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Synthesis and molecular structure of [CpRu(PPh$_3$)(Phterpy-N,N′)]Cl complex: Hdentate nature of Phterpy and diterpy

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Abstract—Ligand displacement reactions of the complex [CpRu(PPh$_3$)$_2$Cl] were investigated with N_3 terdentate ligands, 4′-phenyl-2,2′ : 6,2″-terpyridine (Phterpy) and 1,4-bis(2,2′ : 6′,2″-terpyridin-4-yl)benzene (diterpy). The [CpRu(PPh$_3$)$_2$Cl] reacted with these ligands to form stable complexes of the type [CpRu(PPh$_3$)(Phterpy)]X (X = Cl$^-$, PF$_6^-$) and [{CpRu(PPh$_3$)}(diterpy){Ru(PPh$_3$)Cp}]X$_2$ (X = Cl$^-$, PF$_6^-$) where the respective ligands coordinate in a bidentate fashion. The X-ray crystal structure of the former complex was determined showing octahedral geometry about the metal center assuming the cyclopentadienyl ligand occupying three coordination sites and Phterpy acts as a bidentate ligand. © 1997 Elsevier Science Ltd

Keywords: terpyridine; hypodentate; charge transfer; cyclopentadienyl; meridional; quasi-reversible.

During recent years, the complex [CpRu(PPh$_3$)$_2$Cl] and its derivatives have generated a lot of interest due to their high reactivity [1] and catalytic activity [2]. The chemistry of this complex is characterized by the ready displacement of one or both triphenylphosphine and chloride ligands which occur under mild conditions [3]. The electron rich metal center contributes to the stabilization of unusual ligands such as vinylidines and allenylidines [3(a)]. The steric interactions of the two triphenylphosphine ligands often lead to the displacement of one of them by other ligands. Many of the reactions of these complexes are centered around displacement of either both the PPh$_3$ units or one of them along with chloride to yield neutral or cationic complexes [3–5]. Very few reports are available on the reactions where all three ligands are displaced [4(a)–(c)].

Interest in the synthesis and study of ruthenium complexes of terpyridine ligands is because of their catalytic activity in photochemical [6–8] and redox reactions [6,7,9]. These planar N_3 donor ligands usually bind to the metal in a terdentate fashion if meridional coordination geometry is available [6]. If such geometry is not possible bidentate chelate bonding may occur leaving one of the pyridyl rings uncoordinated [10]. Recently this has been demonstrated in the complexes of ruthenium(II) [11,12], rhenium(I) [13–16], platinum(IV) [14,17(a)], and palladium(IV) [17(b)].

In this paper we describe ligand substitution reactions of [CpRu(PPh$_3$)$_2$Cl] with 4-substituted terpyridines *viz*, 4′-phenyl-2,2′ : 6,2″ terpyridine (Phterpy) and 1,4-bis(2,2′ : 6′,2″-terpyridin-4-yl)benzene (diterpy) (Fig. 1). The results are presented and discussed.

EXPERIMENTAL

A Bruker WM-200 MHz spectrometer was used for recording the ^{1}H NMR spectra of the complexes and ^{31}P NMR spectrum at 80.8 MHz in $CDCl_3$. IR spectra were recorded on a Jasco FT/IR-5300 spectrophotometer. Electrochemical measurements were recorded by using a Cypress system model CS-1090/model CS-1087 computer controlled electroanalytical system. Cyclic voltammograms were recorded in a single-compartment cell by using a Pt-disc working electrode, an Ag/AgCl reference electrode and a Pt-wire as an auxillary electrode, in dichloromethane solvent with 0.1 M Bu_4NClO_4 as supporting electrolyte. [CpRu(PPh$_3$)$_2$Cl] [18,19] and ligands (4′-phenyl-2,2′ : 6′,2″-terpyridine), (Phterpy) [20], {1,4-

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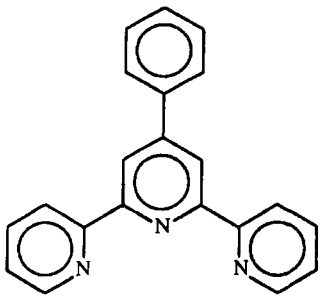
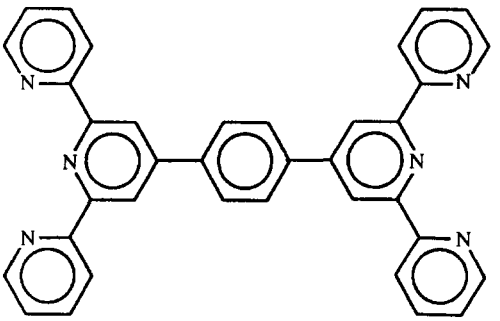


Phterpy



Diterpy

Fig. 1. Structure of the ligands.

bis(2,2′ : 6′,2″-terpyridin-4-yl)benzene}, (diterpy) [21] were prepared by literature methods.

Synthesis of [CpRu(PPh$_3$)(Phterpy)]Cl · 2H$_2$O (**1**)

To a suspension of [CpRu(PPh$_3$)$_2$Cl] (0.1 g, 0.14 mmol) in dry ethanol (20 cm^3) Phterpy (0.050 g, 0.16 mmol) was added. The reaction mixture was refluxed for 4 h whereby the color of the solution changed to red. The solution was evaporated to approximately 5 cm^3 and excess of ether was added to get the red complex. The precipitate was dissolved in dichloromethane (10 cm^3) and layered with ether to give orange-red crystals suitable for X-ray analysis. Found: C, 65.6; H, 3.9; N, 5.4; Calc. for $C_{44}H_{39}N_3O_2PClRu$: C, 65.1; H, 5.1; N, 5.2%. IR (KBr, cm^{-1}): 1612 m, 1537 m, 1479 m, 1412 m, 1092 m, 696 s, 557 s, 524 s. ^{1}H NMR (CDCl$_3$): 4.39 (s, 5H, Cp), multiplets were observed in the range 6.8 ppm to 9.2 ppm for PPh$_3$ and Phterpy ligand protons. ^{31}P NMR (CDCl$_3$): 47.8 ppm (s, PPh$_3$).

Synthesis of [CpRu(PPh$_3$)(Phterpy)]PF$_6$ (**2**)

To a suspension of [CpRu(PPh$_3$)$_2$Cl] (0.1 g, 0.14 mmol) in ethanol (20 cm^3), Phterpy (0.050 g, 0.16 mmol) and NH$_4$PF$_6$ (0.025 g, 0.15 mmol) were added. The reaction mixture was refluxed for 4 h whereby the color of the solution changed to red. The solution was evaporated to near dryness and was dissolved in 10 cm^3 of dichloromethane and filtered. To the filtrate excess of hexane was added whereby a red complex precipitated and was filtered, washed with hexane and dried. Found: C, 59.5; H, 3.7; N, 4.9; Calc. for $C_{44}H_{35}N_3P_2F_6Ru$: C, 59.7; H, 4.2; N, 4.7%. IR (KBr, cm^{-1}): 1612 m, 1537 m, 1479 m, 1412 m, 1092 m, 839 s, 696 s, 557 s, 524 s. ^{1}H NMR (CDCl$_3$): 4.4 (s, 5H, Cp), multiplets were observed in the range 6.8 ppm to 9.2 ppm for PPh$_3$ and Phterpy ligand protons. ^{31}P NMR (CDCl$_3$): 47.8 ppm (s, PPh$_3$).

Synthesis of [{CpRu(PPh$_3$)}(diterpy){Ru(PPh$_3$)Cp}]Cl$_2$ (**3**)

To a suspension of [CpRu(PPh$_3$)$_2$Cl] (0.1 g, 0.14 mmol) in ethanol (20 cm^3) was added diterpy (0.040 g, 0.074 mmol). The reaction mixture was refluxed for 8 h whereby the color of the solution changed to dark red. The solution was evaporated to approximately 5 cm^3 and excess of ether was added to precipitate the red complex, which was dissolved in dichloromethane (10 cm^3) and layered with ether to give orange-red crystals. Found: C, 66.5; H, 4.7; N, 5.4; Calc. for $C_{82}H_{64}N_6P_2Cl_2Ru_2$: C, 66.9; H, 4.6; N, 5.7%. IR (KBr, cm^{-1}): 1612 m, 1537 m, 1479 m, 1412 m, 1092 m, 839 s, 696 s, 557 s, 524 s. ^{1}H NMR (CDCl$_3$): 4.43 and 4.37 (s, 5H, Cp), multiplets were observed in the range 6.8 ppm to 9.2 ppm for PPh$_3$ and diterpy ligand protons. ^{31}P NMR (CDCl$_3$): 47.5 ppm (s, PPh$_3$).

Synthesis of [{CpRu(PPh$_3$)}(diterpy){Ru(PPh$_3$Cp)}](PF$_6$)$_2$ (**4**)

To a suspension of [CpRu(PPh$_3$)$_2$Cl] (0.1 g, 0.14 mmol) in ethanol (20 cm^3), diterpy (0.040 g, 0.074 mmol) and NH$_4$PF$_6$ (0.050 g, 0.31 mmol) were added. The reaction mixture was refluxed for 8 h whereby the color of the solution changed to dark red. The solution was evaporated to near dryness and dissolved in 10 cm^3 of dichloromethane and filtered. To this was added excess of hexane whereby a red complex was precipitated which was filtered, washed with hexane and dried. Found: C, 57.4; H, 4.3; N, 5.5; Calc. for $C_{82}H_{64}N_6P_4F_{12}Ru_2$: C, 58.2; H, 4.0; N, 5.0%. IR (KBr, cm^{-1}): 1612 m, 1537 m, 1479 m, 1412 m, 1092 m, 839 s, 696 s, 557 s, 524 s. ^{1}H NMR (CDCl$_3$): 4.43

and 4.37 (s, 5H, Cp), multiplets were observed in the range 6.8 ppm to 9.2 ppm for PPh_3 and diterpy ligand protons. ^{31}P NMR ($CDCl_3$) : 47.5 ppm (s, PPh_3).

X-ray structural characterization of [CpRu(PPh_3)(Phterpy)]Cl·$2H_2O$ (**1**)

An orange crystal of **1** having approximate dimensions $0.30 \times 0.30 \times 0.40$ mm was used for data collection. The crystallographic data is collected in Table 1. Data were collected at 21°C on a Siemens R3m/V diffractometer using graphite-monochromated Mo-K_α radiation using an ω-2θ scan technique to a maximum 2θ of 45°. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [22] and expanded using Fourier techniques [23]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. There were 5917 unique reflections of which 4533 with $I > 4.00\sigma(I)$ were used for structure solution. Refinement converged at a final $R = 0.044$ and $R_w = 0.0575$ (469 variable parameters). Minimum and maximum final electron density was -0.73 and 0.81 e/Å^{-3}. Bond lengths and bond angles are listed in Table 2.

RESULTS AND DISCUSSION

The reaction of Phterpy and diterpy ligands with [CpRu(PPh_3)$_2$Cl] in dry ethanol yielded red solutions which upon concentration and dilution with ether or hexane gave orange-red crystalline products of the formula [CpRu(PPh_3)(Phterpy)]Cl·$2H_2O$ (**1**) [or PF_6 (**2**)] and [{CpRu(PPh_3)}(diterpy){CpRu(PPh_3)}]Cl_2 (**3**) [or PF_6 (**4**)] respectively. The complexes were crystallized by diffusion of hexane into the concentrated dichloromethane solutions. The purity of the compounds was checked by C, H and N elemental analysis. The IR spectra of the complexes exhibit sharp bands with medium intensity in the range 1600 to 1400 cm^{-1} which originate from the terpyridine ligands. In addition to this the complex **2** gave rise to a sharp band at 840 cm^{-1} due to $\nu_{P\text{-}F}$ of PF_6^-. Electronic spectra of the representative complexes **1** and **3** in dichloromethane solvent exhibited metal-to-ligand charge transfer (mlct) bands at $\lambda_{max} = 480$ nm ($\varepsilon = 2780$ dm^3 mol^{-1} cm^{-1}) and at $\lambda_{max} = 504$ nm ($\varepsilon = 9035$ dm^3 mol^{-1} cm^{-1}) respectively. A shift in λ_{max} towards lower energy (red shift) with increased ε value was observed in the dimer compared to the monomeric complex **1** and is attributed to the conjugated bridging ligand between the two ruthenium centres [21].

Table 1. Crystallographic data for [CpRu(PPh_3)(Phterpy)]Cl·$2H_2O$

Empirical formula	$C_{44}H_{39}ClN_3O_2PRu$
fw	811.23
Space group	*C*2/*c* (15)
a (Å)	29.303 (11)
b (Å)	16.077 (9)
c (Å)	19.613 (10)
β (°)	125.360 (10)
V (Å^3)	7534 (4)
Z	8
D calc. (g cm^{-3})	1.420
T (°C)	21.0
λ (Mo-K_α) (Å)	0.71073
μ (Mo-K_α) (cm^{-1})	5.71
R^a	0.044
R_w^b	0.0575

[a] $R = \Sigma\|F_o\| - |F_c\|/\Sigma|F_o|$,
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Selected bond distances (Å) and bond angles (°) in [CpRu(PPh_3)(Phterpy)]Cl[a]

Ru—P(1)	2.322(2)	Ru—C(1)	2.205(5)
Ru—C(2)	2.215(5)	Ru—C(3)	2.197(5)
Ru—C(4)	2.180(7)	Ru—C(5)	2.181(7)
Ru—N(1)	2.095(4)	Ru—N(2)	2.156(6)

N(1)—Ru—P	89.9(1)
N(2)—Ru—P	91.8(1)
N(1)—Ru—N(2)	76.7(2)
N(2)—C(15)—C(16)	122.1(6)
C(12)—C(13)—C(21)	124.2(5)
C(14)—C(15)—C(16)	115.8(6)
C(14)—C(13)—C(21)	119.9(6)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

An interesting aspect of these reactions is the formation of cationic complexes similar to the reactions of bidentate ligands like bipyridine or *o*-phenanthroline [24] where the bases replace one PPh_3 and the Cl^- ligand. An X-ray crystallographic study of complex **1** was done to determine whether these terpy ligands act as a bidentate or tridentate. The structure of complex **1** is shown in Fig. 2. The most obvious feature of the structure is that the Phterpy ligand coordinates in a bidentate fashion. The coordination is similar to the few known terpyridine ruthenium complexes [11,12]. The geometry of complex **1** is octahedral about the metal center assuming the cyclopentadienyl ligand occupying three coordination sites. This is evident by the near 90° bond angles between the noncyclopentadienyl ligands (N_1—Ru—P = 89.9° (1); N_2—Ru—P = 91.8° (1)) and the metal center as seen in the crystal structure (Table 2). The steric strain in the complex seems to be diminished compared to the parent complex as is evident from the decrease of the bond angle {P_1—Ru—P_2 = 103.99° (4)} [4(d)], to P—Ru—N_1 = 89.9° (1) or P—Ru—N_2 = 91.8° (2). This is also reflected in the shortened Ru—P bond length (Ru—P_1 = 2.322(2)Å) compared to the parent complex molecule [Ru—P_1 = 2.337(1); Ru—P_2 = 2.335(1)Å] [4(d)]. The ruthenium–nitrogen bond lengths are considerably longer [Ru—

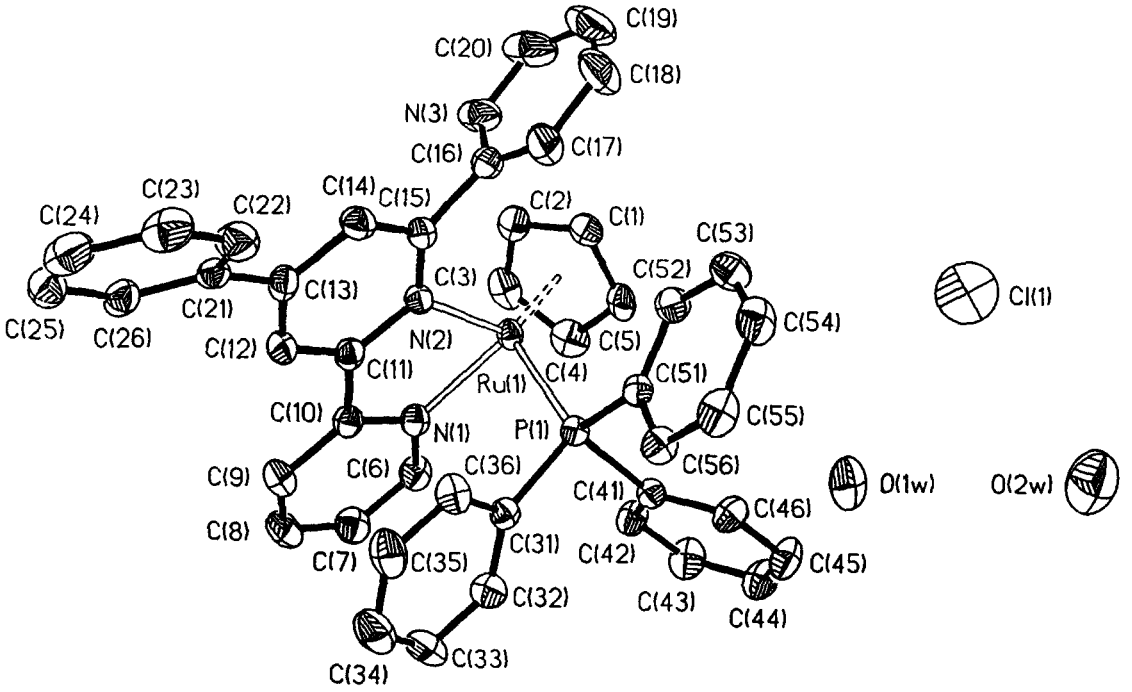


Fig. 2. Crystal and molecular structure of complex $[CpRu(PPh_3)(Phterpy)]Cl \cdot 2H_2O$.

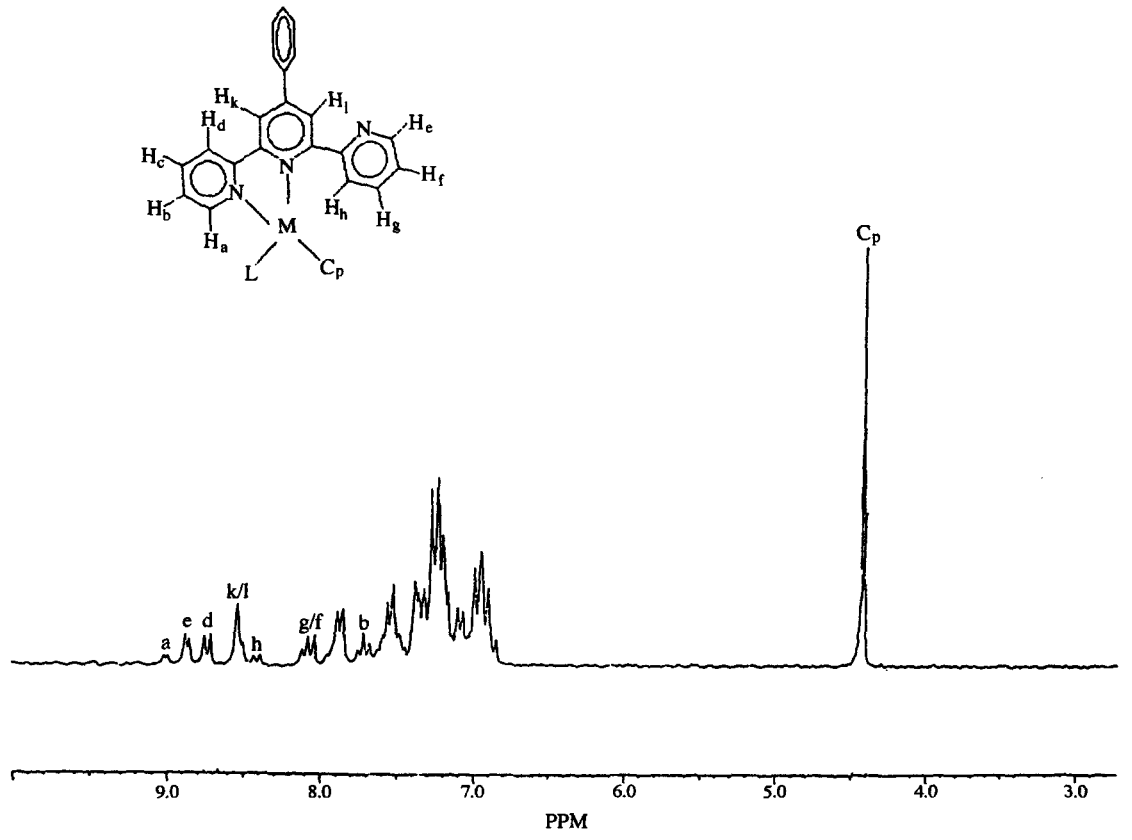


Fig. 3. The 200 MHz ^1H NMR spectrum of $[CpRu(PPh_3)(Phterpy)]Cl$ in $CDCl_3$ solution.

$N_1 = 2.095(4)$; Ru—$N_2 = 2.156(6)$Å] compared to other bidentate terpy complexes [12], $[Ru(bipy\text{-}N,N')_2(terpy\text{-}N,N'')](PF_6)_2$, $[Ru(bbipy\text{-}N,N')_2(terpy\text{-}N,N'')](PF_6)_2$, {Ru—$N_1 = 2.052(6)$; Ru—$N_2 = 2.133(6)$Å}. However, these are found in the same range of some terpy complexes, $[RuX_2(CO)_2(terpy)]$ (X = Cl, Br) [11]. The Ru—N_2 bond lengthened significantly in comparison to Ru—N_1, because of steric factors arising from the presence of a non-coordinating pyridine ring and is position relative to the adjacent cyclopentadienyl group. The Ru—C distances are in the usual range except for Ru—C(4, 5) bonds which are shorter than the Ru—C(1–3) bonds arising as a consequence of possible *trans* influences [25].

The PMR spectrum of complex **1** consisted of a complex pattern of overlapping signals which were clearly associated with an unsymmetrical coordination of terpyridine [12]. All terpy protons were observed in the range 6.8 to 9.2 ppm as multiplets. A sharp resonance was observed at 4.4 ppm for the Cp protons. The PMR spectrum of complex **1** is shown in Fig. 3. ^{31}P NMR signals were observed due to PPh_3 at 47.8 ppm for the chloride complex **1** whereas the PF_6^- analog showed an additional resonance at −143.0 ppm as a septet.

The dimeric complexes (**3**) and (**4**) showed characteristic IR bands in the region 1600–1400 cm^{-1} similar to the mono complexes. The complex **4** exhibited an additional band due to PF_6^- at 840 cm^{-1}. These complexes exhibit two Cp signals at 4.43 and 4.37 ppm respectively apart from very broad signals due to diterpy and triphenylphosphine ligands. On the basis of analytical, NMR data, and comparison with the structure of $[CpRu(PPh_3)(Phterpy)]^+$ in Fig. 2 these complexes are assigned a dimeric structure where the diterpy ligand bridges two ruthenium metal centers in a bidentate fashion as shown in Fig. 4. The coordination environment of the ruthenium is expected to be similar to that of complex **1**.

Complex **1** exhibits two quasi-reversible redox couples at *ca* 1.02 V and at *ca.* −1.43 V *vs* Ag/AgCl reference electrode. The redox couple at 1.02 V corresponds to Ru^{II}/Ru^{III} one electron oxidation process with ΔE_p value of 182 mV, which is at a higher potential compared to $[CpRu(PPh_3)_2Cl]$ which undergoes a reversible one-electron oxidation process at 0.53 V [26]. However, this potential is in the range found for bipyridine, phenanthroline and terpyridine ruthenium(II) complexes [12]. The redox couple at −1.43 V corresponds to one-electron reduction process with ΔE_p value of 94 mV centred on the ligand Phterpy [27].

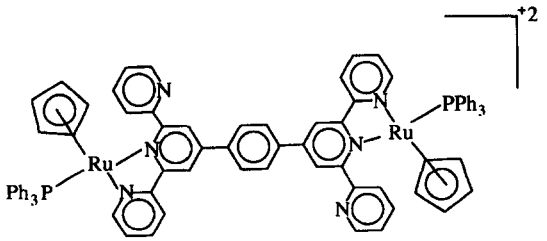


Fig. 4. Proposed structure of complex $[\{CpRu(PPh_3)\}(diterpy)\{CpRu(PPh_3)\}]^{2+}$.

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