Bis(pyrazol-1-yl)acetato Ligands in Ruthenium Chemistry: Syntheses and Structures of Ruthenium(II) and Ruthenium(III) Complexes with bpza and bdmpza

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New ruthenium(II) and ruthenium(III) complexes with the ligands bis(pyrazol-1-yl)acetate (bpza) and bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) are reported. The reaction of ruthenium trichloride hydrate, H[bpza], and excess PPh_3 yielded $[Ru(bpza)Cl(PPh_3)_2]$ as a racemic mixture of an unsymmetrical isomer with traces of a symmetrical isomer. Similar reaction conditions using the more bulky H[bdmpza] yielded $[Ru(bdmpza)Cl_2(PPh_3)]$. Reaction of K[bpza] with $[RuCl_2(PPh_3)_3]$ offered a second route to $[Ru(bpza)Cl(PPh_3)_2]$. Also, $[Ru(bdmpza)Cl(PPh_3)_2]$ was accessed by this synthetic approach. All three new complexes were characterized by X-ray structure determination.

Introduction

The cyclopentadienylruthenium(II) complex $[Ru(Cp)Cl(PPh_3)_2]$ has been used for more than 30 years as a versatile starting material in thousands of reactions in organometallics.[1–6] In the last ten years this chemistry has been extended to $[Ru(Cp^*)Cl(PPh_3)_2]$[7–9] and, due to the firmly established analogy between the cyclopentadienyl ligand and the hydrotris(pyrazol-1-yl)borato ligand (Tp), also to $[Ru(Tp)Cl(PPh_3)_2]$.[10,11] It is thought that the differences in the reactivity of these complexes are essentially determined by the cone angle of triphenylphosphane (145°) as well as the cone angles of the Cp (150°), Cp* (182°), and Tp (199°) ligands.[10–14] Structural data of the complexes, confirming these steric effects, have been available for a long time.[4–6,8–10] Therefore, these bulky ligands are an important factor in the chemistry of these complexes by inducing lability of one of the triphenylphosphane ligands.

Recently, bis(pyrazol-1-yl)acetato ligands, a new class of scorpionate ligands with binding properties similar to those of the cyclopentadienyl or the hydrotris(pyrazol-1-yl)borato ligand (Figure 1), have been introduced to organometallic and coordination chemistry.[15–20] The binding properties as well as the steric hindrance of the two new ligands bis(pyrazol-1-yl)acetate (bpza) and bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) are between those of a Cp ligand and a Cp* ligand.

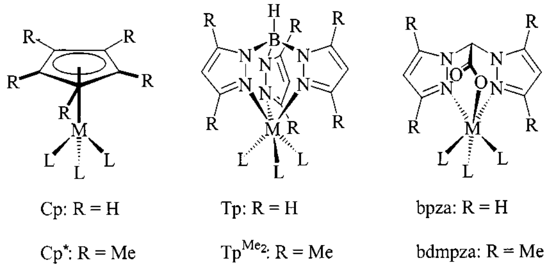
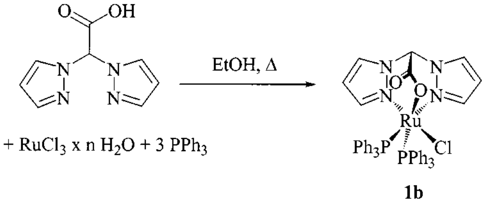


Figure 1. Metal complexes with Cp, Cp*, Tp, $Tp^{Me}{}_2$, bpza, and bdmpza ligands

Recently, we studied iron(II) complexes with these ligands – although with our main focus on bioinorganic model complexes for iron enzymes.[17] Now we report on a route to ruthenium(II) and ruthenium(III) complexes with these new bis(pyrazol-1-yl)acetato ligands.

Results and Discussion

First we investigated a one-step synthesis analogous to the synthesis of $[Ru(Cp)Cl(PPh_3)_2]$ reported by Bruce et al.[3] Reaction of $RuCl_3 \times nH_2O$ with bis(pyrazol-1-yl)acetic acid (H[bpza]) and an excess of PPh_3 in ethanol under refluxing conditions yielded $[Ru(bpza)Cl(PPh_3)_2]$ as the unsymmetrical isomer **1b** [Equation (1)].



1b

(1)

There are two possible isomeric products: (a) a symmetrical one (**1a**) with the chloride ion in *trans* position to the

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carboxylate group of the ligand and (b) an unsymmetrical one (**1b**) with the carboxylate group *trans* to a PPh_3 ligand. The main isomer **1b** obtained in this one-step synthesis is a racemic mixture of two enantiomers. The ^1H NMR spectra of the crude reaction product showed only traces of the symmetrical **1a**. Pure product **1b** could be obtained by column chromatography over silica followed by recrystallization in methanol. The solubility of **1b** in methanol is much lower than that of **1a**.

The coordination of the bpza ligand follows from the IR signal in KBr matrix $\nu_{asym}(CO_2^-) = 1653\ cm^{-1}$. The observation of two doublets in the ^{31}P NMR spectra [$\delta = 43.8$ ($^2J_{PP} = 31.0$ Hz), 49.5 ($^2J_{PP} = 31.0$ Hz)] and of two sets of signals for the pyrazolyl groups in the ^1H and ^{13}C NMR spectra indicates an unsymmetrical coordination of the triphenylphosphane ligands in **1b**. Finally, the molecular structure was proven by CHN analysis, mass spectra, and an X-ray structure determination (Figure 2) of crystals of **1b** obtained from a solution of **1b** in ethanol layered with diethyl ether. Selected bond lengths and angles are summarized in Tables 1 and 2.

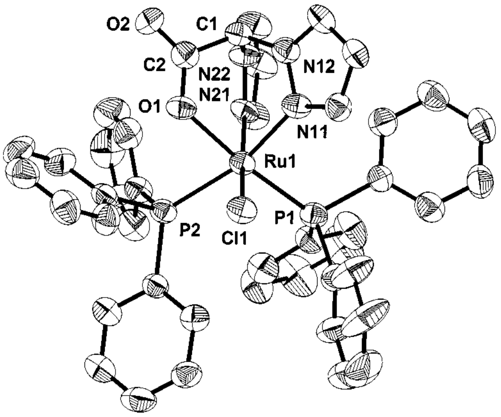


Figure 2. Molecular structure of $[Ru(bpza)Cl(PPh_3)_2]$ (**1b**); thermal ellipsoids are shown at a 50% probability level; hydrogen atoms and co-crystallised solvent are omitted for clarity

Table 1. Selected distances of the complexes **1b**, **2**, and **3**

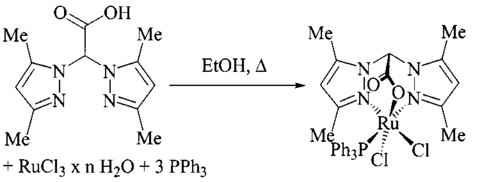
Distance [Å]	1b	2	3
Ru−N(11)	2.157(6)	2.109(3)	2.199(4)
Ru−N(21)	2.100(6)	2.184(3)	2.173(4)
Ru−O(1)	2.181(6)	2.045(3)	2.133(3)
Ru−Cl(1)	2.440(3)	2.346(2)	2.4157(17)
Ru−Cl(2)	−	2.3581(19)	−
Ru−P(1)	2.360(3)	2.3715(18)	2.3555(17)
Ru−P(2)	2.378(4)	−	2.3688(18)
O(2)−C(2)	1.241(9)	1.225(3)	1.241(5)
O(1)−C(2)	1.309(9)	1.298(3)	1.281(5)
C(1)−C(2)	1.566(10)	1.562(4)	1.539(6)

Table 2. Selected angles of the complexes **1b**, **2**, and **3**

Angle [°]	1b	2	3
N(11)−Ru−N(21)	86.5(2)	84.05(9)	78.40(15)
O(1)−Ru−N(11)	82.1(2)	86.50(10)	88.23(14)
O(1)−Ru−N(21)	86.3(2)	87.73(10)	87.68(13)
O(1)−Ru−Cl(1)	87.79(14)	175.36(6)	170.52(9)
O(1)−Ru−P(1)	174.37(14)	85.45(8)	86.50(10)
O(1)−Ru−P(2)	81.58(15)	−	91.36(9)
N(11)−Ru−P(1)	93.07(19)	97.14(8)	169.31(11)
N(21)−Ru−P(1)	90.57(18)	172.99(6)	92.08(11)
N(11)−Ru−P(2)	163.46(18)	−	95.30(12)
N(21)−Ru−P(2)	95.07(18)	−	173.65(11)
N(11)−Ru−Cl(1)	85.35(17)	89.62(9)	84.92(12)
N(21)−Ru−Cl(1)	170.51(17)	89.34(9)	84.58(11)
Cl(1)−Ru−Cl(2)	−	90.90(6)	−
Cl(1)−Ru−P(1)	94.74(8)	97.57(6)	99.16(7)
Cl(1)−Ru−P(2)	91.36(10)	−	95.79(6)
Cl(2)−Ru−P(1)	−	88.27(5)	−
P(1)−Ru−P(2)	103.36(10)	−	94.12(6)

The molecular structure shows one PPh_3 ligand positioned *trans* to the carboxylate group of the bpza ligand and the other phosphane ligand *trans* to a pyrazolyl group. The distances of the bonds in the *cis* geometry [P(1)−Ru = 2.360(3) Å and N(21)−Ru = 2.100(6) Å] are slightly shorter than those in a *trans* geometry [P(2)−Ru = 2.378(4) Å and N(11)−Ru = 2.157(6) Å]. This might be due to the *trans* influence of the triphenylphosphane ligand and the pyrazolyl group.

An analogous reaction of $RuCl_3$ with excess PPh_3 and bis(3,5-dimethylpyrazol-1-yl)acetic acid (H[bdmpza]) yielded $[Ru(bdmpza)Cl_2(PPh_3)]$ (**2**) as an orange, air-sensitive complex [Equation (2)].



2

(2)

Complex **2** is paramagnetic, and therefore was only characterized by mass spectrometry, CHN analysis, and infrared spectroscopy (KBr matrix). The $\nu_{asym}(CO_2^-)$ at $1682\ cm^{-1}$ established the coordination of bdmpza to the ruthenium ion. An X-ray structural analysis of **2** finally confirmed a constitution with the PPh_3 ligand *trans* to one of the pyrazolyl groups (Figure 3). Selected bond lengths and bond angles are summarised in Tables 1 and 2.

Apart from the distances Ru−N(21) [2.184(3) Å] and Ru−P(1) [2.3715(18) Å], all other distances Ru−O, Ru−N, and Ru−Cl are significantly shorter compared to those of **1b**. This is caused by the ruthenium(III) centre in **2** instead of ruthenium(II) in **1b**. These two significantly longer distances again imply a *trans* influence between the PPh_3 ligand and the pyrazolyl group of the bdmpza ligand.

In a second attempt to obtain the target molecule $[Ru(bdmpza)Cl(PPh_3)_2]$, potassium bis(3,5-dimethylpyrazol-1-yl)acetate was allowed to react with $[RuCl_2(PPh_3)_3]$ [Equation (3)].

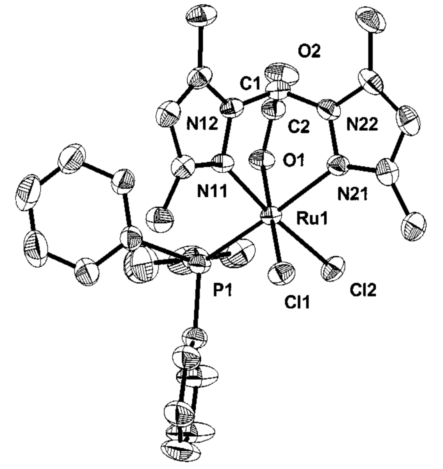


Figure 3. Molecular structure of [Ru(bdmpza)Cl_2(PPh_3)] (**2**); thermal ellipsoids are shown at a 50% probability level; hydrogen atoms and co-crystallised solvent are omitted for clarity

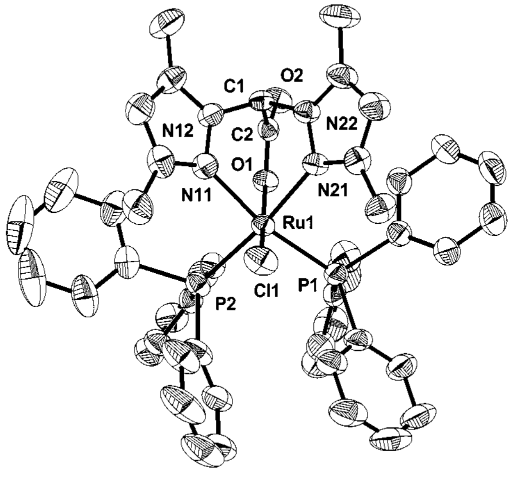
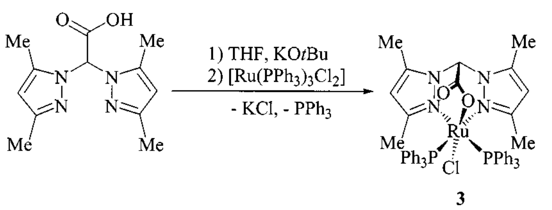


Figure 4. Molecular structure of [Ru(bdmpza)Cl(PPh_3)$_2$] (**3**); thermal ellipsoids are shown at a 50% probability level; hydrogen atoms and co-crystallised solvent are omitted for clarity



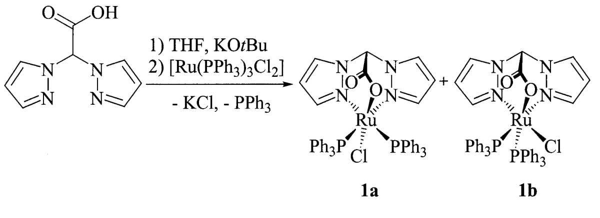
(3)

In an analogous reaction with potassium hydrotris(pyrazol-1-yl)borate and [$RuCl_2$(PPh_3)$_3$] the complex [Ru(Tp)Cl(PPh_3)$_2$] was obtained by Hill et al.[10] Very recently the complex [RuCl(PPh_3)$_2$(TPM)]Cl was synthesized from tris(pyrazol-1-yl)methane (TPM) and [$RuCl_2$(PPh_3)$_3$] by Field and Messerle.[21] [Ru(bdmpza)Cl(PPh_3)$_2$] (**3**) was obtained in good yield after simply washing with degassed water and diethyl ether and was fully characterized. A single signal in the ^{31}P NMR spectrum as well as one set of signals for the pyrazolyl groups in the ^{1}H and ^{13}C NMR spectra indicate a symmetric geometry for **3**. Proton signals of **3** were assigned on the basis of cross-peaks observed in a rotating frame Overhauser spectroscopy (ROESY) experiment. The ^{13}C NMR resonances of the methyl groups were assigned by correlating them to the assigned proton resonances using a heteronuclear multiple quantum coherence (HMQC) experiment. The methyl group at position 3 of the pyrazolyl groups (Me^3) was found in the ^{1}H NMR spectra at $\delta = 1.72$ [^{13}C NMR: $\delta = 15.5$], the methyl group at position 5 (Me^5) at $\delta = 2.35$ [^{13}C NMR: $\delta = 11.1$]. A distinction of the quaternary pyrazolyl carbon resonances was possible with a heteronuclear multiple bond correlation (HMBC) experiment [^{13}C NMR: $\delta = 140.6$ (C^5), 157.3 (C^3)]. The assignment of the NMR signals is in good agreement with those reported by Otero for similar niobium complexes.[16] The symmetric structure was also proven by a single-crystal X-ray structure analysis of **3** (Figure 4). Selected bond lengths and bond angles of **3** are summarized in Tables 1 and 2.

The IR spectrum of **3** shows bands at 1668 and 1570 cm^{-1} [$\nu_{asym}(CO_2^-)$ and $\nu(C{=}N)$]. For all three complexes **1a**/**1b**, **2**, and **3** we were not able to assign $\nu_{sym}(CO_2^-)$ properly to one of the resonances in the region between 1400 and 1500 cm^{-1}. This was due to the weakness of the signals and several resonances of the PPh_3 ligand in that region.

Complex **3** is rather sensitive to oxygen (especially compared to the almost air-stable complexes **1a** or **1b**). This is caused by the bigger steric hindrance of **3**, causing a labilisation of the PPh_3 ligands. This hindrance is indicated by a much smaller angle N(11)−Ru−N(21) of 78.40(15)° compared to 86.5(2)° in **1b**. Another explanation might be, that bdmpza is a better donor ligand compared to bpza due to the four methyl groups in the pyrazolyl rings.

Also [Ru(bpza)Cl(PPh_3)$_2$] could be obtained in good yield by reaction of potassium bis(pyrazol-1-yl)acetate with [$RuCl_2$(PPh_3)$_3$]. Both isomers **1a** and **1b** were formed [Equation (4)].



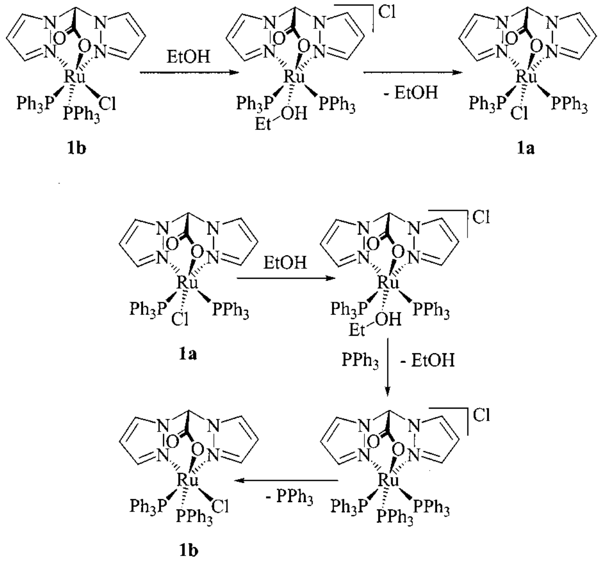
(4)

Due to the simple workup and high yield, we now favour this second synthetic route to **1a**/**1b**. Potassium chloride and traces of excess base are removed by washing with degassed water. Thus, ruthenium complexes with bis(pyrazol-1-yl)-

acetato ligands are stable against hydrolysis, an imminent advantage compared to hydrotris(pyrazolyl)borato ligands. In contrast to unsymmetrical **1b**, only a single ^{31}P NMR signal at $\delta = 40.4$ and one set of ^1H NMR signals is found for **1a**. Both isomers of **1a/1b** are rather stable and can be stored under air as a solid. Assignment of the proton signals of **1a/1b** was accomplished from the cross-peaks observed in correlation spectroscopy (COSY) experiments and ROESY experiments. HMQC experiments were used for correlation of these assigned proton resonances with ^{13}C NMR resonances. In the NMR spectra of the symmetrical isomer **1a** only three proton resonances [$\delta = 5.89$ (H^4), 6.87 (H^3), 7.55 (H^5)] and three carbon resonances [$\delta = 107.6$ (C^4), 132.6 (C^5), 146.6 (C^3)] were detected for the pyrazolyl groups. The pyrazolyl groups in **1b** are no longer spectroscopically equivalent causing six ^1H NMR signals [$\delta = 5.20$ (H^3), 5.46 (H^4), 5.97 ($H^{4'}$), 7.44 ($H^{3'}$), 7.79 ($H^{5'}$), 7.79 (H^5)] and six ^{13}C NMR signals [$\delta = 106.5$ (C^4), 107.4 ($C^{4'}$), 131.9 (C^5 or $C^{5'}$), 132.0 (C^5 or $C^{5'}$), 145.7 ($C^{3'}$), 147.9 (C^3)]. In the ROESY experiment of **1b** an NOE correlation was observed between a signal at $\delta = 7.84$ (six *ortho*-H of the PPh_3 ligand *trans* to the carboxylate donor group) and H^3 indicating a close spherical contact.

From the fact that the unsymmetrical isomer could be isolated by recrystallization, it follows that it is stable against conversion into **1a** at ambient temperature for a reasonable time. To investigate whether one of the isomers is thermodynamically favoured, a mixture of the isomers and PPh_3 in ethanol was heated under reflux. After 4 h in ethanol under refluxing conditions, surprisingly only traces of **1b** were detected by ^1H NMR spectroscopy besides **1a**. Since this formation of the symmetrical isomer **1a** seemed to be incompatible with the one-step synthesis of **1b**, a solution of **1a** with traces of **1b** and PPh_3 in ethanol was heated under reflux for 5 h. After this time **1b** was the main product and only traces of **1a** were left. Obviously, the ratio **1a/1b** depends on whether excess PPh_3 is present in the reaction mixture or not. Very likely, this is due to the intermediate formation of a cationic solvent complex. For alcoholic solutions of $[Ru(Cp)Cl(PPh_3)_2]$ dissociation of a chloride ligand and formation of a cationic alcohol complex is well known.[1,3] The most likely position of the ethanol ligand is the position *trans* to the carboxylate donor group. Exchange of the ethanol ligand by a chloride ion will therefore result in the symmetrical isomer **1a** (Scheme 1). With excess PPh_3 an intermediate cationic complex $[Ru(bpza)(PPh_3)_3]Cl$ might be formed. Similar complexes $[Ru(Cp)(dppm)(PPh_3)]PF_6$ and $[Ru(Cp^*)(PHPh_2)_3]Cl$ were recently reported.[22,23] Both PPh_3 ligands *trans* to pyrazolyl groups are more labile than the one *trans* to the carboxylate donor group because of the *trans* influence of the pyrazolyl groups. Therefore, in this case substitution for a chloride ion will result in formation of the unsymmetrical isomer **1b** (Scheme 1).

Finally, we observed that traces of alcohols or THF in NMR samples caused significant changes in the NMR spectra again indicating an interaction between **1a/1b** and traces of these donor solvents. In protic solvents the carboxylate group might also interact with protons and therefore be a less efficient donor, causing this behaviour. In future experiments we will concentrate on the question of whether such interactions of the carboxylate donor and protons, or even Lewis acids, could be used for changing the reactivity of the complexes.



Scheme 1. Proposed mechanism for the conversion of **1b** in **1a** in ethanol and of **1a** in **1b** in ethanol with excess PPh_3

Conclusions

A simple synthetic route to the ruthenium(II) complexes $[Ru(bpza)Cl(PPh_3)_2]$ (**1a/1b**) and $[Ru(bdmpza)Cl(PPh_3)_2]$ (**3**) was established by reaction of the potassium bis(pyrazol-1-yl)acetates with $[RuCl_2(PPh_3)_3]$. Complex **3** seemed to be more active towards exchange of a PPh_3 ligand by another donor, whereas in **1a/1b** the ratio of the symmetrical isomer **1a** to the unsymmetrical isomer **1b** could be influenced by adding PPh_3 during heating under reflux. Thus, both complexes are promising starting complexes for future organometallic experiments.

Experimental Section

All experiments were carried out in Schlenk tubes under argon. The solvents were dried by standard procedures, distilled, and stored under argon. Microcrystalline precipitates were separated by filtration or centrifugation with a Hettich Rotina 46 R Schlenk tube centrifuge. IR: Biorad FTS 60, CaF_2 cuvettes (0.5 mm) or KBr matrix. ^1H NMR and ^{13}C NMR: Bruker WM 250, Bruker AC 250, δ values relative to TMS. ^{31}P NMR: JEOL GX 400. Two-dimensional NMR experiments: Bruker DRX 600 (Avance). EI-MS and FAB-MS: modified Finnigan MAT 312. Elemental analyses: Analytical Laboratory of the Fachbereich Chemie. A modified Siemens P4 diffractometer was used for X-ray structure determinations. Bis(pyrazol-1-yl)acetic acid and bis(3,5-dimethylpyrazol-1-yl)acetic acid were synthesised from pyrazole and 3,5-dimethylpyrazole as reported recently.[17,18] $[RuCl_2(PPh_3)_3]$ was prepared according to the literature.[24] Hydrated ruthenium trichloride (35−40% Ru) was used as purchased from Merck.

Synthesis of $[Ru(bpza)Cl(PPh_3)_2]$ (1a/1b). − Method A: A solution of $RuCl_3 \times n\ H_2O$ (670 mg, 2.65 mmol) and bis(pyrazol-1-yl)acetic acid (578 mg, 3.00 mmol) in EtOH (40 mL) was added over a period of 10 min to a refluxing solution of PPh_3 (2.09 g, 7.95 mmol) in EtOH (80 mL). The mixture was maintained under reflux for 3 h, cooled to ambient temperature and the solvent was evaporated. The crude product was loaded with CH_2Cl_2 on a short column of silica (length 6 cm, i.d. 4 cm). The column was washed with CH_2Cl_2 (150 mL). Finally, the pure product was recovered with MeOH. The dark yellow MeOH solution was concentrated in vacuo to 20 mL. The precipitated yellow product was filtered off and dried in vacuo. It was dissolved in CH_2Cl_2, precipitated with *n*-pentane, filtered off, and dried in vacuo. The unsymmetrical isomer **1b** was obtained as a yellow crystal powder. Suitable crystals of **1b** for X-ray structure analysis were obtained from a solution in EtOH layered with diethyl ether. Yield 1.23 g (1.44 mmol, 54%), m.p. 194−196 °C. − **Method B:** To a solution of bis(pyrazol-1-yl)acetic acid (200 mg, 1.04 mmol) in THF (25 mL) potassium *tert*-butoxide (117 mg, 1.04 mmol) was added and the mixture stirred for 1 h at ambient temperature. A white precipitate formed during this time indicated the formation of the potassium carboxylate. $[RuCl_2(PPh_3)_3]$ (1.00 g, 1.04 mmol) was added and the mixture was stirred at ambient temperature for 30 min, during which time the colour of the brown suspension changed to orange. The solvent was removed in vacuo and the residue was washed with degassed water (2 × 20 mL) and diethyl ether (2 × 20 mL) and dried in vacuo to yield a mixture of **1a/1b** as an orange crystal powder. Yield 760 mg (0.89 mmol, 86%), m.p. 188−192 °C. FAB-MS (NBOH matrix): *m*/*z* (%) = 853 (2) $[MH^+]$, 817 (4) $[(MH - Cl)^+]$, 590 (11) $[MH^+ - PPh_3]$, 555 (5) $[(MH - PPh_3 - Cl)^+]$. $C_{44}H_{37}ClN_4O_2P_2Ru \times H_2O \times EtOH$ (916.36): calcd. C 60.29, H 4.95, N 6.11; found C 60.58, H 4.73, N 6.00. − **1a:** ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 5.89$ (vt, $^3J_{H,H} = 2.3$ Hz, 2 H, H^4), 6.61 (s, 1 H, CH), 6.87 (d, $^3J_{H,H} = 1.9$ Hz, 2 H, H^3), 7.04 (m, 12 H, *m*-PPh_3), 7.21 (m, 6 H, *p*-PPh_3), 7.43(m, 12 H, *o*-PPh_3), 7.55 (d, $^3J_{H,H} = 2.5$ Hz, 2 H, H^5). ^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta = 75.5$ (CH), 107.6 (C^4), 127.1 (vt, $J_{C,P} = 3.7$ Hz, *m*-PPh_3), 128.8 (*p*-PPh_3), 132.6 (C^5), 134.9 (vt, $J_{C,P} = 4.5$ Hz, *o*-PPh_3), 135.0 (d, $J_{C,P} = 40.1$ Hz, *i*-PPh_3), 146.6 (C^3), 166.1 (CO_2^-). ^{31}P NMR ($CDCl_3$, 161.8 MHz): $\delta = 40.4$. IR (THF): $\tilde{\nu} = 1670$ s (CO_2^-), 1653 m, 1507 w cm^{-1}. IR (KBr): $\tilde{\nu} = 1653$ s (CO_2^-), 1482 w, 1433 m, 1408 w cm^{-1}. − **1b:** ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 5.20$ (s, 1 H, H^3), 5.46 (s, 1 H, H^4), 5.97 (s, 1 H, $H^{4'}$), 6.84 (s br, 6 H, *o*-PPh_3), 7.07 (m, 16 H, CH and *p*-PPh_3 and *m*-PPh_3), 7.26 (m, 3 H, *p*-PPh_3), 7.44 (s, 1 H, $H^{3'}$), 7.84(m, 8 H, *o*-PPh_3 and H^5 and $H^{5'}$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta = 74.2$ (CH), 106.5 (C^4), 107.4 ($C^{4'}$), 127.3 (d, $J_{C,P} = 9.1$ Hz, *m*-PPh_3), 127.6 (d, $J_{C,P} = 9.0$ Hz, *m*-PPh_3), 128.7 (*p*-PPh_3), 129.2 (*p*-PPh_3), 131.9 (C^5 or $C^{5'}$), 132.0 (C^5 or $C^{5'}$), 133.9 (d, $J_{C,P} = 9.0$ Hz, *o*-PPh_3), 134.4 (d, $J_{C,P} = 9.4$ Hz, *o*-PPh_3), 134.5 (d, $J_{C,P} = 40.4$ Hz, *i*-PPh_3), 135.3 (d, $J_{C,P} = 40.5$ Hz, *i*-PPh_3), 145.7 ($C^{3'}$), 147.9 (C^3), 166.6 (CO_2^-). ^{31}P NMR ($CDCl_3$, 161.8 MHz): $\delta = 43.8$ ($^2J_{PP} = 31.0$ Hz), 49.5 ($^2J_{PP} = 31.0$ Hz). IR (CH_2Cl_2): $\tilde{\nu} = 1661$ s (CO_2^-), 1481 w cm^{-1}. IR (KBr): $\tilde{\nu} = 1653$ s (CO_2^-), 1482 w, 1433 m cm^{-1}.

Synthesis of $[Ru(bdmpza)Cl_2(PPh_3)]$ (2): A solution of $RuCl_3 \times n\ H_2O$ (383 mg, 1.52 mmol) in EtOH (20 mL) was added over a period of 10 min to a solution of bis(3,5-dimethylpyrazol-1-yl)acetic acid (376 mg, 1.51 mmol) and PPh_3 (1.20 g, 4.57 mmol) in EtOH (30 mL). The mixture was heated under reflux for 1 h, cooled in an ice bath and the precipitate was collected by filtration. The brownish residue was washed with CH_2Cl_2 (30 mL) and the now orange residue was dried in vacuo. Crystals suitable for a X-ray structure determination were obtained from a solution of **2** in acetonitrile and also from a solution in $CHCl_3$. Yield 660 mg (0.97 mmol, 64%), m.p. 260−265 °C (dec.). FAB MS (NBOH matrix): *m*/*z* (%) = 722 (4) $[M^+ + CH_3CN]$, 681 (4) $[M^+]$, 646 (18) $[(M - Cl)^+]$, 611 (6) $[(M - Cl_2)^+]$, 566 (6) $[(M - Cl_2 - CO_2)^+]$. IR (KBr): $\tilde{\nu} = 1682$ s (CO_2^-), 1560 w (C=N), 1482 w, 1458 w, 1436 w cm^{-1}. $C_{30}H_{30}Cl_2N_4O_2PRu \times CH_3CN$ (722.60): calcd. C 53.19, H 4.60, N 9.69; found C 53.32, H 4.23, N 9.83.

Synthesis of $[Ru(bdmpza)Cl(PPh_3)_2]$ (3): Reaction of bis(3,5-dimethylpyrazol-1-yl)acetic acid (248 mg, 1.00 mmol) in THF (25 mL) with potassium *tert*-butoxide (112 mg, 1.00 mmol) and $[RuCl_2(PPh_3)_3]$ (953 mg, 0.99 mmol) according to Method B yielded **3** as an orange crystal powder. Suitable crystals of **3** for X-ray structure analysis were obtained from a solution in $CHCl_3$. Yield 815 mg (0.90 mmol, 91%), m.p. 201−205 °C (dec.). ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 1.72$ (s, 3 H, Me^3), 2.35 (s, 3 H, Me^5), 5.42 (s, 2 H, H^4), 6.45 (s, 1 H, CH), 6.90 (m, 12 H, PPh_3), 7.04 (m, 6 H, PPh_3), 7.31 (m, 12 H, PPh_3). ^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta = 11.1$ (Me^5), 15.5 (Me^3), 69.1 (CH), 109.3 (C^4), 126.5 (vt, $J_{C,P} = 4.2$ Hz, *m*-PPh_3), 128.0 (*p*-PPh_3), 134.5 (vt, $J_{C,P} = 4.2$ Hz, *o*-PPh_3), 136.2 (d, $J_{C,P} = 39.1$ Hz, *i*-PPh_3), 140.6 (C^5), 157.3 (C^3), 168.2 (CO_2^-). ^{31}P NMR ($CDCl_3$, 161.8 MHz): $\delta = 35.3$. FAB-MS (NBOH-matrix): *m*/*z* (%) = 908 (0.5) $[M^+]$, 873 (1) $[(M - Cl)^+]$, 648 (3) $[MH^+ - PPh_3]$, 611 (2) $[(MH - PPh_3 - Cl)^+]$. IR (THF): $\tilde{\nu} = 1672$ s (CO_2^-), 1571 w (C=N) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu} = 1662$ s (CO_2^-), 1571 w (C=N) cm^{-1}. IR (KBr): $\tilde{\nu} = 1668$ s (CO_2^-), 1570 w (C=N), 1482 w, 1458 w, 1432 m cm^{-1}. $C_{48}H_{45}ClN_4O_2P_2Ru \times 3CHCl_3$ (1266.52): calcd. C 48.37, H 3.82, N 4.42; found C 48.50, H 3.98, N 4.21.

X-ray Structure Determinations: Single crystals of **1b**, **2**, and **3** were sealed in glass capillaries at room temperature. A modified Siemens P4-diffractometer was used for data collection (Wyckhoff technique, graphite monochromator, Mo-K_α radiation, $\lambda = 0.71073$ Å, scan rate 4−30 °min^{-1} in ω). The structures were solved and refined using the SHELX-97 program package (refined with full-matrix least squares against F^2).[25] A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \max(F_o^2,0)]/3$. Hydrogen atoms were included in their calculated positions and refined in a "riding model". One molecule of ethanol and water co-crystallised per asymmetric unit in **1b**, one molecule of $CHCl_3$ in **2**, and three molecules of $CHCl_3$ in **3**. The co-crystallised water in the structure of **1b** can be explained as being due to the crystallisation of **1b** in an open flask. Crystals of **2** were also obtained from a solution in acetonitrile. The X-ray structure determination of these crystals resulted in an almost identical structure model but with higher *R* factors. Therefore, this structure **2**×CH_3CN is not discussed here although the data were deposited with CCDC (see below). Two of the $CHCl_3$ molecules in the structure of **3** are severely disordered causing relatively high *R* factors. All details and parameters of the measurements are summarised in Table 3. 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-168912 (**1b**×H_2O×EtOH), -168913 (**2**×$CHCl_3$), -168914 (**2**×CH_3CN) and -168915 (**3**×3$CHCl_3$). Copies of the data can be obtained free

Table 3. Structure determination details of compounds **1b**, **2**, and **3**

	1b	**2**	**3**
Empirical formula	$C_{44}H_{37}ClN_4O_2P_2Ru \times H_2O \times H_5C_2OH$	$C_{30}H_{30}Cl_2N_4O_2PRu \times CHCl_3$	$C_{48}H_{45}ClN_4O_2P_2Ru \times 3CHCl_3$
Formula mass	916.32	800.89	1266.44
Crystal colour/habit	yellow cube	orange cube	orange prism
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a [Å]	9.969(10)	10.113(7)	14.057(6)
b [Å]	19.37(3)	11.908(9)	31.792(19)
c [Å]	22.96(3)	15.583(10)	14.421(10)
α [°]	90	91.48(7)	90
β [°]	96.64(8)	108.59(3)	115.72(5)
γ [°]	90	103.07(6)	90
V [Å^3]	4405(10)	1723(2)	5806(6)
θ [°]	2.07−25.01	2.13−27.00	2.02−27.01
h	−11 to 11	−6 to 12	−17 to 0
k	−9 to 23	−15 to 14	−40 to 0
l	−27 to 27	−19 to 18	−16 to 18
$F(000)$	1888	810	2568
Z	4	2	4
μ(Mo-K_α) [mm^{-1}]	0.536	0.924	0.827
Crystal size [mm]	0.4 × 0.2 × 0.2	0.4 × 0.35 × 0.35	0.6 × 0.4 × 0.4
D_c [gcm^{-3}]	1.382	1.544	1.449
T [K]	239(2)	232(2)	242(2)
Reflections collected	10245	8278	13162
Independent reflections	7653	7482	12654
Observed reflections [$> 2\sigma(I)$]	3899	6311	9115
Parameter	530	397	703
Restraints	2	0	132
Wt. parameter a	0.0769	0.0437	0.0950
Wt. parameter b	2.4297	1.1694	10.8122
R_1 (obsd.)	0.0586	0.0354	0.0635
R_2 (overall)	0.1447	0.0462	0.0944
wR_1 (obsd.)	0.1328	0.0873	0.1660
wR_2 (overall)	0.1872	0.0934	0.1908
Diff. peak/hole [e/Å^3]	0.900/−1.022	0.757/−0.756	1.503/−1.121

of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Structure figures were prepared with the program Diamond 2.1c.[26]

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