Phosphanyl-Substituted Phosphaferrocenes as *P,P*-Chelate Ligands

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Dicyclohexyl- and diphenylphosphanyl-substituted phosphaferrocenes **2** and **3** were synthesized by substitution of the amino group in 2-dimethylaminomethyl-3,4,-dimethylphosphaferrocene **1**. Homologization of 2-formyl-3,4-dimethylphosphaferrocene **4** by one CH_2 unit via Wittig olefination provided access to the phosphanylethyl derivative **9**. Ligands **2**, **3** and **9** formed *P,P*-chelate complexes with tetracarbonyl metal fragments in good yield. X-ray crystal structure determinations were carried out for the five-ring chelate complex **2** · $Mo(CO)_4$ (= **10**), and the six-ring chelate complex **9** · $Mo(CO)_4$ (= **13**).

There is continuing interest in the development of homogeneous catalysis by transition metal complexes.[1] The progress in asymmetric catalytic transformations brought about by chiral metal-ligand assemblies is particularly noteworthy.[2] Within that context, the development and improvement of ligand systems plays an essential role. Thus, the tuning of the steric and electronic properties of the ligand allows one to control the reactivity of the catalyst and the selectivity of a catalytic reaction proceeding in the coordination sphere of a metal–ligand fragment. We have recently presented a new type of planar chiral chelate ligand based on phosphaferrocene bearing aminoalkyl- and phosphinite donor moieties in the α position of the phospholyl ring.[3] Since *P,P*-chelate ligands are among the most important ligands in coordination chemistry and catalysis and in order to establish a greater variety of donor substituents at our new ligands we sought an access to phosphinoalkyl-substituted phosphaferrocenes. We report here the syntheses of such new *P,P*-chelate ligands as well as their complexation behavior toward tetracarbonyl metal fragments.

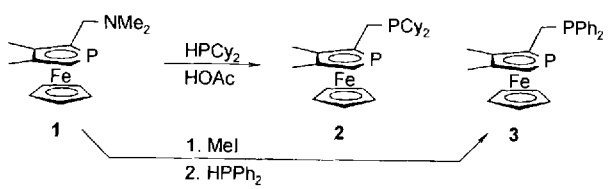
Results

Ligand Syntheses

The dicyclohexylphosphanyl-substituted ligand **2** is synthesized straightforwardly from the aminomethyl phosphaferrocene **1** by treatment with $HPCy_2$[4] in refluxing acetic acid (Scheme 1). This substitution of an aminoalkyl by a phosphanyl group is a well known reaction in the chemistry of ferrocene derivatives and has been utilized by Togni et al. for the preparation of a variety of α-phosphanylalkyl ferrocene compounds.[5]

The phosphanyl compound **2** was isolated as an orange oil in analytically pure form in 75% yield after chromatography on alumina. The ^{31}P NMR spectrum ($CDCl_3$) of **2** shows two doublets at $\delta = -75.5$ (PFc-P) and -0.7 (Cy_2P), respectively, with a coupling constant of $^3J(PP) = 29.7$ Hz.

Scheme 1. Preparation of ligands **2** and **3**

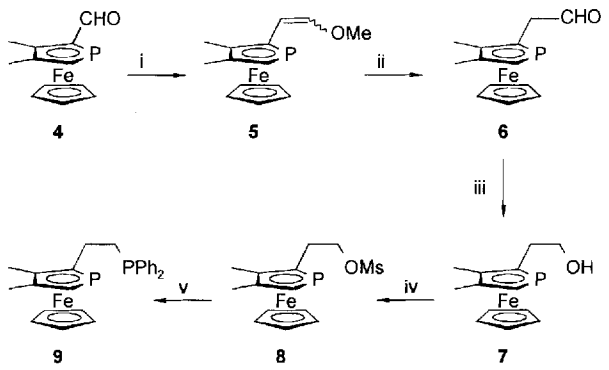


In contrast, when the amino compound **1** was treated with diphenylphosphane instead of dicyclohexylphosphane no conversion to the desired product could be observed even after prolonged reaction times. Obviously, the reduced nucleophilicity of diphenylphosphane is insufficient to force the reaction to proceed to a measureable extent under these reaction conditions. However, the diphenylphosphanyl-substituted derivative **3** was successfully prepared – although in low yield – when the amino compound **1** was transformed to the respective methiodide prior to treatment with diphenylphosphane. While ligands **2** and **3** provide the possibility to form five-membered chelate complexes with metal fragments, we considered it desirable to have also access to ligands with a backbone extended by one more C atom which allow the formation of six-membered chelate complexes. Thus, the synthesis of the CH_2-prolonged aldehyde **6** was devised in the following manner, which might afterwards serve as a starting material for the preparation of six-ring forming chelate ligands (Scheme 2).

The aldehyde **4**, which is readily available from 3,4-dimethylphosphaferrocene by Vilsmeyer formylation,[6] reacts with $Ph_3PCHOMe$ in a Wittig reaction to give the enol ether **5** as a mixture of *E/Z* isomers in 82% yield. Cleavage of the enol ether with formic acid in dichloromethane leads to the desired aldehyde **6**, which is obtained in 98% yield as an orange-red oil. The alcohol **7**, obtained by reduction of **6** with $NaBH_4$ in ether was subsequently transformed to

  0009–2940/97/1212–1771 $ 17.50+.50/0

Scheme 2. Synthesis of ligand **9**[a]



[a] Reagents: i: $Ph_3P{=}CHOMe$, Et_2O, 82%. – ii: HCO_2H, CH_2Cl_2, 95%. – iii: $NaBH_4$, THF, 71%. – iv: MsCl, NEt_3, CH_2Cl_2, 70%. – v: $LiPPh_2$, THF, 98%.

the mesylate **8** by treatment with CH_3SO_2Cl in 70% yield. Addition of $LiPPh_2$ to the mesylate **8** results in the smooth formation of the diphenylphosphanyl compound **9**, which was isolated in 98% yield as a red oil after chromatography on alumina. In the ^{31}P-NMR spectrum of **9** the ^4J(PP) coupling between the two phosphorus nuclei is too small to be detected. Two slightly broadened singlet resonances are recorded at $\delta = -81.3$ (PFc-P) and -16.0 (Ph_2P), respectively. The new ligands **2**, **3** and **9** are the first examples of phosphaferrocenes with phosphanylalkyl side chains. Mathey has prepared 1,1′-diphosphaferrocenes which have phosphanyl substituents directly attached to the α position of the phospholyl rings.[7] These compounds coordinated to metal fragments via the phosphanyl P atoms while the phospholyl phosphorus atoms remained uncomplexed. The coordination behavior of Mathey's 2,2′-diphosphanyl-substituted phosphaferrocenes thus resembled very closely that of the dppf ligand.[8]

Complexation Experiments

In order to investigate the ability of the new compounds **2**, **3** and **9** to act as chelate ligands complexation experiments were carried out using (NBD)$Mo(CO)_4$ as a source of $Mo(CO)_4$ fragments (Scheme 3). When equimolar mixtures of (NBD)$Mo(CO)_4$ and the ligands **2**, **3** or **9**, respectively, were refluxed in THF for three hours the corresponding chelate complexes **2** · $Mo(CO)_4$ (≡ **10**), **3** · $Mo(CO)_4$ (≡ **12**) and **9** · $Mo(CO)_4$ (≡ **13**) were isolated in virtually quantitative yield as crude products.

Crystals could be obtained from ether/hexane. Refluxing a mixture of $Cr(CO)_6$ and ligand **2** in xylene gave the chromium complex **2**·$Cr(CO)_4$ (≡ **11**) in 80% yield. The NMR spectra show several characteristic features upon complexation of the metal fragments (Tables 1 and 2).

The ^{31}P resonances are considerably shifted to lower field in the complexes for both the phospholyl and phosphanyl P nuclei. The ^3J(PP) coupling constants in the free ligands **2** and **3** are reduced upon complexation.[9] As usual in the coordination chemistry of phosphaferrocenes[10] the ^2J(HP) coupling constant of 36 Hz for the α proton in the phospholyl ring of the free ligands decreases to 32–34 Hz in the complexes. In the ^{13}C-NMR spectra of the complexes four resonances are observed for the carbonyl C atoms which can be assigned to the equatorial (*trans* to P) and axial (*trans* to CO) CO groups on the basis of chemical shifts and ^2J(PC) coupling constants. As is common for tetracarbonyl molybdenum complexes with two *cis*-coordinated phosphanes[11] the equatorial carbonyls appear at lower field and show a large coupling with the *trans* phosphorus [$^2J(PC_{trans}) = 21-35$ Hz] whereas the axial CO groups show significantly smaller coupling with the two *cis*-oriented P atoms of $^2J(PC_{cis}) = 6-13$ Hz.

Scheme 3. Synthesis of chelate complexes

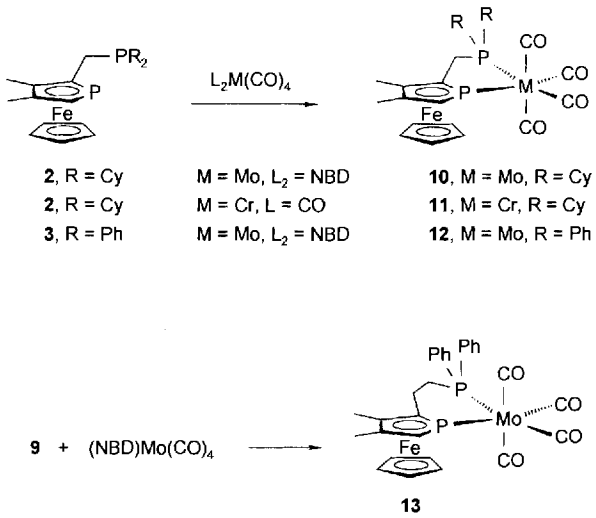


Table 1. ^{31}P-NMR data ($CDCl_3$, J in Hz) for the ligands **2**, **3**, **9** and the complexes **10**–**13**

	δ ^{31}P (PFc)	δ ^{31}P (R_2P)	J(PP)	J(HP) (α-H)
2	−75.5	−0.7	29.7	36.0
3	−76.4	−12.6	28.0	36.0
9	−81.3	−16.0	–[a]	36.0
10	−0.8	81.0	–[a]	33.0
11	37.3	102.3	14.8	32.0
12	−1.4	64.5	5.0	33.6
13	−30.9	16.7	32.2	33.9

[a] Not observed.

Table 2. ^{13}C{^{1}H}-NMR ($CDCl_3$, J in Hz) and IR data for the complexes **10**–**13**

	axial CO: δ ^{13}C, J(CP)		equatorial CO: δ ^{13}C, J(CP)		ν(CO) [cm^{-1}]
10	208.7 (12.0/7.1)	209.2 (12.0/7.1)	216.0 26.0/9.0	216.4 34.9/8.0	2017, 1906, 1889[a]
11	228.4 8.8/2.0	228.9 12.6	220.9 21.4/10.4	221.1 20.9/9.4	2008, 1896, 1884[a]
12	206.2 11.0/6.0	209.2 12.0/8.0	216.3 25.0/8.5	216.7 27.0/6.5	2025, 1908, 1887[b]
13	208.2 11.5/8.8	208.8 11.5/8.3	213.6 33.4/9.8	215.0 22.5/10.4	2022, 1905, 1888[b]

[a] Et_2O. – [b] THF.

Structures of Complexes 10 and 13

Crystals suitable for X-ray diffraction analysis were obtained from ether/hexane (**10**) and $CHCl_3$/hexane (**13**), respectively. The structures (Figures 1 and 2) confirm the chelating coordination mode for ligands **2** and **9** with distorted octahedrally coordinated molybdenum centres. Some prominent geometrical parameters for the two structures are compiled in Table 3.

Figure 1. Molecular structure of **10**

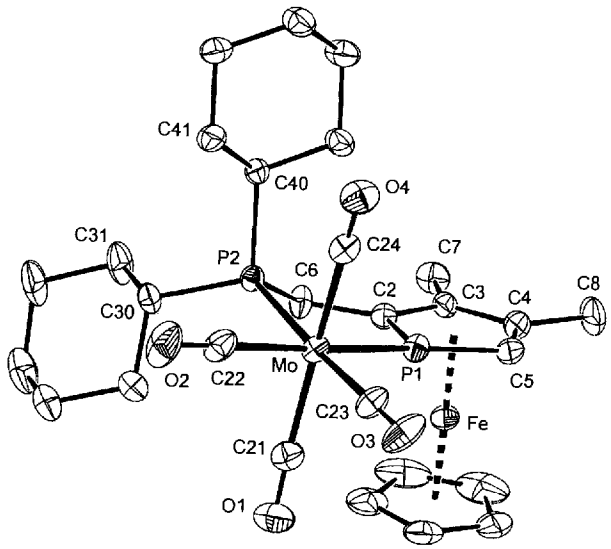
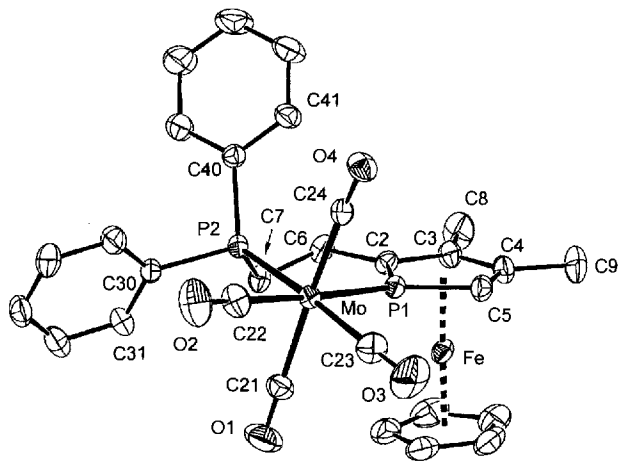


Figure 2. Molecular structure of **13**



In both compounds the two phosphorus atoms P1 and P2 behave quite different in their donor/acceptor properties resulting in different Mo–P distances.

While the Mo–P2 distances of 2.565(1) Å (**10**) and 2.529(1) Å (**13**) are typical for aryl and alkyl phosphanes[11b][11c][12] the Mo–P1 distances of 2.492(1) Å (**10**) and 2.446(1) Å (**13**) are shorter and fall in the range observed for $Mo(CO)_4$ complexes with more π-acidic phosphorus ligands.[13] The differences in the Mo–C distances are much less pronounced. The axial Mo–C bonds tend to be a bit longer than those to the equatorial carbonyl C atoms. However, the *trans* position to the two different phosphorus donors does not significantly affect the two equatorial Mo–C distances which are almost equal within experimental error. The chelate rings show an envelope conformation in **10** and a half-chair conformation for the six-membered ring in complex **13**. More serious deviations from an idealized geometry are evident for the five-ring chelate complex **10** with a P–Mo–P bite angle of 76.15(3)° as compared to 81.59(2)° in **13**. We believe that the longer Mo–P distances in **10** than in **13** (vide supra) are the consequence of the smaller bite angle of ligand **2**. Furthermore, the Mo–P1 vector does not radially point away from P1 but is tilted toward the chelate ring. Thus, since the angle C2–P1–C5 is close to 90° a value of 135° is expected for the angle φ (Mo–P1–C2) in an idealized situation whereas 114.3(1)° is found for **10**. The corresponding value of φ = 129.5(1)° for **13** demonstrates a much more relaxed geometry for the six-membered chelate ring. In both structures the substituents on P2 each adopt one axial and one equatorial position with the axial residue (C40) oriented *trans* to the CpFe moiety resulting in an almost eclipsed conformation with respect to one carbonyl ligand (C24) [torsion angle C40–P2–Mo–C24: 3.0(2)° (**10**) and 6.9(2)° (**13**)].

Table 3. Selected bond lengths [Å] and angles [°] of complexes **10** and **13**

	10	**13**
Mo–P1	2.492(1)	2.446(1)
Mo–P2	2.565(1)	2.529(1)
Mo–C21	2.027(5)	2.022(3)
Mo–C22	1.975(5)	2.005(3)
Mo–C23	1.983(5)	1.972(3)
Mo–C24	2.043(5)	2.025(3)
P1–Mo–P2	76.15(3)	81.59(2)
Mo–P1–C2	114.3(1)	129.5(1)
Mo–P1–C5	154.0(3)	138.6(1)
C2–P1–C5	90.7(2)	91.5(1)
C24–Mo–P2–C40	3.0(2)	6.9(2)
C24–Mo–P1–C5	62.6(3)	64.2(2)

Conclusion

We have demonstrated that phosphanyl-substituted phosphaferrocenes are available in good yield by synthetic routes that allow to vary both the nature of the phosphanyl group and the chain length of the phosphanylalkyl side chain. The new ligands cleanly formed *P,P*-chelate complexes with tetracarbonyl metal fragments. The structure of the five-membered chelate complex **10** turned out to be considerably more strained than the six-ring chelate in **13**. We are currently focussing our attention to complexes with metals which might be useful in catalytic applications.

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

Experimental Section

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, ^1H, int. TMS; 125.639 MHz, $^{13}C\{^1H\}$, APT, int. TMS; 202.265 MHz, $^{31}P\{^1H\}$, 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 (**4**),[6] 2-dimethylaminomethyl-3,4-dimethylphosphaferrocene (**1**)[3] and its methiodide[3] were prepared as described in the literature.

[(3,4-Dimethylphosphaferrocen-2-yl)methyl]dicyclohexylphosphane (**2**): [(3,4-Dimethylphosphaferrocen-2-yl)methyl]dimethylamine (**1**, 1.44 g, 4.98 mmol) was dissolved in 15 ml of glacial acetic acid. Dicyclohexylphosphane (1.0 ml, 6.0 mmol) was added and the solution was refluxed for 12 h. After the addition of 15 ml of CH_2Cl_2 20 ml of dil. NaOH was added and the phases were separated. The organic layer was washed twice with water and brine and dried with Na_2SO_4. Filtration and evaporation of the solvent in vacuo gave an orange oil. Chromatography on alumina gave **2** as an orange oil, which crystallizes after several weeks (1.65 g, 3.72 mmol, 75%). – ^1H NMR ($CDCl_3$): δ = 0.90–2.26 (m, 22 H, Cy-H), 2.19 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.30 (m, 2 H, CH_2PCy_2), 3.66 (d, ^2J = 36.0 Hz, 1 H, α-*H*), 4.08 (s, 5 H, Cp). – ^{13}C NMR ($CDCl_3$): δ = 13.5 (d, *J* = 4.3 Hz, CH_3), 16.1 (CH_3), 23.0 (dd, *J* = 18.9 Hz, *J* = 18.9 Hz, CH_2PCy_2), 25.4 (d, *J* = 6.1 Hz, CH_2), 26.1 (d, *J* = 3.6 Hz, CH_2), 26.3 (d, *J* < 1.0 Hz, CH_2), 26.4 (CH_2), 26.5 (CH_2), 26.7 (CH_2), 28.1 (d, *J* = 8.7 Hz, CH_2), 28.6 (d, *J* = 10.4 Hz, CH_2), 29.3 (d, *J* = 3.0 Hz, CH_2), 29.4 (d, *J* = 7.4 Hz, CH_2), 32.1 (d, *J* = 14.1 Hz, C_{ipso}-Cy), 32.7 (d, *J* = 14.7 Hz, C_{ipso}-Cy), 71.3 (Cp), 74.2 (d, *J* = 59.2 Hz, α-*C*H), 92.4 (d, *J* = 4.9 Hz, CCH_3), 94.5 (d, *J* = 6.7 Hz, CCH_3), 96.3 (dd, *J* = 17.1 Hz, *J* = 56.2 Hz, CCH_2PCy_2). – ^{31}P NMR ($CDCl_3$): δ = –75.5 (d, ^3J = 29.7 Hz, cycl. P), –0.7 (d, ^3J = 29.7 Hz, PCy_2). – MS (70 eV); *m/z* (%): 442.2 (30) [M^+], 245 (100) [$(M - PCy_2)^+$], 199 (10) [$(HPCy_2)^+$]. – $C_{24}H_{36}{}^{56}FeP_2$; calcd. C 65.10, H 8.20; found C 64.50, H 8.38.

[(3,4-Dimethylphosphaferrocen-2-yl)methyl]diphenylphosphane (**3**): [(3,4-Dimethylphosphaferrocen-2-yl)methyl]trimethylammonium iodide (1.45 g, 3.36 mmol) was dissolved in 20 ml of acetonitrile. After the addition of K_2CO_3 (0.93 g, 6.7 mmol) and $HPPh_2$ (0.75 g, 4.0 mmol) the solution was refluxed for 4 days. After cooling to room temp. the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 and the solution was acidified with dil. HCl. The phases were separated and the organic phase was washed twice with water and dried with Na_2SO_4. Filtration and evaporation of the solvent in vacuo gave an orange residue. Chromatography on alumina gave **3** as an orange oil (253 mg, 0.57 mmol, 17%). – ^1H NMR ($CDCl_3$): δ = 1.96 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.87 (m, 2 H, CH_2PPh_2), 3.56 (d, ^2J = 36.0 Hz, 1 H, α-*H*), 3.98 (s, 5 H, Cp), 7.19–7.45 (m, 10 H, Ph-H). – ^{13}C NMR ($CDCl_3$): δ = 12.9 (d, *J* = 2.3 Hz, CH_3), 16.1 (CH_3), 30.3 (dd, ^2J = 14.1 Hz, ^1J = 18.9 Hz, CH_2), 71.2 (Cp), 75.0 (d, ^1J = 58.6 Hz, α-*C*H), 92.4 (s, CCH_3), 93.2 (dd, ^2J = 22.6 Hz, ^1J = 60.3 Hz, α-CCH_2), 94.3 (d, ^3J = 6.7 Hz, CCH_3), 127.2 (*C*H), 127.3 (*C*H), 127.9 (*C*H), 131.4 (d, *J* = 17.7 Hz, *C*H), 132.6 (d, *J* = 19.6 Hz, *C*H), 136.7 (d, *J* = 15.3 Hz, C_{ipso}), 138.0 (d, *J* = 15.9 Hz, C_{ipso}). – ^{31}P NMR ($CDCl_3$): δ = –76.4 (d, ^3J = 28 Hz, cycl. *P*), –12.6 (d, ^3J = 28 Hz, PPh_2). – MS (70 eV); *m/z* (%): 430.1 (10) [M^+]. – $C_{24}H_{24}{}^{56}FeP_2$; calcd. 430.07026; found 430.07032 (MS).

(E/Z)-1-Methoxy-2-(3,4-dimethylphosphaferrocen-2-yl)ethene (**5**): $[Ph_3PCH_2OCH_3]Cl$ (3.43 g, 10.1 mmol) was suspended in 100 ml of dry diethyl ether. At 0°C PhLi (0.89 M, 11.3 ml, 10.1 mmol) was slowly added. The deep red solution was stirred for 10 min at 0°C. A solution of (3,4-dimethylphosphaferrocen-2-yl)carbaldehyde (**4**, 2.38 g, 9.1 mmol) in 30 ml of ether was slowly added. After 12 h of stirring at room temp. the pale brown solution was hydrolyzed with 10 ml of water and acidified with dil. HCl. The phases were separated and the organic phase was washed twice with water and brine and dried with Na_2SO_4. Filtration and evaporation of the solvent in vacuo gave an orange oil. After addition of 50 ml of hexane insoluble Ph_3PO was separated by filtration. Evaporation of the solvent in vacuo and chromatography on alumina gave the *E*/*Z* isomers (ratio *E*/*Z* = 40/60) of 1-methoxy-2-(3,4-dimethylphosphaferrocen-2-yl)ethene (**5**) as an orange oil (2.15 g, 7.47 mmol, 82%).

(Z)-1-Methoxy-2-(3,4-dimethylphosphaferrocen-2-yl)ethene: ^1H NMR ($CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 3.71 (s, 3 H, OCH_3), 3.82 (d, ^2J = 36.0 Hz, 1 H, α-*H*), 4.07 (s, 5 H, Cp), 5.03 (dd, ^3J = 6.41 Hz, ^3J = 13.74 Hz, 1 H, $CHCHOCH_3$), 6.05 (d, ^3J = 6.41 Hz, 1 H, $CHCHOCH_3$). – ^{13}C NMR ($CDCl_3$): δ = 13.9 (CCH_3), 16.9 (CCH_3), 59.7 (OCH_3), 72.3 (Cp), 77.5 (d, α-*C*, ^1J = 58.1 Hz), 88.7 (d, ^1J = 63.1 Hz, α-*C*), 91.6 (d, ^2J = 6.0 Hz, CCH_3), 94.7 (d, ^2J = 6.0 Hz, CCH_3), 104.5 (d, ^2J = 13.2 Hz, *C*H=CHOCH$_3$), 146.1 (CH=*C*HOCH$_3$). – ^{31}P NMR ($CDCl_3$): δ = –74.1. – MS (70 eV); *m/z* (%): 288 (20) [M^+]. – $C_{14}H_{17}{}^{56}FeOP$; calcd. 288.03664; found 288.0366 (MS).

(E)-1-Methoxy-2-(3,4-dimethylphosphaferrocen-2-yl)ethene: ^1H NMR ($CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 3.58 (s, 3 H, OCH_3), 3.72 (d, ^2J = 36.6 Hz, 1 H, α-*H*), 4.10 (s, 5 H, Cp), 5.43 (dd, ^3J = 9.16 Hz, ^3J = 12.51 Hz, *C*H = CHOCH$_3$), 6.04 (d, ^3J = 6.4 Hz, CH=*C*HOCH$_3$). – ^{13}C NMR ($CDCl_3$): δ = 13.9 (CCH_3), 16.9 (CCH_3), 56.7 (OCH_3), 72.3 (Cp), 74.9 (d, ^1J = 58.7 Hz, α-*C*), 91.3 (d, ^2J = 6.0 Hz, CCH_3), 92.9 (d, ^1J = 57.0 Hz, α-*C*), 95.7 (d, ^2J = 7.1 Hz, CCH_3), 102.9 (d, ^2J = 14.3 Hz, *C*H=CHOCH$_3$), 147.2 (d, ^2J = 7.1 Hz, CH=*C*HOCH$_3$). – ^{31}P NMR ($CDCl_3$): δ = –87.8. – MS (70 eV); *m/z* (%): 288 (20) [M^+]. – $C_{14}H_{17}{}^{56}FeOP$; calcd. 288.03664; found 288.0366 (MS).

(3,4-Dimethylphosphaferrocen-2-yl)acetaldehyde (**6**): (*E*/*Z*)-**5** (2.17 g, 7.53 mmol) was dissolved in 20 ml of CH_2Cl_2. After addition of 5 ml of concd. formic acid the solution was refluxed for 12 h. The solution was made alkaline with dil. NaOH, the organic phase was separated and washed twice with water and brine. Filtration and evaporation of the solvent in vacuo gave **6** as an analytically pure orange oil (1.96 g, 7.15 mmol, 95%). – ^1H NMR ($CDCl_3$): δ = 2.12 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3),3.12–3.27 (m, 2 H, CH_2), 3.82 (d, ^2J = 36.6 Hz, 1 H, α-*H*), 4.15 (s, 5 H, Cp), 9.58 (dd, ^3J = 2.44 Hz, ^3J = 2.14 Hz, *C*HO). – ^{13}C NMR ($CDCl_3$): δ = 13.6 (CCH_3), 16.8 (CCH_3), 44.8 (d, ^2J = 17.5 Hz, CH_2), 72.1 (Cp), 76.6 (d, ^1J = 58.7 Hz, *C*H), 87.7 (d, ^1J = 59.3 Hz, CCH_2), 93.7 (d, ^2J < 1.0 Hz, CCH_3), 96.0 (d, ^2J < 1.0 Hz, CCH_3), 199.3 (d, ^3J = 4.4 Hz, CHO). – ^{31}P NMR ($CDCl_3$): δ = –77.4. – MS (70 eV); *m/z* (%): 274 (25) [M^+], 244.9 (20) [$(M - CH_2O)^+$]; 153 (20) [$(M - CpFe)^+$]. – $C_{13}H_{15}{}^{56}FeOP$; calcd. 274.02099; found 274.02113 (MS).

2-(3,4-Dimethylphosphaferrocen-2-yl)ethanol (**7**): To a suspension of $NaBH_4$ (70 mg, 1.82 mmol) in 20 ml of THF a solution of **6** (2.00 g, 7.30 mmol) in 15 ml of THF was added. After 12 h of stirring the solvent was evaporated in vacuo and the residue was dissolved in 40 ml of dry ether. The solution was acidified carefully with 20 ml of diluted HCl. The phases were separated and the organic phase was washed twice with H_2O and dried with Na_2SO_4. Filtration and evaporation of the solvent in vacuo gave an orange oil. Chromatography on alumina gave **7** as an orange oil (1.42 g, 4.9 mmol, 70.5%). – ^1H NMR ($CDCl_3$): δ = 2.06 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.22–2.44 (m, 2 H, CH_2CH_2OH), 3.58 (br. s, 1 H, OH), 3.62 (d, ^2J = 36.0 Hz, 1 H, α-*H*), 4.02 (s, 5 H, Cp), 3.99–4.07 (m, 2 H, CH_2CH_2OH). – ^{13}C NMR ($CDCl_3$): δ = 12.8 (CCH_3), 16.1 (CCH_3), 32.8 (d, ^2J = 17.7 Hz, CH_2CH_2), 62.9 (d,

^3J = 6.1 Hz, CH_2CH_2), 72.1 (Cp), 74.6 (d, ^1J = 58.0 Hz, *C*H), 92.5 (d, ^2J = 4.9 Hz, CCH_3), 94.0 (d, ^1J = 58.6 Hz, CCH_2), 94.9 (d, ^2J = 6.7 Hz, CCH_3). – ^{31}P NMR ($CDCl_3$): δ = −79.3. MS (70 eV); *m/z* (%): 276 (20) [M^+]; 244.9 (20) [$(M - CH_2O)^+$]; 229.9 (10) [$(M - C_2H_5OH)^+$]; 121 (10) [$(CpFe)^+$]. – $C_{13}H_{17}{}^{56}FeP$; calcd. 276.03679; found 276.03681 (MS).

[2-(3,4-Dimethylphosphaferrocen-2-yl)ethyl] Methylsulfonate (**8**): To a solution of **7** (1.42 g, 5.14 mmol) in 30 ml of CH_2Cl_2 at 0°C NEt_3 (0.5 g, 5.14 mmol) and CH_3SO_2Cl (0.58 g, 5.14 mmol) was added dropwise. After 3 h of stirring the solution was acidified with dil. HCl. The phases were separated and the organic phase was washed twice with H_2O and dried with Na_2SO_4. Filtration and evaporation of the solvent in vacuo gave an orange residue. Chromatography on alumina gave **8** as an orange oil (1.27 g, 3.58 mmol, 70%). – ^{1}H NMR ($CDCl_3$): δ = 2.09 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.40–2.65 (m, 2 H, CH_2CH_2O), 2.88 (s, 3 H, SO_2CH_3), 3.65 (d, ^2J = 36.5 Hz, 1 H, α-*H*), 4.05 (s, 5 H, Cp), 3.97–4.08 (m, 2 H, CH_2CH_2O). – ^{13}C NMR ($CDCl_3$): δ = 13.6 (CCH_3), 16.8 (CCH_3), 30.6 (d, ^2J = 18.6 Hz, CH_2CH_2O), 37.3 (OSO_2CH_3), 70.3 (d, ^3J = 6.0 Hz, CH_2CH_2O), 72.0 (Cp), 75.8 (d, ^1J = 58.1 Hz, *C*H), 92.4 (d, ^1J = 59.2 Hz, CCH_2), 93.5 (d, ^2J = 3.0 Hz, CCH_3), 95.9 (d, ^2J = 6.5 Hz, CCH_3). – ^{31}P NMR ($CDCl_3$): δ = −79.1. – MS (70 eV); *m/z* (%): 353.9 (10) [M^+]; 262.1 (15) [$(PfcCH_2OH)^+$]; 149 (30) [$(CpFeC_2H_4)^+$]. – $C_{14}H_{19}{}^{56}FeO_3PS$; calcd. 354.02238; found 354.02242 (MS).

[2-(3,4-Dimethylphosphaferrocen-2-yl)ethyl]diphenylphosphane (**9**): **8** (252 mg, 0.71 mmol) was dissolved in 10 ml of dry THF. After cooling to −78°C a solution of $LiPPh_2$ (273 mg, 1.42 mmol) in 10 ml of THF was added. The deep red solution was allowed to warm to room temp. to 0°C. After 6 h of stirring 10 ml of water was added. The phases were separated and the organic phase was washed twice with H_2O and dried with Na_2SO_4. Filtration and evaporation of the solvent in vacuo gave an orange oil. Chromatography on alumina gave **9** as an orange oil (310 mg, 0.70 mmol, 98%). – ^{1}H NMR ($CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.03–2.20 (m, 4 H, $CH_2CH_2PPh_2$), 3.57 (d, ^2J = 36.0 Hz, 1 H, α-*H*), 3.92 (s, 5 H, Cp), 7.16–7.45 (m, 10 H, Ph-H). – ^{13}C NMR ($CDCl_3$): δ = 12.6 (CH_3), 16.0 (CH_3), 26.5 (dd, ^2J = 18.9 Hz, ^1J = 18.7 Hz, CH_2), 30.3 (dd, ^1J = 41.0 Hz, ^3J = 7.7 Hz, CH_2), 70.9 (Cp), 74.3 (d, ^1J = 58.0 Hz, α-*C*H), 91.7 (d, *J* = 4.9 Hz, CCH_3), 94.7 (d, *J* = 6.3 Hz, CCH_3), 99.8 (dd, ^3J = 15.5 Hz, ^1J = 60.3 Hz, α-CCH_2), 127.2 (d, *J* = 4.0 Hz, *C*H), 127.3 (d, *J* = 6.6 Hz, *C*H), 127.7 (*C*H), 128.2 (*C*H), 128.5 (d, *J* = 4.2 Hz, *C*H), 131.8 (d, *J* = 24.2 Hz, C_{ipso}), 132.6 (d, *J* = 15.2 Hz, *C*H), 134.2 (*C*H), 135.6 (d, *J* = 5.7 Hz, *C*H), 138.0 (d, *J* = 15.9 Hz, C_{ipso}). – ^{31}P NMR ($CDCl_3$): δ = −81.3 (cycl. *P*), −16.0 (PPh_2). – MS (70 eV); *m/z* (%): 443.9 (100) [M^+]. – $C_{25}H_{26}P_2{}^{56}Fe$; calcd. 444.09034; found 444.09032 (MS).

General Procedure for the Synthesis of Tetracarbonylmolybdenum Complexes: Tetracarbonyl(norbornadiene)molybdenum (147 mg, 0.49 mmol) was suspended in 10 ml of THF. A solution of the respective ligand (0.49 mmol) in 10 ml of THF was added. The solution was refluxed for 3 h and the solvent was evaporated in vacuo. The yellow residue obtained in quantitative yield was essentially pure according to ^{1}H-NMR analysis. Recrystallization of the crude product from Et_2O/hexane afforded orange needles.

Tetracarbonyl{[(3,4-dimethylphosphaferrocen-2-yl)methyl]dicyclohexylphosphane}molybdenum (**10**): Tetracarbonyl(norbornadiene)molybdenum (147 mg, 0.49 mmol) and **2** (216 mg, 0.49 mmol) were treated in the above manner to yield orange needles of **10**, suitable for X-ray diffraction analysis (250 mg, 78%). – ^{1}H NMR ($CDCl_3$): δ = 0.9–2.26 (m, 22 H, Cy-H), 2.20 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.10–2.20 (m, 2 H, CH_2PCy_2), 3.57 (d, ^2J = 33.0 Hz, 1 H, α-*H*), 4.19 (s, 5 H, Cp). – ^{13}C NMR ($CDCl_3$): δ = 14.4 (d, *J* = 3.3 Hz, CH_3), 15.9 (d, *J* = 3.8 Hz, CH_3), 20.7 (dd, *J* = 19.5 Hz, *J* = 22.7 Hz, CH_2PCy_2), 24.9 (d, *J* = 1.0 Hz, CH_2), 25.3 (d, *J* = 1.0 Hz, CH_2), 25.7 (d, *J* = 11.5 Hz, CH_2), 25.8 (d, *J* = 9.9 Hz, CH_2), 26.3 (CH_2), 26.4 (d, *J* = 7.9 Hz, CH_2), 26.5 (d, *J* = 6.1 Hz, CH_2), 27.6 (d, *J* = 4.1 Hz, CH_2), 28.4 (CH_2), 28.5 (d, *J* = 1.7 Hz, CH_2), 36.5 (d, *J* = 13.9 Hz, C_{ipso}-Cy), 36.9 (dd, *J* = 15.3 Hz, *J* = 3.3 Hz, C_{ipso}-Cy), 66.0 (dd, *J* = 18.4 Hz, *J* = 5.6 Hz, α-*C*H), 72.7 (Cp), 89.2 (dd, *J* = 5.1 Hz, *J* = 11.0 Hz, CCH_3), 91.2 (CCH_3), 93.7 (dd, *J* = 2.8 Hz, *J* = 27.3 Hz, CCH_2PCy_2), 208.7 (dd, *J* = 7.1 Hz, *J* = 12.0 Hz, *C*O), 209.2 (dd, *J* = 7.1 Hz, *J* = 12.0 Hz, *C*O), 216.0 (dd, *J* = 26.0 Hz, *J* = 9.0 Hz, *C*O), 216.4 (dd, *J* = 34.9 Hz, *J* = 8.0 Hz, *C*O). – ^{31}P NMR ($CDCl_3$): δ = −0.8 (s, cycl. *P*), 81.0 (s, PCy_2). – MS (70 eV); *m/z* (%): 652 (10) [M^+]; 624 (20) [$(M - CO)^+$]; 596 (20) [$(M - 2\ CO)^+$]; 442 (20) [$(M - Mo(CO)_4)^+$]. – IR (Et_2O): ν(CO) = 2017 m, 1906 vs, 1889 cm^{-1} m. – $C_{28}H_{36}FeMoO_4P_2$; calcd. C 51.71, H 5.58; found C 51.78, H 5.69.

Tetracarbonyl{[(3,4-dimethylphosphaferrocen-2-yl)methyl]diphenylphosphane}molybdenum (**12**): Treatment of (norbornadiene)tetracarbonylmolybdenum (123 mg, 0.41 mmol) and **3** (176 mg, 0.41 mmol) according to the general procedure gave **12** as orange needles (99 mg, 38%). – ^{1}H NMR ($CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.52 (m, 1 H, CH_2PPh_2), 3.00 (m, 1 H, CH_2PPh_2), 3.67 (d, ^2J = 33.6 Hz, 1 H, α-*H*), 4.11 (s, 5 H, Cp), 7.12–7.83 (m, 10 H, Ph-H). – ^{13}C NMR ($CDCl_3$): δ = 15.4 (d, *J* = 2.8 Hz, CH_3), 16.8 (d, *J* = 3.3 Hz, CH_3), 30.0 (dd, ^2J = 16.6 Hz, ^1J = 25.2 Hz, CH_2), 67.3 (dd, *J* = 6.1 Hz, *J* = 16.5 Hz, α-*C*H), 73.8 (5 C, Cp), 90.2 (dd, ^2J = 3.0 Hz, ^3J = 12.6 Hz, CCH_3), 92.7 (s, CCH_3), 93.6 (d, ^2J = 28.5 Hz, α-CCH_2), 128.5 (d, *J* = 8.7 Hz, *C*H), 128.7 (d, *J* = 9.9 Hz, *C*H), 129.1 (*C*H), 129.9 (d, *J* = 11.5 Hz, *C*H), 130.6 (*C*H), 130.9 (*C*H), 131.7 (*C*H), 133.2 (d, *J* = 13.2 Hz, *C*H), 135.9 (dd, *J* = 31.8 Hz, *J* = 6 Hz, C_{ipso}), 139.8 (d, *J* = 31.8 Hz, C_{ipso}), 206.2 (dd, *J* = 11.0 Hz, *J* = 6.0 Hz, *C*O), 209.2 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, *C*O), 216.3 (dd, *J* = 8.5 Hz, *J* = 25.0 Hz, *C*O), 216.7 (dd, *J* = 6.5 Hz, *J* = 27.0 Hz, *C*O). – ^{31}P NMR ($CDCl_3$): δ = −1.4 (d, ^3J = 5.0 Hz, cycl. *P*), + 64.5 (d, ^3J = 5.0 Hz, PPh_2). – MS (70 eV); *m/z* (%): 638 (45) [M^+]; 610 (80) [$(M - CO)^+$]; 582 (60) [$(M - 2\ CO)^+$]; 526 (100) [$(M - 4\ CO)^+$]. – IR (THF): ν(CO) = 2025 m, 1908 vs, 1887 cm^{-1} m. – $C_{28}H_{24}FeMoO_4P_2$; calcd. C 52.60, H 3.80; found C 52.10, H 3.60.

Tetracarbonyl{[2-(3,4-dimethylphosphaferrocen-2-yl)ethyl]diphenylphosphane}molybdenum (**13**): (Norbornadiene)tetracarbonylmolybdenum (128 mg, 0.43 mmol) and **9** (190 mg, 0.43 mmol) were treated according to the general procedure to afford orange needles of **13**, suitable for X-ray diffraction analysis (95 mg, 34%). – ^{1}H NMR ($CDCl_3$): δ = 1.98 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), 2.25 (m, 1 H, $CH_2CH_2PPh_2$), 2.40 (m, 1 H, $CH_2CH_2PPh_2$), 2.62 (m, 2 H, $CH_2CH_2PPh_2$), 3.47 (d, ^2J = 33.9 Hz, 1 H, α-*H*), 4.20 (s, 5 H, Cp), 7.26–7.54 (m, 10 H, Ph-H). – ^{13}C NMR ($CDCl_3$): δ = 12.8 (d, *J* = 2.7 Hz, CH_3), 16.4 (d, *J* = 4.4 Hz, CH_3), 24.5 (d, ^1J = 14.3 Hz, CH_2), 30.3 (dd, ^2J = 13.2 Hz, ^2J = 3.3 Hz, CH_2), 67.9 (dd, ^3J = 7.7 Hz, ^1J = 5.5 Hz, α-*C*H), 73.0 (Cp), 87.8 (dd, ^3J = 6.5 Hz, ^1J = 3.8 Hz, α-CCH_2), 91.6 (d, ^3J = 3.8 Hz, CCH_3), 92.5 (CCH_3), 128.3 (d, *J* = 8.8 Hz, *C*H), 128.5 (d, *J* = 4.9 Hz, *C*H), 128.6 (d, *J* = 3.3 Hz, *C*H), 129.2 (*C*H), 130.0 (*C*H), 130.9 (d, *J* = 11.5 Hz, *C*H), 131.5 (d, *J* = 6.6 Hz, *J* = 6.6 Hz, *C*H), 132.5 (d, *J* = 12.7 Hz, *C*H), 135.2 (d, *J* = 29.3 Hz, C_{ipso}), 138.6 (dd, *J* = 3.8 Hz, *J* = 15.9 Hz, C_{ipso}), 208.2 (dd, *J* = 11.5 Hz, *J* = 8.8 Hz, *C*O), 208.9 (dd, *J* = 8.3 Hz, *J* = 11.5 Hz, *C*O), 213.6 (dd, *J* = 9.8 Hz, *J* = 33.4 Hz, *C*O), 215.0 (dd, *J* = 10.4 Hz, *J* = 22.5 Hz, *C*O). – ^{31}P NMR (202 MHz, $CDCl_3$): δ = −30.9 (d, *J* = 32.2 Hz, cycl.

P), 16.7 (d, J = 32.2 Hz, PPh_2). – MS (70 eV); *m/z* (%): 654 (45) [M^+]; 596 (100) [$(M - H_2 - 2\ CO)^+$]; 540 (40) [$(M - H_2 - 4\ CO)^+$]. – IR (THF): ν(CO) = 2022 m, 1905 s, 1888 cm^{-1} m. – $C_{29}H_{26}FeMoO_4P_2$; calcd. C 53.35, H 4.02; found C 53.07, H 3.97.

Tetracarbonyl{[(3,4-dimethylphosphaferrocen-2-yl)methyl]-dicyclohexylphosphane}chromium (**11**): Hexacarbonylchromium (108 mg, 0.49 mmol) was suspended in 20 ml of xylene. A solution of **2** (216 mg, 0.49 mmol) in 10 ml of xylene was added. The solution was stirred for 1 hour at 50°C. Then the temperature was raised for 10°C every 30 minutes. Subliming hexacarbonylchromium was shaken back into the flask. The solution was then refluxed overnight. The solvent was evaporated in vacuo and the residue was dissoluted in $CHCl_3$. The solution was filtrated over a short column of alumina. Evaporation of a part of the solvent and addition of 5 ml of hexane afforded **11** as yellow needles (237 mg, 80%). – ^1H NMR ($CDCl_3$): δ = 0.89–2.17 (m, 22 H, Cy-H); 2.17–2.21 (m, 2 H, CH_2PCy_2); 2.21 (s, 3 H, CH_3); 2.26 (s, 3 H, CH_3); 3.53 (d, ^2J = 32.0 Hz, 1 H, α-*H*); 4.21 (s, 5 H, Cp). – ^{13}C NMR ($CDCl_3$): δ = 15.2 (d, J = 2.7 Hz, CH_3); 16.8 (d, J = 3.8 Hz, CH_3); 21.3 (dd, J = 28.5 Hz, J = 29.7 Hz, CH_2PCy_2); 25.8 (CH_2); 26.2 (CH_2); 26.8 (d, J = 10.9 Hz, CH_2); 27.0 (d, J = 11.5 Hz, CH_2); 27.0 (CH_2); 27.5 (CH_2); 27.5 (d, J = 9.9 Hz, CH_2); 28.0 (d, J = 2.1 Hz, CH_2); 29.0 (CH_2); 29.3 (d, J < 1.0 Hz, CH_2); 38.4 (d, J = 13.2 Hz, C_{ipso}-Cy); 38.9 (dd, J = 14.8 Hz, J = 4.4 Hz, C_{ipso}-Cy); 66.8 (dd, J = 16.0 Hz, J = 8.3 Hz, α-*C*H); 73.6 (Cp); 89.2 (dd, J = 5.5 Hz, J = 11.5 Hz, CCH_3); 91.9 (CCH_3); 93.4 (dd, J = 3.8 Hz, J = 29.1 Hz, CCH_2PCy_2); 220.9 (dd, J = 10.4 Hz, J = 21.4 Hz, *C*O); 221.1 (dd, J = 9.4 Hz, J = 20.9 Hz, *C*O); 228.4 (dd, J = 8.8 Hz, J = 2.0 Hz, *C*O); 228.9 (d, J = 12.6 Hz, *C*O). – ^{31}P NMR ($CDCl_3$): δ = 37.3 (d, ^2J = 14.8 Hz, cycl. *P*); 102.3 (d, ^2J = 14.8 Hz, PCy_2). – MS (70 eV); *m/z* (%): 606 (15) [M^+]; 494 (40) [$(M - (CO)_4)^+$]; 442 (40) [$(M - Cr(CO)_4)^+$]. – IR (Et_2O): ν(CO) = 2008 m, 1896 vs, 1884 cm^{-1} sh. – $C_{28}H_{36}CrFeO_4P_2$; calcd. C 55.46, H 6.00; found C 55.45, H 6.02.

Table 4. Crystal data and structure refinement parameters

	10	**13**
formula	$C_{28}H_{36}FeMoO_4P_2$	$C_{29}H_{26}FeMoO_4P_2$
formula weight	650.3	652.3
crystal size [mm^3]	0.30 × 0.25 × 0.10	0.20 × 0.08 × 0.08
crystal system	orthorhombic	monoclinic
Space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
a [Å]	14.893(2)	10.464(2)
b [Å]	18.928(2)	17.882(7)
c [Å]	20.705(3)	15.796(2)
β [°]	90	104.02(2)
V [$Å^3$]	5837(2)	2868(2)
d_{calcd} [g cm^{-3}]	1.480	1.511
Z	8	4
$F(000)$	2672	1320
μ [cm^{-1}]	10.54	10.73
scan range [°]	2.0 < θ < 30.0	1.8 < θ < 35.0
total no. of data	10442	13461
unique observed data	5291, I > 1.0 σ(I)	6520, I > 2.0 σ(I)
no. of variables	449	438
residual R	0.064	0.039
R_w [$w^{-1} = \sigma^2(F_O)$]	0.045	0.040
GOF	1.180	1.200
max res. density [10^{-6} e pm^{-3}]	0.724, 200.9 pm from O_2	0.443, 80.6 pm from Fe

X-ray Structural Analysis of 10 and **13**: ENRAF-Nonius CAD4, ω-2θ scan, Mo-K_α radiation (0.71073 Å), graphite monochromator, data collection at 298 K. Structure solution with Patterson methods.[14] All non-hydrogen atoms were refined[14] with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier synthesis and refined isotropically. For **13** an empirical absorption correction (ψ-scans) was applied (min, max transmission: 0.899, 1.000). The crystal data and refinement parameters are listed in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100473. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: int. +44 (0)1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk).

[1] See for example: W. A. Herrmann, B. Cornils, *Angew. Chem.* **1997**, *109*, 1074–1095; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1048–1067.

[2] [2a] I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, VCH, Weinheim, **1993**. – [2b] R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**.

[3] C. Ganter, L. Brassat, C. Glinsböckel, B. Ganter, *Organometallics* **1997**, *16*, 2862–2867.

[4] The following abbreviations are used throughout this paper: Cy: cyclohexyl; NBD: norbornadiene; PFc: 3,4-dimethylphosphaferrocen-2-yl; Ms: CH_3SO_2-.

[5] [5a] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066. – [5b] H. C. L. Abbenhuis, U. Burckhardt, V. Gramlich, C. Köllner, P. S. Pregosin, R. Salzmann, A. Togni, *Organometallics* **1995**, *14*, 759–766.

[6] G. dc Lauzon, B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, *J. Am. Chem. Soc.* **1980**, *102*, 994–1000.

[7] B. Deschamps, F. Mathey, *Organometallics* **1992**, *11*, 1411–1413.

[8] K.-S. Gan, T. S. A. Hor in *Ferrocenes: homogenous catalysis, organic synthesis, materials science*. (Eds.: A.Togni, T. Hayashi), VCH, Weinheim, **1995**, chapter 1.

[9] For a discussion of through-backbone and through-metal contributions to the observed J_{PP} coupling see: [9a] S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, J. P. Jesson, *Inorg. Chem.* **1974**, *13*, 1095–1100. – [9b] S. O. Grim, R. C. Barth, J. D. Mitchell, J. del Gaudio, *Inorg. Chem.* **1977**, *16*, 1776–1779. – [9c] A. L. Crumbliss, R. J. Topping in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: L. D. Quinn, J. G. Verkade), VCH, Weinheim, **1987**, chapter 15.

[10] [10a] F. Mathey, *J. Organomet. Chem.* **1978**, *154*, C13–C15. – [10b] B. Deschamps, F. Mathey, J. Fischer, J. H. Nelson, *Inorg. Chem.* **1984**, *23*, 3455–3462. – [10c] G. de Lauzon, B. Deschamps, F. Mathey, *New J. Chem.* **1980**, *4*, 683–685.

[11] [11a] G. E. Herberich, S. Moss, *Chem. Ber.* **1995**, *128*, 689–693. – [11b] J. L. Bookham, W. McFarlane, M. Thornton-Pett, S. Jones, *J. Chem. Soc., Dalton Trans.* **1990**, 3621–3627. – [11c] A. Varshney, G. M. Gray, *Inorg. Chem.* **1991**, *30*, 1748–1754.

[12] [12a] F. A. Cotton, D. J. Darensbourg, S. Klein and B. W. S. Kolthammer, *Inorg. Chem.* **1982**, *21*, 294–299, 1651–1655 and 2661–2666. – [12b] I. Bernal, G. M. Reisner, G. R. Dobson, C. B. Dobson, *Inorg. Chim. Acta* **1986**, *121*, 199–206.

[13] See for example: [13a] T. G. Hill, C. Haltiwanger, T. R. Prout and A. D. Norman, *Inorg. Chem.* **1989**, *28*, 3461–3467. – [13b] E. H. Wong, F. C. Bradley and E. J. Gabe, *J. Organomet. Chem.* **1983**, *244*, 235–245. – [13c] M. S. Balakrishna, T. K. Prakasha, S. S. Krishnamurthy, U. Siriwardane and N. S. Hosmane, *J. Organomet. Chem.* **1990**, *390*, 203–216.

[14] MolEN, *An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, The Netherlands, **1990**.

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