Coordination Chemistry and Catalytic Application of Bidentate Phosphaferrocene−Pyrazole and −Imidazole Based P,N-Ligands

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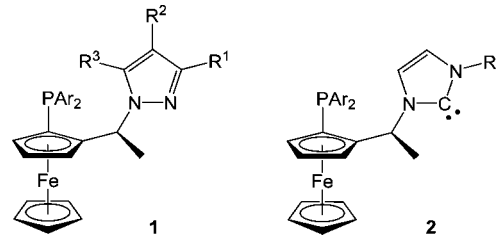
The synthesis of new planar chiral P,N-ligands based on 3,4-dimethylphosphaferrocene and either pyrazole or 1-methylimidazole is described. The coordination chemistry of the hemilabile pyrazole derivatives **3a** and **3b** (**a** features a methylene bridge between the heterocycles, **b** an ethylene bridge) was investigated and afforded complexes [Mo(**3**)$(CO)_5$], *cis*-[Mo(**3**)$_2(CO)_4$], [Cp*RuCl(**3**)], [Cp*Ru-(**3**)$_2$]OTf, [Cp*RuCl(**3**)(PPh_3)], and [Pd(η^3-allyl)(**3**)]PF_6. Reaction of the imidazole derivatives **4a** and **4b** with [Pd(η^3-allyl)Cl]$_2$ and $TlPF_6$ yielded [Pd(η^3-allyl)(**4**)]PF_6. The Pd complexes of **3** and **4** were tested in the catalytic asymmetric allylic alkylation reaction of 1,3-diphenylallyl acetate with sodium dimethylmalonate. X-ray structures of one Ru complex and one Pd complex of **3a** were determined.

Introduction

In view of declining resources and an increasing demand for green chemistry, homogeneous and especially asymmetric catalysis has become one main goal of organometallic chemistry.[1] The latter usually requires complexes of transition metals with chiral ligands to allow for a substantial degree of enantiodiscrimination. However, reactions such as Pd-catalyzed asymmetric allylic substitution have shown that not only the steric properties of the ligand decide on the level of enantioselectivity but also its electronic structure plays an important role. Numerous bidentate ligands with two different donor atoms, mostly P and N,[2] have been employed to investigate the phenomenon of electronic differentiation, i.e., the different *trans* influence of the coordinating atoms on the complex during the catalytic cycle and thus the observation of nucleophiles attacking selectively *trans* to the stronger π-acceptor.[3,4a]

Such behavior was found, for example, for Togni's ligands of type **1** (Chart 1) and elucidated by means of X-ray crystal structure analyses, 2D-NMR spectroscopy, and DFT calculations.[4] The ferrocene-based P,N-ligands were more active and showed higher enantioselectivities in the allylic amination than the isostructural P,C-ligands of type **2**. This is due to their higher electronic differentiation and the lower electron density at the metal center as compared to the NHC-based complexes.[5] Examination of several derivatives of **1** with either electron-donating or -withdrawing substituents at the donor groups in the rhodium-catalyzed hydroboration suggested that "high enantioselectivities are obtained when both the N-ligand is a good σ-donor and the P-ligand a good π-acceptor".[6]

Chart 1. Related P,C- and P,N-Ligands Studied by Togni



As phosphaferrocene is considered to be a good π-acceptor ligand and in extension of our previous research on imidazoline-2-ylidenes with phosphaferrocenyl substituents,[7] we have studied the synthesis, coordination properties, and catalytic application[8] of the new planar chiral phosphaferrocene-based P,N-ligands **3a** and **3b**. Moreover, their catalytic activity in the asymmetric allylic alkylation reaction was compared to the imidazole analogues **4a** and **4b**.

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§ X-ray structure determination.

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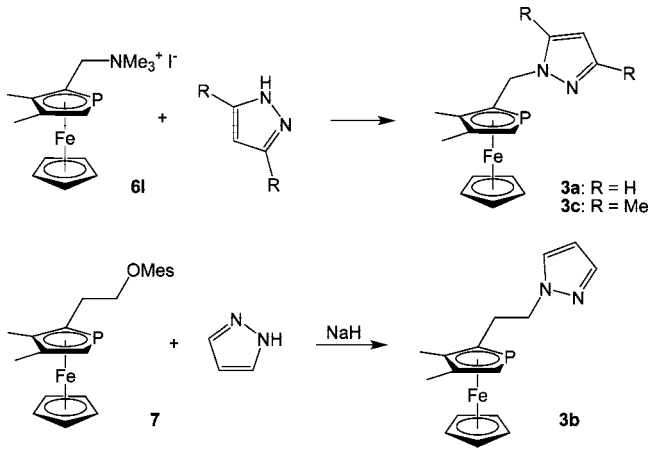
Scheme 1. Synthesis of Pyrazole-Based Ligands



Results and Discussion

Ligand Synthesis. The exploratory complexation studies described in this paper were carried out with racemic mixtures of the ligands. However, for the application in asymmetric catalysis all ligands were obtained in enantiomerically pure form after resolution of the racemic 3,4-dimethylphosphaferrocene-2-carbaldehyde **5** as starting material.[9] The new P,N-ligand **3a** was easily prepared in high yield by heating the trimethylammonium salt **6I**, available from the aldehyde **5** in two steps,[7] with excess pyrazole in acetic acid (Scheme 1). Performing the same reaction with 3,5-dimethylpyrazole in acetonitrile afforded ligand **3c**. The analogue of **3a** with an elongated alkyl bridge, **3b**, was synthesized by refluxing the mesylate **7**[10] with sodium pyrazolide in THF overnight.

The related imidazole-based P,N-ligands **4a** and **4b** were obtained by reaction of aldehyde **5** with lithiated 1-methylimidazole or 1,2-dimethylimidazole, respectively, and subsequent reduction of the resulting alcohols **8** with sodium borohydride and trifluoroacetic acid (Scheme 2).

Complexation Studies. In a first attempt to obtain insight into the coordination chemistry of the new bidentate ligands **3a** and **3b** we tried to synthesize Mo chelate complexes **9** of the type $[Mo(PN)(CO)_4]$, the structure of which should be compared to the Mo complexes of the previously investigated phosphaferrocenyl-substituted NHC ligands.[7] When a THF solution of $[Mo(nbd)(CO)_4]$ was treated with equimolar amounts of ligand **3a** or **3b**, the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures showed a singlet in each case that must be assigned to the desired chelate complexes **9a** and **9b**, respectively, as the main products. In addition to that, two smaller singlets were detected in both spectra that were attributed to Mo complexes *cis*-$[Mo(\mathbf{3})_2(CO)_4]$ (**10**) featuring two P,N-ligands binding monodentate only via their P-donor functions (Scheme 3). Note the presence of two adjacent singlets for **10** due to the racemic nature of the ligands leading to two diastereomeric complexes. Evaporation of the solvent led to a transformation of complex **9a** into the bis-ligand complex **10a**. However, prior to workup via column chromatography this transformation was not complete in the case of complex **9b**, containing the elongated P,N-ligand **3b**. The mixture of **9b** and **10b** was dissolved in $CDCl_3$, and **9b** was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy of this mixture. The higher stability of complex **9b** as compared to complex **9a** is a consequence of the larger bite angle of its P,N-ligands[7] and thus the reduced hemilability (vide infra).

When the ligands **3a** and **3b** were heated with $[Mo(CO)_6]$ in a 1:1 ratio, not even traces of the desired chelate complexes could be detected in the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures. After workup via column chromatography $[Mo(\mathbf{3})(CO)_5]$ (**11**) and *cis*-$[Mo(\mathbf{3})_2(CO)_4]$ (**10**) were isolated (Scheme 4). The coordination of the phosphaferrocene moiety in these complexes and also in the chelate complexes **9** is visible from a downfield shift in the $^{31}P\{^1H\}$ NMR spectra of more than 50 ppm compared to the free ligands and a decrease of the $^2J_{PH}$ coupling constant for the phospholyl α-protons in the ^1H NMR spectra. Mass spectrometry and IR spectroscopy confirm the assumed monodentate coordination mode of the ligands in complexes **11** and **10**. In conclusion, we note that the anticipated chelate complexes **9a** and **9b** could not be isolated in pure form, while the chelate complexes featuring the closely related NHC ligands with imidazoline-2-ylidene groups in place of the pyrazole moieties could be obtained in good yields as pure compounds.[7]

In a next step ligands **3a** and **3b** were treated with $[Cp^*RuCl]_4$, which has been a suitable precursor for many phosphaferrocene complexes, including P,N-ligands based on phosphaferrocene and pyridine.[11] Mixing of one of the ligands with the metal source in a 1:1 ratio in THF led to immediate formation of the expected complexes **12a** and**12b**, respectively (Scheme 5). The quantitative conversion is confirmed by $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixture in THF at 223 K, which show only one diastereomer for **12a** and **12b** each with sharp singlets at 7.7 and 16.4 ppm, respectively. The diastereoselective formation of complexes **12** indicates the preference for the diastereomer permitting the larger distance between the Cp and Cp* moieties. Measurement of the same samples at ambient temperature reveals a broadening of the signals and thus suggests dangling of the pyrazole and a hemilabile character of the P,N-ligands. However, this broadening is far less pronounced in the case of **12b**. The reduced hemilability of **12b** is assumed to be a consequence of its less strained seven-membered chelate.[7] If the ligands were not coordinated in a chelating mode in **12**, one would expect formation of complexes $[Cp^*RuCl(PN)_2]$ with two ligands coordinating monodentate via their P donor while half of the Ru precursor would remain unreacted.[12]

When complex **12a** was subjected to column chromatography over neutral alumina, a transformation took place and afforded complex **13aCl** in a moderate yield of about 50%. Indeed, it was not possible to further purify this complex bearing two P,N-ligands, one in a chelating mode and the other one coordinating

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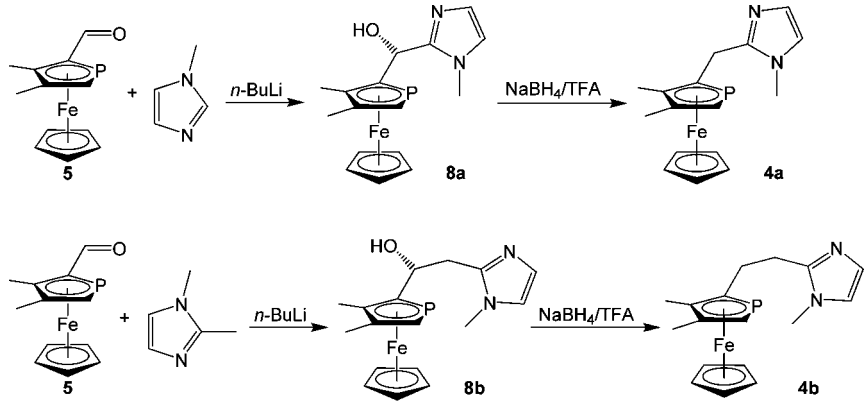
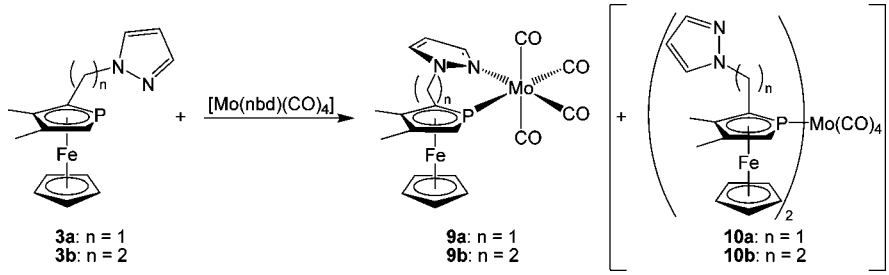
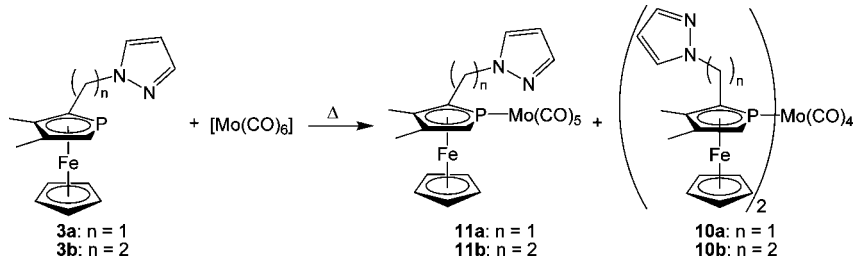
Scheme 2. Synthesis of Imidazole-Based Ligands



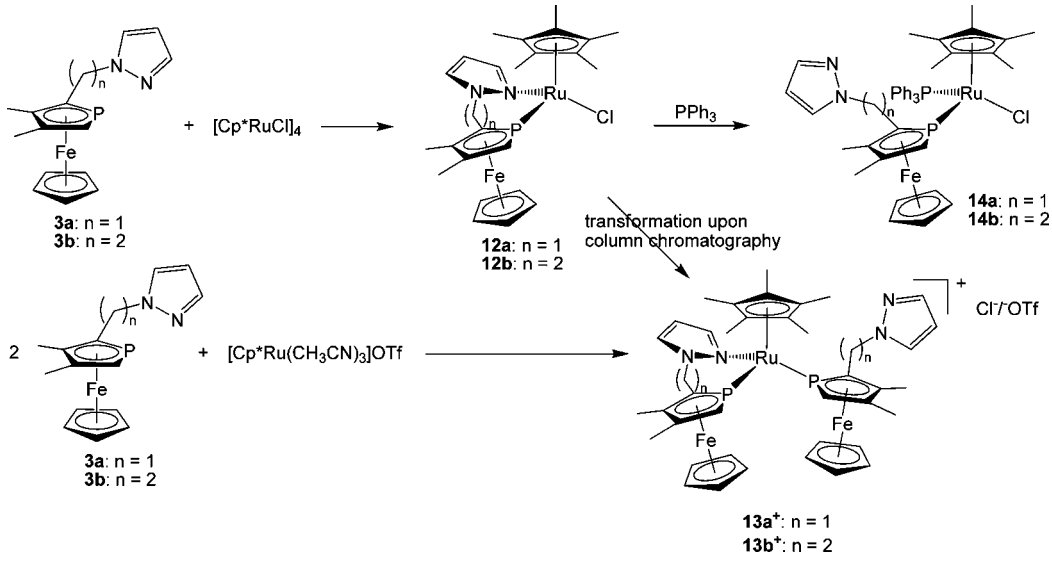
Scheme 3. Synthesis of Mo Chelate Complexes 9



Scheme 4. Synthesis of Mo Complexes 11 and 10



Scheme 5. Synthesis of Several Ru Complexes of the Bidentate P,N-Ligands of Type 3



only via its phosphorus atom. Hence, **13aOTf** was selectively synthesized by reaction of $[Cp^*Ru(CH_3CN)_3]OTf$ with 2 equiv of **3a**. As **13aOTf** is obtained as a mixture of two diastereomers, the $^{31}P\{^1H\}$ NMR spectrum displays two pairs of doublets with $^2J_{PP}$ coupling constants of 55.1 and 56.4 Hz in a 1:1 ratio. The ^1H NMR spectrum shows four sets of signals for the different P,N-ligands, and the MALDI mass spectrum contains the expected peak for $\mathbf{13a}^+$. The same procedure was applied to ligand **3b** with a longer alkyl bridge and yielded complex **13bOTf** almost quantitatively in a 1:1 ratio of the two diastereomers. The constitution was again proven by multinuclear NMR and mass spectra, the $^{31}P\{^1H\}$ NMR spectrum

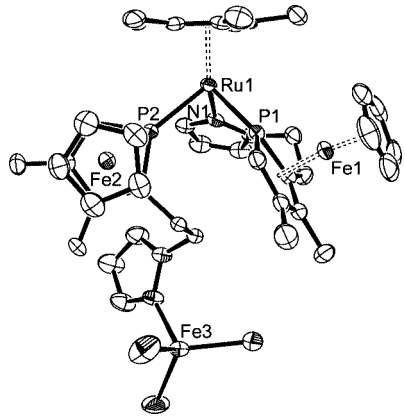


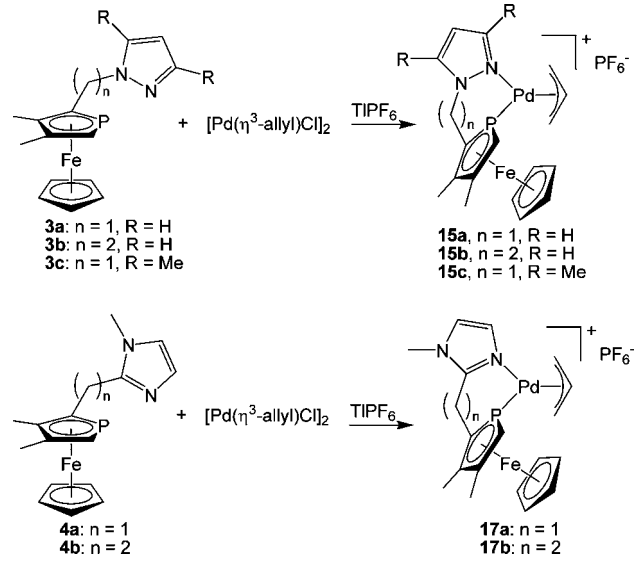
Figure 1. Molecular structure of complex **13bFeCl$_3$** in the solid state with the solvating CH_2Cl_2 and all hydrogen atoms omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å] and angles [deg]: Ru1−P1 2.3080(13), Ru1−P2 2.2918(12), Ru1−N1 2.149(4), Ru−Cp* 1.870, P1−Ru−N1 91.70(11).

showing coupling constants of 61.2 and 64.1 Hz for the two diastereomers. Additionally, orange crystals suitable for X-ray diffraction could be grown by slow diffusion of hexane into a dichloromethane solution of **13bCl**. For these crystals space group $P2_1/n$ was uniquely determined and the structure solution shows the complex cation **13**$^+$ to be coordinated to a $FeCl_3^-$ fragment via its dangling pyrazole moiety (Figure 1). The $FeCl_3^-$ could originate from partial decomposition of phosphaferrocene. The Ru−P distances for the dangling ligand (Ru1−P2 2.2918(12) Å) and the ligand forming the seven-membered chelate ring (Ru1−P1 2.3080(13) Å) are almost identical and lie in the upper range observed for other Ru complexes of phosphaferrocene-based chelate ligands (2.232(4)−2.2912(13) Å).[7,12,13] The P−Ru vector of the chelating ligand is tilted out of the phospholyl mean plane by 19.9° to minimize steric repulsion with the Cp* ligand. In the case of the dangling ligand this angle is 9.7°. The bite angle of the chelating ligand (P1−Ru1−N1) is 91.70(11)° and thus causes only a marginal deviation of the ideal octahedral geometry.

Knowing about their hemilability,[14] the new complexes **12a** and **12b** were treated with PPh_3. Displacement of the nitrogen donors by the phosphine gave the complexes **14a** and **14b**, respectively. The $^{31}P\{^1H\}$ NMR spectrum of compound **14a** before workup shows two pairs of doublets with $^2J_{PP}$ couplings constants of 65.1 and 54.1 Hz in a 11:1 ratio (de = 84%). Complex **14b** features a slightly less distinct de of about 80% with $^2J_{PP}$ coupling constants of 67.5 Hz for the major and 54.7 Hz for the minor diastereomer. The opening of chelate rings in Cp*Ru complexes bearing bidentate phosphaferrocene-based P,N-ligands with further donors such as PPh_3 or CO is well-known, and comparable diastereoselectivities have been observed.[11,15]

Palladium complexes of the new P,N-ligands were synthesized in order to evaluate their electronic influence and applicability in asymmetric catalysis. Reaction of ligands **3a**, **3b** and **3c** with [Pd(η^3-allyl)Cl]$_2$ in acetone and subsequent addition of $TlPF_6$ afforded the desired complexes **15a**, **15b** and **15c**, respectively (Scheme 6).

Scheme 6. Coordination of Ligands 3 and 4 to Pd



Unfortunately, it was impossible to fully separate the orange complexes from small impurities of palladium black, which prevented the characterization by elemental analysis. However, the identity of complexes **15** was established by multinuclear NMR and mass spectra, and no free ligands remained in solution. The ^1H NMR spectrum of **15a** at ambient temperature shows one set of signals for the coordinated ligand, but the very broad signal in the $^{31}P\{^1H\}$ NMR spectrum suggests dynamic behavior of the complex. Indeed, the ^{31}P resonance splits at lower temperature. At 223 K the $^{31}P\{^1H\}$ NMR spectrum reveals four singlets—two of which are still broad—and one pair of doublets with a $^2J_{PP}$ coupling constant of 62.7 Hz. Accordingly, the ^1H NMR spectrum recorded at this temperature shows six different singlets for Cp rings, including two broad ones. The ^1H NMR spectrum of **15b** shows one set of signals at ambient temperature and a more complex pattern at 223 K; the $^{31}P\{^1H\}$ spectrum gives two broad signals at room temperature and four baseline-separated singlets in the range between −64.7 and −38.4 ppm at 223 K. The singlets in the $^{31}P\{^1H\}$ NMR spectra of **15a** and **15b** may be explained by different rotational and conformational isomers due to the orientation of the allyl moiety, which have been studied intensively by Togni and co-workers in the case of the related ferrocene-based ligands.[4a,b] The doublets observed for **15a** are believed to originate from a polynuclear complex, as the formation of an insoluble compound was found for a related phosphaferrocene−pyridine-based ligand with comparable bite angle.[11] However, no tests were carried out to identify the different low-temperature isomers of **15a** or **15b** because all of them interconvert at ambient temperature, which is relevant for the successive catalytic experiments. Moreover, it has to be considered that no allyl ligand but a 1,3-diphenylallyl ligand is present during the catalytic cycle. **15c**, formed by reaction of [Pd(η^3-allyl)Cl]$_2$ with the sterically more demanding and electron-rich pyrazole derivative **3c**, gives three sharp singlets and one pair of doublets in the expected range of the $^{31}P\{^1H\}$ NMR spectrum at 223 K. This splitting is still partially evident at room temperature. Accordingly, a temperature of 333 K is necessary to achieve a single set of signals in the ^1H NMR spectrum of **15c**. With a view to catalytic application, encouraging data come from the $^{13}C\{^1H\}$ NMR spectrum of complex **15b**. The terminal allyl carbon atoms show

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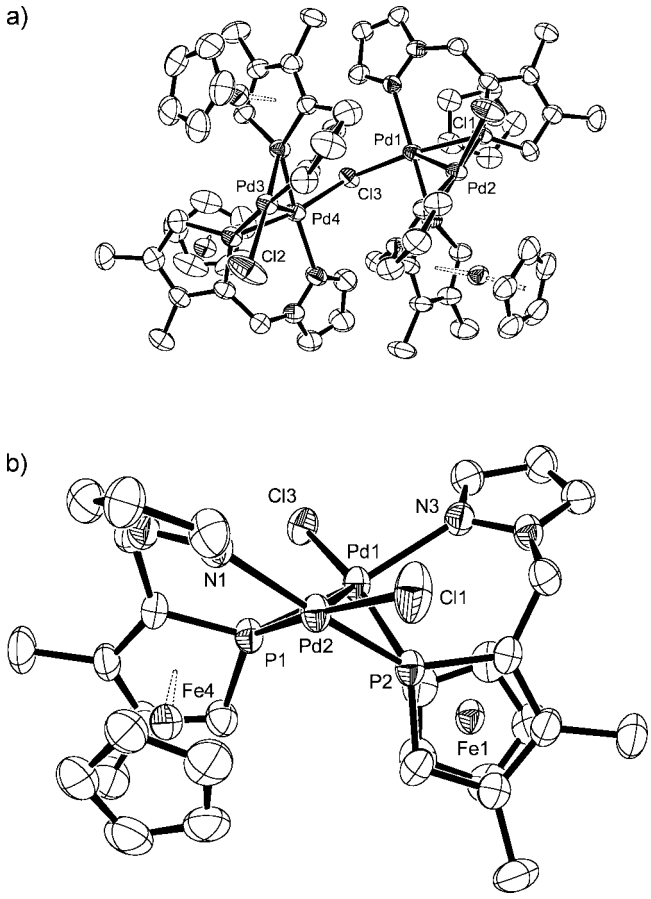
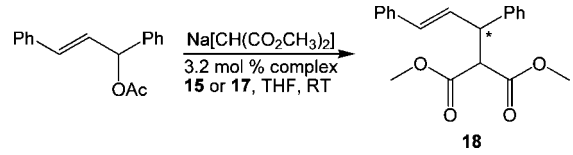


Figure 2. (a) Structure of complex $\mathbf{16}^+$ in the solid of $\mathbf{16}BF_4 \cdot 3(CH_3)_2CO$. All hydrogen atoms are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å] and angles [deg]: Pd1−Pd2 2.7633(8), Pd3−Pd4 2.7645(9), Pd1−Cl3−Pd4 111.09(8). (b) Section of the molecular structure of complex $\mathbf{16}^+$ in the solid of $\mathbf{16}BF_4 \cdot 3(CH_3)_2CO$ showing one of the two dinuclear subunits. All hydrogen atoms are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å] and angles [deg]: Pd1−P1 2.273(2), Pd1−P2 2.258(2), Pd2−P1 2.2917(19), Pd2−P2 2.223(2), Pd1−N3 2.256(6), Pd1−Cl3 2.486(2), Pd2−N1 2.182(6), Pd2−Cl1 2.430(2), P1−Pd1−P2 82.92(7), P2−Pd1−N3 94.06(16), P1−Pd2−P2 83.26(7), P1−Pd2−N1 95.07(17), Pd1−P1−Pd2 74.51(6), Pd1−P2−Pd2 76.14(7).

very different chemical shifts for the atom *trans* to P (84.8 ppm) and *trans* to N (56.8 ppm), respectively. Although this feature does not necessarily correlate with high enantioselectivities in asymmetric catalysis, this difference of 28 ppm is similar to values found for Togni's Pd allyl complexes of the phosphinoferrocene−pyrazole-based PN-ligands (with a 3-*tert*-butyl-substituted pyrazole moiety)[5] and points out the high electronic differentiation induced by the new P,N-ligand. Usually, the shift difference between the terminal allyl carbons in the analogous 1,3-diphenylallyl complexes is even higher. Reaction of ligand **3a** with $[Pd(\eta^3\text{-allyl})Cl]_2$ and $AgBF_4$ in acetone and subsequent diffusion of hexane into the separated supernatant solution incidentally afforded X-ray quality crystals containing complex $\mathbf{16}^+$ in low yield (Figure 2a). Although being a byproduct or formed by degradation of other complexes, $\mathbf{16}^+$ confirms the ability of **3a** to act as a bidentate ligand. Complex $\mathbf{16}BF_4$, crystallizing with 3 equiv of acetone in space group $P2_1/n$, features two subunits within $\mathbf{16}^+$ (Figure 2b), which have identical constitution and are linked by a bridging chloride ligand

Scheme 7. Asymmetric Allylic Alkylation with Pd Complexes 15 and 17 as Catalysts



(Pd1−Cl3−Pd4 111.09(8)°). Each subunit—the one containing Pd1 and Pd2 will be discussed here—possesses two palladium(I) atoms in distorted square-planar coordination environments (P2−Pd1−N3 94.06(16)°, P1−Pd1−P2 82.92(7)°; P1−Pd2−N1 95.07(17)°, P1−Pd2−P2 83.26(7)°), the coordination planes of which form an angle of 71.8°. The deviation from the ideal square-planar geometry is slightly higher for the inner Pd atom (Pd1) as compared to the terminal one (Pd2), reflected by angular sums of 362.94° and 359.95°, respectively. Two ligands **3a** are bound to both Pd atoms in the rare[16] μ^2-bridging mode via their sp^2-hybridized phosphorus atoms, while coordinating to one Pd each via their pyrazole donor functions. The P2−Pd1 and P2−Pd2 vectors are tilted out of the phospholyl mean plane by 41.4° and 30.5°, and the two rings of both phosphaferrocenes deviate by 11.2° and 12.1° from coplanarity. The coordination geometry around the palladium atoms is completed by a terminal or the bridging chloride ligand, respectively. The Pd−P bond lengths (2.223(2)−2.2917(19) Å) fall in the usual range.[16] The Pd−P distances in the chelate assemblies (Pd1−P2 and Pd2−P1) are slightly longer than the bonds from P to Pd that are not part of the particular chelate ring (Pd1−P1 and Pd2−P2). The Pd1−Pd2 distance of 2.7633(8) Å is significantly shorter than the one found for Mathey's dinuclear Pd(I) unit of 3.0996(3) Å[16] and indicates the existence of a Pd−Pd bond in addition to the square-planar coordination environment. The shortest Fe−Pd distances for Pd1 (to Fe2: 3.222 Å) and Pd2 (to Fe1: 3.275 Å) indicate that no Fe−Pd interaction is present.

Coordination of the imidazole-derived ligands **4** to Pd via reaction with $[Pd(\eta^3\text{-allyl})Cl]_2$ in acetone and subsequent addition of $TlPF_6$ yielded complexes **17a** and **17b** (Scheme 6), which could not be fully freed from small amounts of Pd black. Both compounds give one sharp set of signals in the ^1H NMR spectra at 333 K or room temperature, respectively, which broaden and partially split at 223 K. The $^{31}P\{^1H\}$ NMR spectrum of **17a** at 223 K shows two singlets and one pair of doublets in the same range as observed for the complexes with phosphaferrocene−pyrazole-based ligands. Again these signals broaden with rising temperature. An analogous behavior was found for the ^1H NMR spectra of complex **17b**; however only a broad signal was detected in the $^{31}P\{^1H\}$ NMR spectrum even at 223 K. The $^{13}C\{^1H\}$ shifts of the terminal allyl carbon atoms show values as extreme as for the pyrazole-based P,N-ligand **15b** (82.2 and 56.1 ppm) and thus reflect the high electronic differentiation in **17b**.

Catalysis. Complexes **15** and **17** were tested in the asymmetric allylic alkylation reaction. 1,3-Diphenylallyl acetate was reacted with sodium dimethylmalonate in THF at room temperature in the presence of 3.2 mol % of the corresponding complex (Scheme 7). After stirring overnight the alkylation product **18** was purified by column chromatography and isolated in >90% yield.

The observed enantioselectivities are summarized in Table 1. The highest enantiomeric excess of this screening is achieved

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Table 1. Results of the Asymmetric Alkylation Reaction According to Scheme 7

entry	catalyst (ligand)	% ee[b]	abs conf[c]
1	**15a** (*R*-**3a**)	42	(+)-*R*
2	**15a** (*R*-**3a**), NH_4F[a]	13	(+)-*R*
3	**15b** (*R*-**3b**)	19	(−)-*S*
4	**15c** (*R*-**3c**)	6	(+)-*R*
5	**17a** (*S*-**4a**)	33	(+)-*R*
6	**17b** (*S*-**4b**)	39	(+)-*R*

[a] 2 equiv, added as 1.0 M solution in THF. [b] Determined by chiral HPLC (see Experimental Section). [c] Determined by polarimetry and comparison with published data.[18]

with ligand **3a**, with an unsubstituted pyrazole moiety (entry 1). Although the observed ee of 42% clearly exceeds the values found for pyridine-substituted phosphaferrocene ligands (11−19%),[11] these results do not reflect the high electronic differentiation that was expected and cannot reach the enantioselectivities of up to 99% found for Togni's phosphinoferrocene−pyrazole-based P,N-ligands[4a] or Fu's phosphaferrocene−oxazoline-based P,N-ligands (68−82%).[8j] Moreover, the parameters that have been successfully varied to increase the ee in Togni's experiments, i.e., the substitution pattern of the pyrazole and the complex anion, showed a detrimental influence in our studies. Methylation of the pyrazole moiety to make the nitrogen donor more electron rich and thus to enhance the electronic differentiation caused a decline of the ee from 42 to only 6% (entry 4). Addition of the coordinating anion F^-, which was found to be beneficial in the case of the ferrocene derivatives[17] because of enabling a Curtin−Hammet regime by a hypothetical pentacoordinated complex, also led to a decrease of the observed ee from 42 to 13% (entry 2). Even more surprising is the fact that in comparison to the methylene-bridged ligand **3a** the elongated ethylene-bridged derivative **3b** yields the substitution product **18** with opposite absolute configuration (entry 3). The additional methylene group was not anticipated to have a major steric influence nor to be able to invert the electronic properties of the ligand. In the case of the imidazole-based ligands, elongation of the alkyl bridge has only a minor impact on the enantiomeric excess, and values of 33 and 39% are achieved with complexes **17a** and **17b** (entries 5 and 6). The substitution product **18** was again obtained with *R*-configuration although the absolute configuration of the planar chiral phosphaferrocene unit was changed from *R* to *S*. In conclusion, the poor performance of the ligands presented in this study in terms of enantioselectivity is presumably not a consequence of a missing electronic differentiation but most likely due to a lack of pronounced steric interaction between the allylic substrate and the ligand during the catalytic cycle. Considering previous successful applications of planar chiral phosphaferrocene derivatives in asymmetric catalytic reactions,[8] substitution of the Cp by a Cp* unit in ligand **3a** and introduction of additional sterically demanding substituents to the phospholyl or pyrazole rings is expected to improve the ee of the asymmetric allylic alkylation by favoring a specific orientation of the allylic substrate and a regioselective attack of the nucleophile *trans* to the P-donor group. Further research into optimized ligand structures is currently in progress in our laboratory.

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Experimental Section

General Comments. 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 oxygen-free water (5%), and stored under nitrogen. NMR spectra were recorded on a Bruker Avance DRX 500 and a Bruker Avance DRX 200 spectrometer. ^1H and $^{13}C\{^1H\}$ spectra are referenced to the residual solvent signal, and $^{31}P\{^1H\}$ spectra to external H_3PO_4 (85%). Mass spectra were recorded on a Finnigan MAT 8200 (FAB, EI), a Thermo Finnigan Trace DSQ (EI), a Bruker Ultraflex I TOF (MALDI), or a Finnigan LCQ Deca (ESI). 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 Digilab Excalibur FTS 3500 (ATR). Enantiomeric excesses were determined by HPLC using a Daicel Chiralpak IA column and eluting with a *n*-hexane/*i*-PrOH mixture (95:5 v/v; 0.3 mL/min; RT; injection volume 1 μL; retention times (*S*)-**18** 36.2 min, (*R*)-**18** 44.4 min; UV 254 nm). Pfc denotes a 3,4-dimethylphosphaferrocene-2-yl group. (3,4-Dimethylphosphaferrocene-2-yl)methyltrimethylammonium iodide (**6I**),[7] [2-(3,4-dimethylphosphaferrocene-2-yl)ethyl] methylsulfonate (**7**),[10] [Mo(nbd)-$(CO)_4$],[19] $[Cp^*RuCl]_4$,[20] and $[Pd(\eta^3\text{-allyl})Cl]_2$[21] were prepared by published procedures.

Synthesis of 3a. A solution of (3,4-dimethylphosphaferrocene-2-yl)methyltrimethylammonium iodide (**6I**, 1.29 g, 3.00 mmol, 1 equiv) and pyrazole (2.04 g, 30.0 mmol, 10 equiv) in acetic acid (10 mL) was heated for 24 h at 90 °C bath temperature. After alkalizing with aqueous NaOH (2 N) the product was extracted with CH_2Cl_2 and washed three times with aqueous NaOH (2 N) and once with water and saturated aqueous NaCl solution. The organic layer was then dried over anhydrous sodium sulfate, filtered under nitrogen, and evaporated to dryness to give a red oil (805 mg, 86%). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −73.9 (s) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.19 (s, 3H, CCH_3), 2.19 (s, 3H, CCH_3), 3.82 (d, $^2J_{PH}$ = 36.4 Hz, 1H, α-CH), 4.18 (s, 5H, Cp), 4.76 (dd, $^2J_{HH}$ = 14.6 Hz, $^3J_{PH}$ = 7.0 Hz, 1H, CH_2), 4.96 (dd, $^2J_{HH}$ = 14.6 Hz, $^3J_{PH}$ = 14.6 Hz, 1H, CH_2), 6.18 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, CHC*H*CH), 7.30 (d, $^3J_{HH}$ = 2.1 Hz, 1H, C*H*CHCH), 7.45 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CHCHC*H*) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K): δ 13.5 (s, C*C*H$_3$), 16.8 (s, C*C*H$_3$), 51.7 (d, $^2J_{PC}$ = 22.8 Hz, CH_2), 71.1 (s, Cp), 77.0 (d, $^1J_{PC}$ = 59.2 Hz, α-CH), 91.6 (d, $^1J_{PC}$ = 58.0 Hz, α-*C*CH$_2$), 94.1 (d, $^2J_{PC}$ = 4.7 Hz, *C*CH$_3$), 96.6 (d, $^2J_{PC}$ = 7.1 Hz, *C*CH$_3$), 105.4 (br s, CH*C*HCH), 128.2, 138.7 (2 br s, *C*HCH*C*H) ppm. MS (FAB): *m/z* 312 (M^+, 100%), 245 ($[PfcCH_2]^+$, 62%). Anal. Calcd for $C_{15}H_{17}FeN_2P$: C, 57.72; H, 5.49; N, 8.98. Found: C, 57.50; H, 5.64; N, 8.72.

Synthesis of 3b. NaH was added to a solution of pyrazole (1.622 g, 23.83 mmol, 10 equiv) in THF (10 mL) until cessation of the hydrogen evolution. The resulting cloudy solution was treated with [2-(3,4-dimethylphosphaferrocene-2-yl)ethyl] methylsulfonate (**7**, 844 mg, 2.38 mmol, 1 equiv) dissolved in THF (10 mL). The reaction mixture was heated under reflux overnight and then quenched with water (100 mL). The product was extracted with CH_2Cl_2 and washed with aqueous NaOH (2 N) several times and once with water and saturated aqueous NaCl solution. The organic

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layer was then dried over anhydrous sodium sulfate, filtered under nitrogen, and evaporated to dryness to give a red oil (737 mg, 95%). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −78.4 (s) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.01 (s, 3H, CCH_3), 2.18 (s, 3H, CCH_3), 2.70 (m, 2H, PfcCH_2CH_2), 3.71 (d, $^2J_{PH}$ = 36.4 Hz, 1H, α-CH), 4.09 (s, 5H, Cp), 4.13 (m, 2H, PfcCH$_2$CH_2), 6.20 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, CHC*H*CH), 7.25 (d, $^3J_{HH}$ = 2.1 Hz, 1H, C*H*CHCH), 7.51 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CHCHC*H*) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K): δ 13.1 (s, CCH_3), 16.8 (s, CCH_3), 31.8 (d, $^2J_{PC}$ = 19.1 Hz, PfcCH_2CH_2), 53.8 (d, $^3J_{PC}$ = 6.3 Hz, PfcCH$_2$CH_2), 71.9 (s, Cp), 75.6 (d, $^1J_{PC}$ = 58.2 Hz, α-CH), 93.3 (d, $^2J_{PC}$ = 4.7 Hz, *C*CH$_3$), 94.5 (d, $^1J_{PC}$ = 59.1 Hz, α-*C*CH$_2$), 95.6 (d, $^2J_{PC}$ = 6.6 Hz, *C*CH$_3$), 105.0 (s, CH*C*HCH), 129.2, 139.1 (2 s, *C*HCH*C*H) ppm. MS (EI): *m*/*z* 326 (M^+, 42%), 259 ([PfcCH$_2$CH]$^+$, 100%), 245 ([PfcCH$_2$]$^+$, 8%), 121 ([CpFe]$^+$, 14%). Anal. Calcd for $C_{16}H_{19}FeN_2P$: C, 58.92; H, 5.87; N, 8.59. Found: C, 58.86; H, 5.73; N, 7.80.

Synthesis of 3c. A solution of (3,4-dimethylphosphaferrocene-2-yl)methyltrimethylammonium iodide (**6I**, 500 mg, 1.16 mmol, 1 equiv) and 3,5-dimethylpyrazole (1.115 g, 11.60 mmol, 10 equiv) in acetonitrile (10 mL) was heated under reflux overnight. The solvent was removed under high vacuum, and the residue was subjected to column chromatography on neutral alumina. Elution with hexane/diethyl ether (1:1) and subsequent removal of the solvents gave **3c** as a yellow solid (257 mg, 65%). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −74.3 (s) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.18 (s, 3H, CCH_3), 2.19 (s, 3H, CCH_3), 2.28 (br s, 3H, CCH_3), 2.32 (s, 3H, CCH_3), 3.73 (d, $^2J_{PH}$ = 36.4 Hz, 1H, α-CH), 4.16 (s, 5H, Cp), 4.63 (dd, $^2J_{HH}$ = 15.2 Hz, $^3J_{PH}$ = 6.9 Hz, 1H, CH$_2$), 4.79 (dd, $^2J_{HH}$ = 15.2 Hz, $^3J_{PH}$ = 12.3 Hz, 1H, CH$_2$), 5.73 (s, 1H, CCH$_3$C*H*CCH$_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 11.8 (d, $^3J_{PC}$ = 8.5 Hz, CCH_3), 13.5 (s, CCH_3), 14.2 (s, CCH_3), 16.9 (s, CCH_3), 49.0 (d, $^2J_{PC}$ = 21.6 Hz, CH$_2$), 72.1 (s, Cp), 76.3 (d, $^1J_{PC}$ = 58.0 Hz, α-CH), 93.0 (d, $^2J_{PC}$ = 5.0 Hz, *C*CH$_3$), 94.0 (d, $^1J_{PC}$ = 58.6 Hz, α-*C*CH$_2$), 96.2 (d, $^2J_{PC}$ = 6.9 Hz, *C*CH$_3$), 105.0 (s, CCH$_3$*C*HCCH$_3$), 138.2, 146.5 (2 s, *C*CH$_3$CH*C*CH$_3$) ppm. MS (EI): *m*/*z* 340 (M^+, 14%), 244 ([PfcCH]$^+$, 87%), 121 ([CpFe]$^+$, 100%), 56 (Fe^+, 76%).

Synthesis of 4a. Trifluoroacetic acid (5 mL) was carefully added to sodium borohydride (500 mg) at 0 °C. After termination of the vivid reaction alcohol **8a** (702 mg, 2.05 mmol) dissolved in CH_2Cl_2 (10 mL) was dropped into the reaction mixture, which was then stirred overnight. The suspension was alkalized with aqueous NaOH (2 N), and the product was extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous sodium sulfate, filtered under nitrogen, and evaporated to dryness. The residue was subjected to column chromatography on neutral alumina. Elution with diethyl ether/THF (1:1) and subsequent removal of the solvents gave **4a** as an orange oil (382 mg, 57%). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −75.4 (s) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.18 (s, 3H, CCH_3), 2.27 (s, 3H, CCH_3), 3.50 (dd, $^2J_{HH}$ = 15.7 Hz, $^3J_{PH}$ = 8.1 Hz, 1H, CH$_2$), 3.63 (dd, $^2J_{HH}$ = 15.7 Hz, $^3J_{PH}$ = 5.3 Hz, 1H, CH$_2$), 3.62 (s, 3H, NCH_3), 3.68 (d, $^2J_{PH}$ = 36.2 Hz, 1H, α-CH), 4.15 (s, 5H, Cp), 6.74 (br s, 1H, *H*C═CH), 6.90 (br s, 1H, HC═C*H*) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 14.0 (s, CCH_3), 16.9 (s, CCH_3), 28.6 (d, $^2J_{PC}$ = 21.1 Hz, CH$_2$), 33.3 (d, $^5J_{PC}$ = 8.0 Hz, NCH_3), 72.2 (s, Cp), 75.2 (d, $^1J_{PC}$ = 57.7 Hz, α-CH), 94.0 (d, $^2J_{PC}$ = 3.3 Hz, *C*CH$_3$), 94.7 (d, $^1J_{PC}$ = 58.1 Hz, α-*C*CH$_2$), 95.8 (d, $^2J_{PC}$ = 5.5 Hz, *C*CH$_3$), 120.6 (s, H*C*═CH), 127.0 (s, HC═*C*H), 147.6 (br s, NCN) ppm. MS (EI): *m*/*z* 326 (M^+, 55%), 261 ([M − Cp]$^+$, 100%), 205 ([M − CpFe]$^+$, 13%), 121 ([CpFe]$^+$, 45%), 56 (Fe^+, 36%).

Synthesis of 4b. Trifluoroacetic acid (5 mL) was carefully added to sodium borohydride (500 mg) at 0 °C. After termination of the vivid reaction alcohol **8b** (819 mg, 2.30 mmol) dissolved in CH_2Cl_2 (10 mL) was dropped into the reaction mixture, which was then stirred overnight. The suspension was alkalized with aqueous NaOH (2 N), and the product was extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous sodium sulfate, filtered under nitrogen, and evaporated to dryness. The residue was subjected to column chromatography on neutral alumina. Elution with diethyl ether/THF (3:1) and subsequent removal of the solvents gave **4b** as an orange oil (625 mg, 80%). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −79.4 (s) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.10 (s, 3H, CCH_3), 2.19 (s, 3H, CCH_3), 2.55−2.80 (m, 4H, CH_2CH_2), 3.48 (s, 3H, NCH_3), 3.69 (d, $^2J_{PH}$ = 36.2 Hz, 1H, α-CH), 4.10 (s, 5H, Cp), 6.77 (d, $^3J_{HH}$ = 1 Hz, 1H, *H*C═CH), 6.94 (d, $^3J_{HH}$ = 1 Hz, 1H, HC═C*H*) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 13.0 (s, CCH_3), 16.6 (s, CCH_3), 28.7 (d, $^2J_{PC}$ = 19.3 Hz, CH$_2$), 29.3 (d, $^3J_{PC}$ = 7.0 Hz, CH$_2$), 32.4 (s, NCH_3), 71.6 (s, Cp), 75.0 (d, $^1J_{PC}$ = 58.1 Hz, α-CH), 92.7 (d, $^2J_{PC}$ = 4.9 Hz, *C*CH$_3$), 95.4 (d, $^2J_{PC}$ = 6.5 Hz, *C*CH$_3$), 98.1 (d, $^2J_{PC}$ = 58.5 Hz, α-*C*CH$_2$), 120.4 (s, H*C*═CH), 126.7 (s, HC═*C*H), 148.3 (br s, NCN) ppm. MS (EI): *m*/*z* 340 (M^+, 40%), 275 ([M − Cp]$^+$, 100%), 219 ([M − CpFe]$^+$, 7%), 121 ([CpFe]$^+$, 22%). Anal. Calcd for $C_{17}H_{21}FeN_2P$: C, 60.02; H, 6.22; N, 8.23. Found: C, 59.87; H, 6.46; N, 8.08.

Synthesis of 8a. 1-Methylimidazole (0.40 mL, 2.67 mmol, 1 equiv) was dissolved in THF (5 mL), cooled to −78 °C, and treated with *n*-BuLi (1.6 M in hexane, 1.83 mL, 2.94 mmol, 1.1 equiv). After stirring for 1 h at this temperature aldehyde **5** (694 mg, 2.67 mmol, 1 equiv) was added to the yellow solution and stirring was continued overnight. The reaction mixture was quenched with water, and the product was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, filtered under nitrogen, and subjected to column chromatography on neutral alumina. Elution with THF/MeOH (5%) and subsequent removal of the solvents gave **8a** as an orange powder (702 mg, 77%). Only one of the two possible diastereomers was obtained. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −81.2 (s) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.12 (s, 3H, CCH_3), 2.17 (s, 3H, CCH_3), 3.69 (s, 3H, NCH_3), 3.75 (d, $^2J_{PH}$ = 36.8 Hz, 1H, α-CH), 4.24 (s, 5H, Cp), 5.57 (dd, $^3J_{PH}$ = 6.7 Hz, $^3J_{HH}$ = 4.3 Hz, 1H, *H*COH), 6.72 (br s, 1H, *H*C═CH), 6.87 (br s, 1H, HC═C*H*) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 14.2 (s, CCH_3), 16.7 (s, CCH_3), 34.1 (d, $^5J_{PC}$ = 9.4 Hz, NCH_3), 68.9 (d, $^2J_{PC}$ = 12.7 Hz, HCOH), 72.4 (s, Cp), 75.6 (d, $^1J_{PC}$ = 58.0 Hz, α-CH), 92.6 (d, $^2J_{PC}$ = 4.9 Hz, *C*CH$_3$), 96.8 (d, $^2J_{PC}$ = 6.9 Hz, *C*CH$_3$), 101.0 (d, $^1J_{PC}$ = 58.4 Hz, α-*C*HCOH), 122.1 (br s, H*C*═CH), 126.0 (br s, HC═*C*H), 148.6 (br s, NCN) ppm. The signal of the hydroxyl proton cannot be assigned. MS (EI): *m*/*z* 342 (M^+, 94%), 277 ([M − Cp]$^+$, 100%), 121 ([CpFe]$^+$, 24%). Anal. Calcd for $C_{16}H_{19}FeN_2OP$: C, 56.17; H, 5.60; N, 8.19. Found: C, 56.34; H, 5.79; N, 7.91.

Synthesis of 8b. 1,2-Dimethylimidazole (277 mg, 2.88 mmol, 1 equiv) was dissolved in THF (5 mL), cooled to −78 °C, and treated with *n*-BuLi (1.6 M in hexane, 1.98 mL, 3.17 mmol, 1.1 equiv). After stirring for 1 h at this temperature aldehyde **5** (750 mg, 2.88 mmol, 1 equiv) was added to the yellow solution and stirring was continued overnight. The reaction mixture was quenched with water, and the product was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, filtered under nitrogen, and subjected to column chromatography on neutral alumina. Elution with pure THF and subsequent removal of the solvents gave **8b** as a yellow-orange powder (881 mg, 86%). The diastereomers were obtained in a 5:1 ratio. Major diastereomer: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ −85.9 (s) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.14 (s, 3H, CCH_3), 2.20 (s, 3H, CCH_3), 2.77 (m, 2H, CH$_2$), 3.45 (s, 3H, NCH_3), 3.75 (d, $^2J_{PH}$ = 36.5 Hz, 1H, α-CH), 4.23 (s, 5H, Cp), 4.83 (m, 1H, *H*COH), 6.78 (br s, 1H, *H*C═CH), 6.95 (br s, 1H, HC═C*H*) ppm. The signal of the hydroxyl proton cannot be assigned. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 13.6 (s, CCH_3), 16.5 (s, CCH_3), 32.5 (s, NCH_3), 36.7 (d, $^3J_{PC}$ = 2.8 Hz, CH$_2$), 69.8 (d, $^2J_{PC}$ = 12.3 Hz, HCOH), 72.0 (s, Cp), 75.9 (d, $^1J_{PC}$ = 58.3 Hz, α-CH), 91.2 (d, $^2J_{PC}$ = 5.2

Hz, *C*CH$_3$), 96.2 (d, $^2J_{PC}$ = 7.0 Hz, *C*CH$_3$), 104.1 (d, $^1J_{PC}$ = 60.0 Hz, α-*C*HCOH), 120.2 (s, H*C*═CH), 126.6 (s, HC═CH), 145.9 (s, NCN) ppm. Minor diastereomer: ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 298 K): δ −83.5 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.17 (s, 3H, CCH$_3$), 2.31 (s, 3H, CCH$_3$), 3.07 (m, 2H, CH$_2$), 3.64 (s, 3H, NCH$_3$), 3.79 (d, $^2J_{PH}$ = 36.6 Hz, 1H, α-CH), 4.15 (s, 5H, Cp), 4.97 (m, 1H, *H*COH), 6.84 (br s, 1H, *H*C═CH), 6.94 (br s, 1 H, HC═C*H*) ppm. The signal of the hydroxyl proton cannot be assigned. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 298 K): δ 13.7 (s, C*C*H$_3$), 16.6 (s, C*C*H$_3$), 32.5 (s, NCH$_3$), 33.5 (d, $^3J_{PC}$ = 15.1 Hz, CH$_2$), 69.0 (d, $^2J_{PC}$ = 16.7 Hz, HCOH), 71.8 (s, Cp), 76.0 (d, $^1J_{PC}$ = 57.4 Hz, α-CH), 94.2 (d, $^2J_{PC}$ = 5.1 Hz, *C*CH$_3$), 96.8 (d, $^2J_{PC}$ = 6.8 Hz, *C*CH$_3$), 99.7 (d, $^1J_{PC}$ = 60.8 Hz, α-*C*HCOH), 120.2 (s, H*C*═CH), 126.5 (s, HC═CH), 146.7 (s, NCN) ppm. MS (EI): *m*/*z* 356 (M$^+$, 61%), 273 ([M − Cp − H$_2$O]$^+$, 100%), 121 ([CpFe]$^+$, 42%). Anal. Calcd for $C_{17}H_{21}FeN_2OP$: C, 57.33; H, 5.94; N, 7.86. Found: C, 57.19; H, 6.18; N, 7.63.

Synthesis of 9b. A solution of ligand **3b** (65 mg, 0.20 mmol) in THF (10 mL) was slowly added to a solution of [Mo(nbd)(CO)$_4$] (60 mg, 0.20 mmol) in THF (5 mL). The reaction mixture was stirred for 4 h at ambient temperature. After evaporation of the solvent the NMR spectra in $CDCl_3$ showed the desired chelate complex **9b** and the bis-ligand complex **10b** in a 2:1 ratio. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 298 K): δ −24.7 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.11 (s, 3H, CCH$_3$), 2.18 (s, 3H, CCH$_3$), 2.67 (m, 2H, PfcC*H*$_2$CH$_2$), 3.71 (d, $^2J_{PH}$ = 34.3 Hz, 1H, α-CH), 4.11 (s, 5 H, Cp), 4.79 (m, 2H, PfcCH$_2$C*H*$_2$), 6.33 (vt, $^3J_{HH}$ = 2.4 Hz, 1H, CHC*H*CH), 7.52 (d, $^3J_{HH}$ = 2.6 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*CHCH), 7.81 (dd, $^3J_{HH}$ = 2.4 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, CHCHC*H*) ppm.

Synthesis of 10a and 11a. Ligand **3a** (241 mg, 0.77 mmol) and [Mo(CO)$_6$] (205 mg, 0.77 mmol) were dissolved in THF (10 mL) and heated at 60 °C overnight. The solution was then evaporated to dryness, and the residue was subjected to column chromatography on neutral alumina. **11a** was eluted with hexane/diethyl ether (3:1) to 1:1; **10a** with pure diethyl ether. Removal of the solvents afforded **11a** as a yellow powder (169 mg, 40%) and **10a** as an orange solid (36 mg, 11%). **10a**: ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 298 K): δ −18.0 (s), −17.9 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.12 (s, 6H, CCH$_3$), 2.14 (s, 12H, CCH$_3$), 2.15 (s, 6H, CCH$_3$), 3.56 (d, $^2J_{PH}$ = 33.0 Hz, 2H, α-CH), 3.57 (d, $^2J_{PH}$ = 33.0 Hz, 2H, α-CH), 4.25 (s, 20H, Cp), 4.79 (m, 8H, CH$_2$), 6.05 (vt, $^2J_{HH}$ = 2.1 Hz, 2H, CHC*H*CH), 6.09 (vt, $^2J_{HH}$ = 2.1 Hz, 2H, CHC*H*CH), 7.09 (d, $^3J_{HH}$ = 2.2 Hz, 2H, C*H*CHCH), 7.15 (d, $^3J_{HH}$ = 2.2 Hz, 2H, C*H*CHCH), 7.38 (d, $^3J_{HH}$ = 2.1 Hz, 2H, CHCHC*H*), 7.39 (d, $^3J_{HH}$ = 2.1 Hz, 2H, CHCHC*H*) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 298 K): δ 13.7 (s, C*C*H$_3$), 16.6 (s, C*C*H$_3$), 16.6 (s, C*C*H$_3$), 50.3 (br s, CH$_2$), 72.5 (br s, α-CH), 73.9 (s, Cp), 84.7 (br s, *C*CH$_3$), 93.1 (br s, α-*C*CH$_2$), 94.6 (d, $^2J_{PC}$ = 4.6 Hz, *C*CH$_3$), 107.0 (br s, CH*C*HCH), 128.8 (br s, *C*HCHCH), 139.6 (br s, CHCH*C*H), 206.5 (m, CO) 212.2 (m, CO) ppm. MS (FAB): *m*/*z* 750 ([M − 3CO]$^+$, 23%), 494 ([M − **3a** − CO]$^+$, 50%), 410 ([M − **3a** − 4CO]$^+$, 100%), 312 ([**3a**]$^+$, 64%), 245 ([PfcCH$_2$]$^+$, 38%), 121 ([CpFe]$^+$, 70%), 56 (Fe$^+$, 41%). IR ν_{CO} (ATR, cm^{-1}): 2028, 1933, 1906, 1897. **11a**: ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 298 K): δ −21.4 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.21 (s, 3H, CCH$_3$), 2.22 (s, 3H, CCH$_3$), 3.81 (d, $^2J_{PH}$ = 33.7 Hz, 1H, α-CH), 4.31 (s, 5H, Cp), 4.65−4.98 (m, 2H, CH$_2$), 6.21 (br s, 1H, CHC*H*CH), 7.30 (br s, 1H, C*H*CHCH), 7.47 (br s, 1H, CHCHC*H*) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 298 K): δ 13.6 (d, $^3J_{PC}$ = 2.9 Hz, C*C*H$_3$), 16.6 (d, $^3J_{PC}$ = 4.6 Hz, C*C*H$_3$), 49.6 (d, $^2J_{PC}$ = 19.1 Hz, CH$_2$), 72.3 (d, $^1J_{PC}$ = 3.2 Hz, α-CH), 73.9 (s, Cp), 84.6 (d, $^2J_{PC}$ = 6.0 Hz, *C*CH$_3$), 93.4 (d, $^2J_{PC}$ = 5.4 Hz, *C*CH$_3$), 95.2 (s, α-*C*CH$_2$), 105.7 (br s, CH*C*HCH), 128.0, 139.2 (2 br s, *C*HCH*C*H), 204.0 (d, $^2J_{PC}$ = 10.9 Hz, *cis*-CO), 208.0 (d, $^2J_{PC}$ = 31.9 Hz, *trans*-CO) ppm. MS (EI): *m*/*z* 410 ([M − 5CO]$^+$, 24%), 312 ([**3a**]$^+$, 48%), 244 ([PfcCH]$^+$, 8%), 121 ([CpFe]$^+$, 70%), 56 (Fe$^+$, 41%). IR ν_{CO} (ATR, cm^{-1}): 2078, 1956. Anal. Calcd for $C_{20}H_{17}FeMoN_2O_5P$: C, 43.83; H, 3.13; N, 5.11. Found: C, 43.88; H, 3.74; N, 5.40.

Synthesis of 10b and 11b. Ligand **3b** (401 mg, 1.23 mmol) and [Mo(CO)$_6$] (327 mg, 1.23 mmol) were dissolved in THF (10 mL) and heated at 60 °C for 36 h. The solution was then evaporated to dryness, and the residue was subjected to column chromatography on neutral alumina. **11b** was eluted with hexane/diethyl ether 3:1); **10b** with pure diethyl ether. Removal of the solvents afforded **11b** (244 mg, 35%) and **10b** (170 mg, 32%) as yellow solids. **10b**: ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 298 K): δ −22.6 (s), −22.5 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.01 (s, 6H, CCH$_3$), 2.02 (s, 6H, CCH$_3$), 2.16 (s, 12H, CCH$_3$), 2.70 (m, 8H, PfcC*H*$_2$CH$_2$), 3.59 (d, $^2J_{PH}$ = 32.6 Hz, 4H, α-CH), 4.06 (m, 8H, PfcCH$_2$C*H*$_2$), 4.19 (s, 10H, Cp), 4.23 (s, 10H, Cp), 6.19 (br s, 4H, CHC*H*CH), 7.19 (d, $^3J_{HH}$ = 2.2 Hz, 2H, C*H*CHCH), 7.22 (d, $^3J_{HH}$ = 2.1 Hz, 2H, C*H*CHCH), 7.51 (d, $^3J_{HH}$ = 1.8 Hz, 4H, CHCHC*H*) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 298 K): δ 13.1 (br s, C*C*H$_3$), 16.6 (br s, C*C*H$_3$), 30.6 (d, $^2J_{PC}$ = 16.8 Hz, Pfc*C*H$_2$CH$_2$), 30.7 (d, $^2J_{PC}$ = 15.0 Hz, Pfc*C*H$_2$CH$_2$), 53.4 (d, $^3J_{PC}$ = 5.0 Hz, PfcCH$_2$*C*H$_2$), 71.2 (br s, α-CH), 73.7 (s, Cp), 88.3 (d, $^2J_{PC}$ = 4.8 Hz, *C*CH$_3$), 88.4 (d, $^2J_{PC}$ = 4.9 Hz, *C*CH$_3$), 92.4 (br s, *C*CH$_3$), 93.8 (s, α-*C*CH$_2$), 105.3 (s, CH*C*HCH), 129.1 (s, *C*HCHCH), 139.3 (s, CHCH*C*H), 207.1 (m, CO), 212.6 (m, CO) ppm. MS (FAB): *m*/*z* 778 ([M − 3CO]$^+$, 22%), 508 ([M − **3b** − CO]$^+$, 56%), 424 ([M − **3b** − 4CO]$^+$, 100%), 326 ([**3b**]$^+$, 75%). IR ν_{CO} (ATR, cm^{-1}): 2027, 1921, 1894. **11b**: ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 298 K): δ −27.5 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.99 (s, 3H, CCH$_3$), 2.18 (s, 3H, CCH$_3$), 2.68 (m, 2H, PfcC*H*$_2$CH$_2$), 3.69 (d, $^2J_{PH}$ = 33.7 Hz, 1H, α-CH), 4.05 (m, 2H, PfcCH$_2$C*H*$_2$), 4.23 (s, 5H, Cp), 6.20 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, CHC*H*CH), 7.22 (d, $^3J_{HH}$ = 2.1 Hz, 1H, C*H*CHCH), 7.52 (d, $^3J_{HH}$ = 2.1 Hz, 1H, CHCHC*H*) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 298 K): δ 13.0 (d, $^3J_{PC}$ = 3.4 Hz, C*C*H$_3$), 16.5 (d, $^3J_{PC}$ = 4.7 Hz, C*C*H$_3$), 30.4 (d, $^2J_{PC}$ = 17.0 Hz, Pfc*C*H$_2$CH$_2$), 53.4 (d, $^3J_{PC}$ = 2.2 Hz, PfcCH$_2$*C*H$_2$), 70.9 (d, $^1J_{PC}$ = 3.4 Hz, α-CH), 73.8 (s, Cp), 88.0 (d, $^2J_{PC}$ = 7.5 Hz, *C*CH$_3$), 92.6 (d, $^2J_{PC}$ = 5.5 Hz, *C*CH$_3$), 94.3 (s, α-*C*CH$_2$), 105.4 (s, CH*C*HCH), 129.1 (s, *C*HCHCH), 139.5 (s, CHCH*C*H), 204.3 (d, $^2J_{PC}$ = 10.9 Hz, *cis*-CO), 208.1 (d, $^2J_{PC}$ = 30.9 Hz, *trans*-CO) ppm. MS (FAB): *m*/*z* 564 (M$^+$, 15%), 508 ([M − 2CO]$^+$, 57%), 480 ([M − 3CO]$^+$, 34%), 452 ([M − 4CO]$^+$, 17%), 424 ([M − 5CO]$^+$, 74%), 326 ([**3b**]$^+$, 92%), 258 ([PfcCH$_2$CH]$^+$, 100%), 245 ([PfcCH$_2$]$^+$, 29%). IR ν_{CO} (ATR, cm^{-1}): 2075, 1949.

Synthesis of 12a. [Cp*RuCl]$_4$ (137 mg, 0.13 mmol, 1 equiv) was dissolved in THF (5 mL) and treated with a solution of **3a** (157 mg, 0.50 mmol, 4 equiv) in THF (5 mL). The solution was stirred for a few minutes and then evaporated to dryness, affording a brownish powder in quantitative yield according to the NMR spectra (294 mg, 100%). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 223 K): δ 5.8 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 223 K): δ 1.60 (d, $^4J_{PH}$ = 2.6 Hz, 15H, Cp*), 2.18 (s, 3H, CCH$_3$), 2.21 (s, 3H, CCH$_3$), 3.87 (d, $^2J_{PH}$ = 34.1 Hz, 1H, α-CH), 3.94 (s, 5H, Cp), 4.50 (m, 2H, CH$_2$), 6.32 (br s, 1H, CHC*H*CH), 7.41 (br s, 1H, C*H*CHCH), 8.13 (br s, 1H, CHCHC*H*) ppm. MS (MALDI): *m*/*z* 549 ([M − Cl]$^+$, 100%).

Synthesis of 12b. [Cp*RuCl]$_4$ (101 mg, 0.09 mmol, 1 equiv) was dissolved in THF (5 mL) and treated with a solution of **3b** (121 mg, 0.37 mmol, 4 equiv) in THF (5 mL). The solution was stirred for a few minutes and then evaporated to dryness, affording a red powder in quantitative yield according to the NMR spectra (222 mg, 100%). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 298 K): δ 16.4 (s) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.62 (d, $^4J_{PH}$ = 2.7 Hz, 15H, Cp*), 2.11 (s, 3H, CCH$_3$), 2.17 (s, 3H, CCH$_3$), 2.39−2.85 (m, 2H, PfcC*H*$_2$CH$_2$), 3.56 (d, $^2J_{PH}$ = 33.6 Hz, 1H, α-CH), 3.86 (s, 5H, Cp), 4.23 (m, 1H, PfcCH$_2$C*H*$_2$), 4.99 (vt, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 13.3 Hz, 1H, PfcCH$_2$C*H*$_2$), 6.39 (vt, $^3J_{HH}$ = 2.4 Hz, 1H, CHC*H*CH), 7.55 (d, $^3J_{HH}$ = 2.4 Hz, 1H, C*H*CHCH), 8.41 (d, $^3J_{HH}$ = 2.4 Hz, 1H, CHCHC*H*) ppm. MS (MALDI): *m*/*z* 563 ([M − Cl]$^+$, 100%). Anal. Calcd for $C_{26}H_{34}ClFeN_2PRu$: C, 52.23; H, 5.73; N, 4.69. Found: C, 51.56; H, 4.97; N, 4.40.

Synthesis of 13aOTf. [Cp*Ru(CH_3CN)$_3$]OTf (68 mg, 0.13 mmol, 1 equiv) was suspended in THF (5 mL), and ligand **3b** (84 mg, 0.27 mmol, 2 equiv) was slowly added. The reaction mixture was stirred for 5 min and then filtered through a G3 frit. Evaporation of the yellow filtrate yielded the product as an orange powder (135 mg, 99%). The diastereomers were obtained in a 1:1 ratio. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 0.3 (d, $^2J_{PP}$ = 55.1 Hz), 13.4 (d, $^2J_{PP}$ = 56.4 Hz), 25.2 (d, $^2J_{PP}$ = 56.4 Hz), 31.1 (d, $^2J_{PP}$ = 55.1 Hz) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.42 (vt, $^4J_{PH}$ = 2.9 Hz, 15H, Cp*), 1.68 (vt, $^4J_{PH}$ = 3.1 Hz, 15H, Cp*), 2.23 (s, 6H, CCH_3), 2.30 (s, 3H, CCH_3), 2.32 (s, 6H, CCH_3), 2.40 (s, 6H, CCH_3), 2.41 (s, 3H, CCH_3), 3.34 (s, 5H, Cp), 3.61 (d, $^2J_{PH}$ = 33.0 Hz, 1H, α-CH), 3.63 (d, $^2J_{PH}$ = 33.1 Hz, 1H, α-CH), 3.88 (d, $^2J_{PH}$ = 32.3 Hz, 1H, α-CH), 4.14 (s, 5H, Cp), 4.19 (s, 5H, Cp), 4.28−4.65 (m, 4H, CH_2), 4.54 (s, 5H, Cp), 4.85 (dd, $^2J_{HH}$ = 14.5 Hz, $^3J_{PH}$ = 8.7 Hz, 1H, CH_2), 5.09 (dd, $^2J_{HH}$ = 14.4 Hz, $^3J_{PH}$ = 9.3 Hz, 1H, CH_2), 5.35−5.70 (m, 2H, CH_2), 6.14 (vt, $^3J_{HH}$ = 2.0 Hz, 1H, CHC*H*CH), 6.20 (vt, $^3J_{HH}$ = 2.0 Hz, 1H, CHC*H*CH), 6.26 (vt, $^3J_{HH}$ = 2.5 Hz, 1H, CHC*H*CH), 6.45 (vt, $^3J_{HH}$ = 2.4 Hz, 1H, CHC*H*CH), 7.07 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C*H*CHCH), 7.15 (br s, 1H, C*H*CHCH), 7.19 (d, $^3J_{HH}$ = 2.3 Hz, 1H, C*H*CHCH), 7.40 (d, $^3J_{HH}$ = 2.1 Hz, 1H, C*H*CHCH), 7.43 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CHCHC*H*), 7.71 (br s, 1H, CHCHC*H*), 8.04 (d, $^3J_{HH}$ = 2.3 Hz, 1H, CHCHC*H*), 8.39 (d, $^3J_{HH}$ = 2.4 Hz, 1H, CHCHC*H*) ppm. MS (MALDI): *m*/*z* 861 (M^+, 3%), 549 ([M − **3a**]$^+$, 100%). Anal. Calcd for $C_{41}H_{49}F_3Fe_2N_4O_3P_2RuS$: C, 48.78; H, 4.89; N, 5.55. Found: C, 48.08; H, 4.54; N, 5.20.

Synthesis of 13bOTf. [Cp*Ru(CH_3CN)$_3$]OTf (76 mg, 0.15 mmol, 1 equiv) was suspended in THF (5 mL), and ligand **3b** (97 mg, 0.30 mmol, 2 equiv) was slowly added. The reaction mixture was stirred for 5 min and then filtered through a G3 frit. Evaporation of the yellow filtrate yielded the product as an orange powder (152 mg, 98%). The diastereomers were obtained in a 1:1 ratio. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 10.9 (d, $^2J_{PP}$ = 61.2 Hz), 13.7 (d, $^2J_{PP}$ = 64.1 Hz), 18.8 (d, $^2J_{PP}$ = 61.2 Hz), 26.6 (d, $^2J_{PP}$ = 64.1 Hz) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.85 (dd, $^4J_{PH}$ = 2.6/3.1 Hz, 15H, Cp*), 1.92 (vt, $^4J_{PH}$ = 2.8 Hz, 15H, Cp*), 1.98 (s, 6H, CCH_3), 2.02 (s, 6H, CCH_3), 2.11 (s, 3H, CCH_3), 2.20 (s, 3H, CCH_3), 2.21 (s, 3H, CCH_3), 2.26 (s, 3H, CCH_3), 2.54−2.93 (m, 8H, PfcCH_2CH_2), 3.13 (d, $^2J_{PH}$ = 32.6 Hz, 1H, α-CH), 3.22 (d, $^2J_{PH}$ = 33.1 Hz, 1H, α-CH), 3.47 (d, $^2J_{PH}$ = 31.8 Hz, 1H, α-CH), 3.49 (d, $^2J_{PH}$ = 32.4 Hz, 1H, α-CH), 3.54 (s, 5H, Cp), 3.94 (s, 5H, Cp), 4.40 (s, 5H, Cp), 4.43 (s, 5H, Cp), 4.50−5.10 (m, 8H, PfcCH_2CH_2), 6.07 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, CHC*H*CH), 6.23 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, CHC*H*CH), 6.24 (vt, $^3J_{HH}$ = 2.6 Hz, 1H, CHC*H*CH), 6.37 (vt, $^3J_{HH}$ = 2.5 Hz, 1H, CHC*H*CH), 6.62 (d, $^3J_{HH}$ = 2.2 Hz, 1H, C*H*CHCH), 7.11 (d, $^3J_{HH}$ = 2.2 Hz, 1H, C*H*CHCH), 7.14 (d, $^3J_{HH}$ = 2.1 Hz, 1H, C*H*CHCH), 7.35 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H*CHCH), 7.40 (br s, 1H, CHCHC*H*), 7.46 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CHCHC*H*), 8.04 (d, $^3J_{HH}$ = 2.8 Hz, 1H, CHCHC*H*), 8.06 (d, $^3J_{HH}$ = 2.9 Hz, 1H, CHCHC*H*) ppm. MS (MALDI): *m*/*z* 889 (M^+, 2%), 563 ([M − **3b**]$^+$, 100%). Anal. Calcd for $C_{43}H_{53}F_3Fe_2N_4O_3P_2RuS$: C, 49.77; H, 5.15; N, 5.40. Found: C, 50.28; H, 5.34; N, 5.35.

Synthesis of 14a. Ru complex **12a** (176 mg, 0.30 mmol) was dissolved in CH_2Cl_2 and treated with a solution of PPh_3 (78 mg, 0.30 mmol) in CH_2Cl_2 (5 mL). The resulting red solution was stirred for 5 min and then evaporated to dryness. The NMR spectrum of the crude product shows quantitative formation of the desired complex. Further purification is possible by column chromatography on neutral alumina and elution with pure diethyl ether. Removal of the solvent yielded the product as a red powder (104 mg, 41%). The diastereomers were obtained in a 11.4:1 ratio. Major diastereomer: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 22.5 (d, $^2J_{PP}$ = 65.1 Hz, Pfc), 49.5 (d, $^2J_{PP}$ = 65.1 Hz, PPh_3) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.20 (dd, $^4J_{PH}$ = 2.7 Hz, $^4J_{PH}$ = 1.7 Hz, 15H, Cp*), 2.17 (s, 3H, CCH_3), 2.45 (s, 3H, CCH_3), 2.98 (d, $^2J_{PH}$ = 30.0 Hz, 1H, α-CH), 3.45 (s, 5H, Cp), 4.81 (dd, $^2J_{HH}$ = 14.6 Hz, $^3J_{PH}$ = 14.6 Hz, 1H, CH_2), 4.99 (dd, $^2J_{HH}$ = 14.4 Hz, $^3J_{PH}$ = 10.4 Hz, 1H, CH_2), 6.16 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, CHC*H*CH), 7.35 (m, 15H, PPh_3), 7.42 (dd, $^3J_{HH}$ = 1.8 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, C*H*CHCH), 8.18 (dd, $^3J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, CHCHC*H*) ppm. Minor diastereomer: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 24.1 (d, $^2J_{PP}$ = 54.1 Hz, Pfc), 45.7 (d, $^2J_{PP}$ = 54.1 Hz, PPh_3) ppm. MS (MALDI): *m*/*z* 811 ([M − Cl]$^+$, 5%), 549 ([M − Cl − PPh_3]$^+$, 100%).

Synthesis of 14b. Ru complex **12b** (222 mg, 0.37 mmol) was dissolved in THF and treated with a solution of PPh_3 (97 mg, 0.37 mmol) in THF (5 mL). The resulting red solution was evaporated to dryness to afford a red powder (319 mg, 100%). Further purification is possible by column chromatography on neutral alumina and elution with pure diethyl ether (144 mg, 45%). The diastereomers were obtained in a 8.9:1 ratio. Major diastereomer: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 17.1 (d, $^2J_{PP}$ = 67.5 Hz, Pfc), 49.8 (d, $^2J_{PP}$ = 67.5 Hz, PPh_3) ppm. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.26 (dd, $^4J_{PH}$ = 1.8/2.5 Hz, 15H, Cp*), 2.22 (s, 6H, CCH_3), 2.39 (m, 1H, PfcCH_2CH$_2$), 2.94 (m, 1H, PfcCH_2CH$_2$), 3.07 (d, $^2J_{PH}$ = 30.1 Hz, 1H, α-CH), 3.49 (s, 5H, Cp), 3.98 (m, 1H, PfcCH$_2$CH_2), 4.29 (m, 1H, PfcCH$_2$CH_2), 6.16 (dd, $^3J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 1.8 Hz, 1H, CHC*H*CH), 7.33 (m, 15H, PPh_3), 7.46 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H*CHCH), 8.02 (d, $^3J_{HH}$ = 2.2 Hz, 1H, CHCHC*H*) ppm. Minor diastereomer: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): δ 25.7 (d, $^2J_{PP}$ = 54.6 Hz, Pfc), 48.4 (d, $^2J_{PP}$ = 54.6 Hz, PPh_3) ppm. MS (MALDI): *m*/*z* 825 ([M − Cl]$^+$, 1%), 563 ([M − Cl − PPh_3]$^+$, 100%).

Synthesis of 15a. Pd(η^3-allyl)Cl]$_2$ (116 mg, 0.32 mmol, 1 equiv) was dissolved in hot acetone (5 mL). A solution of **3a** (200 mg, 0.64 mmol, 2 equiv) in acetone (5 mL) was dropped into the solution. After stirring for a few minutes a solution of $TlPF_6$ (223 mg, 0.64 mmol, 2 equiv) in acetone (2 mL) was added. The precipitated TlCl was removed by filtration through Celite, and the filtrate was evaporated to dryness. Yield: quantitative (according to the NMR spectra). $^{31}P\{^1H\}$ NMR (81 MHz, acetone-d_6, 223 K): δ −143.1 (sept, $^1J_{PF}$ = 708.6 Hz, PF_6^-), −50.6 (br s), −41.5 (br s), −38.2 (d, $^2J_{PP}$ = 62.7 Hz), −36.3 (s), −34.5 (s), −33.1 (d, $^2J_{PP}$ = 62.7 Hz) ppm. ^1H NMR (200 MHz, acetone-d_6, 298 K): δ 2.32 (s, 3H, CCH_3), 2.38 (s, 3H, CCH_3), 2.90 (br m, 1H, allyl-H), 3.90 (br m, 1H allyl-H), 4.27 (s, 5H, Cp), 4.46 (d, $^2J_{PH}$ = 36.7 Hz, 1H, α-CH), 5.05 (br m, 2H, allyl-H), 5.10 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{PH}$ = 9.0 Hz, 1H, CH_2), 5.39 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{PH}$ = 19.6 Hz, 1H, CH_2), 6.14 (br m, 1H, allyl-H), 6.59 (s, 1H, CHC*H*CH), 8.13 (s, 1H, C*H*CHCH), 8.25 (s, 1H, CHCHC*H*) ppm. MS (ESI): *m*/*z* 459 ([M − PF_6]$^+$, 100%).

Synthesis of 15b. [Pd(η^3-allyl)Cl]$_2$ (68 mg, 0.18 mmol, 1 equiv) was dissolved in hot acetone (5 mL). A solution of **3b** (122 mg, 0.37 mmol, 2 equiv) in acetone (5 mL) was dropped into the solution. After stirring for a few minutes a solution of $TlPF_6$ (131 mg, 0.37 mmol, 2 equiv) in acetone (2 mL) was added. The precipitated TlCl was removed by filtration through Celite, and the filtrate was evaporated to dryness. Yield: quantitative (according to the NMR spectra). $^{31}P\{^1H\}$ NMR (81 MHz, acetone-d_6, 223 K): δ −143.1 (sept, $^1J_{PF}$ = 708.6 Hz, PF_6^-), −64.7 (br s), −56.4 (br s), −40.0 (br s), −38.4 (s) ppm. ^1H NMR (200 MHz, acetone-d_6, 298 K): δ 2.22 (s, 3H, CCH_3), 2.26 (s, 3H, CCH_3), 2.96 (m, 2H, PfcCH_2CH$_2$), 4.25 (d, $^2J_{PH}$ = 36.1 Hz, 1H, α-CH), 4.28 (s, 5H, Cp), 4.82 (m, 2H, PfcCH$_2$CH_2), 6.13 (br m, 1H, allyl-H), 6.67 (vt, $^3J_{HH}$ = 2.3 Hz, 1H, CHC*H*CH), 8.02 (d, $^3J_{HH}$ = 2.3 Hz, 1H, C*H*CHCH), 8.20 (d, $^3J_{HH}$ = 2.3 Hz, 1H, CHCHC*H*) ppm. The signals of the other allyl protons cannot be assigned unambiguously. $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6, 298 K): δ 14.4 (d, $^3J_{PC}$ = 3.3 Hz, C*C*H$_3$), 17.4 (d, $^3J_{PC}$ = 5.0 Hz, C*C*H$_3$), 33.9 (d, $^2J_{PC}$ = 12.8 Hz, Pfc*C*H$_2$CH$_2$), 53.9 (d, $^3J_{PC}$ = 11.9 Hz, PfcCH$_2$*C*H$_2$), 56.8 (br s, *C*H$_2$CHCH$_2$), 70.7 (br s, α-CH), 75.8 (s, Cp), 84.8 (br d, $^2J_{PC}$ = 34.0 Hz, CH$_2$CH*C*H$_2$), 94.6 (d, $^2J_{PC}$ = 5.4 Hz, *C*CH$_3$), 96.5 (s, α-*C*CH$_2$), 110.2 (s, CH*C*HCH), 122.5 (br s, CH$_2$*C*HCH$_2$), 135.8, 145.7 (2 s, *C*HCH*C*H) ppm. The signal of the remaining phospholyl carbon atom could not be assigned. MS (MALDI): *m*/*z* 473 ([M − PF_6]$^+$, 100%).

Synthesis of 15c. [Pd(η^3-allyl)Cl]$_2$ (44 mg, 0.12 mmol, 1 equiv) was dissolved in hot acetone (5 mL). A solution of **3c** (82 mg, 0.24

Table 2. Crystallographic Data for Compounds 16$BF_4 \cdot 3(CH_3)_2CO$ and 13b$FeCl_3 \cdot CH_2Cl_2$

	16$BF_4 \cdot 3(CH_3)_2CO$	**13b**$FeCl_3 \cdot CH_2Cl_2$
formula	$C_{69}H_{86}BCl_3F_4Fe_4N_8O_3P_4Pd_4$	$C_{43}H_{55}Cl_5Fe_3N_4P_2Ru$
M	2041.50	1135.72
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a/Å	12.7190(7)	10.6217(7)
b/Å	40.852(3)	30.3377(19)
c/Å	15.2655(8)	15.2301(9)
β/deg	90.774(7)	97.290(8)
V/Å^3	7931.2(8)	4868.1(5)
Z	4	4
D_c/g cm^{-3}	1.710	1.550
$F(000)$	4080	2312
μ(Mo Kα)/mm^{-1}	1.835	1.555
$2\theta_{max}$/deg	52.28	50.00
total reflns	114 385	35 167
indep reflns	15 616	8202
obsd reflns [$I > 2\sigma(I)$]	6470	5055
params refined	826	532
R_1/wR_2 [$I > 2\sigma(I)$]	0.0446, 0.0850	0.0427, 0.0965
R_1/wR_2 (all data)	0.1059, 0.0879	0.0666, 0.0993

mmol, 2 equiv) in acetone (5 mL) was dropped into the solution. After stirring for a few minutes a solution of $TlPF_6$ (84 mg, 0.24 mmol, 2 equiv) in acetone (2 mL) was added. The precipitated TlCl was removed by filtration through Celite, and the filtrate was evaporated to dryness. Yield: quantitative (according to the NMR spectra). $^{31}P\{^1H\}$ NMR (81 MHz, acetone-d_6, 223 K): δ −143.1 (sept, $^1J_{PF}$ = 708.5 Hz, PF_6^-), −36.8 (s), −30.7 (d, $^2J_{PP}$ = 63.3 Hz), −29.6 (s), −29.4 (s), −27.3 (d, $^2J_{PP}$ = 63.3 Hz) ppm. ^1H NMR (200 MHz, acetone-d_6, 333 K): δ 2.33 (s, 3H, CCH_3), 2.40 (s, 3H, CCH_3), 2.43 (s, 3H, CCH_3), 2.46 (s, 3H, CCH_3), 4.21 (d, $^2J_{PH}$ = 36.6 Hz, 1H, α-CH), 4.37 (s, 5H, Cp), 4.91 (s, 1H, CH_2), 4.98 (s, 1H, CH_2), 6.05 (m, 1H, allyl-H), 6.18 (s, 1H, CCH_3CHCCH_3) ppm. The signals of the other allyl protons cannot be assigned unambiguously. MS (MALDI): m/z 487 ([M − PF_6]$^+$, 100%).

Synthesis of 17a. [Pd(η^3-allyl)Cl]$_2$ (120 mg, 0.33 mmol, 1 equiv) was dissolved in hot acetone (5 mL). A solution of **4a** (215 mg, 0.66 mmol, 2 equiv) in acetone (5 mL) was dropped into the solution. After stirring for a few minutes a solution of $TlPF_6$ (230 mg, 0.66 mmol, 2 equiv) in acetone (2 mL) was added. The precipitated TlCl was removed by filtration through Celite, and the filtrate was evaporated to dryness. Yield: quantitative (according to the NMR spectra). $^{31}P\{^1H\}$ NMR (81 MHz, acetone-d_6, 223 K): δ −143.2 (sept, $^1J_{PF}$ = 708.4 Hz, PF_6^-), −37.5 (d, $^2J_{PP}$ = 63.5 Hz), −34.5 (s), −37.7 (s), −30.9 (d, $^2J_{PP}$ = 63.5 Hz) ppm. ^1H NMR (200 MHz, acetone-d_6, 333 K): δ 2.34 (s, 3H, CCH_3), 2.40 (s, 3H, CCH_3), 3.89 (s, 3H, NCH_3), 3.91 (dd, $^2J_{HH}$ = 19.0 Hz, $^3J_{PH}$ = 5.7 Hz, 1H, CH_2), 4.19 (dd, $^2J_{HH}$ = 19.0 Hz, $^3J_{PH}$ = 19.0 Hz, 1H, CH_2), 4.34 (s, 5H, Cp), 4.56 (d, $^2J_{PH}$ = 37.0 Hz, 1H, α-CH), 6.05 (m, 1H, allyl-H), 7.31 (d, $^3J_{HH}$ = 1.6 Hz, 1H, *H*C═CH), 7.33 (d, $^3J_{HH}$ = 1.6 Hz, 1H, HC═C*H*) ppm. The signals of the other allyl protons cannot be assigned unambiguously. MS (MALDI): m/z 473 ([M − PF_6]$^+$, 100%).

Synthesis of 17b. [Pd(η^3-allyl)Cl]$_2$ (71 mg, 0.20 mmol, 1 equiv) was dissolved in hot acetone (5 mL). A solution of **4b** (133 mg, 0.39 mmol, 2 equiv) in acetone (5 mL) was dropped into the solution. After stirring for a few minutes a solution of $TlPF_6$ (137 mg, 0.39 mmol, 2 equiv) in acetone (2 mL) was added. The precipitated TlCl was removed by filtration through Celite, and the filtrate was evaporated to dryness. Yield: quantitative (according to the NMR spectra). $^{31}P\{^1H\}$ NMR (81 MHz, acetone-d_6, 223 K): δ −143.1 (sept, $^1J_{PF}$ = 708.5 Hz, PF_6^-), −37.6 (br s) ppm. ^1H NMR (200 MHz, acetone-d_6, 298 K): δ 2.21 (s, 3H, CCH_3), 2.26 (s, 3H, CCH_3), 2.72 (m, 1H, CH_2), 2.87 (m, 1H, CH_2), 3.31 (m, 1H, CH_2), 3.39 (m, 1H, CH_2), 3.88 (s, 3H, NCH_3), 4.17 (d, $^2J_{PH}$ = 36.5 Hz, 1H, α-CH), 4.30 (s, 5H, Cp), 5.90 (m, 1H, allyl-H), 7.23 (d, $^3J_{HH}$ = 1.5 Hz, 1H, *H*C═CH), 7.36 (d, $^3J_{HH}$ = 1.5 Hz, 1H, HC═C*H*) ppm. The signals of the other allyl protons cannot be assigned unambiguously. $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6, 298 K): δ 14.3 (d, $^3J_{PC}$ = 3.4 Hz, C*C*H$_3$), 17.4 (d, $^3J_{PC}$ = 4.9 Hz, C*C*H$_3$), 27.7 (d, $^2J_{PC}$ = 11.8 Hz, CH_2), 29.7 (d, $^3J_{PC}$ = 11.2 Hz, CH_2), 56.1 (br s, *C*H$_2$CHCH$_2$), 70.8 (br s, α-CH), 75.8 (s, Cp), 82.2 (br d, $^2J_{PC}$ = 34.9 Hz, CH$_2$CH*C*H$_2$), 94.5 (d, $^2J_{PC}$ = 4.4 Hz, *C*CH$_3$), 96.4 (s, α-*C*CH$_2$), 121.8 (br s, CH$_2$*C*HCH$_2$), 124.9 (s, H*C*═CH), 131.4 (s, HC═*C*H), 153.0 (s, NCN) ppm. The signal of the remaining phospholyl carbon atom could not be assigned. MS (MALDI): m/z 487 ([M − PF_6]$^+$, 100%).

Catalysis. Palladium complex **15** or **17** (10 mg, 0.016 mmol) and 1,3-diphenyl-2-propenyl acetate (114 μL, 0.5 mmol) were suspended in THF (5 mL). NaH (24 mg, 1.0 mmol) and dimethyl malonate (115 μL, 1.0 mmol) were dissolved in THF (5 mL) and added to the suspension by syringe. The resulting red solution was stirred overnight. Then acetic acid (1 mL) was added to the mixture, and the solvent was removed in vacuo. Water (40 mL) was added to the residue, and the product was extracted with diethyl ether. Then the organic layers were washed with water and brine, dried over anhydrous sodium sulfate, and filtrated. After removal of the solvent in vacuo the resulting yellow oil was further purified by column chromatography on neutral alumina with hexane/diethyl ether (4:1) to yield pure product **17**. The configuration of **18** was determined by polarimetry, the enantiomeric excess by chiral HPLC. The NMR data of **18** are consistent with those reported in the literature.[22]

X-ray Crystallographic Study. Isometric crystals of compounds **16**$BF_4 \cdot 3(CH_3)_2CO$ and **13b**$FeCl_3 \cdot CH_2Cl_2$ were investigated with a Stoe IPDS using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. The space group type $P2_1/n$ was uniquely determined for both compounds. *Lp* corrections were applied to all the intensity data. The structures were solved by direct methods,[23] and the positions of all but the H atoms of the solvent molecules were found via ΔF syntheses. Refinements[24] by full-matrix least-squares calculations on F^2 converged to the indicators given in Table 2 (max. shift/s.u.: 0.000 and 0.001, respectively). Anisotropic displacement parameters were refined for all atoms heavier than hydrogen, with the exception of the B atom and the C and O atoms of the acetone solvent molecules of the ruthenium compound. The acetone molecules have been included in the refinement as rigid groups with idealized geometry. Furthermore, idealized bond lengths and angles were used for all the CH_3, CH_2, and CH groups of both compounds; the riding model was applied for their H atoms. 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. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-709215 (**16**$BF_4 \cdot 3(CH_3)_2CO$) and CCDC-709216 (**13b**$FeCl_3 \cdot CH_2Cl_2$). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: int. +1223/336-033; e-mail: teched@chemcrys.cam.ac.uk) or via the Internet at http://www.ccdc.cam.ac.uk.

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Supporting Information Available: X-ray structural information for compounds **13b**$FeCl_3 \cdot CH_2Cl_2$ and **16**$BF_4 \cdot 3(CH_3)_2CO$). NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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