Titanium-Mediated Reductive Coupling of Chiral Formylphosphaferrocenes: Formation of Bis(phosphaferrocenyl)-Substituted Ethylenes and Pinacols

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Treatment of 3,4-dimethylphosphaferrocen-2-carbaldehyde (**1**) with the standard McMurry reagent [$TiCl_3$·$(DME)_{1.5}$] and Zn(Cu) gives good yields of either the 1,2-bis(phosphaferrocenyl)-ethenes **2** as a mixture of *E*- and *Z*-isomers or the respective pinacol coupling products, depending on the reaction conditions. The stereochemical course of the pinacol coupling was investigated. Starting from enantiomerically pure aldehyde **1**, only one isomeric diol **3** is obtained, while racemic starting material leads to the formation of two diastereomeric products. Configurations of all coupling products were determined by a combination of NMR spectroscopy and X-ray diffraction. The distribution of stereoisomers can be rationalized assuming the formation of a titanaoxirane as an intermediate. The configuration of the oxirane C atom is determined by the chirality of the adjacent heterometallocene unit. Insertion of another molecule of aldehyde into the Ti−C bond yields a titanapinacolate as the coupling product. The chirality of the inserting aldehyde seems to be unimportant for the stereochemical course of this step. Diol **3** and its bis(methyl)ether derivative were employed as P,P chelate ligands in the formation of metal complexes with Cp*RuCl and $Mo(CO)_4$ fragments, respectively, and the latter complex was characterized by X-ray diffraction.

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Introduction

The reductive coupling of carbonyl compounds leading to diols or olefins is a well-recognized C−C bond forming reaction, and quite a number of different reducing agents have been tested in these reactions. Titanium-based systems have attracted particular interest, and the McMurry reaction has become a frequently used transformation in both pinacol and olefin synthesis. The applicability of the procedure to α,ω-dicarbonyl compounds leading to cyclic products has made the McMurry reaction a powerful tool in natural products synthesis because it gives straightforward access to medium and large rings, which are obtained only with difficulty by other methods.[1] [$TiCl_3$·$(DME)_{1.5}$] in combination with Zn(Cu) is a standard reagent for performing the reductive coupling, and it was long assumed that the reaction proceeds via the formation of zerovalent Ti particles, which were supposed to be the active reagents leading to the formation of ketyl radicals from the carbonyl substrates. Dimerization of the ketyl radicals would lead to a pinacolate intermediate, which might be either hydrolyzed to the diol or reduced further to the olefinic product. However, more recent studies of this system revealed that the titanium is not reduced below the +II oxidation state and an alternative mechanistic rationale was proposed involving a metallaoxirane intermediate instead of ketyl radicals.[2] DFT calculations support the latter mechanistic assumptions.[3] In most cases, a pinacolate is assumed to be an intermediate on the way to the olefinic product. However, examples are known where a pinacolate can be excluded as an intermediate.[4] Thus, it seems that several reaction pathways are accessible in these McMurry systems, and it strongly depends on the reaction conditions which of the available reaction coordinates is followed.

Besides the interest in the mechanism of the McMurry reaction and its importance for organic synthesis, the stereochemical course of this and related reactions is another point of current interest. Provided a prochiral carbonyl substrate is used, the olefinic product may be obtained as *E*-/*Z*-isomers, whereas *rac*- and *meso*-

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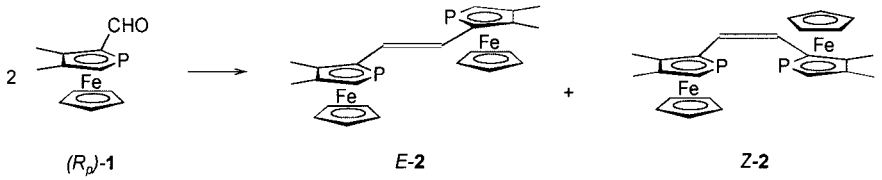
Scheme 1



(R_p)-**1** *E*-**2** *Z*-**2**

diastereomers are conceivable products in the case of the pinacol coupling. The diastereoselective pinacol coupling of those prochiral substrates has been studied in some detail,[5] and enantioselective modifications of the protocol using chiral enantiopure additives (i.e., a reagent-controlled approach) are currently emerging,[6] partly making use of low-valent metal compounds other than titanium. On the other hand, pinacol coupling reactions of chiral carbonyl compounds offer the possibility of a substrate control of the stereoselectivity, but this strategy has found much less attention.[7] The pinacol coupling of planar chiral organometallic aldehydes, in particular of (benzaldehyde)tricarbonyl chromium derivatives and ferrocencarboxaldehydes, has been investigated recently,[8] mostly making use of SmI_2 as reducing agent.

In the course of our investigations of chiral phosphaferrocene derivatives[9] we became interested in compounds featuring two phosphaferrocene units within one molecule which might serve as bidentate P,P ligands. In this paper we describe the results of reductive coupling reactions of the phosphaferrocene aldehyde **1** under McMurry conditions.

Results

Olefinic Products. Treatment of enantiopure aldehyde (R_p)-**1** with $[TiCl_3{\cdot}(DME)_{1.5}]$ and Zn(Cu) in the presence of pyridine in DME at reflux for 30 min gave a mixture of the olefins *E*- and *Z*-**2** in a ratio of ca. 8:1, which were isolated in 65% yield after workup (Scheme 1). The isomer ratio was only slightly dependent on the reaction conditions, and the isomers could be separated by column chromatography on alumina and were completely characterized by standard techniques. The initial assignment of *E*- and *Z*-configurations to the two isomers was based on NMR spectroscopy. In both cases, due to the C_2 symmetry, the same number of NMR signals are observed. Furthermore, the $^3J_{HH}$ coupling between the olefinic protons is not available from the spectra, due to their chemical equivalence. However, a closer look at the ^{13}C satellites in the ^{31}P-decoupled ^1H NMR spectra allowed the two isomers to be distinguished: in the ^{13}C isotopomer with one olefinic carbon being ^{13}C, the two olefinic protons are no longer chemically equivalent, and hence the characteristic $^3J_{HH}$ coupling can be extracted from the signal for the proton attached to the ^{13}C nucleus. This signal thus appears as a doublet ($^1J_{CH}$) of doublets ($^3J_{HH}$) with the latter coupling constant having characteristic values of 15.3 Hz for the *E*- and 11.6 Hz for the *Z*-isomer, respectively (Figures 1 and 2). This assignment could be confirmed by X-ray diffraction studies carried out on both compounds, and ORTEP representations are shown in Figures 3 and 4 together with selected bond lengths and angles.

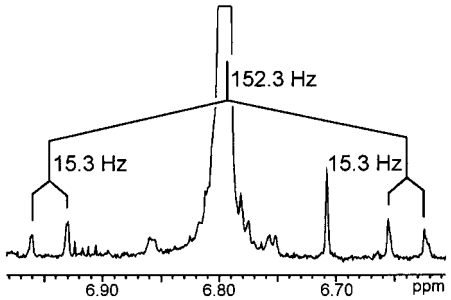


Figure 1. Olefinic region of the $^1H\{^{31}P\}$ NMR spectrum of olefin *E*-**2**.

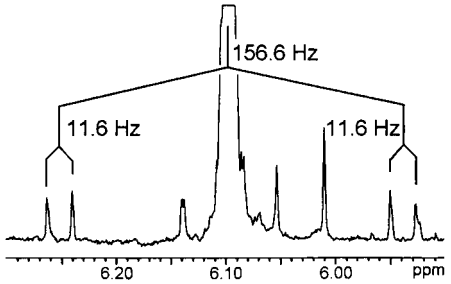


Figure 2. Olefinic region of the $^1H\{^{31}P\}$ NMR spectrum of olefin *Z*-**2**.

When the coupling reaction was carried out starting from racemic **1**, a statistical mixture of coupling products was observed.

Pinacol Products. From a stereochemical point of view the McMurry pinacol coupling of aldehyde **1** is a much more interesting reaction than the formation of olefinic products, since two new stereogenic centers are

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(5) See for example: (a) Li, T.; Cui, W.; Liu, J.; Zhao, J.; Wang, Z. *J. Chem. Soc., Chem. Commun.* **2000**, 139−140. (b) Gansäuer, A.; Moschioni, M.; Bauer, D. *Eur. J. Org. Chem.* **1998**, 1923−1927. (c) Clerici, A.; Clerici, L.; Porta, O. *Tetrahedron Lett.* **1996**, *37*, 3035−3038. (d) Barden, M. C.; Schwartz, J. *J. Am. Chem. Soc.* **1996**, *118*, 5484−5485

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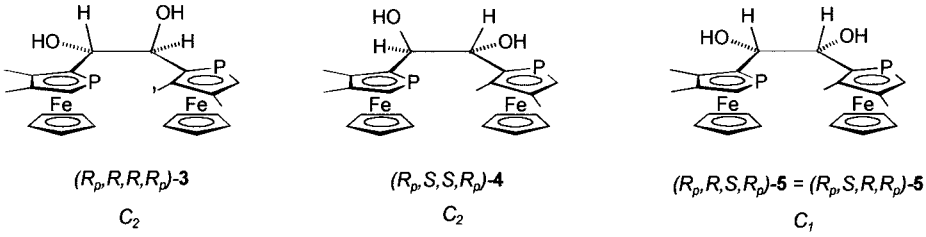
Scheme 2



(R_p,R,R,R_p)-**3** C_2 (R_p,S,S,R_p)-**4** C_2 (R_p,R,S,R_p)-**5** = (R_p,S,R,R_p)-**5** C_1

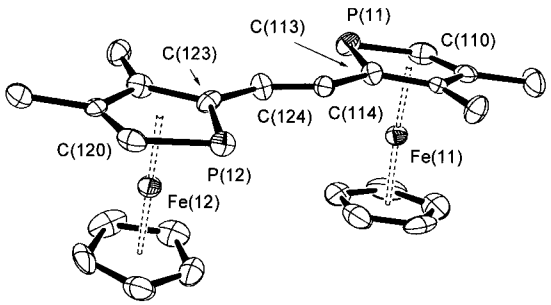


Figure 3. Molecular structure of olefin *E*-**2**. Only one of two molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): P(11)−C(110) 1.750(12), P(11)−C(113) 1.788(10), P(12)−C(120) 1.741(10), P(12)−C(123) 1.755(10), C(114)−C(124) 1.296(11); C(110)−P(11)−C(113) 87.8(5), C(120)−P(12)−C(123) 88.0(5), C(124)−C(114)−C(113) 127.3(9), C(114)−C(124)−C(123) 127.5(9).

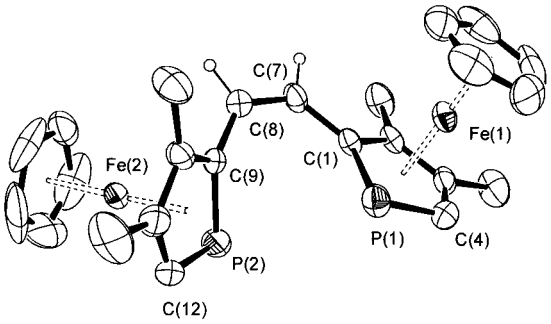


Figure 4. Molecular structure of olefin *Z*-**2**. Selected bond lengths (Å) and angles (deg): P(1)−C(4) 1.758(5), P(1)−C(1) 1.780(4), P(2)−C(9) 1.767(4), P(2)−C(12) 1.767(5), C(7)−C(8) 1.338(5); C(4)−P(1)−C(1) 88.5(2), C(9)−P(2)−C(12) 88.2(2), C(8)−C(7)−C(1) 129.5(4), C(7)−C(8)−C(9) 128.3(4).

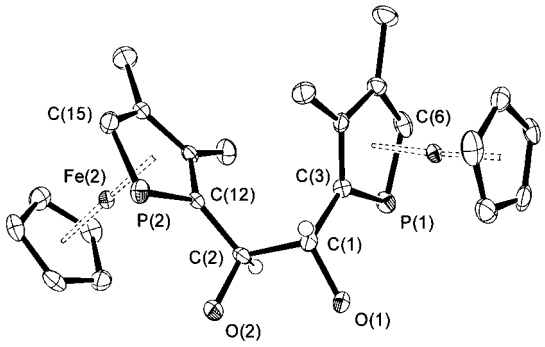


Figure 5. Molecular structure of diol (R_p,R,R,R_p)-**3**. Selected bond lengths (Å) and angles (deg): P(1)−C(6) 1.760(6), P(1)−C(3) 1.798(5), P(2)−C(15) 1.775(6), P(2)−C(12) 1.789(5), O(1)−C(1) 1.429(7), O(2)−C(2) 1.445(6), C(1)−C(3) 1.510(8), C(1)−C(2) 1.544(7), C(2)−C(12) 1.516(7); C(6)−P(1)−C(3) 88.8(2), C(15)−P(2)−C(12) 88.0(3), O(1)−C(1)−C(3) 113.0(4), O(1)−C(1)−C(2) 102.9(4), C(3)−C(1)−C(2) 113.0(4), O(2)−C(2)−C(12) 107.5(4), O(2)−C(2)−C(1) 108.6(4), C(12)−C(2)−C(1) 113.5(4).

created at the former carbonyl carbon atoms. For enantiopure (R_p)-**1** three diastereomeric diols may be formed in the reaction, two C_2-symmetric *threo*-isomers (R_p,R,R,R_p)-**3**[10] and (R_p,S,S,R_p)-**4**, respectively, and a C_1-symmetric *erythro*-isomer (R_p,R,S,R_p)-**5** (Scheme 2).

When (R_p)-**1** was treated with [$TiCl_3$•$(DME)_{1.5}$] and Zn(Cu) in the presence of pyridine in DME at 0 °C for 1 h, the formation of the diol as a single isomer was observed and it was isolated in 67% yield after chromatography. The NMR data suggested the presence of a C_2-symmetric molecule, and the X-ray diffraction study established this assumption and revealed the compound to be (R_p,R,R,R_p)-**3**. Figure 5 shows an ORTEP plot of the diol **3** together with relevant geometric parameters. Obviously, the planar chirality of the phosphaferrocene moiety controls the configuration of the new stereogenic centers in the coupled diol. We have observed complete diastereoselectivity in nucleophilic additions of Grignard reagents to aldehyde **1** earlier.[11] In the case of enantiopure planar chiral ferrocene aldehydes, it was shown that the SmI_2-mediated coupling led to a single diastereomeric diol when the reaction was carried out at −78 °C. At room temperature the other two diastereomers were formed as well to a certain extent (<10%). It is interesting to note that in the case of a diphenylphosphanyl-substituted ferrocene the selectivity was fairly low even at low temperature.[8a,b]

With the selectivity of the aforementioned coupling of the enantiopure aldehyde in mind, we turned our attention to the diol coupling of racemic aldehyde **1** under similar reaction conditions. A maximum of 10 stereoisomers may arise from this coupling reaction, four pairs of enantiomers and two *meso* compounds. In extension to the result described above for the enantiopure starting material, we expected the formation of the homo-coupled diol (R_p,R,R,R_p)-**3** again—of course accompanied by its enantiomer (S_p,S,S,S_p)-**3** in this case—and at least one diastereomeric hetero-coupled diol, in which two phosphaferrocene moieties with different configurations are linked. On the basis of the above observation that the metallocene configuration (R_p) efficiently controls the configuration of the new adjacent stereogenic center (*R*), the *meso* compound with (R_p,R,S,S_p) configuration seemed to be a reasonable

(10) Throughout this paper, stereochemical descriptors are given in the order of chemical connectivity in the molecules, i.e., planar chirality−C(OH)−C(OH)−planar chirality.

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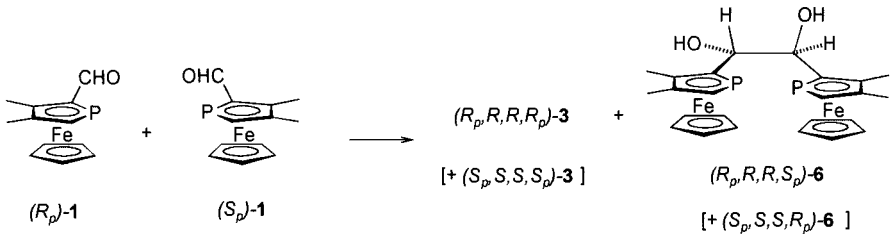
Scheme 3



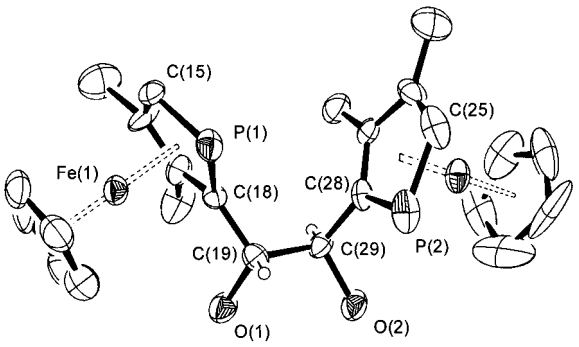


Figure 6. Molecular structure of diol (R_p,R,R,S_p)*-**6**. Only one of two molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): P(1)−C(15) 1.784(8), P(1)−C(18) 1.800(7), P(2)−C(25) 1.746(9), P(2)−C(28) 1.770(7), O(1)−C(19) 1.458(8), O(2)−C(29) 1.437(8), C(18)−C(19) 1.497(10), C(19)−C(29) 1.568(9), C(28)−C(29) 1.531(9); C(15)−P(1)−C(18) 89.0(4), C(25)−P(2)−C(28) 88.5(4), O(1)−C(19)−C(18) 110.2(6), O(1)−C(19)−C(29) 106.3(6), C(18)−C(19)−C(29) 111.1(6), O(2)−C(29)−C(28) 109.4(6), O(2)−C(29)−C(19) 106.7(6), C(28)−C(29)−C(19) 109.7(6).

assumption for this hetero dimer. When the experiment was actually carried out, the formation of two diastereomers was observed which could be separated by column chromatography (Scheme 3). One product was identified as the anticipated homo-coupled racemic diol (R_p,R,R,R_p)*-**3**,[12] giving the same spectral data as the enantiomerically pure compound **3** (vide supra). However, for the other diastereomer the appearance of a complete set of NMR signals precluded a C_s symmetric *meso* form. Instead, this product was identified as the hetero diol **6** with (R_p,R,R,S_p)* configuration as determined by X-ray diffraction (Figure 6). The diols **3** and **6** were formed in a ratio of 1:1.

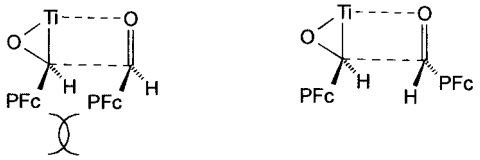
From this result it became evident that the planar chirality of the phosphaferrocene does not solely control the configuration of the adjacent stereogenic center because in isomer **6** a *like* (R_p,R) as well as an *unlike* (S_p,R) combination of configurations is present.

According to calculations carried out by Frenking and co-workers,[3] two reasonable pathways exist for the formation of pinacolate species by the titanium-mediated coupling of two aldehyde molecules: one involves the dimerization of two titanaoxirane intermediates, while the energetically more favorable pathway is characterized by an insertion of an (almost free) aldehyde molecule into the Ti−C bond of a titanaoxirane.

On the basis of these calculational results the insertion pathway offers a particularly plausible explanation

(12) The symbol * as a postscript of a chirality descriptor indicates the presence of a racemic compound, and only the descriptors for one enantiomer are given for the sake of brevity.

Scheme 4



for the selectivities observed by us. The basic assumption is that the formation of a titanaoxirane by coordination of an aldehyde molecule to the Ti reagent proceeds diastereospecifically, i.e., with the formation of a (R_p,R)* sequence. Thus, the configuration of the C atom in the titanaoxirane is determined by the configuration of the adjacent phosphaferrocene moiety. The configuration of the second stereogenic center, however, is controlled in the following insertion step. Determined by the minimization of steric interference between the two sterically demanding heterometallocene moieties (Scheme 4), a *threo* arrangement for the two adjacent stereogenic centers is established, irrespective of the planar chirality of the inserting formylphosphaferrocene. Thus, in the case of enantiomerically pure starting material (R_p)-**1** a single product isomer with (R_p,R,R,R_p) configuration results. In the case of racemic aldehyde **1** as starting material, the diastereospecific formation of titanaoxiranes with (R_p,R)* configuration is again assumed. In this case, however, a molecule of either (S_p)-**1** or (R_p)-**1** may insert into the Ti−C bond of the intermediate titanaoxirane with equal probability. The *threo* selectivity of the insertion step therefore gives rise to the formation of equal amounts of (R_p,R,R,R_p)*- and (R_p,R,R,S_p)*-configurated products, in agreement with our experimental observation. In other words, the planar chirality controls the configuration of the stereogenic carbon center in the oxirane, and this latter central chirality determines the stereochemical course of the following insertion step.

It is much less convincing to rationalize the experimental results on the basis of the dimerization pathway. The formation of the (R_p,R,R,R_p)* product is straightforwardly explained by the dimerization of two (R_p,R)* oxiranes. However, the (R_p,R,S,S_p)* diol, expected to arise from the coupling of a (R_p,R) with a (S_p,S) oxirane, is not observed. To explain the observed (R_p,R,R,S_p)* product, a (S_p,S) oxirane would have to epimerize to the (S_p,R) oxirane prior to the coupling with a (R_p,R) molecule. As both the (R_p,R,R,R_p)* and (R_p,R,R,S_p)* products are formed in almost equal amounts, this would imply a very low configurational stability for the stereogenic C atom in the oxirane. However, the selective formation of the (R_p,R,R,R_p) product from the enantiopure starting material **1** seems to preclude a low configurational stability of the C atom, since a $(R_p,S,S,$-

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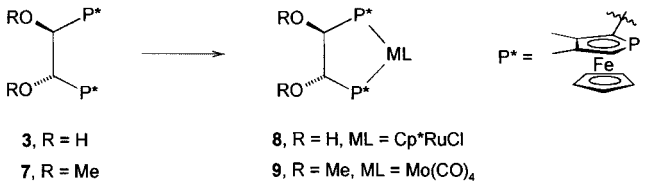
Scheme 5



R_p)* product should then also be observed. Thus, the insertion mechanism appears to provide the more plausible explanation for the observed stereochemical result.

Interestingly, when racemic 2-methylferrocenecarbaldehyde was coupled with SmI_2, a complex diol mixture of unspecified composition was obtained.[8a,e]

Complexation Studies. To examine the coordination properties of the new type of bis(phosphaferrocene), the diol **3** was converted to the bis(methoxy) compound **7** by treatment with NaH and MeI in order to make it compatible with metal fragments sensitive to hydroxy groups. The capability of diol **3** and its bis(methyl)ether derivative **7** to function as bidentate P,P chelate ligands was investigated (Scheme 5). Thus, treatment of **3** with 0.25 equiv of $[Cp^*RuCl]_4$ in DME gave a clean and quantitative conversion to yield the complex [Cp*RuCl·**7**] (**8**), which was isolated in 55% yield after crystallization from CH_2Cl_2. In the ^{31}P NMR spectrum a downfield shift of ca. 100 ppm is observed upon coordination of the free ligand, and two resonances are found for complex **8** with a $^2J_{PP}$ coupling of 85 Hz for the two chemically inequivalent P nuclei due to coordination to the Cp*RuCl fragment.

In another experiment, the bis(methoxy) compound **7** was treated with (nbd)$Mo(CO)_4$ (nbd = norbornadiene), and the P,P chelate complex [$Mo(CO)_4$·**7**] (**9**) was obtained in 93% yield as red crystals. In solution, complex **9** displays effective C_2 symmetry, as only one signal is observed in the ^{31}P NMR spectrum at −19.3 ppm. An X-ray structure determination confirmed the chelating coordination of ligand **7**, and an ORTEP representation of complex **9** is shown in Figure 7 together with selected geometrical data. The most prominent deviation from the octahedral geometry concerns the P−Mo−P angle of 79.8°. The Mo−P distances of 249.8(1) and 245.0(1) Å are in the range observed for other phosphaferrocene-$Mo(CO)_4$ complexes.[13] The Mo−C distances of the CO ligands *trans* to the P atoms (197.0 and 197.9 Å) are shorter than those of the carbonyl ligands occupying *trans* positions to each other (203.4 and 204.2 Å). This feature again demonstrates that although the phosphaferrocene is a good π-acceptor, compared to CO it behaves as a better donor as well, leading to an enhanced back-donation to the CO ligands *trans* to P.

Interestingly, when diol **3** was treated with *p*-toluenesulfonic acid in refluxing toluene, a pinacol rearrangement occurred, leading to the corresponding 1,2-diphosphaferrocenylethan-1-one **10** selectively (Scheme 6), which was isolated in 66% yield as an orange solid after chromatographic workup. Obviously, in this rearrangement a hydrogen atom exhibits a superior migratory aptitude as compared to the phosphaferrocenyl group.

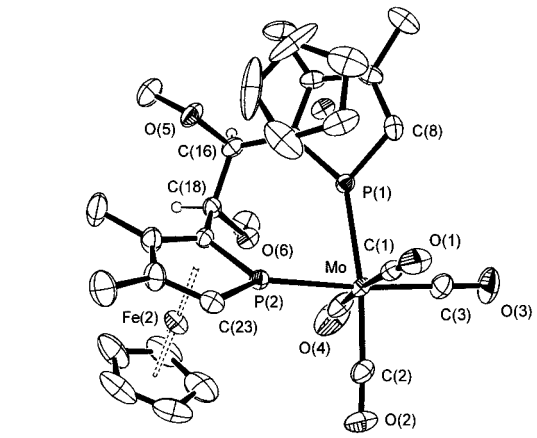
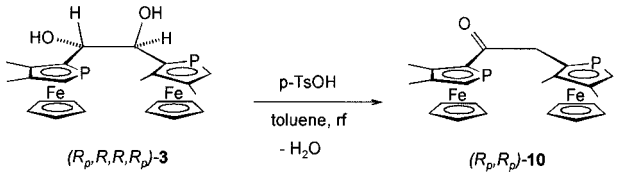


Figure 7. Molecular structure of complex **9**. Selected bond lengths (Å) and angles (deg): Mo−C(1) 2.034(6), Mo−C(2) 1.970(6), Mo−C(3) 1.979(6), Mo−C(4) 2.042(6), Mo−P(2) 2.4498(15) Mo−P(1) 2.4985(13), P(1)−C(8) 1.739(5), P(1)−C(5) 1.780(5), P(2)−C(23) 1.752(5), P(2)−C(20) 1.756(5), O(1)−C(1) 1.135(6), O(2)−C(2) 1.158(6), O(3)−C(3) 1.153(7), O(4)−C(4) 1.134(6), C(16)−C(18) 1.549(7); C(2)−Mo−C(3) 93.1(2), C(1)−Mo−C(4) 174.3(2), C(3)−Mo−P(2) 175.04(18), C(2)−Mo−P(1) 171.38(18), P(2)−Mo−P(1) 79.81(5), C(8)−P(1)−C(5) 91.1(3), C(8)−P(1)−Mo 127.7(2), C(5)−P(1)−Mo 140.87(17), C(23)−P(2)−C(20) 91.3(3), C(23)−P(2)−Mo 136.5(2), C(20)−P(2)−Mo 131.40(18), O(1)−C(1)−Mo 174.5(5), O(2)−C(2)−Mo 177.0(5), O(3)−C(3)−Mo178.3(6), O(4)−C(4)−Mo 174.2(6).

Scheme 6



Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dry nitrogen by means of conventional Schlenk techniques. Solvents were dried and purified by standard methods. Alumina was heated at 220 °C for 12 h, cooled to room temperature under high vacuum, deactivated with 5% water, and stored under nitrogen. NMR spectra were recorded on a Varian Unity 500 spectrometer (^1H, 500 MHz; $^{31}P\{^1H\}$, 202 MHz; $^{13}C\{^1H\}$, 126 MHz). ^1H spectra are referenced to the residual solvent signal 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). [$TiCl_3$·$DME_{1.5}$],[14] Zn(Cu),[15] $[Cp^*RuCl]_4$,[16] and (R_p)-**1**[17] were synthesized according to literature procedures.

Synthesis of 2. (R_p)-Formylphosphaferrocene **1** (774.2 mg, 2.98 mmol) was added to a suspension of [$TiCl_3$·$DME_{1.5}$] (3.66 g, 11. 6 mmol), Zn(Cu) (3.36 g, 47.3 mmol), and pyridine (1 mL, 12.4 mmol) in dry DME (10 mL). The mixture was heated

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to reflux for 30 min. Hexane (30 mL) was added, and the mixture was filtered over alumina. The solvents were evaporated in a vacuum, giving an orange powder. NMR of the crude product shows an *E* to *Z* ratio of 8:1. Separation of isomers was carried out by careful chromatography on alumina. *E*-**2** was eluted first with hexane, *Z*-**2** with hexane/Et_2O, 100:1. Removal of the solvent gave *E*-2 (0.878 mmol, 59.0%) and *Z*-**2** (0.086 mmol, 5.8%, decomposes slowly at room temperature) both as orange powders. Recrystallization of *E*- and *Z*-**2** from hexane/CH_2Cl_2 and Et_2O/MeOH, respectively, gave dark red crystals suitable for X-ray analysis. ^{1}H NMR (500 MHz, CD_2Cl_2): *E*-**2**, 2.21 (s, 12 H, Me), 3.84 (d, ^2J(H,P) = 36.9 Hz, 2 H, α-H), 4.15 (s, 10 H, Cp), 6.42 (d, ^3J(H,P) = 5.2 Hz, 2 H, =CH); *Z*-**2**, 2.21 (s, 6 H, Me), 2.24 (s, 6 H, Me), 3.84 (m, $\sum J$(H,P) = 36.0 Hz, 2 H, α-H), 4.05 (s, 10 H, Cp), 6.10 (t, J(H,P) = 4.8 Hz, 2 H, =CH). ^{13}C NMR (126 MHz, CD_2Cl_2): *E*-**2**, 14.1 (s, CH_3), 17.1 (s, CH_3), 73.1 (s, Cp), 76.8 (d, ^1J(C,P) = 58.7 Hz, phospholyl-α-CH), 92.6 (d, ^2J(C,P) = 3.8 Hz, phospholyl-β-C), 95.4 (d, ^1J(C,P) = 57.0 Hz, phospholyl-α-C(q)), 97.4 (s, phospholyl-β-C), 127.8 (t, J(C,P) = 15.3 Hz, =CH); *Z*-**2**, 14.4 (s, CH_3), 17.1 (s, CH_3), 72.8 (s, Cp), 77.5 (m, $\sum J$(C,P) = 58.6 Hz, phospholyl-α-CH), 91.7 (d, $\sum J$(C,P) = 54.3 Hz, phospholyl-α-C(q)), 94.8 (s, phospholyl-β-C), 95.9 (d, ^2J(C,P) = 3.3 Hz, phospholyl-β-C), 127.8 (t, J(C,P) = 8.3 Hz, =CH). ^{31}P NMR (202 MHz, CD_2Cl_2): *E*-**2**, −85.9 (s); *Z*-**2**, −74.5 (s). MS: *E*-**2**, 488 (M^+), 423 (M^+ − Cp); *Z*-**2**, 488 (M^+), 423 (M^+ − Cp). HRMS: *E*-**2**, $C_{24}H_{26}P_2Fe_2$ calcd 488.02085; found 488.02086; *Z*-**2**, $C_{24}H_{26}P_2Fe_2$ calcd 488.02085; found 488.02078. *E*-**2** calcd for $C_{24}H_{26}P_2Fe_2$ (488.1) C 59.06, H 5.37; found C 58.48, H 5.18.

Synthesis of (*R*$_p$,*R*,*R*,*R*$_p$)-3. (*R*$_p$)-Formylphosphaferrocene **1** (261.3 mg, 1.05 mmol) was added to a suspension of [$TiCl_3$·$DME_{1.5}$] (1.09 g, 3.8 mmol), Zn(Cu) (1.076 mg, 15.1 mmol), and pyridine (0.31 mL, 3.8 mmol) in dry DME (15 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and quenched by addition of a saturated aqueous solution of K_2CO_3 (10 mL). The mixture was filtered and the solid residue washed once with ethyl acetate. The organic layer was separated, and the aqueous phase was extracted once with ethyl acetate. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated to dryness, giving an orange powder, which was further purified by chromatography on alumina with CH_2Cl_2/MeOH (100:1). (*R*$_p$,*R*,*R*,*R*$_p$)-**3** (0.352 mmol, 67.0%) was obtained as an orange powder. Recrystallization from CH_2Cl_2/hexane gave red crystals suitable for X-ray analysis. ^{1}H NMR (500 MHz, CD_2Cl_2): 1.62 (s, 6 H, Me), 2.10 (s, 6 H, Me), 2.53 (s(br), 2 H, OH), 3.75 (d, ^2J(H,P) = 36.9 Hz, 2 H, phospholyl-α-H), 3.98 (d, ^3J(H,P) = 6.4 Hz, 2 H, C*H*OH), 4.16 (s, 10 H, Cp). ^{13}C NMR (126 MHz, CD_2Cl_2): 15.4 (d, ^3J(C,P) = 1.1 Hz, CH_3), 16.7 (s, CH_3), 72.3 (s, Cp), 76.7 (d, ^1J(C,P) = 58.2 Hz, phospholyl-α-CH), 77.6 (d, ^2J(C,P) = 13.1 Hz, CHOH), 93.6 (d, ^2J(C,P) = 5.0 Hz, phospholyl-β-C), 97.1 (d, ^2J(C,P) = 7.1 Hz, phospholyl-β-C), 101.1 (d, ^1J(C,P) = 59.2 Hz, phospholyl-α-C(q)). ^{31}P NMR (202 MHz, CD_2Cl_2): −83.1 (s). MS: 522 (M^+), 504 ($M^+ - H_2O$), 475 ($M^+ - H_2O$ − CHO), 410 ($M^+ - H_2O$ − CHO − Cp). $C_{24}H_{28}O_2P_2Fe_2$ (522.1) calcd C 55.21, H 5.41; found C 54.92, H 5.40.

Synthesis of (*R*$_p$,*R*,*R*,*S*$_p$)*-6. The same procedure as for the synthesis of (*R*$_p$,*R*,*R*,*R*$_p$)-**3** using *rac*-**1** (598.1 mg, 2.230 mmol) was used. A ^{31}P NMR spectrum of the crude product indicates a (*R*$_p$,*R*,*R*,*R*$_p$)*-**3**/(*R*$_p$,*R*,*R*,*S*$_p$)*-**3** ratio of 1:1. Upon chromatography on alumina (*R*$_p$,*R*,*R*,*S*$_p$)*-**3** was eluted first with hexane/Et_2O, 1:1, followed by (*R*$_p$,*R*,*R*,*R*$_p$)*-**3** using CH_2Cl_2/MeOH, 20:1. Evaporation to dryness gave (*R*$_P$,*R*,*R*,*S*$_P$)*-**6** (0.254 mmol, 22.1%) and (*R*$_p$,*R*,*R*,*R*$_p$)-**3** (0.333 mmol, 28.9%) both as orange powders. Recrystallization of **6** from CH_2Cl_2/hexane gave red crystals suitable for X-ray diffraction. ^{1}H NMR (500 MHz, C_6D_6): 1.62 (s, 3 H, Me), 1.77 (s, 3 H, Me), 1.91 (s, 3 H, Me), 2.36 (s, 3 H, Me), 2.39 (d, ^2J(H,H) = 2.5 Hz, 1 H, OH), 2.83 (d, ^2J(H,H) = 2.7 Hz, 1 H, OH), 3.57 (d, ^2J(H,P) = 36.0 Hz, 1 H, α-H), 3.65 (d, ^2J(H,P) = 36.6 Hz, 1 H, α-H), 3.93 (s, 5 H, Cp), 4.08 (s, 5 H, Cp), 4.16 (m, $\sum J$ = 17.4 Hz, 1 H, C*H*OH), 4.35 (m, $\sum J$ = 17.7 Hz, 1 H, C*H*OH). ^{13}C NMR (126 MHz, C_6D_6): 14.6 (s, CH_3), 14.7 (s, CH_3), 16.6 (s, CH_3), 16.7 (s, CH_3), 72.0 (s, Cp), 72.4 (s, Cp), 74.3 (d, ^2J (C,P) = 11.5 Hz, CHOH), 74.3 (d, ^1J(C,P) = 58.1 Hz, phospholyl-α-CH), 77.8 (d, ^1J(C,P) = 58.7 Hz, phospholyl-α-CH), 79.4 (dd, ^2J(C,P) = 26.3 Hz, ^3J(C,P) = 4.1 Hz, CHOH), 92.5 (d, ^2J(C,P) = 4.9 Hz, phospholyl-β-C), 93.6 (d, ^2J(C,P) = 5.4 Hz, phospholyl-β-C), 96.1 (d, ^2J(C,P) = 6.6 Hz, phospholyl-β-C), 96.3 (d, ^2J(C,P) = 7.1 Hz, phospholyl-β-C), 96.9 (d, ^1J(C,P) = 61.7 Hz, phospholyl-α-C(q)), 103.6 (d, ^1J(C,P) = 60.9 Hz, phospholyl-α-C(q)). ^{31}P NMR (202 MHz, C_6D_6): −69.7 (d, ^5J(P,P) = 10.5 Hz, phospholyl-P), −87.1 (d (br), ^5J(P,P) = 6.5 Hz, phospholyl-P). MS: 522 (M^+), 504 ($M^+ - H_2O$), 475 ($M^+ - H_2O$ − CHO), 410 ($M^+ - H_2O$ − CHO − Cp). HRMS: $C_{24}H_{28}O_2P_2Fe_2$ calcd 522.02633, found 522.02715.

Synthesis of (*R*$_p$,*R*,*R*,*R*$_p$)-7. (*R*$_p$,*R*,*R*,*R*$_p$)-**3** (337.5 mg, 0.646 mmol) was dissolved in DME (20 mL) and cooled to −78 °C, and CH_3I (0.121 mL, 1.94 mmol) was added. The resulting solution was then treated with NaH (41.9 mg, 1.75 mmol). The mixture was left to warm to room temperature overnight and subsequently hydrolyzed with water (0.5 mL). The solution was then dried over Na_2SO_4, filtered, and evaporated to dryness. Chromatography of the crude product on alumina gave (*R*$_p$,*R*,*R*,*R*$_p$)-**7** (0.375 mmol, 58.7%) as an orange powder. ^{1}H NMR (500 MHz, CD_2Cl_2): 1.68 (s, 6 H, phospholyl-CH_3), 2.09 (s, 6 H, phospholyl-CH_3), 3.53 (s, 6 H, OCH_3), 3.60 (d, 2 H, ^3J(H,P) = 9.2 Hz, C*H*OCH_3), 3.65 (d, 2 H, ^2J(H,P) = 36.0 Hz, phospholyl-α-H), 4.09 (s, 10 H, Cp). ^{13}C NMR (126 MHz, CD_2Cl_2): 15.8 (s, CH_3), 16.7 (s, CH_3), 60.3 (s, OCH_3), 72.1 (s, Cp), 76.8 (d, ^1J(C,P) = 58.2 Hz, phospholyl-α-CH), 87.5 (t, J(C,P) = 6.0 Hz, *C*HOCH_3), 92.8 (d, ^2J(C,P) = 4.9 Hz, phospholyl-β-C), 96.2 (d, ^2J(C,P) = 6.5 Hz, phospholyl-β-C), 100.5 (d, ^1J(C,P) = 59.2 Hz, phospholyl-α-C(q)). ^{31}P NMR (202 MHz, CD_2Cl_2): −77.4 (s, phospholyl-P). MS: 550 (M^+), 488 (M^+ − 2 OMe), 423 (M^+ −2 OMe −Cp), 367 (M^+ − 2 OMe − Cp − Fe). HRMS: $C_{26}H_{32}O_2P_2Fe_2$ calcd 550.05763; found 550.05757.

Synthesis [(*R*$_p$,*R*,*R*,*R*$_p$)-3·Cp*RuCl] (8). (*R*$_p$,*R*,*R*,*R*$_p$)-**3** (135.4 mg, 0.259 mmol) and [Cp*RuCl]$_4$ (70.3 mg, 0.065 mmol) were dissolved in DME (3 mL) at room temperature, giving a red-brown mixture, which was stirred for 2.5 h. After filtration and evaporation of the solvent a brown oil was obtained. Recrystallization from CH_2Cl_2 yielded complex **8** (0.141 mmol, 54.2%) as an orange powder. ^{1}H NMR (500 MHz, CD_2Cl_2): 1.78 (t, ^3J(H,P) = 2.4 Hz, 15 H, Cp*-CH_3), 1.81 (s, 3 H, phospholyl-CH_3), 1.89 (m, 1 H, OH), 1.99 (s, 3 H, phospholyl-CH_3), 2.00 (s, 3 H, phospholyl-CH_3), 2.21 (s, 3 H, phospholyl-CH_3), 3.36 (d, 1 H, ^2J(H,P) = 33.3 Hz, phospholyl-α-CH), 3.52 (d, 1 H, ^2J(H,P) = 33.0 Hz, phospholyl-α-CH), 3.86 (s, 5 H, Cp), 4.45 (s, 5 H, Cp), 4.56−4.74 (m, 3 H, 2 C*H*OH, OH). ^{13}C NMR (126 MHz, CD_2Cl_2): 10.9 (s, Cp*-CH_3), 14.2 (d, ^3J(C,P) = 2.7 Hz, phospholyl-CH_3), 14.6 (s, phospholyl-CH_3), 16.3 (d, ^3J(C,P) = 4.4 Hz, phospholyl-CH_3), 16.8 (d, ^3J(C,P) = 4.4 Hz, phospholyl-CH_3), 62.7 (s, phospholyl-α-CH), 63.4 (s (br), phospholyl-α-CH), 73.1 (d, ^2J(C,P) = 11.5 Hz, *C*HOH), 73.3 (s, Cp), 73.8 (s, Cp), 74.5 (d, ^2J(C,P) = 10.9 Hz, *C*HOH), 90.0 (s, phospholyl-α-C(q)), 91.0 (s, phospholyl-β-C), 91.1 (s, phospholyl-β-C), 91.6 (s, phospholyl-α-C(q)), 92.0 (s, Cp* (q)), 92.9 (d, ^2J(C,P) = 3.9 Hz, phospholyl-β-C), 93.0 (s, phospholyl-β-C). ^{31}P NMR (202 MHz, CD_2Cl_2): 16.6 (d, ^2J(P,P) = 85.3 Hz, phospholyl-P), 23.1 (d, ^2J(P,P) = 85.3 Hz, phospholyl-P). MS: 794 (M^+), 776 ($M^+ - H_2O$), 758 ($M^+ - 2\ H_2O$), 741 ($M^+ - 2\ H_2O$ − Cl), 260 ($PFcCHO^+$). $C_{34}H_{43}O_2P_2ClFe_2Ru$ (793.8) calcd C 51.44, H 5.46; found C 50.75, H 5.10.

Synthesis of [(*R*$_p$,*R*,*R*,*R*$_p$)-7·Mo(CO)$_4$] (9). (Norbornadien)$Mo(CO)_4$ (22.6 mg, 0.075 mmol) was dissolved in DME (1.5 mL), and a solution of (*R*$_p$,*R*,*R*,*R*$_p$)-**7** (41.0 mg, 0.074 mmol) in DME (2 mL) was slowly added at room temperature. The resulting solution was then stirred for 1 h. The solvent was evaporated in a vacuum, and the residue redissolved in Et_2O and filtered over alumina. The resulting solution was evaporated to dryness, giving complex **9** (0.069 mmol, 93.0%) as a light orange powder. ^{1}H NMR (500 MHz, CD_2Cl_2): 2.20 (s, 6 H,

Table 1. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for *E*-2, *Z*-2, and (R_p,*R*,*R*,R_p)-3

	E-**2**	*Z*-**2**	(R_p,*R*,*R*,R_p)-**3**
formula	$C_{24}H_{26}Fe_2P_2$	$C_{24}H_{26}Fe_2P_2$	$C_{24}H_{28}Fe_2O_2P_2$
fw	488.12	488.12	522.16
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a, Å	12.1244(10)	7.1207(10)	7.6150(10)
b, Å	13.688(3)	13.312(2)	10.6901(12)
c, Å	26.330(2)	23.707(3)	13.924(2)
β, deg	90	90	96.01(2)
V, Å^3	4369.6(11)	2247.1(6)	1127.3(2)
d_{calcd}, g·cm^{-3}·	1.48	1.443	1.538
Z	8	4	2
F(000)	2016	1008	540
μ, cm^{-1}	14.76	14.40	13.68
cryst dimens, mm	0.6 × 0.6 × 0.4	0.38 × 0.13 × 0.1	0.2 × 0.2 × 0.15
T, K	223	293	293
radiation	Mo Kα	Mo Kα	Mo Kα
scan mode	$\omega-2\theta$	ω	ϕ
scan range, deg	$3 < \theta < 26$	$2 < \theta < 28$	$2 < \theta < 28$
no. of reflns measd	14 433	18 250	13 584
no. of indep reflns	8537	5603	5404
no. of obsd data	4324 ($I > 2\sigma(I)$)	2600 ($I > 2\sigma(I)$)	4181 ($I > 2\sigma(I)$)
no. of variables	513	253	320
R, R_w [$w^{-1} = \sigma^2(F_o)$], GOF	0.0782; 0.1395; 0.929	0.0431; 0.0629; 0.716	0.0433; 0.0776; 1.042
max resid density, e Å^{-3}	1.3	0.41	0.46

	(R_p,*R*,*R*,S_p)*-**6**	**9**
formula	$C_{24}H_{28}Fe_2P_2O_2$	$C_{30}H_{32}Fe_2P_2O_6Mo$
fw	522.16	758.14
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	12.101(2)	10.5929(15)
b, Å	14.525(1)	16.5064(8)
c, Å	15.104(2)	17.7960(5)
α, deg	118.330(7)	90
β, deg	90.80(1)	90
γ, deg	90.708(8)	90
V, Å^3	2336.1(5)	3111.6(5)
d_{calcd}, g·cm^{-3}	1.48	1.62
Z	4	4
F(000)	1080	1536
μ, cm^{-1}	114.8	14.60
cryst dimens, mm	0.2 × 0.1 × 0.1	0.32 × 0.2 × 0.12
T, K	291	213
radiation	Cu Kα	Mo Kα
scan mode	$\omega-2\theta$	$\omega-2\theta$
scan range, deg	$3 < \theta < 72$	$2 < \theta < 26$
no. of reflns measd	29 169	7834
no. of indep reflns	9162	6077
no. of obsd data	3148 ($I > 2\sigma(I)$)	4764 ($I > 2\sigma(I)$)
no. of variables	549	253
R, R_w [$w^{-1} = \sigma^2(F_o)$], GOF	0.0813; 0.1623; 0.944	0.0407; 0.0789; 0.950
max resid density, e Å^{-3}	0.56	0.35

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phospholyl-CH_3), 2.21 (s, 6 H, phospholyl-CH_3), 3.43 (s, 6 H, OCH_3), 3.71 (m, 2 H, $\sum J$(H,P) = 36.0 Hz, phospholyl-α-CH), 4.04 (s (br), 2 H, C*H*OCH_3), 4.13 (s, 10 H, Cp). ^{13}C NMR (126 MHz, CD_2Cl_2): 14.8 (s, CH_3), 16.7 (s, CH_3), 58.5 (s, OCH_3), 72.1 (s, phospholyl-α-CH), 74.1 (s, Cp), 80.1 (s (br), *C*HOCH_3), 90.3 (s (br), phospholyl-α-C(q)), 93.2 (s, phospholyl-β-C), 93.8 (s, phospholyl-β-C), 207.8 (m, ΣJ(C,P) = 11.5 Hz, CO), 215.4 (s (br), CO). ^{31}P NMR (202 MHz, CD_2Cl_2): −19.3 (s, phospholyl-P). IR [CH_2Cl_2, ν(CO), cm^{-1}]: 2026, 1930, 1916, 1885. MS: 760 (M^+), 732 (M^+ − CO), 702 (M^+ − 2 CO), 648 (M^+ − 4 CO), 550 (**7**$^+$). HRMS: $C_{30}H_{32}O_6P_2Fe_2Mo$ calcd 759.94280; found 759.94279.

Synthesis of (R_p,R_p)-10. (R_p,*R*,*R*,R_p)-**3** (182.4 mg, 0.349 mmol) and *p*-toluenesulfonic acid (17.5 mg) were heated to reflux in toluene (10 mL) for 4 h. The solution was then evaporated to dryness. Chromatography of the raw product gave (R_p,R_p)-**10** (0.229 mmol, 65.6%) as an orange powder. ^{1}H NMR (500 MHz, CD_2Cl_2): 2.98 (s, 3 H, phospholyl-CH_3), 2.21 (s, 3 H, phospholyl-CH_3), 2.22 (s, 3 H, phospholyl-CH_3), 2.42 (s, 3 H, phospholyl-CH_3), 3.48 (m, $\sum J$ (H,P) 54.8 Hz, 2 H, CH_2), 3.74 (d, ^2J(H,P) = 36.0 Hz, 1 H, α-H), 4.13 (d, ^2J(H,P) = 37.1 Hz, 1 H, α-H), 4.14 (s, 5 H, Cp), 4.26 (s, 5 H, Cp). ^{13}C NMR (126 MHz, CD_2Cl_2): 14.2 (s, CH_3), 15.5 (s, CH_3), 16.9 (s, CH_3), 17.2 (s, CH_3), 44.7 (dd, ^2J(C,P) = 21.1, ^3J(C,P) = 11.5, CH_2),72.5 (s, Cp), 73.8 (s, Cp), 76.4 (d, ^1J(C,P) = 58.1 Hz, phospholyl-α-CH), 81.2 (d, ^1J(C,P) = 58.4 Hz, phospholyl-α-CH), 87.7 (d, ^1J(C,P) = 64.5 Hz, phospholyl-α-C(q)), 92.9 (d, ^1J(C,P) = 56.8 Hz, phospholyl-α-C(q)), 94.8 (d, ^2J(C,P) = 4.9 Hz, phospholyl-β-C), 95.1 (d, ^2J(C,P) = 4.6 Hz, phospholyl-β-C), 96.3 (d, ^2J(C,P) = 6.6 Hz, phospholyl-β-C), 100.8 (d, ^2J(C,P) = 7.4 Hz, phospholyl-β-C), 204.9 (d, ^2J(C,P) = 20.9 Hz, C═O). ^{31}P NMR (202 MHz, CD_2Cl_2): −75.3 (d, ^5J(P,P) = 8.6 Hz), 57.9 (d, ^5J(P,P) = 8.6 Hz).MS: 504 (M^+), 488 (M^+ −O). HRMS: $C_{24}H_{26}OP_2Fe_2$ calcd: 504.01576; found: 504.01590.

X-ray Structure Determinations. Geometry and intensity data were collected on an ENRAF-Nonius CAD4 diffractometer (for (*E*)-**2**, **6**, **9**), a Bruker SMART APEX CCD detector on a D8 goniometer (for (*Z*)-**2**), and a Stoe IPDS image plate

diffractometer (for **3**). A summary of crystallographic data, data collection parameters, and refinement parameters are collected in Table 1. Detailed X-ray structural information for all compounds is available free of charge via the Internet at http://www.acs.org.

Furthermore, crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-182322 (*E*-**2**), 182323 (*Z*-**2**), 182324 (**3**), 182325 (**6**), and 182326 (**9**). 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).

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Supporting Information Available: X-ray structural information for compounds *E*-**2**, *Z*-**2**, **3**, **6**, and **9**. This material is available free of charge via the Internet at http://www.acs.org.

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