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Hybrid Ligands with N-Heterocyclic Carbene and Chiral Phosphaferrocene Components

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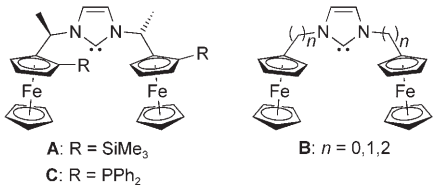
Abstract: N-Heterocyclic carbenes (NHCs) possessing one or two 3,4-dimethylphosphaferrocenyl substituents and either methylene or ethylene alkyl bridges have been prepared. These carbenes turned out to be remarkably stable and were characterized by NMR methods and partly by mass spectrometry. Their molybdenum and ruthenium complexes were examined in order to determine the electronic properties and the coordination behaviour of these chiral PC- and PCP-chelate ligands, which combine a NHC unit as a strong σ-donor with π-accepting phosphaferrocene moieties. Crystal structures of one ligand precursor and of three complexes have been determined.

Keywords: chelates · molybdenum · N-heterocyclic carbenes · phosphaferrocenes · ruthenium

Introduction

N-Heterocyclic carbenes (NHCs) have become an intensively studied class of ligands for coordination chemistry and homogeneous catalysis. Because of their modular structures, many modifications of the basic imidazole-based motif have been produced.[1] While one area of these studies has been directed towards the elucidation of the factors determining the stabilities of the free carbenes in terms of electronic and steric effects,[2] another part of the investigations has focused on potential applications of NHCs, mainly as ligands for transition-metal-catalysed reactions.[3] In the latter context, significant recent developments include, for example, the incorporation of NHC moieties into multidentate chelate ligands[4] and the chiral modification of NHCs with implications for their use in asymmetric catalysis.[5] Ferrocenyl-based substituents have been used both as sterically demanding groups (**A** and **B**; Scheme 1), some of which are chiral,[6] and as scaffolds for the attachment of additional donor groups in multidentate NHC ligands (**C**).[7] On the other hand, phosphaferrocene derivatives are interesting chiral ligands featuring electron-poor, good acceptor-type P atoms in a unique topological arrangement. They have proven to be useful in stereodiscriminating stoichiometric and catalytic reactions,[8] while the number of NHC complexes affording high *ee* values is still quite limited.[5]



A: R = $SiMe_3$
C: R = PPh_2
B: n = 0,1,2

Scheme 1. Ferrocenyl-substituted NHCs published by Togni (**A**, **C**) and Bildstein (**B**).

Here we report a new type of multidentate hybrid ligand in which a powerful σ-donor NHC is functionalized with one (**4**, **13**) or two (**5**, **14**, **15**) chiral π-acidic phosphaferrocene groups, giving bidentate PC- or tridentate PCP-ligands. These ligands are believed to be well suited for asymmetric catalysis, because of the closeness of the chiral information to the metal,[8e] the bulky substituents,[5b] and the electronic differentiation, which should be more distinct than in other well investigated PN-ligands.[9]

Results and Discussion

Ligand synthesis: Imidazolium cations $\mathbf{2}^+$ and $\mathbf{3}^+$ were straightforwardly prepared by treatment of the trimethylammonium salt **1I** (available from 3,4-dimethylphosphaferrocene-2-carbaldehyde by reductive amination[8f] and subsequent methylation of the amine) with imidazole or N-methylimidazole, respectively (Scheme 2). If desired, the ammo-

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nium salt **1I** may be obtained in enantiomerically pure form in gram quantities. However, for the sake of preparative convenience, the exploratory investigations described in this paper were carried out with the racemic compound. Thus, cation $\mathbf{2}^+$ was obtained as a racemic mixture, while $\mathbf{3}^+$ was formed as its diastereomeric *rac* and *meso* forms, which gave rise to slightly different $^{31}P\{^1H\}$ NMR resonances at δ −72.6 and −72.8 ppm, respectively ($CDCl_3$). The ^1H resonance for the proton at C2 in compound $\mathbf{3}^+$ depends strongly on the counter anion and varies from 8.61 ppm for the PF_6 salt to 11.26 ppm for the chloride. Such behaviour was also observed for the related ferrocene compounds and led to an investigation of their application as anion receptors.[10] The molecular connectivity of the imidazolium cation $\mathbf{3}^+$ as the iodide salt containing an additional molecule of water could be unambiguously confirmed by X-ray crystal structure determination (Figure 1). However, because of the poor crystal quality the precision of the geometrical parameters does not allow for a meaningful discussion.

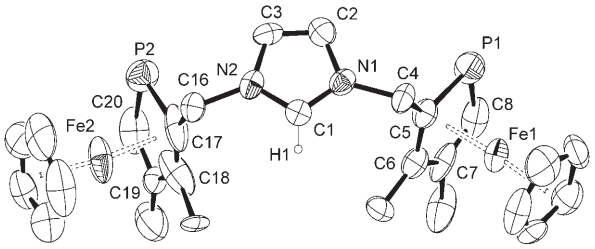
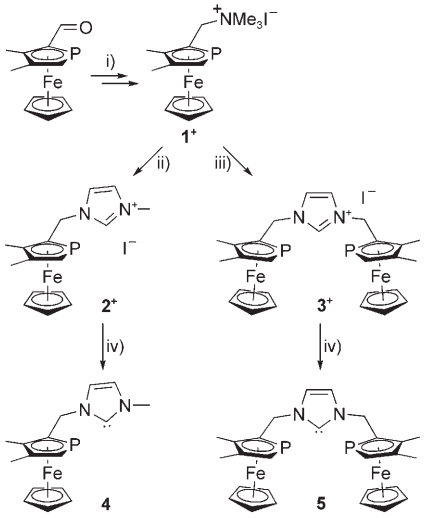


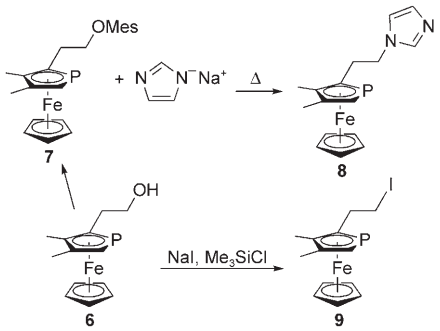
Figure 1. Molecular structure of imidazolium cation $\mathbf{3}^+$ in the solid state. Iodide, the water molecule and all hydrogen atoms except the one at C1 are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level.



Scheme 2. Synthesis of phosphaferrocenyl-substituted imidazolin-2-ylidenes with single methylene groups between the heterocycles. i) $HNMe_2$ (1 equiv), NEt_3 (2 equiv), $TiCl_4$ (1 equiv), CH_2Cl_2, −70 °C→RT, 12 h, then $NaBH_3CN$ (1.5 equiv), MeOH; after workup: MeI (1.1 equiv), CH_2Cl_2/Et_2O; ii) 1-methylimidazole (1 equiv), CH_3CN, reflux, 6 h; iii) imidazole (0.475 equiv), CH_3CN, reflux, 12 h; iv) NaH (excess), DMSO/THF.

Subsequent deprotonation of the imidazolium salts with NaH in THF in the presence of catalytic amounts of DMSO yielded the carbenes **4** and **5** in virtually quantitative yields within five minutes. Carbene **4** is stable for days in THF solution in the absence of air, **5** even for weeks. To the best of our knowledge this is the highest stability so far observed for NHCs with metallocene substituents,[6i] even in comparison with the structurally very similar ferrocenyl-substituted NHCs **B** ($n=1$) and **C** prepared by Bildstein[6d] and Togni.[7a] Both carbenes were characterized by EI mass spectrometry and NMR spectroscopy. As expected, the ^1H NMR signals for the protons at C4 and C5, and also the $^{31}P\{^1H\}$ resonances, are shifted to higher field than in their imidazolium precursors ($[D_8]$THF). No $^{13}C\{^1H\}$ signal could be detected for the carbene C atoms, as is frequently observed.

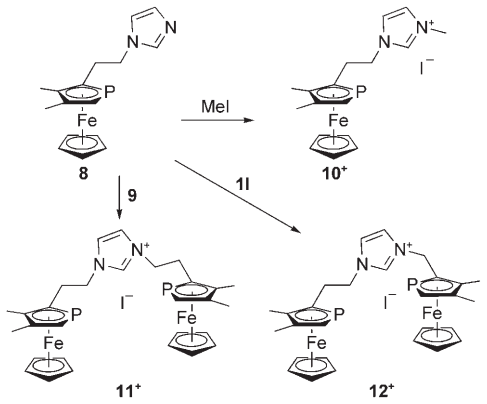
The synthesis of related carbenes incorporating longer alkyl chains between the phosphaferrocenyl substituents and the NHC cores is more elaborate. Granting access to several new imidazolium salts, the imidazole derivative **8** (Scheme 3) proved to be the first target molecule of the reaction sequence. The crucial step was the elongation of the phosphaferrocene aldehyde by one CH_2 group by an established procedure.[11] The extended aldehyde was then converted into the alcohol **6** by reduction with sodium borohydride. The mesylate **7** available from this reacted with sodium imidazolide in THF at reflux to give the desired intermediate **8** as a red oil in good yield (Scheme 3). Heating



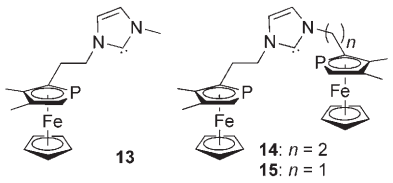
Scheme 3. Synthesis of new phosphaferrocene compounds.

of **8** variously with methyl iodide, iodide **9** (available from the elongated phosphaferrocene alcohol **6** as described by Olah[12]), or the ammonium salt **1I** in acetonitrile led to the solid imidazolium salts **10I**, **11I**, and **12I**, respectively (Scheme 4). As the phosphaferrocene aldehyde had been used as a racemic mixture, cation $\mathbf{11}^+$ was obtained as a mixture of *rac* and *meso* diastereomers showing signals at δ −77.2 and −77.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Cation $\mathbf{10}^+$ was isolated as a racemic mixture, while $\mathbf{12}^+$ consists of two diastereomers, each racemic.

Just like their methylene-bridged analogues, cations $\mathbf{10}^+$, $\mathbf{11}^+$ and $\mathbf{12}^+$ can be deprotonated with NaH in THF/DMSO to afford the NHCs **13**, **14** and **15**, respectively. However,

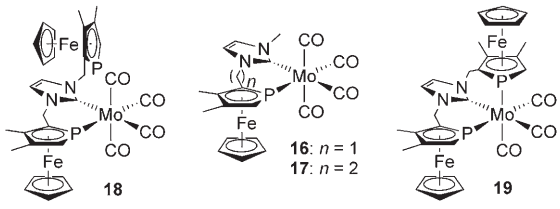


Scheme 4. Synthesis of the NHC precursors with extended alkyl bridges.



the stabilities of the carbenes with longer alkyl bridges are reduced in relation to **4** and **5**, which may be explained by the less efficient steric protection of the carbene centre. As the phosphaferrocenyl groups are attached to the heterocyclic carbene through alkyl spacers, any electronic interaction between the NHC and the substituents can be neglected for all ligands discussed in this paper.[6a–c] Because of their limited stabilities, the complete characterization of the carbenes **13**, **14** and **15** proved difficult, as the ^{1}H NMR spectra showed minor signals corresponding to unknown impurities.

Complexation studies: The abilities of the phosphaferrocenyl-substituted NHCs to act as bi- and tridentate chelate ligands were demonstrated by the preparation of molybdenum and ruthenium complexes. Heating of ligands **4**, **5** and **13** with [Mo(CO)$_6$] yielded Mo carbonyl complexes **16**, **18**



and **17**, respectively.[13] Treatment of **5** with [Mo(MeCN)$_3$(CO)$_3$] gave *fac*-**19**. In all cases, coordination leads to a considerable downfield shift in the ^{31}P{^{1}H} NMR spectra and reduction of the ^{2}J(P,H) coupling constants for the α-protons of the phospholyl rings in the ^{1}H NMR spectra. The ^{13}C{^{1}H} spectrum of **16** in [D$_8$]THF shows a doublet for the carbene carbon at a typical shift[13] of 189 ppm with a ^{2}J(P,C) coupling of 15 Hz. This signal could not be observed in the case of complex **17**, with the expanded chelate ring. Both diastereomers of **18**, however, again showed doublets for the carbene carbons at the expected chemical shifts. The two isomers *rac*- and *meso*-**5** each give rise to a pair of enantiomeric complexes of type **18**, so four singlets are observed in the ^{31}P{^{1}H} NMR spectrum, two in the range for coordinated phosphaferrocene units and two in the region expected for the free P-donor. In complex **19**, containing *meso*-**5** as ligand, the two P atoms are equivalent, so one singlet is observed in the ^{31}P{^{1}H} spectrum, while *rac*-**5** affords a C_1-symmetric complex **19**, due to the facial ligand arrangement. Two doublets are accordingly recorded in the ^{31}P{^{1}H} NMR spectrum for the latter isomer, with a ^{2}J(P,P) coupling of 36 Hz.

Orange crystals of complexes **16** and **17** suitable for X-ray analysis were obtained by layering chloroform solutions of **16** and **17** with hexane. Each complex crystallizes in the monoclinic space group type $P2_1/n$ with $Z=4$. Representative geometrical data for both structures are summarized in Table 1.

Table 1. Selected interatomic distances [Å] and angles [°] in molybdenum complexes **16** and **17**.

	16	**17**
Mo1–C1	2.300(4)	2.268(5)
Mo1–P1	2.4863(11)	2.5057(13)
Mo1–C18	1.979(5)	1.966(6)
Mo1–C17	1.988(5)	1.968(5)
Mo1–C19	2.036(4)	2.040(6)
Mo1–C20	2.050(4)	2.038(6)
P1-Mo1-C1	79.85(10)	82.75(11)
C5-P1-Mo1	116.27(13)	132.63(14)
C8-P1-Mo1	153.27(14)	137.0(2)
N1-C1-Mo1	129.0(3)	128.3(3)
N2-C1-Mo1	128.1(3)	129.2(4)
N1-C1-N2	102.8(3)	102.0(4)
C5-P1-C8	90.36(19)	90.2(2)
C18-Mo1-P1-C8	25.4(3)	34.3(3)
P1-Mo1-C1-N1	−36.2(3)	−43.3(3)

The molecular structure of **16** (Figure 2) features a distorted octahedral arrangement around the central Mo atom (P1-Mo1-C1 79.85(10)°) and a distorted coordination mode of the P-ligand (C5-P1-Mo1 116.27(13)°; C8-P1-Mo1 153.27(14)°). The Mo–CO distances *trans* to P and NHC are identical within experimental error and do not reflect the different donor/acceptor properties of these two ligand moieties. However, these Mo–CO distances are significantly shorter than those involving the other two, mutually *trans*, CO groups.

The IR spectrum of complex **19** shows a sharp band at 1924 cm^{-1} and a broad one at 1823 cm^{-1} for the CO stretching vibrations. These wavenumbers fall in the middle of the range observed for *fac*-[MoL$_3$(CO)$_3$] complexes of ligands with different π-acceptor strengths and are comparable to the values of 1934 and 1835 cm^{-1} found for [Mo(PPh$_3$)$_3$(CO)$_3$].[1c] Such an averaging of the electronic effects

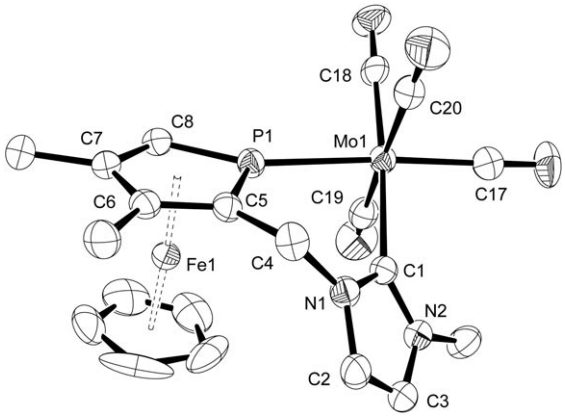


Figure 2. Molecular structure of complex **16** in the solid state. Hydrogen atoms are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

would be expected for the interaction of the NHC—which can be mainly regarded as a σ-donor—and the π-accepting phosphaferrocene moieties.

The Mo–P distance of 2.4863(11) Å in **16** lies well within the range of bond lengths found in comparable Mo complexes with bidentate phosphaferrocene ligands.[8k,l,11] The Mo–$C_{carbene}$ distance of 2.300(4) Å falls in the upper range usually observed for related complexes, while the N-C-N angle (102.8(3)°) is remarkably acute.[14]

The X-ray structure of **17** (Figure 3), with a seven-membered chelate ring, shows a less distorted octahedrally coordinated molybdenum centre than is seen in complex **16** (P1-Mo1-C1 82.75(11)°). The elongation of the alkyl bridge further allows the phosphaferrocene unit to coordinate almost symmetrically to molybdenum (C5-P1-Mo1 132.63(14)°; C8-P1-Mo1 137.0(2)°).

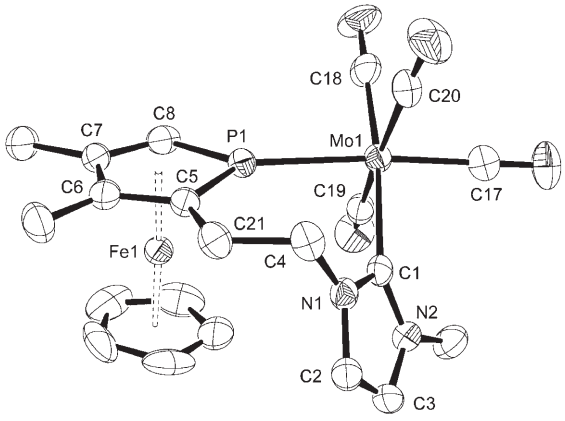
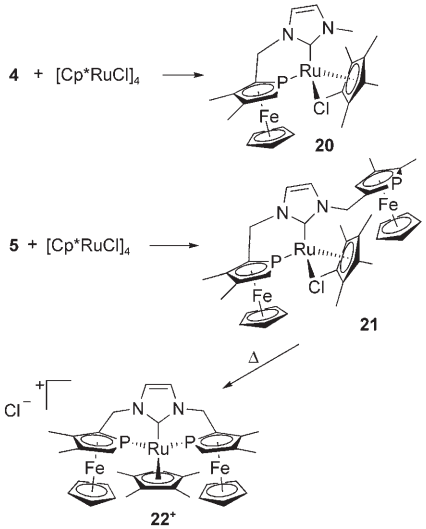


Figure 3. Molecular structure of complex **17** in the solid state. Hydrogen atoms are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

A seven-membered chelate ring is thus essential in order to achieve a relaxed geometry for phosphaferrocenes with additional NHC-donor function, whereas six-membered chelate rings are sufficient for bidentate ligands bearing one phosphaferrocene and one phosphine unit.[11] The other angles and bond lengths show no significant differences, except for the fact that the N-C-N angle (102.0(4)°) is even more acute than in **16**. The tridentate, facial coordination mode in complex **19** could also be confirmed by X-ray diffraction. However, although the connectivity of the complex was unambiguously determined, the final refinement of the structural model was not suitable for extraction of meaningful distances and angles, due to the poor crystal quality.

Addition of carbene **4** to a suspension of $[Cp^*RuCl]_4$[15] in THF afforded complex **20** (Scheme 5) with a stereogenic Ru atom. This complex was obtained as a single diastereomer, due to the steric demand of the bulky Cp*Ru and CpFe fragments, as also observed earlier with other bidentate phosphaferrocene-based ligands.[8f–j] The carbene carbon couples to the phosphorus atom with a coupling constant of 27 Hz at a chemical shift of 174.3 ppm and thus confirms the bidentate coordination mode of ligand **4**.



Scheme 5. Ruthenium complexes with phosphaferrocenyl-substituted NHCs.

Treatment of **5** with the same Ru precursor complex gave complex **21**, as shown by a $^{31}P\{^1H\}$ NMR spectrum of the crude product that featured several signals for coordinated and uncoordinated phosphaferrocene groups in a 1:1 ratio. The intermediate complex **21**, with a bidentate ligand coordination mode, could not be isolated in pure form because it transformed into the cationic species $\mathbf{22}^+$ either on heating or upon changing of the solvent, which was essential for column chromatography. Because of the tridentate PCP coordination of the ligand **5**, complex $\mathbf{22}^+$ containing *meso*-**5** is C_s-symmetric and features one singlet in the $^{31}P\{^1H\}$ NMR spectrum, while $\mathbf{22}^+$ with *rac*-**5** exhibits C_1 symmetry and is characterized by two doublets, each with a ^2J(P,P) coupling constant of 52 Hz.

Crystals suitable for X-ray diffraction containing the complex cation **22**$^+$ with the *meso* ligand were obtained by slow diffusion of hexane into a chloroform/dichloromethane solution. Although an elemental analysis confirmed the composition of complex **22Cl** as the chloride, the recrystallisation procedure to obtain X-ray quality crystals led to the formation of **22**$^+$ as the tetrachloroferrate salt, in which the charge of two cations is compensated by one $FeCl_4^{2-}$ dianion, the origin of which is unknown, though presumably it is formed by partial decomposition of the phosphaferrocene unit in cation **22**$^+$. Complex $(\mathbf{22})_2FeCl_4$ crystallizes in the monoclinic $P2_1/n$ spacegroup as a solvate containing one $CHCl_3$ and two CH_2Cl_2 molecules. The complex shows a distorted octahedral coordination sphere at the Ru atom (C1-Ru1-P1 82.5(3)°; P1-Ru1-P2 105.03(14)°; Figure 4), with the bonds (2.232(4) and 2.250(4) Å) are also rather short. The C-P-C angles[8f–h] in the phospholyl rings, of 86.9(6) and 88.6(7)°, and the N-C-N angle[16,17] at the carbene carbon of 98.6(10)°—usually about 102 to 104°—are exceptionally acute and thus confirm the steric strain in this air-stable complex.

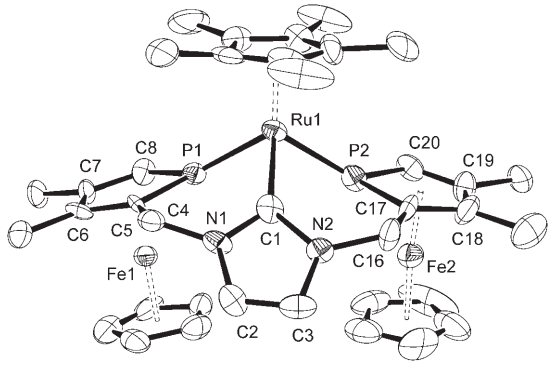
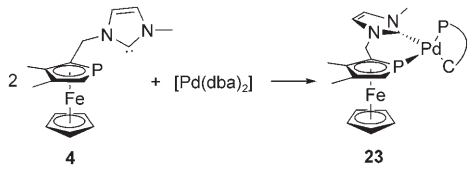


Figure 4. Molecular structure of one cation of $(\mathbf{22})_2FeCl_4$ with *meso*-**5** as ligand in the solid state. The $FeCl_4^{2-}$ anion, the solvating $CHCl_3$ and CH_2Cl_2 molecules and all hydrogen atoms are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å] and angles [°]: Ru1–C1 2.028(13), Ru1–P1 2.232(4), Ru1–P2 2.250(4), C1–N1 1.385(14), N1–C2 1.345(13), C2–C3 1.323(15), C3–N2 1.369(13), N2–C1 1.426(14), P1–C5 1.722(11), C5–C6 1.396(14), C6–C7 1.400(15), C7–C8 1.399(15), C8–P1 1.711(11), P1-Ru1-P2 105.03(14), C1-Ru1-P1 82.5(3), C1-Ru1-P2 84.0(4), N1-C1-N2 98.6(10), C5-P1-Ru1 116.6(4), C8-P1-Ru1 149.6(4), C5-P1-C8 86.9(6), C17-P2-C20 88.6(7).

Several attempts to prepare palladium complexes of the new NHC ligands by treatment of solutions of carbenes **4** or **5** with several Pd precursor complexes were made. In all cases except for one, however, decomposition occurred and palladium black was obtained. The only successful transformation was the reaction of **4** with $[Pd(dba)_2]$, leading to the bis(carbene) Pd^0 complex **23**, which could be isolated in low yield (Scheme 6). The proton NMR spectrum confirms the bidentate coordination mode of the ligands through the reduction of the ^2J(P,H) coupling constant for the α-protons and the typical shift of the protons at C4 and C5 of the N-heterocycle to higher field. In the $^{31}P\{^1H\}$ NMR spectrum, one singlet and two doublets each with a ^2J(P,P) coupling constant of 543 Hz are observed. From racemic ligand, one would expect two doublets for the C_1-symmetric, heterochiral complex with one pair of enantiomers and two singlets for the two possible diastereomers of the C_2-symmetric, homochiral complex. The lack of one singlet in the recorded $^{31}P\{^1H\}$ spectrum implies that the formation of complex **23** proceeds diastereoselectively. No peaks confirming the identity of the new palladium complex could be detected by mass spectrometry. Layering a methylene chloride solution of **23** with hexane gave red crystals that were unfortunately too small for X-ray analysis.



Scheme 6. Synthesis of bis(carbene) bischelate complex **23**.

Cp* ligand and the two CpFe moieties extending in opposite directions of space. Because of additional repulsion between the two CpFe fragments the P–Ru vectors are tilted out of the phospholyl mean planes away from the CpFe fragments by 18.6 and 26.5°, respectively. To the best of our knowledge this is the highest displacement so far observed.[8f,j] Even the C–Ru vector is tilted out of the NHC mean plane by 4.5°. Moreover, the P ligand shows a distorted coordination mode involving the Ru-P-C angles (C5-P1-Ru1 116.6(4)°; C8-P1-Ru1 149.6(4)°). The $Ru–C_{carbene}$ distance of 2.028(13) Å is shorter than those in published complexes with a NHC coordinated to a $Cp^{(*)}Ru$ fragment (about 2.10 Å)[16] and fits in the range typically observed for Ru complexes with PCP pincer-type NHCs.[7a,17] In comparison with previously reported Ru complexes with bidentate phosphaferrocene ligands (2.238(1)–2.2912(13) Å)[8f–h] the Ru–P

It is important to note that all imidazolium precursors of the NHCs with phosphaferrocenyl substituents described in this paper failed to give NHC complexes upon treatment with precursors bearing basic ligands such as $Pd(OAc)_2$, $Hg(OAc)_2$ or $[Ir_2(\mu\text{-}OMe)_2(\eta^4\text{-}cod)_2]$,[18] which are frequently used in NHC chemistry to give the desired carbene complexes. Thionation of the free carbenes with elemental sulfur is also impossible. In all cases, either decomposition or no reaction at all was observed. Hence it was also impossible to use the ligand-transfer protocol with Ag_2O established by Lin.[19] This discrepancy in the chemical reactivity in relation to the ferrocenyl-substituted NHCs[6d] must be ascribed to the phosphaferrocene groups. Any influence of the length of the alkyl spacer can be ruled out, as further preliminary coordination experiments on the elongated NHCs showed the same behaviour.

Catalysis: Given the recent successful application of bidentate phosphine-NHC ligands in cross-coupling reactions,[4d,7f] a preliminary study relating to the catalytic applicability of the new palladium complex **23** in the Suzuki cross-coupling reaction[20] between *p*-bromoacetophenone and phenylboronic acid was undertaken. The reaction was conducted in the presence of **23** (0.01 mol%) and K_2CO_3 as base. After the reaction mixture had been heated at reflux in toluene for 2 h (3, 4 h), 88% (92, 97%) conversion had been achieved, and pure *p*-phenylacetophenone was isolated in >95% yield after workup.

Conclusion

We have introduced phosphaferrocenyl-substituted N-heterocyclic carbenes as a new class of chiral chelate ligands. Because of their remarkable stabilities in solution under inert atmosphere—particularly in relation to the analogous ferrocene compounds—these carbenes could be characterized by NMR spectroscopy and partly by mass spectrometry. Molybdenum and ruthenium complexes were prepared in order to study the coordination behaviour of the new bi- and tridentate NHC ligands. X-ray analyses of the former complexes did not reveal the expected electronic differences between the strong σ-donor NHC and the π-accepting phosphaferrocene substituents but indicated the seven-membered chelate ring to be less strained than the six-membered one. A palladium complex of one of the new ligands showed catalytic activity in the Suzuki cross-coupling reaction. Further studies of the coordination chemistry and catalytic applications of the new compounds are currently in progress.

Experimental Section

General: All reactions were carried out under dry nitrogen by conventional Schlenk techniques. Solvents were dried and purified by standard methods. Alumina was heated at 200°C for 12 h, cooled to room temperature under high vacuum, deactivated with water (5%), and stored under nitrogen. NMR spectra were recorded on a Bruker Avance DRX 500 and a Bruker Avance DRX 200 spectrometer. ^{1}H and ^{13}C{^{1}H} spectra are referenced to the residual solvent signal, and ^{31}P{^{1}H} spectra to external H_3PO_4 (85%). Mass spectra were recorded on a Finnigan MAT 8200 (FAB, EI). Elemental analyses were performed by the Institute for Pharmaceutical Chemistry at the Heinrich-Heine-Universität Düsseldorf on a Perkin–Elmer 2400 Series II CHN elemental analyzer. IR spectra were obtained with a Bruker IFS 66 (KBr) and a Digilab Excalibur FTS 3500 (ATR). Pfc denotes a 3,4-dimethylphosphaferrocenyl group. 2-Dimethylaminomethyl-3,4-dimethylphosphaferrocene,[8f] 2-(3,4-dimethylphosphaferrocen-2-yl)ethanol (**6**),[11] [2-(3,4-dimethylphosphaferrocen-2-yl)ethyl] methylsulfonate (**7**),[11] and [Cp*RuCl]$_4$[15] were prepared by published procedures.

(3,4-Dimethylphosphaferrocen-2-yl)methyltrimethylammonium iodide (1I): A solution of 2-dimethylaminomethyl-3,4-dimethylphosphaferrocene (6.735 g, 23.30 mmol) in CH_2Cl_2 (60 mL)/diethyl ether (60 mL) was treated with methyl iodide (1.60 mL, 25.6 mmol, 1.1 equiv). After a few minutes a yellow solid precipitated. The crude product was filtered off and washed with diethyl ether (2×20 mL) to give **1I** as a yellow powder (8.710 g, 86%). ^{1}H NMR (200 MHz, [D$_6$]acetone, 25°C): δ=2.27 (s, 3H; CH_3), 2.48 (s, 3H; CH_3), 3.27 (s, 9H; NMe$_3$), 4.10 (d, ^2J(P,H)=37.1 Hz, 1H; α-CH), 4.35 (s, 5H; Cp), 4.41 (dd, ^2J(H,H)=13.8, ^3J(P,H)=5.5 Hz, 1H; CH_2NMe$_3$), 4.82 ppm (dd, ^2J(H,H)=13.8, ^3J(P,H)=15.6 Hz, 1H; CH_2NMe$_3$); ^{13}C{^{1}H} NMR (126 MHz, [D$_6$]DMSO, 25°C): δ=14.2 (s; CCH_3), 16.4 (s; CCH_3), 51.0 (d, ^4J(P,C)=3.4 Hz; NMe$_3$), 65.0 (d, ^2J(P,C)=19.5 Hz; CH_2), 72.5 (s; Cp), 78.8 (d, ^1J(P,C)=57.6 Hz; α-CH), 80.7 (d, ^1J(P,C)=60.4 Hz; α-CCH_2), 95.8 (d, ^2J(P,C)=4.3 Hz; CCH_3), 97.4 ppm (d, ^2J(P,C)=7.2 Hz; CCH_3); ^{31}P{^{1}H} NMR (81 MHz, [D$_6$]acetone, 25°C): δ=−57.8 ppm (s); MS (FAB): *m*/*z* (%): 304 (24) [*M*]$^+$, 245 (100) [PfcCH$_2$]$^+$; elemental analysis calcd (%) for $C_{15}H_{23}FeINP$ (431.1): C 41.76, H 5.38, N 3.25; found: C 41.50, H 5.12, N 3.22.

1-[(3,4-Dimethylphosphaferrocen-2-yl)methyl]-3-methylimidazolium iodide (2I): A solution of compound **1I** (500 mg, 1.16 mmol) in acetonitrile (10 mL) was treated with 1-methylimidazole (92 μL, 1.2 mmol). After the reaction mixture had been heated under reflux for 6 h, removal of the solvent gave **2I** as a yellow powder. The product can optionally be washed with HCl (2N, 2×5 mL) and water (1×5 mL) and then dried under vacuum. Yield without wash: 527 mg (100%); ^{1}H NMR (200 MHz, [D$_8$]THF+[D$_6$]DMSO (5%), 25°C): δ=2.26 (s, 3H; CH_3), 2.37 (s, 3H; CH_3), 3.92 (d, ^2J(P,H)=36.9 Hz, 1H; α-CH), 4.01 (s, 3H; NCH_3), 4.39 (s, 5H; Cp), 4.98 (dd, ^2J(H,H)=14.7, ^3J(P,H)=6.2 Hz, 1H; CH_2), 5.57 (dd, ^2J(H,H)=14.7, ^3J(P,H)=14.7 Hz, 1H; CH_2), 7.73 (brs, 1H; *H*C=CH), 7.79 (brs, 1H; HC=C*H*), 9.47 ppm (s, 1H; NC*H*N); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25°C): δ=14.1 (s; CCH_3), 16.8 (s; CCH_3), 37.1 (s; NCH_3), 50.3 (d, ^2J(P,C)=23.3 Hz; CH_2), 72.6 (s; Cp), 77.7 (d, ^1J(P,C)=58.6 Hz; α-CH), 87.0 (d, ^1J(P,C)=59.4 Hz; α-CCH_2), 94.3 (d, ^2J(P,C)=4.5 Hz; CCH_3), 97.6 (d, ^2J(P,C)=7.5 Hz; CCH_3), 121.1 (s; HC=CH), 123.5 (s; HC=C*H*), 135.4 ppm (s; NC*H*N); ^{31}P{^{1}H} NMR (81 MHz, [D$_8$]THF+[D$_6$]DMSO (5%), 25°C): δ=−73.8 ppm (s); MS (FAB): *m*/*z* (%): 327 (44) [*M*]$^+$, 245 (100) [PfcCH$_2$]$^+$; elemental analysis calcd (%) for $C_{16}H_{20}FeIN_2P$ (454.1): C 42.32, H 4.44, N 6.17; found: C 42.38, H 4.62, N 5.93.

***rac*-/*meso*-1,3-Bis-[(3,4-dimethylphosphaferrocen-2-yl)methyl]imidazolium iodide (3I)**: Imidazole (167 mg, 2.45 mmol, 0.475 equiv) was added to a solution of compound **1I** (2.226 g, 5.16 mmol) in acetonitrile (50 mL). The reaction mixture was heated at reflux overnight and then evaporated to dryness. The yellow-red solid was treated with HCl (2N, 20 mL) and ultrasound until the powder was clear yellow and the aqueous phase slightly red. The crude product was filtered off, washed with HCl (2N, 2×20 mL) and water (1×20 mL), and then dried under vacuum (1.361 g, 81%); the diastereomers were obtained in a 1:1 ratio; ^{1}H NMR (200 MHz, CDCl$_3$, 25°C): δ=2.18, 2.19, 2.23, 2.27 (4×s, 24H; CH_3), 3.88 (d, ^2J(P,H)=36.8 Hz, 4H; α-CH), 4.28 (s, 20H; Cp), 4.71 (dd, ^2J(H,H)=14.6, ^3J(P,H)=5.9 Hz, 4H; CH_2), 5.45 (dd, ^2J(H,H)=14.6, ^3J(P,H)=14.6 Hz, 4H; CH_2), 7.03 (brs, 4H; *H*C=C*H*), 10.45, 10.51 ppm (2×s, 2H; NC*H*N); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25°C): δ=14.1, 14.2 (2×s; CCH_3), 16.8 (2×s; CCH_3), 50.4 (brd, ^2J(P,C)=23.3 Hz; CH_2), 72.7 (s; Cp), 77.6 (d, ^1J(P,C)=58.6 Hz; α-CH), 87.3, 87.4 (2×d, ^1J(P,C)=59.2 Hz; α-CCH_2), 94.3, 94.4 (2×d, ^2J(P,C)=4.5 Hz; CCH_3), 97.6 (brd, ^2J(P,C)=7.0 Hz; CCH_3), 120.7 (brs; HC=C*H*), 134.5 ppm (2×s; NC*H*N); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 25°C): δ=−72.8 (s), −72.6 ppm (s); MS (FAB): *m*/*z* (%): 557 (16) [*M*]$^+$, 245 (100) [PfcCH$_2$]$^+$; elemental analysis calcd (%) for $C_{27}H_{31}Fe_2IN_2P_2$ (684.1): C 47.40, H 4.57, N 4.09; found: C 47.32, H 4.71, N 4.00. Red crystals suitable for X-ray analysis were grown by slowly cooling down a hot solution of **3I** in MeOH.

General procedure for the preparation of the N-heterocyclic carbenes: In a small Schlenk tube the corresponding NHC precursor was dissolved or suspended in an appropriate volume of DMSO/THF and treated with an excess of NaH. During the reaction, which could be tracked by means of the hydrogen evolution, the colour of the solution changed from yellow to orange or red. When the gas evolution had stopped, either the desired precursor complex was added to the suspension containing the carbene or the Schlenk tube was centrifuged until the sedimentation of NaI and excess NaH. The supernatant carbene solution was then transferred to the other reaction mixture by syringe.

1-[(3,4-Dimethylphosphaferrocen-2-yl)methyl]-3-methylimidazolin-2-ylidene (4): In a small Schlenk tube, NHC precursor **2I** (80 mg, 0.18 mmol) was suspended in DMSO (0.2 mL)/THF (2.0 mL) and deprotonated by

the general procedure. Yield: quantitative (according to the NMR spectra); ^{1}H NMR (200 MHz, [D$_8$]THF+[D$_6$]DMSO (10%), 25°C): δ=2.23 (s, 3H; CCH_3), 2.31 (s, 3H; CCH_3), 3.74 (s, 3H; NCH_3), 3.80 (d, ^2J(P,H)=36.3 Hz, 1H; α-CH), 4.29 (s, 5H; Cp), 4.65 (dd, ^2J(H,H)=14.5, ^3J(P,H)=6.9 Hz, 1H; CH_2), 5.57 (dd, ^2J(H,H)=14.5, ^3J(P,H)=14.5 Hz, 1H; CH_2), 7.05 (s, 1H; HC=CH), 7.10 ppm (s, 1H; HC=CH); ^{13}C{^{1}H} NMR (126 MHz, [D$_8$]THF+[D$_6$]DMSO (10%), 25°C): δ=12.9 (s; CCH$_3$), 15.8 (s; CCH$_3$), 36.6 (s; NCH$_3$), 49.9 (d, ^2J(P,C)=21.0 Hz; CH$_2$), 71.7 (s; Cp), 76.0 (d, ^1J(P,C)=58.5 Hz; α-CH), 93.7 (d, ^2J(P,C)=4.9 Hz; CCH$_3$), 94.5 (d, ^1J(P,C)=58.4 Hz; α-CCH$_2$), 96.0 (d, ^2J(P,C)=6.8 Hz; CCH$_3$), 117.6 (d, ^4J(P,C)=2.8 Hz; HC=CH), 119.2 ppm (s; HC=CH); ^{31}P{^{1}H} NMR (81 MHz, [D$_8$]THF+[D$_6$]DMSO (10%), 25°C): δ=−74.9 ppm (s); MS (EI, 70 eV): m/z (%): 326 (5) $[M]^+$, 245 (100) [PfcCH$_2$]$^+$.

***rac*-/*meso*-1,3-Bis-[(3,4-dimethylphosphaferrocen-2-yl)methyl]imidazolin-2-ylidene (5)**: In a small Schlenk tube NHC precursor **3I** (100 mg, 0.15 mmol) was dissolved in DMSO (0.1 mL)/THF (2.0 mL) and deprotonated by the general procedure. Yield: quantitative (according to the NMR spectra); ^{1}H NMR (200 MHz, [D$_8$]THF+[D$_6$]DMSO (5%), 25°C): δ=2.20, 2.21, 2.27, 2.30 (4×s, 24H; CH_3), 3.76 (d, ^2J(P,H)=36.8 Hz, 4H; α-CH), 4.26 (s, 20H; Cp), 4.61 (dd, ^2J(H,H)=14.4, ^3J(P,H)=6.9 Hz, 4H; CH_2), 5.04 (dd, ^2J(H,H)=14.4, ^3J(P,H)=14.4 Hz, 4H; CH_2), 6.94 ppm (brs, 4H; HC=CH); ^{13}C{^{1}H} NMR (126 MHz, [D$_8$]THF+[D$_6$]DMSO (5%), 25°C): δ=13.0 (2×s; CCH$_3$), 15.8 (2×s; CCH$_3$), 49.7 (brd, ^2J(P,C)=21.3 Hz; CH$_2$), 71.9 (s; Cp), 76.2 (d, ^1J(P,C)=58.4 Hz; α-CH), 92.7 (brd, ^1J(P,C)=62.3 Hz; α-CCH$_2$), 93.8, 93.9 (2×d, ^2J(P,C)=3.9 Hz; CCH$_3$), 96.3 (d, ^2J(P,C)=6.6 Hz; CCH$_3$), 118.8 ppm (brs; HC=CH); ^{31}P{^{1}H} NMR (81 MHz, [D$_8$]THF+[D$_6$]DMSO (5%), 25°C): δ=−75.2 (s), −75.0 ppm (s); MS (EI, 70 eV): m/z (%): 556 (2) $[M]^+$, 312 (49) $[M-$PfcCH$_2$+H]$^+$, 245 (100) [PfcCH$_2$]$^+$, 121 (44) [CpFe]$^+$.

1-[2-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]imidazole (8): Imidazole (482 mg, 7.08 mmol, 2 equiv) was dissolved in THF (20 mL) and deprotonated with excess NaH until the gas evolution had ceased. Mesylate **7** (1,111 g, 3.14 mmol) in THF (15 mL) was added, and the reaction mixture was then heated at reflux overnight. After quenching with water (5 mL), the crude product was extracted with dichloromethane and washed several times with aqueous NaOH (2N). The organic layer was dried over anhydrous sodium sulfate, filtered under nitrogen, and evaporated to dryness to give a red oil (892 mg, 87%). ^{1}H NMR (200 MHz, CDCl$_3$ 25°C): δ=1.90 (s, 3H; CCH_3), 2.13 (s, 3H; CCH_3), 2.55 (m, 2H; PfcCH_2CH$_2$), 3.69 (d, ^2J(P,H)=36.5 Hz, 1H; α-CH), 3.85 (m, 2H; PfcCH$_2$CH_2), 4.04 (s, 5H; Cp), 6.79 (brs, 1H; HC=CH), 6.98 (brs, 1H; HC=CH), 7.30 ppm (brs, 1H; NCHN); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25°C): δ=13.1 (s; CCH$_3$), 16.8 (s; CCH$_3$), 32.7 (d, ^2J(P,C)=19.6 Hz; PfcCH$_2$CH$_2$), 49.1 (brs; PfcCH$_2$CH_2), 71.9 (s; Cp), 75.8 (d, ^1J(P,C)=58.2 Hz; α-CH), 93.3 (d, ^2J(P,C)=4.8 Hz; CCH$_3$), 94.1 (d, ^1J(P,C)=58.8 Hz; α-CCH$_2$), 95.8 (d, ^2J(P,C)=6.7 Hz; CCH$_3$), 119.0 (brs; HC=CH), 129.2 (brs; HC=CH), 137.1 ppm (brs; NCHN); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 25°C): δ=−78.3 ppm (s); MS (FAB): m/z (%): 327 (98) $[M$+H]$^+$, 326 (100) $[M]^+$, 259 (44) [PfcCH$_2$CH$_2$]$^+$, 245 (29) [PfcCH$_2$]$^+$.

2-(3,4-Dimethylphosphaferrocen-2-yl)ethyl iodide (9): Alcohol **6** (475 mg, 1.72 mmol) and sodium iodide (773 mg, 5.16 mmol, 3 equiv) were dissolved in acetonitrile (5 mL) and treated with Me$_3$SiCl (0.44 mL, 3.44 mmol, 2 equiv). After the mixture had been stirred overnight at 50°C, diethyl ether (20 mL) and water (5 mL) were added with vigorous stirring. The organic layer was separated and washed successively with water (10 mL), aqueous Na$_2$S$_2$O$_3$ solution (10%, 3 mL) and brine (3 mL). The red solution was then dried over anhydrous sodium sulfate, filtered under nitrogen and evaporated to dryness to give an orange oil. The crude product was purified by column chromatography on neutral alumina (hexane). Yield: 293 mg (44%); ^{1}H NMR (500 MHz, CDCl$_3$, 25°C): δ=2.14 (s, 3H; CH_3), 2.19 (s, 3H; CH_3), 2.70 (m, 2H; CH_2CH$_2$I), 3.08 (m, 2H; CH$_2$CH_2I), 3.73 (d, ^2J(P,H)=36.3 Hz, 1H; α-CH), 4.11 ppm (s, 5H; Cp); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25°C): δ=4.7 (d, ^3J(P,C)=7.3 Hz; CH$_2$CH$_2$I), 13.6 (s; CCH$_3$), 17.0 (s; CCH$_3$), 35.6 (d, ^2J(P,C)=19.3 Hz; CH$_2$CH$_2$I), 72.0 (s; Cp), 75.8 (d, ^1J(P,C)=58.6 Hz; α-CH), 92.7 (d, ^2J(P,C)=4.9 Hz; CCH$_3$), 95.8 (d, ^2J(P,C)=6.8 Hz; CCH$_3$), 97.9 ppm (d, ^1J(P,C)=58.7 Hz; α-CCH$_2$); ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$, 25°C): δ=−78.4 ppm (s); MS (EI, 70 eV): m/z (%): 386 (100) $[M]^+$, 259 (71) [PfcCH$_2$CH$_2$]$^+$, 121 (33) [CpFe]$^+$.

1-[2-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]-3-methylimidazolium iodide (10I): Methyl iodide (0.18 mL, 2.8 mmol, 2 equiv) was added to a solution of **8** (461 mg, 1.41 mmol) in acetonitrile (10 mL). The reaction mixture was heated at reflux for 3 h and then evaporated to dryness. The residue was taken up in dichloromethane and washed with HCl (2N, 2× 10 mL) and water (1×10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. Evaporation of the solvent gave an orange solid (480 mg, 73%). ^{1}H NMR (200 MHz, CDCl$_3$, 25°C): δ=2.06 (s, 3H; CCH_3), 2.09 (s, 3H; CCH_3), 2.66 (m, 2H; PfcCH_2CH$_2$), 3.59 (d, ^2J(P,H)=36.5 Hz, 1H; α-CH), 3.97 (s, 3H; NCH_3), 4.04 (s, 5H; Cp), 4.22 (m, 2H; PfcCH$_2$CH_2), 7.28 (brs, 1H; HC=CH), 7.51 (brs, 1H; HC=CH), 9.72 ppm (brs, 1H; NCHN); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25°C): δ=13.7 (s; CCH$_3$), 16.8 (s; CCH$_3$), 32.6 (d, ^2J(P,C)=18.3 Hz; PfcCH$_2$CH$_2$), 38.9 (s; NCH$_3$), 49.5 (brs; PfcCH$_2$CH_2), 72.3 (s; Cp), 74.8 (d, ^1J(P,C)=52.3 Hz; α-CH), 92.9 (d, ^1J(P,C)=55.0 Hz; α-CCH$_2$), 93.1 (d, ^2J(P,C)=5.5 Hz; CCH$_3$), 95.2 (d, ^2J(P,C)=5.7 Hz; CCH$_3$), 121.2 (s; HC=CH), 121.8 (s; HC=CH), 136.3 ppm (brs; NCHN); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 25°C): δ=−77.3 ppm (s); MS (FAB): m/z (%): 341 (100) $[M]^+$, 259 (38) [PfcCH$_2$CH$_2$]$^+$, 245 (16) [PfcCH$_2$]$^+$.

***rac*-/*meso*-1,3-Bis-[2-(3,4-dimethylphosphaferrocen-2-yl)ethyl]imidazolium iodide (11I)**: A solution of imidazole **8** (280 mg, 0.86 mmol) and iodide **9** (331 mg, 0.86 mmol) in acetonitrile (10 mL) was heated at reflux overnight. After evaporation of the solvent, the residue was dissolved in dichloromethane (20 mL) and washed with HCl (2N, 2×10 mL) and water (10 mL). The organic layer was dried over sodium sulfate and filtered. The crude product was then freed from organometallic impurities by column chromatography on neutral alumina (1–2 cm). The product was eluted with THF/MeOH 50:1. Yield: 407 mg (67%); the diastereomers were obtained in a 1:1 ratio; ^{1}H NMR (200 MHz, CDCl$_3$, 25°C): δ=2.15 (s, 12H; CCH_3), 2.18 (s, 6H; CCH_3), 2.19 (s, 6H; CCH_3), 2.78 (m, 8H; PfcCH_2CH$_2$), 3.69 (d, ^2J(P,H)=36.6 Hz, 4H; α-CH), 4.13 (s, 20H; Cp), 4.27 (m, 8H; PfcCH$_2$CH_2), 6.94 (d, ^3J(H,H)=1.4 Hz, 2H; HC=CH), 6.96 (d, ^3J(H,H)=1.4 Hz, 2H; HC=CH), 10.71 ppm (brs, 2H; NCHN); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25°C): δ=13.9 (s; CCH$_3$), 16.9 (s; CCH$_3$), 31.7 (d, ^2J(P,C)=19.8 Hz; PfcCH$_2$CH$_2$), 31.8 (d, ^2J(P,C)=20.2 Hz; PfcCH$_2$CH$_2$), 51.4 (brs; PfcCH$_2$CH_2), 72.3 (s; Cp), 75.8, 75.9 (2×d, ^1J(P,C)=58.3 Hz; α-CH), 92.0 (d, ^1J(P,C)=59.4 Hz; α-CCH$_2$), 93.6 (2×d, ^2J(P,C)=4.2, 4.8 Hz; CCH$_3$), 96.2 (d, ^2J(P,C)=6.2 Hz; CCH$_3$), 96.3 (d, ^2J(P,C)=6.6 Hz; CCH$_3$), 121.9 (s; HC=CH), 137.2 ppm (2×s; NCHN); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, 25°C): δ=−77.2 (s), −77.3 ppm (s); MS (FAB): m/z (%): 585 (100) $[M]^+$, 259 (91) [PfcCH$_2$CH$_2$]$^+$, 245 (35) [PfcCH$_2$]$^+$.

1-[2-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]-3-[(3,4-dimethylphosphaferrocen-2-yl)methyl]imidazolium iodide (12I): Imidazole **8** (149 mg, 0.46 mmol) and ammonium iodide **1I** (197 mg, 0.46 mmol) were dissolved in acetonitrile (10 mL) and heated at reflux overnight. After evaporation of the solvent the crude product was purified by column chromatography on neutral alumina (1–2 cm). Impurities were removed with THF/MeOH 50:1 as eluent, and the product was eluted with THF/MeOH 20:1. Yield: 283 mg (88%); the diastereomers were obtained in a 1:1 ratio. (In the following analysis of the NMR spectra two abbreviations are used: sac=*N*-substituent with *s*hort *a*lkyl *c*hain, lac=*N*-substituent with *l*ong *a*lkyl *c*hain). ^{1}H NMR (200 MHz, CDCl$_3$, 25°C): δ=2.11, 2.11 (2×s, 6H; sac CCH_3), 2.16, 2.19 (2×s, 12H; lac CCH_3), 2.21, 2.25 (2×s, 6H; sac CCH_3), 2.75 (m, 4H; lac PfcCH_2CH$_2$), 3.64, 3.66 (2×d, ^2J(P,H)=36.5 Hz, 2H; sac α-CH), 3.89 (d, ^2J(P,H)=36.7 Hz, 2H; lac α-CH), 4.11, 4.12 (2×s, 10H; lac Cp), 4.26, 4.27 (2×s, 10H; sac Cp), 4.29 (m, 4H; lac PfcCH$_2$CH_2), 4.72, 4.73 (2×dd, ^2J(H,H)=14.7, ^3J(P,H)=5.8 Hz, 2H; sac CH_2), 5.41 (dd, ^2J(H,H)=14.7, ^3J(P,H)=14.7 Hz, 2H; sac CH_2), 7.00, 7.03 (2×d, ^3J(H,H)=1.8 Hz, 2H; HC=CH), 7.13, 7.14 (2×d, ^3J(H,H)=1.6 Hz, 2H; HC=CH), 10.12 ppm (brs, 2H; NCHN); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25°C): δ=13.7, 13.7, 13.9, 14.0, 16.5, 16.6, 16.6 (7×s; CCH$_3$), 31.1 (d, ^2J(P,C)=19.3 Hz; lac PfcCH$_2$CH$_2$), 50.0 (d, ^2J(P,C)=23.1 Hz; sac PfcCH$_2$), 51.2 (brs; lac PfcCH$_2$CH_2), 71.8, 72.2 (2×s; Cp), 75.7 (d, ^1J(P,C)=58.4 Hz; α-CH), 77.3 (d, ^1J(P,C)=58.8 Hz; α-CH), 86.5 (d, ^1J(P,C)=58.9 Hz; α-CCH$_2$), 91.3 (d, ^1J(P,C)=59.6 Hz; α-CCH$_2$), 93.0,

93.9, 95.8, 97.1 (4 brs; CCH_3), 120.6, 122.3, 122.4 (3×s; HC=*C*H), 134.5 ppm (brs; N*C*HN); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -77.0$ (s; lac), −72.1 (s; sac), −71.9 ppm (s; sac); MS (FAB): *m*/*z* (%): 571 (19) $[M]^+$, 245 (100) $[PfcCH_2]^+$.

1-[2-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]-3-methylimidazolin-2-ylidene (13): In a small Schlenk tube, NHC precursor **10I** (200 mg, 0.43 mmol) was dissolved in DMSO (0.1 mL)/THF (2.0 mL) and deprotonated by the general procedure. Yield: quantitative (according to the NMR spectra); ^1H NMR (500 MHz, $[D_8]$THF+$[D_6]$DMSO (5%), 25 °C): $\delta = 2.22$ (s, 3H; CCH_3), 2.23 (s, 3H; CCH_3), 2.72 (m, 2H; PfcCH_2CH_2), 3.70 (d, $^2J(P,H) = 36.6$ Hz, 1H; α-C*H*), 3.95 (s, 3H; NCH_3), 4.20 (s, 5H; Cp), 4.24 (m, 2H; PfcCH_2CH_2), 7.68 (brs, 1H; *H*C=CH), 7.71 ppm (brs, 1H; HC=C*H*); $^{31}P\{^1H\}$ NMR (81 MHz, $[D_8]$THF+$[D_6]$DMSO (5%), 25 °C): $\delta = -78.1$ ppm (s).

***rac*-/*meso*-1,3-Bis-[2-(3,4-dimethylphosphaferrocen-2-yl)ethyl]imidazolin-2-ylidene (14)**: In a NMR tube, NHC precursor **11I** (20 mg, 0.04 mmol) was dissolved in DMSO (0.03 mL)/THF (0.6 mL) and deprotonated with excess NaH. When the gas evolution had ceased, the NMR tube was centrifuged and spectra were recorded instantly. Yield: not determined, partial decomposition; ^1H NMR (200 MHz, $[D_8]$THF+$[D_6]$DMSO (5%), 25 °C): $\delta = 2.12$, 2.18, 2.21, 2.25 (4×s, 24H; CCH_3), 2.55 (m, 8H; PfcCH_2CH_2), 3.66 (d, $^2J(P,H) = 36.6$ Hz, 2H; α-C*H*), 3.72 (d, $^2J(P,H) = 36.5$ Hz, 2H; α-C*H*), 4.12 (s, 10H; Cp), 4.17 (s, 10H; Cp), 4.17 (m, 8H; PfcCH_2CH_2), 7.53 (brs, 2H; *H*C=C*H*), 7.54 ppm (brs, 2H; *H*C=C*H*); $^{31}P\{^1H\}$ NMR (81 MHz, $[D_8]$THF+$[D_6]$DMSO (5%), 25 °C): $\delta = -78.3$ ppm (s).

[(4)Mo(CO)$_4$] (16): In a small Schlenk tube, NHC precursor **2I** (80 mg, 0.18 mmol) was dissolved in DMSO (0.2 mL)/THF (2.0 mL) and treated with an excess of NaH. When the hydrogen evolution had stopped, solid $Mo(CO)_6$ (47 mg, 0.18 mmol) was added to the suspension containing the carbene. The reaction mixture was allowed to stir for 2 h at 60 °C, giving a deep red suspension. After quenching with a small volume of water the suspension was evaporated to dryness. The residue was then purified by column chromatography on neutral alumina. Elution with diethyl ether/THF 5:1 and subsequent removal of the solvents gave **16** as a yellow solid (49 mg, 52%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.19$ (s, 3H; CCH_3), 2.22 (s, 3H; CCH_3), 3.79 (d, $^2J(P,H) = 34.2$ Hz, 1H; α-C*H*), 3.97 (s, 3H; NCH_3), 4.03 (s, 5H; Cp), 4.49 (dd, $^2J(H,H) = 14.7$, $^3J(P,H) = 14.7$ Hz, 1H; CH_2), 4.61 (dd, $^2J(H,H) = 14.7$, $^3J(P,H) = 12.5$ Hz, 1H; CH_2), 6.87 (d, $^3J(H,H) = 1.8$ Hz, 1H; *H*C=CH), 6.89 ppm (d, $^3J(H,H) = 1.8$ Hz, 1H; HC=C*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $[D_8]$THF, 25 °C): $\delta = 11.8$ (d, $^3J(P,C) = 2.1$ Hz; CCH_3), 15.1 (d, $^3J(P,C) = 4.0$ Hz; CCH_3), 38.6 (s; NCH_3), 49.5 (d, $^2J(P,C) = 13.4$ Hz; CH_2), 69.0 (d, $^1J(P,C) = 15.2$ Hz; α-C*H*), 72.5 (s; Cp), 87.0 (d, $^1J(P,C) = 3.0$ Hz; α-CCH_2), 90.8 (d, $^2J(P,C) = 2.5$ Hz; CCH_3), 91.6 (d, $^2J(P,C) = 1.6$ Hz; CCH_3), 120.7 (s; HC=CH), 122.8 (s; HC=*C*H), 188.9 (d, $^2J(P,C) = 15.3$ Hz; N*C*N), 207.5 (d, $^2J(P,C) = 11.3$ Hz; *C*O), 209.4 (d, $^2J(P,C) = 11.8$ Hz; *C*O), 216.6 (d, $^2J(P,C) = 40.1$ Hz; *C*O), 216.8 ppm (d, $^2J(P,C) = 11.2$ Hz; *C*O); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -17.8$ ppm (s); IR (ATR): $\tilde{\nu} = 2010$, 1896, 1869 cm^{-1} (C=O); MS (FAB): *m*/*z* (%): 536 (54) $[M]^+$, 480 (100) $[M-2CO]^+$, 424 (98) $[M-4CO]^+$; elemental analysis calcd (%) for $C_{20}H_{19}FeMoN_2O_4P$ (534.1): C 44.97, H 3.59, N 5.24; found: C 45.08, H 3.62, N 5.27. Layering a chloroform solution of **16** with hexane afforded orange crystals suitable for X-ray analysis.

[(13)Mo(CO)$_4$] (17): In a small Schlenk tube, NHC precursor **10I** (205 mg, 0.44 mmol) was dissolved in DMSO (0.1 mL)/THF (2.0 mL) and treated with an excess of NaH. When the hydrogen evolution had stopped, solid $[Mo(CO)_6]$ (116 mg, 0.44 mmol) was added to the suspension containing the carbene. The reaction mixture was allowed to stir for 2 h at 60 °C, giving a deep red suspension. After quenching with a small volume of water, the suspension was evaporated to dryness. The residue was then purified by column chromatography on neutral alumina. Elution with diethyl ether to THF and subsequent removal of the solvents gave **17** as a yellow powder (192 mg, 80%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.09$ (s, 3H; CCH_3), 2.16 (s, 3H; CCH_3), 2.61 (m, 2H; PfcCH_2CH_2), 3.61 (d, $^2J(P,H) = 33.9$ Hz, 1H; α-C*H*), 3.93 (s, 3H; NCH_3), 4.15 (brs, 5H; Cp), 4.38 (m, 1H; PfcCH_2CH_2), 4.88 (m, 1H; PfcCH_2CH_2), 6.91 (d, $^3J(H,H) = 1.8$ Hz, 1H; *H*C=CH), 6.93 ppm (d, $^3J(H,H) = 1.8$ Hz, 1H; HC=C*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 13.3$ (d, $^3J(P,C) = 2.5$ Hz; CCH_3), 16.4 (d, $^3J(P,C) = 4.3$ Hz; CCH_3), 33.4 (d, $^2J(P,C) = 10.7$ Hz; PfcCH_2CH_2), 39.9 (s; NCH_3), 49.9 (d, $^3J(P,C) = 10.4$ Hz; PfcCH_2CH_2), 69.8 (brs; α-CH), 73.4 (s; Cp), 88.5 (d, $^1J(P,C) = 15.8$ Hz; α-CCH_2), 91.5 (brs; CCH_3), 93.3 (s; CCH_3), 121.0 (s; HC=CH), 122.8 (s; HC=*C*H), 208.6 (d, $^2J(P,C) = 11.0$ Hz; *C*O), 216.5 ppm (d, $^2J(P,C) = 10.1$ Hz; *C*O); two further signals for CO could not be detected unambiguously; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -23.1$ ppm (brs); IR (ATR): $\tilde{\nu} = 2010$, 1891, 1861 cm^{-1} (C=O); MS (FAB): *m*/*z* (%): 550 (22) $[M]^+$, 522 (6) $[M-CO]^+$, 494 (100) $[M-2CO]^+$, 438 (53) $[M-4CO]^+$; elemental analysis calcd (%) for $C_{21}H_{21}FeMoN_2O_4P$ (548.2): C 46.01, H 3.86, N 5.11; found: C 46.22, H 4.14, N 5.03. Layering a chloroform solution of **17** with hexane afforded orange crystals suitable for X-ray analysis.

[(5)Mo(CO)$_4$] (18): In a small Schlenk tube, NHC precursor **3I** (100 mg, 0.15 mmol) was dissolved in DMSO (0.1 mL)/THF (2.0 mL) and treated with an excess of NaH. When the hydrogen evolution had stopped, solid $[Mo(CO)_6]$ (39 mg, 0.15 mmol) was added to the suspension containing the carbene. The reaction mixture turned deep red while being allowed to stir for 2 h at 60 °C. After quenching with a small volume of water, the suspension was evaporated to dryness. The residue was then subjected to column chromatography on neutral alumina. Elution with diethyl ether and subsequent removal of the solvents gave **18** as a yellow powder; additionally a small amount of complex **19** was eluted with diethyl ether/THF 2:1. Yield: 77 mg **18** (69%), 21 mg **19** (20%); the diastereomers of **18** were obtained in a 1:1 ratio; ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.10$, 2.13, 2.21, 2.22 (4×s, 24H; CH_3), 3.80, 3.82 (2×d, $^2J(P,H) = 34.3$ Hz, 2H; α-C*H*), 3.87 (d, $^2J(P,H) = 36.1$ Hz, 2H; α-C*H*), 3.98 (s, 5H; Cp), 4.03 (s, 5H; Cp), 4.29 (s, 10H; Cp), 4.34–4.70 (m, 4H; CH_2), 4.70 (dd, $^2J(H,H) = 14.3$, $^3J(P,H) = 6.5$ Hz, 1H; CH_2), 4.96 (dd, $^2J(H,H) = 14.4$, $^3J(P,H) = 6.2$ Hz, 1H; CH_2), 5.33 (dd, $^2J(H,H) = 14.8$, $^3J(P,H) = 14.8$ Hz, 1H; CH_2), 5.47 (dd, $^2J(H,H) = 14.4$, $^3J(P,H) = 14.4$ Hz, 1H; CH_2), 6.75 ppm (m, 4H; *H*C=C*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 13.4$, 13.6, 16.5, 16.9, 17.0 (5×s; CCH_3), 50.6 (d, $^2J(P,C) = 14.1$ Hz; CH_2), 50.7 (d, $^2J(P,C) = 13.7$ Hz; CH_2), 52.3 (d, $^2J(P,C) = 22.9$ Hz; CH_2), 52.5 (d, $^2J(P,C) = 23.5$ Hz; CH_2), 69.7 (d, $^1J(P,C) = 14.2$ Hz; α-C*H*), 69.8 (d, $^1J(P,C) = 13.4$ Hz; α-C*H*), 72.6, 73.0, 73.0 (3×s; Cp), 77.7 (d, $^1J(P,C) = 2.5$ Hz; α-C*H*), 86.9 (d, $^1J(P,C) = 48.1$ Hz; α-CCH_2), 87.0 (d, $^1J(P,C) = 48.0$ Hz; α-CCH_2), 89.4 (d, $^1J(P,C) = 58.1$ Hz; α-CCH_2), 90.1 (d, $^1J(P,C) = 58.7$ Hz; α-CCH_2), 90.9 (d, $^2J(P,C) = 20.3$ Hz; CCH_3), 92.0 (d, $^2J(P,C) = 20.5$ Hz; CCH_3), 95.0 (brd, $^2J(P,C) = 3.5$ Hz; CCH_3), 96.9 (d, $^2J(P,C) = 6.6$ Hz; CCH_3), 97.1 (d, $^2J(P,C) = 6.9$ Hz; CCH_3), 118.0, 118.0, 122.1, 122.5 (4×s; HC=*C*H), 188.8 (d, $^2J(P,C) = 15.7$ Hz; N*C*N), 188.9 (d, $^2J(P,C) = 17.5$ Hz; N*C*N), 207.1 (d, $^2J(P,C) = 11.1$ Hz; *C*O), 207.9 (d, $^2J(P,C) = 11.5$ Hz; *C*O), 209.2 (d, $^2J(P,C) = 11.5$ Hz; *C*O), 210.1 (d, $^2J(P,C) = 11.8$ Hz; *C*O), 217.2 (d, $^2J(P,C) = 39.7$ Hz; *C*O), 217.3 (d, $^2J(P,C) = 39.1$ Hz; *C*O), 217.6 (d, $^2J(P,C) = 10.9$ Hz; *C*O), 217.7 ppm (d, $^2J(P,C) = 10.0$ Hz; *C*O); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -70.9$ (s), −69.8 (s), −20.1 (s), −18.9 ppm (s); IR (ATR): $\tilde{\nu} = 2008$, 1952, 1880, 1847 cm^{-1} (C=O); MS (FAB): *m*/*z* (%): 766 (2) $[M]^+$, 682 (13) $[M-3CO]^+$, 589 (3) $[M-4CO-Cp]^+$, 533 (17) $[M-4CO-CpFe]^+$, 468 (12) $[M-4CO-CpFe-Cp]^+$, 412 (8) $[M-4CO-2CpFe]^+$, 245 (100) $[PfcCH_2]^+$.

[(5)Mo(CO)$_3$] (19): Imidazolium iodide **3I** (100 mg, 0.15 mmol) was dissolved in DMSO (0.1 mL)/THF (2.0 mL) and converted into the free carbene **5** by the general procedure. The red solution containing the carbene was then added to $[Mo(MeCN)_3(CO)_3]$ (44 mg, 0.15 mmol), which had been freshly dissolved in acetonitrile (2 mL). The solution was allowed to stir for a few minutes before the solvents were evaporated under vacuum. The product was then purified by column chromatography on neutral alumina (diethyl ether/THF 2:1) and a yellow powder was obtained (72 mg, 65%). Compound **19** with *rac* ligand was obtained in a higher proportion than **19** with *meso* ligand; ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.09$, 2.12, 2.14, 2.19, 2.25 (5×s; CH_3), 3.42 (s; $Cp^{rac\text{-}5}$), 3.72 (d, $^2J(P,H) = 34.3$ Hz; α-C*H*), 3.76 (d, $^2J(P,H) = 33.8$ Hz; α-C*H*), 4.12 (dd, $^2J(H,H) = 14.4$, $^3J(P,H) = 20.4$ Hz; CH_2), 4.35 (s; $Cp^{meso\text{-}5}$), 4.39 (s; $Cp^{rac\text{-}5}$), 4.54 (dd, $^2J(H,H) = 14.4$, $^3J(P,H) = 20.0$ Hz; CH_2), 4.82 (dd, $^2J(H,H) = 14.4$, $^3J(P,H) = 6.2$ Hz; CH_2), 5.00 (dd, $^2J(H,H) = 14.4$, $^3J(P,H) = 5.4$ Hz; CH_2), 5.12 (dd, $^2J(H,H) = 14.4$, $^3J(P,H) = 6.0$ Hz; CH_2), 6.64 (s; *H*C=C*H*), 6.76 (d, $^3J(H,H) = 1.7$ Hz; *H*C=CH), 6.84 ppm (d, $^3J(H,H) = 1.7$ Hz; HC=

C*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 13.3$ (s; C*C*H$_3$), 13.4 (2×d, ^3J(P,C) = 1.9, 2.0 Hz; C*C*H$_3$), 16.4 (d, ^3J(P,C) = 3.4 Hz; C*C*H$_3$), 16.5 (s; C*C*H$_3$), 16.8 (d, ^3J(P,C) = 3.0 Hz; C*C*H$_3$), 50.5 (d, ^2J(P,C) = 13.0 Hz; *C*H$_2$), 51.0 (d, ^2J(P,C) = 14.5 Hz; *C*H$_2$), 69.7 (d, ^2J(P,C) = 15.8 Hz; *C*H$_2$), 70.0 (d, ^1J(P,C) = 24.0 Hz; α-*C*H), 70.8 (d, ^1J(P,C) = 19.8 Hz; α-*C*H), 71.9, 73.4, 73.5 (3×s; Cp), 87.0 (s; α-*C*CH$_2$), 87.4 (d, ^1J(P,C) = 4.6 Hz; α-*C*CH$_2$), 88.3 (d, ^1J(P,C) = 4.8 Hz; α-*C*CH$_2$), 89.2 (s; *C*CH$_3$), 89.3 (d, ^2J(P,C) = 1.6 Hz; *C*CH$_3$), 91.2 (d, ^2J(P,C) = 8.5 Hz; *C*CH$_3$), 91.4 (d, ^2J(P,C) = 3.4 Hz; *C*CH$_3$), 120.0, 120.3, 121.8 ppm (3×s; H*C*=*C*H); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -22.2$ (d, ^2J(P,P) = 36.3 Hz), −10.9 (s), −10.6 ppm (d, ^2J(P,P) = 36.3 Hz); IR (KBr): $\tilde{\nu} = 1934$, 1835 cm^{-1} (C=O); MS (FAB): *m*/*z* (%): 557 (6) $[\mathbf{3}]^+$, 245 (100) $[PfcCH_2]^+$.

[Cp*(4)RuCl] (20): In a small Schlenk tube, NHC precursor **2I** (133 mg, 0.29 mmol, 4 equiv) was dissolved in DMSO (0.2 mL)/THF (2 mL) and treated with an excess of NaH. When the hydrogen evolution had stopped, solid $[Cp^*RuCl]_4$ (100 mg, 0.07 mmol, 1.25 equiv) was added to the suspension containing the carbene. The deep red suspension was quenched with a small volume of water and then evaporated to dryness. The residue was subjected to column chromatography on neutral alumina (THF/MeOH 10:1). Evaporation of the yellow eluate gave an orange–brown solid (150 mg, 85%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.63$ (d, ^4J(P,H) = 3.0 Hz, 15H; Cp*), 2.29 (s, 3H; CC*H*$_3$), 2.46 (s, 3H; CC*H*$_3$), 3.35 (d, ^2J(P,H) = 34.0 Hz, 1H; α-C*H*), 4.04 (s, 3H; NC*H*$_3$), 4.21 (s, 5H; Cp), 4.43 (dd, ^2J(H,H) = 16.3, ^3J(P,H) = 2.4 Hz, 1H; C*H*$_2$), 5.68 (dd, ^2J(H,H) = 16.3, ^3J(P,H) = 18.0 Hz, 1H; C*H*$_2$), 7.18 (d, ^3J(H,H) = 1.8 Hz, 1H; *HC*=CH), 8.24 ppm (d, ^3J(H,H) = 1.8 Hz, 1H; HC=C*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 10.0$ (s; Me of Cp*), 13.4 (d, ^3J(P,C) = 3.2 Hz; C*C*H$_3$), 16.3 (d, ^3J(P,C) = 5.0 Hz; C*C*H$_3$), 39.0 (s; N*C*H$_3$), 51.0 (d, ^2J(P,C) = 10.1 Hz; *C*H$_2$), 59.8 (s; α-*C*H), 74.3 (s; Cp), 78.1 (d, ^2J(P,C) = 11.8 Hz; α-*C*CH$_2$), 91.8 (d, ^2J(P,C) = 4.2 Hz; *C*CH$_3$), 92.5 (s; *C*CH$_3$), 93.7 (s; Cp*), 122.3 (s; H*C*=CH), 127.1 (s; HC=*C*H), 174.3 ppm (d, ^2J(P,C) = 26.5 Hz; N*C*N); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 15.7$ ppm (s); MS (FAB): *m*/*z* (%): 563 (100) $[M-Cl]^+$, 245 (30) $[PfcCH_2]^+$.

[Cp*(5)Ru]Cl (22Cl): Imidazolium iodide **3I** (100 mg, 0.15 mmol, 4 equiv) was converted into the free carbene **5** by the general procedure. The red solution containing the carbene was then added to $[Cp^*RuCl]_4$ (40 mg, 0.04 mmol) dissolved in THF (1 mL). At this point a $^{31}P\{^1H\}$ NMR of the crude reaction mixture showed the existence of complex **21** with ligand **5** in a bidentate coordination mode. The suspension was then freed from all solvents, and the residue was subjected to column chromatography on neutral alumina (THF/MeOH 10:1). Evaporation of the eluate afforded an orange solid (85 mg, 70%), compound **22Cl** with *rac* ligand was obtained in a higher proportion than **22Cl** with *meso* ligand; ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.51$, 1.92 (t/virtual t, ^4J(P,H) = 2.9 Hz; Cp*), 2.14, 2.21, 2.24, 2.32, 2.34, 2.38 (6×s; CC*H*$_3$), 3.29 (d, ^2J(P,H) = 32.2 Hz; α-C*H*), 3.40 (s; Cp$^{rac\text{-}5}$), 3.44 (d, ^2J(P,H) = 33.5 Hz; α-C*H*), 4.18 (s; Cp$^{meso\text{-}5}$), 4.40 (m; C*H*$_2$), 4.41 (s; Cp$^{rac\text{-}5}$), 4.78 (dd, ^2J(H,H) = 14.8, ^3J(P,H) = 21.8 Hz; C*H*$_2$), 5.07 (m; C*H*$_2$), 7.52 (brs; *HC*=CH), 7.64 (brs; HC=C*H*), 7.67 ppm (brs; *HC*=C*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 10.5$, 11.3 (2×s; Me of Cp*), 13.3 (s; C*C*H$_3$), 13.4, 13.6 (2×d, ^3J(P,C) = 3.1 Hz; C*C*H$_3$), 16.4 (d, ^3J(P,C) = 4.6 Hz; C*C*H$_3$), 16.7 (s; C*C*H$_3$), 16.7 (d, ^3J(P,C) = 4.5 Hz; C*C*H$_3$), 49.4 (d, ^3J(P,C) = 15.8 Hz; *C*H$_2$), 49.8 (d, ^3J(P,C) = 11.2 Hz; *C*H$_2$), 51.2 (brs; *C*H$_2$), 61.5 (dd, ^1J(P,C) = 5.2, ^3J(P,C) = 3.6 Hz; α-*C*H), 63.4 (dd, ^1J(P,C) = 5.3, ^3J(P,C) = 5.3 Hz; α-*C*H), 64.8 (d, ^1J(P,C) = 4.5 Hz; α-*C*H), 72.7, 73.7, 74.1 (3×s; Cp), 80.2 (brs; α-*C*CH$_2$), 82.3 (brs; α-*C*CH$_2$), 84.0 (brs; α-*C*CH$_2$), 89.8 (d, ^2J(P,C) = 4.3 Hz; *C*CH$_3$), 89.8 (s; *C*CH$_3$), 91.4 (d, ^2J(P,C) = 5.5 Hz; *C*CH$_3$), 91.6 (s; *C*CH$_3$), 91.7 (s; *C*CH$_3$), 92.4 (s; *C*CH$_3$), 92.7, 94.0 (2×s; Cp*), 122.8 (s; H*C*=CH), 124.4 (s; HC=*C*H), 124.6 ppm (s; HC=CH); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 10.5$ (s), 18.8 (d, ^2J(P,P) = 52.3 Hz), 22.2 ppm (d, ^2J(P,P) = 52.3 Hz); MS (FAB): *m*/*z* (%): 793 (100) $[M]^+$, 245 (65) $[PfcCH_2]^+$; elemental analysis calcd (%) for $C_{37}H_{45}ClFe_2N_2P_2Ru$ (827.9): C 53.68, H 5.48, N 3.38; found: C 53.59, H 5.68, N 3.26. Layering of a chloroform/dichloromethane solution of **22Cl** with hexane afforded red crystals of $(\mathbf{22})_2FeCl_4$ suitable for X-ray analysis.

[(4)$_2$Pd] (23): Imidazolium iodide **2I** (80 mg, 0.18 mmol, 2 equiv) was converted into the free carbene **4** by the general procedure. The red solution containing the carbene was then added to $[Pd(dba)_2]$ (51 mg, 0.09 mmol) suspended in THF (2 mL). The resulting dark suspension was evaporated to dryness, and the residue was subjected to column chromatography on neutral alumina. Elution with THF and subsequent removal of the solvents gave a mixture of dba and complex **23**. Layering of a CH_2Cl_2 solution of this mixture with hexane afforded red crystals of the homochiral diastereomer of **23**. Yield: 5 mg (7%).

Homochiral 23: ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.27$ (s, 6H; CC*H*$_3$), 2.28 (s, 6H; CC*H*$_3$), 3.57 (s, 6H; NC*H*$_3$), 4.14 (d, ^2J(P,H) = 32.0 Hz, 2H; α-C*H*), 4.26 (s, 10H; Cp), 4.40 (m, 2H; C*H*$_2$), 5.50 (dd, ^2J(H,H) = 15.1, ^3J(P,H) = 3.6 Hz, 2H; C*H*$_2$), 6.81 (d, ^3J(H,H) = 1.8 Hz, 2H; *HC*=CH), 6.86 ppm (d, ^3J(H,H) = 1.8 Hz, 2H; HC=C*H*); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 43.1$ ppm (s).

Heterochiral 23: ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.22$ (s, 6H; CC*H*$_3$), 2.28 (covered s, 3H; CC*H*$_3$), 2.30 (s, 3H; CC*H*$_3$), 3.18 (s, 3H; NC*H*$_3$), 3.93 (d, ^2J(P,H) = 32.6 Hz, 2H; α-C*H*), 4.29 (s, 5H; Cp), 4.33 (s, 5H; Cp), 4.39 (s, 3H; NC*H*$_3$), 4.43 (m, 1H; C*H*$_2$), 4.49 (m, 1H; C*H*$_2$),5.38 (dd, ^2J(H,H) = 15.1, ^3J(P,H) = 3.1 Hz, 1H; C*H*$_2$), 5.79 (dd, ^2J(H,H) = 14.6, ^3J(P,H) = 6.3 Hz, 1H; C*H*$_2$), 6.56, 6.66 (2×d, ^3J(H,H) = 1.9 Hz, 2H; H*C*=C*H*), 6.98, 7.01 ppm (2×d, ^3J(H,H) = 1.9 Hz, 2H; *HC*=C*H*); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -45.7$ (d, ^2J(P,P) = 543.0 Hz), −27.7 ppm (d, ^2J(P,P) = 543.0 Hz).

Catalysis: A Schlenk flask was charged under nitrogen with *p*-bromoacetophenone (3.38 g, 17.0 mmol, 1.0 equiv), phenylboronic acid (3.11 g, 25.5 mmol, 1.5 equiv) and potassium carbonate (4.70 g, 34.0 mmol, 2.0 equiv). Crystals of complex **23** (1.0 mg, 1.3×10^{-6} mmol, 0.01 mol%) were then added, and the reaction mixture was heated at reflux in toluene (30 mL) for 4 h. Samples were taken after 2, 3 and 4 h, and the progress of the conversion was determined by integration of the ^1H NMR resonances of the methyl groups of the starting material and of *p*-phenylacetophenone. After aqueous workup the crude product was purified by column chromatography.

X-ray crystallographic study: Crystals of compounds $[\mathbf{3I}]\cdot H_2O$, **16**, **17** and $[(\mathbf{22})_2FeCl_4]\cdot 2\,CH_2Cl_2\cdot CHCl_3$ were investigated with a Stoe IPDS with use of graphite-monochromatised $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 291 K. In the case of $[\mathbf{3I}]\cdot H_2O$ only crystals of very limited quality were obtained, while in the case of $[(\mathbf{22})_2FeCl_4]\cdot 2\,CH_2Cl_2\cdot CHCl_3$ only small crystals were available. The space group type $P2_1/n$ was exclusively determined for all four compounds. Lp corrections were applied to all the intensity data, and absorption corrections using symmetry equivalent reflections were performed. The structures were solved by direct methods,[21] and the positions of all but some of the H atoms of the iodide and of the ruthenium compound were found by ΔF syntheses. Refinements[22] by full-matrix, least-squares calculations on F^2 converged to the indicators given in Table 2. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. Appropriate restraints had to be applied in the case of the ruthenium compound. Idealized bond lengths and angles were used for all the CH_3, CH_2 and CH groups and the solvent water molecule of the iodide; the riding model was applied for their H atoms. In addition, the H atoms of the CH_3 groups, with the exceptions of those at C9 and C10 of $[\mathbf{3I}]\cdot H_2O$, were allowed to rotate around the neighbouring C–C bonds; the H atoms of the water molecule were allowed for free rotation. The isotropic displacement parameters of the H atoms were kept equal to 120% of the equivalent isotropic displacement parameters of the parent "aromatic" or secondary carbon atom and equal to 150% of the parent primary carbon or oxygen atom, respectively. A summary of further crystallographic data, data collection parameters, and refinement parameters is collected in Table 2.

CCDC 659378 ($[\mathbf{3I}]\cdot H_2O$), 659379 (**16**), 659380 ($[(\mathbf{22})_2FeCl_4]\cdot 2\,CH_2Cl_2\cdot CHCl_3$) and 659381 (**17**) 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.

Table 2. Crystallographic data for compounds **3I**·H_2O, **16**, **17** and $[(\mathbf{22})_2FeCl_4]\cdot 2\,CH_2Cl_2\cdot CHCl_3$.

Compound	**3I**·H_2O	**16**	**17**	$[(\mathbf{22})_2FeCl_4]\cdot 2\,CH_2Cl_2\cdot CHCl_3$
formula	$C_{27}H_{33}Fe_2IN_2OP_2$	$C_{20}H_{19}FeMoN_2O_4P$	$C_{21}H_{21}FeMoN_2O_4P$	$C_{77}H_{95}Cl_{11}Fe_5N_4P_4Ru_2$
M	702.09	534.13	548.16	2071.79
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	7.5930(5)	11.200(2)	11.0112(8)	20.6545(12)
b [Å]	28.1741(19)	16.911(4)	17.4908(16)	18.7192(12)
c [Å]	13.9685(10)	11.364(2)	11.5612(8)	23.3704(13)
β [°]	102.85(3)	98.84(2)	95.089(9)	97.364(7)
V [Å^3]	2913.4(5)	2126.8(7)	2217.8(3)	8961.3(9)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.601	1.668	1.642	1.536
$F(000)$	1408	1072	1104	4200
$\mu(Mo_{K\alpha})$ [mm^{-1}]	2.188	1.375	1.321	1.556
$2\Theta_{max}$ [°]	52.16	52.16	51.80	52.20
total reflections	29225	19050	15846	127936
independent reflections	5701	4170	4207	17629
observed reflections [$I > 2\sigma(I)$]	2488	2831	2686	4195
parameters refined	324	265	274	946
$R1/wR2$ [$I > 2\sigma(I)$]	0.1022, 0.2754	0.0385, 0.0864	0.0410, 0.0792	0.0665, 0.1225
$R1/wR2$ (all data)	0.1625, 0.2879	0.0549, 0.0891	0.0616, 0.0807	0.2097, 0.1348

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