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Synthesis, structures, spectroscopic and electrochemical studies of Ru(II) complexes containing bis(phosphino)amine ligands. Crystal and molecular structures of *trans*-[$RuCl_2\{Ph_2PN(Me)PPh_2$-κP,κP$\}_2$] and *trans*-[$RuCl_2\{Ph_2PN(^iPr)PPh_2$-κP,κP$\}_2$]

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Abstract

The synthesis, characterization and X-ray crystal study of the monomeric neutral complexes of general formula *trans*-[$RuCl_2\{Ph_2PN(R)PPh_2$-κP,κP$\}_2$] (R = H **1**, Me **2**, Et **3**, ^{n}Pr **4**, ^{i}Pr **5**, ^{n}Bu **6**, Ph **7**) is described. The analogous *cis* complexes, *cis*-[$RuCl_2\{Ph_2PN(R)PPh_2$-κP,κP$\}_2$] (R = H **8**, Me **9**), have also been synthesized and are characterized. The *trans*-[$RuCl_2\{Ph_2PN(Me)PPh_2$-κP,κP$\}_2$] complex reacts with Ag_2SO_4 to give a *cis* neutral complex, [$Ru\{(SO_4)$-κO,κO$\}\{Ph_2PN(Me)PPh_2$-κP,κP$\}_2$] (**10**) in good yield. Cyclic voltammograms of the complexes show two one-electron oxidation waves, one being quasi-reversible (Ru^{III}/Ru^{II}) and the other chemically irreversible (Ru^{IV}/Ru^{III}) with $E_{1/2}(Ru^{III}/Ru^{II})^{cis} > E_{1/2}(Ru^{III}/Ru^{II})^{trans}$. The more positive ($Ru^{III}/Ru^{II}$) potential for the *cis* isomer compared to that of *trans* isomer is consistent with stabilization of the dπ levels in the *cis* compared to the *trans* complex.

Keywords: Bis(phosphino)amines, ruthenium; Octahedral complexes; Crystal structures; Cyclic voltammetry

1. Introduction

The chemistry of Ru(II) complexes has gained considerable attention due to their wide-range of utility in homogeneous catalysis [1]. In particular, Ru(II) complexes containing phosphine ligands have been extensively used in catalytic processes such as homogeneous hydrogenation [2], epoxidation of olefins [3], oxidation of alcohols [4], reductive elimination and oxidative addition of C–H bonds [5], C–O, C–S [6] C–H [7] and C–C [1b] bond activations. To date, several six-coordinate complexes of Ru(II) containing bis(phosphines) with the P–C–P framework [8–13] have been reported but analogous complexes of bis(phosphino)amines are less extensive [14,15]. As a part of our continued interest [16] in synthesizing and studying the complexes of phosphorus based ligands, we report herein the synthesis of isomerically pure *cis*- and *trans*-[$RuCl_2\{Ph_2PN(R)PPh_2$-κP,κP$\}_2$] complexes. The reactivity, electrochemical properties, spectroscopic, and structural investigations are also described.

2. Results and discussion

In the present work a series of bis(phosphino)amines of the type $PPh_2N(R)PPh_2$ (R = H, Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, Ph) have been used. Treatment of [$RuCl_2(PPh_3)_3$] with 2 equiv. of these ligands in CH_2Cl_2 afforded the neutral, mononuclear *trans*-octahedral complexes of the type *trans*-[$RuCl_2\{Ph_2PN(R)PPh_2$-κP,κP$\}_2$] (**1**–**7**) (Scheme 1) with the elimination of PPh_3 ligands. The reactions of bis(phosphino)amines with [$RuCl_2(PPh_3)_3$] in equimolar ratios did not give complexes of the type [$RuCl_2(PPh_3)\{Ph_2PN(R)PPh_2\}$]; instead the same neutral *trans*-octahedral complexes were obtained in lower

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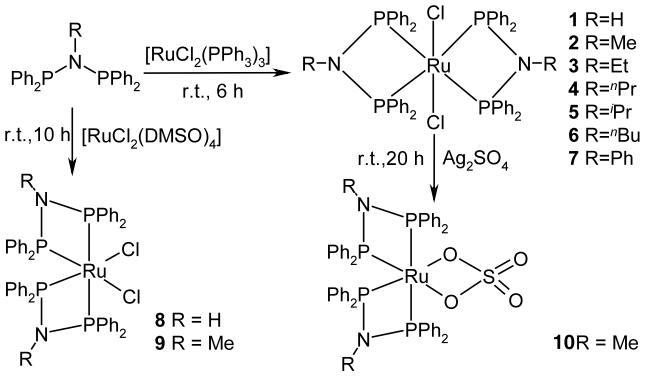


Scheme 1.

yield. Analogous *trans*-octahedral complexes with other bis(phosphines) have been prepared using rather forced reaction conditions and more complex routes [17,18]. In the present study the reactions occur smoothly under mild conditions to give exclusively the *trans* isomers in good yield. All the complexes are yellow or orange microcrystalline solids, stable to air but in solution they decompose gradually to give an insoluble green substance that could not be further characterized. All the complexes were characterized by NMR (^{1}H and ^{31}P{^{1}H}) and UV spectroscopic data. The compositions of the complexes have been confirmed by elemental analyses.

The ^{31}P{^{1}H} NMR (Table 1) spectra of *trans* complexes show sharp single resonances around δ 70–80 indicating the symmetric nature of the complexes. These resonances are downfield of the signals for the 'free' ligands, the deshielding being more pronounced for *iso*-propyl derivative, *trans*-[RuCl$_2${Ph$_2$PN(^{i}Pr)PPh$_2$-κP,κP}$_2$] (**5**) ($\Delta\delta = 27.1$) whereas it is least ($\Delta\delta = 1.6$) for methyl analog, *trans*-[RuCl$_2${Ph$_2$PN(Me)PPh$_2$-κP,κP}$_2$] (**2**). The coordination shifts ($\Delta\delta$) of all the compounds are given in Table 1 which follows the order: ^{i}Pr > H > Et ≈ ^{n}Bu ≈ ^{n}Pr > Ph > Me. The ^{1}H NMR spectra of all the complexes show the expected resonances for the ligand protons. The ^{1}H NMR spectrum of **2** shows a triplet at δ 3.03 for NCH_3 with $^3J_{PH} = 4.2$ Hz.

Table 1
^{31}P {^{1}H} NMR spectroscopic data [a] for the complexes **1**–**10**

Compound	^{31}P δ, J in Hz	$\Delta\delta$ [b]
trans-[RuCl$_2${Ph$_2$PN(H)PPh$_2$-κP,κP}$_2$] (**1**)	61.4	18.0
trans-[RuCl$_2${Ph$_2$PN(Me)PPh$_2$-κP,κP}$_2$] (**2**)	75.3	1.6
trans-[RuCl$_2${Ph$_2$PN(Et)PPh$_2$-κP,κP}$_2$] (**3**)	76.8	15.0
trans-[RuCl$_2${Ph$_2$PN(^{n}Pr)PPh$_2$-κP,κP}$_2$] (**4**)	76.6	13.6
trans-[RuCl$_2${Ph$_2$PN(^{i}Pr)PPh$_2$-κP,κP}$_2$] (**5**)	75.9	27.1
trans-[RuCl$_2${Ph$_2$PN(^{n}Bu)PPh$_2$-κP,κP}$_2$] (**6**)	76.5	14.0
trans-[RuCl$_2${Ph$_2$PN(Ph)PPh$_2$-κP,κP}$_2$] (**7**)	79.4	10.7
cis-[RuCl$_2${Ph$_2$PN(H)PPh$_2$-κP,κP}$_2$] (**8**)	61.7 (t), 35.8 (t), $^2J_{PP} = 37.8$	
cis-[RuCl$_2${Ph$_2$PN(Me)PPh$_2$-κP,κP}$_2$] (**9**)	75.7 (t), 52.4 (t), $^2J_{PP} = 36.3$	
cis-[Ru{Ph$_2$PN(Me)PPh$_2$-κP,κP}$_2$SO$_4$] (**10**)	79.6 (t), 59.3 (t), $^2J_{PP} = 35.5$	

[a] In $CDCl_3$; δ (^{31}P) in ppm vs. 85% H_3PO_4.
[b] $\Delta\delta = \delta_{complex} - \delta_{ligand}$ in ppm. t, triplet.

The electronic spectra of both *cis* and *trans* complexes show two intense bands around 236 and 262 cm^{-1}. The intense high-energy absorption bands have been assigned to intraligand $\pi \rightarrow \pi^*$ transitions. Similar bands were also observed in the free ligands.

The redox properties of compounds **1**–**7** and **9** in CH_2Cl_2 solution are summarized in Table 2. All potentials are referred to SCE. Both *cis*- and *trans*-[RuCl$_2${Ph$_2$PN(R)PPh$_2$-κP,κP}$_2$] exhibit two one-electron oxidation waves in CH_2Cl_2 solution with 0.1 M NBu_4PF_6 as supporting electrolyte. As shown in Fig. 1, the first oxidation wave is quasi-reversible but the second one is chemically irreversible. The one-electron nature of the responses is confirmed by comparing the current heights with that of the standard ferrocene/ferrocenium couple under identical experimental conditions. For the *trans* compounds, the quasi-reversible oxidation occurs in the range 0.24–0.133 V and is assigned to Ru^{III}/Ru^{II} couple. The formal potential of the couple varies depending on the 'R' groups present in the system in the order **7** < **4** < **1** < **3** < **6** < **2** < **5** < **9**. At the positive side of the SCE the complexes display one irreversible reductive process near 1.2–1.5 V assigned to Ru^{IV}/Ru^{III} couple. Comparisons between $E_{1/2}(Ru^{III}/Ru^{II})$ values for the *cis* and *trans* isomers show that $E_{1/2}(Ru^{III}/Ru^{II})^{cis}$ is larger than $E_{1/2}(Ru^{III}/Ru^{II})^{trans}$.

Table 2
Electrochemical data for compounds **1**–**7** and **9** in CH_2Cl_2 at 298 K [a]

Compound	E°_{298}/V (ΔE_p/mV)	
	Couple I Ru(III)–Ru(II)	Couple II Ru(IV)–Ru(III)
1	0.175 (103)	1.35
2	0.240 (106)	1.56
3	0.188 (100)	1.52
4	0.163 (113)	1.52
5	0.308 (80)	1.50
6	0.201 (139)	1.58
7	0.133 (133)	1.19
9	0.35 (133)	1.76

[a] Solvent, CH_2Cl_2; supporting electrolyte [NBu_4][PF_6]; reference electrode, SCE; solute concentration, approximately 10^{-3} mol dm^{-3}; working electrode, platinum wire. Cyclic voltammetry data: scan rate, 50 mV s^{-1}; $E^\circ_{298} = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

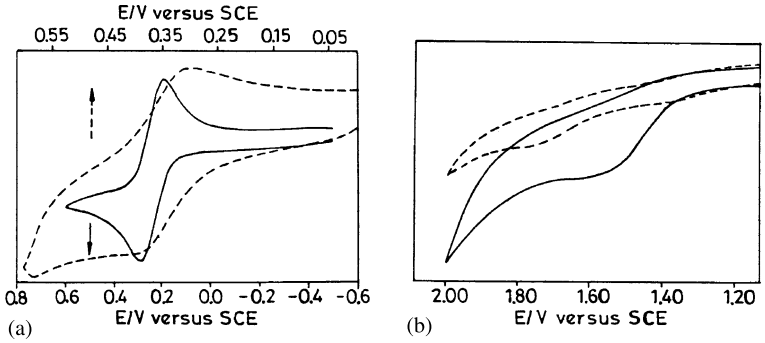


Fig. 1. CV traces of $\approx 10^{-3}$ mol dm^{-3} solution of the *trans*-[$RuCl_2${$Ph_2PN(Me)PPh_2$-κP,κP}$_2$] (**2**) (—) and *cis*-[$RuCl_2${$Ph_2PN(Me)PPh_2$-κP,κP}$_2$] (**9**) (---) in dry CH_2Cl_2. (a) First oxidative wave (quasi-reversible); and (b) second oxidative wave (irreversible).

Similar observations were made by Sullivan et al. for the *cis*–*trans* isomeric pair of [$RuCl_2(dppm)_2$] and also for the complexes of the type [(terpy)$RuLCl_2$] (L = PPh_3, P(*p*-$C_6H_4Me)_3$, pyridine; terpy = 2,2′,2″-terpyridine) [19,20]. The electronic preference for the *cis* isomer over the *trans* is based on metal–ligand back bonding. For the *cis* isomer there are two axial Cl–M–P groupings in place of the Cl–M–Cl and P–M–P groupings of the *trans* isomer. The net effect leads to enhanced back-bonding with phosphorus through the common metal d orbital via a pπ(Cl) → dπ(Ru) → dπ or σ*(P) interactions.

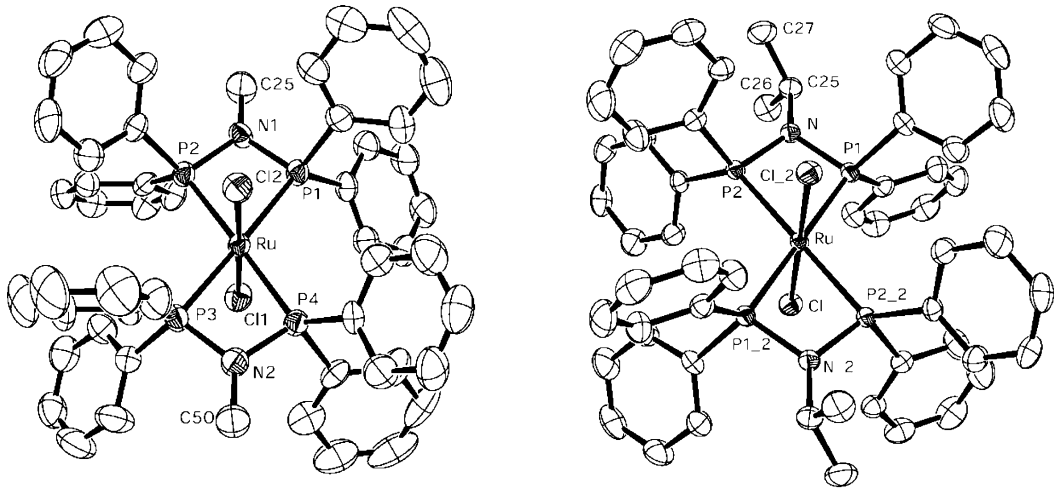
The Ru(II) derivative [$RuCl_2(DMSO)_4$] reacts cleanly with $Ph_2PN(R)PPh_2$ (R = H, Me) under mild reaction conditions to afford exclusively the *cis* isomers, *cis*-[$RuCl_2${$Ph_2PN(R)PPh_2$-κP,κP}$_2$] (R = H **8**, Me **9**) (Scheme 1). However, similar reactions with other bis(phosphino)amines, $Ph_2PN(R)PPh_2$ (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu) led to the isolation of only the *trans* isomers. We have no ready explanation for the differing stereochemical results here but do note that it is the ligands having the larger R groups attached to nitrogen that form exclusively the *trans* isomers. We thus tentatively ascribe the difference to steric factors. The ^{31}P NMR spectra show two triplets at δ 61.7 and 35.8 and δ 75.7 and 52.4, respectively for complexes **8** and **9**. The low field ^{31}P shifts for **8** and **9** which are comparable with those of their *trans* analogues can be readily assigned to two mutually *trans* phosphorus centers of the two chelating ligands whereas the remaining two high field shifts at δ 35.8 and 52.4 are assigned to the two phosphorus centers in a mutually *cis* disposition [21]. In case of compound **9** the ^{1}H NMR spectrum shows a triplet at δ 2.77 for the *N*-methyl protons with a $^3J_{PH}$ coupling of 4.8 Hz.

In another reaction, treatment of *trans*-[$RuCl_2$-{$Ph_2PN(Me)PPh_2$-κP,κP}$_2$] with Ag_2SO_4 affords *cis*-[Ru{(SO_4)-κO,κO}{$Ph_2PN(Me)PPh_2$-κP,κP}$_2$] (**10**), where SO_4^{-2} is acting as an anionic bidentate chelating ligand (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of **10** consists of two triplets at δ 79.6 and 59.3 with a $^2J_{PP}$ coupling of 35.5 Hz which strongly supports the formation of the *cis* product. The ^{1}H NMR spectrum shows a triplet at δ 2.82 for the *N*-methyl protons with a $^3J_{PH}$ coupling of 4.6 Hz.

The structures of the compounds **2** and **5** were determined by single crystal X-ray diffraction studies. Perspective views of the molecules and the atom numbering schemes are shown in Fig. 2. The crystallographic data are given in Table 3 with selected bond lengths and angles listed in Table 4.

The molecular structures show that the Ru(II) atom is in a typical octahedral environment with two bis(phosphino)amines in the equatorial plane and two chlorine atoms being axial with a *trans*-conformation. The *trans* angles around Ru(II) in case of two ranges from 177° to 179°. In the complex **5** the ruthenium atom is sited on a crystallographic center of inversion; therefore only half of the molecule is independently located in the asymmetric unit and the *trans* angles around Ru(II) are 180°.

In both the complexes the chelate ring is very much constrained as is evident from the P(1)–Ru–P(2) bite angles: 69.261(5)° in case of *trans*-[$RuCl_2${$Ph_2PN(Me)$-PPh_2-κP,κP}$_2$] (**2**) and 68.91(2)° in *trans*-[$RuCl_2${Ph_2P-$N(^iPr)PPh_2$-κP,κP}$_2$] (**5**). The average Ru–P distance is 2.3305(14) Å in **2** and 2.352(6) Å in **5** which are longer than those in the *trans*-[$RuCl_2${$Ph_2PN(C_6H_4OMe$-*o*)-PPh_2-κP,κP}$_2$] (2.348(3), 2.2332(2) Å) [15b] and [CpRu-Cl{$Ph_2PN(H)PPh_2$-κP,κP}] (2.2813(10), 2.4607(10) Å) [15c]. The Ru–Cl and P–N bond distances are comparable in these complexes. In all these complexes, the P-atoms that are *trans* disposed to another P-atom exhibit significantly larger distances than those *trans* to chloride ligand. It is due to the stronger *trans* influence exerted by phosphorus donors. The P–N–P_{ave} bond angles in both complexes is 102.24(6)° which is considerably less than the expected trigonal angle if the N-atom were sp^2 hybridized. The P–N_{ave} bond length of 1.707(5) Å is shorter than the normally accepted value for P–N single bond (1.77 Å) [22] suggesting a degree of P–N π bonding. Consistent with this, the nitrogen atoms are nearly planar as evidenced by the sum of the bond angles around the nitrogen atom: 359.5(3)° for **2** and 359.09(16)° for **5**, respectively.



2 **5**

Fig. 2. Perspective views of *trans*-[$RuCl_2\{Ph_2PN(Me)PPh_2$-κP,κP$\}_2$] (**2**) and *trans*-[$RuCl_2\{Ph_2PN(^iPr)PPh_2$-κP,κP$\}_2$] (**5**) as 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3
Crystallographic data for the complexes **2** and **5**

	2	**5**
Empirical formula	$C_{50}H_{46}Cl_2N_2P_4Ru$	$C_{54}H_{54}Cl_2N_2P_4Ru$
M	970.74	1024.84
T (K)	293	293
Crystal system	orthorhombic	triclinic
Space group	$Pca2_1$ (no. 29)	$P\bar{1}$ (no. 2)
a (Å)	20.526(2)	10.3399(6)
b (Å)	11.6569(12)	11.4368(6)
c (Å)	19.072(3)	12.3889(4)
α (°)		113.993(3)
β (°)		93.733(4)
γ (°)		113.395(5)
V (Å^3)	4563.3(10)	1182.74(13)
Z	4	1
D_{calc} (g cm^{-3})	1.413	1.442
μ (mm^{-1})	0.6	0.6
Total reflections	6368	4905
Unique reflections	4719	4635
R_{int}	0.034	0.023
R_1	0.0343	0.0265
wR_2	0.0907	0.0732

Table 4
Selected bond distances (Å) and bond angles (°) for **2** and **5**

Bond distances		Bond angles	
2			
Ru–Cl(1)	2.423(2)	P(1)–Ru–(P2)	69.26(5)
Ru–Cl(2)	2.412(2)	P(3)–Ru–P(4)	69.28(5)
Ru–P(1)	2.332(15)	P(1)–N(1)–P(2)	102.4(2)
Ru–P(2)	2.315(15)	P(3)–N(2)–P(4)	103.6(2)
Ru–P(3)	2.341(15)	P(2)–Ru–P(3)	109.90(5)
Ru–P(4)	2.334(2)	P(1)–Ru–P(4)	111.68(5)
P(1)–N(1)	1.700(4)	Cl(2)–Ru–P(4)	92.52(6)
P(2)–N(1)	1.689(5)	Cl(2)–Ru–P(3)	89.40(6)
N(1)–C(25)	1.476(6)	Cl(1)–Ru–P(1)	92.92(6)
N(2)–C(50)	1.478(7)	Cl(1)–Ru–P(2)	89.71(6)
P(3)–N(2)	1.689(5)	P(1)–Ru–P(3)	177.00(6)
P(4)–N(2)	1.692(5)	P(4)–Ru–P(2)	177.76(7)
		Cl(2)–Ru–P(1)	178.78(6)
5			
Ru–Cl	2.418(7)	P(1)–Ru–P(2)	68.91(2)
Ru–P(1)	2.3391(6)	Cl–Ru–P(1)	92.52(2)
Ru–P(2)	2.365(6)	Cl–Ru–P(2)	95.04(2)
P(1)–N	1.714(2)	P(1)–N–P(2)	101.48(10)
P(2)–N	1.724(2)	Cl–Ru–P(1_a) [a]	87.48(2)
N–C(25)	1.498(3)	Cl–Ru–P(2_a) [a]	84.96(2)
		P(1)–Ru–P(2_a) [a]	111.09(2)

[a] Atom 1_a related to atom 1, etc. by center.

3. Experimental

3.1. General

All experimental manipulations were performed under an atmosphere of dry nitrogen or Ar, using standard Schlenk and vacuum line techniques. Solvents were dried and distilled by standard methods prior to use. The bis(diphenylphosphino)amines, $Ph_2PN(R)PPh_2$ (R = H [23] Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu [24], Ph [25], $[RuCl_2(PPh_3)_3]$ [26] and $[RuCl_2(DMSO)_4]$ [27]) were prepared according to the published procedures. Silver sulfate was purchased from the Strem Chemical Co. and used as received.

3.2. Physical measurements

The multinuclear NMR (^{1}H and $^{31}P\{^1H\}$) were recorded on a VXR 300S spectrometer (operating at frequencies 300 and 121.421 MHz, respectively) using TMS and 85% H_3PO_4, respectively as the external standards. $CDCl_3$ was used both as solvent and as an

internal lock. Positive shifts lie downfield of the standard in all cases (δ is reported in ppm). Microanalyses were carried out on a Carlo–Erba Model 1112 elemental analyzer. The electronic absorption spectra were recorded on a 160A UV–Vis spectrophotometer. The electrochemical data were acquired with an EG&G model 273 system. The supporting electrolyte was $[NBu_4]PF_6$ (0.1 mol dm^{-3}) and solute concentration was 10^{-3} mol dm^{-3}. All experiments performed under an inert atmosphere.

3.3. General* procedure for the preparation of trans-[$RuCl_2\{Ph_2PN(R)PPh_2$-$\kappa P,\kappa P\}_2$] ($R = H$ **1**, Me **2**, Et **3**, ^{n}Pr **4**, ^{i}Pr **5**, ^{n}Bu **6**, Ph **7**)

A solution of bis(diphenylphosphino)amine, $X_2PN(R)PX_2$ (X = Ph, R = H, Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, Ph) (0.1 mmol) in CH_2Cl_2 (7 ml) was added dropwise to a solution of $[RuCl_2(PPh_3)_3]$ (0.048 g, 0.05 mmol) in CH_2Cl_2 (7 ml) at room temperature (r.t.). The reaction mixture was stirred for 6 h to get a yellow/orange solution. This was concentrated to 1–2 ml and Et_2O (5 ml) was added slowly whereupon analytically pure samples of the complexes **1**–**7** were precipitated out from the solution as yellow/orange crystalline solids.

*In the case of bis(diphenylphosphino)isopropylamine the duration of the reaction was 14 h.

3.4. trans-[$RuCl_2\{Ph_2PN(H)PPh_2$-$\kappa P,\kappa P\}_2$] (**1**)

Yield: 0.035 g, 74%, m.p. > 230 °C (dec.). *Anal*. Calc. for $C_{48}H_{42}Cl_2N_2P_4Ru$: C, 61.15; H, 4.49; N, 2.97. Found: C, 61.30; H, 4.23; N, 2.75%. UV–Vis: λ (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 197 (5500), 257 (38 000). ^{1}H NMR ($CDCl_3$, δ ppm): 7.16–7.38 (m, 40H, –*Ph*), 5.00 (br s, 2H, –N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 61.4 (s).

3.5. trans-[$RuCl_2\{Ph_2PN(Me)PPh_2$-$\kappa P,\kappa P\}_2$] (**2**)

Yield: 0.039 g, 80%, m.p. > 202 °C (dec.). *Anal*. Calc. for $C_{50}H_{46}Cl_2N_2P_4Ru$: C, 61.85; H, 4.78; N, 2.88. Found: C, 61.69; H, 4.63; N, 2.79%. UV–Vis: λ (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 235 (16 000), 265 (14 200). ^{1}H NMR ($CDCl_3$, δ ppm): 7.04–7.42 (m, 40H, –*Ph*), 3.03 (t, $^3J_{PH} = 4.2$ Hz, 6H, –NC*H*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 75.3 (s).

3.6. trans-[$RuCl_2\{Ph_2PN(Et)PPh_2$-$\kappa P,\kappa P\}_2$] (**3**)

Yield: 0.039 g, 78%, m.p. > 200 °C (dec.). *Anal*. Calc. for $C_{52}H_{50}Cl_2N_2P_4Ru$: C, 62.51; H, 5.05; N, 2.80. Found: C, 62.38; H, 5.15; N, 2.74%. UV–Vis: λ (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 232 (38 400), 262 (34 500). ^{1}H NMR ($CDCl_3$, δ ppm): 7.10–7.38 (m, 40H, –*Ph*), 3.50 (q, $^3J_{HH} = 6.0$ Hz, 4H, N–C*H*$_2$–CH$_3$,), 1.14 (t, $^3J_{HH} = 6.0$ Hz, 6H, N–CH$_2$–C*H*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 76.8 (s).

3.7. trans-[$RuCl_2\{Ph_2PN(^nPr)PPh_2$-$\kappa P,\kappa P\}_2$] (**4**)

Yield: 0.037 g, 72%, m.p. > 210 °C (dec.). *Anal*. Calc. for $C_{54}H_{54}Cl_2N_2P_4Ru$: C, 63.15; H, 5.30; N, 2.72. Found: C, 63.32; H, 5.37; N, 2.58%. UV–Vis: λ (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 236 (44 400), 265 (46 500). ^{1}H NMR ($CDCl_3$, δ ppm): 7.10–7.41 (m, 40H, –*Ph*), 3.31 (m, 4H, N–C*H*$_2$–CH$_2$–CH$_3$), 1.57 (m, 4H, N–CH$_2$–C*H*$_2$–CH$_3$), 0.68 (t, $^3J_{HH} = 6.8$ Hz, 6H, N–CH$_2$–CH$_2$–C*H*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 76.6 (s).

3.8. trans-[$RuCl_2\{Ph_2PN(^iPr)PPh_2$-$\kappa P,\kappa P\}_2$] (**5**)

Yield: 0.038 g, 73%, m.p. > 200 °C (dec.). *Anal*. Calc. for $C_{54}H_{54}Cl_2N_2P_4Ru$: C, 63.15; H, 5.30; N, 2.72. Found: C, 63.02; H, 5.24; N, 2.63%. UV–Vis: λ (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 236 (44 400), 262 (47 100). ^{1}H NMR ($CDCl_3$, δ ppm): 7.10–7.39 (m, 40H, –*Ph*), 3.86 (septet, $^3J_{HH} = 6.6$ Hz, 2H, N–C*H*–(CH$_3$)$_2$), 1.02 (d, $^3J_{HH} = 6.6$ Hz, 12H, N–CH–(C*H*$_3$)$_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 75.9 (s).

3.9. trans-[$RuCl_2\{Ph_2PN(^nBu)PPh_2$-$\kappa P,\kappa P\}_2$] (**6**)

Yield: 0.043 g, 82%, m.p. > 220 °C (dec.). *Anal*. Calc. for $C_{56}H_{58}Cl_2N_2P_4Ru$: C, 63.75; H, 5.54; N, 2.65. Found: C, 64.02; H, 5.63; N, 2.58%. UV–Vis: λ (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 236 (44 400), 265 (46 500). ^{1}H NMR ($CDCl_3$, δ ppm): 7.09–7.36 (m, 40H, –*Ph*), 3.36 (m, 4H, N–C*H*$_2$–(CH$_2$)$_2$–CH$_3$), 1.56 (m, 4H, N–CH$_2$–(*CH*$_2$)–CH$_2$–CH$_3$), 1.06 (sextet, $^3J_{HH} = 7.2$ Hz, 4H, N–(CH$_2$)$_2$–*CH*$_2$–CH$_3$), 0.72 (t, $^3J_{HH} = 7.2$ Hz, 6H, N–(CH$_2$)$_3$–C*H*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 76.5 (s).

3.10. trans-[$RuCl_2\{Ph_2PN(Ph)PPh_2$-$\kappa P,\kappa P\}_2$] (**7**)

Yield: 0.042 g, 76%, m.p. > 200 °C (dec.). *Anal*. Calc. for $C_{60}H_{50}Cl_2N_2P_4Ru$: C, 65.81; H, 4.60; N, 2.56. Found: C, 65.66; H, 4.49; N, 2.45%. UV–Vis: λ (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 236 (44 400), 265 (55 100). ^{1}H NMR ($CDCl_3$, δ ppm): 6.68–7.36 (m, 50H, –*Ph*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 79.4 (s)

3.11. cis-[$RuCl_2\{Ph_2PN(R)PPh_2$-$\kappa P,\kappa P\}_2$] ($R = H$ **8**, Me **9**)

A solution of bis(diphenylphosphino)amine $X_2PN(R)PX_2$ (X = Ph, R = H, Me) (0.2 mmol) in CH_2Cl_2 (8 ml) was added to a solution of $[RuCl_2(DMSO)_4]$ (0.048 g, 0.1 mmol) also in CH_2Cl_2 (5 ml). The reaction mixture was stirred for 10 h at r.t. and then solvent was removed under vacuum to get a yellow sticky mass. This was washed with $C_6H_5CH_3$ and the yellow residue was

dissolved in CH_2Cl_2/*n*-C_6H_{14} (1:1) which, upon cooling to 0 °C, gave analytically pure crystalline samples of **8** and **9**.

3.12. *cis*-[$RuCl_2\{Ph_2PN(H)PPh_2$-κ*P*,κ*P*$\}_2$] (**8**)

Yield: 0.072 g, 77%, m.p. >215 °C (dec.). *Anal*. Calc. for $C_{48}H_{42}Cl_2N_2P_4Ru$: C, 61.15; H, 4.49; N, 2.97. Found: C, 61.05; H, 4.57; N, 2.83%. ^{1}H NMR ($CDCl_3$, δ ppm): 6.40–8.05 (m, 40H, –*Ph*), 4.88 (br s, 2H, –N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 61.7 (t, 2P), 35.7 (t, 2P), $^2J_{PP} = 37.8$ Hz.

3.13. *cis*-[$RuCl_2\{Ph_2PN(Me)PPh_2$-κ*P*,κ*P*$\}_2$] (**9**)

Yield: 0.082 g, 85%, m.p. >260 °C (dec.). *Anal*. Calc. for $C_{50}H_{46}Cl_2N_2P_4Ru$: C, 61.85; H, 4.78; N, 2.88. Found: C, 62.03; H, 4.84; N, 2.81%. UV–Vis: λ (nm) (ε, $M^{-1}\,cm^{-1}$) (CH_2Cl_2): 234 (38 400), 264 (20 600). ^{1}H NMR ($CDCl_3$, δ ppm): 6.38–8.15 (m, 40H, –*Ph*), 2.77 (t, $^3J_{PH} = 4.8$ Hz, 6H, –NC*H*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 75.7 (t, 2P), 52.4 (t, 2P), $^2J_{PP} = 36.3$ Hz.

3.14. *cis*-[*Ru*{(SO_4)-κ*O*,κ*O*}{$Ph_2PN(Me)PPh_2$-κ*P*,κ*P*$\}_2$] (**10**)

A mixture of *trans*-[$RuCl_2\{Ph_2PN(Me)PPh_2$-κ*P*,κ*P*$\}_2$] (**2**) (0.068 g, 0.07 mmol) and Ag_2SO_4 (0.044 g, 0.14 mmol) was stirred at r.t. in dry CH_2Cl_2 (10 ml) for 20 h. The yellow colored solution was filtered through celite, the filtrate was concentrated to 3 ml and upon cooling to 0 °C gave analytically pure **10**. Yield: 0.053 g, 76%, m.p. >290 °C (dec.). *Anal*. Calc. for $C_{50}H_{46}N_2O_4P_4RuS$: C, 60.29; H, 4.66; N, 2.81. Found: C, 60.08; H, 4.39; N, 2.72%. ^{1}H NMR ($CDCl_3$, δ ppm): 6.32–8.11 (m, 40H, –*Ph*), 2.82 (t, $^3J_{PH} = 4.6$ Hz, 6H, –NC*H*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 79.6 (t, 2P), 59.3 (t, 2P), $^2J_{PP} =$ 35.5 Hz.

3.15. *X-ray crystallography*

Crystals of **2** and **5** were mounted on Pyrex filaments with epoxy resin. General procedures for crystal orientation, unit cell determination, refinement and collection of intensity data have been published. Intensity data were collected at r.t. using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation with a Enraf–Nonius CAD-4 diffractometer. Intensities were corrected for Lp effects (XCAD4) [28] and for absorption. The structures were solved by direct methods (SHELXS-97). Refinements were done by full-matrix least-squares based on F^2 using SHELXTL-PLUS [29] program package. Details of the data collections and refinements are summarized in Table 3.

4. Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 175550 (**2**) and 175551 (**5**) . Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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