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# Ruthenium(II) complexes with 2-(diphenylphosphinomethyl)aniline

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Dedicated to Professor Reinhard Kirmse on the occassion of his 65th birthday.

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#### ABSTRACT

2-(Diphenylphosphinomethyl)aniline,  $H_2L^1$ , reacts with  $[RuCl_2(PPh_3)_3]$  to yield the monomeric complexes  $[RuCl_2(H_2L^1)(PPh_3)(CH_3CN)]$ ,  $[RuCl_2(H_2L^1)_2]$  and the chloro-bridged dimer  $[(H_2L^1)(PPh_3)Ru(\mu-Cl)_2Ru(PPh_3)(H_2L^1)]$  depending on the conditions applied. Exclusively the monochelate  $[RuCl_2(H_2L^1)(dmso)_2]$  is formed during reactions of  $H_2L^1$  with  $[RuCl_2(dmso)_4]$ .  $H_2L^1$  acts as a neutral, bidentate ligand in all complexes. The products are studied spectroscopically and by X-ray diffraction.

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#### 1. Introduction

Ruthenium complexes are of permanent interest for applications in homogenous and heterogenous catalysis [1]. During the recent years, another field of interest entered the focus of the coordination chemistry of this element: possible applications in treatment of cancer and other diseases [2]. The latter area has been mainly stimulated by the organometallic approach using so-called RAPTA compounds (halfsandwich complexes with 1,3,5-triaza-7phosphaadamantane co-ligands) [3] and the promising clinical trials of trans-tetrachloridobis(1H-indazole)ruthenate(III) complexes ("Keppler-type" compounds) [4] and ruthenium(II) dmso complexes (NAMI) [5]. Both fields of interest require exact knowledge of the basic coordination chemistry of the metal, which stimulates also fundamental studies including hitherto underrepresented ligand systems.

Hybrid ligands with 'hard' and 'soft' donor atoms are currently under discussion for applications in several fields of chemistry, particularly as catalysts in homogeneous catalysis [6]. But still some fundamental research has to be done to understand the unique structural and reactivity patterns of complexes with such systems. In the present paper, we describe reaction patterns of the *P*,*N*-donor ligand 2-(diphenylphosphinome thyl)aniline,  $H_2L^1$ , with common ruthenium(II) precursors such as



[RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and [RuCl<sub>2</sub>(dmso)<sub>4</sub>]. Phosphines bearing o-amino moieties are versatile ligands, which form stable complexes with a variety of transition metal ions [7]. Most of these studies, however, were done with 2-(diphenylphosphino)aniline,  $H_2L^2$ , which can readily be synthesized. With its combination of hard and soft donor atoms,  $H_2L^2$  is well able to stabilize metals in different oxidation states. In previous reports dealing with rhenium(V) compounds, we had to consider that  $H_2L^1$  does not fully resemble the coordination behavior of the familiar ligand H<sub>2</sub>L<sup>2</sup> [7,8]. Ruthenium complexes with unsubstituted H<sub>2</sub>L<sup>2</sup> are only described in three papers, in which the ligand was found to act as a neutral bidentate chelate in  $[RuCl(\eta^6-p-cymene)(H_2L^2)]^+$  [9], while single deprotonation was observed in some complexes, in which the nitrogen donor bridges two ruthenium atoms [10]. Some more information about P,N-bidentate coordination in ruthenium complexes is available for the methyl-substituted derivatives MeHL<sup>2</sup> [11] and Me<sub>2</sub>L<sup>2</sup> [12].



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### 2. Results and discussion

A suspension of  $[RuCl_2(PPh_3)_3]$  and  $H_2L^1$  in acetonitrile reacts under exclusion of air, irrespective of the amount of ligand used, under formation of a clear yellow solution. After evaporation of the solvent, the monochelate  $[RuCl_2(H_2L^1)(PPh_3)(CH_3CN)]$  precipitated as a microcrystalline yellow solid. The compound is stable under an atmosphere of dry argon. Exposure to air results in slow conversion into an insoluble green powder, which also deposits from the reaction mixture, when it is exposed to air.

The presence of coordinated acetonitrile is evident by a weak IR band at 2268 cm<sup>-1</sup>. NH stretches can be detected at 3350 and 3102 cm<sup>-1</sup>, which indicates the coordination of the phosphineamine as non-deprotonated H<sub>2</sub>L<sup>1</sup>. The detection of two doublets in the <sup>31</sup>P NMR spectrum (47.4 and 60.6 ppm) evidences one remaining PPh<sub>3</sub> ligand in addition to the coordinated H<sub>2</sub>L<sup>1</sup> in the coordination sphere of ruthenium, which indicates the formation of a monochelate. Yellow single crystals of  $[RuCl_2(H_2L^1)(PPh_3)(CH_3CN)]$ could be obtained by slow diffusion of diethyl ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. Fig. 1 shows the molecular structure of the compound. Selected bond lengths are summarized in Table 1. Ruthenium is coordinated in a distorted octahedral environment with the two phosphorus atoms in *cis* position to each other. This is in agreement with the product of a related reaction of  $[RuCl_2(PPh_3)_3]$  with Me<sub>2</sub>L<sup>2</sup>, which gives the five-coordinate complex  $[RuCl_2(PR_3)(Me_2L^2)]$  (R = 4-toloyl) [12a]. The chlorido ligands in  $[RuCl_2(H_2L^1)(PPh_3)(CH_3CN)]$  coordinate trans to the phosphorus atom of H<sub>2</sub>L<sup>1</sup> and the acetonitrile ligand. Consequently, the Ru–Cl1 bond is slightly longer (2.476(2) versus 2.411(2)Å) than the Ru-Cl2 bond due to the trans influence of the phosphine. The coordination of acetonitrile seems to stabilize the monochelate and prevents ongoing ligand reactions. At least, we were not successful in our attempts to produce a bis-chelate with H<sub>2</sub>L<sup>1</sup> in this solvent (see also Scheme 1).

A different course of the reaction is observed in CH<sub>2</sub>Cl<sub>2</sub>, where obviously a five-coordinate intermediate of the composition {RuCl<sub>2</sub>(PPh<sub>3</sub>)(H<sub>2</sub>L<sup>2</sup>)} is formed. Unlike the more bulky [RuCl<sub>2</sub>(PR<sub>3</sub>) (Me<sub>2</sub>L<sup>2</sup>)] (R = 4-toloyl), which was isolated in the monomeric form, the compound with H<sub>2</sub>L<sup>1</sup> dimerises to the sparingly soluble [(H<sub>2</sub>L<sup>1</sup>)(PPh<sub>3</sub>)Ru( $\mu$ -Cl)<sub>2</sub>Ru(PPh<sub>3</sub>)(H<sub>2</sub>L<sup>1</sup>)]. The red complex rapidly precipitates from the reaction mixture. Its low solubility prevents from a rapid formation of the bis-chelate [RuCl<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>2</sub>] under mild conditions, but also restricts the spectroscopic methods which could



**Fig. 1.** Ellipsoid representation [22] of the molecular structure of  $[RuCl_2(PPh_3) (H_2L^1)(CH_3CN)]$ . Thermal ellipsoids represent 50% probability. H atoms on C atoms have been omitted for clarity.

#### Table 1

Selected bond lengths (Å) and angles (°) in  $[RuCl_2(PPh_3)(H_2L^1)(CH_3CN)]$ ·CHCl<sub>3</sub> and  $[(H_2L^1)(PPh_3)Ru(\mu-Cl)_2Ru(PPh_3)(H_2L^1)]$ ·0.5CH<sub>2</sub>Cl<sub>2</sub>.

	[RuCl <sub>2</sub> (PPh <sub>3</sub> )(H <sub>2</sub> L <sup>1</sup> )( CH <sub>3</sub> CN)]·CHCl <sub>3</sub>	$\begin{array}{l} [(H_2L^1)(PPh_3)Ru(\mu\text{-}Cl)_2Ru\\ (PPh_3)(H_2L^1)]\text{-}0.5CH_2Cl_2{}^a \end{array}$
Ru-Cl1	2.476(2)	2.390(3), 2.389(3)
Ru-Cl2	2.411(2)	2.441(3), 2.445(2)
Ru-N1	2.157(5)	2.195(8), 2.185(8)
Ru-P1	2.285(2)	2.257(3), 2.265(3)
Ru–P2	2.330(2)	2.311(3), 2.315(3)
Ru-N10/Cl2'	2.001(6)	2.563(3), 2.573(3)
Cl1-Ru-Cl2	92.80(7)	162.76(9), 164.45(9)
N10-Ru-N1	85.5(2)	_
N10-Ru-P1	93.4(2)	_
N1-Ru-P1	87.5(2)	87.9(2), 88.5(2)
N10-Ru-P2	93.3(2)	_
N1-Ru-P2	167.7(2)	170.8(2), 168.6(2)
P1-Ru-P2	104.88(8)	98.9(1), 100.2(1)
N10-Ru-Cl2	170.8(2)	_
N1-Ru-Cl2	85.3(2)	84.2(2), 84.5(2)
P1-Ru-Cl2	87.04(7)	88.56(8), 87.77(9)
P2-Ru-Cl2	95.50(7)	102.1(1), 102.92(9)
N10-Ru-Cl1	85.0(2)	-
N1-Ru-Cl1	81.2(2)	83.3(2), 84.5(2)
P1-Ru-Cl1	168.57(7)	102.8(1), 101.7(1)
P2-Ru-Cl1	86.52(7)	89.1(1), 87.7(1)
N1-Ru-Cl2'	-	77.9(2), 76.6(2)
P1-Ru-Cl2'	-	161.5(1), 160.6(1)
P2-Ru-Cl2'	-	96.69(9), 96.22(9)
Cl1-Ru-Cl2'	_	87.30(9), 89.10(9)
Cl2-Ru-Cl2'	_	78.44(9), 78.58(9)
Ru-Cl2-Ru'	_	101.2(1), 101.42(9)

<sup>a</sup> Values for two crystallographically independent species; symmetry transformations used: (') -x + 2, -y + 1, -z.

be applied to study this compound. Fortunately, we were able to obtain single crystals by slow diffusion of the two reactants. X-Ray diffraction confirms the dimeric structure of the product with two bridging chlorido ligands (Fig. 2). The compound crystallizes with two halves of centrosymmetric molecules in the asymmetric unit. The molecules are completed by inversion symmetry. Selected bond lengths and angles are compared with the values of the monomeric complex [RuCl<sub>2</sub>(PPh<sub>3</sub>)(H<sub>2</sub>L<sup>1</sup>)(CH<sub>3</sub>CN)] in Table 1.

The formation of chlorido-bridged dimers is a common feature in the coordination chemistry of ruthenium [13–15] and has been explained by the formation of an equilibrium in solution between [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and "[RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]" with subsequent dimerization of the latter compound to [(PPh<sub>3</sub>)Ru( $\mu$ -Cl)<sub>2</sub>Ru(PPh<sub>3</sub>)] [13,15]. The product of this dimerization shows a square-pyramidal coordination of the metal ions. Replacement of each one PPh<sub>3</sub> ligand of this intermediate by H<sub>2</sub>L<sup>1</sup> finally gives [(H<sub>2</sub>L<sup>1</sup>)(PPh<sub>3</sub>)Ru( $\mu$ -Cl)<sub>2</sub>Ru(PPh<sub>3</sub>) (H<sub>2</sub>L<sup>1</sup>)], which precipitates as an almost insoluble solid.

When the reaction between  $[RuCl_2(PPh_3)_3]$  and  $H_2L^1$  is performed in CH<sub>2</sub>Cl<sub>2</sub> under reflux and using an excess of the aminophosphine, the bis-chelate  $[RuCl_2(H_2L^1)_2]$  can be synthesized. The reaction proceeds via  $[(H_2L^1)(PPh_3)Ru(\mu-Cl)_2Ru(PPh_3)(H_2L^1)]$ , as it can be concluded from the intermediate formation of a red precipitate, which slowly re-dissolves upon prolonged heating under reflux. Finally, a yellow solid was formed, which is only sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> or alcohols. Nevertheless, the product slightly dissolves in dmso, which allowed the measurement of NMR spectra. The integration of the signals of the proton spectrum indicates the formation of a complex without additional PPh<sub>3</sub>. This is supported by the <sup>31</sup>P NMR spectrum, which shows only one signal at 67.2 ppm proving that the two phosphorus atoms are magnetically equivalent. The detection of a peak in the +EI mass spectrum at m/z = 719.97, which can be assigned to  $[RuCl(H_2L^1)_2]^+$ suggests the formation of the bis-chelate, which was finally confirmed by the results of an X-ray diffraction study. Single crystals



Scheme 1.



**Fig. 2.** (a) Ellipsoid representation [22] of the structure of  $[(H_2L^1)(PPh_3)Ru(\mu-CI)_2Ru(PPh_3)(H_2L^1)]$ . Thermal ellipsoids represent 50% probability. H atoms on C atoms have been omitted for clarity.

of the compound could only be obtained, when a saturated solution of  $[RuCl_2(PPh_3)_3]$  was overlayered with a solution of the ligand. Slow diffusion of the solutions initially resulted in the formation of red crystals of  $[RuCl_2(PPh_3)(H_2L^1)]$  at the phase interphase, which slowly (8 weeks) disappeared and were replaced by bright yellow single crystals of  $[RuCl_2(H_2L^1)_2]$ .

The molecular structure of  $[RuCl_2(H_2L^1)_2]$  is shown in Fig. 3. Selected bond lengths and angles are given in Table 2. The ruthenium atom is coordinated in a distorted octahedral environment. The organic ligands coordinate in one plane in cis configuration. This results in some repulsions of the phosphine donor sites, which is evident by the P1-Ru-P2 angle of 98.63(6)°. Consequently, the N1-Re-N2 angle is smaller, 84.7(2)°, and both chlorido ligands are bent away from the sterically overloaded phosphine hemisphere of the molecule. This results in a relatively small trans Cl-Ru–Cl angle of 162.69(6)°. The preference of the *cis* configuration can be explained by a larger structural *trans* influence due to the phosphine donors compared with the amine sides, and consequently they are arranged trans to each other. Similar ligand arrangements were also found for ruthenium complexes with other aminophosphine ligands [15-17], as well in the nitridorhenium(V) and oxidorhenium(V) bis-chelates [ReNCl(H<sub>2</sub>L<sup>1</sup>)<sub>2</sub>]Cl and  $[\text{ReO}_2(\text{H}_2\text{L}^1)_2]$ Cl [7,8].

An insoluble yellow solid was formed during the reaction of  $[RuCl_2(dmso)_4]$  with one equivalent of  $H_2L^1$  (Scheme 2). No other



**Fig. 3.** Ellipsoid representation [22] of the molecular structure of  $[RuCl_2(H_2L^1)_2]$ . Thermal ellipsoids represent 50% probability. H atoms on C atoms have been omitted for clarity.

products could be obtained irrespective of the ratio of the reactants used or the reaction conditions applied. The main reason for this fact seems to be the very low solubility of the compound in all common solvents. Elemental analysis and IR spectra strongly suggest a composition of  $[RuCl_2(dmso)_2(H_2L^1)]$ , with S-bonded dmso ligands. This was concluded from the appearance of a strong IR band at 1087 cm<sup>-1</sup>, which can be assigned to the S=O stretch. An X-ray study on single crystals, which were obtained in a similar diffusion procedure as described for  $[RuCl_2(H_2L^1)_2]$ , confirm the composition of the product.

The structure of  $[RuCl_2(dmso)_2(H_2L^1)]$  is shown in Fig. 4a. Table 3 summarizes selected bond lengths and angles. The coordination polyhedron of the ruthenium atom is a distorted octahedron. The two chlorido ligands and the dmso ligands are *cis* coordinated each. The aminophosphine occupies the two remaining coordination positions in a way that the phosphorus atom is arranged *trans* to Cl<sup>-</sup>. Dimethylsulfoxide is S-bonded as is expected for Ru(II) complexes. The bond lengths in  $[RuCl_2(dmso)_2(H_2L^1)]$  are unexceptional and the slight differences in the Ru–Cl (2.465(2) versus 2.436(1) Å) and Ru–S bonds (2.309(1) versus 2.271(1) Å) reflect the influence of the respective trans ligands. Hydrogen bonds are established between both amine protons and the chlorido ligands

Table 2	
Selected bond lengths (Å) and angles (°) in [RuCl <sub>2</sub>	(H <sub>2</sub> L <sup>1</sup> ) <sub>2</sub> ].

		[	
Ru-Cl1	2.423(2)	Ru-P1	2.266(2)
Ru-Cl2	2.397(2)	Ru-N2	2.231(5)
Ru-N1	2.238(5)	Ru-P2	2.277(2)
Cl1-Ru-Cl2	162.69(6)	Cl2-Ru-N2	85.7(1)
Cl1-Ru-N1	85.15(16)	Cl2-Ru-P2	101.97(6)
Cl1-Ru-P1	100.18(6)	N1-Ru-P1	88.5(1)
Cl1-Ru-N2	83.1(2)	N1-Ru-N2	84.7(2)
Cl1-Ru-P2	90.86(6)	N1-Ru-P2	172.3(2)
Cl2-Ru-N1	80.7(1)	N2-Ru-P1	172.2(2)
Cl2-Ru-P1	89.43(6)	N2-Ru-P2	88.4(1)
P1-Ru-P2	98.63(6)		



of an adjacent molecule and arrange each two of them to dimeric units in the solid state. Details are depicted in Fig. 4b.

## 3. Experimental

[RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] [18] and [RuCl<sub>2</sub>(dmso)<sub>4</sub>] [19] were prepared by literature procedures. Unlike to a previous synthesis [20],  $H_2L^2$ was prepared from *N-tert*-butylcarbonate(BOC)-protected o-toluidine, by lithiation of the methyl group and subsequent reaction with PPh<sub>2</sub>Cl [8]. IR spectra were measured as KBr pellets on a Shimadzu FTIR-spectrometer 8300. ESI mass spectra were measured with an Agilent 6210 ESI-TOF. All MS results are given in the form: m/z, assignment. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. The values determined for hydrogen are systematic too low. This does not refer to impure samples, but most probably to incomplete combustion and/or the formation of hydrides. Similar findings have been observed for analogous rhenium complexes with the same type of ligands before [7,8]. We left these values uncorrected. Additional proof for the identity of the products is given by high-resolution mass spectra for the complexes with sufficient solubility. NMR spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

## 3.1. [RuCl<sub>2</sub>(PPh<sub>3</sub>)(H<sub>2</sub>L<sup>1</sup>)(CH<sub>3</sub>CN)]

 $[RuCl_2(PPh_3)_3]$  (100 mg, 0.1 mmol) was suspended in 20 mL of degassed acetonitrile under an atmosphere of dry argon.  $H_2L^1$  (29 mg, 0.1 mmol) was added as a solid in small portions over a period of 15 min. The mixture was stirred at room temperature for 3 h, which gave a clear yellow solution. The volume of the solvent was reduced to 5 mL. A yellow solid precipitated upon standing over night. The product was filtered off and washed with hexane.

Single crystals for X-ray diffraction were obtained by slow diffusion of diethyl ether in a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. Yield: 48 % (37 mg). IR( $\nu_{max}$ , cm<sup>-1</sup>): 3350 (w), 3102 (w), 3051 (st), 2908 (w), 2268 (w), 1577 (m), 1481 (m), 1435 (st), 1191 (m), 1153 (w), 1091 (st), 1064 (w), 1026 (m), 871 (m), 841 (w), 740 (st), 698 (st), 528 (st), 517 (st), 498 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 1.94 (s, 3H, CH<sub>3</sub>CN), 3.19 (m, 1H, PCH<sub>2</sub>), 3.61 (m, 1H, PCH<sub>2</sub>), 6.30 (m, 1H, CH<sub>arom.</sub>), 6.59 (m, 2H, CH<sub>arom.</sub>), 6.93–7.14 (m, 16H, CH<sub>arom.</sub>), 7.23 (m, 2H, CH<sub>arom.</sub>), 7.54 (m, 6H, CH<sub>arom.</sub>), 7.80 (m, 2H, CH<sub>arom.</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 47.39 (d, *J* = 26.4 Hz), 60.55 (d, *J* = 26.4 Hz) ppm. +ESI-MS: 654 [M–Cl–HCl–CH<sub>3</sub>CN]<sup>+</sup>, 690 [M–Cl–CH<sub>3</sub>CN]<sup>+</sup>, 731 [M–Cl]<sup>+</sup>. High resolution MS of the ion [M–Cl]<sup>+</sup> calcd: 371.1086, found: 371.1051.



**Fig. 4.** (a) Ellipsoid representation [22] of the molecular structure of  $[RuCl_2(dm-so)_2(H_2L^1)]$ . Thermal ellipsoids represent 50% probability. H atoms on C atoms have been omitted for clarity. (b) Hydrogen bond between each two of the complex molecules.

Selected bond lengths (Å) and angles (°) in $[RuCl_2(dmso)_2(H_2L^1)] \cdot CH_2Cl_2$ .				
Ru-Cl1	2.465(2)		Ru-P1	2.304(2)
Ru-Cl2	2.436(1)		Ru-S1	2.309(1)
Ru–N1	2.165(4)		Ru-S2	2.271(1)
Cl1-Ru-Cl2	87.91(5)		Cl2-Ru-S1	92.69(5)
Cl1-Ru-N1	83.9(1)		Cl2-Ru-S2	174.69(5)
Cl1-Ru-P1	169.04(4)		N1-Ru-P1	88.9(1)
Cl1-Ru-S1	88.68(5)		N1-Ru-S1	170.4(1)
Cl1-Ru-S2	90.56(5)		N1-Ru-S2	93.8(1)
Cl2-Ru-N1	81.0(1)		S1-Ru-P1	97.53(5)
Cl2-Ru-P1	82.81(5)		S1-Ru-S2	92.36(5)
P1-Ru-S2	98.15(5)			
_	Hydrogen bonds			
	d(D-H)	<i>d</i> (HA)	<i>d</i> (DA)	∠(D–HA)
N1-H1BCl1′	0.90	2.48	3.260(4)	144.9
N1-H1ACl2'	0.90	2.60	3.377(5)	145.1

Symmetry transformations used: (') -x, -y, -z + 1.

Table 3

## 3.2. $[(H_2L^1)(PPh_3)Ru(\mu-Cl)_2Ru(PPh_3)(H_2L^1)]$

 $[RuCl_2(PPh_3)_3]$  (100 mg, 0.1 mmol) was suspended in 20 mL of degassed  $CH_2Cl_2$  under an atmosphere of dry argon.  $H_2L^1$  (30 mg, 0.11 mmol) was added as a solid in small portions over a period of 15 min. The mixture was stirred for 4 h at room temperature.

Table 4	ole 4			
X-ray structure data collection and refinement parameters	ay structure data	collection and	d refinement	parameters.

	$[RuCl_2(PPh_3)(H_2L^1)(CH_3CN)] \cdot CHCl_3$	$[(H_2L^1)(PPh_3)Ru(\mu-Cl)_2Ru(PPh_3)(H_2L^1)]\cdot 0.5CH_2Cl_2$	$[RuCl_2(H_2L^1)_2]$	$[RuCl_2(dmso)_2(H_2L^1)] \cdot CH_2Cl_2$
Formula	C40H37Cl5N2P2Ru	C74.5H67Cl5N2P4Ru2	C38H36Cl2N2P2Ru	C24H32Cl4NO2PRuS2
M <sub>w</sub>	885.98	1493.57	754.60	704.51
Crystal system	monoclinic	triclinic	monoclinic	triclinic
a (Å)	10.393(1)	13.285(2)	20.698(2)	9.205(2)
b (Å)	22.807(2)	14.175(2)	16.289(1)	13.615(3)
<i>c</i> (Å)	17.106(1)	18.120(2)	10.213(1)	14.031(3)
α (°)	90	103.830(10)	90	61.31(2)
β(°)	93.72(1)	91.230(10	103.57(1)	84.53(2)
γ (°)	90	95.860(10)	90	87.41(2)
V (Å <sup>3</sup> )	4046.1(6)	3292.3(8)	3347.2(5)	1535.5(6)
Space group	$P2_1/n$	PĪ	$P2_1/c$	PĪ
Ζ	4	2	4	2
$D_{\rm calc}$ (g cm <sup>-3</sup> )	1.454	1.507	1.497	1.524
$\mu$ (mm <sup>-1</sup> )	0.828	0.805	0.755	1.069
Number of reflections	19078	25383	18439	16451
Number of independent	7017	12767	7221	8080
Number of parameters	453	802	407	339
$R_1$ , $wR_2$	0.0683, 0.1116	0.0790, 0.1254	0.0536, 0.1416	0.0591, 0.1530
GOF	0.893	0.860	0.892	0.833

The color of the solution turned to orange-brown and a pink solid precipitated. The complex was filtered off and washed with diethyl ether. The product is almost insoluble in all common solvents. Thus, red single crystals for X-ray diffraction were produced by slow diffusion of a solution of  $H_2L^1$  in diethyl ether into a saturated CHCl<sub>3</sub> solution of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]. Yield: 43 mg (59%). *Anal.* Calc. for C<sub>74</sub>H<sub>66</sub>Cl<sub>4</sub>N<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>: C, 60.25; H, 4.58; N, 1.93. Found: C, 59.87; H, 2.92; N, 1.77%. IR( $\nu_{max}$ , cm<sup>-1</sup>): 3317 (w), 3224 (w), 3051 (st), 2958 (w), 2916 (w), 1562 (m), 1481 (m), 1434 (st), 1188 (w), 1157 (w), 1087 (m), 1034 (m), 871 (m), 841 (m), 744 (st), 694 (st), 524 (st), 501 (m) cm<sup>-1</sup>.

## 3.3. $[RuCl_2(H_2L^1)_2]$

 $H_2L^1$  (60 mg, 0.2 mmol) was dissolved in 10 mL of degassed CH<sub>2</sub>Cl<sub>2</sub> under an atmosphere of dry argon. [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (100 mg, 0.1 mmol) was added to the colorless solution. The color changed within a few minutes to red. The reaction was heated under reflux for 4 h, which resulted in another color change and a sparingly soluble, yellow solid precipitated from the resulting yellow solution, which was filtered off and washed with diethyl ether. Single crystals for X-ray diffraction were obtained by a slow diffusion of H<sub>2</sub>L<sup>1</sup> (60 mg, 0.2 mmol) into a saturated CHCl<sub>3</sub> solution of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]. The initially formed red crystals redissolve within a few weeks and finally only clear yellow single-crystals of [RuCl<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>2</sub>] were obtained. Yield: 35 mg (46 mg). Anal. Calc. for C<sub>38</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Ru: C, 60.48; H, 4.81; N, 3.71. Found: C, 59.97; H, 3.76; N, 3.34%. IR(v<sub>max</sub>, cm<sup>-1</sup>): 3283 (m), 3232 (w), 3133 (w), 3056 (w), 2946 (w), 2905 (w), 1613 (w), 1574 (m), 1496 (m), 1456 (m), 1433 m), 1309 (w), 1262 (w), 1243 (m), 1220 (w), 1187 (w), 1091 (st), 1073 (m), 1048 (m), 1027 (st), 921 (w), 865 (m), 830 (st), 756 (st), 745 (m), 736 (st), 691 (st), 616 (m), 595 (st), 562 (m). <sup>1</sup>H NMR (dmso- $d_6$ ,  $\delta$ , ppm): 3.78 (m, 4H, PCH<sub>2</sub>), 6.68 (m, 2H, CH<sub>arom</sub>), 6.85 (m, 10H, CH<sub>ar-</sub> om), 6.90–7.12 ppm (m, 16H, CH<sub>arom</sub>). <sup>31</sup>P NMR (dmso, *δ*): 64.17 ppm. +ESI-MS: 720 [M-Cl]<sup>+</sup>, 797 [M-Cl+dmso]<sup>+</sup>. High resolution MS of the ion [M–Cl]<sup>+</sup> calcd: 719.1086, found: 719.1069.

## 3.4. $[RuCl_2(dmso)_2(H_2L^1)]$

 $[RuCl_2(dmso)_4]$  (50 mg, 0.1 mmol) was dissolved in 10 mL of degassed  $CH_2Cl_2$  and  $H_2L^1$  (30 mg, 0.11 mmol) was added. The solution was stirred for 4 h at room temperature. During this time, a pale yellow solid precipitated. Yield: 34 mg (48%). Single crystals of the almost insoluble compound for X-ray diffraction were obtained by the method described for  $[RuCl_2(PPh_3)(H_2L^1)(CH_3CN)]$ .

Anal. Calc. for  $C_{23}H_{30}Cl_2NP_2S_2Ru$ : C, 44.59; H, 4.88; N, 2.26; S, 10.35. Found: C, 44.21; H, 3.51; N, 2.20; S, 10.75%.  $IR(v_{max}, cm^{-1})$ : 3240 (m), 3190 (m), 3109 (st), 3058 (m), 3004 (m), 2916 (w), 1608 (m), 1581 (m), 1496 (m), 1458 (m), 1434 (st), 1404 (m), 1307 (w), 1137 (m), 1114 (st), 1087 (st), 1022 (m), 968 (m), 910 (m), 871 (m), 837 (m), 767 (st), 744 (m), 698 (st), 516 (st), 428 (m).

#### 3.5. X-ray structure determinations

The intensities for the X-ray determinations were collected on a STOE IPDS automated single crystal diffractometer with Mo K $\alpha$  radiation at 200(2) K. The structures were solved by direct ([RuCl<sub>2</sub>(PPh<sub>3</sub>)(H<sub>2</sub>L<sup>1</sup>)(CH<sub>3</sub>CN)], [RuCl<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>2</sub>], [RuCl<sub>2</sub>(dmso)<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)]) and Patterson methods ([(H<sub>2</sub>L<sup>1</sup>)(PPh<sub>3</sub>)Ru( $\mu$ -Cl)<sub>2</sub>Ru(PPh<sub>3</sub>)(H<sub>2</sub>L<sup>1</sup>)]) using shelxs-97 [21]. Subsequent Fourier difference map analyses yielded the position of the non-hydrogen atoms. Refinement was performed using shelxL-97 [21]. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of shelxL. Crystal data and more details of the data collections and refinements are contained in Table 4.

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## Appendix A. Supplementary data

CCDC 842635, 842636, 842637 and 842636 contain the supplementary crystallographic data for  $[RuCl_2(PPh_3)(H_2L^1)(CH_3CN)]$ ,  $[(H_2L^1)(PPh_3)Ru(\mu-Cl)_2Ru(PPh_3)(H_2L^1)]$ ,  $[RuCl_2(H_2L^1)_2]$  and  $[RuCl_2(dmso)_2(H_2L^1)]$ , respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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