# A New Concept for Chelate Ligands with Planar Chirality†

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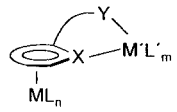
The chiral donor substituted phosphaferrocene derivatives CpFe(3,4-$Me_2$-2-R-$C_4$HP) **6** (R = $CH_2CH_2NMe_2$), **7** (R = $CH_2NMe_2$), and **8** (R = $CH_2OPPh_2$) were synthesized as racemates starting from 2-formyl-3,4-dimethylphosphaferrocene. The P,N-ligand **6** reacted with $[Cp^*RuCl]_4$ in THF to give the six-ring chelate complex $Cp^*RuCl$(**6**) (≡**10**) which was characterized by single-crystal X-ray diffraction analysis. The complexation reaction was found to proceed diastereoselectively with respect to the newly created stereogenic center on the ruthenium atom. Under similar conditions, the reaction of ligand **7** with $[Cp^*RuCl]_4$ did not lead to chelate formation. Instead, two isomers of the bis-P-coordinated complex $Cp^*RuCl(\mathbf{7})_2$ (≡**11**) were observed by NMR spectroscopy. Reaction of the phosphinite ligand **8** with $(PhCN)_2PdCl_2$ in toluene produced the six-ring chelate complex *cis*-$PdCl_2$(**8**) (≡**12**). The crystal structure of **12** has been determined.



## Introduction

Chiral ligands play an important role in coordination chemistry. In particular, the increasing interest in asymmetric catalysis over the past two decades has stimulated the development of a huge number of chiral ligands, among which the bidentate chelate ligands are by far the most numerous.[1] Whereas the $C_2$ symmetry of these chelate ligands was considered to be a prerequisite for excellent asymmetric inductions,[2] it has been shown in recent years that ligands lacking any symmetry at all may perform equally well or even superior in certain catalytic reactions.[3] Ligands owing their chirality to the presence of stereogenic centers are legion, while those with planar chirality are so far restricted to $\pi$-complexed disubstituted carbocycles (e.g. 1,2-disubstituted ferrocenes[4] and tricarbonylchromium complexes of *ortho* disubstituted benzene derivatives[5]). We considered a new approach to a novel class of bidentate chelate ligands with planar chirality *via* $\pi$-complexed monosubstituted heterocycles which are able to coordinate to a metal fragment M′L′$_m$ *via* both the heteroatom X of the $\pi$-complexed heterocycle and an appropriate donor group Y at the substituent (Chart 1). Within this arrangement the coordinated metal atom M′ is positioned in immediate proximity to the element of planar chirality. This situation may prove advantageous for stereoselective reactions at the metal center which involve chirality transfer from the ligand to a metal-coordinated substrate as is the case in asymmetric catalysis. We present here the first results obtained from our studies with phosphaferrocenes, i.e. the syntheses of appropriately substituted phosphaferrocene derivatives and their application as chelate ligands toward transition metal fragments.

**Chart 1**




## Results

**Choice of Ligands.** Among the heterocycles considered as potential candidates were thiophene, pyridine, and the pyrrolyl and phospholyl anions. The $CpFe^+$ and the $Cr(CO)_3$ moieties might serve as appropriate metal fragments for $\pi$-complexation of the heterocycles. From the possible combinations of the fragments, phosphaferrocene, i.e. the combination of the phospholyl anion with the $CpFe^+$ cation, was chosen for several reasons. Firstly, from the pioneering work of Mathey[6] et al. it is known that the phosphorus atom in the phosphaferrocene molecule is still nucleophilic enough to act as a Lewis base toward metal centers.[7] Secondly, the phosphaferrocenes are reasonably stable and tolerate a wide range of experimental conditions so that the risk of degradation in the course of the intended complexation reactions is appreciably low. Furthermore, the synthesis of phosphaferrocenes is

† Dedicated to Professor Gerhard E. Herberich on the occasion of his 60th birthday.

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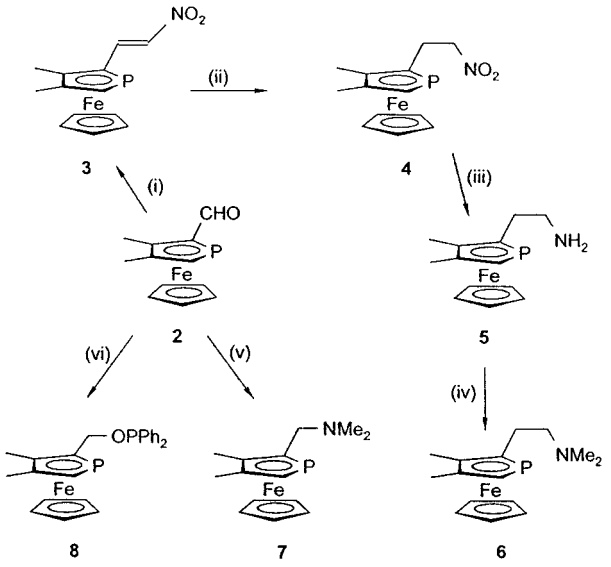
**Scheme 1. Synthesis of Ligands 6, 7, and 8[a]**




[a] Reagents and conditions: (i) $CH_3NO_2$, MeOH, cat.; (ii) $NaBH_4$, $NiCl_2$, MeOH; (iii) $LiAlH_4$, $Et_2O$; (iv) $H_2CO$, $NaBH_3CN$, $ZnCl_2$, MeOH; (v) $HNMe_2$, $NEt_3$, $TiCl_4$, $NaBH_3CN$, $CH_2Cl_2$; (vi) $LiAlH_4$, $Et_2O$; then $Ph_2PCl$, $NEt_3$, $Et_2O$.

quite straightforward. For synthetic reasons the dimethyl-substituted derivative 3,4-dimethylphosphaferrocene (**1**) was chosen as the starting material, which was prepared in 65% yield using an optimized modification of Mathey's original procedure[7a] (see the Experimental Section). Introduction of a substituent in the 2-position of the phospholyl ring establishes the element of planar chirality. Great progress has been achieved in the stereoselective synthesis of planar chiral ferrocene derivatives *via* both diastereo[8]- and most recently enantioselective[9] deprotonation of monosubstituted ferrocenes. Unfortunately, the analogous approach of enantioselective metalation in the 2-position of the phospholyl ring of **1** is hampered by the fact that strong nucleophiles such as BuLi add to the phosphorus atom of phosphaferrocene,[10] leading to subsequent degradation. We therefore decided to utilize the Vilsmeyer formylation of **1**[11] as an entry into 2-substituted phosphaferrocene derivatives although this reaction is not stereoselective and leads to racemic 2-formyl-3,4-dimethylphosphaferrocene (**2**). Starting from aldehyde **2** the P∧N ligands **6** and **7** and the P∧P ligand **8** were prepared by standard organic transformations (Scheme 1). Reductive amination of **2** affords the (dimethylamino)methyl-substituted ligand **7**, which should give rise to five-membered chelate rings on complexation to a metal fragment. In contrast, nitroaldol condensation of aldehyde **2** with nitromethane enables the extension of the alkyl spacer by one $CH_2$ unit and leads after stepwise reduction and dimethylation to the amino compound **6**, appropriate for six-membered chelate ring formation.

**Scheme 2**

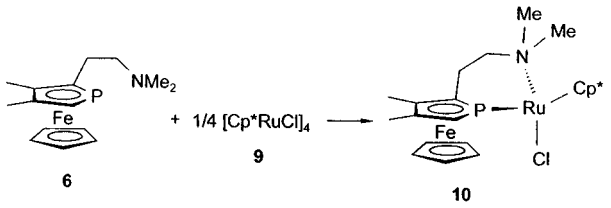



**Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 10**

| | | | |
|---|---|---|---|
| (a) Distances | | | |
| Ru−Cl | 2.475(2) | Fe−P | 2.262(2) |
| Ru−P | 2.238(1) | Fe−C2 | 2.077(6) |
| Ru−N | 2.296(5) | Fe−C3 | 2.048(6) |
| Ru−C20 | 2.214(6) | Fe−C4 | 2.036(6) |
| Ru−C21 | 2.145(6) | Fe−C5 | 2.070(6) |
| Ru−C22 | 2.149(5) | Fe−C12 | 2.031(8) |
| Ru−C23 | 2.184(6) | Fe−C13 | 2.037(8) |
| Ru−C24 | 2.252(6) | Fe−C14 | 2.020(8) |
| P−C2 | 1.752(5) | Fe−C15 | 2.037(8) |
| P−C5 | 1.761(6) | Fe−C16 | 2.040(8) |
| C2−C3 | 1.425(8) | C6−C7 | 1.51(1) |
| C3−C4 | 1.423(9) | N−C7 | 1.512(8) |
| C4−C5 | 1.421(8) | N−C10 | 1.471(9) |
| C2−C6 | 1.498(9) | N−C11 | 1.479(8) |
| (b) Angles | | | |
| Ru−P−Fe | 140.88(7) | Cl−Ru−N | 85.0(1) |
| P−Ru−N | 84.4(1) | Cl−Ru−P | 94.64(6) |
| C2−P−C5 | 90.8(3) | Ru−P−C2 | 126.4(2) |
| Ru−P−C5 | 141.9(2) | P−C2−C3 | 112.6(4) |
| P−C2−C6 | 122.1(4) | C3−C2−C6 | 125.3(5) |
| C2−C3−C4 | 111.9(5) | C3−C4−C5 | 112.7(5) |
| P−C5−C4 | 112.0(5) | | |

**Complexation Studies.** Complexation reactions of the P∧N ligands **6** and **7** were carried out using $[Cp^*RuCl]_4$ **9**,[12] which is known to provide a source of Cp*RuCl fragments with two vacant coordination sites and reacts with a variety of hard and soft bidentate ligands L∧L including phosphines and nitrogen donors to give chelate complexes of the type Cp*RuCl(L∧L).[13] Different results were obtained for the reaction of $[Cp^*RuCl]_4$ with ligands **6** and **7**, respectively. When ligand **6** was treated with 0.25 equiv of **9** in THF at room temperature, we observed within minutes the formation of the desired chelate complex [Cp*RuCl(**6**)] **10** (Scheme 2), which was isolated in analytically pure form as an orange red powder in quantitative yield simply by evaporating the solvent. Recrystallization from acetone afforded red crystals suitable for X-ray diffraction. Selected bond distances and angles are given in Table 1; a PLATON plot of the structure of **10** is depicted in Figure 1 and reveals the chelating coordination of ligand **6** to the ruthenium atom. The phospholyl ring shows only slight deviation from planarity and forms an angle of 4(2)° with the Cp ring plane. The Ru−P vector is tilted from the mean phospholyl plane by 8.2(2)° away from iron. A similar tilt angle of 8.4(2)° was found for the Fe−P vector in tetracarbonyl(3,4-dimethylphospha-

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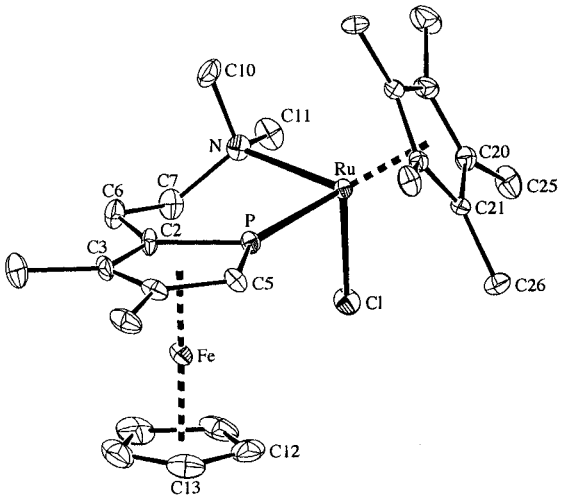
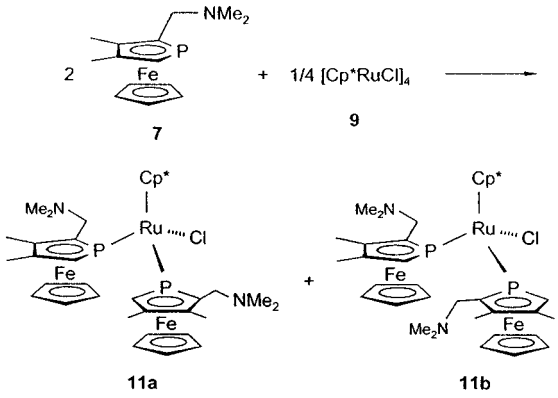



**Figure 1.** Thermal ellipsoid plot (PLATON)[28] of complex **10**. Ellipsoids are scaled to 30% probability.

ferrocene-*P*)iron.[7b] The six-membered chelate ring shows a half-chair conformation with only C7 and N deviating considerably from its mean plane by −0.300(7) and 0.614(5) Å, respectively. The Ru−P distance of 2.238(1) Å is remarkably short and falls in the range observed for Cp*RuCl{P(OR)$_3$}$_2$ complexes [2.212(9)−2.250(9) Å][14] while 2.276(2) and 2.278(2) Å are found in Cp*RuCl-($Ph_2PCH_2CHMePPh_2$).[15] The Ru−N and Ru−Cl distances are comparable to those found in related complexes.[13a,16] A new stereogenic center is created on the ruthenium atom in the course of the complexation reaction. The crystal examined contains only one diastereomer with the relative configuration of the central and planar elements of chirality as depicted in Figure 1, i.e. ($R_{Ru}$),($S$)[17] and —consistent with the centrosymmetric space group $P2_1/c$—its ($S_{Ru}$),($R$) enantiomer as we started from the racemic ligand **6**. Since the quantitatively obtained crude product of **10** as well as the crystals give identical NMR spectra, we conclude that complex **10** is formed diastereoselectively since we observe only one set of NMR signals consistent with the presence of only one diastereomer. In the $^1$H NMR spectrum of **10** the protons of the Cp* ligand appear as a doublet due to the coupling with the phosphorus atom of coordinated **6** with $J_{HP}$ = 2.7 Hz. The coupling constant $^2J_{HP}$ for the α phospholyl H decreases on complexation from 36.0 Hz in **6** to 31.7 Hz in **10**, which is a known phenomenon in the coordination chemistry of phosphaferrocenes.[7a,d,e] At room temperature the protons of the $NMe_2$ group give one broad signal, which coalesces on cooling to 6 °C (500 MHz) and splits into two sharp resonances ($\Delta\nu$ = 212 Hz) at −40 °C. We attribute this observation to a dynamic hemilabile behavior of dissociation/association of the $NMe_2$ moiety that is fast on the NMR time scale at ambient temperature. For this dangling process an activation enthalpy of $\Delta G^{\ddagger}$ = 53.6 ± 1 kJ mol$^{-1}$ is calculated from the recorded data. In the $^{31}$P NMR spectrum the signal of **6** (−80.2 ppm) experiences a downfield shift to $\delta(^{31}P)$ = 25.5 ppm in **10**. No sign of line broadening was observed for the $^{31}$P resonance down to −80 °C. Although we cannot as yet exclude tentatively a fast epimerization of the chiral ruthenium center on the NMR time scale which should also lead to a single $^{31}$P resonance for the interconverting diastereomers, we believe that the formation of **10** proceeds stereoselectively and only one diastereomer is present in the crystal as well as in solution. The fact that Consiglio et al. were able to observe both diatsereoisomers of CpRuCl(P∧P) with chiral bidentate diphosphines[15,18] points to an appreciable epimerization barrier for the ruthenium atom and supports our assumption.

**Scheme 3**




Completely different results were obtained for the reaction of ligand **7** with the ruthenium complex **9**. No chelate formation was observed. Instead, when **7** was reacted with 0.25 equiv of [Cp*RuCl]$_4$ in THF-$d_8$, we observed the formation of the 2:1 complex [Cp*RuCl-(**7**)$_2$] **11** by NMR spectroscopy while half of the [Cp*-RuCl]$_4$ remains unreacted and insoluble (Scheme 3). Addition of another equivalent of ligand **7** to the mixture results in complete consumption of **9** with complex **11** again being the only detectable species in the NMR spectrum. The 2:1 stoichiometry of complex **11** is evident from the integration of the Cp and Cp* protons which appear in a 10:15 ratio. Both phosphaferrocene molecules **7** are coordinated *via* their phosphorus atoms to the ruthenium center, which leads to a triplet structure of the signal for the Cp* protons due to coupling to the two phosphorus nuclei with $J_{HP}$ = 2.7 Hz. The $^{31}$P NMR spectrum consists of a singlet [$\delta(^{31}P)$ = 30.7 ppm] and a pair of doublets at $\delta(^{31}P)$ = 35.5 and $\delta(^{31}P)$ = 24.7 ppm, respectively, with $J_{PP}$ = 56.8 Hz in a 4:1 ratio. We assume that two isomers of **11** are formed in the complexation reaction. While the $C_s$ symmetric **11a** gives rise to one $^{31}$P NMR signal for the two equivalent phosphorus atoms, the phosphorus nuclei in the $C_1$ symmetric isomer **11b** are inequivalent and lead to the observed AB pattern. Consistently, the $^1$H NMR spectrum shows, besides the signal set for $C_s$ symmetric **11a**, the expected resonances for the $C_1$ symmetric isomer **11b** in the same 4:1 ratio. Due to the lower symmetry of **11b**, two singlets for the Cp protons are observed and the signal for the Cp* protons appears as a doublet of doublets with identical coupling constants to the two inequivalent P atoms of $J_{HP}$ = 2.5 Hz. Attempts to separate and isolate the isomers **11a**

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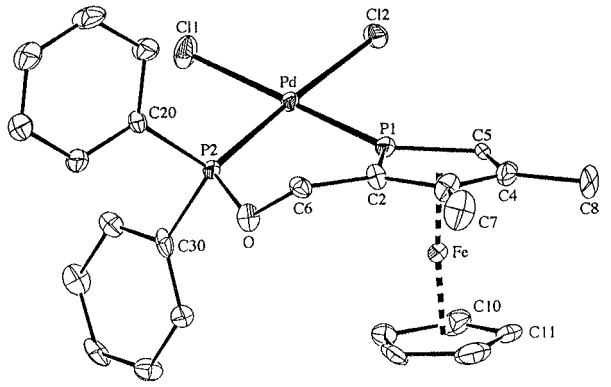
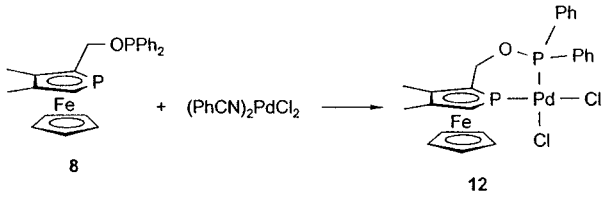



**Figure 2.** Thermal ellipsoid plot (PLATON)[28] of complex **12**. Ellipsoids are scaled to 30% probability.

**Scheme 4**




and **11b** in pure form have so far been unsuccessful. The Ru atom in the achiral isomer **11a** is an achirotopic but stereogenic unit, i.e. it is a center of pseudoasymmetry. Thus, the formation of another achiral diastereomer may be anticipated, which can formally be constructed by interchanging the positions of the two phosphaferrocene ligands in formula **11a**. This would result in a ligand arrangement with the aminoalkyl side chains pointing toward each other, a situation which is very likely less favorable for steric reasons as compared to the arrangement depicted in formula **11a** with the side chains lying far apart from each other. The NMR spectra indicate the presence of only one achiral complex, and we therefore consider the arrangement **11a** to belong to the observed species.

Another complexation experiment was carried out with the P∧P ligand **8**. The synthesis of the phosphinite **8** was complicated by the formation of $Ph_2P(O)PPh_2$ in a consecutive reaction.[19] Furthermore, since it is quite sensitive and decomposes on chromatography, **8** could not be obtained in pure form. Therefore, ligand **8** was prepared *in situ* without isolation and immediately treated with $(PhCN)_2PdCl_2$ in toluene (Scheme 4). The resulting red precipitate was collected and recrystallized from dichloromethane and ether to give the palladium chelate complex **12** in low yield as dark red crystals suitable for an X-ray diffraction study (Figure 2, Table 2). The structure determination confirms the chelating coordination mode of the phosphinite ligand **8**, which leads to a boat conformation for the six-membered chelate ring. The structure shows a distorted square planar geometry about the palladium atom with a rather short Pd−P1 distance of 2.201(4) Å, which is comparable to 2.229(1) Å found for *cis*-$PdCl_2$-$[P(OSiMe_3)_3]_2$.[20] The distance Pd−P2 of 2.243(3) Å falls in the range observed for other $PdCl_2$ complexes with chelating diphosphines.[21] The bite angle P1−Pd−P2 adopts a value of 89.3(1)°. The Pd-Cl1 distance of 2.329(4) Å *trans* to the phospholyl phosphorus is shorter than the Pd−Cl2 distance of 2.367(3) Å reflecting the different donor/acceptor properties of the two phosphorus centers. The mean planes for the Cp and phospholyl rings form an angle of 8(2)°. The Pd−P1 vector is inclined against the phospholyl mean plane by 10.4(2)°. In the $^{31}P$ NMR spectrum the signal for the phospholyl P atom is shifted downfield from −78.0 ppm in ligand **8** to −14.3 ppm in the complex **12**, while the signal for the phosphinite phosphorus atom remains practically unchanged (**8**, 116.7 ppm; **12**, 109.7 ppm).

**Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 12**

(a) Distances

| | | | |
|---|---|---|---|
| Pd−Cl1 | 2.329(4) | Fe−P1 | 2.224(4) |
| Pd−Cl2 | 2.367(3) | Fe−C2 | 2.08(1) |
| Pd−P1 | 2.201(4) | Fe−C3 | 2.06(1) |
| Pd−P2 | 2.243(3) | Fe−C4 | 2.03(2) |
| P1−C2 | 1.74(1) | Fe−C5 | 2.06(1) |
| P1−C5 | 1.74(1) | Fe−C10 | 2.05(1) |
| C2−C3 | 1.40(2) | Fe−C11 | 2.03(1) |
| C3−C4 | 1.42(2) | Fe−C12 | 2.03(1) |
| C4−C5 | 1.42(2) | Fe−C13 | 2.05(1) |
| C2−C6 | 1.49(2) | Fe−C14 | 2.06(2) |
| O−C6 | 1.44(1) | P2−C20 | 1.82(1) |
| P2−O | 1.604(9) | P2−C30 | 1.81(1) |

(b) Angles

| | | | |
|---|---|---|---|
| Pd−P1−Fe | 142.1(3) | Pd−P2−O | 117.0(4) |
| C2−P1−C5 | 92.8(7) | P1−Pd−P2 | 89.3(1) |
| Cl1−Pd−Cl2 | 93.5(1) | Cl2−Pd−P1 | 88.6(1) |
| Cl1−Pd−P1 | 176.6(1) | Cl2−Pd−P2 | 176.9(1) |
| Cl1−Pd−P2 | 88.7(1) | Pd−P1−C2 | 121.7(5) |
| Pd−P1−C5 | 143.8(6) | P1−C2−C3 | 111.2(9) |
| C2−C3−C4 | 113(1) | C3−C4−C5 | 113(1) |
| P1−C5−C4 | 110(1) | | |

## Discussion

Some aspects of the reported findings deserve a further comment. Comparing ligands **6** and **7**, we note that chelate formation only occurs with **6** leading to a six-membered chelate ring, while no five-membered ring was observed with ligand **7**. As both ligands can be supposed to have similar donor/acceptor properties, their different coordination modes toward the Cp*RuCl fragment must be attributed to their different conformational flexibility resulting in a better ring size fit for ligand **6**. Complexation of two molecules of **7** *via* their phosphorus atoms shows that P-coordination of the ligand is prefered for electronic reasons as compared to coordination *via* the $NMe_2$ donor moiety. In the chelate complex **10** on the other hand, this electronic preference is overcome by the chelate effect. A further, quite encouraging point concerns the diastereoselectivity observed in the formation of the Ru complex **10**. Consiglio et al. have reported the synthesis of several CpRuCl(P∧P) chelate complexes with chiral diphosphine ligands. In most cases, low diastereoselectivities were observed for the formation of the stereogenic center on the ruthenium atom resulting in almost 1:1 mixtures of diastereomers.[15,18] An argument for the increased stereoselectivity observed in the complexation reaction with our new ligand **6** is provided by inspection of the structure of the ruthenium complex **10**: formally, interchanging the positions of the Cl and Cp* ligands on the ruthenium atom results in the other diastereomer. Model inspection of that hypothetical ligand

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arrangement suggests an unfavorable approach of the Cp and Cp* ligands for that particular diastereomer.

## Conclusion and Outlook

Phosphaferrocene derivatives bearing donor substituents in the 2-position have been synthesized and were shown to react as bidentate chelate ligands forming metal complexes with six-membered chelate rings. The planar chirality of the ligand **6** provided effective stereocontrol in the formation of the stereogenic ruthenium center in complex **10** which was obtained diastereoselectively. This clearly demonstrates that our approach to a topologically new class of planar chiral chelate ligands bears a potential for stereoselective reactions being carried out at a coordinated metal center. We are currently investigating the resolution of the racemic aldehyde **2** in order to obtain enantiopure ligands. Further work will be directed toward the development of ligands with other donor substituents as well as their use in coordination chemistry and asymmetric catalysis.

## Experimental Section

**General Procedures.** Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Solvents were purified and deoxygenated by conventional methods. Kieselguhr and alumina (Woelm, N-super O, activity I) were heated at 250 °C for 12 h, cooled to room temperature under high vacuum, and stored under dinitrogen. Alumina was deactivated with 5% deoxygenated water after cooling.

NMR spectra were recorded on a Varian Unity 500 spectrometer ($^1$H, 500 MHz; $^{13}$C{$^1$H}, 125.7 MHz; $^{31}$P{$^1$H}, 202.3 MHz), a Bruker AM 250 PFT ($^1$H, 250 MHz; $^{13}$C, 62.9 MHz), and a Bruker WP 80 PFT ($^1$H, 80 MHz). $^1$H and $^{13}$C spectra are referenced to internal TMS and $^{31}$P spectra to external $H_3PO_4$ (85%). Mass spectra were recorded on a Finnigan MAT-95 spectrometer (EI, 70 eV nominal electron energy). 3,4-Dimethylphosphaferrocene (**1**) was prepared by an optimized modification of Mathey's original procedure[7a] (see below). 2-Formyl-3,4-dimethylphosphaferrocene (**2**),[11] 2-(hydroxymethyl)-3,4-dimethylphosphaferrocene,[11] and [Cp*RuCl]$_4$ (**9**)[12] were prepared as described in the literature.

**Preparation of 3,4-Dimethylphosphaferrocene (1).** 1-*tert*-Butyl-3,4-dimethylphosphole[22] (10.4 g, 62 mmol) and 12.0 g (34 mmol) of [CpFe(CO)$_2$]$_2$ were refluxed in 75 mL of xylene for 15 h. The solvent was evaporated under vacuum and the residue dissolved in dichloromethane (30 mL). Alumina (30 g) was added, and the solvent was removed under vacuum. The dry residue was loaded onto a 20 cm alumina column and eluted with hexane. Evaporation of the dark orange main band gave 9.3 g (65%) of **1** as an orange solid which yielded spectroscopic data similar to those quoted in the literature.[7a] Crystalline **1** can be obtained by recrystallization of the crude product from hot methanol.

**Preparation of 3**. Aldehyde **2** (2.45 g, 9.4 mmol), nitromethane (0.63 g, 10.3 mmol), and ethylenediamine diacetate (170 mg, 0.94 mmol) were stirred in methanol (20 mL) at room temperature for 4 days. The solvent was removed, and the residue was chromatographed on alumina (15 cm) with hexane/ether (4:1) to give 2.23 g (78%) of **3** as a dark purple powder after removal of the eluent under vacuum. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.23 (s, 3H, Me), 2.27 (s, 3H, Me), 4.21 (s, 5H, Cp), 4.24 (d, $J$ = 37.3 Hz, 1H, α-H), 7.27 (dd, $J$ = 13.1/1.2 Hz, 1H, CCH), 7.98 (dd, $J$ = 13.1/12.2 Hz, 1H, $CHNO_2$). $^{13}$C{$^1$H} NMR (125.7 MHz, $CDCl_3$): $\delta$ = 13.94 (Me), 16.97 (Me), 73.60 (Cp), 80.99 (d, $J$ = 59.7 Hz, α-CH), 82.34 (d, $J$ = 59.2 Hz, α-C), 96.06 (d, $J$ = 4.4 Hz, β-C), 99.83 (d, $J$ = 7.6 Hz, β-C), 134.36 (d, $J$ = 14.8 Hz, =CH), 144.49 (d, $J$ = 17.0 Hz, =CH). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ = −75.6. MS: 303 ($M^+$). Anal. Calcd for $C_{13}H_{14}FePNO_2$: C, 51.52; H, 4.66; N, 4.62. Found: C, 51.14; H, 4.67; N, 4.34.

**Preparation of 4.** $NaBH_4$ (211 mg, 5.58 mmol) was added to a solution of $NiCl_2 \cdot 6H_2O$[23] (439 mg, 1.85 mmol) in 25 mL of MeOH portionwise, and the mixture was stirred vigorously for 0.5 h. A solution of **3** (1.12 g, 3.7 mmol) in 10 mL of MeOH and 3 mL of THF was then added followed by 485 mg (12.83 mmol) of $NaBH_4$ in several portions. Stirring was continued for 0.5 h at room temperature, and the mixture was filtered through Kieselguhr. The filtrate was evaporated to dryness, dissolved in 30 mL of $CH_2Cl_2$, and washed with 0.1 N HCl and brine. The organic phase was dried over $Na_2SO_4$ and filtered, and the solvent was removed under vacuum to yield 1.00 g (89%) of **4** as a red oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.14 (s, 3H, Me), 2.16 (s, 3H, Me), 2.84 (m, 2H, $CH_2$), 3.72 (d, $J$ = 36.9 Hz, α-H), 4.10 (s, 5H, Cp), 4.34 (t, $J$ = 7.8 Hz, 2H, $CH_2NO_2$). $^{13}$C{$^1$H} NMR (125.7 MHz, $CDCl_3$): $\delta$ = 13.50 (Me), 16.89 (Me), 28.93 (d, 19.7 Hz, $CH_2$), 72.23 (Cp), 76.03 (d, $J$ = 58.7 Hz, α-CH), 76.38 (d, $J$ = 6.6 Hz, $CH_2NO_2$), 92.33 (d, $J$ = 59.2 Hz, α-C), 93.36 (d, $J$ = 5.0 Hz, β-C), 96.26 (d, $J$ = 6.6 Hz, β-C). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ = −79.6. HRMS: calcd for $C_{13}H_{16}FePNO_2$ 305.026 804, found 305.026 764.

**Preparation of 5**. To a suspension of 500 mg (13.16 mmol) of $LiAlH_4$ in 25 mL of ether was added a solution of **4** (1.00 g, 3.3 mmol) in 5 mL of THF dropwise at 0 °C, and the mixture was strirred for 1 h at room temperature. Water (0.5 mL), 1 mL of NaOH (2 M), and again 1 mL of water were added subsequently to give a granular precipitate which could easily be removed by filtration through Kieselguhr. The filtrate was evaporated to dryness under vacuum and treated with ether, water and HCl (2 M). The acidic aqueous phase was separated, treated with 2 M NaOH until pH 11, and extracted twice with ether. The combined extracts were washed with brine and dried over $Na_2SO_4$, and the solvent was removed under vacuum to give 667 mg (74%) of **5** as a red oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.32 (br s, 2H, $NH_2$), 2.14 (s, 3H, Me), 2.19 (s, 3H, Me), 2.24 (m, 1H, $CH_2$), 2.36 (m, 1H, $CH_2$), 2.78 (m, 2H, $CH_2NH_2$), 3.68 (d, $J$ = 36.0 Hz, 1H, α-H), 4.08 (s, 5H, Cp). $^{13}$C{$^1$H} NMR (125.7 MHz, $CDCl_3$): $\delta$ = 13.61 (Me), 16.85 (Me), 35.62 (d, $J$ = 16.4 Hz, $CH_2$), 43.74 (br s, $CH_2$), 71.85 (Cp), 75.35 (d, $J$ = 58.2 Hz, α-CH), 93.12 (d, $J$ = 4.9 Hz, β-C), 95.58 (d, $J$ = 6.6 Hz, β-C), 96.48 (d, $J$ = 58.7 Hz, α-C). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ = −79.06. HRMS: calcd for $C_{13}H_{18}FeNP$ 275.052 625, found 275.052 317.

**Preparation of 6**. To a solution of **5** (590 mg, 2.14 mmol) and 3 equiv of formaldehyde (37% aqueous solution) in 15 mL of MeOH and 5 mL of THF was added a solution of $NaBH_3CN$[24] (135 mg, 2.14 mmol) and $ZnCl_2$ (146 mg, 1.07 mmol) in 5 mL of MeOH, and the mixture was stirred for 3 h. Water was added and the pH adjusted to 10. The organic solvents were removed under vacuum, more water was added and the mixture was extracted with three portions of ether which were dried over $Na_2SO_4$ and evaporated to dryness. The oily residue was chromatographed on alumina with hexane/ether (1:1) to give 468 mg (72%) of **6** as a red oil after removal of the eluent under vacuum. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.10 (s, 3H, Me), 2.14 (s, 3H, Me), 2.21 (s, 6H, $NMe_2$), 2.27 (m, 4H, $CH_2CH_2$), 3.63 (d, $J$ = 36.0 Hz, α-H), 4.04 (s, 5H, Cp). $^{13}$C{$^1$H} NMR (125.7 MHz, $CDCl_3$): $\delta$ = 13.89 (Me), 16.81 (Me), 28.96 (d, $J$ = 18.1 Hz, $CH_2$), 45.31 ($NMe_2$), 61.64 (d, $J$ = 7.1 Hz, $CH_2NMe_2$), 71.72 (Cp), 75.23 (d, $J$ = 58.2 Hz, α-CH), 92.85 (d, $J$ = 5.5 Hz, β-C), 95.31 (d, $J$ = 6.0 Hz, β-C), 96.81 (d, $J$ = 58.7 Hz, α-C). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ = −80.2. MS: 303 ($M^+$). The methylammonium iodide was prepared for the purpose of an elemental analysis by addition of an excess of MeI to a solution

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of **6** in ether and collecting the resulting precipitate [Me-**6**]$I^-$ on a frit. Anal. Calcd for $C_{16}H_{25}NPFeI$: C, 43.17; H, 5.66; N, 3.15. Found: C, 42.94; H, 5.83; N, 3.11.

**Preparation of 7**. To a solution of **2** (2.054 g, 7.90 mmol), dimethylamine (356 mg, 7.90 mmol), and trimethylamine (1.60g, 15.8 mmol) in 30 mL of dichloromethane was added 1.50 g (7.9 mmol) of $TiCl_4$, and the mixture was stirred overnight at room temperature. A solution of $NaBH_3CN$ (750 mg, 11.94 mmol) in 5 mL of dichloromethane was added dropwise at 0 °C, and stirring was continued for another 2 h at ambient temperature. The mixture was hydrolyzed by the careful addition of 2 mL of water, filtered through Kieselguhr, and concentrated under vacuum. $CH_2Cl_2$ (15 mL) was added, and the solution was washed with $NaHCO_3$ solution and brine and dried over $Na_2SO_4$. The solvent was removed under vacuum, and the residue was chromatographed on alumina with hexane/ether (1:1). Evaporation of the eluent yielded 1.43 g (63%) of **7** as a dark red oil which solidified slowly on standing. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.15$ (s, 3H, Me), 2.16 (br s, 9H, Me + $NMe_2$), 2.88 (dd, $J = 13.0/6.0$ Hz, 1H, $CH_2$), 3.10 (dd, $J = 16.0/13.0$ Hz, 1H, $CH_2$), 3.73 (d, $J = 35.7$ Hz, 1H, α-H), 4.07 (s, 5H, Cp). $^{13}$C{$^1$H} NMR (125.7 MHz, $CDCl_3$): $\delta = 14.02$ (Me), 17.00 (Me), 45.17 ($NMe_2$), 59.33 (d, $J = 19.2$ Hz, $CH_2$), 72.02 (Cp), 76.63 (d, $J = 55.1$ Hz, α-CH), 94.23 (d, $J = 5.0$ Hz, β-C), 94.42 (d, $J = 58.0$ Hz, α-C), 96.10 (d, $J = 6.0$ Hz, β-C). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta = -72.9$. MS: 289 ($M^+$). Anal. Calcd for $C_{14}H_{20}FePN$: C, 58.15; H, 6.97; N, 4.84. Found: C, 58.08; H, 7.14; N, 4.78.

**Preparation of 10**. **6** (83.0 mg (0.274 mmol) was added to a suspension of $[Cp^*RuCl]_4$ **9** (74.4 mg, 0.068 mmol) in 5 mL THF at room temperature, and the mixture was stirred for 5 min until a clear dark red solution had formed. Evaporation of the solvent under vacuum gave pure **10** as an orange brown powder in quantitative yield. The crude product could be recrystallized by cooling an acetone solution to −20 °C to give 102 mg (65%) of **10** as dark red crystals. $^1$H NMR (500 MHz, THF-$d_8$): $\delta = 1.62$ (d, $J = 2.7$ Hz, 15H, Cp*), 2.08 (s, 3H, Me), 2.22 (s, 3H, Me), 2.49 (m, 2H, $CH_2$), 2.64 (br s, 6H, $NMe_2$), 3.57 (d, $J = 31.7$ Hz, 1H, α-H), 3.97 (m, 2H, $CH_2$), 4.36 (s, 5H, Cp). $^{13}$C{$^1$H} NMR (125.7 MHz, THF-$d_8$): $\delta = 10.92$ (Cp*), 12.80 (Me), 16.62 (Me), 28.20 (d, $J = 14.1$ Hz, $CCH_2$), 54.29 ($NMe_2$), 59.97 (d, $J = 7.3$ Hz, $CH_2NMe_2$), 73.08 (Cp), 74.02 (d, $J = 35.2$ Hz, α-CH), 83.03 (Cp*), 88.72 (β-C), 89.56 (β-C), 91.01 (d, $J = 35.4$ Hz, α-C). $^{31}$P{$^1$H} NMR (THF-$d_8$): $\delta = 25.5$. SIMS (DTE/DTT matrix): 540 ($M^+$ − Cl). Anal. Calcd for $C_{25}H_{37}NPClFeRu$: C, 52.23; H, 6.49; N, 2.44. Found: C, 52.16; H, 6.63; N, 2.29.

**Complexation Experiment with Ligand 7**. A NMR tube was charged with 24.0 mg (0.088 mmol) of **9** and THF-$d_8$. Ligand **7** (51.1 mg, 0.177 mmol) was added, and the NMR tube was shaken several times until a clear solution resulted. $^1$H NMR (500 MHz, THF-$d_8$): major isomer ($C_s$ symmetry): $\delta =$ 1.82 (t, $J = 2.7$ Hz, 15H, Cp*), 2.10 (s, 12H, $NMe_2$), 2.15 (s, 6H, Me), 2.21 (s, 6H, Me), 2.48 (dm, $J = 12.2$ Hz, 2H, $CH_2$), 3.41 (dm, $J = 12.2$ Hz, 2H, $CH_2$), 3.88 (dm, $J = 26.6$ Hz, 2H, α-H), 4.01 (s, 10H, Cp); minor isomer ($C_1$ symmetry) $\delta = 1.60$ (t, $J = 2.5$ Hz, 15H, Cp*), 2.07 (s, 6H, $NMe_2$), 2.17 (s, 6H, $NMe_2$), 2.25 (s, 3H, Me), 2.26 (s, 3H, Me), 2.27 (s, 3H, Me), 2.28 (s, 3H, Me), 2.88 (m, 2H, $CH_2$), 3.03 (m, 2H, $CH_2$), 4.19 (s, 5H, Cp), 4.28 (s, 5H, Cp). $^{31}$P{$^1$H} NMR (THF-$d_8$): major isomer ($C_s$ symmetry) $\delta = 30.7$; minor isomer ($C_1$ symmetry) $\delta = 24.7$ (d, $J = 56.8$ Hz), 35.5 (d, $J = 56.8$ Hz). Ratio major/minor isomer: 4:1.

**Preparation of 12**. To a solution of 2-(hydroxymethyl)-3,4-dimethylphosphaferrocene[11] (198 mg, 0.76 mmol) and triethylamine (0.5 mL) in 30 mL of ether was added a solution of chlorordiphenylphosphine (167 mg, 0.76 mmol) in 5 mL of ether dropwise at 0 °C. After the mixture was stirred for 1 h at room temperature, hexane (10 mL) was added and the precipitated hydrochloride was removed by filtration through Kieselguhr. The filtrate was evaporated to dryness under vacuum, and the residue was dissolved in toluene (5 mL). The resulting solution of ligand **8** was added to a solution of dichlorobis(benzonitrile)palladium (289 mg, 0.76 mmol) in 30 mL of toluene. A red voluminous precipitate formed instantaneously, which was collected on a frit after the mixture was stirred for 0.5 h. The solid was dried under vacuum, dissolved in dichloromethane (20 mL), and layered with ether (30 mL) to give **12** (56 mg, 12%) as dark red crystals. $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta = 2.07$ (s, 3H, Me), 2.18 (s, 3H, Me), 4.46 (s, 5H, Cp), 7.5 (m, 5H, Ph), 8.0 (m, 5H, Ph). $^{31}$P{$^1$H} NMR ($CD_2Cl_2$): $\delta = -14.3$ (br s), 109.7 (br s). Anal. Calcd for $C_{24}H_{24}FeP_2OPdCl_2$: C, 46.23; H, 3.88. Found: C, 47.21; H, 3.89.

**Table 3. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for 10 and 12**

| | **10** | **12** |
|---|---|---|
| formula | $C_{25}H_{37}ClFeNPRu$ | $C_{24}H_{24}Cl_2FeOP_2Pd$ |
| fw | 574.92 | 623.56 |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/c$ (No. 14) | $P2_1/n$ (No. 14) |
| $a$, Å | 10.479(2) | 8.728(5) |
| $b$, Å | 16.171(3) | 13.65(1) |
| $c$, Å | 14.647(6) | 20.12(1) |
| $\beta$, deg | 95.32(2) | 94.21(5) |
| $V$, Å$^3$ | 2471(2) | 2391(5) |
| $d_{calcd}$, g·cm$^{-3}$ | 1.545 | 1.733 |
| $Z$ | 4 | 4 |
| $F$(000) | 1184 | 1248 |
| $\mu$, cm$^{-1}$ | 13.72 | 17.23 |
| cryst dimens, mm | 0.10 × 0.20 × 0.28 | 0.25 × 0.25 × 0.10 |
| $T$, K | 203 | 203 |
| scan mode | $\omega-2\theta$ | $\omega-2\theta$ |
| scan range, deg | $3 < \theta < 28$ | $3 < \theta < 28$ |
| total no. of data | 6479 | 6353 |
| no. of unique obsd data | 4002 ($I > \sigma(I)$) | 2962 ($I > \sigma(I)$) |
| no. of variables | 418 | 280 |
| $R$, $R_w$ [$w^{-1} = \sigma^2(F_o)$], GOF | 0.057, 0.049, 1.090 | 0.084, 0.066, 1.193 |
| max resid density, e Å$^{-3}$ | 0.83 (1.13 Å from Ru) | 1.23 (1.36 Å from O) |

**X-ray Structure Determinations**. Geometry and intensity data were collected on an ENRAF-Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ Å, graphite monochromator). A summary of crystallographic data, data collection parameters, and refinement parameters are collected in Table 3. The structures were solved with Patterson methods and refined on structure factors.[25] In the final least squares full-matrix refinement, all non-hydrogen atoms for both structures were refined with anisotropic thermal displacement parameters. Hydrogen atoms for compound **10** were refined isotropically and for **12** were included as riding atoms with an idealized geometry (C−H = 0.98 Å, $B_H = 1.3\,B_c$). For **10** an empirical absorption correction (Ψ scans) was applied.[26,27]

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**Supporting Information Available:** Complete tables of unit cell parameters, H atom parameters, thermal parameters, bond distances, bond angles, and positional and anisotropic thermal parameters for **10** and **12** (11 pages). Ordering information is given on any current masthead page.

OM970059N

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