A New Diruthenium(II,III) Compound, $Ru_2(C{\equiv}CPh)(PhNpy)_4 \cdot 2CH_2Cl_2$, with an Axial η^1-Acetylide Ligand

AKHIL R. CHAKRAVARTY and F. ALBERT COTTON*

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A & M University, College Station, Tex. 77843, U.S.A.

Received June 11, 1985

Abstract

The compound $Ru_2(C{\equiv}CPh)(PhNpy)_4$ was prepared by reacting $Ru_2Cl(PhNpy)_4$ and $Li(C{\equiv}CPh)$ in a toluene–tetrahydrofuran mixture. The product, which was purified by column chromatography on a neutral alumina column using benzene as an eluting agent, was obtained in *ca.* 70% yield. Crystals of composition $Ru_2(C{\equiv}CPh)(PhNpy)_4 \cdot 2CH_2Cl_2$ (1), obtained from a CH_2Cl_2–hexane mixture (1:1 V/V) at −20 °C, belong to the triclinic system, space group $P\bar{1}$, with unit cell dimensions of a = 13.857(6), b = 19.338(9), c = 10.463(4) Å, α = 104.03(4)°, β = 108.25(4)°, γ = 93.55(4)°, V = 2554(2) Å^3, Z = 2. The structure was refined to R = 0.064 (R_w = 0.073). The complex has a diruthenium(II,III) unit bridged by four $PhNpy^-$ ligands, all oriented in the same direction. The axial ligand on the ruthenium is an η^1-acetylide, C≡CPh. The Ru(1)–Ru(2) distance in 1 is 2.319(2) Å. The Ru(1)–C(1) and average Ru–N distances are 2.08(3) and 2.07[2] Å, respectively. The C(1)–C(2) distance is 1.14(3) Å and the Ru(2)–Ru(1)–C(1) group is essentially linear. The Ru(1)–C(1)–C(2) and C(1)–C(2)–C(3) angles are 172(3) and 173(3)°, respectively. The complex is paramagnetic, exhibiting a moment of 3.92 μ_B (308 K). The Ru–Ru bond order is 2,5 with a $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$ ground electronic configuration. The electronic spectrum of the compound in CH_2Cl_2 displays two absorption bands in the visible region, *viz.*, at 735 nm (ϵ = 1050 M^{-1} cm^{-1}) and at 480 nm (ϵ = 1630 M^{-1} cm^{-1}). Cyclic voltammetry in CH_2Cl_2 in the presence of 0.1 M $(TBA)PF_6$ at 100 mV s^{-1} shows nearly reversible metal-centered one-electron oxidation and reduction processes at +0.235 V (ΔE_p = 70 mV) and −0.985 V (ΔE_p = 70 mV), respectively, *vs.* an Ag–AgCl reference electrode. A quasireversible oxidation at +1.050 V is also observed.

Introduction

In the chemistry of multiply bonded diruthenium complexes, an important feature is the sensitivity of the HOMO and LUMO levels towards the nature of axial and equatorial ligands [1]. Besides the carboxylates of type $Ru_2Cl(O_2CR)_4$ [2–8], a variety of new diruthenium compounds have been reported [1, 9–28] in recent years. In most cases [10–20] the compounds have the Ru_2^{5+} core. Spectral and electrochemical studies done on such systems show a dramatic shift of the visible band energy and the redox potentials of the oxidation and reduction couples on changing the equatorial and axial ligand(s).

To a synthetic inorganic chemist, such an observation provides an idea of selective use of ligand(s) that will lead to the formation of a diruthenium complex with higher bond order. The Ru(III)–Ru(III) state in $Ru_2Cl(O_2CR)_4^+$ is unstable even in the cyclic voltammetric time scale since the oxidation potential of the Ru(II)–Ru(III)/Ru(III)–Ru(III) is very high e.g., irreversible oxidation takes place in $Ru_2Cl(O_2CC_3H_7)_4$ above 1.6 V [10, 29, 30]. Substituting carboxylates by acetamidato bridges, Bear and coworkers have reported [11] a diruthenium(II,III) compound, $Ru_2Cl(HNOCCH_3)_4$, which has a Ru(II)–Ru(III)/Ru(III)–Ru(III) couple at +0.47 V in Me_2SO. Oxypyridine ligands have a reverse effect and stabilize the lower oxidation states [17, 18, 31]. The same is true with a diphosphine ligand [25]. The air-stable Ru(II)–Ru(II) compound, $[Ru_2Cl(Me_2PCH_2PMe_2)_2(PhNpy)_2][BPh_4]$, has recently been obtained [25] in this laboratory. Other known diruthenium(II,II) complexes with four bridging ligands are $Ru_2(mhp)_4 \cdot CH_2Cl_2$ [21, 22] and $Ru_2(O_2CCH_3)_4(THF)_2$ [23]. These compounds are air-sensitive.

Wilkinson and his coworkers [9] were able to isolate a Ru(III)–Ru(III) compound, Ru_2R_6 (R = CH_2SiMe_3, CH_2Bu^t), by reacting $Ru_2Cl(O_2CCH_3)_4$ with Grignard reagents, but the Ru–Ru bond is not supported by any bridging ligand. To get the

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

shortest Ru–Ru distances, it would be desirable to isolate a diruthenium(III,III) species in which the dimetallic core will be held by four bridging ligands. The best choice of ligands would be those giving a product with an oxidation potential favorable to a stable Ru(III)/Ru(III) state. Besides the acetamidato ligand, the $PhNpy^-$ ligand, with N,N donor set, forms a complex, $Ru_2Cl(PhNpy)_4$, which has a Ru(II)–Ru(III)/Ru(III)–Ru(III) reversible couple at +0.50 V (ΔE_p = 60 mV) [15, 31]. The Ru–Cl bond is strong and the polar arrangement of bridging ligands makes one ruthenium atom unavailable for axial coordination. Replacement of the axial chloride by an acetylide would be expected to (and does) shift the potential to such an extent that the isolation of a compound with a Ru≡Ru bond is near reality.

In this paper we wish to report the initial step along this direction by presenting the synthesis and characterization of a new diruthenium(II,III) compound, $Ru_2(C{\equiv}CPh)(PhNpy)_4 \cdot 2CH_2Cl_2$. Further investigations on this system including study of the η^1-acetylide ligand are in progress.

Experimental

Materials

The compound $Ru_2Cl(PhNpy)_4$ was prepared [15] by reacting $Ru_2Cl(O_2CCH_3)_4$ [3] and molten PhNHpy. Phenyl acetylene was purchased from Aldrich Chemical Company. Tetrabutylammonium hexafluorophosphate, $(TBA)PF_6$, was used as a supporting electrolyte in electrochemical studies.

Preparation of $Ru_2(C{\equiv}CPh)(PhNpy)_4 \cdot 2CH_2Cl_2$, (1)

A 0.09 g (*ca.* 0.1 mmol) of $Ru_2Cl(PhNpy)_4$ was placed in a three-necked flask containing 10 ml of toluene under an argon atmosphere. In a separate flask *ca.* 0.05 ml of PhC≡CH (*ca.* 0.5 mmol) was added to 10 ml of tetrahydrofuran (THF) under an argon atmosphere. The acetylene was converted to the lithium salt, Li(C≡CPh), by adding 0.3 ml *n*-butyllithium (1.6 M in hexane). The toluene solution of $Ru_2Cl(PhNpy)_4$ was cooled to –40 °C and the THF solution containing Li(C≡CPh) was added slowly to it. The flask was allowed to warm slowly to room temperature, and the solution was then stirred for another 24 h. The color of the solution changed from green to brown. At this stage, the solution was evaporated to dryness, and the brown residue was dissolved in benzene and subjected to chromatography on a neutral alumina (supplier E. Merck, F.R.G.) column of 20.0 × 1.5 cm in benzene. The brown band was eluted with benzene. Upon evaporation of the benzene, the brown solid product was obtained in *ca.* 70% yield. Crystals of the composition $Ru_2(C{\equiv}CPh)(PhNpy)_4 \cdot 2CH_2Cl_2$ (**1**) were obtained by cooling a CH_2Cl_2–hexane (1:1 v/v) solution of the compound to –20 °C. The solvent of crystallization was found to be volatile. The compound is soluble in common organic solvents other than hexane. *Anal.* Calc. for $Ru_2(C{\equiv}CPh)(PhNpy)_4$($Ru_2N_8C_{52}H_{41}$): C, 63.74; H, 4.19; N, 11.44. Found: C, 63.32; H, 4.28; N, 11.29%. Infrared spectrum (KBr phase): 3060(w), 3040(w), 3020(w), 1590(s), 1580(s), 1530(m), 1475(s), 1460(s), 1425(s), 1410(w), 1350(s), 1280(s), 1250(m), 1215(s), 1200(w), 1150(m), .065(m), 1040(w), 1025(w), 1015(s), 915(s), 860(s), 755(s), 735(s), 695(s), 535(w), 505(s), 440(m), 380(s), 325(w), 310(s) cm^{-1} (s, strong; m, medium; w, weak). Magnetic moment (in CH_2Cl_2 by Evans' method [32]): μ_{eff} = 3.92 μ_B (308 K). Electronic spectrum in CH_2Cl_2 solvent: λ_{max} = 735 nm (ϵ = 1050 M^{-1} cm^{-1}), 480 (1630), 330 (7860).

Measurements

The elemental analysis was obtained from Galbraith Laboratories, Inc. The infrared and electronic spectra were recorded with Perkin-Elmer 785 and Cary 17D spectrophotometers, respectively. Magnetic measurements were made in CH_2Cl_2 solution by the Evans' method [32] on a Varian EM 390 spectrometer. Electrochemical measurements were carried out with a Bioanalytical System, Inc., Model BAS100 electrochemical analyzer instrument in connection with a Bausch and Lomb, Houston Instruments Model DMP 40 digital plotter. Measurements were made in CH_2Cl_2 solution containing 0.1 M $(NBu_4)PF_6$ as supporting electrolyte. In a three electrode cell system, a platinum disk Model BAS MF 2032 and a platinum wire were used as working and auxiliary electrodes, respectively, along with a BAS MAF 2020 Ag–AgCl reference electrode (against which ferrocene is oxidized at $E_{1/2}$ = +0.52 V). All potentials were referenced to the Ag–AgCl electrode at 22 ± 2 °C and are uncorrected for junction potentials.

X-ray Crystallographic Procedures

Although the dark brown crystalline mass seemed to be homogeneous, the crystals turned into powder on removal from the mother liquor, and it was necessary to mount a crystal inside a sealed capillary containing mother liquor. The procedures followed to determine the structure of **1** are described in the literature [33]*. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I.

The crystals belong to the triclinic space group $P\bar{1}$ with two molecules per unit cell. Measurements of unit cell constants and data collection were per-

---

*Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A & M University, College Station, Tex. with a VAX-SDP software package.

TABLE I. Crystallographic Parameters

Formula	$Ru_2(C{\equiv}CPh)(PhNpy)_4 \cdot 2CH_2Cl_2$
Formula weight	1149.97
Space group	$P\bar{1}$
Systematic absences	None
a (A)	13.857(6)
b (A)	19.338(9)
c (A)	10.463(4)
α (deg)	104.03(4)
β (deg)	108.25(4)
γ (deg)	93.55(4)
V (A^3)	2554(2)
Z	2
D_c (g/cm^3)	1.495
Crystal dimensions (mm)	0.5 × 0.3 × 0.1
μ(Mo Kα) (cm^{-1})	8.343
Data collection instrument	Syntex $P\bar{1}$
Radiation (monochromated in incident beam)	Mo (Kα = 0.71073 Å)
Orientation reflections. number, range (2θ)	15, 15–25°
Temperature (°C)	5
Scan method	$\omega-2\theta$
Data collection range, 2θ (deg)	$5 \leq 2\theta \leq 50$
Number unique data; total	4805
with $F_o^2 > 3\sigma(F_o^2)$	2387
Number of parameters refined	493
Transmission factors; max./min.	99.69/76.87%
R^a	0.064
R_w^b	0.073
Quality-of-fit indicator^c	1.256
Largest shift/e.s.d., final cycle	0.87
Largest peak (e/Å^3)	0.67

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

formed using a Syntex $P\bar{1}$ diffractometer at 5 °C. There was 7.4% decay in intensity during 138.4 h of exposure time. The ruthenium atom positions were obtained from the direct methods program MULTAN. The remainder of the structure was developed by using least-squares refinement and difference Fourier maps. There was one complete dimer and two CH_2Cl_2 molecules per asymmetric unit. The carbon atoms of the phenyl groups of $PhNpy^-$ ligands were refined isotropically while other atoms were refined anisotropically in order to keep a reasonable ratio between the number of reflections and the number of parameters. In the final cycle, 2387 unique data with $I > 3\sigma(I)$ were used to refine 493 parameters to final values of $R = 0.064$ and $R_w = 0.073$.

Results and Discussion

The compound $Ru_2(C{\equiv}CPh)(PhNpy)_4$ was prepared by reacting $Ru_2Cl(PhNpy)_4$ with $Li(C{\equiv}CPh)$. Although the latter reagent was used in excess, it has substituted only the axial Cl from $Ru_2Cl(PhNpy)_4$ [15], with the cage of bridging ligands remaining intact, and no reduction of the Ru_2^{5+} core having occurred. This is in interesting contrast to the reaction between $Ru_2Cl(O_2CCH_3)_4$ and Grignard reagent in 1:1 molar proportion [23], where reduction occurs to produce $Ru_2(O_2CCH_3)_4(THF)_2$, instead of the substitution product $Ru_2(R)(O_2CCH_3)_4$. When the Grignard reagent is used in excess, disintegration of the cage structure is known [9] to occur to produce Ru_2R_6 (R = CH_2SiMe_3, CH_2Bu^t). The difference in reactivity can probably be attributed to the steric rigidity of the polar molecule. In $Ru_2Cl(PhNpy)_4$, the arrangement of the ligands results in perfect screening of one axial site of the ruthenium and the amine nitrogen atoms are also covered by phenyl groups, thus preventing any attack in this general part of the molecule. The only way the incoming nucleophile can approach is along the Ru–Cl end. Compared to this, in $Ru_2Cl(O_2CCH_3)_4$ the weak Ru–Cl bonds can easily dissociate in polar solvent leaving the $[Ru_2(O_2CCH_3)_4]^+$ core more attractive to any incoming, negatively charged species. Nor is the cage around the Ru_2^{5+} core in this case sterically encumbered.

Alkali metal salts of oxypyridine and aminopyridine ligands are known [21, 27] to substitute the bridging acetates but the reaction pathways are not as simple as those found in other dimetallic species. The reactions between $Ru_2Cl(O_2CCH_3)_4$ with Na(mhp) and Li(ap) are known to produce $Ru_2(mhp)_4 \cdot CH_2Cl_2$ [21] and $Ru_2(ap)_6(PMe_2Ph)_2$ [27], respectively, where Hmhp and Hap are 2-hydroxy-6-methylpyridine and 2-aminopyridine.

Magnetic measurements on compound 1 in CH_2Cl_2 by Evans' method [32] show a μ_{eff} value of 3.92 μ_B (308 K) which is consistent with the presence of three unpaired spins [34]. From this we infer that the ground electronic configuration is $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$ and the Ru–Ru bond order is 2.5. We use the notation $(\delta^*\pi^*)^3$ to imply that the δ^* and π^* orbitals are of very similar energy and we are not certain of their relative positions. The presence of a strong axial interaction doubtless has an effect on the Ru–Ru distance but evidently does not lift the near degeneracy of the π^* and δ^* orbitals which is characteristic of Ru_2(II,III) complexes of this general class.

TABLE II. Table of Positional Parameters and Their Estimated Standard Deviations for $Ru_2(C\equiv CPh)(PhNpy)_4\cdot 2CH_2Cl_2$

Atom	*x*	*y*	*z*	*B* (A2)
Ru(1)	0.0385(1)	0.24011(9)	0.0716(2)	2.65(4)
Ru(2)	0.2013(1)	0.30754(9)	0.1722(2)	2.57(4)
Cl(1)	−0.7058(6)	−0.1271(4)	−0.311(1)	10.8(3)
Cl(2)	−0.7310(7)	−0.2709(5)	−0.0304(1)	15.0(3)
Cl(3)	0.1126(7)	0.9640(5)	0.4476(8)	11.5(3)
Cl(4)	0.3186(9)	1.0051(6)	0.471(1)	15.2(4)
N(11)	0.068(1)	0.2090(7)	0.257(1)	3.0(4)
N(21)	0.240(1)	0.2465(8)	0.308(1)	2.8(4)
N(31)	0.106(1)	0.1550(8)	−0.008(2)	3.7(4)
N(41)	0.250(1)	0.2368(8)	0.036(1)	3.8(4)
N(51)	−0.017(1)	0.3330(7)	0.159(1)	2.7(4)
N(61)	0.150(1)	0.3773(7)	0.307(1)	2.4(4)
N(71)	0.019(1)	0.2777(7)	−0.107(1)	2.6(4)
N(81)	0.160(1)	0.3666(8)	0.033(1)	3.1(4)
C(1)	−0.107(1)	0.179(1)	−0.012(3)	5.9(7)
C(2)	−0.191(2)	0.152(1)	−0.061(2)	4.5(6)
C(3)	−0.301(1)	0.116(1)	−0.108(2)	4.2(6)
C(4)	−0.382(2)	0.155(1)	−0.157(2)	7.2(8)
C(5)	−0.483(2)	0.117(1)	−0.195(3)	7.2(8)
C(6)	−0.501(2)	0.050(2)	−0.174(3)	9(1)
C(7)	−0.426(2)	0.011(2)	−0.128(3)	8.1(9)
C(8)	−0.322(2)	0.043(1)	−0.091(2)	6.1(7)
C(9)	−0.650(2)	−0.188(1)	−0.218(3)	9(1)
C(10)	0.193(2)	0.983(2)	0.357(3)	8.8(9)
C(11)	−0.013(1)	0.182(1)	0.288(2)	3.7(5)
C(12)	0.003(2)	0.156(1)	0.407(2)	4.4(6)
C(13)	0.108(2)	0.159(1)	0.497(2)	4.9(6)
C(14)	0.188(2)	0.1872(9)	0.464(2)	4.7(6)
C(15)	0.166(1)	0.211(1)	0.344(2)	3.8(5)
C(21)	0.344(1)	0.242(1)	0.377(2)	3.5(5)[a]
C(22)	0.380(2)	0.177(1)	0.370(2)	4.4(5)[a]
C(23)	0.484(2)	0.169(1)	0.432(2)	5.4(6)[a]
C(24)	0.551(2)	0.235(1)	0.504(2)	6.1(6)[a]
C(25)	0.519(2)	0.301(1)	0.511(2)	5.3(6)[a]
C(26)	0.415(1)	0.307(1)	0.449(2)	3.9(5)[a]
C(31)	0.056(2)	0.0836(9)	−0.058(2)	4.8(6)
C(32)	0.095(2)	0.028(1)	−0.130(2)	5.6(7)
C(33)	0.184(2)	0.044(1)	−0.160(2)	5.2(6)
C(34)	0.239(2)	0.113(1)	−0.107(2)	4.3(6)
C(35)	0.199(1)	0.169(1)	−0.029(2)	3.0(5)
C(41)	0.330(1)	0.260(1)	−0.010(2)	3.4(4)[a]
C(42)	0.426(1)	0.286(1)	0.095(2)	4.3(5)[a]
C(43)	0.507(2)	0.315(1)	0.055(2)	5.3(6)[a]
C(44)	0.488(2)	0.318(1)	−0.081(2)	6.2(6)[a]
C(45)	0.395(2)	0.294(1)	−0.180(2)	5.9(6)[a]
C(46)	0.310(1)	0.264(1)	−0.147(2)	4.3(5)[a]
C(51)	−0.114(1)	0.338(1)	0.114(2)	3.7(5)
C(52)	−0.157(1)	0.395(1)	0.175(2)	4.3(6)
C(53)	−0.089(1)	0.450(1)	0.296(2)	4.0(5)
C(54)	0.012(1)	0.4436(9)	0.342(2)	3.7(5)
C(55)	0.049(1)	0.3858(9)	0.273(2)	3.1(5)
C(61)	0.219(1)	0.4190(9)	0.441(2)	3.1(4)[a]
C(62)	0.218(1)	0.397(1)	0.558(2)	3.4(4)[a]
C(63)	0.290(1)	0.436(1)	0.690(2)	4.4(5)[a]
C(64)	0.360(2)	0.493(1)	0.706(2)	5.4(6)[a]
C(65)	0.365(2)	0.514(1)	0.588(2)	6.4(6)[a]
C(66)	0.292(2)	0.476(1)	0.451(2)	5.6(6)[a]
C(71)	−0.056(1)	0.244(1)	−0.234(2)	4.1(6)
C(72)	−0.075(2)	0.275(1)	−0.345(2)	4.3(6)
C(73)	−0.015(1)	0.340(1)	−0.328(2)	4.3(6)
C(74)	0.063(1)	0.373(1)	−0.201(2)	3.3(5)
C(75)	0.080(1)	0.338(1)	−0.091(2)	3.4(5)
C(81)	0.201(1)	0.440(1)	0.073(2)	3.4(4)a
C(82)	0.143(1)	0.495(1)	0.099(2)	3.2(4)[a]
C(83)	0.187(2)	0.570(1)	0.148(2)	4.5(5)[a]
C(84)	0.290(2)	0.584(1)	0.166(2)	4.5(5)[a]
C(85)	0.351(2)	0.533(1)	0.142(2)	4.9(5)[a]
C(86)	0.308(2)	0.459(1)	0.095(2)	4.5(5)[a]

[a] Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE III. Selected Bond Distances (A) and Angles (deg) in $Ru_2(C\equiv CPh)(PhNpy)_4\cdot 2CH_2Cl_2$ (**1**)[a]

Bond Distances (A)	
Ru(1)–Ru(2)	2.319(3)
Ru(1)–C(1)	2.08(3)
Ru(1)–N(11)	2.095(14)
Ru(1)–N(31)	2.07(2)
Ru(1)–N(51)	2.114(15)
Ru(1)–N(71)	2.116(15)
C(1)–C(2)	1.14(3)
C(2)–C(3)	1.51(3)
C(15)–N(11)	1.37(2)
C(15)–N(21)	1.38(2)
C(35)–N(31)	1.40(2)
C(35)–N(41)	1.36(2)
Cl(1)–C(9)	1.78(3)
Cl(2)–C(9)	1.75(3)
Ru(2)–N(21)	2.03(2)
Ru(2)–N(41)	2.04(2)
Ru(2)–N(61)	2.030(14)
Ru(2)–N(81)	2.03(2)
C(55)–N(51)	1.39(2)
C(55)–N(61)	1.37(2)
C(75)–N(71)	1.35(2)
C(75)–N(81)	1.38(2)
N(21)–C(21)	1.41(2)
N(41)–C(41)	1.43(2)
N(61)–C(61)	1.43(2)
N(81)–C(81)	1.41(2)
Cl(3)–C(10)	1.75(3)
Cl(4)–C(10)	1.73(2)
Bond angles (deg)	
Ru(2)–Ru(1)–C(1)	178.0(8)
Ru(2)–Ru(1)–N(11)	86.9(5)
Ru(2)–Ru(1)–N(31)	87.7(5)
Ru(2)–Ru(1)–N(51)	87.2(5)
Ru(2)–Ru(1)–N(71)	88.8(5)

(continued on facing page)

TABLE III. *(continued)*

C(1)–C(2)–C(3)	173(3)
C(2)–C(3)–C(4)	119(2)
C(2)–C(3)–C(8)	119(2)
N(11)–C(15)–N(21)	113(3)
N(31)–C(35)–N(41)	115(2)
Ru(1)–Ru(2)–N(21)	89.4(5)
Ru(1)–Ru(2)–N(41)	89.5(5)
Ru(1)–Ru(2)–N(61)	89.6(4)
Ru(1)–Ru(2)–N(81)	89.2(4)
Ru(1)–C(1)–C(2)	172(3)
Ru(1)–N(11)–C(11)	119(2)
Ru(1)–N(11)–C(15)	122(1)
Ru(1)–N(31)–C(31)	123(1)
Ru(1)–N(31)–C(35)	120(1)
Ru(1)–N(51)–C(51)	120(2)
Ru(1)–N(51)–C(55)	120(1)
Ru(1)–N(71)–C(71)	122(2)
Ru(1)–N(71)–C(75)	117(2)
Ru(2)–N(21)–C(15)	121(1)
Ru(2)–N(21)–C(21)	121(1)
Ru(2)–N(41)–C(35)	121(1)
Ru(2)–N(41)–C(41)	121(1)
Ru(2)–N(61)–C(55)	121(1)
Ru(2)–N(61)–C(61)	121(1)
Ru(2)–N(81)–C(75)	120(1)
Ru(2)–N(81)–C(81)	120(1)
N(51)–C(55)–N(61)	115(2)
N(71)–C(75)–N(81)	119(2)
C(1)–Ru(1)–N(11)	91(1)
C(1)–Ru(1)–N(31)	92.6(8)
C(1)–Ru(1)–N(51)	92.6(8)
C(1)–Ru(1)–N(71)	93.1(9)
N(11)–Ru(1)–N(31)	89.6(6)
N(11)–Ru(1)–N(51)	90.8(6)
N(11)–Ru(1)–N(71)	175.6(7)
N(31)–Ru(1)–N(51)	174.8(7)
N(31)–Ru(1)–N(71)	91.2(6)
N(51)–Ru(1)–N(71)	88.0(6)
N(21)–Ru(2)–N(41)	89.5(6)
N(21)–Ru(2)–N(61)	90.6(6)
N(21)–Ru(2)–N(81)	178.6(6)
N(41)–Ru(2)–N(61)	179.1(6)
N(41)–Ru(2)–N(81)	90.1(6)
N(61)–Ru(2)–N(81)	89.8(6)
Cl(1)–C(9)–Cl(2)	105(2)
Cl(3)–C(10)–Cl(4)	109(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The molecular structure of **1** was obtained by an X-ray crystallographic analysis. The positional parameters are presented in Table II. Selected bond distances and angles are given in Table III. An ORTEP view of the molecule is shown in Fig. 1 along with the atom labelling scheme.

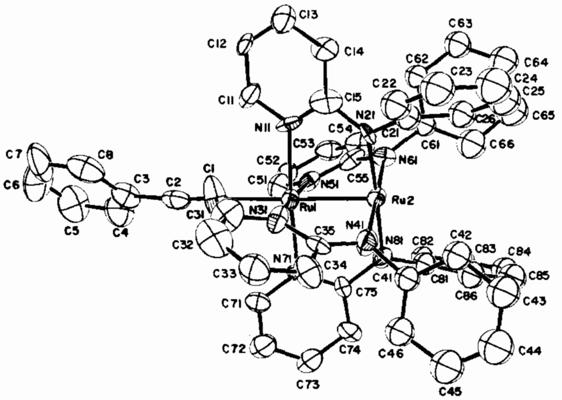

Fig. 1. An ORTEP representation of the $Ru_2(C\equiv CPh)$-$(PhNpy)_4$ molecule. The atom-numbering scheme is defined. Thermal ellipsoids are at the 50% probability level.

The molecular structure of $Ru_2Cl(PhNpy)_4$ has already been reported [15]. The two molecules are very similar in structure except that the Ru–Cl bond in $Ru_2Cl(PhNpy)_4$ is replaced by Ru–C≡CPh in **1**. This change has a large effect on the Ru–Ru distance, changing it from 2.275(3) Å in $Ru_2Cl(PhNpy)_4$ to 2.319(3) Å in $Ru_2(C\equiv CPh)(PhNpy)_4$. We are surprised by the magnitude of this effect and for the present have no definite explanation to propose.

The arrangement of the PhNpy ligands in **1** is still the completely polar or unidirectional one, as in $Ru_2Cl(PhNpy)_4$ [15]. The average Ru–N distance is 2.07[2] Å. The axial Ru(1)–C(1) distance is 2.08(3) Å which is a normal M–C σ-bond distance. The C(1)–C(2) distance of 1.14(3) Å is consistent with the retention of the C≡C triple bond. In the $Ru_2(PhNpy)_4$ unit, the polar arrangement of equatorial ligands has caused a severe twist in the ligand system, with an average torsion angle of 19.45°. Torsion angles observed in other complexes [15, 19, 25, 35] having $PhNpy^-$ ligands are presented for comparison in Table IV.

The visible and near UV spectrum of **1** in CH_2Cl_2 is shown in Fig. 2. There are two absorption bands in the visible range at 735 nm ($\epsilon = 1050\ M^{-1}\ cm^{-1}$) and 480 nm (1630). One more absorption is seen at 330 nm (7860). In $Ru_2Cl(PhNpy)_4$ two more intense bands are known [15] to occur at 764 nm (6910) and 415 (5770). In $Ru_2Cl(O_2CCH_3)_4$, the two prominent bands are assigned [34] to the $O(\pi) \rightarrow Ru_2(\pi^*)$ and $Cl \rightarrow Ru_2(\pi^*$ or $\delta^*)$ transitions. The low-energy band in **1** is possibly due to $PhNpy(\pi) \rightarrow Ru_2(\pi^*)$ transition. The 480 nm band in **1** could be due to $PhC\equiv C(\pi) \rightarrow Ru_2(\pi^*$ or $\delta^*)$ transition. Since the band positions in **1** are considerably shifted from those of $Ru_2Cl(PhNpy)_4$, a more definite assignment would require a thorough MO calculation on the system.

The redox behavior of **1** has been studied by cyclic voltammetry in CH_2Cl_2 with 0.1 M $(TBA)PF_6$ as a supporting electrolyte. The pattern of electron-

TABLE IV. Comparison of Torsional Angles in 1 and Related Species

Compound	Atom 1	Atom 2	Atom 3	Atom 4	Angle (deg)
$Ru_2(C{\equiv}CPh)(PhNpy)_4 \cdot 2CH_2Cl_2$	N(11)	Ru(1)	Ru(2)	N(21)	19.8
	N(31)	Ru(1)	Ru(2)	N(41)	19.5
	N(51)	Ru(1)	Ru(2)	N(61)	20.1
	N(71)	Ru(1)	Ru(2)	N(81)	18.4
$Ru_2Cl(PhNpy)_4$[a]	N(2)	Ru(1)	Ru(2)	N(1)	22.8
	N(4)	Ru(1)	Ru(2)	N(3)	22.6
$Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)_2 \cdot CH_2Cl_2$[b]	O(1)	Ru(1)	Ru(2)	O(4)	2.6
	O(3)	Ru(1)	Ru(2)	O(2)	2.1
	N(2)	Ru(1)	Ru(2)	N(1)	5.2
	N(4)	Ru(1)	Ru(2)	N(3)	1.3
$[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4] \cdot 1.5MeOH$[c]	P(1)	Ru(1)	Ru(2)	P(3)	22.2
	P(2)	Ru(1)	Ru(2)	P(4)	22.5
	N(1)	Ru(1)	Ru(2)	N(4)	17.7
	N(2)	Ru(1)	Ru(2)	N(3)	16.9
$Os_2Cl_3(PhNpy)_3$[d]	N(1)	Os(1)	Os(2)	N(4)	12.5
	N(2)	Os(1)	Os(2)	N(5)	16.1
	N(3)	Os(1)	Os(2)	N(6)	14.7

[a]Ref. 15. [b]Ref. 19. [c]Ref. 25. [d]Ref. 35.

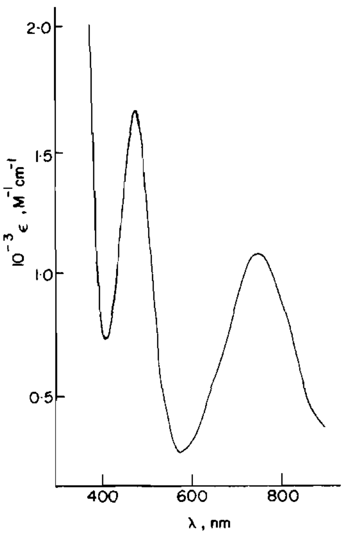

Fig. 2. The electronic absorption spectrum of $Ru_2(C{\equiv}CPh)(PhNpy)_4$ in CH_2Cl_2.

transfer processes is quite similar to those reported [17, 18, 31] for other polar diruthenium(II,III) complexes. Figure 3 shows the cyclic voltammograms of 1 in CH_2Cl_2 at $\nu = 100$ mV s^{-1}.

Constant potential electrolysis has shown that the nearly reversible process occurring at +0.235 V (ΔE_p = 70 mV) is an oxidation. A second oxidation occurring at +1.050 V (ΔE_p = 580 mV) is irreversible although a return wave is observed at E_{pc} = +0.76 V. The anodic peak potential, E_{pa} of + 1.340 V and the high ΔE_p value indicates a sluggish electron transfer process. Further studies have shown* that this process is involved in an ECE mechanism. The Ru(III)–Ru(III) species produced at +0.235 V undergoes an oxidation to Ru(III)–Ru(IV) species at +1.34 V, but this oxidized species then decomposes to unknown products. The current height of this peak is greater than others indicating that the species generated at this potential oxidizes other Ru(III)–Ru(III) species. On the negative side of the Ag–AgCl reference electrode a quasireversible reduction was

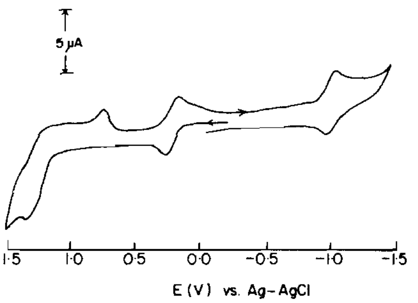

Fig. 3. Cyclic voltammogram of $Ru_2(C{\equiv}CPh)(PhNpy)_4$ in CH_2Cl_2-0.1 M $(TBA)PF_6$ at a scan rate of 100 mV s^{-1}.

---

*When the potential is scanned much higher than the E_{pa} of this oxidation step, the return waves are not observable even for the other two couples. We believe after oxidation at +1.34 V, the Ru(III)Ru(IV) compound undergoes spontaneous decomposition and affects the platinum working electrode.

observed at –0.985 V (ΔE_p = 70 mV). Electrochemical results on **1** can be summarized as follows:

$$\begin{array}{lccccccc} & [\mathrm{Ru^{III}Ru^{IV}}]^{2+} & \xleftarrow[-e]{} & [\mathrm{Ru^{III}Ru^{III}}]^{+} & \underset{-e}{\overset{+e}{\rightleftharpoons}} & \underset{\mathbf{1}}{[\mathrm{Ru^{II}Ru^{III}}]^{\circ}} & \underset{-e}{\overset{+e}{\rightleftharpoons}} & [\mathrm{Ru^{II}Ru^{II}}]^{-} \\ E_{1/2}\ (\mathrm{V}) & & +1.340(E_{pa}) & & +0.235 & & -0.985 & \\ \Delta E_p\ (\mathrm{mV}) & & & & 70 & & 70 & \end{array}$$

The potential for the Ru(III)–Ru(III)/Ru(II)–Ru(III) couple is the lowest among all diruthenium complexes having bridging ligands. A lower potential for this couple is known in $[RuL]^+$ complexes (–0.2 V in MeCN *vs.* Ag–AgClO$_4$ reference electrode), where L = tetraazaannulene but in this complex the diruthenium core is not supported by any bridging ligand(s) [20].

In $Ru_2Cl(PhNpy)_4$, the reversible one-electron oxidation and reduction are observed [31] at +0.50 V (60 mV) and –0.75 V (67 mV), respectively. A large negative shift of *ca.* 250 mV has occurred on substituting Ru–Cl by Ru–C≡CPh. This is consistent with the longer, weaker Ru–Ru bond in **1**.

The electron transfer behavior in $Ru_2Cl(HNOCCH_3)_4$, reported [11] by Bear and coworkers, should be mentioned in this context. This compound has a Ru(III)–Ru(III)/Ru(II)–Ru(III) couple at a very similar potential to that for **1**, namely, at +0.47 V *vs.* SCE. However, there is an interpretational problem with this compound, as mentioned by the authors, because of its ability to undergo axial coordination by solvent molecules.

The electron transfer behavior of **1** indicates that generating a Ru(III)–Ru(III) system from Ru(II)–Ru(III) complex by means of chemical oxidation should be feasible, and work in this direction is in progress.

Acknowledgement

We thank the National Science Foundation for support.

Supplementary Material

Details of the crystal structure determination and listings of bond angles, anisotropic thermal parameters, bond distances, observed and calculated structure factors, and root-mean-square amplitudes (22 pages). A copy may be obtained from author F.A.C.

References

1 F. A. Cotton and R. A. Walton, *Struct. Bonding (Berlin), 62,* 1 (1985).
2 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms', Wiley, New York, 1982.
3 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 28,* 2285 (1966).
4 M. J. Bennett, K. G. Caulton and F. A. Cotton, *Inorg. Chem., 8,* 1 (1969).
5 A. Bino, F. A. Cotton and T. R. Felthouse, *Inorg. Chem., 18,* 2599 (1979).
6 (a) M. Mukaida, T. Nomura and T. Ishimori, *Bull. Chem. Soc. Jpn., 40,* 2462 (1967); *45,* 2143 (1972); (b) T. Togano, M. Mukaida and T. Nomura, *Bull. Chem. Soc. Jpn., 53,* 2085 (1980).
7 D. S. Martin, R. A. Newman and L. M. Vlasnik, *Inorg. Chem., 19,* 3404 (1980).
8 T. Kimura, T. Sakurai, M. Shima, T. Togano, M. Mukaida and T. Nomura, *Bull. Chem. Soc. Jpn., 55,* 3927 (1982).
9 R. P. Tooze, M. Motevalli, M. B. Hursthouse and G. Wilkinson, *J. Chem. Soc., Chem. Commun.,* 799 (1984).
10 T. Malinski, D. Chang, F. N. Feldman, J. L. Bear and K. M. Kadish, *Inorg. Chem., 22,* 3225 (1983).
11 M. Y. Chavan, F. N. Feldman, X. Q. Lin, J. L. Bear and K. M. Kadish, *Inorg. Chem., 23,* 2373 (1984).
12 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *J. Am. Chem. Soc., 106,* 6409 (1984).
13 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Polyhedron, 4,* 1097 (1985).
14 A. R. Chakravarty and F. A. Cotton, *Polyhedron,* in press.
15 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem., 24,* 172 (1985).
16 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem., 23,* 1263 (1985).
17 A. R. Chakravarty, F. A. Cotton and W. Schowtzer, *Polyhedron, in press.*
18 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem., 24,* 2857 (1985).
19 A. R. Chakravarty and F. A. Cotton, *Inorg. Chim. Acta, 105,* 19 (1985).
20 L. F. Warren and V. L. Goedken, *J. Chem. Soc., Chem. Commun.,* 909 (1978).
21 M. Berry, C. D. Garner, I. H. Hillier and W. Clegg, *Inorg. Chim. Acta, 45,* L209 (1980).
22 W. Clegg, *Acta Crystallogr., Sect. B:, 36,* 3112 (1980).
23 A. J. Lindsay, R. P. Tooze, M. Motevalli, M. B. Hursthouse and G. Wilkinson, *J. Chem. Soc., Chem. Commun.,* 1383 (1984).
24 J. B. Collman, C. E. Barnes, P. N. Swepton and J. A. Ibers, *J. Am. Chem. Soc., 106,* 3500 (1984); J. P. Collman, C. E. Barnes, T. J. Collins, P. J. Brothers, J. Gallucci and J. A. Ibers, *J. Am. Chem. Soc., 103,* 7030 (1981).
25 A. R. Chakravarty, F. A. Cotton and L. R. Falvello, *Inorg. Chem.,* in press.
26 M. T. Flood, R. F. Ziolo, J. E. Early and H. B. Gray, *Inorg. Chem., 12,* 2153 (1973).
27 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem., 23,* 4030 (1984).
28 A. R. Chakravarty and F. A. Cotton, *Inorg. Chem., 24,* 3584 (1985).
29 F. A. Cotton and E. Pedersen, *Inorg. Chem., 14,* 388 (1975).
30 C. R. Wilson and H. Taube, *Inorg. Chem., 14,* 2276 (1975).
31 A. R. Chakravarty, F. A. Cotton, D. A. Tocher and J. H. Tocher, *Polyhedron, 4,* 1475 (1985).

32 D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

33 (a) A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem.*, *18*, 3358 (1979); (b) F. A. Cotton, B. A. Frenz, G. Deganello and A. Shaver, *J. Organomet. Chem.*, *50*, 227 (1973); (c) A. C. T. North, D. C. Phillips and F. A. Mathews, *Acta Crystallogr., Sect. A:*, *24*, 351 (1968).

34 J. G. Norman, Jr., G. E. Renzoni and P. A. Case, *J. Am. Chem. Soc.*, *101*, 5256 (1979).

35 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem.*, *23*, 4693 (1984).