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Syntheses, characterization and structure determination of $\{[CpRu(X)]_2(\eta^2,\mu_2\text{-dppe})_2\}$ complexes (X=Cl, N_3; dppe= $Ph_2PCH_2CH_2PPh_2$) Chelating vs. bridging behavior of a classical bidentate ligand

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Abstract

Phosphine substitution reactions between $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (**1**) and 1,2-bis(diphenylphosphino)ethane ($Ph_2P(CH_2)_2PPh_2$, dppe), in refluxing benzene or in toluene at 80°C afforded a mixture of complexes where dppe behaves both as a bridging and as a chelating ligand. $CpRu(\eta^2\text{-dppe})Cl$ (**2**) and $\{[CpRu(Cl)]_2(\eta^2,\mu_2\text{-dppe})_2\}$ (**3**) were separated by fractional precipitation from the reaction mother-liquor, and were characterized by ^1H, ^{13}C, ^{31}P NMR, elemental analysis and IR spectroscopy. The (**2**):(**3**) ratio in the composition of the reaction product was found to be independent of the reaction time. In solution and at room temperature, (**3**) exists in both boat and chair conformers of a 10-membered ring, while at lower temperatures, and in the solid-state, only the chair conformer is observed. Compounds (**2**) and (**3**) undergo halide-displacement upon reacting with NaN_3 in the presence of ethanol to yield $CpRu(\eta^2\text{-dppe})(N_3)$ (**4**) and $\{[CpRu(N_3)]_2(\eta^2,\mu_2\text{-dppe})_2\}$ (**5**), respectively. The crystal structures of (**3**) and (**5**) were determined.

Keywords: Ruthenium; Diphosphine; Dimer; dppe; Azide; Cyclopentadienyl

1. Introduction

Interest in the cyclopentadienyl diphosphine ruthenium(II) fragment has increased in past years due to its use as an auxiliary unit towards the development of organometallic-assisted organic synthesis [1–4]. For instance, the facile replacement of both the phosphines and the chloride in $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ by a wide variety of neutral or anionic ligands has been used [5,6] as a means to prepare several complexes containing a metal-bound organic moiety. These compounds have been used to promote modifications of such organic fragments even under mild conditions [1,5–8]. Also, interest in these compounds can be attributed to the catalytic activity of phosphino-complexes of Ru(II) on the decarbonylation of both aliphatic and aromatic aldehydes as previously pointed out in the literature [9,10] as well as in hydroformylation reactions carried out at low temperatures [13–15] and more recently on the anti-Markovnikov hydration of terminal alkynes under relatively mild conditions [16].

Transition metal azido (N_3^-) complexes, on the other hand, have been widely used in a series of organometallic-assisted reactions such as oxidations [11,12] and 1,3-cycloadditions [17,18]. In addition, photolysis of azido complexes leads to the formation of azido radicals, which have found industrial use on the photoinitiation of radical polymerization [19].

The phosphine replacement reaction between $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (**1**) and bis(diphenylphosphino)ethane ($Ph_2P(CH_2)_2PPh_2$, dppe) was first carried out by Bruce and coworkers [20]. They reported that when the reaction was carried out in refluxing benzene, $CpRu(\eta^2\text{-dppe})Cl$

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(**2**), in which dppe acts as a chelating ligand, was formed in high yield as the sole product. When attempting to reproduce the synthesis of this compound in order to further study its ligand-exchange reactions, we observed several signals on the ^{31}P NMR spectrum of the crude product, in addition to those due to (**2**), that could not be assigned to it or to free PPh_3. These signals were later assigned to the dimeric complex, $\{[CpRu(Cl)]_2(\eta_2,\mu_2\text{-dppe})_2\}$ (**3**), which is formed in the 17 to 30 mol% yield range. Compounds (**2**) and (**3**) are the co-products of the reaction and their relative distribution in the final product is not dependent upon the reaction time. We have thus decided to further study this reaction and try to identify its intermediates in order to explain the observed product distribution. We have also prepared several derivatives of (**2**) and (**3**). Our results are described below.

2. Experimental

2.1. Physical measurements

IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer or in a Mattson Galaxy FTIR instrument as pressed KBr or CsI pellets. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were recorded at 400, 50 and 162 MHz, respectively, on a Bruker DRX 400 spectrometer, using $CDCl_3$ or C_6D_6 as solvents. ^{13}C and ^1H NMR spectra were referenced to TMS ($\delta=0$ ppm). ^{31}P NMR spectra were referenced to an external 85% H_3PO_4/D_2O standard ($\delta=0$ ppm). Elemental analyses were carried out on a Perkin-Elmer PE2400CHN instrument using copper sample-tubes. Melting points were measured using a Medtler FP90 melting point apparatus with digital calibration. Chlorine analysis was carried out by X-ray fluorescence in a Rigaku-Geigerflex spectrometer.

2.2. Preparation and characterization of the compounds

$RuCl_3\cdot 3H_2O$, $Ph_2P(CH_2)_2PPh_2$ (1,2-diphenylphosphinoethane, dppe) and PPh_3 were purchased from Aldrich Chemical Co. and used as supplied. Cyclopentadiene (Aldrich) was distilled under dry N_2 prior to use. EtOH was freshly distilled from a Mg/I_2 still and stored under N_2 over 4 Å molecular sieves. Benzene and toluene were distilled from a Na/benzophenone ketyl still and stored under N_2 over 3 Å molecular sieves. All reactions were carried out using standard Schlenk and glove-bag techniques, under dry dinitrogen.

$CpRu(PPh_3)_2Cl$ (**1**) was prepared according to published methods [21], from the reaction between $RuCl_3\cdot 3H_2O$, C_5H_6 and PPh_3 in dry EtOH. The air-stable $CpRu(\eta^2\text{-dppe})Cl$ (**2**) was also prepared according to published procedures [20] from the reaction between (**1**) and dppe in refluxing benzene.

The orange–yellow, air-stable, $\{[CpRu(Cl)]_2(\eta^2,\mu_2\text{-dppe})_2\}$ (**3**), a co-product from the synthesis of (**2**), was separated from the crude reaction product by extraction with cold toluene. It can alternatively be separated from (**2**), by means of fractional precipitation from the mother-liquor. Reacting 0.37 g (5.1×10^{-4} mol) of (**1**) and 0.21 g (5.4×10^{-4} mol) of dppe in 100 ml of refluxing benzene for 10 h, followed by reduction of the original volume of the reaction mother-liquor by 80% and adding an equal volume of *n*-hexane, causes the precipitation of considerably pure (**3**), with (**2**) remaining in solution. Compound (**3**) was re-dissolved in cold toluene (25 ml) and re-precipitated by addition of cold *n*-hexane (20 ml). Melting point: 327°C (dec.). Elemental analysis data for (**3**): calculated (*found*): C 62.00 (*62.23*); H 4.87 (*4.72*); Cl 5.90 (*5.82*). ^1H NMR (ppm, $CDCl_3$): δ 2.17 (broad, CH_2), δ 3.01 (broad, CH_2), δ 3.94 (s, η^5-Cp), δ 7.41–7.92 (m, C_6H_5). ^{13}C NMR (ppm, $CDCl_3$): δ 27.8 (s, CH_2), δ 79.6 (s, η^5-Cp), δ 127.8–133.9 (m, C_6H_5). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): δ 37.10 (s, μ-dppe), δ 45.69 (s, μ-dppe, see text).

Compounds (**2**) and (**3**) may also be separated by means of column chromatography using silica gel as stationary phase and toluene:$CHCl_3$ as eluent. While (**3**) follows closely the solvent front, (**2**) virtually does not undergo any elution.

$CpRu(\eta^2\text{-dppe})(N_3)$ (**4**), and $\{[CpRu(N_3)]_2(\eta^2,\mu_2\text{-dppe})_2\}$ (**5**) were prepared by salt metathesis reactions between a large stoichiometric excess of NaN_3 (0.10 g, 1×10^{-3} mol) and (**2**) or (**3**) (1.7×10^{-4} mol) respectively, in refluxing 4:1 EtOH:benzene solution (100 ml). While the reaction with the dimeric compound reaches completion after ca. 4 h, the reaction with its monomeric counterpart requires up to 6 h under the same conditions. Upon cooling down to room temperature, most of the excess of NaN_3 precipitated out is separated by filtration and the filtrate evaporated under vacuum. The products were further purified by re-crystallization. Bulk (**4**) was dissolved in 4.5 ml of CH_2Cl_2 and re-precipitated by the addition of ca. 30 ml of chilled *n*-hexane or *n*-pentane. Overall yield was 85%. Compound (**5**) was purified in the same way, but using 6 ml of CH_2Cl_2, instead. Overall yield was 81%. Both products are obtained as air-stable, reddish–orange powders.

Caution! Although the authors had no accidents while carrying out these syntheses, care should be taken when handling azides due to their explosive nature. These complexes, as well as NaN_3, should be handled with a glass or ceramic spatula.

Melting point for (**4**): 251°C (dec.). Elemental analysis data for (**4**): calculated (*found*) C 61.28 (*59.95*); H 4.81 (*4.10*); N 6.92 (*6.69*). Spectroscopic data for (**4**): IR (cm^{-1}, CsI): 2000 (ν_{N_3}); 680 (δ_{N_3}); 393 (ν_{Ru-N}). ^1H NMR (ppm, $CDCl_3$): δ 2.24 (broad, CH_2), δ 4.51 (s, η^5-Cp), δ 6.69–7.86 (m, C_6H_5); ^{13}C NMR (ppm, $CDCl_3$): δ 31.0 (s, CH_2); δ 81.9 (s, η^5-Cp); δ 127.8–135.8 (m, C_6H_5). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): δ 81.6 (s, dppe).

Table 1
Crystal data and refinement parameters for $\{[CpRuCl]_2(\mu_2dppe)_2\}\cdot 2CH_2Cl_2$ (**3**), and $\{[CpRu(N_3)]_2(\mu_2\text{-}dppe)_2\}$ (**5**)[a]

	$\{[CpRuCl]_2(\mu_2\text{-}dppe)_2\}\cdot 2CH_2Cl_2$ (**3**)	$\{[CpRu(N_3)]_2(\mu_2\text{-}dppe)_2\}$ (**5**)
Empirical formula	$C_{64}H_{62}Cl_6P_4Ru_2$	$C_{62}H_{58}N_6P_4Ru_2$
Formula weight	1369.86 Da	1213.16 Da
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a=13.1493(1)$ Å; $\alpha=90°$	$a=11.2329(1)$ Å; $\alpha=90°$
	$b=16.6125(1)$ Å; $\beta=101.3185(4)°$	$b=19.0047(1)$ Å; $\beta=94.735(1)°$
	$c=14.0232(1)$ Å; $\gamma=90°$	$c=12.8452(1)$ Å; $\gamma=90°$
Unit cell volume, Z	3003.70(4) Å^3, 2	2732.81(4) Å^3, 2
Density (calculated)	1.515 Mg/m^3	1.474 Mg/m^3
Absorption coefficient	0.916 mm^{-1}	0.716 mm^{-1}
$F(000)$	1392	1240
Crystal size	0.36×0.26×0.22 mm	0.38×0.12×0.10 mm
θ range for data collection	1.92 to 28.31°	1.92 to 28.19°
Limiting indices	$-16\le h\le 17$, $-22\le k\le 21$, $-18\le l\le 18$	$-14\le h\le 14$, $-25\le k\le 24$, $-17\le l\le 16$
Reflections collected	32 046	28 333
Independent reflections	7207 ($R_{int}=0.0221$)	6467 ($R_{int}=0.0457$)
Observed reflections ($I>2\sigma(I)$)	6533	5219
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transm.	0.862 and 0.747	0.9465 and 0.8286
Data/restraints/parameters	7207/0/467	6466/0/450
Goodness-of-fit on F^2	0.999	1.058
Final R indices ($I>2\sigma(I)$)	$R1=0.0250$, $wR2=0.0645$	$R1=0.0346$, $wR2=0.0637$
R indices (all data)	$R1=0.0294$, $wR2=0.0671$	$R1=0.0526$, $wR2=0.0701$
Largest diff. peak and hole	0.800 and −0.877 e Å^{-3}	0.379 and −0.520 e Å^3

[a] Weighting scheme: $w=1/[\sigma^2(F_o^2)+(AP)^2+(BP)]$ where $P=(F_o^2+2F_c^2)/3$.

Melting point for (**5**): 321°C (dec.). Elemental analysis data for (**5**), calculated (*found*): C 61.28 (*59.68*); H 4.81 (*4.22*); N 6.92 (*6.61*). Spectroscopic data for (**5**): IR (cm^{-1}, CsI): 2003 (ν_{N_3}); 682 (δ_{N_3}); 387 (ν_{Ru-N}). ^{1}H NMR (ppm, $CDCl_3$): δ 2.17 (d, CH_2, $J_{H_a-H_e}=12$ Hz); δ 4.12 (s, η^5-Cp); δ 7.14–7.42 (m, C_6H_5). ^{13}C NMR (ppm, $CDCl_3$): δ 27.77 (s, CH_2); δ 79.61 (s, η^5-Cp); δ 127.80–133.90 (m, C_6H_5). ^{31}P NMR (ppm, $CDCl_3$): δ 39.19 (s, dppe).

2.3. Crystallographic measurements and structure determinations

Columnar crystals of (**3**) and (**5**) were grown from the slow evaporation of $CHCl_3$ or CH_2Cl_2:$CHCl_3$ (1:1) solutions. Approximate spheres of data were collected at 173(2) K on a Siemens Smart 1 K CCD system using a graphite monochromator (wavelength Mo Kα=0.71073 Å). Structures were solved and refined using the SHELX software [22]. Refinement was full-matrix least-squares on F^2 over all data. Absorption corrections were applied using multi-scan data [23] (SADABS). Hydrogen atoms were located from difference-Fourier maps and refined isotropically. Other crystal data and structure refinement parameters for (**3**) and (**5**) are summarized in Table 1.

3. Discussion

The ^{31}P{^{1}H} NMR spectrum of the crude product from the reaction between (**1**) and dppe displayed three singlets at δ 80.3, δ 45.7 and δ 37.1 ppm, Fig. 1(a). Fractional crystallization of the crude product leads to the separation of two fractions. The first one is insoluble in chilled toluene and characterized by the sole presence of the signal at δ 80.3 ppm, due to (**2**), as previously reported [21]. The second fraction, soluble in chilled toluene, is characterized by the peaks at δ 37.1 and δ 45.7 ppm and was tentatively assigned to a complex or mixture of complexes (**3**). The ^{31}P{^{1}H} NMR spectrum for the fraction containing (**3**) after purification is shown in Fig. 1(b).

In spite of these differences, (**3**) displays the same elemental analysis and IR results as those found for (**2**), within the expected intrinsic error. Considering that bis-(dialkylphosphino)alkyl ligands may often behave as bridging ligands, and due to the large difference in the melting point values observed for (**2**) and (**3**), we postulated the latter to be comprised of a dimer with formula $\{[CpRuCl](\eta^2,\mu_2\text{-}dppe)_2\}$. This composition would lead to a compound displaying a 10-membered ring conducive to the existence of both *boat* and *chair* conformers, Fig. 2. The possible existence of these conformers would then explain the presence of the peaks at δ 37.1 and δ 45.7 ppm in the ^{31}P NMR of (**3**), a spectral region typical of non-chelating phosphines.

Further, ^{1}H NMR for the crude reaction product displays two signals assigned to η^5-Cp. The first signal, at δ 4.53 ppm was assigned to (**2**), in agreement with previously published work [20]. The other signal, a slightly broad resonance line at δ 3.94 ppm was assigned to the dimeric compound, upon analysis of the NMR spectrum of pure

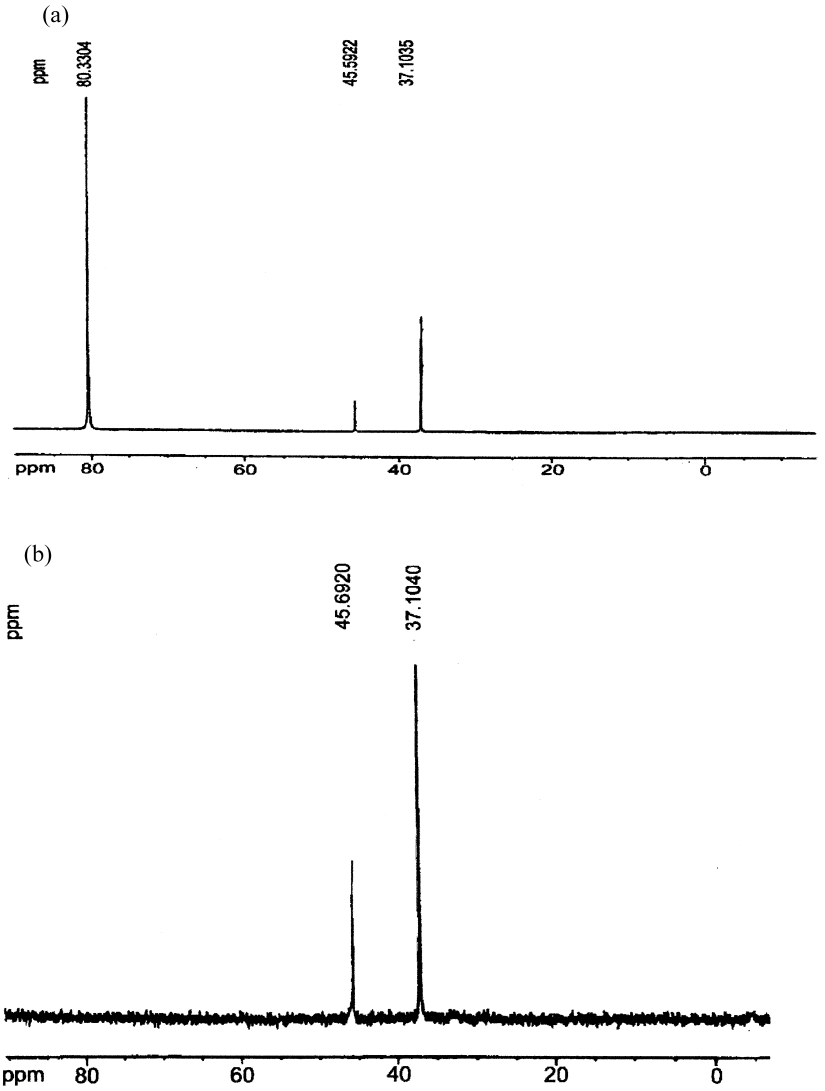

Fig. 1. $^{31}P\{^{1}H\}$ NMR in $CDCl_3$ of the crude product from the synthesis of (**2**) (a), and after fractional crystallization to yield the dimer (**3**) (b).

(**3**). Together, $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR results are indicative of the considerably different chemical environments to which dppe is subjected when bound as a chelating or as a bridging ligand.

Although bridging diphosphine complexes are relatively common when the phosphorus atoms are separated by only one CH_2 group, such as in $Ph_2PCH_2PPh_2$ (dppm), and the two metal centers are connected by a metal–metal bond, compounds with structures similar to those of (**3**) and (**5**) are relatively rare. To date, only nine of such complexes [24–31] have been fully characterized, mostly for group 11 metals.

These complexes are normally formed in low-yield due to the equilibrium between the monomeric (chelato, entropy favored) and the dimeric (bridged) complexes, Eq. (1).

$$L_{2n}M_2(\mu\text{-dppe})_2 \leftrightarrows 2L_nM(\text{dppe}) \quad (1)$$

The occurrence of such a equilibrium is dependent upon the lability of both species involved, thus depending on the electronic configuration of the metal center. Such equilibrium may be responsible, at least in part, for the equivalence [28] of the four phosphorus atoms around each copper observed in the ^{31}P NMR spectrum of $\{[Cu(dmpe)]_2(\eta^2,\mu_2\text{-dmpe})_2\}^{2+}$ at room-temperature. In the case of d^6-octahedral complexes, such as those of Ru(II), ligand lability is at its minimum and the equilibrium illustrated by Eq. (1) in no longer a preponderant factor on describing the product distribution. This explains our yield of 17 to 30 mol% of dimer from the syntheses of (**2**). Once the dimer is formed, it does not tend to dissociate to yield the entropy-favored monomer.

The structure of (**3**) is shown in Fig. 3. In this structure, the two Cp rings are parallel to each other and the '$Ru_2P_4C_4$' ring adopts the chair conformation in the solid state. This causes the hydrogen atoms of each CH_2 group

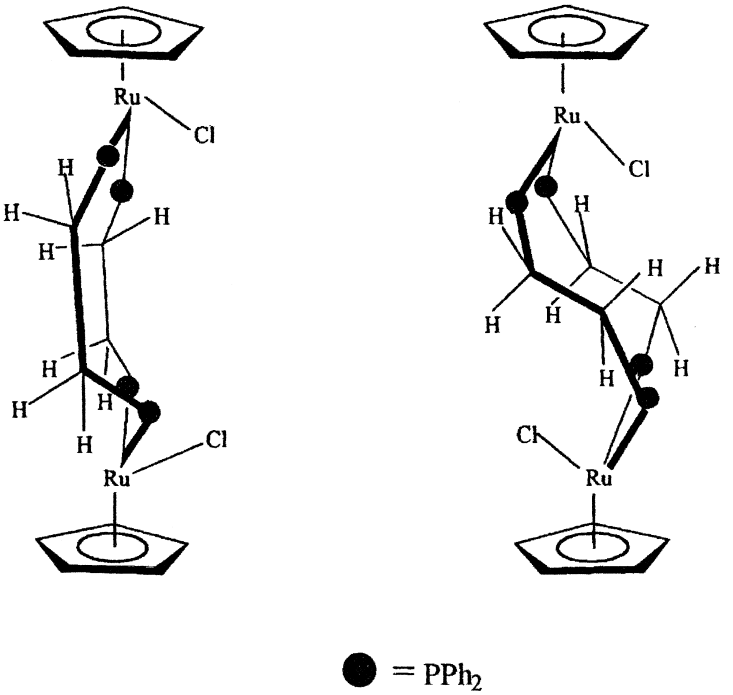

Fig. 2. Possible boat and chair conformers of $\{[CpRuCl]_2(\eta^2,\mu_2\text{-dppe})_2\}$, (**3**).

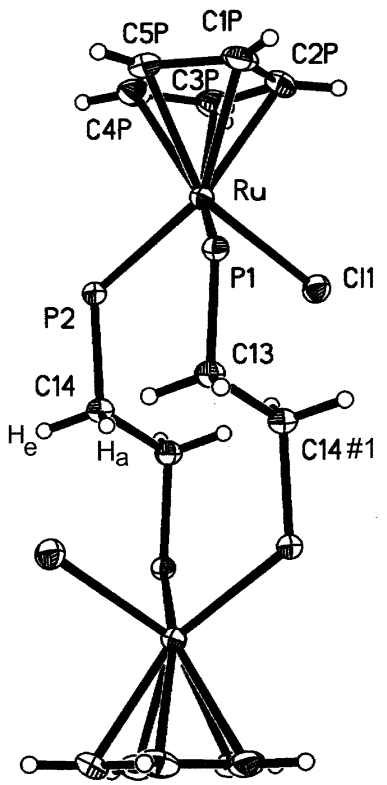

Fig. 3. Displacement ellipsoid diagram (50% probability) for the centrosymmetric $\{[CpRuCl]_2(\eta^2,\mu_2\text{-dppe})_2\}$, (**3**). Phenyl groups at each P atom have been omitted for clarity. C*n*P labels denote carbon atoms of the Cp ring. Relevant bond lengths are: Ru(1)–Cl(1) = 2.4643(4) Å; Ru–P(1) = 2.3289(4) Å; Ru–P(2) = 2.3133(4) Å. Average of Ru–C(*n*P) = 2.2096(4) Å. Relevant bond angles: P(1)–Ru–P(2) = 95.059(15)°; P(1)–Ru–Cl(1) = 96.122(14)°; P(2)–Ru–Cl(1) = 93.888(15)°.

to become non-equivalent. One becomes axial (H_a) and the other equatorial (H_e). In case an equilibrium between the chair and the boat conformers is forbidden, H_a and H_e should each yield a doublet in the ^1H NMR spectrum of (**3**) and $^{31}P\{^1H\}$ NMR should yield a single resonance to the four equivalent P atoms in the chair.

In solution, at room temperature, the opposite is observed for (**3**). The $^{31}P\{^1H\}$ NMR spectrum shows two signals at 37.10 and 45.69 ppm while the ^1H NMR spectrum shows two very broad signals in the 2.17 to 3.01 ppm region. We postulated these observations to be due to the proposed chair-to-boat equilibrium. For (**5**), on the other hand, only one signal is observed in the ^{31}P NMR and the hydrogen atoms in each CH_2 are clearly non-equivalent.

VT ^{31}P NMR of (**3**) in $CDCl_3$, in the 60 to −50°C range shows that the two signals in Fig. 1(b) are due to two species in equilibrium. Upon cooling the sample, the signal at 37.10 ppm (tentatively assigned to the chair conformer) disappears while the signal at 45.7 ppm shows a remarkable intensity increase. The process is reversible, and warming up the sample to above room-temperature leads to the opposite behavior.

Boat–chair interconversion can only be achieved for those cases for which the ligands *endo* in the boat conformer (e.g. the chlorides in Fig. 2) do not cause considerable sterical hindrance. When larger groups such as N_3 and $SnCl_3$ replace Cl, formation of the boat-conformer is precluded and only the chair conformer should be observed. This is observed for the salt metathesis reaction between pure (**3**) and NaN_3 in refluxing

EtOH:benzene (4:1), which leads to the formation of the substitution product *only* in the chair conformation. Salt metathesis reactions with $CpRuL_2Cl$ compounds in polar solvents, such as EtOH, are known to proceed via a chloride-dissociation mechanism [1], leading to the formation of the intimate ion-pair $[CpRuL_2^+][Cl^-]$, as the reaction intermediate. This imposes a considerable flattening of the $L_2RuCp^+_{(centroid)}$ fragment, and the subsequent addition of N_3^- leads to the formation of the less sterically hindered chair conformer. Formation of the boat conformer is made impossible due to the consequent overlap of the two azido groups.

Compound (**3**) crystallizes as a solvate with two molecules of CH_2Cl_2 in the unit cell. Each solvent molecule interacts with one molecule of (**3**) through a weak hydrogen bond, with the distance between the coordinated Cl and one of the hydrogen atoms in the methylene chloride being 2.63(3) Å and C–H . . . Cl angle of 157(2)°.

The structure of (**5**) is shown in Fig. 4. Internuclear distances in the N_3^- ligand are within the expected range for coordinated azido [32–36]. Ru–N(1) distance and the N(2)–N(1)–Ru angle fall outside their expected [32–35] range of values, though. Ru–N(1) distance in (**5**) is from ca. 0.07 to 0.2 Å longer than previously recorded M–N_3 distances. N(2)–N(1)–Ru angle of 114.8° is 3° smaller than previously observed for Ru(II) complexes and falls well outside the range from 118 to 132° normally observed for other azido complexes [32–35], the azido group being 'pushed away' from the dppe.

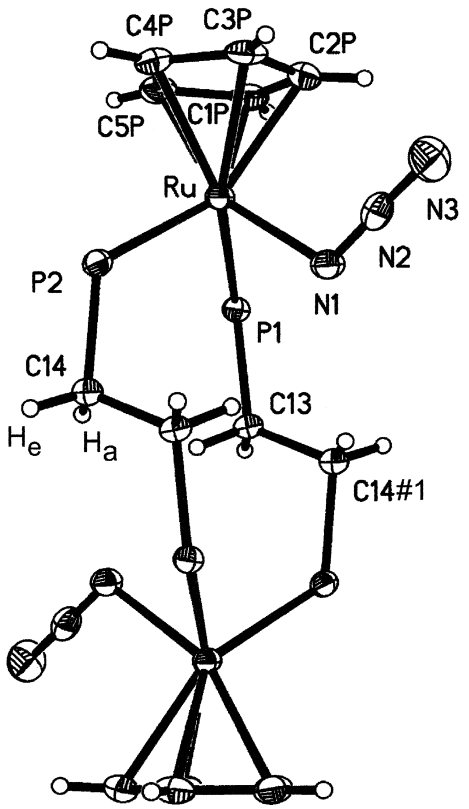

Fig. 4. Displacement ellipsoid diagram (50% probability) for the centrosymmetric $\{[CpRu(N_3)]_2(\eta^2,\mu_2\text{-dppe})_2\}$, (**5**). Phenyl groups at each P atom have been omitted for clarity. Relevant bond lengths are: Ru–N(1) = 2.194(2) Å; Ru–P(2) = 2.3263(7) Å; Ru–P(1) = 2.3312(6) Å; N(1)–N(2) = 1.193(3) Å; N(2)–N(3) = 1.169(3) Å. Average of Ru–C(*n*P) = 2.2119(3) Å. Relevant bond angles are: N(1)–N(2)–N(3) = 177.9(3)°; N(1)–Ru–P(2) = 92.97(6)°; P(2)–Ru–P(1) = 97.17(2)°; N(1)–Ru–P(1) = 89.12(6)°; N(2)–N(1)–Ru = 114.8(2)°. H_a and H_e denote, respectively, the axial and equatorial hydrogen atoms in each CH_2 group.

We suggest that these observations are due to both the $d_\pi(Ru)$–$p_\pi(N)$ repulsion, what finds some support in the structure of other ruthenium–azido complexes [33,34], as well as to the sterical hindrance provided by the phenyl groups of dppe. Also, although the $^{31}P\{^1H\}$ NMR spectrum of (**5**) did not indicate the presence of any residual (**3**), fortuitous co-crystallization of trace amounts of the latter compound may have taken place, leading to the measurement of a longer Ru–N_3 distance.

VT $^{31}P\{^1H\}$ NMR spectra of (**5**) in $CDCl_3$ did not show any changes in the −60 to 50°C range, indicating that conversion of the *chair* into the *boat* conformer, achievable only through dissociative mechanisms in the case of this complex is not observed.

In order to elucidate the nature of possible intermediate species from the reaction between (**1**) and dppe, a time dependent $^{31}P\{^1H\}$ NMR study of the reaction was carried out. Spectra were collected at $t = 0$, 1, 2, 4, 6 and 8 h of reaction. After this time virtually all the starting material had been converted into the products.

Upon mixing the reagents, only trace amounts of (**2**) are detected, in addition to the reagents. After 1 h of reaction, a considerably complex spectrum is observed. This spectrum is characterized by intense resonances due to (**2**) at 80.3 ppm, to free PPh_3 at −4.5 ppm and by a complex resonance pattern between 30 ppm and 50 ppm, a spectral region characteristic of metal-bonded monodentate or non-chelating phosphines. Careful analysis of the signals in this region, taking into account both the line position and J^2_{P-P} values allowed the identification of three reaction intermediates, named (**A**), (**B**) and (**C**), Fig. 5. Assignments of line position and J_{P-P} values for complexes containing monodentate dppe were estimated based on similar values found by Bruce [37] for the complex $[CpRu(PPh_3)(\eta^1\text{-dppm})Cl]$ (dppm = bis-(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$) in which only one P atom of dppm is coordinated to Ru. Our results are also in agreement with more recent work by Bergman and Andersen [38] with bridging dimers containing both $(\eta^2,\mu_2\text{-dmpm})$ and η^1-dmpm, and that by Girolami [39], with related $Cp^*Ru^{II}(dmpm)$ derivatives.

Without a more complete mechanistic study it is difficult to infer about the reaction path followed by any of the reaction intermediates. It is though reasonable to presume that (**A**) and (**C**) are more suitable to yield (**3**), while (**B**) would be a more appropriate intermediate for the forma-

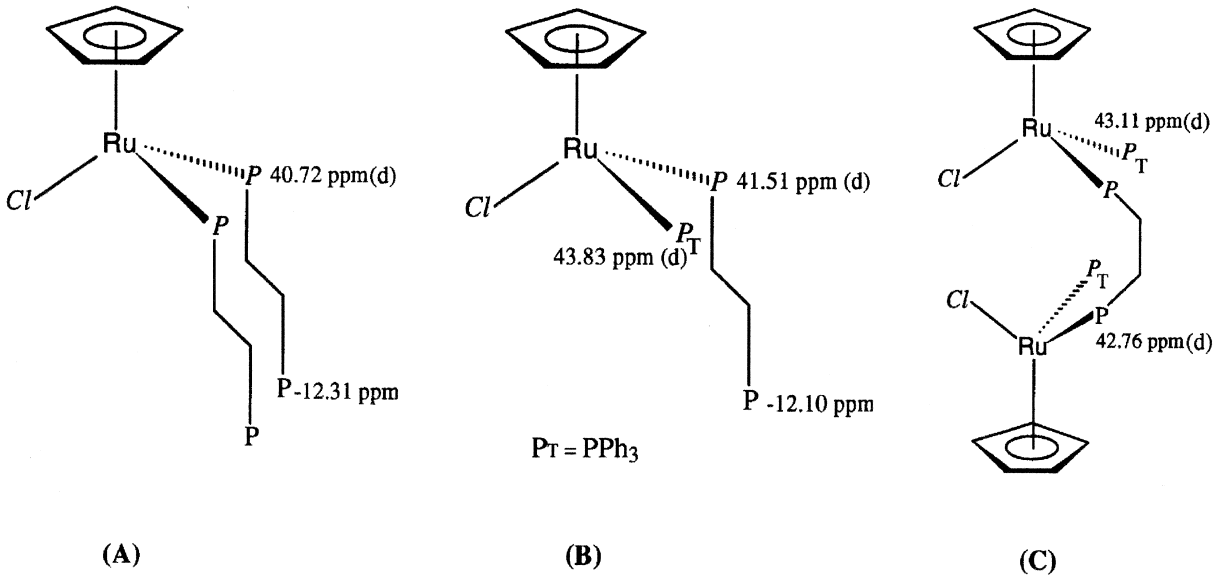

Fig. 5. Proposed structures for the intermediates from the reaction between (**1**) and dppe, at 80°C, after 1 h.

tion of (**2**). Evaporation of the reaction mother liquor after approximately 1 h of reaction led invariably to the formation of a mixture of (**1**), (**2**), (**3**) and free phosphines. No conversion of (**2**) into (**3**) (or vice-versa) was observed upon refluxing a solution of each of them for several hours.

4. Conclusions

Syntheses of CpRu(η^2-dppe)Cl, the most often used precursor to a wide range of derivatives of the CpRu(dppe) moiety also yields the dimeric compound containing bridging dppe in considerable amounts. The complete separation of the monomeric and the dimeric complexes can only be achieved by repetitive fractional crystallization, solvent extraction or column chromatography. The dimeric chloro-derivative is present both as chair and boat conformers in solution and at room temperature, while the azido derivative is formed solely in the chair configuration. Boat and chair conformers are in equilibrium in polar solvents and their relative concentration is dependent on the temperature. The chair conformer of {[CpRu(η^2,μ_2-dppe)Cl]$_2$} is the only conformer isolated in the solid state.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 115527 and 115528 for the structures of (**3**) and (**5**), respectively.

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