Optically active transition metal complexes. Part 123:† new chiral half-sandwich ruthenium complexes, in which the arene ligand is tethered to a PN ligand

H. Brunner,* C. Valério and M. Zabel‡

Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg, Germany

Received (in Strasbourg, France) 22nd November 1999, Accepted 7th February 2000
Published on the Web 13th April 2000

A concept is presented to fix the otherwise labile metal configuration in chiral half-sandwich ruthenium complexes by three-point-attachment ligands. Ligands of this type are prepared by tethering the backbone of the PN ligand **1** to a cyclopentadienyl (**2**) or arene system (**3**, **4**). In half-sandwich ruthenium complexes the arene-PN ligands bind in a three-point attachment (**5**, **6**) and in a bidentate PN coordination (**7**–**9**).

A wealth of arene–ruthenium complexes [(arene)Ru(LL′)X] is known, in which the arene can be a five-membered or a six-membered ring, LL′ is an unsymmetrical chelate ligand and X is a unidentate ligand. The complexes are neutral or cationic depending on the arene and the nature of LL′ and X. These complexes have a pseudo-tetrahedral structure (three-legged piano stool geometry) containing a chiral central atom. A series of these complexes has been resolved with respect to the stereogenic Ru atom.[2–18] Most of these complexes turned out to be configurationally labile at the metal center. As some of these complexes have served as enantioselective catalysts in organic transformations[19–25] it seemed desirable to stabilize the ruthenium configuration such that it cannot change. According to a concept presented in ref. 26 this can be done by using a ligand with three different bonding sites. If such a ligand, taken as a pure enantiomer, binds to a ruthenium atom in a three-point attachment, it fixes the metal configuration even if hemi-labile ligand arms dissociate intermediately, because a chiral three-armed ligand necessarily must regenerate the original ruthenium configuration. Such a three-point attachment results on tethering a bidentate PN ligand *via* its backbone to a π-bonded five- or six-membered arene. In these ligands the carbon atom in the branching position becomes a chiral center. Thus, these compounds are the centrally chiral analogues of the planar chiral approach of Ward and coworkers,[27,28] in which an arene with two different *meta*-substituents is used to fix the ruthenium configuration.

In this paper we describe our attempts to tether bidentate PN ligands to arene rings in half-sandwich ruthenium complexes. As arene-containing ligand arms we chose η^5-C_5H_4–, η^6-$C_6H_2(CH_3)_3CH_2$– and η^6-$C_6H_5(CH_2)_2$–. In all these PN ligands N was 2-pyridyl and P was diphenylphosphanyl, both attached to the chiral carbon atom in the branching position.

Results and discussion

Synthesis of the arene-PN ligands 1–4

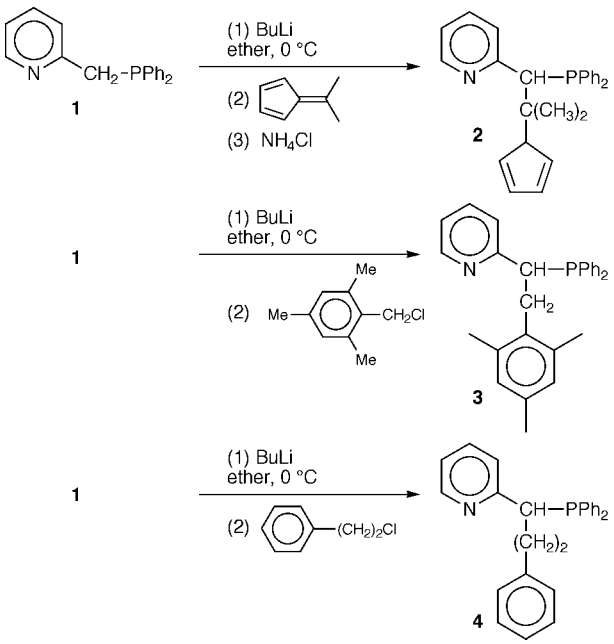
The bidentate PN precursor 2-(diphenylphosphanylmethyl)-pyridine **1**[29] was prepared by deprotonation of 2-methylpyridine with *n*-butyllithium in ether at 0 °C, followed by reaction with chlorodiphenylphosphine at −78 °C.[30,31] For the synthesis of the tridentate arene-PN ligands the same methodology was applied: deprotonation of **1** with *n*-butyllithium in ether at 0 °C and successive addition of 6,6′-dimethylfulvene or the halide compounds at 0 °C to give the ligands **2**–**4** (Scheme 1).

The reaction of **1** with 6,6′-dimethylfulvene required the addition of 1 equiv. of NH_4Cl to obtain the ligand **2** in its neutral form. A mixture of two isomers (**2a** : **2b** = 80 : 20) differing in the positions of the carbon–carbon double bonds of the cyclopentadiene part of the molecule was obtained with 69% yield. The compound was characterized by resonances at −10.29 and −9.83 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Resonances at 6.50, 6.20, 5.80 and 2.55 ppm in the ^1H NMR spectrum confirmed the presence of the cyclopentadiene ring.

The ligands **3** and **4** were isolated with 57 and 20% yields, respectively. In the $^{31}P\{^1H\}$ NMR spectra there were resonances at −2.74 (s) for **3** and 0.44 (s) ppm for **4**.

Synthesis of the ruthenium complexes 5–7

The ligand **2** was added in a CH_2Cl_2 solution to a suspension of $Ru(PPh_3)_3Cl_2$ in dried ethanol. After 3 h of reflux an orange solution had formed. Chromatography of the yellow



Scheme 1

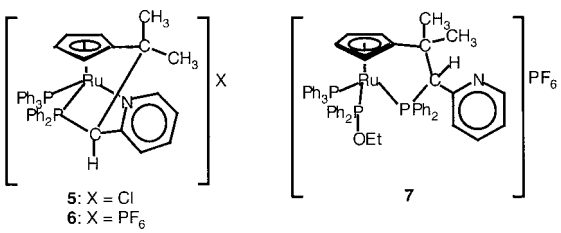
† Part 122: ref. 1.
‡ X-Ray structure analyses.

residue gave complex **5** in 92% yield as an orange yellow powder. The $^{31}P\{^{1}H\}$ NMR spectrum shows the presence of the main product **5** and a by-product (with NMR spectra similar to **5**) in a ratio of 85 : 15. Each spin system consists of two doublets, for the major compound **5** at 62.49 and 42.84 ppm (coupling constant of 36 Hz) and for the minor compound at 74.45 and 42.71 ppm (J = 34 Hz). The resonances at about 42 ppm are assigned to the triphenylphosphine ligand[32] and the resonances at 74.45 and 62.49 ppm to the phosphine substituent of ligand **2** in agreement with the $^{31}P\{^{1}H\}$ NMR data for [(*p*-cymene)Ru(**1**)Cl]PF_6, **8** and **9**.

The ^{1}H NMR spectrum of **5** exhibits an unexpected high field shift for one proton of the cyclopentadienyl ring. The Cp resonances are expected to occur at 4.5–5.5 ppm. For **5** there are three resonances at 4.53, 4.84 and 5.33 ppm with the integration 1, 2 and 1. Of these 4 protons, three belong to the cyclopentadienyl ring, the fourth is the proton of the chiral carbon atom as shown by comparison of the ^{1}H and $^{1}H\{^{31}P\}$ NMR spectra. The fourth cyclopentadienyl proton resonance appears at 3.13 ppm in agreement with literature data.[32] The FD mass spectrum of the mixture contains peaks due to $\mathbf{5}^+$, $[\mathbf{5} - Cl]^+$ and $[\mathbf{5} - PPh_3]^+$. Attempts to separate the 85 : 15 mixture were unsuccessful.

Metathesis of **5** with NH_4PF_6 in methanol replaced the Cl^- anion by the PF_6^- anion to give **6**. In the crude product, in addition to complex **6**, a similar by-product was present. However, crystallization from acetone–ethanol–ether (2 : 1 : 1) afforded the main product **6** in a pure form. The $^{31}P\{^{1}H\}$ NMR spectrum of **6** exhibits two doublets at 52.24 and 55.60 ppm (J = 37 Hz) and a resonance for PF_6 at −142.56 ppm. In the ^{1}H NMR spectrum of **6** the pyridine proton H^6 is displaced to high field (8.21 compared to 8.45 ppm for **5**). For **6** all the cyclopentadienyl proton resonances appear between 6.0 and 4.3 ppm. The X-ray structure analysis of **6** shows that the deprotonated ligand **2** coordinates in a three-point attachment through the Cp, the pyridine and the phosphine moiety (Fig. 1). The crystals contain the racemate of complex **6**.

We tried to replace the triphenylphosphine ligand in complex **6** by the optically active ligand (*S*)-$PPh_2N(Me)CHMePh$.[33] The expected product should be a pair of diastereomers that could be separated. First, the reaction of complex **6** and (*S*)-$PPh_2N(Me)CHMePh$ was carried out in dichloromethane. After 2 days at room temperature complex **6** was isolated unchanged. Then, the reaction was conducted in refluxing ethanol for 12 h. After chromatography on silica gel with diethyl ether–dichloromethane (50 : 50) a 41 : 59 mixture of compounds was obtained. The NMR data showed that none of them was the expected product. In the $^{31}P\{^{1}H\}$ NMR spectrum there were two different sets of three doublets of doublets, indicating the presence of three coordinated phosphine ligands in each of the new complexes. The ^{31}P NMR chemical shifts were 45.32, 63.03 and 133.74 ppm for the minor complex **7**, and 141.76, 140.33 and 63.04 ppm for the major compound, probably a complex with the deprotonated ligand **2** coordinating by η^5-C_5H_4 and PPh_2 and two additional PPH_2OEt ligands. Thus, in the formation of complex **7** by reaction of **6** with (*S*)-$PPh_2N(Me)CHMePh$ in ethanol the pyridine arm of ligand **2** was de-coordinated and a diphenyl(ethoxy)phosphine ligand was bound, resulting from the solvolytic cleavage of the P–N bond in (*S*)-$PPh_2N(Me)CHMePh$ while refluxing in ethanol. This was



5: X = Cl
6: X = PF_6

7

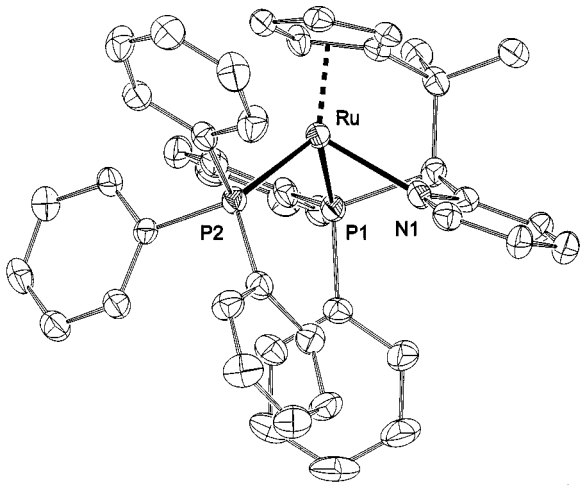


Fig. 1 View of the cation of compound **6**. Displacement ellipsoids for non-H atoms drawn at the 30% probability level (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–P1 2.289(2), Ru–P2 2.315(2), Ru–N1 2.120(6); P1–Ru–P2 106.46(8), P1–Ru–N1 77.1(1), P2–Ru–N1 101.6(1).

corroborated by the FD mass spectrum. The peak m/z = 976 could be assigned to the cation of complex **7**. The structure of complex **7** was confirmed by X-ray structural analysis of a pale yellow crystal obtained by diffusion of *n*-hexane into a solution of **7** in dichloromethane at room temperature (Fig. 2). The crystals contain the racemate of complex **7**.

Synthesis of the ruthenium complexes 8 and 9

We attempted to synthesize complexes analogous to **5** and **6** with the η^6-arene-PN ligands **3** and **4**. As a precursor we chose $[(p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$. The first step was the synthesis of complexes in which the ligands **3** or **4** were PN-coordinated to ruthenium. In the next step the *p*-cymene ligand should be replaced by the arene of ligands **3** and **4**. In the literature there are a few reports of such arene exchange reactions.[34,35]

The reaction of $[(p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ with ligands **3** and **4**, respectively, was carried out analogously to similar reactions reported in ref. 36, giving complexes **8** and **9** as pairs of diastereomers. For both complexes the less soluble diastereoisomers (the major diastereomers in the mixtures obtained) could be separated by repeated fractional crys-

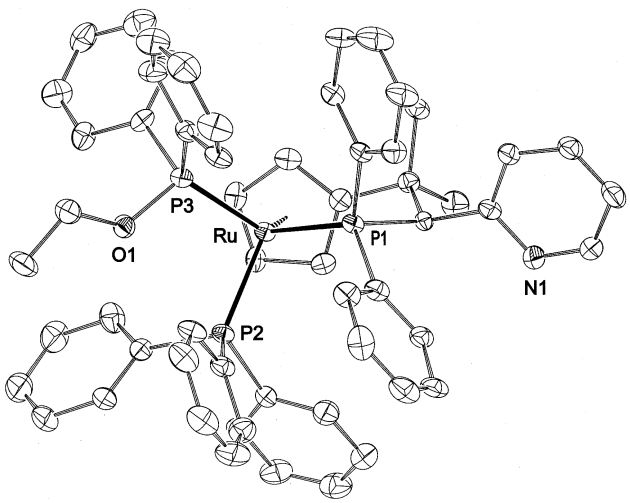
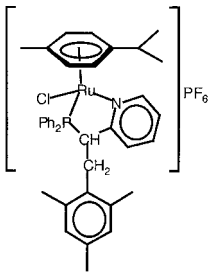
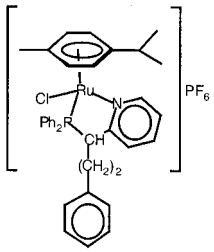


Fig. 2 View of the cation of compound **7**. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–P1 2.363(2), Ru–P2 2.352(2), Ru–P3 2.324(2); P1–Ru–P2 101.78(8), P1–Ru–P3 105.02(8), P2–Ru–P3 92.95(8).



8



9

tallization of the diastereoisomer mixtures from acetone–ethanol. Up to now it has not been possible to exchange the cymene ligand in **8** and **9** for the arene of the PN-coordinated ligands **3** and **4** (reflux in dichloromethane, chlorobenzene, and acetonitrile, irradiation).

Experimental

All the syntheses were carried out under an atmosphere of dry nitrogen with standard Schlenk techniques. The solvents were dried and saturated with N_2 before use. Chromatography: silica gel 60 (Merck). NMR spectra: Bruker ARX 400 spectrometer; IR spectra: Beckman IR 4240; mass spectra: Finnigan Mat 95 (FD and FAB) and Finnigan 112 S (EI). 6,6′-Dimethylfulvene,[37] $Ru(PPh_3)_3Cl_2$[38] and $[(p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$[39] were prepared according to published methods.

2-(Diphenylphosphanylmethyl)pyridine 1

The compound was synthesized as described.[29–31] Distillation under high vacuum (bp 140 °C/10^{-3} mmHg) gave a pale yellow solid, which was dissolved in ether and filtered to obtain a colourless solution. After evaporation of the solvent the residue was washed several times with pentane. The product was a fine white powder.

1: Yield 50–57%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.38 (m, 1H, H^6-py), 7.36–7.31 (m, 5H + 4H, Ph + H^4-py), 7.21–7.17 (m, 6H, Ph), 6.92 (m, 1H, H^3-py), 6.87 (m, 1H, H^5-py), 3.66 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): δ −9.75 (s).

1-Diphenylphosphanyl-2,2-dimethyl-2-cyclopentadienyl-1-(2-pyridyl)ethane 2

n-Butyllithium (6.07 mmol, 3.8 mL of a 1.6 M solution in *n*-hexane) was added dropwise (1 h) at 0 °C to a solution of **1** (1.69 g, 6.07 mmol) in 70 mL of diethyl ether. To the deep red solution was added dropwise a solution of 2,2-dimethylfulvene (0.75 mL, 6.22 mmol) in 5 mL of diethyl ether. The solution was stirred for 2 h at 0 °C and 1 h at room temperature. Then a degassed solution of ammonium chloride (0.325 g, 6.07 mmol) in water was added and the solution was stirred for 30 min. The yellow solution was filtered to remove lithium chloride and evaporated to dryness. The residue obtained was dissolved in diethyl ether and chromatographed on a short SiO_2 column with diethyl ether. After evaporation of the solvent the product was washed with pentane. It was obtained as a fine white powder (mixture of isomers 81 : 19).

2: Yield 1.60 g (4.19 mmol, 69%). Mp 90 °C. $C_{26}H_{26}NP$ (383.5). EI-MS: *m/z* 383 (M, 18), 277 [M − $C(CH_3)_2C_5H_5$, 100]. ^{1}H NMR (400 MHz, $CDCl_3$, TMS; signals of minor isomer in parentheses): δ 8.35 (8.34) (m, 1H, H^6-py), 7.67 (m, 2H, Ph), 7.25 (m, 6H, Ph + H^4-py), 6.95–6.90 (m, 4H, Ph + H^3-py), 6.82 (m, 1H, H^5-py), 6.53 (6.19) (m, 1H, Cp), 6.17 (6.09) (m, 1H, Cp), 5.80 (6.05) (m, 1H, Cp), 4.25 (m, 1H, CH), 2.55 (2.70) (m, 2H, CH_2), 1.43 (1.38) (s, 3H, CH_3), 1.23 (1.29) (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): δ −10.29 (−9.83) (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.38 (160.43) (d, C^2-py, J_{CP} = 5.2 Hz), 154.03 (156.20) (s, C_q, Cp), 148.17 (s, C^6-py), 139.21 (139.29) (d, C_q, PhP, J_{CP} = 15.4 Hz), 138.16 (138.03) (d, C_q, PhP, J_{CP} = 12.9 Hz), 134.72 (134.69) (s, C^4-py), 134.29 (134.47) (d, *o*-PhP, J_{CP} = 22.1 Hz), 133.80 (133.73) (d, *o*-PhP, J_{CP} = 22.5 Hz), 133.07 (131.51) (s, Cp), 132.81 (131.29) (d, Cp, J_{CP} = 1.2 Hz), 128.34 (128.43) (d, Cp, J_{CP} = 0.7 Hz), 128.14 (d, *p*-PhP, J_{CP} = 7.9 Hz), 127.89 (d, *m*-PhP, J_{CP} = 8.1 Hz), 127.40 (127.42) (d, *m*-PhP, J_{CP} = 8.2 Hz), 126.06 (s, *p*-PhP), 125.47 (125.31) (d, C^3-py, J_{CP} = 6.4 Hz), 120.52 (s, C^5-py), 57.97 (55.78) (d, CH, J_{CP} = 19.1 Hz), 40.62 (41.13) (s, CH_2), 39.59 (41.02) (d, C_q, J_{CP} = 17.8 Hz), 27.78 (d, CH_3, J_{CP} = 10.1 Hz), 26.25 (d, CH_3, J_{CP} = 11 Hz).

1-Diphenylphosphanyl-3-(2,4,6-trimethylphenyl)-1-(2-pyridyl)-ethane 3 and 1-diphenylphosphanyl-3-phenyl-1-(2-pyridyl)-propane 4

n-Butyllithium (5.65 mmol, 3.53 mL of a 1.6 M solution in *n*-hexane) was added dropwise (1 h) at 0 °C to a solution of **1** (1.57 g, 5.65 mmol) in 70 mL of diethyl ether. To the deep red solution was added dropwise 5.75 mmol of aryl halide in 5 mL diethyl ether. The solution was stirred for 2 h at 0 °C and 1 h at room temperature. The yellow solution was filtered to remove lithium chloride and evaporated to dryness. The yellow residue was purified by chromatography in diethyl ether on a short SiO_2 column. After removal of the solvent the product was washed with pentane. It was obtained as a fine white powder.

3: Aryl halide = 2,4,6-trimethylbenzylchloride. Yield 1.32 g (3.22 mmol, 57%). Mp 105–107 °C. $C_{28}H_{28}NP$ (409.5). EI-MS: *m/z* 409 (M, 17.5), 394 (M − CH_3, 100). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.47 (m, 1H, H^6-py), 7.67 (m, 2H, Ph), 7.34 (m, 6H, Ph + H^4-py), 7.13 (m, 3H, Ph), 6.93 (m, 1H, H^3-py), 6.70 (m, 1H, H^5-py), 6.58 (s, 2H, C_6H_2), 3.72 (ddd, 1H, J_{HP} = 7.6 Hz, J = 11.2 Hz, J = 3.4 Hz, CH), 3.27 (ddd, 1H, J_{HP} = 6.0 Hz, J = 11.2 Hz, J = 13.8 Hz, CH_2), 2.84 (ddd, 1H, J_{HP} = 6.7 Hz, J = 13.8 Hz, J = 3.4 Hz, CH_2), 2.13 (s, 3H, *p*-CH_3), 1.62 (s, 6H, *o*-CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): δ −2.74 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.47 (d, C^2-py, J_{CP} = 6.2 Hz), 149.38 (s, C^6-py), 138.21 (d, C_q, PhP, J_{CP} = 17.5 Hz), 136.93 (d, C_q, PhP, J_{CP} = 14.9 Hz), 136.74 (s, *o*-Ar), 135.47 (s, C^4- py), 135.01 (s, *p*-Ar), 134.90 (d, *o*-PhP, J_{CP} = 21.5 Hz), 133.45 (d, C_q, Ar, J_{CP} = 12.3 Hz), 133.39 (d, *o*-PhP, J_{CP} = 19.1 Hz), 129.23 (s, *p*-PhP), 128.74 (s, *m*-Ar), 128.26 (d, *m*-PhP, J_{CP} = 7.6 Hz), 128.22 (s, *p*-PhP), 127.97 (d, *m*-PhP, J_{CP} = 6.8 Hz), 124.59 (d, C^3-py, J_{CP} = 4.9 Hz), 121.04 (s, C^5-py), 47.89 (d, CH, J_{CP} = 11.6 Hz), 32.94 (d, CH_2, J_{CP} = 24.5 Hz), 20.70 (s, *p*-CH_3), 19.56 (s, *o*-CH_3).

4: Aryl halide = 1-chloro-2-phenylethane. Yield 0.43 g (1.13 mmol, 20%). Mp 63–65 °C. $C_{26}H_{24}NP$ (381.5). EI-MS: *m/z* 381.3 (M, 18), 277 (M − $CHCH_2C_6H_5$, 100). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.54 (m, 1H, H^6-py), 7.48 (m, 2H, Ph), 7.44 (m, 3H, Ph), 7.25 (m, 1H, H^4-py), 7.15 (m, 2H, Ph), 7.10–7.00 (m, 6H, Ph), 6.92 (m, 1H, H^3-py), 6.83 (m, 2H, Ph), 6.70 (m, 1H, H^5-py), 3.67 (m, 1H, CH), 2.60 (m, 1H, CH_2), 2.41 (m, 2H, CH_2), 2.00 (m, 1H, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): δ 0.44 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.95 (d, C^2-py, J_{CP} = 7.2 Hz), 149.24 (s, C^6-py), 141.44 (s, C_q, Ph, 136.91 (d, C_q, PhP, J_{CP} = 14.5 Hz), 136.38 (d, C_q, PhP, J_{CP} = 16.0 Hz), 135.99 (s, C^4-py), 133.85 (d, *o*-PhP, J_{CP} = 20.6 Hz), 133.12 (d, *o*-PhP, J_{CP} = 19.0 Hz), 129.11 (s, *p*-PhP), 128.59 (s, *m*-Ph), 128.49 (d, *m*-PhP, J_{CP} = 7.3 Hz), 128.29 (s, *p*-PhP), 128.23 (s, *o*-Ph), 127.82 (d, *m*-PhP, J_{CP} = 6.9 Hz), 125.80 (s, *p*-Ph), 124.22 (d, C^5-py, J_{CP} = 5.9 Hz), 121.11 (s, C^3-py), 46.42 (d, CH, J_{CP} = 13.2 Hz), 33.93 (d, CH_2, J_{CP} = 22.3 Hz), 33.88 (d, CH_2, J_{CP} = 13.5 Hz).

{[η^5-$C_5H_4C(CH_3)_2CH(PPh_2)C_5H_4N$]Ru($PPh_3$)}Cl 5

To a solution of 1.1 mmol (1.06 g) of $Ru(PPh_3)_3Cl_2$ in 100 mL of dried ethanol was added 1.1 mmol (0.42 g) of **2** in 25 mL of dichloromethane. After 3 h reflux the solution was orange-red.

The residue obtained after evaporation was washed several times with pentane to remove free triphenylphosphine. Chromatography with CH_2Cl_2–acetone (50 : 50) on a SiO_2 column gave a 85 : 15 mixture of two compounds as a broad orange band.

5 (and by-product): Yield 92%. Mp 195 °C (decomp.). Anal. found: C, 66.35; H, 5.48; N, 1.72. Calcd.: C, 66.07; H, 5.30; N, 1.75% for $C_{44}H_{40}ClNP_2Ru \cdot H_2O$ (799.3). FD-MS (CH_2Cl_2): *m/z* 781 (M, 100), 746 (M − Cl, 8), 519 (M − PPh_3, 64). ^1H NMR (400 MHz, $CDCl_3$, TMS; signals of by-product in parentheses): δ 8.45 (8.40) (dd, 1H, H^6-py), 7.86 (br t, 2H, Ph), 6.65–7.40 (m, 26H, PPh_3 + PPh_3 + H-py), 6.01 (5.97) (d, 1H, H-py), 5.33 (5.23) (br s, 1H, Cp), 4.84 (5.10) (m, 1H, Cp), 4.84 (m, 1H, CH), 4.53 (4.75) (br s, 1H, Cp), 3.13 (3.44) (m, 1H, Cp), 1.32 (1.13) (s, 3H, CH_3), 1.02 (1.12) (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): δ 62.49, 42. 84 (d, J = 36 Hz) [74.45, 42.71 (d, J = 34 Hz)].

{[η^5-$C_5H_4C(CH_3)_2CH(PPh_2)C_5H_4N$]Ru($PPh_3$)}$PF_6$ 6

5 (135 mg, 0.173 mmol) was dissolved in dried methanol and 43 mg (0.26 mmol) of NH_4PF_6 were added. The mixture was stirred for 4 h at room temperature. The solvent was evaporated and the solution in dichloromethane was filtered to remove inorganic salts. After chromatography on a short silica gel column with acetone–methanol (60 : 40) **6** was obtained as a yellow powder. The crystallization at −25 °C in a mixture of acetone–ethanol–diethyl ether led to the formation of small orange needles suitable for X-ray analysis.

6: Yield 70%. Mp 220 °C (decomp.). Anal. found: C, 55.35; H, 5.14; N, 1.36. Calcd.: C, 55.38; H, 4.34; N, 1.44% for $C_{44}H_{40}F_6NP_3Ru \cdot CH_2Cl_2$ (975.7). FD-MS (CH_2Cl_2): *m/z* 746 (cation of **6**). ^1H NMR (400 MHz, acetone-d_6, TMS): δ 8.21 (m, 2H, Ph + H^6-py), 8.07 (m, 3H, Ph), 7.57–7.09 (m, 20H, Ph + H^4-py), 6.94 (m, 2H, Ph), 6.48 (m, 2H, $H^{3,5}$-py), 6.09 (s, 1H, Cp), 5.70 (d, 1H, Cp, J = 10.7 Hz), 5.10 (br s, 1H, CH), 4.61 (s, 1H, Cp), 4.33 (s, 1H, Cp), 1.27 (s, 3H, CH_3), 1.15 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6, H_3PO_4 ext.): δ 52.24, 55.60 (d) (J = 37 Hz), −142.56 (PF_6). $^{13}C\{^1H\}$ NMR (acetone-d_6, TMS): δ 166.57 (d, C^2-py, J = 5.3 Hz), 160.81 (d, C^6-py, J = 1.9 Hz), 138.77 (s, C^4-py), 137.42 (d, C_q, PPh_3, J = 41.7 Hz), 136.49 (d, C_q, PPh_2, J = 40.0 Hz), 136.20 (d, C_q, PPh_2, J = 31.4 Hz), 134.52 (d, *o*-PhP, PPh_3, J = 12.1 Hz), 132.36 (d, *o*-PPh, PPh_2, J = 9.9 Hz), 132.26 (d, *p*-PPh, PPh_2, J = 2.4 Hz), 130.79 (d, *p*-PhP, PPh_3, J = 2.0 Hz), 130.22 (d, *p*-PPh, PPh_2, J = 2.4 Hz), 129.68 (d, *o*-PPh, PPh_2, J = 10.4 Hz), 129.38 (d, *m*-PPh, PPh_2, J = 9.5 Hz), 128.96 (d, *m*-PhP, PPh_3, J = 9.6 Hz), 127.99 (d, *m*-PPh, PPh_2, J = 7.8 Hz), 124.91 (s, C^3-py), 100.90 (s, C^5-py), 93.66 (d, C_q, Cp, J = 11.9 Hz), 84.85 (d, Cp, J = 10.6 Hz), 84.58 (s, Cp), 83.13 (d, Cp, J = 6.7 Hz), 82.88 (d, Cp, J = 6.5 Hz), 72.25 (s, CH), 39.95 (d, C_q, J = 7.8 Hz), 28.57 (d, CH_3, J = 43.0 Hz), 28.53 (d, CH_3, J = 52.3 Hz).

Synthesis of {η^5-$C_5H_4C(CH_3)_2CH(PPh_2)C_5H_4N$]Ru-[$PPh_2(OCH_2CH_3)$]$PPh_3$}$PF_6$ 7

6 (90 mg, 0.1 mmol) and 96 mg (0.3 mmol) of (*S*)-$PPh_2N(Me)CHMePh$ in 50 mL of dried ethanol were refluxed for 12 h under nitrogen. The pale yellow solution was evaporated and the yellow residue was washed several times with pentane–diethyl ether to remove free phosphine ligands. After purification by chromatography on silica gel with CH_2Cl_2–diethyl ether (50 : 50) the NMR spectrum of the mixture showed that two compounds were present: **7** (41%) and another ruthenium complex with deprotonated **2** and two diphenyl(ethoxy)phosphane ligands. By slow diffusion of *n*-hexane into a solution of the mixture in dichloromethane it was possible to crystallize **7** as pale yellow crystals suitable for X-ray structure analysis.

7: Mp 160 °C (decomp.). Anal. found: C, 59.35; H, 5.53; N, 0.99. Calcd.: C, 58.76; H, 4.76; N, 1.16% for $C_{58}H_{55}F_6NOP_4Ru \cdot CH_2Cl_2$. FAB-MS ($CH_2Cl_2$): *m/z* 976 (M, 32) (M = cation of **7**), 714 (M − PPh_3, 100). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.46 (m, 1H, H^6-py), 7.85 (m, 2H, Ph), 7.76 (m, 2H, Ph), 7.60–6.87 (m, 34H, PPh_3, PPh_2, H-py), 5.42 (d, 1H, Cp, J = 8.0 Hz), 5.02 (d, 1H, Cp, J = 9.2 Hz), 4.90 (br s, 1H, Cp), 4.62 (br s, 1H, Cp), 4.16 (m, 1H, CH), 3.15 (m, 2H, CH_2O), 1.02 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 0.23 (t, 3H, CH_3, J = 7.1 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): δ 133.74 (dd, PPh_2O, $J_{PO\text{-}PPh_3}$ = 27.0 Hz, $J_{PO\text{-}P2}$ = 35.1 Hz), 63.03 (dd, PPh_2**2**, $J_{P2\text{-}PPh_3}$ = 51.6 Hz), 45.32 (dd, PPh_3), −143.58 (PF_6).

[(p-$CH_3C_6H_4CH(CH_3)_2$)Ru(3)Cl]PF_6 8 and [(p-$CH_3C_6H_4$-$CH(CH_3)_2$)Ru(4)Cl]PF_6 9

[(p-$CH_3C_6H_4CH(CH_3)_2$)$RuCl_2$]$_2$ (310 mg, 0.5 mmol) and 1.1 mmol of ligand **3** or **4** were dissolved in 6 mL of ethanol and 2 mL of dichloromethane was added. After 20 h stirring at room temperature the red solution was filtered and evaporated. The red-orange residue was dissolved in 10 mL of methanol and 195 mg (1.02 mmol) of NH_4PF_6 was added. After 1 h an orange powder had precipitated. The solution was half-evaporated and filtered. The orange precipitate was **8a**/**b** or **9a**/**b**, respectively, enriched in the **a** isomers. The mother liquor was evaporated. The residue was dissolved in CH_2Cl_2 and filtered to remove inorganic salts. After concentration and addition of diethyl ether a yellow powder precipitated containing **8a**/**b** or **9a**/**b** enriched in the **b** isomers.

8: Yield 77% (diastereomer ratio 71 : 29). Mp 150 °C (decomp.). Anal. found: C, 55.53; H, 5.26; N, 1.70. Calcd.: C, 55.31; H, 5.13; N, 1.69% for $C_{38}H_{42}ClF_6NP_2Ru$. FAB-MS (CH_2Cl_2): *m/z* 680.2 (cation of **8**).

8a (major diastereomer): ^1H NMR (400 MHz, acetone-d_6, TMS): δ 9.75 (m, 1H, H^6-py), 8.12 (m, 2H, *o*-PhP), 7.80–7.50 (m, 11H, $H^{3,4,5}$-py + PPh_2), 6.70 (d, 2H, C_6H_2), 6.50 (d, 1H, cymene, J = 7.3 Hz), 6.42 (d, 1H, cymene, J = 7.3 Hz), 6.14 (d, 1H, cymene, J = 6.3 Hz), 5.94 (d, 1H, cymene, J = 6.3 Hz), 5.10 (m, 1H, CH), 4.60 (m, 1H, CH_2), 3.47 (m, 1H, CH_2), 2.45 (m, 1H, Pr^i-CH), 2.19 (s, 3H, CH_3, *p*-arene), 2.17 (s, 3H, CH_3, cymene), 1.88 (s, 3H, CH_3, *o*-arene), 1.83 (s, 3H, CH_3, *o*-arene), 0.98 (d, 3H, J = 6.9 Hz, CH_3, cymene), 0.63 (d, 3H, J = 6.9 Hz, CH_3, cymene). $^{31}P\{^1H\}$ NMR (acetone-d_6, H_3PO_4 ext.): δ 60.55 (s), −143.59 (PF_6).

8b (minor diastereomer): ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 9.43 (m, 1H, H^6-py), 8.06 (m, 2H, *o*-PhP), 7.70–7.32 (m, 10H, $H^{3,5}$-py + PPh_2), 7.16 (m, 1H, H^4-py), 6.70 (d, 2H, C_6H_2), 5.79 (d, 1H, cymene, J = 6.2 Hz), 5.74 (d, 1H, cymene, J = 6.2 Hz), 5.66 (d, 1H, cymene, J = 6.2 Hz), 5.62 (d, 1H, cymene, J = 6.2 Hz), 4.95 (m, 1H, CH), 3.40 (m, 1H, CH_2), 3.16 (m, 1H, CH_2), 2.19 (m, 1H, Pr^i-CH), 2.18 (s, 3H, CH_3, cymene), 1.87 (s, 6H, CH_3, *m*-arene), 1.68 (s, 3H, CH_3, *p*-arene), 0.96 (d, 3H, J = 6.9 Hz, CH_3, cymene), 0.90 (d, 3H, J = 6.9 Hz, CH_3, cymene). $^{31}P\{^1H\}$ NMR ($CDCl_3$, H_3PO_4 ext.): δ 72.00 (s), −143.58 (PF_6).

9: Yield 81% (diastereomer ratio 78 : 22). Mp 140 °C (decomp.) Anal. found: C, 51.46; H, 4.71; N, 1.51. Calcd.: C, 50.39; H, 4.58; N, 1.59% for $C_{36}H_{38}ClF_6NP_2Ru \cdot CH_2Cl_2$. FAB-MS ($CH_2Cl_2$): *m/z* 652.2 (cation of **9**).

9a (major diastereomer): ^1H NMR (400 MHz, acetone-d_6, TMS): δ 9.69 (m, 1H, H^6-py), 8.20–6.90 (m, 18H, $H^{3,4,5}$-py + PPh_2 + Ph), 6.10 (d, 1H, cymene, J = 6.2 Hz), 6.07 (d, 1H, cymene, J = 6.2 Hz), 5.80 (d, 1H, cymene, J = 6.2 Hz), 5.34 (d, 1H, cymene, J = 6.2 Hz), 4.61 (m, 1H, CH), 2.86 (s, 1H, CH_2), 2.82 (s, 1H, CH_2), 2.61 (m, 1H, CH_2), 2.58 (m, 1H, Pr^i-CH), 2.20 (s, 1H, CH_2), 1.93 (s, 3H, CH_3, cymene), 0.99 (d, 3H, J = 6.9 Hz, CH_3, cymene), 0.77 (d, 3H, J = 6.9 Hz, CH_3, cymene). $^{31}P\{^1H\}$ NMR (acetone-d_6, H_3PO_4 ext.): δ 59.23 (s), −142.55 (PF_6). $^{13}C\{^1H\}$ NMR (acetone-d_6, TMS): δ 167.35 (d, C^2-py, J_{CP} = 7.8 Hz), 159.83 (s, C^6-py), 141.47 (s, C_q, Ph), 141.12 (s, C^4-py), 136.93 (d, *o*-PhP, J_{CP} = 10.4 Hz), 136.58 (s,

C_q, PhP), 136.08 (s, C_q, PhP), 133.35 (d, *p*-PhP, $J_{CP} = 2.7$ Hz), 132.41 (d, *p*-PhP, $J_{CP} = 2.6$ Hz), 132.14 (d, *o*-PhP, $J_{CP} = 8.7$ Hz), 130.28 (d, *m*-PhP, $J_{CP} = 10.1$ Hz), 129.45 (d, *m*-PhP, $J_{CP} = 11.1$ Hz), 129.25 (s, *m*-Ph), 129.19 (s, *o*-Ph), 126.99 (s, *p*-Ph), 126.18 (s, C^3-py), 125.88 (d, C^5-py, $J_{CP} = 11.2$ Hz), 110.92 (s, C_q, cymene), 102.16 (s, C_q, cymene), 96.97 (d, $J = 6.0$ Hz, cymene), 92.01 (d, $J = 8.1$ Hz, cymene), 91.97 (d, $J = 8.7$ Hz, cymene), 89.18 (d, $J = 2.4$ Hz, cymene), 51.71 (d, CH, $J_{CP} = 28.8$ Hz), 35.84 (s, CH_2), 35.13 (d, CH_2, $J_{CP} = 6.7$ Hz), 30.86 (s, Pr^i-CH), 22.52 (s, CH_3, cymene), 21.76 (s, CH_3, cymene), 17.85 (s, CH_3, cymene).

9b (minor diastereomer): ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.47 (m, 1H, H^6-py), 8.00–6.91 (m, 18H, $H^{3,4,5}$-py + PPh_2 + Ph), 5.88 (d, 1H, cymene, $J = 6.2$ Hz), 5.80 (d, 1H, cymene, $J = 6.2$ Hz), 5.50 (s, 2H, cymene), 4.42 (m, 1H, CH), 2.84 (m, 1H, CH_2), 2.56 (m, 2H, CH_2), 2.30 (m, 1H, Pr^i-CH), 2.10 (m, 1H, CH_2), 1.76 (s, 3H, CH_3, cymene), 0.94 (d, 3H, $J = 6.9$ Hz, CH_3, cymene), 0.78 (d, 3H, $J = 6.9$ Hz, CH_3, cymene). $^{31}P\{^1H\}$ NMR (acetone-d_6, H_3PO_4 ext.): δ 74.98 (s), -143.54 (PF_6).

X-Ray structure analysis of 6 and 7

Data were collected with an imaging plate diffraction system (Stoe-IPDS, Stoe & CIE GmbH, Darmstadt, Germany), using Mo-Kα radiation, $\lambda = 0.710\,73$ Å, with a graphite monochromator. No absorption correction was applied. For data reduction the Stoe-IPDS software (Stoe, 1998) was used.[40] The structure was solved with direct methods (SIR-97; Altomare, 1993)[41] and refined by full-matrix least-squares techniques (SHELX97; Sheldrick, 1997).[42] All H atoms were included at calculated positions and refined using a riding model.

Crystal data of 6. $C_{44}H_{40}F_6NP_3Ru$, $M = 890.75$, $T = 297(2)$ K, clear yellow needles, crystal system: monoclinic, $P2_1/c$, $a = 10.8328(12)$, $b = 24.560(2)$, $c = 17.0067(15)$ Å, $\beta = 101.074(12)°$, $U = 4440.4(7)$ Å^3, $Z = 4$, $\mu = 0.52$ mm^{-1}, reflections collected = 57 915, independent = 8584, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0573$, $wR_2 = 0.1154$.

Crystal data of 7. $C_{58}H_{55}F_6NOP_4Ru$, $M = 1120.98$, $T = 297(2)$ K, clear yellow needles, crystal system: triclinic, $P\bar{1}$, $a = 10.9743(11)$, $b = 12.4718(14)$, $c = 21.493(3)$ Å, $\alpha = 92.052(14)°$, $\beta = 94.429(14)°$, $\gamma = 91.384(13)°$, $U = 2930.0(6)$ Å^3, $Z = 2$, $\mu = 0.43$ mm^{-1}, reflections collected = 41 926, independent = 10 664, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0847$, $wR_2 = 0.1836$.

CCDC reference number 440/168. See http://www.rsc.org/suppdata/nj/a9/a909262e/ for crystallographic files in .cif format.

Acknowledgements

We thank the Alexander von Humboldt foundation for a research grant for C.V. and the Fonds der Chemischen Industrie for their support of this work.

References

1 Part 122: H. Brunner, M. Niemetz and M. Zabel, *Z. Naturforsch.*, 1999, in press.
2 N. Gül and J. H. Nelson, *Polyhedron*, 1999, **18**, 1835.
3 N. Gül and J. H. Nelson, *Organometallics*, 1999, **18**, 709.
4 H. D. Hansen, K. Maitra and J. H. Nelson, *Inorg. Chem.*, 1999, **38**, 2150.
5 H. Brunner, B. Nuber and M. Prommesberger, *Tetrahedron: Asymmetry*, 1998, **9**, 3223.
6 H. Brunner, B. Nuber and T. Neuhierl, *Eur. J. Inorg. Chem.*, 1998, 1877.
7 D. Enders, H. Gielen, G. Raabe, J. Runsink and H. J. Teles, *Chem. Ber./Recl.*, 1997, **130**, 1253.
8 H. Brunner, R. Oeschey and B. Nuber, *J. Chem. Soc., Dalton Trans.*, 1996, 1499.
9 H. Brunner, R. Oeschey and B. Nuber, *Organometallics*, 1996, **15**, 3616.
10 I. De los Rios, M. J. Tenorio, M. C. Puerta and P. Valerga, *J. Organomet. Chem.*, 1996, **525**, 57.
11 H. Brunner, R. Oeschey and B. Nuber, *J. Organomet. Chem.*, 1996, **518**, 47.
12 S. Attar, V. J. Catalano and J. H. Nelson, *Organometallics*, 1996, **15**, 2932.
13 S. Attar, J. H. Nelson, J. Fischer, A. de Cian, J.-P. Sutter and M. Pfeffer, *Organometallics*, 1995, **14**, 4559.
14 H. Brunner, R. Oeschey and B. Nuber, *Inorg. Chem.*, 1995, **34**, 3349.
15 (*a*) H. Brunner, R. Oeschey and B. Nuber, *Angew. Chem.*, 1994, **106**, 941; (*b*) *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 866.
16 S. K. Mandal and A. R. Chakravarty, *Inorg. Chem.*, 1993, **32**, 3851.
17 S. K. Mandal and A. R. Chakravarty, *J. Chem. Soc., Dalton Trans.*, 1992, 1627.
18 S. K. Mandal and A. R. Chakravarty, *J. Organomet. Chem.*, 1991, **417**, C59.
19 S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1995, **117**, 7562.
20 J. Takehara, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, *Chem. Commun.*, 1996, 233.
21 K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, *Angew. Chem.*, 1997, **109**, 297; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 285.
22 R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97.
23 D. L. Davies, J. Fawcett, S. A. Garrat and D. R. Russell, *Chem. Commun.*, 1997, 1351.
24 D. Carmona, C. Cativiela, S. Elipe, F. J. Lahoz, M. P. Lamata, M. Pilar, L.-R. de Viu, L. A. Oro, C. Vega and F. Viguri, *Chem. Commun.*, 1997, 2351.
25 H. Brunner and M. Prommesberger, *Tetrahedron: Asymmetry*, 1998, **9**, 3231.
26 H. Brunner, H.-J. Lautenschlager, W. A. König and R. Krebber, *Chem. Ber.*, 1990, **123**, 847.
27 (*a*) B. Therrien and T. R. Ward, *Angew. Chem.*, 1999, **111**, 418; (*b*) *Angew. Chem., Int. Ed.*, 1999, **38**, 405.
28 B. Therrien, A. König and T. R. Ward, *Organometallics*, 1999, **18**, 1565.
29 W. Knebel and R. J. Angelici, *Inorg. Chim. Acta*, 1973, **7**, 713.
30 M. Alvarez, N. Lugan and R. Mathieu, *J. Chem. Soc., Dalton Trans.*, 1994, 2755.
31 H. Yang, M. Alvarez–Gressier, N. Lugan and R. Mathieu, *Organometallics*, 1997, **16**, 1401.
32 A. M. Z. Slawin, D. J. Williams, J. Crosby, J. A. Ramsden and C. White, *J. Chem. Soc., Dalton Trans.*, 1988, 2491.
33 H. Brunner, *Angew. Chem.*, 1999, **111**, 1249; *Angew. Chem., Int. Ed.*, 1999, **38**, 1194.
34 P. D. Smith and A. H. Wright, *J. Organomet. Chem.*, 1998, **559**, 141.
35 B. Therrien, T. R. Ward, M. Pilkington, C. Hoffman, F. Gilardoni and J. Weber, *Organometallics*, 1998, **17**, 330.
36 H. Yang, N. Lugan and R. Mathieu, *An. Quim., Int. Ed.*, 1997, **93**, 28.
37 K. J. Stone and R. D. Little, *J. Chem. Org.*, 1984, **49**, 1849.
38 P. S. Hallman, T. A. Stephenson and G. Wilkinson, *Inorg. Synth.*, 1970, **12**, 237.
39 M. A. Bennett, G. B. Robertson and A. K. Smith, *J. Organomet. Chem.*, 1972, **43**, C41.
40 *STOE IPDS-software*, version 2.89, STOE & Cie GmbH, Darmstadt, Germany, 1998.
41 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
42 G. M. Sheldrick, *SHELXL97*, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.