Synthesis and Coordination Chemistry of a New Chiral Tridentate PCP *N*-Heterocyclic Carbene Ligand Based on a Ferrocene Backbone

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The new chiral imidazolium salt 1,3-bis[(*R*)-1-((*S*)-2-diphenylphosphinoferrocenyl)ethyl]-imidazolium iodide (**4**, (PCPH)I) was prepared in three steps from commercially available *N*,*N*-dimethyl-1-ferrocenylethylamine (**1**) in 55% overall yield. Salt **4** is the precursor for the in situ generation of a novel tridentate carbene ligand that could not be isolated upon deprotonation of **4** with NaO^{t}Bu. Reaction of **4** with $[Pd(OAc)_2]_3$ afforded (SP-4)-1,3-bis[(*R*)-1-((*S*)-2-diphenylphosphino-κP-ferrocenyl)ethyl]imidazol-2-ylideneiodopalladium(II) acetate, [PdI(PCP)]OAc (**6**). Treatment of **4** with NaO^{t}Bu and $[RuCl_2(PPh_3)_3]$ gave the mixed halide complex (SP-5)-1,3-bis[(*R*)-1-((*S*)-2-diphenylphosphino-κP-ferrocenyl)ethyl]imidazol-2-ylidene-chloroiodoruthenium(II) [RuClI(PCP)] (**7a**), as a mixture of two isomers in 60% yield. Additional complexes that could be obtained from **4** are $[PdCl(PCP)]PF_6$ (**5**), $[RuCl_2(PCP)]$ (**7b**), and $[RuI(PCP)(NCCH_3)_2]PF_6$ (**8**). The crystal and molecular structures of **5** and **7a** were determined by X-ray diffraction. The Ru(II) center undergoes a weak agostic interaction with one of the two stereogenic methine units.

Introduction

Metal complexes bearing *N*-heterocyclic carbene (NHC) ligands were reportet by Öfele[1] and Wanzlick[2] in 1968. In 1991 Arduengo achieved the first isolation of free NHCs, whose crystal structure could be determined.[3] Since then, NHCs, their corresponding metal complexes, and their applications in catalysis have progressed to become a well-established area of research in organometallic chemistry.[4−8] NHCs generally form stronger bonds to metal centers than electron-rich phosphines do, their corresponding complexes tend to be air stable, and in catalytic reactions an excess of ligand is usually not required. NHCs are powerful σ-donating but weak π-accepting ligands. This property increases the electron density at the metal center and engenders a higher trans effect/influence as compared to *P*- and *N*-donor ligands.[9−12] Due to these features NHC complexes prove to be robust and active catalysts for several different reactions.[13−18] These are some simple reasons explaining the still growing interest in NHC complexes.

An important step in the development of carbene ligands is chiral modification. The first chiral and optically active carbene was synthesized in 1983 by Lappert.[19] Since then, many chiral NHCs acting as monodentate ligands[20−22] as well as bidentate ligands[23−25] in asymmetric reactions were reported.[7] A possible way to introduce chirality in the *N*-substituents of the NHCs is to use planar chiral ferrocenyl fragments.[26,27] This

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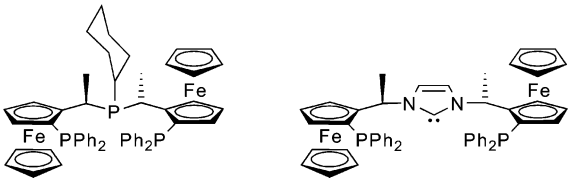
Chart 1

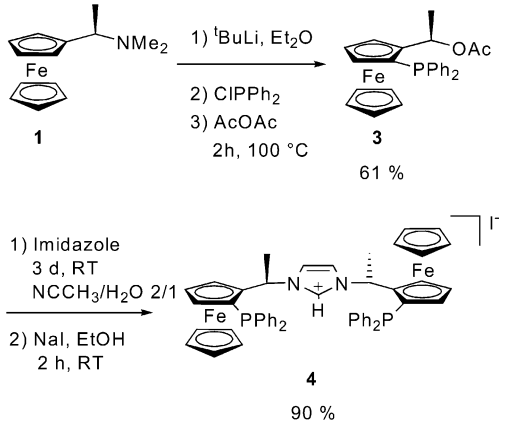


resulted in monodentate ligands[28−30] and a bidentate ligand in combination with a *P*- and *S*-functionality.[31] In this work we disclose a new chiral C_2-symmetric tridentate ligand where an NHC is combined with two ferrocenyl phosphine units. The synthesis and the X-ray crystal structures of a ruthenium and a palladium complex are presented. Our interest in tridentate ligands based on the ferrocene scaffold derives from the successful application of the triphosphine Pigiphos (see Chart 1)[32] in, for example, Ni-catalzed hydroamination reactions of cyanoolefins.[33] However, Pigiphos is not a C_2-symmetric molecule. The replacement of the central P-Cy unit by an NHC fragment generates a C_2-symmetric molecule. We reasoned that this should lead, in the case of square planar complexes, to a chiral environment that is better defined than with Pigiphos.

Results and Discussion

Ligand Synthesis. The diastereoselective ortho functionalization of (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (**1**) is a well-known method for the preparation of phosphines and other compounds displaying both central and planar chirality.[26,27,34,35] The yield in the synthesis of (*R*),(*S*)-PPFA (**2**) could be improved to over 70% by using ^{t}BuLi instead of ^{n}BuLi as described in the literature.[34] The substitution of the dimethylamino group by nucleophiles in compounds such as **2** is known to proceed under retention of configuration at the stereogenic center. However, substitution with imidazole under the conditions reported by Seo[31] for the reaction of (*R*),(*S*)-PPFA with 1-methylimidazole in acetic acid always resulted in phosphine oxidation. Therefore, (*R*),(*S*)-PPFA was converted to the acetate **3**.[35] Only the substitution of the acetate in a 2:1 mixture of acetonitrile and water, a method also described by Dübner,[36] gave the desired product. Ion exchange with NaI afforded the imidazolium salt (PCPH)I, **4**, in good yield (90%) after purification over silica (PCP indicates the deprotonated form of **4**, i.e., the free carbene, Scheme 1). The counterion could be exchanged by chloride in EtOH by the addition of NaCl. However, the

Scheme 1



iodide salt turned out as the most stable form, whereas the chloride as well as the acetate salts were not as easy to handle and were also isolated in lower yields of 64% (Cl^-) and 69% (OAc^-), respectively.

Treatment of **4** with NaO^{t}Bu in THF resulted in the deprotonation of the imidazolium salt. However, despite several attempts we were not successful in isolating the free carbene. The ^{13}C signal of the free carbene could not be observed in spectra of the compound generated in situ. Therefore, the imidazolium salt ^{13}C-**4** containing a ^{13}C label at position 2 of the imidazole[37] was also prepared in 71% yield. The deprotonation of the labeled compound in THF using an excess of NaO^{t}Bu allowed us to observe a broad signal at δ 209.03 ppm with a line width of 36 Hz at room temperature. While this confirms the clean generation of the carbene, it also accounts for the fact that the same signal turns out to be not observable for the nonlabeled compound. Furthermore, also solutions of the carbene in C_6D_6 showed the back formation of the imidazolium ion within minutes, indicating that the acidic sites of the NMR tube glass are sufficient to protonate the carbene.

Synthesis of Palladium Complexes. As the isolation of the free carbene proved not to be possible, we tried to trap the carbene with a transition metal. In a first approach, we investigated the reactivity of the in situ-generated carbene with conventional starting materials for the preparation of Pd(II) complexes via ligand substitution reactions, such as $[PdCl_2(NCCH_3)_2]$, $[PdCl_2(PPh_3)_2]$, and $[PdCl_2(cod)]$. These were dissolved together with 1 equiv of $TlPF_6$ in THF, and a carbene solution was added via a Millipore filter. The best results were obtained using $[PdCl_2(cod)]$, producing $[PdCl(PCP)]PF_6$, **5**, albeit in low isolated yield of 21% (Scheme 2). The ^{1}H NMR spectra no longer showed the imidazolium NCHN$^+$ proton at 9.25 ppm. All the signal sets in the ^{1}H, ^{13}C, and ^{31}P NMR spectra were in agreement with the presence of a C_2-symmetric tridentate complexation mode.

Another method to obtain complexes of this type, without a prior deprotonation step, relies on the use of basic palladium salts.[38] Thus, the reaction of (PCPH)I, **4**, with $[Pd(OAc)_2]_3$ turned out to be the method of choice for the complexation of the PCP ligand to Pd(II), as it

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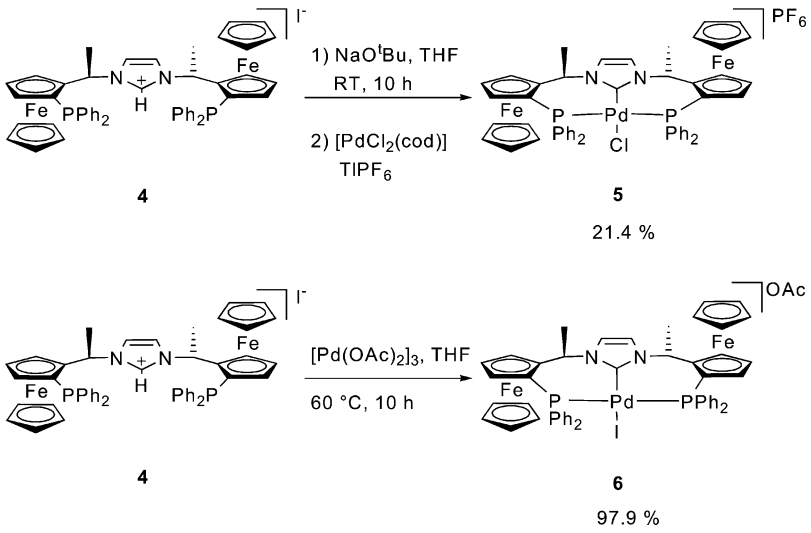
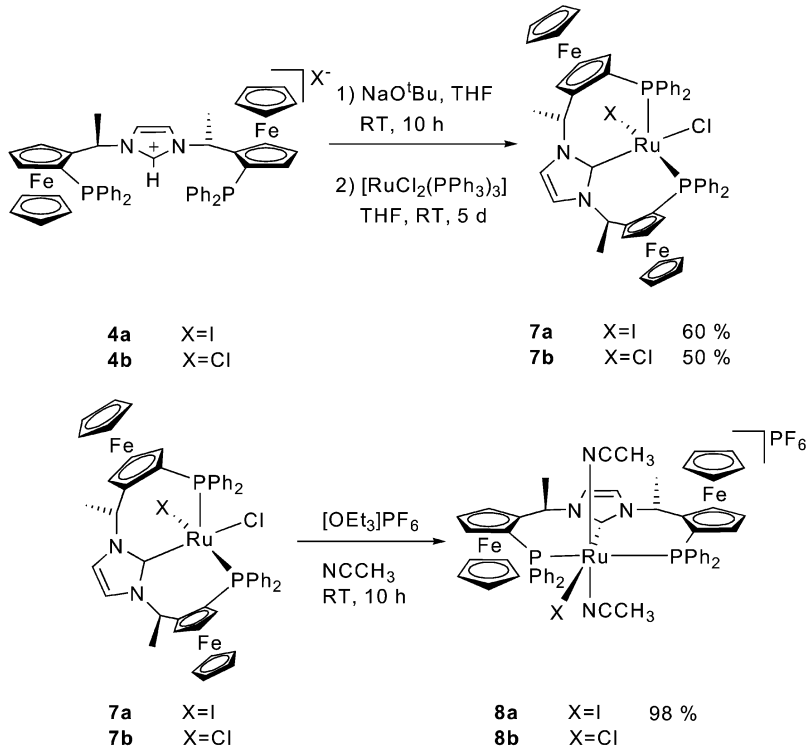
Scheme 2



Scheme 3



afforded complex **6**, [PdI(PCP)]OAc, in virtually quantitative yield (98% isolated). The quantitative formation of derivative **6** seems to indicate that the separate deprotonation step of imidazolium salt **4** is detrimental in view of subsequent ligand exchange processes. The NMR spectra of **6** were very similar to those of **5** and were again in accordance with the formulation of a C_2-symmetric species. Furthermore, the NMR spectroscopic similarity between **5** and **6** is an argument supporting the formulation of the latter derivative as an iodo rather than acetato complex. The acetate ion displays a chemical shift in the ^{1}H NMR spectrum of 2.00 ppm in the form of a broadened singlet. This might implicate ion exchange at palladium to some extent.

For complexes **5** and **6** no signal of the carbene carbon atom bound to the metal was detectable by ^{13}C NMR spectroscopy directly. However, in the case of complex **5**, it was possible to identify the carbene C atom at δ 152.84 ppm by a 2D long-range HMQC experiment. There, the coupling of the two olefinic protons of the imidazole unit with the carbene carbon was used to enhance sensitivity. Due to possible dynamic behavior of [PdI(PCP)]OAc (**6**, vide supra) on the NMR time scale, this method could not be used for this complex.

Synthesis of Ruthenium Complexes. Treating the iodide salt (PCPH)I (**4**) with NaO^{t}Bu in THF in order to generate the free carbene followed by the addition of a solution of [RuCl$_2$(PPh$_3$)$_3$] in THF resulted in the ruthenium complex [RuClI(PCP)], **7a**. The NMR spectra of the crude material, in particular the ^{31}P NMR spectra, indicated the presence of two isomers in a ratio of 1 to 3.3 (Scheme 3). The phosphorus−phosphorus coupling

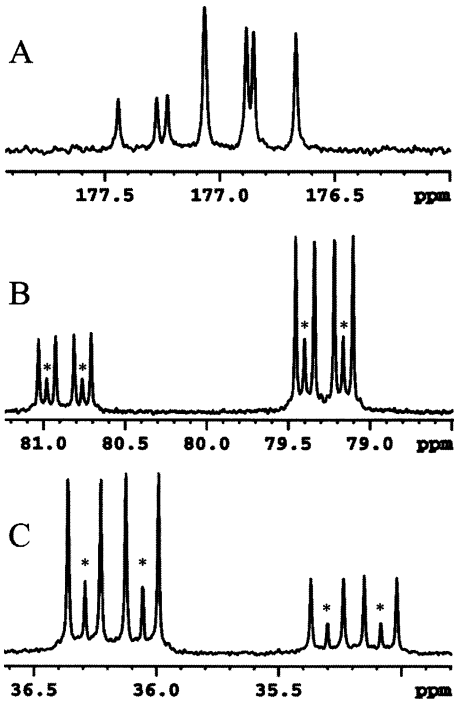


Figure 1. Excerpts from the ^{13}C (A, carbene C atoms) and ^{31}P (B, apical P atoms; C, basal P atoms) NMR spectra of the ^{13}C-labeled mixture of isomeric complexes [RuClI(PCP)], **7a**. Signals marked by an asterisk are due to the unlabeled compound.

constants of 28.7 and 26.5 Hz, respectively, for the two similar species show that the phosphines are in cis position to each other. The different chemical shifts of 36 and 80 ppm point at the fact that one phosphine is trans to a ligand-free position, thus indicating a square pyramidal geometry with the second phosphine trans to a halide. From the mass spectra and the elemental analysis we could determine the presence of both chloride and iodide in the complex. The two isomers result therefore from the two possible orientations of the two different halogens: In the predominant isomer iodide is trans to the basal phosphine (see crystal structure), and in the minor isomer the same phosphine is trans to chloride.

Since it was not possible to observe the chemical shift of the carbene carbon using long-range HMQC experiments, complex **7a** was also prepared using the ^{13}C-labeled imidazolium salt under the same conditions. Parts of the corresponding ^{13}C and ^{31}P NMR spectra are shown in Figure 1, whereas Table 1 collects relevant NMR parameters. The ^{13}C NMR spectra of the mixture showed an AMX spin system for each of the two carbenes at δ 176.87 ppm for the predominant isomer and δ 177.25 ppm for the second one with coupling constants $J_{CP} = 13.8$ Hz, $J_{CP} = 16.2$ Hz and $J_{CP} = 12.7$ Hz, $J_{CP} = 16.2$ Hz, respectively. Each of the phosphorus atoms appears in the ^{31}P NMR spectra as an AMX spin system. Moreover, since the ^{13}C enrichment of the imidazole is only achieved to ca. 60%, the AX spin system of the nonlabeled complex is also apparent. Interestingly, the CP coupling constant is smaller for the coupling to the apical phosphine than to the basal phosphine. The reason for this observation is that the bigger the bite angle between the carbon and the phosphine, the more positive the coupling constant.

Table 1. Chemical Shifts and Coupling Constants of the Carbene and the Phosphines in ^{13}C-Labeled [RuClI(PCP)] (7a)

^{13}C NMR	δ (ppm)	J_{CP} (Hz)
minor	177.25	16,[b] 13[a]
major	176.87	16,[b] 14[a]

^{31}P NMR	δ (ppm) basal P	δ (ppm) apical P	J_{CP} (Hz)	J_{PP} (Hz)
minor ^{13}C	35.19	80.87	16,[b] 13[a]	26
major ^{13}C	36.18	79.28	16,[b] 14[a]	29
minor ^{12}C	35.19	80.87		26
major ^{12}C	36.17	79.28		29

[a] Coupling to/of the apical phosphine. [b]Coupling to/of the basal phosphine.

Table 2. $^{13}C-^{1}H$ Coupling Constants (Hz) of the Fc-*CH*Me Groups in Complexes 5, 6, 7a, and 8

complex	298 K	223 K	193 K
[RuClI(PCP)] (**7a**), agostic C−H	131.3	130.8	130.6
[RuClI(PCP)] (**7a**), nonagostic C−H	141.4	141.5	142.0
$[RuI(PCP)(NCCH_3)_2]PF_6$ (**8**)	141.0		
$[PdCl(PCP)]PF_6$ (**5**)	143.1		
[PdI(PCP)]OAc (**6**)	143.7		

Because the coupling constants in complexes are negative for cis coupling and positive for trans coupling, smaller (less negative) coupling constants are observed for a larger P−Ru−C bite angle.[39] As described later the bite angle from the carbene to the apical phosphine in the predominant isomer is 98.6(7)°, larger than the bite angle to the basal phosphine, which is only 83.8(7)°. The coupling constants are 14.0 Hz for the apical position and 16.3 Hz for the basal one.

In the crystal structure of [RuClI(PCP)] we found an agostic interaction between Ru and the C−H unit of the stereogenic center (C(47)−H(47), vide infra). To validate the presence of such an interaction, the $^{13}C-^{1}H$ coupling constants of the Fc-*CH*Me groups were measured at different temperatures (Table 2). The reduction of the coupling constant for the C(47)−H(47) bond by 7.5% compared to the second Fc-*CH*Me group (131.3 and 141.4 Hz, respectively, at rt) indeed shows the presence of an interaction with ruthenium. However, the extent of reduction of the $^{13}C-^{1}H$ coupling constant as shown by the varible-temperature studies is low, thus indicating that the agostic interaction is weak.

To avoid the formation of isomers, the complexation was repeated with (PCPH)Cl, **4b**, affording the expected single-isomer complex **7b** in 50% yield. The mixture of both isomers of **7a** was used in a further step where we tried to remove one of the halide ligands. The removal was achieved with $[OEt_3]PF_6$ in acetonitrile, giving the cationic complex $[RuI(PCP)(NCCH_3)_2]PF_6$, **8**, in almost quantitative yield (Scheme 3). The ^{31}P NMR spectra, showing only one signal at 17.18 ppm, indicated that there is only one C_2-symmetric species present. According to elemental analysis and mass spectra, the halide abstraction is selective for chloride, affording the monocationic iodo complex **8**. The process is reversible, and the addition of NEt_4Cl results in the formation of **7a** after stirring a CH_2Cl_2 solution for 24 h.

Crystal Structures. Single crystals of the palladium complex $[PdCl(PCP)]PF_6$ (**5**) were obtained by slow

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Table 3. Selected Bond Lengths (Å) and Angles (deg) of [PdCl(PCP)]PF_6, 5, and [RuClI(PCP)], 7a[a]

[PdCl(PCP)]PF_6, **5**			
Pd−C(20)	1.962(8)	Pd−Cl(1)	2.350(2)
Pd−P(1)	2.317(2)	Pd−P(2)	2.357(2)
P(1)−Pd−C(20)	86.6(3)	P(2)−Pd−C(20)	82.2(3)
Cl(1)−Pd−C(20)	164.3(3)	P(1)−Pd−P(2)	168.46(6)
Cl(1)−Pd−P(1)	90.66(8)	Cl(1)−Pd−P(2)	100.87(8)
P(1)−Pd−C(20)−N(1)	−70.4(8)	P(1)−Pd−C(20)−N(2)	107.0(7)
Cl(1)−Pd−C(20)−N(1)	−150.6(7)	Cl(1)−Pd−C(20)−N(2)	26.7(15)
P(2)−Pd−C(20)−N(1)	107.0(8)	P(2)−Pd−C(20)−N(2)	−75.6(7)
[RuClI(PCP)], **7a**			
I(2)−Ru(2)	2.759(3)	Ru(2)−Cl(2)	2.423(7)
Ru(2)−C(61)	2.02(2)	Ru(2)−C(47)	2.94(3)
Ru(2)−P(4)	2.209(7)	Ru(2)−H(47)	2.311
Ru(2)−P(3)	2.309(8)		
P(4)−Ru(2)−C(61)	98.6(7)	Cl(2)−Ru(2)−P(3)	97.6(3)
P(4)−Ru(2)−P(3)	101.8(3)	I(2)−Ru(2)−C(61)	86.2(6)
Cl(2)−Ru(2)−P(4)	105.4(3)	I(2)−Ru(2)−Cl(2)	86.33(18)
I(2)−Ru(2)−P(4)	92.1(2)	Cl(2)−Ru(2)−C(61)	155.0(7)
P(3)−Ru(2)−C(61)	83.8(7)	I(2)−Ru(2)−P(3)	164.0(2)
P(4)−Ru(2)−C(61)−N(4)	−1(3)	P(4)−Ru(2)−C(61)−N(3)	170.9(15)

[a] esd's are given in parantheses.

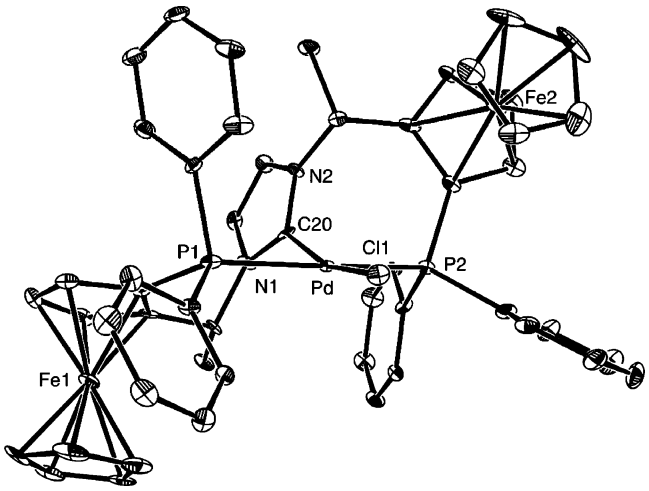

Figure 2. ORTEP representation of the cation of [PdCl(PCP)]PF_6, **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 30% probability.

diffusion of hexane into a methanol solution. The structure is shown in Figure 2, and selected bond length and angles are listed in Table 3. The geometry of the complex is square planar with only a slight tetrahedral distortion, as indicated, among other geometrical parameters, by the Cl(1)−Pd−C(20) angle of 164.3(3)°. The Pd−C(20) bond length of 1.962(8) Å is comparable to other Pd(II)−carbene distances with chloride trans to the carbene C atom (1.943(2),[40] 1.9553(3),[41] 1.973(2),[42] and 1.999(13) Å[43] are values previously reported in the literature). In such structures, the imidazole plane is perpendicular to the coordination plane. This tendency is also visible in the structure of **5**, although the corresponding planes are not exactly perpendicular due to the rigid geometry of the ligand (the torsion angle P(2)−C(20)−Pd−N(2) is −75.6(7)°, the angle between the least-squares plane containing C(20), N(1), C(21), C(22), N(2) and the least-squares plane containing Pd, Cl(1), P(1), P(2), C(20) is 72.9°).

The C_2 symmetry of the [PdCl(PCP)]PF_6 complex as inferred by NMR techniques in solution was not observed in the solid state. The ferrocenyl and phenyl groups on P(1) and P(2) have different orientations, as shown by the ORTEP representation of Figure 2. Additionally, one of the phenyl groups on P(1) is in an axial position and the other is in an equatorial position, whereas the P(2) phenyl groups are both in pseudo-equatorial positions. The seven-membered chelate ring is flexible enough to allow a fast exchange on the NMR scale in solution, so that C_2 symmetry is observed. The P(1)−Pd−C(20) and P(2)−Pd−C(20) bite angles are 86.6(3)° and 82.2(3)°, which is less than the ideal value of 90° and may be due to the steric bulk of the ligand. Although the conformations of the PPh_2 groups are different, one phenyl of each PPh_2 group lies roughly in the coordination plane of palladium, as can be seen in Figure 3 and by the corresponding torsion angles C(20)−Pd−P(1)−C(14) of 168.1(4)° and C(20)−Pd−P(2)−C(36) of −166.4(4)°. This is probably the reason the chloride ligand is slightly pushed out of the coordination plane, causing the tetrahedral distortion of the complex. Indeed, the chlorine atom is located 0.697 Å above the least-squares plane containing Pd, P(1), P(2), and C(20).

Single crystals of [RuClI(PCP)] (**7a**) for X-ray analysis could be obtained from a dichloromethane solution overlayered with 2-propanol. Complex **7a** crystallizes with two crystallographically independent molecules. Since both independent molecules show similar parameters, only one molecule is discussed here (Figure 4). Selected bond lengths and angles are provided in Table 3. The coordination geometry around ruthenium is approximately square pyramidal with a facial coordination mode of the PCP ligand. The apical position is occupied by P(4), and in the basal plane, Cl(2) is trans to the carbene C(61) whereas I(2) is trans to P(3). Ru(2) is displaced by 0.392 Å from the least-squares plane containing the donor atoms C(61), P(3), Cl(2), and I(2). The displacement of ruthenium from the basal plane is also shown by the angles Cl(2)−Ru(2)−C(61) of 155.0(7)° and I(2)−Ru(2)−P(3) of 164.0(2)°. A square pyramidal coordination geometry, but with a different

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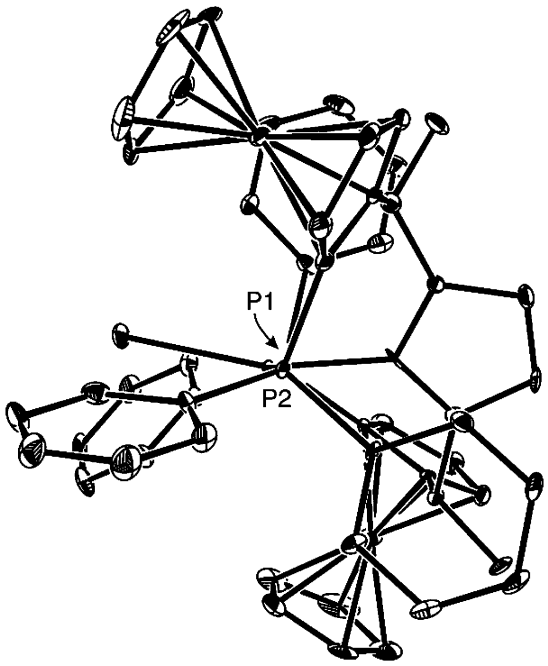

Figure 3. Side view of the cation $[PdCl(PCP)]^+$ showing the equatorial orientation of two phenyl groups.

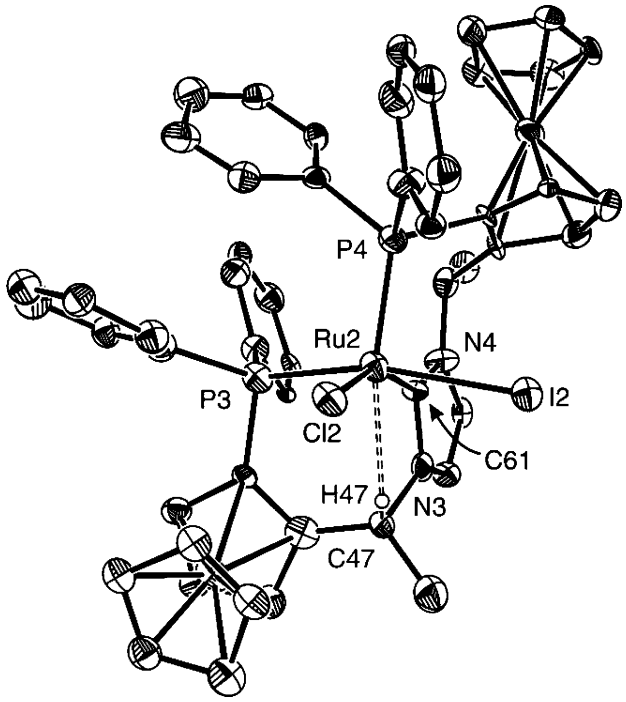

Figure 4. ORTEP representation of [RuClI(PCP)], **7a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 30% probability.

coordination pattern, was also found for Grubbs-type carbene complexes studied by Fürstner,[44] which contain, however, monodentate NHC ligands. A structure with the same coordination geometry as reported here for **7a** containing a tridentate phosphine ligand was reported from these laboratories.[32] The Ru(2)−C(61) bond length of 2.02(2) Å trans to chloride is slightly shorter than other Ru−C(carbene) distances found in the literature.[6,22,44−46] However, this distance can be compared to the Ru−C(carbene) distances of 2.057(8) and 2.067(10) Å in two complexes studied by Fürstner where chloride is also in trans position to the carbene of an NHC ligand.[47]

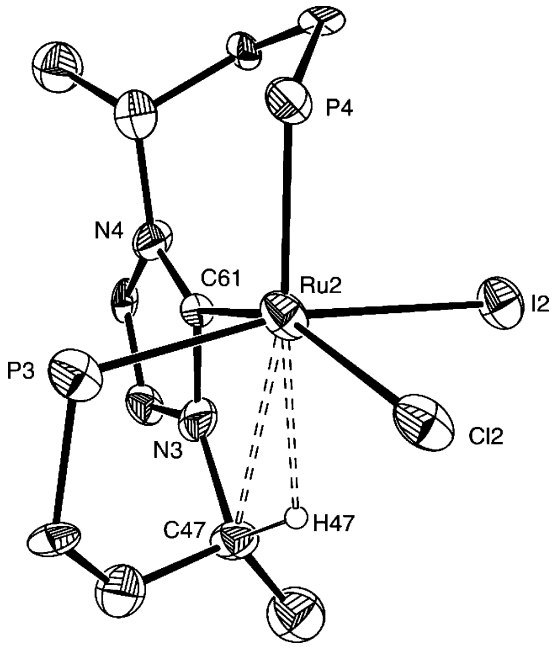

Figure 5. Agostic interaction between Ru(2) and C(47)−H(47) in **7a**.

It is interesting to compare [RuClI(PCP)], **7a**, with the facial coordination geometry, with $[RuI(PCP)(NCCH_3)_2]PF_6$, **8**, which has a meridional octahedral coordination geometry according to ^{31}P NMR data. For the tridentate phosphine complex $[RuCl_2(PPP)]$ (PPP = pigiphos) Barbaro reports that the meridional geometry should be thermodynamically more stable than the facial one.[32] If this is also true for the PCP ligand, there must be an electronic reason for the stability of the facial coordination geometry. The stabilization of the square pyramidal geometry can also be interpreted by the position of one of the ferrocenyl groups, which is placed below the basal plane of the complex. This may prevent the coordination of a sixth ligand. This sixth coordination site can also be involved in the already mentioned agostic interaction between C(47)−H(47) and Ru(2) that results in an octahedral coordination geometry (Figure 5). The calculated Ru(2)−H(47) nonbonded distance is 2.311 Å, and the Ru(2)−C(47) separation is 2.94(3) Å. This contact can also be forced purely by the steric constraints of the complex. A structure of a $[RuCl_2(triphosfer)]$ complex (triphosfer = bis-1-(1′-diphenylphosphinoferrocenyl)phenylphosphine) was reported by Butler. In this complex, also displaying an approximate square pyramidal geometry, an agostic interaction blocking the sixth coordination site with a Ru−H distance of 2.89 Å is observed.[48] For the tungsten

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complex $[W(CO)_3(PCy_3)_2]$, Wassermann reported an agostic interaction with a W−H distance of 2.27 Å and a W−C distance of 2.945(6) Å.[49] The rhenium complex $[Re(CO)_3(PCy_3)_2]$ of Heinekey[50] contains a similar agostic interaction with a Re−C distance of 2.89(5) Å. Finally, the complex $[RuCl_2(=CHPh)(H_2IAdMes)(PCy_3)]$ recently reported by Dinger shows a Ru−C interaction with a distance of 2.883(6) Å between an adamantyl carbon and ruthenium.[51] These examples show that the Ru−(H−C) distance in **7a** falls within a range observed for compounds of second- and third-row transition metals that have been described as involving an agostic interaction. However, the interaction we see in **7a** is undoubtedly a weak one and resembles much more the type of interactions previously discussed by Pregosin for a series of Pt complexes and later dubbed as remote agostic.[52]

Conclusion

The new tridentate chiral carbene ligand precursor (PCPH)I (**4**) with two phosphines and an NHC unit was prepared in three steps from *N*,*N*-dimethyl-1-ferrocenylethylamine (**1**). The isolation of the free carbene could not be achieved. However, it was possible to form in situ complexes of this ligand after deprotonation with NaO^tBu in THF. By this route the complexes $[PdCl(PCP)]PF_6$, **5**, and [RuXCl(PCP)] (X = I, **7a**; X = Cl, **7b**) could be obtained starting from $[PdCl_2(cod)]$ and $[RuCl_2(PPh_3)_3]$, respectively. The ruthenium complex **7a** could only be isolated as a mixture of two isomers. The most efficient route to obtain a palladium complex is the reaction of the imidazolium salt **4** with $[Pd(OAc)_2]_3$ to afford [PdI(PCP)]OAc, **6**. The structures of **5** and **7a** (main isomer) were analyzed by X-ray diffraction. Derivative **5** displayed a slightly distorted square planar coordination geometry. An approximately square pyramidal arrangement of the ligands was found in **7a** with a facial coordination of the tridentate PCP ligand. The nonbonded distances of Ru(2)−H(47) of 2.311 Å and of Ru(2)−C(47) of 2.94(3) Å indicate that an agostic interaction is present. Keeping this in mind, the coordination geometry of the ruthenium complex **7a** can also be interpreted as being octahedral.

First attempts to generate catalytically active species containing the new tridentate carbene ligand have been carried out. Upon reaction with $[Et_3O]PF_6$ in acetonitrile, complex **6** is converted to the dicationic derivative $[Pd(PCP)(NCCH_3)](PF_6)_2$, which acts as a Lewis-acidic catalyst for the enantioselective addition of morpholine to methacrylonitrile. The enantioenriched product is obtained in 96% yield and 37% ee when working with 5 mol % catalyst at room temperature. Although the enantioselectivity is lower than that obtained in the same reaction utilizing the similar dicationic Ni(II) complex containing Pigiphos,[33] we regard this preliminary result as encouraging. The simple and modular synthesis of this new type of diphosphino carbene will allow a fine-tuning of both its steric and electronic properties in view of achieving more selective catalysts. Work along these lines is in progress and will be reported in due course.

Experimental Section

General Methods. (*R*)-*N*,*N*-Dimethyl-1-ferrocenylethylamine (**1**) was generously provided by Solvias AG (Basel) and was recrystallized as tartrate salt according to the reported procedure.[53] The complexes $[RuCl_2(PPh_3)_3]$[54] and $[PdCl_2(cod)]$[55] were prepared following literature procedures. All commercially available reagents were used without further purification. Acetonitrile was freshly distilled from CaH_2, Et_2O from NaK, and THF from Na. All reactions were performed under inert atmosphere, and air-sensitive substances were handled in a glovebox. NMR: The routine ^1H, ^{13}C, and ^{31}P NMR spectra were measured in the given solvent on either a Bruker DPX250 or Bruker DPX300 instrument. The two-dimensional 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 microelemental analysis service of the "Laboratorium für Organische Chemie der ETHZ". Crystallography: X-ray structural measurements were carried out on a Bruker CCD diffractometer (Bruker SMART PLATFORM, with CCD detector, graphite monochromator, Mo Kα 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 palladium complex $[PdCl(PCP)]PF_6$, **5**, all non hydrogen atoms were refined freely with anisotropic displacement parameters. One of the CH_2Cl_2 molecules is disordered over two sites with Cl(4) in common. The C−Cl bond lengths were restrained to standard values. For the ruthenium complex [RuClI(PCP)], **7a**, only the non hydrogen and non carbon atoms were refined freely with anisotropic displacement parameters. Due to low data-to-paremeters ratio, the carbon atoms were refined anisotropically in combination with the ISOR instruction. For both structures 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 4.

(*R*)-*N*,*N*-Dimethyl-1-((*S*)-2-diphenylphosphinoferrocenyl)ethylamine (2). A solution of **1** (12.9 g, 50 mmol) in Et_2O (60 mL) was cooled to −78 °C, and a ^{t}BuLi solution (1.7 N in pentane) (32.4 mL, 55 mmol, 1.1 equiv) was slowly added. After the addition the reaction mixture was warmed to room temperature and stirred for 1 h. $ClPPh_2$ (18.5 mL, 100 mmol, 2 equiv) was added at 0 °C. After refluxing for 2 h aqueous $NaHCO_3$ was slowly added with cooling in an ice bath. The mixture was extracted with Et_2O, and the combined organic layers were washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo to afford a red oil. The oil was chromatographed (silica, hexane/ethyl acetate, 5:1), and the product was purified by recrystallization (EtOH). Yield: 15.34 g (34.8 mmol, 69%), orange crystals. TLC (hexane/EtOAc, 5:1): R_f = 0.28. ^1H NMR ($CDCl_3$): δ 1.27 (d, J_{CHMe} = 6.8 Hz, 3 H, CH*Me*), 1.78 (s, 6 H, N*Me*$_2$), 3.87 (m, J_{CHCH} = 1.1 Hz, 1 H, Cp), 3.95 (s, 5 H, Cp′), 4.16 (dq, J_{CHP} = 2.6 Hz, J_{CHMe} = 6.8 Hz, 1 H, C*H*Me), 4.25 (m, J_{CHCH} = 2.3 Hz, 1 H, Cp), 4.38 (m, J_{CHCH} = 1.1 Hz, 1 H, Cp), 7.19 (m, 5 H, P*Ph*$_2$), 7.36 (m, 3 H, P*Ph*$_2$), 7.00 (m, 2 H, P*Ph*$_2$). ^{13}C NMR ($CDCl_3$): δ 9.36 (CH*Me*), 39.03 (N*Me*$_2$), 57.24 (*C*HMe), 68.38 (CH, Cp), 69.34 (CH, Cp), 69.66 (CH, Cp′), 71.75

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Table 4. Crystallographic Data of [PdCl(PCP)]PF_6 (5) and [RuClI(PCP)] (7a)

	[PdCl(PCP)]PF_6, **5**	[RuClI(PCP)], **7a**
color, shape	yellow needle	deep red plate
empirical formula	$C_{51}H_{46}ClF_6Fe_2N_2P_3Pd\cdot 1.37(CH_2Cl_2)$	$C_{51}H_{46}ClFe_2IN_2P_2Ru\cdot 0.5(CH_2Cl_2)\cdot 0.5(^iPrOH)$
fw	1261.30	1196.47
temp (K)	100	100
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P1$	$P2_1$
unit cell dimens (Å/deg)	$a = 9.2494(16)$	$a = 11.5599(14)$
	$b = 11.382(2)$	$b = 24.807(3)$
	$c = 13.529(2)$	$c = 18.429(2)$
	$\alpha = 96.572(4)$	$\alpha = 90$
	$\beta = 198.18(4)$	$\beta = 96.331(3)$
	$\gamma = 90.485(4)$	$\gamma = 90$
volume (Å^3)	1342.8(4)	5252.7(11)
Z	1	4
calcd density (g cm^{-3})	1.560	1.513
abs coeff (mm^{-1})	1.198	1.616
cryst size (mm)	0.27 × 0.11 × 0.08	0.21 × 0.10 × 0.02
reflns collected, unique	13 672, 12 024	31 414, 12 818
R_{int}	0.0249	0.1401
refinemet method	full-matrix least-squares on F^2	
data, restraints, params	12 024, 9, 655	12 818, 639, 1110
GOF	1.096	0.972
R, R_w	0.0712, 0.1756	0.098, 0.2292
abs struct param	0.03(3)	0.04(5)
min./max. resd (e Å^{-3})	2.411, −1.181	1.708, −0.934

(CH, Cp), 76.80 (C, Cp), 77.22 (C, Cp), 127.13, 127.28, 127.38, 127.81, 127.93, 128.69 (C, CH, P*Ph*$_2$), 132.31 (d, J_{CP} = 18.8 Hz, CH, P*Ph*$_2$), 135.14 (d, J_{CP} = 21.4 Hz, CH, P*Ph*$_2$). ^{31}P NMR ($CDCl_3$): δ −21.67 (*P*Ph$_2$).

(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl Acetate (3). A mixture of (*R*)-(*S*)-PPFA (**2**) (4.37 g, 9.91 mmol) and acetic anhydride (6.2 mL) was heated at 100 °C for 2 h. Cooling at −20 °C for 2 days afforded the crystalline product, which was collected on a glass filter, washed with cooled methanol, and dried in vacuo. Yield: 4.02 g (8.82 mmol, 89%), orange crystals. ^{1}H NMR (C_6D_6): δ 1.19 (s, 3 H, O*Ac*), 1.59 (d, J_{CHMe} = 6.4 Hz, 3 H, CH*Me*), 3.76 (m, 1 H, Cp), 3.83 (s, 5 H, Cp′), 4.02 (m, 1 H, Cp), 4.27 (m, 1 H, Cp), 6.48 (dq, J_{CHP} = 2.8 Hz, J_{CHMe} = 6.4 Hz, 1 H, C*H*Me), 6.94 (m, 3 H, P*Ph*$_2$), 7.06 (m, 3 H, P*Ph*$_2$), 7.15 (m, 2 H, P*Ph*$_2$), 7.29 (m, 2 H, P*Ph*$_2$). ^{13}C NMR (C_6D_6): δ 18.86 (CH_3, CH*Me*), 20.19 (O*Ac*), 68.67 (d, J_{CP} = 9.3 Hz, *C*HMe), 69.73 (d, J_{CP} = 3.8 Hz, CH, Cp), 69.84 (CH, Cp), 70.26 (CH, Cp′), 72.67 (d, J_{CP} = 4.9 Hz, CH, Cp), 77.83 (d, J_{CP} = 11.1 Hz, C, Cp), 92.81 (d, J_{CP} = 24.5 Hz, C, Cp), 128.08, 128.25, 128.33, 128.46, 128.56, 129.40 (CH, P*Ph*$_2$), 133.35 (d, J_{CP} = 18.6 Hz, CH, P*Ph*$_2$), 135.76 (d, J_{CP} = 20.2 Hz, CH, P*Ph*$_2$), 138.20 (d, J_{CP} = 10.3 Hz, C, P*Ph*$_2$), 140.77 (d, J_{CP} = 11.6 Hz, C, P*Ph*$_2$), 169.28 (C, O*Ac*). ^{31}P NMR (C_6D_6): δ −22.96 (*P*Ph$_2$).

1,3-Bis[(*R*)-1-((*S*)-2-diphenylphosphinoferrocenyl)ethyl]-imidazolium Iodide (4). A suspension of **3** (1.44 g, 3.15 mmol) and imidazole (117.8 mg, 1.73 mmol, 0.55 eq) in a mixture of acetonitrile (12 mL) and H_2O (6 mL) was stirred for 3 days to give a clear orange solution. After addition of benzene (8 mL) the organic phase was separated and concentrated in vacuo. The residue was dissolved together with NaI (943 mg, 6.29 mmol, 2 equiv) in ethanol (15 mL) and stirred for 3 h. After evaporating the solvent in vacuo the crude product was chromatographed (silica, CH_2Cl_2 + 2% MeOH). Yield: 1.41 g (1.43 mmol, 90%), orange solid. TLC (CH_2Cl_2 + 4% MeOH): R_f = 0.53. ^{1}H NMR (C_6D_6): δ 1.98 (d, J_{CHMe} = 7.0 Hz, 6 H, CH*Me*), 3.82 (m, 2 H, Cp), 3.91 (s, 10 H, Cp′), 4.31 (t, J_{CHCH} = 2.5 Hz, 2 H, Cp), 5.47 (dq, J_{CHMe} = 7.0 Hz, J_{PH} = 3.5 Hz, 2 H, C*H*Me), 6.06 (m, 2 H, Cp), 6.87 (*t*, J_{CHCH} = 6.8 Hz, 4 H, P*Ph*$_2$), 7.20 (m, 12 H, P*Ph*$_2$), 7.61 (m, 2 H, HC=CH Im), 7.64 (m, 4 H, P*Ph*$_2$), 9.25 (s, 1 H, $^+$CH, Im). ^{13}C NMR (C_6D_6): δ 22.23 (CH_3, CH*Me*), 56.66 (CH, *C*HMe), 70.62 (CH, Cp′), 71.95 (CH, Cp), 72.41 (d, J_{CP} = 4.3 Hz, CH, Cp), 73.17 (d, J_{CP} = 3.63 Hz, CH, Cp), 75.39 (d, J_{CP} = 10.0 Hz, C, Cp), 92.18 (d, J_{CP} = 26.64 Hz, C, Cp), 121.29 (CH, HC=CH Im), 128.49, 128.57, 128.68 (CH, P*Ph*$_2$), 129.04 (d, J_{CP} = 5.4 Hz, CH, P*Ph*$_2$), 129.82 (CH, P*Ph*$_2$), 131.89 (d, J_{CP} = 17.1 Hz, CH, P*Ph*$_2$), 132.91 ($^+$CH, Im), 135.88 (d, J_{CP} = 21.7 Hz, CH, P*Ph*$_2$), 137.60 (d, J_{CP} = 6.9 Hz, C, P*Ph*$_2$), 140.50 (d, J_{CP} = 8.2 Hz, C, P*Ph*$_2$). ^{31}P NMR (C_6D_6): δ −24.81 (*P*Ph$_2$). No correct elemental analysis could be obtained because of partial phosphine oxidation.

(SP-4)-1,3-Bis[(*R*)-1-((*S*)-2-diphenylphosphino-κ*P*-ferrocenyl)ethyl]imidazol-2-ylidenechloropalladium(II) Hexafluorophosphate, [PdCl(PCP)]PF_6 (5). A solution of **4** (50 mg, 0.05 mmol) and NaO^{t}Bu (4.8 mg, 0.05 mmol) in THF (2 mL) was stirred overnight. A THF (1 mL) suspension of [$PdCl_2$(cod)] (14.5 mg, 0.051 mmol) and $TlPF_6$ (18.4 mg, 0.0526 mmol, 1.05 equiv) was prepared, and the carbene solution was added slowly via a Millipore filter (previously washed with NEt_3 and THF). This mixture was stirred for 5 days and then concentrated in vacuo to 1 mL. The product was precipitated by the addition of hexane and filtered off. The crude product was purified by flash chromatography (CH_2Cl_2). Yield: 12.4 mg (0.011 mmol, 21%), yellow crystals. ^{1}H NMR (CD_2Cl_2): δ 1.20 (d, J_{CHMe} = 7.2 Hz, 6 H, CH*Me*), 3.74 (m, 2 H, Cp), 4.23 (s, 10 H, Cp′), 4.51 (t, J_{CHCH} = 2.6 Hz, 2 H, Cp), 4.77 (m, 2 H, Cp), 5.66 (q, J_{CHMe} = 7.2 Hz, 2 H, C*H*Me), 6.74 (s, 2 H, HC=CH Im), 7.03 (qt, J_{CHCH} = 7.2 Hz, J_{CHCH} = 1.2 Hz, 4 H, P*Ph*$_2$), 7.43 (tt, J_{CHCH} = 7.4 Hz, J_{CHCH} = 1.4 Hz, 4 H, P*Ph*$_2$), 7.56 (*tt*, J_{CHCH} = 7.2 Hz, J_{CHCH} = 1.5 Hz, 6 H, P*Ph*$_2$), 7.63 (q, J_{CHCH} = 6.9 Hz, 2 H, P*Ph*$_2$), 7.95 (q, J_{CHCH} = 6.0 Hz, 4 H, P*Ph*$_2$). ^{13}C NMR (CD_2Cl_2): δ 15.54 (CH_3, CH*Me*), 54.58 (CH, *C*HMe), 70.68 (t, J_{CP} = 3.1 Hz, CH, Cp), 70.89 (t, J_{CP} = 3.6 Hz, CH, Cp), 71.30 (CH, Cp′), 75.41 (CH, Cp), 90.46 (t, J_{CP} = 6.8 Hz, C, Cp), (second C, Cp not observed), 118.76 (CH, HC=CH Im), 127.78 (CH, P*Ph*$_2$), 129.21 (t, J_{CP} = 4.9 Hz, CH, P*Ph*$_2$), 130.89 (t, J_{CP} = 6.2 Hz, CH, P*Ph*$_2$), 131.61 (CH, P*Ph*$_2$), 133.85 (t, J_{CP} = 29.4 Hz, C, P*Ph*$_2$), 136.01 (t, J_{CP} = 5.8 Hz, CH, P*Ph*$_2$) 152.84 (C−Pd, Im). ^{31}P NMR (CD_2Cl_2): δ −144.36 (heptet, J_{PF} = 710.5 Hz, PF_6), −2.16 (*P*Ph$_2$). Anal. Calcd for $C_{51}H_{46}ClF_6Fe_2N_2P_3Pd$: C, 53.39; H, 4.04; N, 2.44. Found: C, 53.78; H, 4.62; N, 2.25. MS-ESI: 1000.06 (PdClPCP$^+$), 966.9 (PdPCP$^+$).

(SP-4)-1,3-Bis[(*R*)-1-((*S*)-2-diphenylphosphino-κ*P*-ferrocenyl)ethyl]imidazol-2-ylideneiodopalladium(II) Acetate, [PdI(PCP)]OAc (6). [$Pd(OAc)_2$]$_3$ (68.1 mg, 0.10 mmol) and **4** (300 mg, 0.30 mmol) were dissolved in THF (9 mL) and heated at 60 °C for 12 h. After removing the solvent in vacuo the residue was dissolved in CH_2Cl_2 (1 mL) and the product precipitated with hexane, filtered off, washed three times with hexane, and dried in vacuo. Yield: 313.6 mg (0.272 mmol, 98%), brown-yellow solid. ^{1}H NMR (CD_2Cl_2): δ 1.22 (d, J_{CHMe} = 6.9 Hz, 6 H, CH*Me*), 2.00 (br, 3 H, OAc), 3.74 (m, 2 H, Cp), 4.24 (s, 10 H, Cp′), 4.52 (t, J_{CHCH} = 2.4 Hz, 2 H, Cp), 4.83 (m, 2 H, Cp), 5.72 (br, 2 H, C*H*Me), 6.90 (s, 2 H, HC=CH Im), 7.10 (m, 4 H, P*Ph*$_2$), 7.43 (t, J_{CHCH} = 7.5 Hz, 4 H, P*Ph*$_2$), 7.56 (tt, J_{CHCH} = 7.4 Hz, J_{CHCH} = 1.5 Hz, 6 H, P*Ph*$_2$), 7.63 (q, J_{CHCH} = 7.2 Hz, 2 H, P*Ph*$_2$), 7.84 (br, 4 H, P*Ph*$_2$). ^{13}C NMR (CD_2Cl_2): δ 15.81 (CH_3, CH*Me*), 22.63, 32.56 (CH_3, OAc), 54.42 (CH, *C*HMe), 70.15 (CH, Cp), 70.52 (CH, Cp), 70.82 (CH, Cp), 71.30 (CH, Cp′), 75.15 (C,Cp), 90.53 (t, J_{CP} = 6.9 Hz, C, Cp), 119.19 (CH, HC=CH Im), 127.96 (CH, P*Ph*$_2$), 129.14 (t, J_{CP} = 5.0 Hz, CH, P*Ph*$_2$), 130.89 (CH, P*Ph*$_2$), 131.12 (CH, P*Ph*$_2$), 131.62 (CH, P*Ph*$_2$), 133.56 (C, P*Ph*$_2$), 135.54 (CH, P*Ph*$_2$). ^{31}P NMR (CD_2Cl_2): δ −1.89 (*P*Ph$_2$). MS-ESI: 1093.0 (PdIPCP$^+$), 1001.1, 965.1 (PdPCP$^+$).

(SP-5)-1,3-Bis[(*R*)-1-((*S*)-2-diphenylphosphino-κ*P*-ferrocenyl)ethyl]imidazol-2-ylidenechloroiodoruthenium-(II), [RuClI(PCP)] (7a). A solution of **4a** (300 mg, 0.30 mmol) and NaO^{t}Bu (29 mg, 0.30 mmol) in THF (9 mL) was stirred overnight, affording a suspension. A THF (6 mL) solution of $[RuCl_2(PPh_3)_3]$ (291 mg, 0.30 mmol) was added, and the mixture was stirred for 5 days. The mixture was concentrated to an amount of 2 mL, and the product was precipitated by the addition of hexane. After filtration and washing three times with hexane the crude product was chromatographed (silica, ethyl acetate). Yield: 198 mg (0.18 mmol; 60%), deep red solid, two isomers in a ratio of 1:3.3. ^{1}H NMR (CD_2Cl_2): major isomer, δ 1.38 (d, J_{CHMe} = 7 Hz, 3 H, CH*Me*), 1.86 (d, J_{CHMe} = 7 Hz, 3 H, CH*Me*), 3.01 (m, 1 H, Cp), 3.67 (m, 1 H, Cp), 4.13 (s, 10 H, Cp′), 4.21 (m, 1 H, Cp), 4.27 (s, 10 H, Cp′), 4.36 (m, 1 H, Cp), 4.62 (m, 1 H, Cp), 4.86 (q, 1 H, C*H*Me), 6.71−6.82, 6.95−6.99, 7.13−7.21, 7.32−7.56, 8.55−8.78 (m, 20 H + 2 H, P*Ph*$_2$); minor isomer, δ 1.38 (d, J_{CHMe} = 7 Hz, 3 H, CH*Me*), 3.70 (m, 1 H, Cp), 4.06 (s, 10 H, Cp′), 4.78 (q, 1 H, C*H*Me). ^{31}P NMR (CD_2Cl_2): major isomer, δ 36.17 (d, J_{PP} = 28.7 *P*Ph$_2$), 79.30 (d, J_{PP} = 28.6 *P*Ph$_2$); minor isomer, δ 35.19 (d, J_{PP} = 26.4 *P*Ph$_2$), 80.89 (d, J_{PP} = 26.5 *P*Ph$_2$). Anal. Calcd for $C_{51}H_{46}ClFe_2IN_2P_2Ru$: C, 54.45; H, 4.21; N, 2.49. Found: C, 54.29; H, 4.70; N, 2.25. HiResMALDI: 1089 ($RuPCPI^+$), 997 ($RuPCPCl^+$), 961 ($RuPCP^+$), 841 ($RuPCP^+$ without FeCp), 656 (−PPh$_2$ von 841).

(SP-5)-1,3-Bis[(*R*)-1-((*S*)-2-diphenylphosphino-κ*P*-ferrocenyl)ethyl]imidazol-2-ylidenedichlororuthenium-(II), [RuCl$_2$(PCP)] (7b). A solution of **4** (chloride salt, 200 mg, 0.22 mmol) and NaO^{t}Bu (21 mg, 0.22 mmol) in THF (6 mL) was stirred overnight, affording a suspension. A THF (5 mL) solution of $[RuCl_2(PPh_3)_3]$ (214 mg, 0.22 mmol) was added, and the mixture was stirred for 5 days. The mixture was concentrated to an amount of 2 mL, and the product was precipitated by the addition of hexane. After filtration and washing three times with hexane the crude product was chromatographed (silica, ethyl acetate). Yield: 114 mg (0.11 mmol; 50%), deep red solid. ^{1}H NMR (CD_2Cl_2): δ 1.37 (d, J_{CHMe} = 7.0 Hz, 3 H, CH*Me*), 1.89 (d, J_{CHMe} = 6.0 Hz, 3 H, CH*Me*), 2.96 (m, 1 H, Cp), 3.35 (q, J_{CHMe} = 7.0 Hz, 1 H, C*H*Me), 3.65 (q, J_{CHMe} = 6.0 Hz, 1 H, C*H*Me), 3.67 (m, 1 H, Cp), 4.12 (s, 10 H, Cp′), 4.21 (m, 1 H, Cp), 4.28 (s, 10 H, Cp′), 4.31 (m, 1 H, Cp), 4.33 (m, 1 H, Cp), 4.63 (m, 1 H, Cp), 6.64 (br, 1 H, P*Ph*$_2$), 6.70 (s, 1 H, HC═CH Im), 6.78 (t, J_{CHCH} = 7.0, 3 H, P*Ph*$_2$), 7.00 (s, 1 H, HC═CH Im), 7.16 (t, J_{CHCH} = 7.3, 2 H, P*Ph*$_2$), 7.39 (m, J_{CHCH} = 6.3, 4 H, P*Ph*$_2$), 7.47 (t, J_{CHCH} = 7.3, 2 H, P*Ph*$_2$), 7.52 (t, J_{CHCH} = 7.0, 2 H, P*Ph*$_2$), 7.63 (m, 3 H, P*Ph*$_2$), 8.60 (br, 3 H, P*Ph*$_2$), 9.77 (br, 1 H, P*Ph*$_2$). ^{13}C NMR (CD_2Cl_2): δ 16.21 (CH_3, CH*Me*), 17.92 (CH_3, CH*Me*), 51.46 (CH, *C*HMe), 57.22 (d, J_{CP} = 7.7 Hz, CH, *C*HMe), 66.28 (d, J_{CP} = 7.0 Hz, CH, Cp), 68.03 (d, J_{CP} = 5.5 Hz, CH, Cp), 69.50 (d, J_{CP} = 7.0 Hz, CH, Cp), 70.65 (CH, Cp′), 71.13 (CH, Cp′), 71.21 (CH, Cp), 71.48 (d, J_{CP} = 3.8 Hz, CH, Cp), 74.09 (d, J_{CP} = 8.7 Hz, CH, Cp), 78.92 (d, J_{CP} = 42.8 Hz, C, Cp), 82.36 (d, J_{CP} = 50.7 Hz, C, Cp), 91.53 (d, J_{CP} = 12.8 Hz, C, Cp), 92.82 (d, J_{CP} = 14.0 Hz, C, Cp), 115.14 (CH, HC═CH Im), 116.67 (CH, HC═CH Im), 126.10 (d, J_{CP} = 54.1 Hz, C, P*Ph*$_2$), 127.18 (d, J_{CP} = 8.4 Hz, CH, P*Ph*$_2$), 127.51 (d, J_{CP} = 9.7 Hz, CH, P*Ph*$_2$), 128.50 (CH, P*Ph*$_2$), 128.88 (CH, P*Ph*$_2$), 129.88 (CH, P*Ph*$_2$), 130.15 (CH, P*Ph*$_2$), 130.56 (CH, P*Ph*$_2$), 131.49 (d, J_{CP} = 8.9 Hz, CH, P*Ph*$_2$), 132.68 (d, J_{CP} = 56.7 Hz, C, P*Ph*$_2$), 133.69 (d, J_{CP} = 15.0 Hz, CH, P*Ph*$_2$), 134.06 (d, J_{CP} = 7.6 Hz, CH, P*Ph*$_2$), 136.72 (d, J_{CP} = 10.2 Hz, CH, P*Ph*$_2$), 139.82 (d, J_{CP} = 48.3 Hz, C, P*Ph*$_2$), 141.07 (d, J_{CP} = 48.9 Hz, C, P*Ph*$_2$), 178.70 (t, J_{CP} = 15.5, C−Ru, Im). ^{31}P NMR (CD_2Cl_2): δ 34.03 (d, J_{PP} = 33.3 *P*Ph$_2$), 74.29 (d, J_{PP} = 33.5 *P*Ph$_2$).

(OC-6)-1,3-Bis[(*R*)-1-((*S*)-2-diphenylphosphino-κ*P*-ferrocenyl)ethyl]imidazol-2-ylideneiodobisacetonitriloruthenium(II), [RuI(PCP)(NCCH$_3$)$_2$] (8). A solution of **7a** (140.7 mg, 0.125 mmol) and $[OEt_3]PF_6$ (67.6 mg, 0.27 mmol, 2 equiv) in $NCCH_3$ (9 mL) was stirred overnight. After concentrating the solution in vacuo to a volume of 2 mL the complex was precipitated by the addition of hexane. The product was filtered off and washed three times with Et_2O. Yield: 163 mg (0.123 mmol, 98%), orange solid. ^{1}H NMR (CD_2Cl_2): δ 1.69 (d, J_{CHMe} = 7.2 Hz, 6 H, CH*Me*), 2.16 (s, 6 H, $NCCH_3$), 2.29 (s, 3 H, not coordinating $NCCH_3$), 3.64 (s, 10 H, Cp′), 4.15 (m, 2 H, Cp), 4.43 (t, J_{CHCH} = 2.6 Hz, 2 H, Cp), 4.61 (m, 2 H, Cp), 5.90 (q, J_{CHMe} = 7.2 Hz, 2 H, C*H*Me), 6.73 (br, 4 H, P*Ph*$_2$), 7.26 (s, 2 H, HC═CH Im), 7.40 (m, J_{CHCH} = 7.5 Hz, 6 H, P*Ph*$_2$), 7.75 (m, J_{CHCH} = 7.4 Hz, 6 H, P*Ph*$_2$), 7.56 (m, J_{CHCH} = 6.9 Hz, 4 H, P*Ph*$_2$). ^{13}C NMR (CD_2Cl_2): δ 3.76 (CH_3, not coordinating $NCCH_3$), 4.46 (CH_3, $NCCH_3$), 16.87 (CH_3, CH*Me*), 50.84 (CH, *C*HMe), 66.08 (d, J_{CP} = 3.0 Hz, CH, Cp), 70.45 (CH, Cp′), 70.60 (CH, Cp), 74.40 (d, J_{CP} = 7.6 Hz, CH, Cp), 77.18 (t, J_{CP} = 21.4 Hz, C, Cp), 92.76 (t, J_{CP} = 7.9 Hz, C, Cp), 118.81 (CH, HC═CH Im), 128.22 (t, J_{CP} = 4.5 Hz, CH, P*Ph*$_2$), 128.93 (t, J_{CP} = 5.1 Hz, CH, P*Ph*$_2$), 129.10 (CH, P*Ph*$_2$), 129.52 (C, $NCCH_3$), 129.74 (C, not coordinating $NCCH_3$), 131.40 (t, J_{CP} = 22.1 Hz, C, P*Ph*$_2$), 131.86 (CH, P*Ph*$_2$), 132.00 (t, J_{CP} = 4.8, CH Hz, P*Ph*$_2$), 134.58 (t, J_{CP} = 6.2, CH Hz, P*Ph*$_2$), 135.48 (t, J_{CP} = 23.6 Hz, C, P*Ph*$_2$), 167.17 (C−Ru, Im). ^{31}P NMR (CD_2Cl_2): δ −144.32 (heptet, J_{PF} = 710.9 Hz, PF_6), 17.18 (*P*Ph$_2$).

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Supporting Information Available: Full crystallographic data for compounds **5** and **7a** are provided as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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