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Substitution reactions of $CpRu(PPh_3)_2Cl$ with PPh_2H and dppa [1]

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Abstract

One PPh_3 group of $CpRu(PPh_3)_2Cl$ is easily substituted by PPh_2H to give the asymmetrical complex $CpRu(PPh_3)(PPh_2H)Cl$ (**1**) in a very good yield. Attempts to form the λ^4-phosphanediyl complex $CpRu(PPh_3){=}PPh_2$ (**1'**) by selective dehydrohalogenation of **1** failed. However, by using one equivalent of the chelating diphosphine dppa two PPh_3 ligands are substituted to yield CpRu(dppa)Cl (**2**). With an excess of dppa the reaction yielded the *N*-iminophosphoranyl-substituted dppa complex $CpRu\{(PPh_2)_2NPPh_2{=}NH\}Cl$ (**3**) and PPh_2H. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR, IR and mass spectra of **1–3** are given. Crystals of **1** are monoclinic, space group $P2_1/c$ with $a=11.8446(12)$, $b=14.502(3)$, $c=17.504(2)$ Å and $\beta=95.55(9)°$, $Z=4$ and $R=0.0270$ for 4299 observed reflections. Crystals of **2** are monoclinic, space group $P2_1/c$ with $a=10.7616(14)$, $b=18.263(4)$, $c=13.859(2)$ Å and $\beta=110.41(1)°$, $Z=4$ and $R=0.0327$ for 4227 observed reflections. © 1998 Elsevier Science S.A.

Keywords: Phosphinoamine complexes; Crystal structures; Ruthenium complexes; Iminophosphoranyl complexes

1. Introduction

$CpRu(PPh_3)_2Cl$ has been known since 1966 [1]. It is used as a convenient starting material for substitution reactions [2] and as a catalyst for certain reactions, e.g. HDS catalysis [3], hydrogenation of alkenes [4] or hydrosilylation of alkines [5]. Its substitution reactions with tertiary phosphines and diphosphines such as dppm and dppe are very well documented [2–10]. Our interest in $CpRu(PPh_3)_2Cl$ derives from our investigations of organometalated phosphorus compounds which follow the isolobal relationship [11]. Hitherto we have mainly used the 17-electron fragment $CpFe(CO)_2$ (=ferrio substituent) as the organometallic substituent and have prepared mono-, di- and triferriophosphonium salts. These organometalated salts can be used for the synthesis of the corresponding phosphines and phosphoranes [12–17] by the usual methods known from organic derivatives. Moreover, selective oxidation reactions have led to the first μ_3-bridged PS complexes [18] and to an interesting polynuclear cage compound [19]. Recently, we changed the object of our research from the organometallic substituent $CpFe(CO)_2$ to the isoelectronic CpMn(CO)(NO) fragment and have synthesized the stable manganiophosphonium salts $[C_5R_5Mn(CO)(NO)PPh_2Bz]X$ (R = H, Me) and the unstable manganioalkylidenephosphoranes $C_5R_5Mn(CO)(NO)\{PPh_2{=}CHPh\}$ [20]. In our last paper on this subject we reported the syntheses and reactions of ferrio- and manganioaminophosphonium salts and their corresponding iminophosphoranes [21]. In this paper we describe similar reactions of $CpRu(PPh_3)_2Cl$, which is isoelectronic to $CpFe(CO)_2Cl$, with PPh_2H and $(Ph_2P)_2NH$ (=dppa). It was hoped that the substitution products $CpRu(PPh_3)(PPh_2H)Cl$ and CpRudppaCl would be able to eliminate HCl to give the λ^4-phosphanediyl complex $CpRu(PPh_3){=}PPh_2$ or the imidodiphosphine complex $CpRu\{(PPh_2)_2N\}$.

2. Experimental

All operations were carried out under Ar and all solvents were dried according to known methods. PPh_2H [22], dppa [19] and $CpRu(PPh_3)_2Cl$ [23] were synthesized as published. $^{31}P\{^1H\}$ (109.36 MHz, standard: 85% H_3PO_4), $^{13}C\{^1H\}$ (100.53 MHz) and ^1H (270.16 MHz) NMR spectra were recorded on a Jeol GSX270 spectrometer at 21°C. IR spectra were recorded on a Nicolet 520 Fourier transform IR spectrometer (Nicolet Instrument GmbH) and mass spectra on a MAT 711A (Varian).

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2.1. *Synthesis of $CpRu(PPh_3)(PPh_2H)Cl$ (1)*

0.45 g (0.62 mmol) of $CpRu(PPh_3)_2Cl$ were added to a solution of 0.12 g (0.62 mmol) PPh_2H in 40 ml toluene. The orange solution was stirred for 5 days, after which the solvent was removed in vacuo to give a red solid. Crystals were obtained from thf/petroleum ether (1:1) after 24 h. Yield: 87%. ^1H NMR ($CDCl_3$, Me_4Si): δ 4.35 (s, Cp), 6.27 (d, PH, 359.2 Hz), 6.86–7.72 (m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, Me_4Si): δ 80.07 (s, Cp), 127.70 (d, 9.16 Hz), 128.00 (d, 9.77 Hz), 128.39 (d, 9.15 Hz), 129.19 (d, 1.83 Hz), 129.37 (d, 1.22 Hz), 132.08 (d, 9.77 Hz), 132.50 (d, 9.15 Hz), 132.94 (d, 10.37), 135.40 (d, 34.79 Hz), 135.41 (d, 45.17 Hz), 136.49 (d, 40.89 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.0 (d, PPh_3, $^3J_{pp}=47.0$ Hz), 41.0 (d, PPh_2H, $^3J_{pp}=47.0$ Hz). IR (KBr): ν 3070 (w, Cp, Ph), 2326 (m, PH), 1433 (s, Cp). Fast atom bombardment (FAB-MS) (*m*/*z*): 651 (M^+), 616 (M^+-Cl), 539 ($M^+-Cl-Ph$), 462 ($M^+-Cl-2Ph$). *Anal.* Calc. for $C_{35}H_{31}ClP_2Ru$: C, 64.66; H, 4.81. Found: C, 64.47; H, 4.38%.

2.2. *Synthesis of $CpRu\{(PPh_2)_2NH\}Cl$ (2)*

0.27 g (0.69 mmol) of dppa and 0.50 g (0.69 mmol) of $CpRu(PPh_3)_2Cl$ in 30 ml toluene were refluxed with stirring for 4 h. During this period the color of the solution changed to deep red, and a residue precipitated (see Section 2.3). After filtration the solvent was removed in vacuo and the resulting orange powder washed four times with 15 ml of n-pentane. Recrystallization of the orange powder in thf yielded red crystals which were washed with methanol. Yield: 47%. ^1H NMR ($CDCl_3$, Me_4Si): δ 4.66 (s, Cp), 5.10 (t, NH, 7.08 Hz), 7.35–7.66 (m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, Me_4Si): δ 79.3 (s, Cp), 128.0 (t, 4.88 Hz), 128.4 (t, 4.89 Hz), 129.8 (t, 5.49 Hz), 130.1 (s), 131.9 (t, 4.88 Hz), 134.3 (t, 20.80 Hz), 140.8 (t, 23.40 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 72.5 (s, PPh_2). IR (KBr): ν 3155 (w, Cp, Ph), 3071 (w, Cp, Ph), 1434 (vs, Cp). FAB-MS (*m*/*z*): 587 (M^+), 552(M^+-Cl), 475 ($M^+-Cl-Ph$), 398 ($M^+-Cl-2Ph$). *Anal.* Calc. for $C_{29}H_{26}ClNP_2Ru$: C, 59.34; H, 4.46; N, 2.39. Found: C, 59.27; H, 4.48; N, 2.28%.

2.3. *Synthesis of $CpRu\{(PPh_2)_2NPPh_2{=}NH\}Cl$ (3)*

0.27 g (0.69 mmol) of dppa and 0.50 g (0.69 mmol) of $CpRu(PPh_3)_2Cl$ in 30 ml toluene were refluxed with stirring for 4 h. After filtration (see Section 2.2) the yellow–green residue was washed with 10 ml thf. Yield: 25%. ^1H NMR ($CDCl_3$, Me_4Si): δ 3.99 (s, Cp), 6.42–7.09 (m, Ph), 8.41 (s, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, Me_4Si): δ 89.5 (s, Cp), 127.8 (d, 3.66 Hz), 128.2 (t, 4.88 Hz), 128.7 (t, 5.49 Hz), 129.1 (s), 129.2 (d, 1.84 Hz), 130.2 (t, 6.10 Hz), 131.5 (d, 21.97 Hz), 133.3 (d, 12.21 Hz), 133.8 (d, 19.53 Hz), 135.6 (t, 24.42 Hz), 138.8 (d, 46.38 Hz), 142.5 (t, 25.02 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.2 (d, PRu, $^3J_{pp}=37.6$ Hz), 51.9 Hz (t, PN_2, $^3J_{pp}=37.5$ Hz). IR (KBr): ν 3143 (w, Cp, Ph), 3055 (w, Cp, Ph), 1435 (s, Cp). FAB-MS (*m*/*z*): 785 (M^+-H), 750 (M^+-H-Cl), 736 ($M^+-H-Cl-N$). *Anal.* Calc. for $C_{41}H_{36}ClN_2P_3Ru$: C, 58.65; H, 4.80; N, 5.00. Found: C, 55.26; H, 5.38; N, 5.51%.

3. Results and discussion

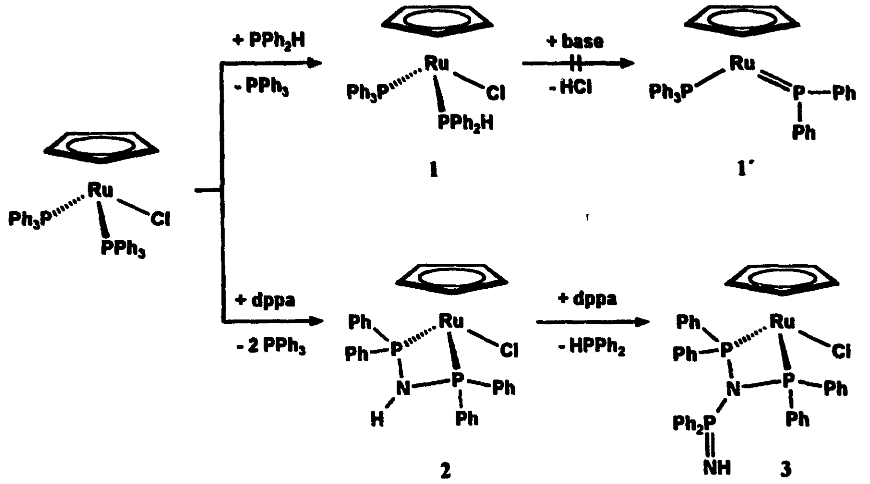
3.1. *Synthesis, spectra and properties*

One equivalent of PPh_2H easily reacts with the neutral half-sandwich complex $CpRu(PPh_3)_2Cl$ at room temperature to give the substitution product $CpRu(PPh_3)(PPh_2H)Cl$ (**1**) in a very good yield. With PPh_2H none of the disubstituted complex is formed. However, both phosphine ligands can be substituted when one equivalent of the bidentate aminodiphosphine ligand dppa is used under more drastic conditions. After refluxing $CpRu(PPh_3)_2Cl$ and dppa in toluene for 4 h we obtain $CpRu\{(PPh_2)_2NH\}Cl$ (**2**) which is found in solution. In the precipitate we find another product, namely $CpRu\{(PPh_2)_2NPPh_2{=}NH\}Cl$ (**3**), which forms in a competing reaction using two equivalents of dppa. Repetition of this reaction with an excess of dppa yields more precipitate and more **3**. In every case the formation and presence of PPh_2H in the solution is proven by $^{31}P\{^1H\}$ NMR spectroscopy. **3** also forms if **2** is treated with dppa in refluxing toluene. Therefore the following pathway for the formation of **3** is plausible. One nucleophilic phosphine group of the free dppa attacks the metal-coordinated dppa ligand at the electrophilic NH moiety. The easy formation and elimination of PPh_2H leads to P–N cleavage, and to coupling of the complex fragment with the new iminophosphoranyl group to yield the stable $CpRu\{(PPh_2)_2NPPh_2{=}NH\}Cl$ (**3**).

The red solids **1** and **2** and the yellow–green solid **3** are atmospherically stable. **1** and **2** are soluble in thf, but insoluble in acetonitrile and n-hexane, whereas **3** is insoluble in thf and soluble in toluene and benzene. Attempts to dehydrohalogenate **1** selectively using nBuLi or DBU to give the λ^4-phosphanediyl complex $CpRu(PPh_3){=}PPh_2$ (**1′**) with a trigonal planar phosphorus atom failed. All of the reactions mentioned above are summarized in Scheme 1.

IR, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra and mass spectra of compounds **1–3** were recorded (for details see Section 2). In their IR spectra the absorptions for ν(CH) and ν(C=C) are found in the same region at 3071–3055 cm^{-1} owing to similar phenyl and cyclopentadienyl ligands in all three complexes (**1**: 3070 cm^{-1}, **2**: 3071 cm^{-1} and **3**: 3055 cm^{-1}) and 1435–1433 cm^{-1} (**1**: 1433 cm^{-1}, **2**: 1434 cm^{-1} and **3**: 1435 cm^{-1}). For **1** a weak ν(PH) absorption is observed at 2326 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectra of **1–3** with their significant peaks reflect the different characters of the phosphorus atoms. For **1** we obtain two doublets at 47.0 ppm ($^2J_{PP}=47.0$ Hz) and 41.0 ppm ($^2J_{PP}=46.9$ Hz) for the PPh_3 and the PPh_2H group. Compound **2** shows a downfield shift of the singlet to 72.5 ppm resulting from the bidentate dppa ligand. At the



Scheme 1.

first glance the $^{31}P\{^1H\}$ NMR spectrum of **3** was puzzling; it surprisingly showed a doublet at 61.2 ppm ($^2J_{PP}$ = 37.6 Hz) and a triplet at 51.9 ppm ($^2J_{PP}$ = 37.6 Hz). However, we found a very useful hint concerning the origin and character of these signals. Ellermann and Wend [24] had synthesized and characterized the similar planar, but symmetrical ligand $N(PPh_2)_3$, which, when bidentately coordinated to a metal as in $(CO)_4Cr\{(PPh_2)_2NPPh_2\}$, shows a very similar pattern of signals.

The multiplets of the phenyl protons in the ^1H NMR spectra of **1–3** lie in the same expected region (**1**: 6.38–7.72 ppm, **2**: 7.35–7.66 ppm, **3**: 6.42–7.09 ppm). The singlets for the Cp protons, however, differ significantly among themselves and lie respectively for **1** and **2** at 4.35 and 4.45 ppm. The Cp protons of **3** are found at higher field, at 3.99 ppm. Moreover, **2** and **3** possess a NH function and this proton appears as a triplet at 5.10 for **2** and a singlet at 8.41 ppm for **3**. The proton at the phosphorus of **1** appears as a doublet at 6.27 ppm ($^1J_{PH}$ = 359.2 Hz).

The $^{13}C\{^1H\}$ NMR spectra of **1–3** are of higher order for the signals in the aromatic region. **1** shows doublets between 127.70–136.49 ppm, whereas **2** has a more complex spin system, so all signals are found as triplets within 128.0 and 140.8 ppm indicating a P–C interaction. **3** exhibits a mixture of triplets and doublets between 127.8 and 142.5 ppm for the two different phenyl groups. The Cp signals, however, appear as singlets at 80.1 ppm for **1**, 79.3 ppm for **2** and 89.5 ppm for **3**.

The mass spectrum of **1** shows the molecular peak at 651 (M^+) and the corresponding fragments at 616 ($M^+ - Cl$), 539 ($M^+ - Cl - Ph$) and 462 ($M^+ - Cl - 2Ph$). In the mass spectrum of **2** the molecular peak is detected at 587 (M^+) with fragments at 552 ($M^+ - Cl$), 475 ($M^+ - Cl - Ph$) and 398 ($M^+ - Cl - 2Ph$). The mass spectrum of **3** shows a molecular peak at 785 which is consistent with ($M^+ - H$) for the structure of **3** mentioned above. Further fragments which were detected are 750 ($M^+ - H - Cl$) and 736 ($M^+ - H - Cl - N$).

3.2. X-ray structural analyses of 1 and 2

Suitable single crystals of **1** and **2** were obtained by recrystallization of the orange residue of **1** in a mixture of thf/petroleum ether (1:1) and recrystallizing the orange powder of **2** in thf. The resulting red crystals of both compounds were washed with methanol.

The bond lengths and angles of **1** and **2** are summarized in Table 1, and their measuring and crystal data in Table 2. Figs. 1 and 2 show the molecular structures of **1** and **2**. In both compounds the central metal atoms, as well as the phos-

Table 1
Selected bond lengths (Å) and angles (°) of **1** and **2**

1		**2**	
Ru(1)–C(4)	2.183(4)	Ru(1)–C(3)	2.146(4)
Ru(1)–C(5)	2.193(4)	Ru(1)–C(2)	2.164(4)
Ru(1)–C(2)	2.200(4)	Ru(1)–C(4)	2.207(4)
Ru(1)–C(3)	2.199(4)	Ru(1)–C(1)	2.223(4)
Ru(1)–C(1)	2.210(4)	Ru(1)–C(5)	2.234(4)
Ru(1)–P(2)	2.2799(9)	Ru(1)–P(2)	2.2777(10)
Ru(1)–P(1)	2.3019(9)	Ru(1)–P(3)	2.2813(10)
Ru(1)–Cl(1)	2.3290(9)	Ru(1)–Cl(1)	2.4607(10)
P(1)–C(6)	1.837(3)	P(2)–N(1)	1.692(3)
P(1)–C(12)	1.840(3)	P(3)–N(1)	1.694(3)
P(1)–C(18)	1.838(3)	P(2)–C(6)	1.823(3)
P(2)–C(24)	1.822(3)	P(2)–C(12)	1.821(3)
P(2)–C(30)	1.837(3)	P(3)–C(24)	1.829(3)
		P(3)–C(18)	1.827(4)
P(2)–Ru(1)–P(1)	92.32(3)	P(3)–Ru(1)–P(2)	69.12(3)
P(2)–Ru(1)–Cl(1)	88.35(3)	P(2)–Ru(1)–Cl(1)	100.19(3)
P(1)–Ru(1)–Cl(1)	89.26(3)	P(3)–Ru(1)–Cl(1)	97.92(3)
C(6)–P(1)–C(12)	102.49(13)	P(3)–N(1)–P(2)	99.6(2)
C(6)–P(1)–C(18)	104.14(13)	Ru(1)–P(2)–N(1)	95.70(10)
C(12)–P(1)–C(18)	100.78(13)	Ru(1)–P(3)–N(1)	95.53(10)
C(6)–P(1)–Ru(1)	112.58(10)	Ru(1)–P(2)–C(6)	127.59(12)
C(12)–P(1)–Ru(1)	116.84(10)	Ru(1)–P(2)–C(12)	117.71(11)
C(18)–P(1)–Ru(1)	117.98(10)	Ru(1)–P(3)–C(24)	131.84(12)
C(24)–P(2)–C(30)	102.27(13)	Ru(1)–P(3)–C(18)	112.64(11)
C(24)–P(2)–Ru(1)	119.89(10)	C(6)–P(2)–C(12)	99.5(2)
C(30)–P(2)–Ru(1)	118.52(9)	C(24)–P(3)–C(18)	101.6(2)

Table 2
Parameters used for the X-ray data collection

	1	**2**
Identification code	$CpRu(PPh_3)(PPh_2H)Cl$	$CpRu((PPh_2)_2NH)Cl$
Empirical formula	$C_{35}H_{31}ClP_2Ru$	$C_{29}H_{26}ClNP_2Ru$
Formula weight	650.06	586.97
Diffractometer	Enraf-Nonius-CAD4	Enraf-Nonius-CAD4
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	11.8446(12)	10.7616(14)
b (Å)	14.502(3)	18.263(4)
c (Å)	17.504(2)	13.859(2)
α (°)	90	90
β (°)	95.55(9)	110.41(1)
γ (°)	90	90
Volume (Å^3)	2992.4(7)	2553.0(7)
Z	4	4
Density (calc.) (Mg m^{-3})	1.443	1.527
Absorption coefficient (mm^{-1})	0.743	0.863
$F(000)$	1328	1192
Crystal size (mm)	0.53×0.40×0.27	0.43×0.53×0.53
θ range (°)	2.77–22.98	2.73–23.97
Index ranges	$-13 \leq h \leq 12$, $0 \leq k \leq 15$, $0 \leq l \leq 19$	$-12 \leq h \leq 0$, $0 \leq k \leq 20$, $-14 \leq l \leq 15$
No. reflections collected	4299	4227
No. independent reflections	4142 [$R_{int}=0.0127$]	3994 [$R_{int}=0.0196$]
Absorption correction	semi-empirical from ψ-scans	semi-empirical from ψ-scans
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Max. and min. transmission	0.9991 and 0.9489	0.9959 and 0.8822
Data/restraints/parameters	4142/0/355	3994/0/307
GOF	1.030	1.137
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0270$, $wR2 = 0.0628$	$R1 = 0.0327$, $wR2 = 0.0851$
R indices (all data)	$R1 = 0.0341$, $wR2 = 0.0675$	$R1 = 0.0380$, $wR2 = 0.0884$
Largest difference peak/hole (e Å^{-3})	0.313/ −0.282	0.739/ −0.529

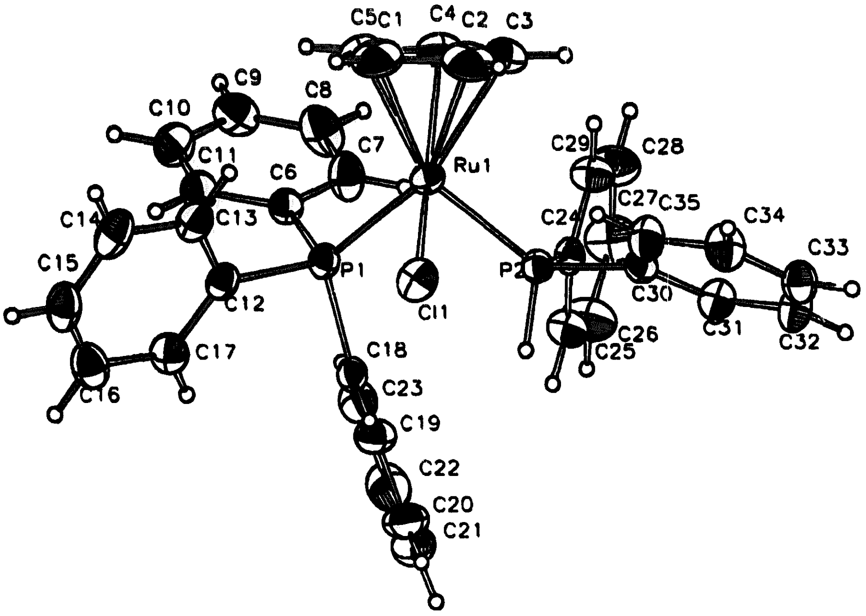


Fig. 1. Molecular structure of **1**.

phine ligands, have distorted tetrahedral configurations. The cyclic ligand C_5H_5 shows an average M–C distance of 2.197 Å for **1** and 2.195 Å for **2**. The metal–phosphorus distances of **1** differ slightly owing to the different phosphorus ligands (Ru(1)–P(2), 2.2799(9) Å; Ru(1)–P(1), 2.3019(9) Å). The metal–phosphorus distances of **2** are as

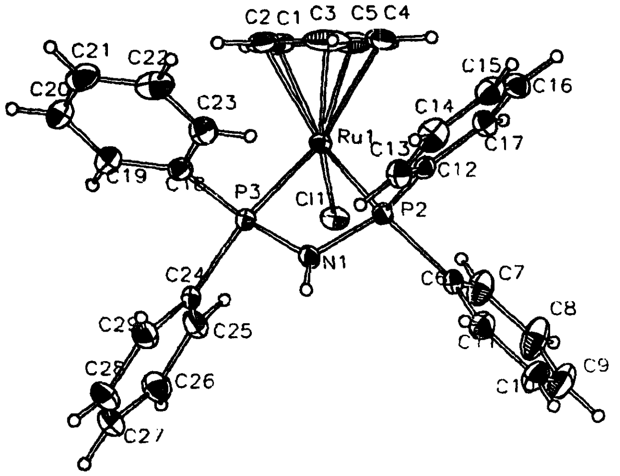


Fig. 2. Molecular structure of **2**.

expected nearly identical at 2.2777(10) and 2.2813(10) Å, and are comparable with those known from the literature [25]. Both phosphorus–nitrogen bonds in **2** are also identical (1.692(3) and 1.694(3) Å). Owing to the stronger *trans*-influencing dppa ligand the metal–chlorine distance of **2** is significantly longer than that of **1** with the two different, but weaker phosphine ligands (**1**: 2.3290(9) Å, **2**: 2.4607(10) Å).

Looking at the P–Ru–P angles we find striking differences between **1** and **2** because of the chelate effect (**1**: 92.32(3)°, **2**: 69.12(3)°). Therefore the P–Ru–Cl angles of **2** (P(2)–Ru(1)–Cl(1), 100.19(3)°; P(3)–Ru(1)–Cl(1), 97.92°) are higher than those of **1** (P(2)–Ru(1)–Cl(1), 88.35(3)°; P(1)–Ru(1)–Cl(1), 89.26(3)°). Summarizing the angles of the Ru–P–N–P ring of **2** we obtain 359.95° which indicates a planar ring system.

4. Supplementary material

Further details of the two crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD 406798 and CSD 406799, the names of the authors, and the journal citation.

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