Pergamon

0277-5387(94)00236-3

Polyhedron Vol. 14, No. 2, pp. 231–237, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277-5387/95 \$9.50+0.00

SYNTHESIS, STRUCTURE AND PROPERTIES OF MONOMERIC COMPLEXES OBTAINED FROM THE CLEAVAGE OF A (μ-OXO)BIS(μ-CARBOXYLATO) DIRUTHENIUM(III) CORE

ARIYANCHIRA SYAMALA and AKHIL R. CHAKRAVARTY*

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012, India

(*Received* 12 *April* 1994; *accepted* 2 *June* 1994)

Abstract—Reaction of $[Ru_2O(O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ (**1**) with 1,2-diaminoethane (en) in MeOH–H_2O yielded a mixture of products from which a diamagnetic ruthenium(II) complex $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ (**2**) and a paramagnetic ruthenium(III) species $[Ru(O_2CR)(en)_2(PPh_3)](BPh_4)_2$ (**3**) (R = Ph, **a**; C_6H_4-*p*-Me, **b**; C_6H_4-*p*-OMe, **c**) were isolated and characterized. The crystal structure of complex **2**, obtained by X-ray diffraction analysis, shows a *cis* arrangement of the unidentate ligands in this octahedral complex. Complex **3** displays an axial EPR spectrum. Complex **2** undergoes two successive irreversible metal-centred one-electron oxidation processes at 1.13 and 1.33 V vs SCE in MeCN–0.1 M $[NBu^n_4]ClO_4$ at 50 mV s^{-1}. The mechanistic aspects of the core cleavage reactions in **1** are discussed.

Current interest[1-9] in the chemistry of (μ-oxo)bis(μ-carboxylato)diruthenium(III) complexes stems from the discovery[10] of a similar core structure in several non-heme metalloproteins. Besides this, the tribridged diruthenium(III) complexes are closely related to the carboxylate bridged (μ_3-oxo)triruthenium[11] and metal–metal bonded[12] diruthenium complexes. Unlike the chemistry of μ_3-oxo trimetal complexes, an intriguing aspect of the tribridged dimetal complexes is the stability of the core. While the presence of a facially capping terdentate ligand renders stability of the core containing 3*d* metal ions,[10] the core can be readily stabilized for a 4*d* element like ruthenium with unidentate or bidentate terminal ligands. However, the susceptibility of the core towards cleavage depends primarily on the nature of the terminal ligands. We have recently shown[6-8] that in $[Ru_2O(O_2CR)_4(PPh_3)_2]$ and $[Ru_2O(O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ (**1**), the bulky π-acceptor PPh_3 terminal ligands exert sufficient influence to weaken the Ru—O bond *trans* to it. In this paper, we present evidence for the cleavage of the tribridged diruthenium(III) core. Complex **1**, on reaction with 1,2-diaminoethane (en), yields yellow monomeric ruthenium complexes of formulations $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ (**2**) and $[Ru(O_2CR)(en)_2(PPh_3)](BPh_4)_2$ (**3**) (R = Ph, **a**; C_6H_4-*p*-Me, **b**; C_6H_4-*p*-OMe, **c**). Herein we report the synthesis, structure and properties of complexes **2** and **3**. Complex **2** has been structurally characterized by X-ray crystallography.

EXPERIMENTAL

The solvents and reagents were purchased from commercial sources. $Ru_2Cl(O_2CMe)_4$, $Ru_2Cl(O_2CR)_4$ and $[Ru_2O(O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ (**1**; R = Ph, **a**; C_6H_4-*p*-Me, **b**; C_6H_4-*p*-OMe, **c**) were prepared by literature methods.[6,13,14]

Preparation of $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ (**2**)

Complex **2** was isolated from the reactions of en with the precursor complexes **1a**–**1c**. A representative procedure is described below.

---

*Author to whom correspondence should be addressed.

A 0.3 M solution of en in MeOH (1.65 cm^3, 0.48 mmol) was treated with a solution of **1c** (270 mg, 0.19 mmol) in MeOH (10 cm^3) under refluxing conditions for 2 h. The resulting purple reaction mixture was added to a 5 cm^3 aqueous solution of $NaClO_4$. The purple precipitate thus obtained was filtered off and the filtrate was slowly evaporated. Needle-shaped crystals of **2** obtained from this solution after 15 days were washed with cold water and dried *in vacuo* over P_4O_{10}. Yield *ca* 20%. Found: C, 39.2; H, 4.7; N, 9.6. Calc. for $C_{24}H_{34}N_5O_8PCl_2Ru$: C, 39.8; H, 4.7; N, 9.7%.

Preparation of $[Ru(O_2CR)(en)_2(PPh_3)](BPh_4)_2$ (**3**) (R = Ph, **a**; R = C_6H_4-*p*-Me, **b**; R = C_6H_4-*p*-OMe, **c**; X = ClO_4; R = Ph, **a′**; C_6H_4-*p*-Me, **b′**; C_6H_4-*p*-OMe, **c′**)

Complexes **3a**–**3c** as well as **3a′**–**3c′** were synthesized by following a general procedure. A representative one is given below.

A solution of **1c** (270 mg, 0.19 mmol) in MeOH (10 cm^3) was treated with a 0.3 M solution of en in MeOH (1.65 cm^3, 0.48 mmol) and the reaction mixture was boiled under reflux for 2 h. The resulting purple reaction mixture was added to a 5 cm^3 aqueous solution of $NaClO_4$ to precipitate a purple solid which was removed by filtration, and the resulting yellow solution was evaporated to dryness. From the residue, which was a mixture of complexes **2** and **3c′**, complex **3c′** was extracted with cold H_2O. An aqueous solution of $NaBPh_4$ was added to this extract to isolate **3c** in an analytically pure form. Yield *ca* 20%. Found: C, 74.0; H, 6.4; N, 4.9. Calc. for $C_{78}H_{78}N_4O_3PB_2Ru$: C, 73.6; H, 6.1; N, 4.4%. Complex **3a**: yield *ca* 20%. Found: C, 74.1; H, 6.1; N, 5.0. Calc. for $C_{77}H_{76}N_4O_2PB_2Ru$: C, 74.4; H, 6.2; N, 4.5%. Complex **3b**: yield *ca* 25%. Found: C, 73.9; H, 6.1; N, 5.1. Calc. for $C_{78}H_{78}N_4O_2PB_2Ru$: C, 74.5; H, 6.2; N, 4.5%.

Physical measurements

The elemental analyses were carried out using a Heraeus CHN-O Rapid instrument. Electronic spectra were recorded on a Hitachi U-3400 Spectrophotometer. The ^1H NMR spectra were obtained using an ACF-200 spectrometer. Conductivity measurements were performed on a Century CC603 digital conductivity meter. Cyclic voltammetric measurements were obtained using a three-electrode set-up on a PAR Model 174A polarographic analyser connected to a Houston Instruments Omnigraphic *X–Y* recorder. A platinum button, a platinum wire and a saturated calomel electrode (SCE) were used as working, auxiliary and reference electrodes, respectively. The measurements were made at 25°C in MeCN containing 0.1 M$[NBu^n_4]ClO_4$(TBAP). The data reported are uncorrected for junction potentials. Ferrocene was used as a standard to verify the potentials observed against the SCE and to obtain the electron-transfer stoichiometries of the redox couples by peak current measurements. The Fe^{II}/Fe^{III} couple of ferrocene was observed at +0.42 V (*vs* SCE) under similar experimental conditions. EPR measurements were carried out on a Varian E-109 X-band spectrometer working at a microwave frequency of 9.05 GHz.

Crystal structure determination of $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$

The pale-yellow, needle-shaped crystal used for data collection was obtained by slow evaporation of a solution of complex **2** in H_2O–MeCN. The crystal, being unstable and becoming powder outside the mother liquor, was sealed in a Lindemann capillary along with the mother liquor.

Crystal data. $C_{24}H_{35}N_5O_{8.5}PCl_2Ru$, $M = 732.5$, monoclinic, $P2_1/c$, $a = 20.493(3)$, $b = 8.923(1)$, $c = 36.605(6)$ Å, $\beta = 92.96(1)°$, $V = 6684(2)$ Å^3, $Z = 8$, $D_c = 1.46$ g cm^{-3}, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 3.58 cm^{-1}, $T = 293$ K.

Data collection, structure solution and refinement

CAD4 diffractometer, ω-scan technique, graphite monochromated Mo-K_α radiation; 7300 reflections measured ($2° \leqslant 2\theta \leqslant 40$), 6236 unique giving 2529 with $F_0 > 5\sigma(F_0)$. The thin crystal was found to diffract weakly at higher angles and hence data were collected only up to $2\theta = 40°$. Since the absorption coefficient value was very small ($\mu = 3.58$ cm^{-1}), the data were not corrected for absorption.

The positions of the ruthenium atoms were derived from the Patterson map. Iterative application of the least-squares refinement and difference Fourier map led to the development of the entire structure. During the structure refinement, the observed data with $F_0 > 5\sigma(F_0)$ were found to be less than that required for a data-to-parameter ratio of 6:1 and hence to reduce the number of parameters phenyl group carbons were refined at the isotropic level. The asymmetric unit consisted of two molecules of the complex along with one lattice water. Several atoms showed high thermal motion. Two of the four ClO_4^- anions were found to have positionally disordered oxygen atoms and the site occupancies of these oxygens were obtained by refining the occupancy factors (s.o.f.) of these atoms. The complex molecules in the asymmetric unit have similar coordination geometry, even though the bond lengths and bond angles were marginally different from each other. Hydrogen atoms of the complex cation, placed at the calculated positions with $d(\text{C—H}) = 1.08$ Å, were constrained to ride on the atoms to which they are attached. The atoms which showed non-positive definite during anisotropic refinement were refined isotropically. Residuals are $R = 0.079$ and $R_w = 0.069$ for $w = [\sigma^2(F_0)]^{-1}$. The maximum peak in the final difference Fourier map was 0.42 e Å^{-3}. All calculations were performed using VAX88 computer and SHELXS-86 and SHELX-76 programs.[15] A full listing of the positional and thermal parameters, bond lengths and angles has been forwarded to the Cambridge Crystallographic Data Centre.

RESULTS

Synthesis and spectral properties

The reaction of complex **1** with en under refluxing conditions in MeOH has led to the formation of a mixture of complexes. TLC of the crude product shows the presence of blue,[16] purple[8a] and yellow coloured complexes in the mixture. The yellow complexes were separated from the other products by precipitating the blue and purple tribridged diruthenium complexes by adding an aqueous solution of $NaClO_4$ to the reaction mixture. The yellow complexes remain soluble in the H_2O–MeOH medium. Complex **2** was isolated in crystalline form by slow evaporation of this solution. The remaining yellow solution, after removal of complex **2**, gives a hygroscopic diperchlorate salt **3′**, which was converted to a non-hygroscopic solid $[Ru(O_2CR)(en)_2(PPh_3)](BPh_4)_2$ (**3**) by treating the solution with $NaBPh_4$.

Complex **2** is sparingly soluble in chloroform and dichloromethane. It is less soluble in water but highly soluble in MeOH and MeCN. Complex **3** is sparingly soluble in water and chloroform but highly soluble in MeOH, MeCN and acetone. The perchlorate salt **3′** is hygroscopic and sparingly soluble in MeOH and MeCN. The complexes are 1 : 2 electrolytes in solution (Table 1). Complex **2** does not show any absorption in the visible region. It shows a peak at 325 nm. However, complex **3** displays a visible band at ~440 nm. Electronic spectral data are presented in Table 1.

The ^{1}H NMR spectrum of complex **2** exhibits a singlet for the MeCN ligand. The CH_2 protons of en appear as four broad peaks within 2.5–4.9 ppm. A complex multiplet which is observed in the aromatic region in the range 7.6–7.7 ppm undergoes exchange with D_2O and this multiplet has been assigned to the NH_2 protons of the en rings. The phenyl protons of PPh_3 appear in the range 7.49–

Table 1. Physicochemical data for complexes **2**, **3** and **3′**

Complex	**2**	**3a**	**3b**	**3c**
Λ_M, Ω^{-1} cm^2 M^{-1}[a]	230	240	237	242
λ_{max}, nm (ε, M^{-1} cm^{-1})[a]	325 (910)	442 (1300)	445 (1290)	438 (1260)
EPR, MeCN glass, 77 K	—	$g_\parallel = 1.89$; $g_\perp = 2.29$	$g_\parallel = 1.90$; $g_\perp = 2.29$	$g_\parallel = 1.89$; $g_\perp = 2.28$
Complex	**2**	**3a′**	**3b′**	**3c′**
^{1}H NMR (δ, ppm)[nH, J][b]				
Me(O_2CR)	—	—	2.35s [3H]	3.80s [3H]
Me(MeCN)	2.59s [3H]	—	—	—
CH_2/NH_2(en)	2.55, 3.20, 4.00, 4.57, 4.86m [8H][c]	2.70, 3.05, 4.52, 4.90, 5.25m [10H]	2.75, 3.00, 4.50, 4.75, 5.20m [10H]	2.70, 3.05, 4.43, 4.62, 5.15m [10H]
NH_2(en)	7.65m [8H]	7.40br [4H] 8.55d [1H] 11.90d [1H]	7.35br [4H] 9.05d [1H] 13.15d [1H]	7.40br [4H] 8.65d [1H] 12.15d [1H]
NH_2,R,PPh_3	7.49–7.58m [15H][d]	7.50–7.80m [20H][d,e]	6.82d [2H, 8][e] 7.94d [2H, 8][e] 7.50–7.60m [15H][d]	6.85d [2H, 7][e] 8.48d [2H, 7][e] 7.45–7.60m [15H][d]

[a] In MeCN.

[b] In CD_3CN. s, singlet; d, doublet; m, multiplet; br, broad.

[c] CH_2 protons of en.

[d] PPh_3 protons.

[e] Aryl group protons of O_2CR.

7.58 ppm as a multiplet. The ^1H NMR data of complex **2** are given in Table 1. Since the phenyl group protons of the BPh_4^- anion in complex **3** obscure the spectral details in the aromatic region, the ^1H NMR spectra of complex **3′** have been investigated (Table 1). Considering the paramagnetism of the ruthenium(III) complex (**3′**), considerably sharp proton resonances are observed except for the en protons. The peaks show downfield shifts. The methyl group of the *para*-substituted carboxylate ligand exhibits a sharp singlet, indicating the presence of only one type of carboxylate ligand in the complex. The two doublets near 6.9 and 8.5 ppm in complexes **3b′** and **3c′** are due to the aryl group of the carboxylate ligand. The PPh_3 protons appear within 7.4–7.6 ppm. The CH_2 protons display broad multiplets but with a small downfield shift. The peaks for the NH_2 protons in complex **3′** are considerably downfield shifted compared to those in complex **2**.

Complex **3** is paramagnetic and it exhibits an axial EPR spectrum in MeCN glass at 77 K. The EPR spectra of complex **3c** is shown in Fig. 1, and the relevant data are presented in Table 1. The complexes are characterized by a $g_\perp$ value of *ca* 2.28 and a $g_\parallel$ value of *ca* 1.89. Based on these data, it can be concluded that the complex has an axial symmetry with *trans* arrangements of the unidentate ligands in an octahedral geometry.

Based on the analytical, conductivity and spectral data, the proposed structure of the cationic complex in **3** and **3′** is shown below. The NH_2 protons of one en ligand are presumably hydrogen bonded to the unidentate carboxylate ligand. This is inferred from the appearance of two doublets near 12 and 9 ppm in the ^1H NMR spectrum of complex **3′**. These protons probably show a doublet because of their inequivalency due to hydrogen bonding. The peak near 12 ppm undergoes fast D_2O exchange. This peak is tentatively assigned to the proton which is not involved in the hydrogen bonding interaction. The doublet near 9 ppm, which also disappears after some time, is assignable to the proton involved in hydrogen bonding. A broad peak near 7.4 ppm also undergoes complete exchange with D_2O, and this peak could be due to amino protons. Similarly, a broad multiplet which appears at 2.7 ppm along with the CH_2 protons has also been found to be exchanged with D_2O and this multiplet is tentatively assigned to the NH_2 protons of the other en ligand. Four multiplets, observed near 3.0, 4.4, 4.6 and 5.1 ppm, are assignable to the CH_2 protons of the en chelate rings.

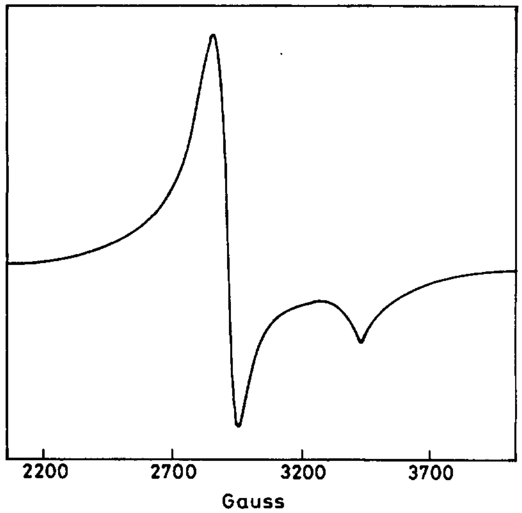
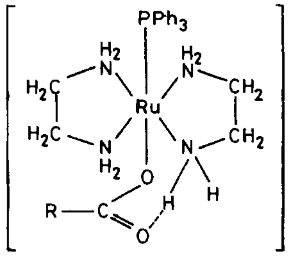


Fig. 1. The EPR spectrum of $[Ru(O_2CC_6H_4\text{-}p\text{-}OMe)(en)_2(PPh_3)](BPh_4)_2$ (**3c**) in MeCN glass at 77 K.



$X = ClO_4$ or BPh_4

Crystal structure of complex **2**

A PLUTO[17] diagram of the asymmetric unit of complex **2** is shown in Fig. 2. The presence of two similar molecules in the asymmetric unit with slightly different bond lengths and angles could be related to the disorderness of the perchlorate anions. In the cationic complex, two en and one PPh_3 ligands, along with one linear MeCN ligand, complete the essentially octahedral coordination geometry around the ruthenium centre. The MeCN and PPh_3 ligands are in *cis* disposition to each other. Selected bond distances and angles are listed in Table 2. The formation of complex **2** takes place from cleavage of the dimeric core in complex **1** with substitution of a carboxylate ligand by en.

Electrochemistry

The redox behaviour of complexes **2** and **3** have been studied by cyclic and differential pulse voltammetry using a platinum button working electrode in MeCN containing 0.1 M $[NBu^n_4]ClO_4$. Complex **2** undergoes two consecutive one-electron oxidations at 1.13 and 1.33 V *vs* SCE (Fig. 3). The

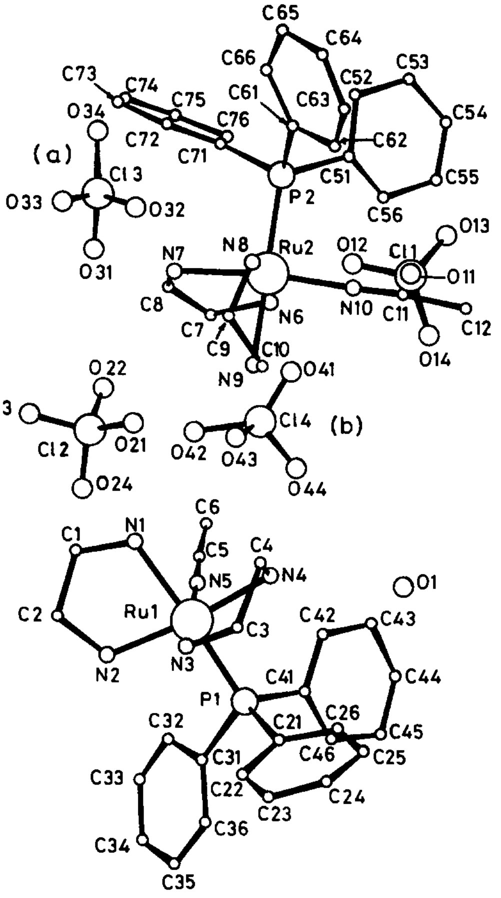


Fig. 2. A PLUTO diagram of two formula units of $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ in the asymmetric unit of the unit cell. The disorder of two perchlorate anions (a and b) is not shown for clarity.

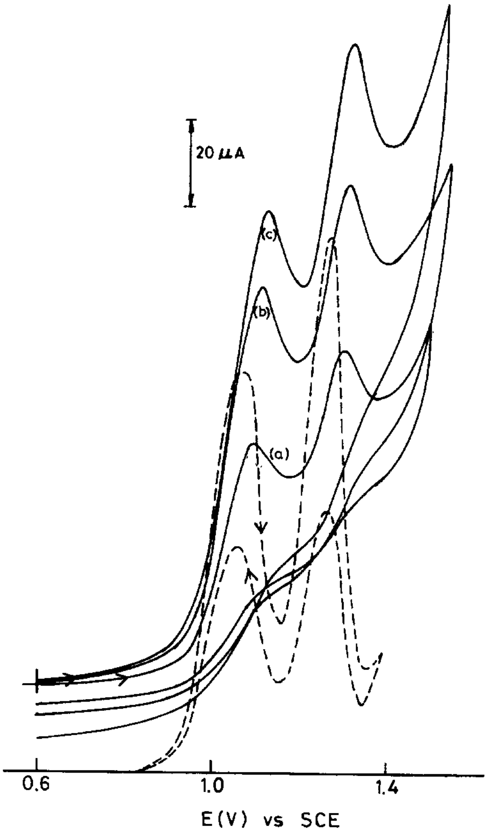


Fig. 3. Cyclic voltammograms (——) at 10 (a), 20 (b) and 50 (c) mV s^{-1} and differential pulse voltammograms (— — —) of $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ at 2 mV s^{-1} in MeCN–0.1 M $[NBu^n_4](ClO_4)$.

electron transfer processes are irreversible and the couples involved are Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV}. The sluggish electron transfer nature of these couples are further evidenced from the differential pulse voltammetric (DPV) results, showing a decrease of the i_{bs}/i_{fs} ratio on increasing the scan rate.[18] The voltammetric data are presented in Table 3 and the differential pulse voltammograms of complex **2** are displayed in Fig. 3.

Complex **3** did not show any metal centred electron transfer process within the potential range of +1.8 to −1.5 V. The only electrochemical response observed during the cyclic voltammetric scan corresponds to an irreversible oxidation of the BPh_4^- anion.

DISCUSSION

Recent studies on the (μ-oxo)bis(μ-carboxylato)diruthenium(III) complexes have shown that the tribridged core can be stabilized in the presence of bidentate and/or unidentate terminal ligands besides the terdentate facially capping ligands. The isolation of two monomeric species from a tribridged precursor shows that the stability of the core is reduced in the presence of π-acceptor and/or bulky terminal ligands. The presence of PPh_3 terminal ligands in complex **1** makes the core susceptible to cleavage. The Ru—$O(O_2CR)$ bond *trans* to the PPh_3 ligand is expected to undergo substitution by en.

In the precursor complex, the terminal MeCN ligand *trans* to the μ-oxo ligand is more labile, as is evidenced from the crystal structure of complex **1a**[6] and $[Ru_2O(O_2CMe)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$.[7] Experimental evidence for this observation is obtained from a study[1] by Sasaki *et al.* showing an exclusive exchange of the pyridine *trans* to the μ-oxo ligand in $[Ru_2O(O_2CMe)_2(py)_6]^{2+}$ with pyridine-d_5 in CD_3CN. Hence, a substitution of MeCN *trans* to the oxo bridge in complex **1** by en could be the first step. A nucleophilic substitution of the Ru—O bond *trans* to the PPh_3 ligand by a potentially bidentate 1,2-diaminoethane explains the cleavage of the core and the formation of the monomeric complexes **2** and **3**.

Table 2. Selected bond distances (Å) and angles (°) for complex **2**

Molecule 1		Molecule 2	
Ru(1)—P(1)	2.276(7)	Ru(2)—P(2)	2.290(7)
Ru(1)—N(1)	2.20(2)	Ru(2)—N(6)	2.15(2)
Ru(1)—N(2)	2.09(2)	Ru(2)—N(7)	2.11(2)
Ru(1)—N(3)	2.12(2)	Ru(2)—N(8)	2.15(2)
Ru(1)—N(4)	2.14(2)	Ru(2)—N(9)	2.15(2)
Ru(1)—N(5)	1.98(2)	Ru(2)—N(10)	1.97(2)
N(5)—C(5)	1.11(3)	N(10)—C(11)	1.13(4)
C(5)—C(6)	1.44(4)	C(11)—C(12)	1.43(4)
P(1)—Ru(1)—N(1)	175.1(5)	P(2)—Ru(2)—N(6)	94.6(6)
P(1)—Ru(1)—N(2)	95.8(5)	P(2)—Ru(2)—N(7)	94.1(5)
P(1)—Ru(1)—N(3)	95.4(5)	P(2)—Ru(2)—N(8)	95.5(5)
P(1)—Ru(1)—N(4)	94.0(5)	P(2)—Ru(2)—N(9)	176.9(6)
P(1)—Ru(1)—N(5)	92.3(6)	P(2)—Ru(2)—N(10)	92.9(6)
N(1)—Ru(1)—N(2)	80.0(6)	N(6)—Ru(2)—N(7)	80.7(8)
N(1)—Ru(1)—N(3)	87.4(7)	N(6)—Ru(2)—N(8)	168.9(7)
N(1)—Ru(1)—N(4)	90.5(7)	N(6)—Ru(2)—N(9)	88.5(8)
N(1)—Ru(1)—N(5)	85.1(7)	N(6)—Ru(2)—N(10)	95.1(9)
N(2)—Ru(1)—N(3)	92.5(7)	N(7)—Ru(2)—N(8)	94.1(7)
N(2)—Ru(1)—N(4)	169.1(7)	N(7)—Ru(2)—N(9)	86.5(7)
N(2)—Ru(1)—N(5)	90.2(7)	N(7)—Ru(2)—N(10)	172.2(8)
N(3)—Ru(1)—N(4)	81.7(7)	N(8)—Ru(2)—N(9)	81.4(7)
N(3)—Ru(1)—N(5)	171.5(7)	N(8)—Ru(2)—N(10)	88.9(8)
N(4)—Ru(1)—N(5)	94.3(7)	N(9)—Ru(2)—N(10)	86.8(8)
Ru(1)—N(5)—C(5)	175(2)	Ru(2)—N(10)—C(11)	178(3)
N(5)—C(5)—C(6)	175(2)	N(10)—C(11)—C(12)	177(4)
Ru(1)—P(1)—C(21)	112.5(8)	Ru(2)—P(2)—C(51)	119.0(8)
Ru(1)—P(1)—C(31)	116.0(8)	Ru(2)—P(2)—C(61)	116.0(8)
Ru(1)—P(1)—C(41)	119.1(8)	Ru(2)—P(2)—C(71)	112.6(8)

Table 3. Electrochemical data for $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ (**2**) in MeCN–0.1 M $[NBu^n_4](ClO_4)$

CV data[a]			
v (mV s^{-1})	$E_{pa}(Ru^{II}/Ru^{III})$ (V)	$E_{pa}(Ru^{III}/Ru^{IV})$ (V)	
10	1.11	1.31	
20	1.12	1.32	
50	1.13	1.33	
DPV data[b]			
v (mV s^{-1})	E_{fs} (V)	E_{bs} (V)	I_{bs}/I_{fs}
Couple: Ru^{II}/Ru^{III}			
2	1.05	1.03	0.58
5	1.06	1.03	0.35
10	1.07	1.01	0.25
Couple: Ru^{III}/Ru^{IV}			
2	1.27	1.26	0.46
5	1.28	1.25	0.30
10	1.28	1.24	0.22

[a] E_{pa}, anodic peak potential.

[b] E_{fs} and E_{bs} are forward and backward scan potentials, respectively. I_{fs}/I_{bs} is the ratio of forward scan and backward scan peak current. v, scan rate. Modulation amplitude = 50 mV (peak to peak). Drop time = 0.5 s.

Acknowledgement—We thank the Department of Science and Technology, Govt. of India, for financial support.

REFERENCES

1. Y. Sasaki, M. Suzuki, A. Nagasawa, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, T. Ochi and T. Ito, *Inorg. Chem.* 1991, **30**, 4903.
2. P. Neubold, K. Wieghardt, B. Nuber and J. Weiss, *Inorg. Chem.* 1989, **28**, 459.
3. A. Llobet, M. E. Curry, H. T. Evans and T. J. Meyer, *Inorg. Chem.* 1989, **28**, 3131.
4. N. Gupta, S. Mukerjee, S. Mahapatra, M. Roy and R. N. Mukherjee, *Inorg. Chem.* 1992, **31**, 139.
5. M. C. Barral, R. Jimenez-Aparicio, E. C. Royer, F. A. Urbanos, A. Monge and C. Ruizvalero, *Polyhedron* 1991, **10**, 113.
6. B. K. Das and A. R. Chakravarty, *Inorg. Chem.* 1990, **29**, 2078.
7. A. Syamala, B. K. Das and A. R. Chakravarty, *Polyhedron* 1992, **11**, 335.
8. (a) A. Syamala and A. R. Chakravarty, *Polyhedron* 1993, **12**, 1545; (b) 1993, **12**, 273.
9. C. Sudha, S. K. Mandal and A. R. Chakravarty, *Inorg. Chem.* 1993, **32**, 3801.
10. (a) S. J. Lippard, *Angew. Chem., Int. Edn Engl.* 1988, **27**, 344; (b) D. M. Kurtz Jr, *Chem. Rev.* 1990, **90**, 585; (c) L. Que Jr and A. E. True, *Prog. Inorg. Chem.* 1990, **38**, 97; (d) J. B. Vincent, G. L. Olivier-Lilley and B. A. Averill, *Chem. Rev.* 1990, **90**, 1447; (e) K. Wieghardt, *Angew. Chem., Int. Edn Engl.* 1989, **28**, 1153; (f) P. C. Wilkins and R. G. Wilkins, *Coord. Chem. Rev.* 1987, **79**, 195.
11. (a) R. D. Cannon and R. P. White, *Prog. Inorg. Chem.* 1988, **36**, 195; (b) B. O. West, *Polyhedron* 1989, **8**, 219.
12. (a) F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*. Wiley-Interscience, New York (1982); (b) F. A. Cotton and R. A. Walton, *Struct. Bonding (Berlin)* 1985, **62**, 1.
13. R. W. Mitchell, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.* 1973, 846.
14. B. K. Das and A. R. Chakravarty, *Polyhedron* 1988, **7**, 685.
15. (a) G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination. University of Cambridge (1976); (b) G. M. Sheldrick, SHELX-86, Program for Crystal Structure Solution. Universität Göttingen (1986); (c) *International Tables for X-ray Crystallography*, Vol. 4. Kynoch Press, Birmingham (1974).
16. A. Syamala, M. Nethaji and A. R. Chakravarty, *Inorg. Chim. Acta*, in press.
17. W. D. S. Motherwell and W. Clegg, PLUTO: Program for Plotting Molecular and Crystal Structures. Cambridge University Press (1978).
18. R. S. Nicholson and I. Shain, *Analyt. Chem.* 1965, **37**, 178.