# New *P,N*-Chelate Ligands Based on Pyridyl-Substituted Phosphaferrocenes

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Received March 24, 1998

**Keywords:** Chelates / P,N ligands / Phosphaferrocene / Catalysis / Heterocycles

The new pyridyl-substituted phosphaferrocene ligands **3** and **6** are prepared by addition of lithiated pyridine or α-picoline to 2-formyl-3,4-dimethylphosphaferrocene (**1**). The ligands **3** and **6** react with $[Cp^*RuCl]_4$ in THF to give the *P,N*-chelate complexes $[Cp^*RuCl\cdot\mathbf{3}]$ (**9**) and $[Cp^*RuCl\cdot\mathbf{6}]$ (**10**) with high diastereoselectivity. Addition of monodentate ligands like CO or $PPh_3$ to the complexes leads by displacement of the Ru-bound pyridyl group to the respective carbonyl or phosphane complexes with monodentate *P*-coordinated phospha-ferrocene ligands. Reaction of the ligand **6** with $[(C_3H_5)PdCl]_2$ and $NH_4PF_6$ gives the seven-membered chelate complex $[(C_3H_5)Pd\cdot\mathbf{6}]PF_6$ (**13**) which was characterized by X-ray diffraction. The ligands **3** and **6** were tested in the palladium-catalyzed asymmetric alkylation of 1,3-diphenylallyl acetate.

Chiral chelate ligands continue to be of interest in coordination chemistry and asymmetric catalysis. Recently, we reported a new concept for chelate ligands with planar chirality based on substituted phosphaferrocenes. Meanwhile, we have prepared a variety of *P,P* and *P,N* compounds comprising, inter alia, those with aminoalkyl, phosphanylalkyl and phosphinite donor substituents attached to the phosphaferrocene nucleus.[1][2] In this contribution we wish to report the syntheses of pyridyl-substituted phosphaferrocenes as well as the coordination behaviour of the new ligands toward transition-metal fragments. Furthermore, preliminary results obtained with the new ligands in the Pd-catalyzed asymmetric alkylation of 1,3-diphenylallyl acetate are reported.

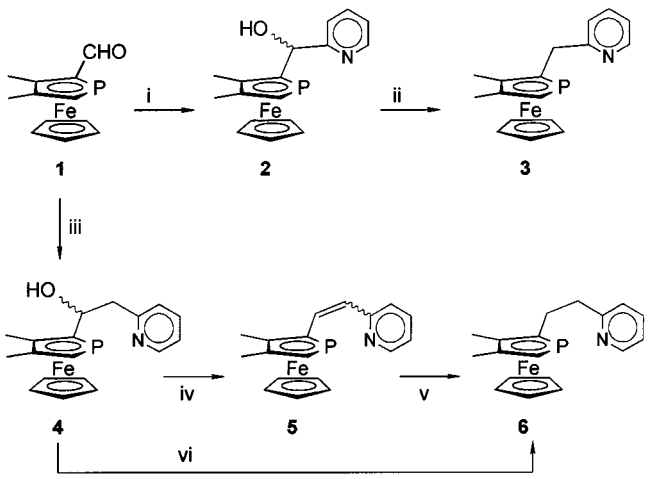
## Results

### Ligand Synthesis

As depicted in Scheme 1, the synthesis of the pyridyl ligands **3** and **6** can be carried out in one-pot procedures starting from 2-formyl-3,4-dimethylphosphaferrocene (**1**) which has already proven to be a versatile building block for the synthesis of phosphaferrocene ligands before.[1][2] Treatment of the aldehyde **1** with 2-lithiopyridine − prepared in situ from 2-bromopyridine and *n*BuLi − leads to the alcohol **2** (de 83%) which can be deoxygenated with $NaBH_4$ and trifluoroacetic acid to yield the pyridylmethyl ligand **3** as a brown oil which crystallizes on standing. The homologous pyridylethyl ligand **6** with a backbone extended by one $CH_2$ unit is obtained in an analogous reaction sequence when 2-(lithiomethyl)pyridine − prepared from 2-methylpyridine by deprotonation with *n*BuLi − is employed as the nucleophilic reagent.

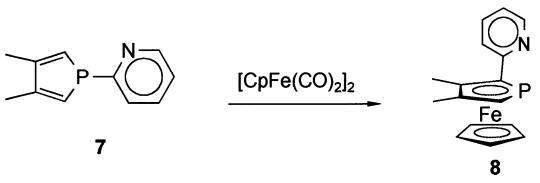
If the work-up procedure of the preliminarily formed alcohol **4** (de 60%) is carried out under slightly acidic conditions, the formation of the olefin **5** (as a mixture of *E* and *Z* isomers) is observed by elimination of water. However, the olefin can successfully be transformed into the desired saturated ligand **6** by treatment with $NaBH_4$ and trifluoroacetic acid. The ligands **3** and **6** are obtained in good yield in analytically pure form after chromatography on deactivated alumina and exhibit resonances in the $^{31}P$-NMR spectra in the expected range [δ = −77.1 (**3**) and −80.2 (**6**)]. Recently, Mathey and coworkers reported the synthesis of the 2-(2′-pyridyl)phosphaferrocene ligand **8** by combining the [1,5]-sigmatropic rearrangement of the *P*-pyridyl-substituted phosphole **7** with the complexation reaction with $[CpFe(CO)_2]_2$ in a one-pot procedure.[3]

Scheme 1. Preparation of ligands **3** and **6**[a]




[a] Reagents: i: 2-Lithiopyridine, $Et_2O$, 55%. − ii: $NaBH_4$, $CF_3CO_2H$, $CH_2Cl_2$, 64%. − iii: 2-(lithiomethyl)pyridine, THF, 77%. − iv: Aqueous acidic conditions. − v, vi: $NaBH_4$, $CF_3CO_2H$, $CH_2Cl_2$, 80%.

  1434−1948/98/0808−1163 $ 17.50+.50/0 




7 8

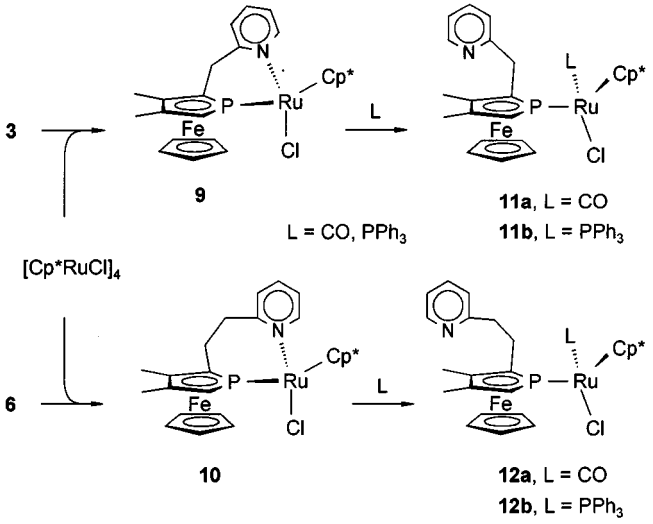
However, since Mathey's synthesis is carried out under non-stereoselective conditions the racemate of ligand **8** was obtained, whereas our approach allows the synthesis of the enantiomerically pure ligands **3** and **6**, starting from the enantiomerically pure aldehyde **1** which is readily available on a preparative scale.[4]

**Complexation Experiments**

*Cp*Ru Complexes:* Reaction of the ligands **3** and **6** with appropriate metal fragments should lead to six- and seven-membered chelate complexes, respectively. First, experiments were carried out with $[Cp^*RuCl]_4$ as a source of Cp*RuCl fragments with two vacant coordination sites.[1][5] If the reactants are mixed in a metal-to-ligand ratio of 1:1 in THF the quantitative formation of the anticipated chelate complexes [Cp*RuCl·**3**] (**9**) and [Cp*RuCl·**6**] (**10**) is observed within a few moments by NMR spectroscopy. The complexes **9** and **10** are isolated in analytically pure form as yellow and orange microcrystalline solids in 95 and 93% yield, respectively. In the $^{31}$P-NMR spectra a characteristic downfield shift of ca. 95 ppm is observed for the phospholyl P atom on going from the free ligands to the complexes. Whereas the typical reduction of the $^2J$(HP) coupling constant for the α-phospholyl proton from 36 Hz to 33 Hz is observed for the complexation of ligand **3**, an unprecedented increase of that coupling constant to 40 Hz was observed for the transformation of the ligand **6** to the complex **10**. The *N*-coordination of the pyridyl group to the Ru centre in that complex leads to a downfield shift for the pyridine 6-H from δ = 8.47 to 9.70. As a result of the chelate formation reaction with the Cp*Ru fragment the Ru atom becomes a stereogenic centre in the complexes. Only one set of signals is observed in the NMR spectra of the six-membered chelate complex **9** indicating the stereoselective formation of only one diastereomer (dr > 99:1). The more flexible seven-membered chelate complex **10** is also formed with high, but significantly decreased selectivity (dr = 95:5). The high diastereoselectivity observed in the reaction of the ligands **3** and **6** with $[Cp^*RuCl]_4$ is in contrast to the findings of Consiglio et al. who observed the formation of almost 1:1 mixtures of diastereomers in the reaction of chiral bidentate *P,P*-chelate ligands with the tetrameric ruthenium complex.[6]

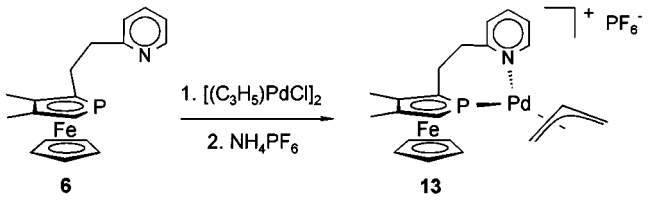
Addition of monodentate ligands such as CO or $PPh_3$ to THF solutions of the chelate complexes **9** and **10** leads under selective rupture of the Ru−N bond to the formation of the respective carbonyl or $PPh_3$ complexes **11** and **12** in which the ligands **3** and **6** behave as monodentate *P* ligands (Scheme 2). The reactions were monitored by IR and multinuclear NMR spectroscopy. The diastereomeric ratios of

Scheme 2. Synthesis of complexes




the reaction products are easily obtained from the integrated $^{31}$P-NMR spectra. Interestingly, the reactions with CO lead to almost complete epimerization at the Ru centre (dr < 60:40), whereas the additions of $PPh_3$ proceed with diastereoselectivities of dr = 92:8 and 86:14; thus, the stereochemical integrity is at least partially preserved in the latter case. The carbonyl complex [Cp*RuCl(CO)·**3**] (**11a**) now exhibits a coupling constant of $^2J$(HP) = 31 Hz in the expected range and the resonance for the pyridyl 6-H at δ = 8.50 is characteristic for an uncoordinated pyridyl group. The carbonyl C signal appears as a doublet with $^2J$(CP) = 36 Hz, comparable to the value reported by Kirchner et al. for the complex $[Cp^*RuCl(CO)(Ph_2PCH_2CH_2NMe_2)]$.[7] In the $PPh_3$ complexes **11b** and **12b** the resonances of the P nuclei appear as doublets with $^2J$(PP) coupling constants in the range of 55 to 68 Hz (see Experimental Section).

*(Allyl)palladium Complexes:* (Allyl)palladium complexes with *P,N*-chelate ligands have been intensively studied in view of their superior performance in catalytic asymmetric allylic substitutions.[8] The reaction of the ligands **3** and **6** with $[(C_3H_5)PdCl]_2$ in ethanol proceeds smoothely and is accompanied by a color change from orange to deep red. The complexes were precipitated by addition of $NH_4PF_6$ and isolated by filtration. The complex formed with ligand **3** turned out to be insoluble in common organic solvents which precluded further characterization. We anticipate the formation of a polymeric structure with the ligand **3** acting in a bridging rather than a chelating manner. In contrast, the complex $[(C_3H_5)Pd\cdot\mathbf{6}]PF_6$ (**13**) is soluble in polar solvents and can be recrystallized from ethanol to give orange needles which were suited for X-ray diffraction analysis.




6 13

A PLATON plot of the molecular structure of the cation of complex **13** is depicted in Figure 1, selected bond lenghts and angles are compiled in Table 1. The structure features the typical parameters for a Pd centre in a distorted square-planar coordination geometry with a bite angle P1−Pd−N of 93.6(3)°.

Figure 1. Molecular structure (PLATON) of the cation of complex **13**; hydrogen atoms have been omitted for clarity

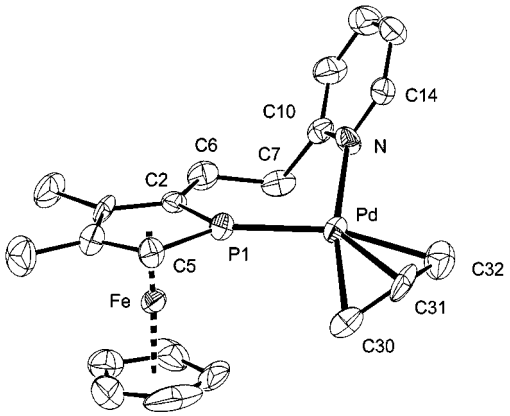



Table 1. Selected bond lengths [A] and angles [°] of complex **13**

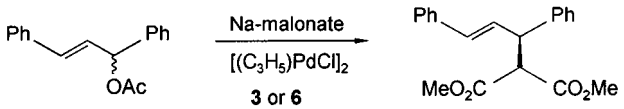
| | | | |
|---|---|---|---|
| Pd−P1 | 2.274(3) | P1−Pd−N | 93.6(3) |
| Pd−N | 2.13(1) | P1−Pd−C30 | 99.0(5) |
| Pd−C30 | 2.12(1) | P1−Pd−C31 | 134.2(7) |
| Pd−C31 | 2.09(1) | N−Pd−C31 | 130.6(7) |
| Pd−C32 | 2.18(2) | N−Pd−C32 | 99.1(6) |
| P1−C2 | 1.75(1) | Pd−P1−C2 | 126.7(5) |
| P1−C5 | 1.71(1) | Pd−P1−C5 | 141.2(5) |
| C30−C31 | 1.39(2) | C2−P1−C5 | 91.4(7) |
| C31−C32 | 1.34(2) | C10−N−C14 | 120(1) |
| N−C10 | 1.33(2) | Pd−C30−C31 | 69.5(8) |
| N−C14 | 1.34(2) | Pd−C32−C31 | 68(1) |
| C2−C3 | 1.41(2) | C30−C31−C32 | 123(2) |
| C4−C5 | 1.39(2) | | |

As is usually observed for palladium complexes with *P,N* ligands the distance Pd−P1 [2.274(3) A] is significantly longer than the corresponding bond to the nitrogen donor [Pd−N: 2.13(1) A], although the differences tend to be more pronounced for *P,N* ligands with phosphane donor groups.[9][10] The high π-acceptor character of the phospholyl P atom leads to the rather short Pd−P distance. This π acidity has another consequence involving the Pd−C bond lenghts: the distances Pd−C30 [2.12(1) A] and Pd−C32 [2.18(2) A] are not very different if compared to (allyl)Pd complexes with softer *P* donors, where the Pd−C bond *trans* to the phosphorus atom is often found to be roughly 10 pm longer than the Pd−C bond *trans* to the $sp^2$ nitrogen donor atom.[9][10] The allyl ligand adopts an almost symmetrical orientation with respect to the coordination plane of the palladium centre as is evident from the virtually identical angles between the plane (P1,Pd,N) and the planes (Pd,C30,C31) (27.8°) and (Pd,C31,C32) (28.4°), respectively. In contrast, a pronounced rotation of the 1,3-diphenylallyl moiety about the (allyl)Pd axis by ca. 15−20° was observed in complexes with ferrocene-derived *P,N* ligands.[9] This rotation seems to be the consequence of the sterically more demanding 1,3-diphenyl substitution on the allyl ligand. In complex **13** the Pd−P1 vector is only slightly tilted out of the phospholyl mean plane away from the CpFe fragment [tilt angle: 3.7(4)°]. The coordination plane about the Pd atom forms an angle with the allyl plane of 112.3(9)°.

The $^{31}$P-NMR spectrum of complex **13** shows one broad signal (δ = −42.6) at room temperature. On cooling to −20°C four baseline-separated signals are observed in the range from δ = −39 to −44 in the ratio of 15:16:39:30. We assume, that these signals are due to the presence of two isomers with *exo* and *endo* orientation of the allyl ligand, which both exist in two different chelate ring conformations. Such conformational isomers of seven-membered (allyl)Pd-*P,N*-chelate complexes have been observed by Togni et al.[9b]

Reaction of the pyridine ligand **6** with $[(1,3\text{-}Ph_2C_3H_3)PdCl]_2$ under the same conditions as above leads to the analogous chelate complex **14** with a (diphenylallyl)palladium fragment which was recrystallized from $CH_2Cl_2$/hexane. At room temperature 3 broad signals are found in the $^{31}$P-NMR spectrum in $CD_2Cl_2$, which split into 4 resonances at −20°C. Obviously, the activation enthalpy for the dynamic interconversion of the isomers is higher in the 1,3-diphenylallyl case.

Preliminary experiments were carried out with ligands **3** and **6** to test their applicability in asymmetric allylic substitutions. 1,3-Diphenylallyl acetate was treated with sodium malonate as *C*-nucleophile in the presence of $[(C_3H_5)PdCl]_2$ and the enantiomerically pure ligands **3** or **6** (5 mol-%) in THF. The substitution reaction is complete after 3 h at room temperature and the product **15** was isolated in 65−80% yield. However, the enantiomeric purity was only 19 and 11%, respectively.




**15**

We are currently modifying the ligands in order to obtain higher selectivity in catalysis. Furthermore, we are looking for other catalytic reactions for which the ligand type described here might be better suited.

Support of this work by the *Deutsche Forschungsgemeinschaft* (SFB 380) is greatfully acknowledged.

## Experimental Section

*General:* All manipulations were carried out under dry $N_2$ in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under $N_2$. − NMR: Varian Unity 500 (499.843 MHz, $^1$H, int. TMS; 125.639 MHz, $^{13}$C{$^1$H}, APT, int. TMS; 202.265 MHz, $^{31}$P{$^1$H}, ext. 85% $H_3PO_4$). − MS: Finnigan MAT 95. − Elemental analysis (C, H, N): Carlo-Erba elemental analyzer, Modell 1106. − IR: Perkin-Elmer 1720 X FTIR. − 2-Formyl-3,4-dimethylphosphaferrocene (**1**),[11] $[Cp^*RuCl]_4$,[5] $[(C_3H_5)PdCl]_2$[12] and di-μ-chlorobis(1,3-diphenyl-π-allyl)dipalladium[13] were prepared as described in the literature.

*(3,4-Dimethylphosphaferrocene-2-yl)(pyridin-2-yl)methanol* (**2**): 2-Bromopyridine (0.83 ml, 8.71 mmol) was dissolved in 5 ml of $Et_2O$, cooled to −78°C and *n*BuLi (5.4 ml of a 1.6 M solution in hexane, 8.71 mmol) was added. After stirring for 30 min at −78°C, a solution of 2-formyl-3,4-dimethylphosphaferrocene (**1**) (1.75 g, 6.3 mmol) in 10 ml $Et_2O$ was added, the cooling bath was removed and the mixture was stirred for additional 3 h. The reaction was quenched by 10 ml of $H_2O$ and the phases were seperated. The aqueous phase was washed twice with $Et_2O$, the combined organic phases were washed with $H_2O$ and brine and dried with $Na_2SO_4$. Filtration and concentration gave the crude product as a brown oil which was further purified by chromatography on alumina (eluent: THF). **2** was isolated as brown crystals (1.25 g, 3.5 mmol, 55%) after removal of the solvent in vacuo, de 83%. − $^1$H NMR ($CDCl_3$, major isomer): δ = 2.21 (s, 3 H, C$H_3$), 2.28 (s, 3 H, C$H_3$), 3.77 (d, $^2J_{PH}$ = 36 Hz, 1 H, α-C*H*), 4.17 (s, 1 H, O*H*), 4.29 (s, 5 H, Cp), 5.43 (br. s, 1 H, C*H*OH), 7.30−8.60 (4 H, pydidine H). − $^{13}$C NMR ($CDCl_3$, major isomer): δ = 14.4 (s, 1 C, *C*$H_3$), 16.6 (s, 1 C, *C*$H_3$), 72.1 (s, 5 C, Cp), 73.2 (d, *J* = 12.5 Hz, 1 C, *C*HOH), 76.4 (d, *J* = 59.1 Hz, 1 C, α-*C*H), 92.6 (s, 1 C, *C*$CH_3$), 96.3 (s, 1 C, *C*$CH_3$), 104.9 (d, *J* = 57.6 Hz, 1 C, α-*C*CHOH), 120.7 (s, 1 C, *C*H), 122.2 (s, 1 C, *C*H), 136.4 (s, 1 C, *C*H), 147.8 (s, 1 C, N*C*H), 162.3 (s, 1 C, N*C*CHOH). − $^{31}$P NMR ($CDCl_3$): δ = −86.1 (major isomer), −77.9 (minor isomer). − MS (70 eV); *m*/*z* (%): 339.0 (100) [$M^+$], 322.8 (10) [$(M - O)^+$], 274.1 (45) [$(M - Cp)^+$], 232.0 (20) [$(M - CHOHC_5H_4N)^+$]. − $C_{17}H_{18}{}^{56}$FeNOP (339.3): calcd. C 339.047539; found 339.047502 (HRMS).

*2-[(3,4-Dimethylphosphaferrocene-2-yl)methyl]pyridine* (**3**): 5 ml of $CF_3COOH$ was cooled to 0°C and 1/2 of an $NaBH_4$ tablet was added. A solution of **2** (0.52 g, 1.48 mmol) in 10 ml of $CH_2Cl_2$ was slowly added and the reaction mixture was stirred over night at room temp. Solvents were evaporated in vacuo and 10 ml of $H_2O$ and 10 ml of $CH_2Cl_2$ were added. Phases were separated, the aqueous phase was washed twice with $CH_2Cl_2$, the combined organic layers were washed with water and brine and dried with $Na_2SO_4$. Filtation and evaporation of the solvent gave the crude product. Chromatography on alumina with hexane/$Et_2O$ (4:1) as eluent gave **3** (0.32 g, 0.95 mmol, 64%) as brown oil, which crystallized within 24 h. − $^1$H NMR ($CDCl_3$): δ = 2.11 (s, 3 H, C$H_3$), 2.18 (s, 3 H, C$H_3$), 3.70 (m, 2 H, C$H_2$), 3.73 (d, *J* = 36.0 Hz, 1 H, α-C*H*), 4.14 (s, 5 H, Cp), 7.05 (m, 2 H, C*H*), 7.51(m, 1 H, C*H*), 8.47 (br. s, 1 H, NC*H*). − $^{13}$C NMR ($CDCl_3$): δ = 13.7 (s, 1 C, *C*$H_3$), 16.9 (s, 1 C, *C*$H_3$), 39.9 (d, *J* = 6.0 Hz, 1 C, *C*$H_2$), 72.1 (s, 5 C, Cp), 76.0 (d, *J* = 57.0 Hz, 1 C, α-*C*H), 93.7 (d, *J* = 3.9 Hz, 1 C, *C*$CH_3$), 95.8 (d, *J* = 6.8 Hz, 1 C, *C*$CH_3$), 96.3 (d, *J* = 57.4 Hz, 1 C, α-*C*$CH_2$), 121.2 (s, 1 C, CH), 122.6 (s, 1 C, *C*H), 136.1 (s, 1 C, *C*H), 148.7 (s, 1 C, N*C*H), 161.6 (s, 1 C, N*C*$CH_2$). − $^{31}$P NMR ($CDCl_3$): δ = −77.1 . − MS (70 eV); *m*/*z* (%): 322.9 (100) [$M^+$], 258.0 (60) [$(M - Cp)^+$]. − $C_{17}H_{18}$FeNP (323.2): calcd. C 63.18, H 5.61, N 4.33; found C 62.93, H 5.71, N 4.28.

*1-(3,4-Dimethylphosphaferrocene-2-yl)-2-(pyridin-2-yl)ethanol* (**4**): To a solution of α-picoline (0.72 ml, 7.27 mmol) in 10 ml of THF at −40°C was added a solution of *n*BuLi in hexane (4.5 ml, 1.6 M solution of *n*BuLi, 1.51 mmol). After warming up to room temp. and stirring for 15 min, the orange solution was again cooled to −40°C and 2-formyl-3,4-dimethylphosphaferrocene (**1**) (1.27 g, 4.85 mmol), dissolved in 10 ml of THF, was added. The reaction mixture was stirred at room temp. for 3 h, then 10 ml of $H_2O$ was added and the organic solvent was evaporated in vacuo. After addition of 10 ml of $CH_2Cl_2$, the phases were separated, the aqueous phase was extracted twice with $CH_2Cl_2$, the combined organic phases were washed with water and brine and dried with $Na_2SO_4$. Filtration and evaporation of the solvent yielded the crude product which was further purified by chomatography on alumina. Elution with $Et_2O$/THF (1:1) and evaporation of solvents gave **3** (1.32 g, 3.73 mmol, 77%) as orange powder, de 60%. − $^1$H NMR ($CDCl_3$, major isomer): δ = 2.12 (s, 3 H, C$H_3$), 2.19 (s, 3 H, C$H_3$), 2.80−3.00 (m, 2 H, C$H_2$), 3.70 (d, *J* = 36.6 Hz, 1 H, α-C*H*), 4.19 (s, 5 H, Cp), 4.57 (s, 1 H, O*H*), 4.68 (m, 1 H, C*H*OH), 7.10−7.60 (m, 3 H, C*H*), 8.50 (d, *J* = 4.9 Hz, 1 H, NC*H*). − $^{13}$C NMR ($CDCl_3$, major isomer): δ =.13.9 (s, 1 C, *C*$H_3$), 16.6 (s, 1 C, *C*$H_3$), 47.1 (s, 1 C, *C*$H_2$), 71.6 (d, *J* = 12,0 Hz, 1 C, *C*HOH), 72.0 (s, 5 C, Cp), 75.5 (d, *J* = 60.0 Hz, 1 C, α-*C*H), 91.7 (s, 1 C, *C*$CH_3$), 96.2 (s, 1 C, *C*$CH_3$), 105.5 (d, *J* = 60.6 Hz,1 C, α-*C*CHOH), 121.7 (s, 1 C, *C*H), 124.2 (s, 1 C, *C*H), 136.4 (s, 1 C, *C*H), 148.4 (s, 1 C, N*C*H), 159.5 (s, 1 C, N*C*$CH_2$). − $^{31}$P NMR ($CDCl_3$): δ = −86.5 (major isomer), −85.0 (minor isomer). − MS (70 eV); *m*/*z* (%): 353.1 (50) [$M^+$], 335.2 (55) [$(M - H_2O)^+$], 232 (70) [$(M - CHOHCH_2C_5H_4N)^+$]. − $C_{18}H_{20}$FeNOP (353.2): calcd. C 61.21, H 5.71, N 3.96; found C 61.53, H 6.12, N 4.14.

*2-[(3,4-Dimethylphosphaferrocene-2-yl)ethyl]pyridine* (**6**): **4** (1.32 g, 3.72 mmol) was treated as described above for the preparation of **3**. The product **6** (0.98 g, 2.91 mmol, 80%) was isolated as a brown oil. − $^1$H NMR ($CDCl_3$): δ = 2.10 (s, 3 H, C$H_3$), 2.18 (s, 3 H, C$H_3$), 2.58 (m, 2 H, C$H_2$), 2.87 (m, 2 H, C$H_2$). 3.67 (d, *J* = 35.7 Hz, 1 H, α-C*H*), 4.07 (s, 5 H, Cp), 7.10 (m, 2 H, C*H*), 7.55 (m 1 H, C*H*), 8.55 (s, 1 H, NC*H*). − $^{13}$C NMR ($CDCl_3$): δ = 13.4 (s, 1 C, *C*$H_3$), 16.8 (s, 1 C, *C*$H_3$), 31.0 (s, 1 C, *C*$H_2$), 41.2 (s, 1 C, *C*$H_2$), 71.8 (s, 5 C, Cp), 75.3 (d, *J* = 58.7 Hz, 1 C, α-*C*H), 93.0 (s, 1 C, *C*$CH_3$), 95.4 (s, 1 C, *C*$CH_3$), 99.1 (d, *J* = 58.6 Hz, 1 C, α-*C*$CH_2$), 121.0 (s, 1 C, *C*H), 123.0 (s, 1 C, *C*H), 136 (s, 1 C, *C*H), 149.1 (s, 1 C, N*C*H), 161.5 (s, 1 C, N*C*$CH_2$). − $^{31}$P NMR ($CDCl_3$): δ = −80.2 . − MS (70 eV); *m*/*z* (%): 337.2 (100) [$M^+$], 272.3 (60) [$(M - Cp)^+$], 245.1 (20) [$(M - CH_2C_5H_4N)^+$]. − $C_{18}H_{20}$FeNP (337.2): calcd. C 64.12, H 5.98, N 4.15; found C 63.46, H 5.87, N 4.01.

*[Cp*RuCl·**3**]* (**9**): **3** (38,0 mg, 0.12 mmol) was dissolved in 3 ml of THF and added to a suspension of $[Cp^*RuCl]_4$ (31.9 mg, 0.029 mmol) in 2 ml of THF. The resulting clear red solution was stirred for 30 min, filtered and the solvent was evaporated. The yellow powder was washed with a small portion of hexane and dried in vacuo to give spectroscopically pure **9** (67.8 mg, 0.11 mmol, 95%), dr > 99:1. − $^1$H NMR ([$D_8$]THF): δ = 1.53 (d, *J* = 2.9 Hz, 15 H, Cp*), 2.20 (s, 3 H, C$H_3$), 2.22 (s, 3 H, C$H_3$), 3.38 (m, 2 H, C$H_2$), 3.58 (d, *J* = 40 Hz, 1 H, α-C*H*), 3.79 (s, 5 H, Cp), 7.10 (m, 1 H, C*H*), 7.18 (m, 1 H, C*H*), 7.59 (m, 1 H, C*H*), 9.70 (d, *J* = 4.9 Hz, 1 H, NC*H*). − $^{13}$C NMR ([$D_8$]THF): δ = 8.5 (s, 5 C, *C*$H_3$-Cp*), 11.5 (s, 1 C, *C*$H_3$), 14.9 (s, 1 C, *C*$H_3$), 36.3 (d, *J* = 13.8 Hz, 1 C, *C*$H_2$), 65.1 (d, *J* = 30 Hz, 1 C, α-*C*H), 71.0 (s, 5 C, Cp), 79.6 (s, 1 C, *C*$CH_3$), 81.2 (d, *J* = 3.1 Hz, 5 C, *C*$CH_3$-Cp*), 87.5 (d, *J* = 35 Hz, 1 C, α-*C*$CH_2$), 120.1 (s, 1 C, *C*H), 123.9 (s, 1 C, *C*H), 134.5 (s, 1 C, *C*H), 158.2 (s, 1 C, N*C*H), 162.1 (d, *J* = 4.9 Hz, 1 C, N*C*$CH_2$). − $^{31}$P NMR ([$D_8$]THF): δ = 14.9 . − SIMS (70 eV); *m*/*z* (%): 560.3 (100) [$(M - Cl)^+$]. − $C_{27}H_{33}$ClFeNPRu (594.9): calcd. C 54.51, H 5.59, N 2.35; found C 54.57, H 5.74, N 2.36.

*[Cp*RuCl·**6**]* (**10**): **6** (56.2 mg, 0.16 mmol) was dissolved in 3 ml of THF and added to a suspension of $[Cp^*RuCl]_4$ (45.2 mg, 0.041 mmol) in 2 ml of THF. The resulting clear red solution was stirred for 30 min, filtered and the solvent was evaporated. The orange powder was washed with a small portion of hexane and dried in vacuo to give spectroscopically pure **10** (94.4 mg, 0.15 mmol, 93%). dr = 95:5. − $^1$H NMR ([$D_8$]THF, major isomer): δ = 1.56 (d, *J* = 2.64 Hz, 15 H, Cp*), 2.09 (s, 3 H, C$H_3$), 2.15 (s, 3 H, C$H_3$), 2.90 (m, 2 H, C$H_2$), 3.10 (m, 2 H, C$H_2$), 3.43 (d, *J* = 33 Hz, 1 H, α-C*H*), 3.62 (s, 5 C, Cp), 7.09 (m, 1 H, C*H*), 7.32 (m, 1 H, C*H*), 7.64

(m, 1 H, C*H*), 9.80 (d, $J$ = 5.18 Hz, 1 H, NC*H*). − $^{13}$C NMR ([D$_8$]THF, major isomer): δ = 10.3 (s, 5 C, *C*H$_3$-Cp*), 13.3 (d, $J$ = 3.0 Hz, 1 C, *C*H$_3$), 16.8 (d, $J$ = 3.2 Hz, 1 C, *C*H$_3$), 33.3 (d, $J$ = 12.4 Hz, 1 C, *C*H$_2$), 39.3 (d, $J$ = 13.2 Hz, 1 C, *C*H$_2$), 67.6 (d, $J$ = 22.0 Hz, 1C, α-CH), 73.9 (s, 5 C, Cp), 83.1 (d, $J$ = 3.0 Hz, 5 C, *C*CH$_3$-Cp*), 87.0 (d, $J$ = 11.2 Hz, 1 C, α*C*), 88.5 (s, 1 C, *C*CH$_3$), 91.1 (s, 1 C, *C*CH$_3$), 121.9 (s, 1 C, *C*H), 124.2 (s, 1 C, *C*H), 136.3 (s, 1 C, *C*H), 158.2 (s, 1 C, N*C*H), 168.8 (s, 1 C, N*C*CH$_2$). − $^{31}$P NMR ([D$_8$]THF): δ = 17.5 (major isomer), 21.8 (minor isomer). − MS (70 eV); *m*/*z* (%): 609.6 (1) [M$^+$], 544.3 (2) [(M − Cp)$^+$], 337.3 (100) [**5**$^+$]. − $C_{28}H_{35}ClFeNPRu$ (608.9): calcd. C 55.23, H 5.79, N 2.30; found C 55.21, H 5.98, N 2.18.

*NMR Experiments:* For the substitution reaction of the pyridine moiety with CO about 30 mg of the complex [Cp*RuCl·**3**/**6**] was prepared in situ by dissolving ligand **3** or **6** and [Cp*RuCl]$_4$ in [D$_8$]THF. Purity was proven by NMR and 10 ml of CO was bubbled through the solution by syringe. Then the NMR spectra were recorded. For the substitution with triphenylphosphane, the complexes **9** and **10** were prepared as described and the stoichiometric amount of $PPh_3$ was added. The resulting clear red solution was analyzed by NMR spectroscopy.

*[Cp*RuCl(CO)·**3**]* (**11a**): dr = 50:50. − $^1$H NMR ([D$_8$]THF): δ = 1.64 (br. s, 15 H, Cp*), 2.20 (br. s, 6 H, C*H*$_3$), 3.46 (d, $J$ = 30.5 Hz, 1 H, α-C*H*, isomer I), 3.70 (d, $J$ = 30.8 Hz, 1 H, α-C*H*, isomer II), 3.84 (br. s, 2 H, C*H*$_2$), 4.31 (s, 5 H, Cp), 7.07 (br. s, 2 H, C*H*), 7.49 (br. s, 1 H, C*H*), 8.49 (s, 1 H, NC*H*). − $^{13}$C NMR ([D$_8$]THF): δ = 9.7 (d, $J$ = 5.8 Hz, 5 C, C*C*H$_3$-Cp*), 13.8 (s, 1 C, *C*H$_3$), 16.4 (s, 1 C, *C*H$_3$), 37.5 (s, 1 C, *C*H$_2$), 74.0 + 74.1 (s, 1 C, Cp), 85.2 (s, 1 C, *C*CH$_3$), 88.1 (s, 1 C, *C*CH$_3$), 91.5 (d, $J$ = 47.8 Hz, 1 C, α-*C*CH$_2$), 96.1 (s, 5 C, *C*CH$_3$-Cp*), 122.0 (br. s, 2 C, *C*H), 135.7 (br. s, 1 C, *C*H), 148.5 (br. s, 1 C, N*C*H), 162.0 (br. s, 1 C, N*C*CH$_2$), 203.7 (d, $J$ = 36 Hz, 1 C, *C*O). − $^{31}$P NMR ([D$_8$]THF): δ = 10.3 (isomer I), 22.0 (isomer II). − IR ([D$_8$]THF): ν = 1940 cm$^{-1}$.

*[Cp*RuCl(CO)·**6**]* (**12a**): dr = 60:40. − $^1$H NMR ([D$_8$]THF): δ = 1.81 (d, $J$ = 2.8 Hz, 15 H, Cp*), 2.00−2.20 (br. s, 6 H, C*H*$_3$), 2.60−3.00 (br. m, 4 H, C*H*$_2$), 3.43 and 3.52 (d, $J$ = 32 Hz, 1 C, α-C*H*), 4.18 and 4.25 (s, 5 H, Cp), 7.00−7.60 (br. m, 3 H, C*H*), 8.46 (br. s, 1 H, NC*H*). − $^{13}$C NMR ([D$_8$]THF): δ = 10.0 (d, $J$ = 4.1 Hz, 5 C, C*C*H$_3$-Cp*), 13.4 (s, 1 C, *C*H$_3$), 16.5 (s, 1 C, *C*H$_3$), 30.0 (d, $J$ = 14.8 Hz, 1 C, *C*H$_2$), 41.5 (br. s, 1 C, *C*H$_2$), 73.9 (s, 5 C, Cp), 91.2 (d, $J$ = 55 8 Hz, 1 C, *C*CH$_3$) 96.2 (s, 5 C, *C*CH$_3$-Cp*), 121.0 (s, 1 C, *C*H), 123.5 (s, 1 C, *C*H), 136.4 (s, 1 C, *C*H), 148.5 (s, 1 C, N*C*H), 163.0 (s, 1 C, N*C*CH$_2$), 204.0 (d, $J$ = 26 Hz, 1 C, *C*O). − $^{31}$P NMR ([D$_8$]THF): δ = 9.7 (major isomer), 18.8 (minor isomer). − IR ([D$_8$]THF): ν = 1940 cm$^{-1}$.

*[Cp*RuCl(PPh$_3$)·**3**]* (**11b**): dr = 92:8. − $^1$H NMR ([D$_8$]THF, major isomer): δ = 1.22 (d/d, 15 H, Cp*), 2.16 (s, 3 H, C*H*$_3$), 2.27 (s, 3 H, C*H*$_3$), 2.53 (br. s, 2H, CH$_2$), 3.03 (d, $J$ = 29.6 Hz, 1 H, α-C*H*), 3.46 (s, 5 H, Cp), 7.00−7.80 (m, 18 H, aromatic H), 8.40 (br. s, 1 H, NC*H*). − $^{31}$P NMR ([D$_8$]THF): major isomer: δ = 21.6 (d, $^3J$ = 65.9 Hz, cycl. P), 51.7 (d, $J$ = 65.9 Hz, PPh$_3$); minor isomer: δ = 28.0 (d, $J$ = 51.3 Hz, cycl. P), 48.6 (d, $J$ = 51.3 Hz, PPh$_3$).

*[Cp*RuCl(PPh$_3$)·**6**]* (**12b**): dr = 86:14. − $^1$H NMR ([D$_8$]THF, major isomer): δ = 1.29 (d/d, 15 H, Cp*), 2.22 (s, 3 H, C*H*$_3$), 2.25 (s, 3 H, C*H*$_3$), 2.50−3.20 (m, 4 H, C*H*$_2$), 3.51 (s, 5 H, Cp), 7.00−8.00 (m, 18 H, aromatic H), 8.40 (d, 1 H, NC*H*). − $^{31}$P NMR ([D$_8$]THF): major isomer: δ = 18.5 (d, $J$ = 67.8 Hz, cycl. P), 51.8 (d, $J$ = 67.8 Hz, PPh$_3$); minor isomer: δ = 29.3 (d, $J$ = 55.0 Hz, cycl. P), 50.5 (d, $J$ = 55.0 Hz, PPh$_3$).

*[(C$_3$H$_5$)Pd·**6**][PF$_6$]* (**13**): [(C$_3$H$_5$)PdCl]$_2$ (28.2 mg, 0,077 mmol) was suspended in 10 ml of EtOH and **6**, (52.0 mg, 0.154 mmol) dissolved in 10 ml of EtOH, was added and the mixture was stirred for 30 min. The clear orange-red solution was treated with $NH_4PF_6$ (25.1 mg, 0.154 mmol) and cooled to 0°C until an orange precipitate formed. The orange powder was filtered off, washed with EtOH and dried in vacuo. Recrystallization from hot EtOH gave pure **13** (85.3 mg, 88%) as orange needles. − $^1$H NMR ($CD_2Cl_2$, room temp.): δ = 2.14 (s, 3 H, C*H*$_3$), 2.20 (s, 3 H, C*H*$_3$), 2.75 (m, 2 H, C*H*$_2$), 3.15−3.25 (m, 2 H, C*H*$_2$), 3.40 (br. m, 1 H, allyl-H), 3.86 (s, 5 H, Cp), 3.9−4.2 (br. m, 2 H, allyl-H), 5.08 (br. m, 1 H, allyl-H), 6.05 (2 br. m, 1 H, 2-allyl-H), 7.45 (s, 1 H, C*H*), 7.61 (s, 1 H, C*H*), 7.97 (s, 1 H, C*H*), 8.71 (s, 1 H, NC*H*). − $^{13}$C NMR ($CD_2Cl_2$, room temp.): δ = 13.5 (s, 1 C, *C*H$_3$), 16.5 (s, 1 C, *C*H$_3$), 32.0 (s, 1 C, *C*H$_2$), 39.5 (s, 1 C, *C*H$_2$), 56.7 (d, $J$ = 57.0 Hz, 1 C, α-*C*H), 74.3 (s, 5 C, Cp), 83.0 (d, $J$ = 30.1 Hz, 1 C, allyl-C), 83.6 (d, $J$ = 32.7 Hz, 1 C, allyl-C), 120.8 (d, $J$ = 19.7 Hz, 1 C, 2-allyl-C), 124.5 (s, 1 C, *C*H), 126.8 (s, 1 C, *C*H), 140.0 (s, 1 C, *C*H), 152.7 (s, 1 C, N*C*H), 165.0 (s, 1 C, N*C*CH$_2$). − $^{31}$P NMR ($CD_2Cl_2$), room temp.: δ = −42.6 (br. s, cycl. P), −144.7 (sept, $J$ = 708 Hz, $PF_6$), −20°C: δ = −43.6, −42.9, −40.6, −39.5 (30:39:16:15) (cycl. P). − SIMS (70 eV); *m*/*z* (%): 483.3 (5) [(M − $PF_6$)$^+$], 338.3 (100) [(**5** + H)$^+$]. − $C_{21}H_{25}F_6FeNP_2Pd$ (629.6): calcd. C 40.03, H 3.97, N 2.22; found C 39.67, H 3.87, N 2.24.

*[(C$_{13}$H$_{13}$)Pd·**6**][PF$_6$]* (**14**): The complex was prepared from [(C$_{13}$H$_{13}$)PdCl]$_2$ as described above for **13**. Recrystallisation from $CH_2Cl_2$/hexane (1:1) afforded orange-red crystals in 54% yield. − $^1$H NMR ($CD_2Cl_2$, −20°C): δ = 1.93 (s, 3 H, C*H*$_3$), 2.03 (s, 3 H, C*H*$_3$), 2.35−2.44 (m, 2 H, C*H*$_2$), 2.78−2.91 (m, 2 H, C*H*$_2$), 3.34−3.53 (m, 1 H, α-C*H*), 3.50−4.25 (4 s, 5 H, Cp), 5.40 (2 d, 1 H, 2-allyl-H), 5.84−5.95 (m, 1 H, allylic H), 6.79−7.07 (m, 1 H, allylic H), 7.30−7.80 (m, 14 H, aromatic H). − $^{13}$C NMR ($CD_2Cl_2$, +23°C): δ = 13.4 (s, 1 C, *C*H$_3$), 16.6 (s, 1 C, *C*H$_3$), 32.2 (s, 1 C, *C*H$_2$), 38.7 (s, 1 C, *C*H$_2$), 63.4 (br. m, 1 C, α-*C*H), 73.5−76.7 (4 s, 5 C, Cp), 93.8 (m, 3 C, quat. phospholyl-C), 97.0 (d, $J$ = 26.3 Hz, 1 C, allylic C), 109.5 (d, $J$ = 7.2 Hz, 1 C, allylic C), 110.4 (br. s, 1 C, allylic C), 124.3−130.2 (m, 13 C, aromatic C), 138.2−139.4 (m, 3 C, aromatic *ipso*-C), 150.4 (s, 1 C, N*C*H), 164.5 (s, 1 C, N*C*CH$_2$). − $^{31}$P NMR ($CD_2Cl_2$, +24°C): δ = −19.7, −29.4, −37.1 (8:42:50), (3 br. s, 1 P, cycl. P), −144.6 (sept, $J$ = 708 Hz, 1 P, $PF_6$), ($CD_2Cl_2$, −20°C): δ = −18.8, −28.8, −36.4, −38.0 (7:46:38:8), (4 s, 1 P, cycl. P), 144.6 (sept, $J$ = 708 Hz, $PF_6$). − SIMS (70 eV); *m*/*z* (%): 636.5 (4)[(M − $PF_6$)$^+$], 338.3 (100) [(**5** + H)$^+$]. − $C_{33}H_{33}F_6FeNP_2Pd \cdot 0.5\ CH_2Cl_2$ (824.3): calcd. C 48.85, H 4.13, N 1.70; found C 48.80, H 4.24, N 1.77.

*General Procedure for the Catalytic Allylic Alkylation*: [(C$_3$H$_5$)PdCl]$_2$ (0.012 mmol, 4.6 mg), the ligand (**3** or **6**, 0.025 mmol) and 1,3-diphenyl-2-propenyl acetate (126.1 mg, 0.5 mmol) were dissolved in 5 ml of THF to give a clear orange solution. NaH (24 mg, 1.0 mmol) and dimethyl malonate (132.1 mg, 1 mmol) were dissolved in 5 ml of THF and added to the orange solution by syringe. The solution was stirred for 13−19 h, then 1 ml of acetic acid was added and the solvent was removed in vacuo. 10 ml of water was added to the mixture, followed by extraction with $Et_2O$. Then the organic layers were washed with water and brine, dried with $Na_2SO_4$ and the solvent was removed in vacuo. The resulting yellow oil was further purified by chromatography on silica gel with hexane/ethyl acetate (5:1) to yield pure product **15**. The enantiomeric excess of **15** was determined by polarimetry, the NMR data are consistent with those reported in the literature.[14]

*X-ray Structural Analysis of* **13**: $C_{21}H_{25}F_6FeNP_2Pd$, $M$ = 629.63 g mol$^{-1}$, orthorhombic space group *Pna*2$_1$ (no. 33), $a$ = 8.978(1), $b$ = 29.010(4), $c$ = 9.102(2) A, $V$ = 2370(1) A$^3$, $Z$ = 4, $d_{calcd.}$ = 1.76 g cm$^{-3}$, μ(Mo-$K_\alpha$) = 15.49 cm$^{-1}$, $F$(000) = 1256. ENRAF-

Nonius CAD4, ω-2θ scan, Mo-$K_\alpha$ radiation (0.71073 Å), graphite monochromator, 7865 reflections at 298 K with $2° \leq \theta \leq 30°$, crystal size 0.04 × 0.30 × 0.60 mm. Structure solution with Patterson methods. Refinement[15] with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.067$, $R_w = 0.049$ for 288 parameters and 2609 independent observations with $I > 1.5\ \sigma(I)$. Hydrogen atoms were treated as riding atoms. A final difference Fourier synthesis showed a residual density of 2.31 (0.51 Å from Pd)/−0.62 $eA^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101282. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: int. code + 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).


[1] C. Ganter, L. Brassat, C. Glinsböckel, B. Ganter, *Organometallics* **1997**, *16*, 2862−2867.
[2] C. Ganter, L. Brassat, B. Ganter, *Chem. Ber.* **1997**, *130*, 1771−1776.
[3] B. Deschamps, L. Ricard, F. Mathey, *J. Organomet. Chem.* **1997**, *548*, 17−22.
[4] C. Ganter, L. Brassat, B. Ganter, *Tetrahedron: Asymmetry* **1997**, *8*, 2607−2611.
[5] P. J. Fagan, W. S. Mahoney, J. C. Calabrese, I. D. Williams, *Organometallics* **1990**, *9*, 1843−1852.
[6] [6a] F. Morandini, G. Consiglio, B. Straub, G. Ciani, A. Sironi, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2293−2298. − [6b] G. Consiglio, F. Morandini, *Chem. Rev.* **1987**, *87*, 761−778. − [6c] G. Consiglio, F. Morandini, F. Bangerter, *Inorg. Chem.* **1982**, *21*, 455−457. − [6d] See also: C. White, E. Cesarotti, *J. Organomet. Chem.* **1985**, *287*, 123.
[7] K. Mauthner, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1997**, *16*, 1956−1961.
[8] For leading reviews on asymmetric allylic substitutions see for example: [8a] B.Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395−422. − [8b] G. Consiglio, R. M. Waymouth, *Chem. Rev.* **1989**, *89*, 257−276.
[9] [9a] A. Togni, U. Burckhardt, V. Gramlich, P. S. Pregosin, R. Salzmann, *J. Am. Chem. Soc.* **1996**, *118*, 1031−1037. − [9b] U. Burckhardt, V. Gramlich, P. Hofmann, R. Nesper, P. S. Pregosin, R. Salzmann, A. Togni, *Organometallics* **1996**, *15*, 3496−3503. − [9c] P. E. Blöchl, A. Togni, *Organometallics* **1996**, *15*, 4125−4132.
[10] N. Baltzer, L. Macko, S. Schaffner, M. Zehnder, *Helv. Chim. Acta* **1996**, *79*, 803−812.
[11] G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, *J. Am. Chem. Soc.* **1980**, *102*, 994−1000.
[12] W. T. Dent, R. Long, A. J. Wilkinson, *J. Chem. Soc.* **1964**, 1585−1588.
[13] T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Am. Chem. Soc.* **1989**, *111*, 6301−6311.
[14] M. Yamaguchi, T. Shima, T. Yamagishi, M. Hida, *Tetrahedron: Asymmetry* **1991**, *2*, 663−666.
[15] *MolEN, An Interactive Structure Solution Procedure*, ENRAF-Nonius, Delft, The Netherlands, **1990**.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