Synthesis of Chiral, Half-Sandwich Ruthenium Complexes from Weakly Coordinated Solvent Species

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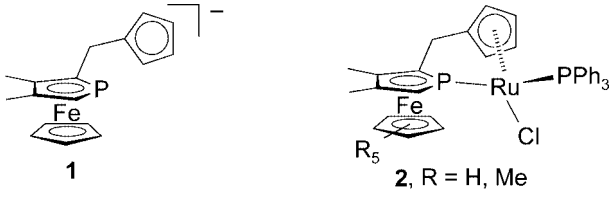
The bis(acetonitrile) species **7** has been synthesized in a multistep protocol. This chiral phosphaferrocene-containing, half-sandwich ruthenium complex easily provides two coordination sites due to the high lability of the coordinated solvent molecules. Although complex **7** could not be isolated in pure form, it serves as a valuable starting material for the preparation of other half-sandwich complexes with, for example, pyridine (**8**), tmeda (**9**), *N*-(2-dimethylaminoethyl)-morpholine (**10**), or tricyclohexylphosphine (**11**) as ligands. Whereas the morpholine complex **10** was obtained as almost a 1:1 mixture of diastereomers, the mixed MeCN/PCy_3 complex **11** was formed with a high level of diastereoselectivity (90% *de*). The molecular structures of complexes **8**, **10**, and the cyclopentadiene derivative **3a** were determined by X-ray diffraction.

Introduction

In a series of previous papers we have outlined the chemistry of a new type of bidentate ligands that contain a substituted phosphaferrocene moiety as a chiral building block.[1–3] The coordination chemistry employing these new ligands, as well as their applicability in asymmetric catalysis, has been studied by us[1,4] and independently by other groups.[5–11] In a more recent project we have tethered the chiral phosphaferrocene unit to a cyclopentadienyl ring and explored the properties of this anionic ligand system **1** (Scheme 1).[12] For example, the half-sandwich complexes **2** were formed in the reaction of the Na salt of the Cp anion **1** with $[RuCl_2(PPh_3)_3]$.[13] A high diastereoselectivity of 90–99% *de* was observed for the formation of the stereogenic Ru atom in complexes **2**.



Scheme 1.

Furthermore, substitution of chloride in complex **2** for other ligands like I, H or H_2 was easily accomplished and proceeded in a stereospecific manner. However, all attempts to replace the tightly bound PPh_3 ligand by other donor ligands were unsuccessful. In order to have access to a larger array of half-sandwich complexes we set out to develop a new synthetic route based on a weakly coordinated bis(solvent) species that allows the weakly bonded ligands to be easily exchanged. Such bis(solvent) complexes might also be of interest for catalytic asymmetric transformations. Indeed, there is an increasing number of recent literature reports on the application of chiral half-sandwich complexes in catalytic asymmetric reactions.[14–19]

Results and Discussion

Our synthetic strategy had to avoid the presence of strongly binding phosphane ligands throughout the synthesis. Therefore, we chose the half-open ruthenocene **5** as a target, which should be easily converted into the cationic pentadiene complex **6** upon protonation. We hoped to exchange the diene ligand in **6** with two molecules of a donor solvent in the final step to yield the desired species with two potential coordination sites available.

A large number of attempts to prepare the half-open ruthenocene from the sodium salt of **1** were unsatisfactory, the product being obtained in low yields. However, exchange of Na for Tl as the cation gave a straightforward access to excellent yields of complex **5**. For this purpose, the Na derivative was hydrolysed in wet THF and the neutral cyclopentadiene derivative **3** was isolated as a pale-orange solid in 91% yield after chromatography. The NMR spectra indicated that **3** was formed as a 2.5:1 mixture of two isomers that differ in the distribution of the double bonds in the cyclopentadiene ring (Scheme 2).

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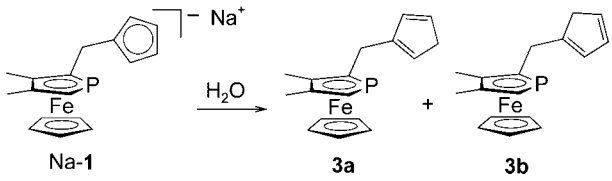


Scheme 2.

Both isomers have the phosphaferrocenylmethyl group attached to an olefinic carbon atom, as indicated by the signals for the CH_2 groups in the DEPT spectra in both cases. The isomers could not be separated by chromatography, but cooling a hexane solution of the mixture afforded crystals of one isomer suitable for X-ray diffraction. The molecular structure of **3a** is depicted in Figure 1 and relevant geometrical data are summarized in Table 1.

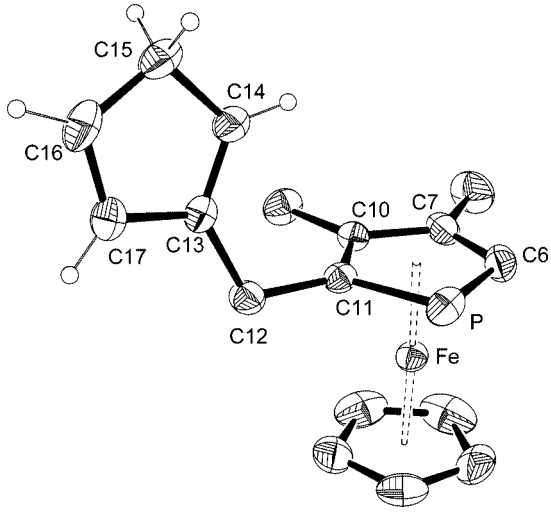
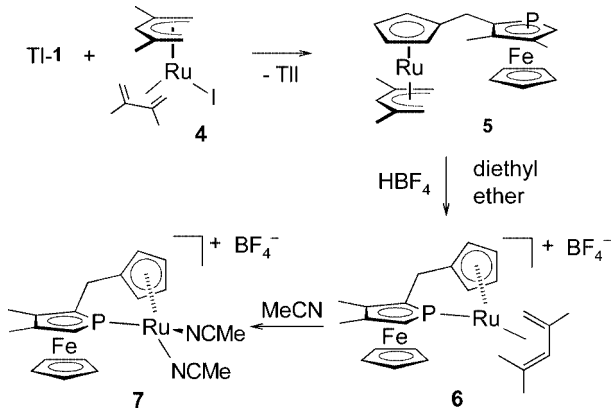


Figure 1. Molecular structure of complex **3a**.

Table 1. Selected bond lengths [Å] and angles [°] for complex **3a**.

Fe–P	2.2799(6)	P–C(6)	1.767(2)
P–C(11)	1.7794(15)	C(6)–C(7)	1.417(3)
C(7)–C(10)	1.437(2)	C(10)–C(11)	1.421(2)
C(13)–C(14)	1.345(2)	C(13)–C(17)	1.450(2)
C(14)–C(15)	1.481(2)	C(15)–C(16)	1.454(3)
C(16)–C(17)	1.368(3)		
C(6)–P–C(11)	88.93(8)	C(7)–C(6)–P	114.30(12)
C(6)–C(7)–C(10)	111.37(14)	C(11)–C(10)–C(7)	111.95(13)
C(10)–C(11)–P	113.37(11)	C(10)–C(11)–C(12)	124.10(14)
C(12)–C(11)–P	122.51(12)		

Treatment of a solution of cyclopentadiene **3** in diethyl ether with TlOEt precipitated the thallium cyclopentadienide Tl-**1**, which was isolated as a pale-yellow powder in almost quantitative yield after filtration and drying. The Tl salt was then allowed to react with the ruthenium butadiene iodide **4** [20] to give the half-open ruthenocene **5** (Scheme 3).



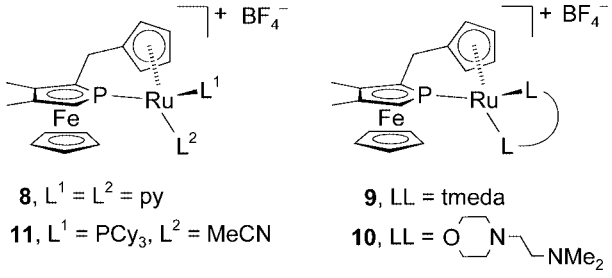
Scheme 3.

The best yield (76%) was obtained when an equimolar mixture of starting materials was heated as a slurry in toluene overnight. Complex **5** was isolated as a pale-yellow solid after removal of TlI by filtration and chromatography on alumina. The analytical data are in agreement with a half-sandwich structure, with the phosphorus not coordinated to the ruthenium atom. When an ethereal solution of complex **5** was treated dropwise with HBF_4 in diethyl ether, protonation of the pentadienyl ligand occurred at the terminal position to give an η^4-coordinated pentadiene ligand. This transformation is accompanied by the intramolecular coordination of the P atom of the phosphaferrocene moiety to the ruthenium atom, which thereby maintains an 18-electron count in the cationic product **6**. Due to the presence of the chiral phosphaferrocene group, the terminal carbons of the pentadienyl ligand are diastereotopic and the protonation leads to a 1:1 mixture of diastereomeric pentadiene complexes which could not be separated. Accordingly, the ^{31}P NMR spectrum shows two resonances at δ = 50.5 and 43.7 ppm, respectively, which are strongly downfield from the signal at δ = –76.0 ppm for the precursor complex **5** with a non-coordinated phosphorus.

The diene ligand in cationic complex **6** could easily be replaced by acetonitrile by stirring the complex in acetonitrile at room temperature for a couple of hours. Monitoring the reaction progress by ^{31}P NMR spectroscopy revealed that this is not a clean transformation. First, a new signal appears in the spectrum which is attributed to the bis(acetonitrile) species **7**; the intensity of this signal increases with time at the expense of the signals for the two isomeric diene complexes **6**. However, the bis(acetonitrile) complex has a limited stability under the reaction conditions and eventually starts to decompose to uncharacterized products before all the diene complex has been consumed. The reproducibility of the reaction is not very good: repeated experiments under identical conditions led, in some cases, to almost pure solutions of the bis(acetonitrile) species **7**, while in other runs considerable degradation occurred. Variation of the reaction parameters (concentration, temperature, irradiation) did not improve the reaction performance. Attempts to isolate complex **7** in pure form failed and the characteri-

zation had therefore to be carried out from the reaction solution.

However, the high reactivity of the bis(solvent) complex **7** could be exploited in subsequent substitution reactions (Scheme 4). For example, when the cation **6** was stirred in acetonitrile in the presence of an excess of pyridine for five hours, the respective bis(pyridine) complex **8** could be isolated in 91% yield after precipitation from the solution with diethyl ether. During the reaction, the characteristic signals of **7** are first detected in the ^{31}P NMR spectrum, followed by the appearance of the signal of complex **8**. The use of acetonitrile as solvent is essential for a fast reaction. Indeed, when acetone was used instead of acetonitrile, the reaction proceeded much slower and the conversion was incomplete even after two days. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetone solution of bis(pyridine) complex **8**. An ORTEP view of the molecular structure is depicted in Figure 2; relevant geometrical data are summarized in Table 2.



Scheme 4.

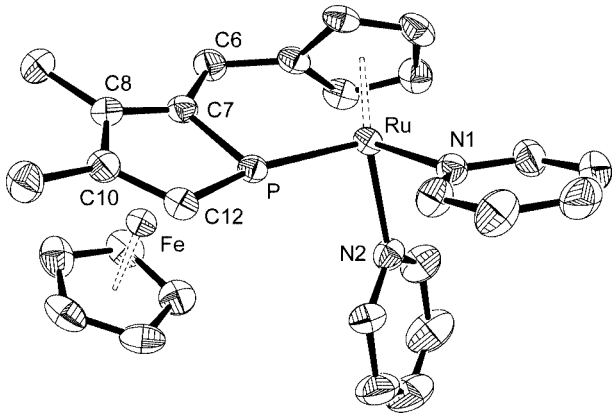


Figure 2. Molecular structure of the cation of complex **8**.

Similarly to the preparation of **8**, the tmeda complex **9** was prepared in 98% isolated yield by treatment of an acetonitrile solution of diene complex **6** with one equivalent of tmeda. When a solution of diene cation **6** in acetonitrile was treated with one equivalent of *N*-(2-dimethylaminoethyl)morpholine complex **10** was formed, with the morpholine derivative coordinated as an *N*,*N* ′-chelate ligand.

In the course of this reaction the ruthenium center becomes stereogenic and complex **10** is formed as two diastereomers in a ratio of approximately 3:2. This poor diastereoselectivity reflects the similar steric demands of the two

Table 2. Selected bond lengths [Å] and angles [°] for complex **8**.

Ru–N(1)	2.139(2)	Ru–N(2)	2.153(2)
Ru–P	2.2797(6)	P–C(7)	1.753(2)
P–C(12)	1.766(2)	C(7)–C(6)	1.521(3)
C(8)–C(7)	1.416(4)	C(8)–C(10)	1.445(4)
C(10)–C(12)	1.422(4)		
N(1)–Ru–N(2)	84.26(8)	N(1)–Ru–P	99.96(6)
N(2)–Ru–P	95.72(6)	C(7)–P–C(12)	90.88(12)
C(7)–P–Ru	108.36(8)	C(12)–P–Ru	159.05(9)
C(8)–C(7)–C(6)	130.5(2)	C(8)–C(7)–P	113.21(18)
C(6)–C(7)–P	116.26(18)		

different nitrogen donor groups of the morpholine derivative. As the two groups on nitrogen are incorporated into the heterocyclic system of the morpholine the flexibility of this donor is fairly low, and it should therefore be sterically less demanding than the open-chain NEt_2 analogue. Thus, the difference in steric bulk of the morpholine and the dimethylamino donor groups is less pronounced than one would expect at first glance. While a chromatographic separation of the two diastereomeric morpholine complexes **10** was not successful, one diastereomer could be obtained in pure form by crystallization. The molecular structure of this complex was determined by X-ray diffraction and is depicted in Figure 3; relevant geometrical data are summarized in Table 3.

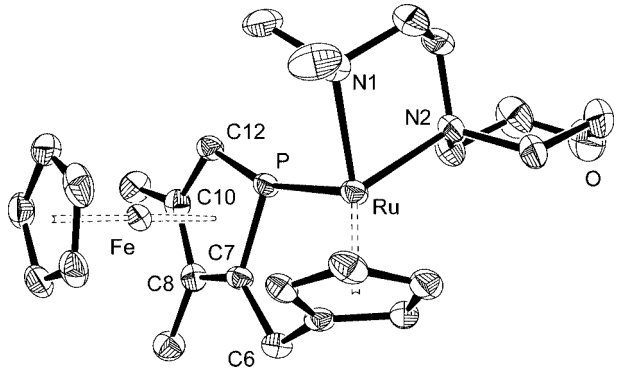


Figure 3. Molecular structure of the cation of complex **10**.

Table 3. Selected bond lengths [Å] and angles [°] for complex **10**.

Ru–N(1)	2.214(4)	Ru–N(2)	2.210(4)
Ru–P	2.2912(13)	P–C(7)	1.750(4)
P–C(12)	1.749(5)	C(7)–C(6)	1.517(6)
C(7)–C(8)	1.409(6)	C(8)–C(10)	1.444(6)
C(12)–C(10)	1.427(6)		
N(2)–Ru–N(1)	80.99(16)	N(1)–Ru–P	97.83(12)
N(2)–Ru–P	97.66(11)	C(12)–P–C(7)	90.6(2)
C(7)–P–Ru	108.69(16)	C(12)–P–Ru	160.74(16)
C(6)–C(7)–P	116.1(3)	C(8)–C(7)–P	113.5(3)
C(8)–C(7)–C(6)	130.1(4)	C(10)–C(12)–P	112.7(3)

The Ru–P distances in the two cationic complexes **8** (228 pm) and **10** (229 pm) are almost identical and slightly longer than in neutral Ru-phosphaferrocene half-sandwich complexes (224–225 pm).[2,13] As expected, the Ru–N bonds are significantly shorter in the pyridine complex **8** (214 pm) than in the morpholine derivative **10** (221 pm) with its terti-

ary amine donor functions. As is usually observed, on going from an uncoordinated phosphaferrocene derivative (**3a**) to the metal complexes **8** and **10** the C–P–C angle in the phospholyl ring increases slightly from 88.9° (**3**) to 90.9° (**8**) and 90.6° (**10**). Furthermore, the P–C bonds in the phospholyl ring contract slightly on coordination from ca. 178 pm to 175–176 pm.

It was also possible to prepare a mono(acetonitrile) derivative starting from the cationic complex **6**. Thus, when an acetonitrile solution of **6** was treated with one equivalent of tricyclohexylphosphane (PCy_3), the mixed P,N complex **11** was formed in 96% yield. In contrast to the morpholine derivative **10**, a high level of stereodiscrimination (90% *de*) was observed for the formation of complex **11**. This reflects the different steric properties of the acetonitrile and PCy_3 ligands.

Conclusions

A high-yield route to half-sandwich ruthenium complexes with a tethered phosphaferrocene donor and two loosely coordinated acetonitrile molecules has been devised. The bis(acetonitrile) complex is very reactive and easily provides two available coordination sites at the ruthenium. The synthetic value of this approach has been corroborated by the subsequent preparation of some derivatives with mono- and bidentate nitrogen ligands. We are currently trying to extend and improve the results with respect to the stereodiscrimination in the complexation of difunctional ligands and the use of the solvent complex for catalytic applications.

Experimental Section

All experiments were performed under nitrogen using Schlenk and vacuum-line techniques. Hexane and toluene were distilled from sodium; $CHCl_3$ and CH_2Cl_2 from CaH_2. THF and diethyl ether were distilled from sodium/benzophenone. Acetonitrile was dried with P_4O_{10} and distilled from CaH_2. Methanol and acetone were dried with magnesium. The solvents were kept in Schlenk flasks under nitrogen. Silica gel or alumina were heated to 200 °C, cooled to room temperature under vacuum, and stored under nitrogen. Alumina (Riedel-de Haën) was deactivated by addition of 5% water. NMR spectra were measured with Varian Mercury 200, VXR 300 and Unity 500 spectrometers. EI and FAB mass spectra were measured on a Finnigan MAT 95 spectrometer. Elemental analyses were performed by the microanalytical laboratory of the Universität Düsseldorf. Na-**1** [12] and ruthenium iodide **4** [20] were prepared as described in the literature.

Cyclopentadiene 3: Na-**1** was obtained by addition of $NaBEt_3H$ (0.62 mmol, 0.4 mL of a 1.5 M solution in THF) to a solution of 6-(3,4-dimethylphosphaferrocen-2-yl)fulvene (127.7 mg, 0.41 mmol) in diethyl ether/THF (1:1, 30 mL) at room temperature. After stirring for 45 min water (5 mL) was added to the orange solution and the phases were separated. The organic phase was washed with water, dried with Na_2SO_4, and the solvent was removed in vacuum. The crude product was filtered through a short plug of alumina with hexane as eluent. After evaporation of the solvent, **3** (115.7 mg, 0.37 mmol, 91%) was isolated as an orange crystalline powder as a mixture of two isomers in a ratio of ca. 1:2.5. Crystals suitable for X-ray diffraction were obtained by slowly cooling a hexane solution to –18 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.21, 2.14 (s, 3 H, CH_3), 2.93 (m, 4 H, CH_2 in C_5H_5R), 3.26 (m, 4 H, PCC*H*$_2$, major + minor), 3.71 (d, $J_{C,P}$ = 35.7 Hz, 2 H, PCH, major + minor), 4.13 (s, 2 × 5 H, Cp, major + minor), 5.9 (s, 1 H, C_5H_5R, major), 6.24, 6.06 (s, 1 H, C_5H_5R, minor), 6.39 (s, 2 H, C_5H_5R, major + minor), 6.47 (s, 1 H, C_5H_5R, major) ppm. ^{13}C{^{1}H} (125.6 MHz, $CDCl_3$): major isomer: δ = 17.1, 13.7 (s, CH_3), 31.1 (d, $J_{C,P}$ = 20.2 Hz, PC*C*H$_2$), 41.0 (s, *C*H$_2$ in C_5H_5R), 72.0 (s, Cp), 75.6 (d, $J_{C,P}$ = 58.5 Hz, PCH), 93.3 (d, $J_{C,P}$ = 5.7 Hz, *C*CH$_3$), 95.6 (d, $J_{C,P}$ = 6.7 Hz, *C*CH$_3$), 97.4 (d, $J_{C,P}$ = 57.6 Hz, P*C*CH$_2$), 134.4, 133.5, 126.5 (s, CH in C_5H_5R), 146.6 (s, CR in C_5H_5R) ppm; minor isomer: δ = 17.1, 13.7 (s, CH_3), 32.0 (d, $J_{C,P}$ = 22 Hz, PC*C*H$_2$), 43.2 (s, *C*H$_2$ in C_5H_5R), 72.0 (s, Cp), 75.5 (d, $J_{C,P}$ = 57.5 Hz, PCH), 93.3 (d, $J_{C,P}$ = 5.7 Hz, *C*CH$_3$), 95.6 (d, $J_{C,P}$ = 6.7 Hz, *C*CH$_3$), 98.3 (d, $J_{C,P}$ = 57.5 Hz, P*C*CH$_2$), 132.2, 130.7, 127.0 (s, CH in C_5H_5), 149.2 (s, CR in C_5H_5R) ppm. ^{31}P NMR (80.95 MHz, $CDCl_3$): δ = –79.7 (s, minor), –80.1 (s, major) ppm. MS (70 eV): *m*/*z* (%) = 310 (42) [M$^+$], 244.9 (47) [M$^+$ – Cp]. $C_{17}H_{19}FeP$ (310.2): calcd. C 65.83, H 6.17; found C 65.61, H 6.08.

Thallium Salt Tl-1: TlOEt (0.22 mL, 3.06 mmol) was added dropwise to a solution of cyclopentadiene **3** (947 mg, 3.06 mmol) in diethyl ether (10 mL) at room temperature. After stirring for 30 min the precipitate was isolated by filtration, washed with diethyl ether, and dried in vacuo to give 1.74 g (3.03 mmol, 99%) of Tl-**1** as a pale-orange powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23 (s, CH_3), 2.26 (s, CH_3), 3.28 (dd, $J_{H,P}$ = 15.3, $J_{H,H}$ = 7.0 Hz, 1 H, CH_2), 3.49 (m, 1 H, CH_2), 3.66 (d, $J_{H,P}$ = 35.7 Hz, 1 H, PCH), 4.12 (s, 5 H, Cp), 5.84 (m, 2 H, C_5H_4), 5.99 (m, 2 H, C_5H_4) ppm. ^{13}C{^{1}H} (125.6 MHz, $CDCl_3$): δ = 14.2 (s, CH_3), 17.2 (s, CH_3), 29.9 (d, $J_{C,P}$ = 20.9 Hz, CH_2), 72.1 (s, Cp), 75.3 (d, $J_{C,P}$ = 58.1 Hz, PCH), 92.9 (d, $J_{C,P}$ = 4.4 Hz, *C*CH$_3$), 95.8 (d, $J_{C,P}$ = 6.5 Hz, *C*CH$_3$), 105.5 (s, C_5H_4), 106.1 (d, $J_{C,P}$ = 54.9 Hz, P*C*CH$_2$), 108.0 (s, C_5H_4), 132.6 (s, *C*CH$_2$) ppm. ^{31}P NMR (80.95 MHz, $CDCl_3$): δ = –77.7 (s) ppm. SIMS (70 eV): *m*/*z* = 514 [M$^+$], 310.2 [M$^+$ – Tl], 205.1 [Tl$^+$]. $C_{17}H_{18}FePTl$ (513.53): calcd. C 39.76, H 3.53, found C 39.01, H 3.39.

(Dimethylpentadienyl)ruthenium Complex 5: Tl-**1** (1.13 g, 2.21 mmol) was added to a suspension of ruthenium iodide **4** (894 mg, 2.21 mmol) in 35 mL of toluene and the mixture was refluxed overnight. TlI was removed by filtration through Kieselguhr and the filtrate was evaporated to dryness. The residue was extracted with hexane, the solution filtered through alumina, and the solvent was removed in vacuo to yield **5** (849 mg, 1.68 mmol, 76%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.29 (d, $J_{H,H}$ = 2.4 Hz, 1 H, H$_{endo}$), 0.31 (d, $J_{H,H}$ = 2.4 Hz, 1 H, H$_{endo}$), 1.87 (s, CH_3), 1.89 (s, CH_3), 1.90 (s, CH_3), 1.92 (s, CH_3), 2.86 (d, $J_{H,H}$ = 2.4 Hz, 1 H, H$_{exo}$), 2.87 (d, $J_{H,H}$ = 2.4 Hz, 1 H, H$_{exo}$), 3.07 (m, 2 H, CH_2), 3.60 (d, $J_{H,P}$ = 36.0 Hz, 1 H, PCH), 3.90 (s, 5 H, Cp), 4.31 (m, 2 H, C_5H_4), 4.56 (m, 2 H, C_5H_4), 5.34 (s, CH) ppm. ^{13}C{^{1}H} (125.6 MHz, $CDCl_3$): δ = 13.9 (s, CH_3), 16.9 (s, CH_3), 27.9 (s, 2 × CH_3), 30.5 (d, $J_{C,P}$ = 20.9 Hz, CH_2), 42.2 (s, =CH_2), 42.3 (s, =CH_2) 72.2 (s, Cp), 76.2 (d, $J_{C,P}$ = 58.8 Hz, PCH), 77.4 (s, RC_5H_4), 78.0 (s, RC_5H_4), 78.5 (s, RC_5H_4), 79.1 (s, RC_5H_4), 92.3 (s, CH_2=*C*), 92.7 (s, CH), 95.7 (d, $J_{C,P}$ = 6.1 Hz, *C*CH$_3$), 98.8 (d, $J_{C,P}$ = 2.8 Hz, *C*CH$_3$), 100.2 (d, $J_{C,P}$ = 58.2 Hz, P*C*CH$_2$) ppm. ^{31}P NMR (80.95 MHz, $CDCl_3$): δ = –76.0 (s) ppm. MS (70 eV): *m*/*z* = 505.8 [M$^+$], 309.9 [M$^+$ – Ru – C_7H_{11}], 244.9 [M$^+$ – Ru – C_7H_{11} – Cp]. HRMS for $C_{24}H_{29}FePRu$: calcd. 506.039346; found 506.039321.

(η^4-2,4-Dimethylpentadiene)ruthenium Complex 6: HBF_4 (0.38 mL, 54% solution in diethyl ether, 2.76 mmol) was added dropwise to a

solution of complex **5** (943 mg, 1.87 mmol) in diethyl ether (50 mL) at –78 °C. After stirring for 30 min at room temperature the precipitate was isolated by filtration, washed twice with diethyl ether, and dried in vacuo to give 1.05 g (1.78 mmol, 95%) of complex **6** as a 1:1 mixture of isomers as an orange powder. ^{1}H NMR (500 MHz, [D$_6$]acetone): isomer 1: δ = 1.46 (d, $J_{H,H}$ = 8.9 Hz, 3 H, CH_3), 2.22 (s, CH_3), 2.28 (s, CH_3), 2.34 (s, CH_3), 2.35 (m, 2 H, =CH_2), 2.40 (s, CH_3), 2.93 (m, 2 H, CH_2), 3.70 (d, $J_{H,P}$ = 32.0 Hz, 1 H, PCH), 3.81 (m, 1 H, =CH-C), 4.63 (m, 1 H, C_5H_4), 4.65 (s, 5 H, Cp), 5.38 (m, 1 H, C_5H_4), 5.61 (m, 1 H, C_5H_4), 5.83 (m, 1 H, C_5H_4) ppm; isomer 2: δ = 1.24 (d, $J_{H,H}$ = 8.4 Hz, 3 H, CH_3), 1.83 (s, CH_3), 1.91 (m, 2 H, = CH_2), 2.30 (s, CH_3), 2.31 (s, CH_3), 2.47 (s, CH_3), 3.01 (m, 2 H, CH_2), 3.38 (m, 1 H, =CH-C), 4.10 (d, $J_{H,P}$ = 32.4 Hz, 1 H, PCH), 4.51 (s, 5 H, Cp), 4.83 (m, 1 H, C_5H_4), 5.25 (m, 1 H, C_5H_4), 5.63 (m, 1 H, C_5H_4), 5.73 (m, 1 H, C_5H_4) ppm. ^{13}C{^{1}H} (125.6 MHz, [D$_6$]acetone): isomer 1: δ = 15.9 (d, $J_{C,P}$ = 6.0 Hz, CH_3), 16.1 (d, $J_{C,P}$ = 5.6 Hz, CH_3), 23.6 (d, $J_{C,P}$ = 15.9 Hz, CH_2), 24.6 (s, CH_3), 26.4 (s, CH_3), 34.3 (s, CH_3), 43.2 (s, =CH_2), 43.3 (s, =*C*H-C), 57.5 (s, PCH), 76.1 (s, Cp), 82.8 (s, RC_5H_4), 85.4 (s, RC_5H_4), 86.9 (s, RC_5H_4), 88.9 (s, RC_5H_4) ppm; isomer 2: δ = 13.9 (s, CH_3), 14.0 (d, $J_{C,P}$ = 5.0 Hz, CH_3), 23.9 (d, $J_{C,P}$ = 16.5 Hz, CH_2), 24.7 (s, CH_3), 26.0 (s, CH_3), 34.0 (s, CH_3), 43.8 (s, =CH_2), 43.9 (s, =*C*H-C), 60.4 (s, PCH), 76.5 (s, Cp), 83.3 (s, RC_5H_4), 83.6 (s, RC_5H_4), 85.8 (s, RC_5H_4), 90.2 (d, $J_{C,P}$ = 4.9 Hz, RC_5H_4) ppm. ^{31}P NMR (80.95 MHz, $CDCl_3$): δ = 50.5 (s, isomer 1), 43.7 (s, isomer 2) ppm. SIMS (70 eV): *m*/*z* = 507 [M$^+$], 411 [M$^+$ – C_7H_{11}]. $C_{24}H_{30}BF_4FePRu$ (593.2): calcd. C 48.59, H 5.10; found C 47.85, H 5.18.

Bis(acetonitrile) Complex 7: A solution of cationic complex **6** (118 mg, 0.20 mmol) in 15 mL of acetonitrile was stirred at room temperature. The reaction progress was monitored by ^{31}P NMR spectroscopy. After 4 h all volatiles were evaporated off under high vacuum to give an orange oil of **7** which was immediately characterized by NMR spectroscopy in CD_3CN. ^{1}H NMR (200 MHz, CD_3CN): δ = 2.20 (s, 6 H, CH_3CN), 2.44, 2.42 (2 × s, 3 H, CH_3), 2.72 (m, 2 H, CH_2), 3.89 (d, $J_{H,P}$ = 34.2 Hz, 1 H, PCH), 4.28 (br. s, 1 H, C_5H_4), 4.52 (s, 5 H, Cp), 5.37, 5.27, 4.71 (3 × br. s, 1 H, C_5H_4) ppm. ^{31}P NMR (202.25 MHz, CD_3CN): δ = 4.2 (s) ppm.

Bis(pyridine) Complex 8: An excess of pyridine (260 µL, 3.21 mmol) was added to a solution of cationic complex **6** (336 mg, 0.57 mmol) in 15 mL of acetonitrile at room temperature. The reaction mixture was stirred for 4 h. The solvents were removed under high vacuum to give an orange oil, which was redissolved in acetone. Complex **8** (338 mg, 0.52mmol, 91%) was isolated as an orange powder upon precipitation with diethyl ether. Red crystals were obtained by diffusion of diethyl ether into an acetone solution. ^{1}H NMR (500 MHz, $[CD_3]_2CO$): δ = 2.27, 2.26 (2 × s, 3 H, CH_3), 2.65 (m, 2 H, CH_2-Phosp.), 3.88 (d, $J_{H,P}$ = 33.3 Hz, 1 H, PCH), 4.11 (s, 5 H, Cp), 5.38, 5.10, 4.73, 4.12 (4 × s, 1 H, C_5H_4R), 7.51, 7.36 (br. t, *J* = 7.0 Hz, 2 H, C_5H_5N-H$_{meta}$), 8.00, 7.88 (2 × br. t, *J* = 7.6 Hz, 1 H, C_5H_5N-H$_{para}$), 8.94 (br. d, *J* = 5.2 Hz, 2 H, C_5H_5N-H$_{ortho}$), 9.19 (br. d, *J* = 4.9 Hz, 2 H, C_5H_5N-H$_{ortho}$) ppm. ^{13}C{^{1}H} (125.6 MHz, $[CD_3]_2CO$): δ = 16.4, 14.3 (2 × s, CH_3), 24.1 (d, $J_{C,P}$ = 16.3 Hz, CH_2), 62.2 (s, C_5H_4), 62.5 (d, $J_{C,P}$ = 36.5 Hz, PCH), 69.9 (s, C_5H_4), 74.8 (s, Cp), 83.2 (d, $J_{C,P}$ = 10.5 Hz, C_5H_4), 85.1 (d, *J* = 5.8 Hz, C_5H_4), 89.2 (s, CR in RC_5H_4), 91.2 (d, *J* = 2 Hz, P*C*CH_2), 111.4 (d, *J* = 7.66 Hz, *C*CH_3), 111.7 (d, *J* = 12.5 Hz, *C*CH_3), 126.6, 126.4 (2 × s, C$_{meta}$-C_5H_5N), 138.3, 138.2 (2 × s, C$_{para}$-C_5H_5N), 158.4, 157.9 (2 × d, $J_{C,P}$ = 7.7 Hz, C$_{ortho}$-C_5H_5N) ppm. ^{31}P NMR (202.25 MHz, $[CD_3]_2CO$): δ = 10.5 (s) ppm. $C_{27}H_{28}BF_4FePN_2Ru$ (655.2): calcd. C 49.49, H 4.31, N 4.28; found C 48.82, H 4.38, N 4.19. FAB MS: *m*/*z* = 490 [cation – py], 411 [cation – 2 py].

Tetramethylethylenediamine Complex 9: tmeda (85 µL, 0.56 mmol) was added to a solution of complex **6** (331.6 mg, 0.56 mmol) in 15 mL of acetonitrile at room temperature. The reaction mixture was stirred for 7 h and the solvent was then evaporated under high vacuum to give **9** as an orange powder (329.4 mg, 96%). ^{1}H NMR (500 MHz, CD_3CN): δ = 2.20, 2.18 (2 × s, 3 H, CCH_3), 2.33 (m, 2 H, C_5H_4-C*H* $_2$), 2.52 (m, 2 H, NCH_2), 2.72 (d, $J_{H,P}$ = 3 Hz, 3 H, NCH_3), 2.72 (m, 1 H, NCH_2), 2.87 (m, 1 H, NCH_2), 3.13 (s, 3 H, NCH_3), 3.15 (d, $J_{H,P}$ = 4 Hz, 3 H, NCH_3), 3.28 (s, 3 H, NCH_3), 3.53 (d, $J_{H,P}$ = 32 Hz, 1 H, PCH), 4.11, 4.09 (2 × m, 1 H, C_5H_4), 4.25 (s, 5 H, Cp), 5.06, 4.64 (2 × m, 1 H, C_5H_4) ppm. ^{13}C{^{1}H} (125.6 MHz, CD_3CN): δ = 14.3 (d, $J_{C,P}$ = 4.8 Hz, CH_3), 16.5 (s, CH_3), 23.8 (d, $J_{C,P}$ = 16.3 Hz, $CpCH_2$), 60.0, 59.4 (2 × s, NCH_3), 61.7 (s, C_5H_4), 61.7 (d, $J_{C,P}$ = 36.5 Hz, PCH), 62.3 (d, *J* = 15.3 Hz, NCH_3), 62.9 (d, *J* = 16.3 Hz, NCH_3), 64.5, 63.8 (2 × s, NCH_2), 66.8 (s, C_5H_4), 75.3 (s, Cp), 77.5 (d, $J_{C,P}$ = 10.5 Hz, C_5H_4), 89.5 (s, C$_{quat.}$), 90.5 (s, C_5H_4), 107.8, 110.6, 117.5 (3 × s, C$_{quat.}$) ppm. ^{31}P NMR (80.95 MHz, CD_3CN): δ = 16.5 (s) ppm. FAB MS (NBA matrix): *m*/*z* = 527 [cation], 87 [BF_4^-]. $C_{23}H_{34}BF_4FeN_2PRu$: calcd C 45.05, H 5.59, N 4.57; found C 45.90, H 5.78, N 3.84.

Morpholine Complex 10: *N*-(2-Dimethylaminoethyl)morpholine (1.3 equiv., 82 µL, 0.48 mmol) was added to a solution of cationic complex **6** (220 mg, 0.37 mmol) in 10 mL of acetonitrile and stirred for 1 d at room temperature. The solvent was evaporated under high vacuum to give **10** as a red powder (223.5 mg, 97%) as a mixture of isomers in a ratio of about 3:2. Crystals suitable for X-ray diffraction were obtained by layering a CH_2Cl_2 solution with hexane. ^{1}H NMR (500 MHz, CD_3CN, mixture of isomers): δ = 2.21, 2.20, 2.20, 2.19 (4 × s, 3 H, CH_3), 3.27, 3.25, 3.24, 3.12 (4 × s, 3 H, NCH_3), 4.24 (s, 5 H, Cp), 4.28 (s, 5 H, Cp) ppm. ^{31}P NMR (202 MHz, CD_3CN): δ = 13.9 (s, major), 12.9 (s, minor) ppm. FAB MS (NBA matrix): *m*/*z* = 569 [cation], 411 [cation – morpholine]. $C_{25}H_{36}BF_4FeN_2OPRu$ (655.3): calcd. C 45.82, H 5.54, N 4.28; found C 45.01, H 5.67, N 4.51.

Tricyclohexylphosphane Complex 11: One equivalent of tricyclohexylphosphane (97 mg, 0.37 mmol) was added to a solution of complex **6** (222 mg, 0.37 mmol) in 10 mL of acetonitrile and stirred for 1 d at room temperature. The solvent was evaporated under high vacuum to give Ru-**9** as an orange foam (291mg, 96%) as a mixture of two isomers in a ratio of about 19:1 (90% *de*). ^{1}H NMR (300 MHz, C_6D_6): major isomer: δ = 1.9–1.1 (m, 36 H, PCy_3 and CH_3CN), 1.94, 1.88 (2 × s, 3 H, CH_3), 2.38 (m, 1 H, $PCCH_2$), 2.59 (m, 1 H, $PCCH_2$), 3.33 (d, $J_{H,P}$ = 32.6 Hz, 1 H, PCH), 3.36 (s, 1 H, C_5H_4), 4.33 (s, 5 H, Cp), 5.01, 5.20, 5.86 (3 × s, 1 H, C_5H_4) ppm. ^{31}P NMR (121.45 MHz, C_6D_6): major isomer: δ = 59.6 (d, $J_{P,P}$ = 55 Hz, PFc), 18.1 (d, $J_{P,P}$ = 55 Hz, PCy_3) ppm; minor isomer: δ = 59.4 (d, $J_{P,P}$ = 48 Hz, PFc), 18.1 (d, $J_{P,P}$ = 48 Hz, PCy_3) ppm.

X-ray Crystallographic Study: Crystal data and details of the structure determination are listed in Table 4. Data collection was performed with a Bruker Smart APEX CCD (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator) area detector. The unit-cell parameters were obtained by the least-squares refinement of 8096 reflections. All the structures were solved by direct methods (SHELXS-97)[21] and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).[22] The SADABS[23] program was used for absorption correction of the structures. All non-hydrogen atoms were refined anisotropically. H atoms were in part located from difference Fourier maps; the remaining hydrogens were introduced at their idealized positions [*d*(CH) = 0.98 Å] and were refined using a riding model. The absolute configuration for complex **3a** was confirmed by evaluation of the Flack parameter.[24] CCDC-237071 (for **3a**), -237069

Table 4. Crystallographic data for compounds **3a**, **8**, and **10**.

Compound	**3a**	**8**	**10**
Formula	$C_{17}H_{19}FeP$	$C_{30}H_{34}BF_4FeN_2OPRu$	$C_{25}H_{36}BF_4FeN_2OPRu$
M	310.14	713.29	655.27
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
a/Å	9.2086(19)	9.6510(9)	8.311(3)
b/Å	11.208(2)	13.1340(13)	21.113(7)
c/Å	14.540(3)	13.3840(13)	14.944(5)
α/°	90	75.710(2)	90
β/°	90	68.860(2)	97.390(9)
γ/°	90	79.530(2)	90
V/Å^3	1500.7(5)	1525.3(3)	2600.3(15)
Z	4	2	4
T/K	293	293	293
D_c/g cm^{-3}	1.373	1.553	1.674
F_{000}	648	724	1336
μ(Mo-K_α)/cm^{-1}	1.095	1.074	1.251
$2\theta_{max}$/°	54.88	56.64	56.74
Total reflections	19492	21164	35782
Independent reflections	3423	7569	6470
Observed reflections [$I > 2\sigma(I)$]	3306	6867	4726
Parameters refined	244	411	329
$R1$/$wR2$ [$I > 2\sigma(I)$]	0.0250, 0.0627	0.0368, 0.0923	0.0577, 0.1201
$R1$/$wR2$ (all data)	0.0259, 0.0631	0.0410, 0.0951	0.0862, 0.1318
Flack's param.	0.039(12)	–	–

(for **8**) and -237070 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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