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Electrochemical behavior and X-ray crystal structure of the unusual dimeric ruthenium(cyclooctadiene) complex, (tri-μ-chloro)(chloro)(acetonitrile)bis(η^4-cyclooctadiene)-diruthenium(II)

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Abstract

A novel Ru(II)(COD) dimer containing triply-bridging chloride ligands has been prepared and its crystal structure determined. The metal atoms each contain axial COD ligands and are separated by a distance of 3.251 Å. Both transition metals possess octahedral coordination geometries. One contains a coordinated molecule of acetonitrile and the other contains an axial halide ligand. Electrochemical investigations show that the complex undergoes two one-electron oxidations that satisfy the criteria for a fully reversible diffusion controlled process. An improved method of preparing this dimeric Ru(II) cycloolefin complex is also presented. The crystals are monoclinic, space group *C2/c*, $a=21.258(6)$, $b=7.179(2)$, $c=27.068(7)$ Å, $\beta=93.18(2)°$, $V=4124(2)$ Å^3. Convergence to conventional R values of $R=0.0368$ and $R_w=0.0394$ with a goodness-of-fit of 0.95 was obtained for 226 variable parameters and 2710 reflections with $I>0\sigma(I)$.

Keywords: Crystal structures; Electrochemistry; Ruthenium complexes; Diene complexes; Dinuclear complexes

1. Introduction

Examples of stable dimeric Ru(II) olefin complexes are well established, although few crystallographically characterized examples exist [1–3]. The paucity of detailed structural information on these Ru(II) olefin complexes is complemented by the virtual absence of electrochemical data on this interesting and important class of compounds.

Ruthenium complexes such as the chloro-bridged ruthenium(II) cyclooctadiene dimer and other ruthenium(II) complexes containing cycloolefin ligands have been shown to be excellent starting materials for the preparation of new dimeric chloro-bridged Ru(II) complexes containing a variety of arene ligands [4]. These compounds are also particularly useful as precursors in the preparation of new ruthenium sandwich complexes containing a variety of arene ligands. Cleavage of the dimer by halide abstraction in acetone leads to the formation of the (arene)Ru(tris(acetone)) dication, and this complex can then be reacted with arenes to form a variety of novel symmetrical and unsymmetrical bis(arene)ruthenium(II) sandwich complexes [4–8].

Recently we completed the preparation of a new series of dimeric Ru(II) sandwich complexes containing a variety of both large and small coordinated arene ligands. During the course of our work we were surprised to find that when the arene was either naphthalene, anthracene or phenanthrene, a quite different product was formed whose structure we were unable to fathom solely on the basis of the available ^{1}H and ^{13}C data. Faced with well-formed single crystals of this product, it seemed only natural to undertake an X-ray crystal structure determination. From the results of the crystal structure determination it became clear that we had succeeded in preparing a new dinuclear chloro-bridged Ru(II) complex characterized by the presence of a tightly coordinated solvent molecule of acetonitrile. Halide-bridged dinuclear Ru(II) complexes are not

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unknown; however, their numbers are small and detailed structural information is scarce [9–12].

The most salient feature of this complex concerns the presence of a pair of transition metals bridged by three halide ligands. Consideration of the way in which the two metals are joined leads to a polyhedral description in which the metals form a pair of face sharing bioctahedra. To the best of our knowledge, this constitutes the first example of a ruthenium cycloolefin complex of this type.

In this paper we report the synthesis of the title compound via two different routes. In addition, we describe its X-ray crystal structure and present the results of our electrochemical investigations.

2. Results and discussion

The X-ray crystal structure of this complex shows it to possess a dimeric structure consisting of a pair of Ru(II) centers bridged by a set of three chloride ligands (Fig. 1). The transition metals each possess octahedral geometries and, overall, the structure can be described as being comprised of a pair of face-sharing bioctahedra. Bonds to the COD ligands by the metal atoms range from 2.163(5) to 2.209(6) Å, and are similar to those observed in other Ru(II) complexes containing these ligand groups [1–3]. Bonds to the bridging halide, in contrast, display substantial variation, varying from a minimum of 2.409(1) Å to a maximum of 2.499(2) Å. The ruthenium atoms are separated by a distance of 3.251 Å, and Ru(2) is bonded to an axial halide (Cl(1)) at a distance of 2.402(2) Å. A molecule of acetonitrile is found in the coordination sphere of the other ruthenium where it coordinates using the N atom (Ru(1)–N(1) = 2.044(4) Å). Atomic coordinates are given in Table 1; bond lengths and bond angles are given in Table 2.

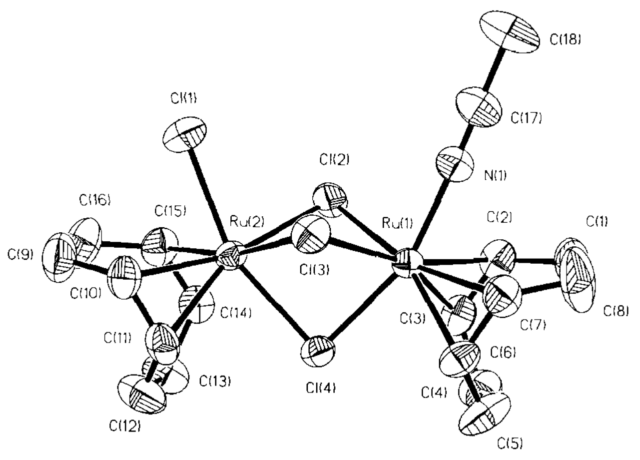

Fig. 1. View of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level and H atoms have been omitted for clarity.

Table 1
Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3)

	x	y	z	U_{eq}[a]
Ru(1)	9268(1)	890(1)	3480(1)	33(1)
Ru(2)	10691(1)	1403(1)	3965(1)	35(1)
Cl(1)	11435(1)	−403(3)	3531(1)	74(1)
Cl(2)	10217(1)	2128(2)	3134(1)	47(1)
Cl(3)	9977(1)	−1364(2)	3899(1)	44(1)
Cl(4)	9683(1)	2731(2)	4167(1)	42(1)
N(1)	9227(2)	−960(6)	2905(2)	44(2)
C(1)	8005(3)	1258(10)	2855(3)	71(3)
C(2)	8613(3)	2316(9)	2942(2)	51(2)
C(3)	8739(3)	3472(8)	3340(2)	52(2)
C(4)	8279(3)	3867(9)	3732(2)	65(2)
C(5)	8149(3)	2263(9)	4064(3)	76(3)
C(6)	8511(2)	508(8)	3992(2)	45(2)
C(7)	8399(3)	−646(9)	3597(2)	54(2)
C(8)	7902(3)	−315(14)	3198(3)	106(4)
C(9)	11946(3)	1078(11)	4588(3)	78(3)
C(10)	11279(3)	325(8)	4577(2)	50(2)
C(11)	10797(3)	1319(8)	4771(2)	48(2)
C(12)	10885(4)	3204(10)	4991(2)	72(3)
C(13)	10932(3)	4792(9)	4652(2)	67(3)
C(14)	10971(3)	4261(8)	4119(2)	47(2)
C(15)	11476(3)	3325(8)	3939(2)	54(2)
C(16)	12043(3)	2707(11)	4252(3)	79(3)
C(17)	9227(3)	−2050(9)	2608(2)	56(2)
C(18)	9231(4)	−3455(9)	2226(2)	77(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The electrochemical behavior of this complex shows that it is readily oxidized at a stationary platinum electrode. Two well-defined oxidations and reductions are observed, both of which satisfy the criteria for a one-electron fully reversible diffusion controlled process (Fig. 2). Interestingly, the electrochemical reversibility of this complex contrasts with preliminary reports of other dimeric Ru(II) complexes containing phosphine or arene ligands [13]. Furthermore, in these latter systems, monocationic complexes were found to be more difficult to oxidize than their neutral counterparts. For the arene systems that were examined in that earlier paper, all were found to undergo a well-defined oxidation in acetonitrile that was chemically irreversible. The reasons for the differences between those results and the results described here remain uncertain. However, one factor that does need to be considered is the choice of solvent. While all of these dimeric transition metal complexes exhibit good solubility in acetonitrile, we found that many of our complexes decomposed in these types of solvents slowly over a period of time. We therefore carried out our electrochemical investigations in nitromethane, and not acetonitrile as did earlier workers. The electrochemical data are given in Table 3.

An interesting question concerns the nature of the oxidized species. Structural changes and rearrangements

Table 2
Bond lengths (Å) and angles (°)

Ru(1)–Cl(2)	2.439(2)	Ru(1)–Cl(3)	2.448(2)
Ru(1)–Cl(4)	2.409(1)	Ru(1)–N(1)	2.044(4)
Ru(1)–C(2)	2.209(6)	Ru(1)–C(3)	2.190(6)
Ru(1)–C(6)	2.199(5)	Ru(1)–C(7)	2.190(6)
Ru(2)–Cl(1)	2.402(2)	Ru(2)–Cl(2)	2.468(1)
Ru(2)–Cl(3)	2.499(2)	Ru(2)–Cl(4)	2.435(1)
Ru(2)–C(10)	2.163(5)	Ru(2)–C(11)	2.184(5)
Ru(2)–C(14)	2.171(5)	Ru(2)–C(15)	2.171(6)
N(1)–C(17)	1.121(7)	C(1)–C(2)	1.505(9)
C(1)–C(8)	1.485(11)	C(2)–C(3)	1.374(8)
C(3)–C(4)	1.509(9)	C(4)–C(5)	1.496(9)
C(5)–C(6)	1.494(9)	C(6)–C(7)	1.361(8)
C(7)–C(8)	1.489(9)	C(9)–C(10)	1.515(8)
C(9)–C(16)	1.504(11)	C(10)–C(11)	1.379(8)
C(11)–C(12)	1.486(9)	C(12)–C(13)	1.471(9)
C(13)–C(14)	1.498(8)	C(14)–C(15)	1.379(8)
C(15)–C(16)	1.500(9)	C(17)–C(18)	1.445(8)
Cl(3)–Ru(1)–Cl(4)	79.3(1)	Cl(2)–Ru(1)–Cl(4)	79.7(1)
Cl(3)–Ru(1)–N(1)	85.5(1)	Cl(2)–Ru(1)–N(1)	86.9(1)
Cl(4)–Ru(1)–C(3)	80.3(2)	Cl(4)–Ru(1)–N(1)	160.5(1)
C(2)–Ru(1)–C(3)	36.4(2)	N(1)–Ru(1)–C(2)	78.5(2)
N(1)–Ru(1)–C(6)	113.4(2)	N(1)–Ru(1)–C(3)	114.8(2)
C(3)–Ru(1)–C(6)	80.1(2)	C(2)–Ru(1)–C(6)	90.9(2)
C(3)–Ru(1)–C(7)	91.3(2)	Cl(4)–Ru(1)–C(7)	116.1(2)
Cl(1)–Ru(2)–Cl(2)	85.1(1)	C(2)–Ru(1)–C(7)	79.8(2)
Cl(2)–Ru(2)–Cl(3)	83.5(1)	C(6)–Ru(1)–C(7)	36.1(2)
Cl(2)–Ru(2)–Cl(4)	78.6(1)	Cl(1)–Ru(2)–Cl(3)	87.1(1)
C(10)–Ru(2)–C(11)	37.0(2)	Cl(1)–Ru(2)–Cl(4)	158.9(1)
C(11)–Ru(2)–C(14)	79.7(2)	Cl(3)–Ru(2)–Cl(4)	77.9(1)
C(11)–Ru(2)–C(15)	90.7(2)	C(10)–Ru(2)–C(14)	92.8(2)
Ru(1)–Cl(2)–Ru(2)	83.0(1)	C(10)–Ru(2)–C(15)	80.7(2)
Ru(1)–Cl(4)–Ru(2)	84.3(1)	C(14)–Ru(2)–C(15)	37.0(2)
C(2)–C(1)–C(8)	116.2(5)	Ru(1)–Cl(3)–Ru(2)	82.1(1)
C(2)–C(3)–C(4)	124.0(5)	Ru(1)–N(1)–C(17)	175.6(5)
C(4)–C(5)–C(6)	117.2(6)	C(1)–C(2)–C(3)	123.7(5)
C(6)–C(7)–C(8)	123.9(6)	C(3)–C(4)–C(5)	115.2(5)
C(10)–C(9)–C(16)	115.1(5)	C(5)–C(6)–C(7)	123.3(5)
C(10)–C(11)–C(12)	122.9(6)	C(1)–C(8)–C(7)	116.9(6)
C(12)–C(13)–C(14)	114.4(5)	C(9)–C(10)–C(11)	121.5(6)
C(14)–C(15)–C(16)	124.1(6)	C(11)–C(12)–C(13)	117.9(5)
N(1)–C(17)–C(18)	179.7(8)	C(13)–C(14)–C(15)	123.4(5)
		C(9)–C(16)–C(15)	116.1(5)

have been previously documented following the oxidation of other transition metal complexes [15]. One possibility is that the two oxidized Ru(III) metal centers become drawn closer together forming a metal–metal bond. Additional investigations would be required in order to firmly establish this point, however, it is worth noting that metal–metal interactions have been documented in other triply-bridged Ru(III) complexes [14,15].

3. Experimental

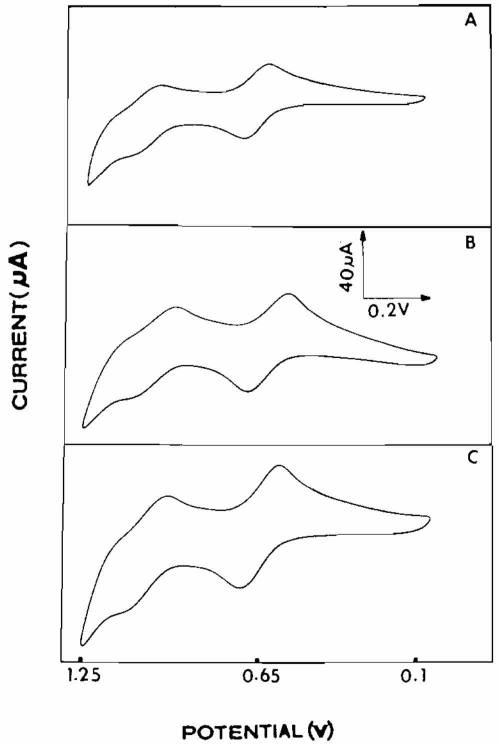

Fig. 2. Cyclic voltammograms of $[(C_8H_{12})_2Ru_2Cl_3Cl)(CH_3CN)]$ at three different scan rates in nitromethane using a Pt electrode: (a) 500, (b) 1000, (c) 1500 mV s^{-1}.

Table 3
Cathodic and anodic peak potentials as a function of scan rate for $[(C_8H_{12})_2Ru_2Cl_3(Cl)(CH_3CN)]^a$

Scan rate (mV s^{-1})	E_{a_1} (V)	E_{c_1} (V)	ΔE_p (V)	E_{a_2} (V)	E_{c_2} (V)	ΔE_p (V)
500	1.062	1.005	0.057	0.720	0.665	0.055
1000	1.078	1.020	0.058	0.710	0.655	0.055
1500	1.083	1.023	0.060	0.705	0.648	0.057

[a] Measured potentials are referenced to an Ag/AgCl reference electrode at 298 K. Supporting electrolyte was 0.1 M $[Bu_4][PF_6]$.

All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or in an inert atmosphere glove box. Solvents were distilled from suitable drying agents prior to use. All reagents were purchased from Aldrich Chemical Company, Inc. or Janssen Chimica, and used as received. Ruthenium(III) chloride hydrate was obtained from the Engelhard Corporation. NMR spectra were recorded on a Bruker AM-250 spectrometer using $CDCl_3$ and referenced to TMS. Crystallographic data were collected on Siemens R3m/V diffractometer. Electrochemical investigations were carried out under N_2 using a Bioanalytical systems CV-27 voltammograph and a cell equipped with a platinum working electrode.

3.1. Preparation of (tri-μ-chloro)(chloro)(acetonitrile)bis(η^4-cyclooctadiene)diruthenium(II), $[(C_8H_{12})_2Ru_2Cl_3(Cl)(CH_3CN)]$

The starting material, (COT)Ru(0)(COD) where COT is cyclooctatetraene, was prepared according to the literature procedure starting from 1.0 g (3.85 mmol) of ruthenium chloride trihydrate [16]. After workup the yellow product was extracted into pentane, then purified by passage through a column packed with alumina. The Ru(0) complex was then reacted with an excess (0.650 g, 5.1 mmol) of naphthalene in 40 ml of freshly distilled pentane. Naphthalene was added at this stage because we were seeking to prepare a new series of dimeric chloro-bridged Ru(II) complexes containing axially coordinated η^6 naphthalene ligands following the metal-catalyzed H_2 reduction of the COD/COT ligands. Pure hydrogen was bubbled slowly into the reaction mixture via a cannula for 4 h, with additional pentane being added on a regular basis to maintain solution volume. The resulting yellow–brown solution was then filtered and transferred to a clean Schlenk flask via a cannula, one end of which was covered with filter paper. The solvent was removed under reduced pressure and the resulting yellow product was redissolved in 10.0 ml of acetonitrile followed by the addition of 4.0 ml of 1.0 M HCl in diethyl ether. The solution was allowed to stir for 12 h and a yellow product was obtained following the addition of 10.0 ml of diethyl ether. This product was isolated by filtration, rinsed with an additional 5.0 ml aliquot of diethyl ether, and purified by recrystallization from nitromethane. The yield was 6.1% (141 mg) of a clean yellow powder, with no evidence of any free or coordinated naphthalene.

^{1}H NMR ($CDCl_3$): δ 2.0 (b, 8H), 2.6 (b, 24H), 4.5 (b, 3H).

^{13}C NMR ($CDCl_3$): δ 29.40, 29.57, 29.69, 29.95, 84.42, 84.64, 89.91, 90.52, 122.09, 123.50.

3.2. *Improved synthesis of (tri-μ-chloro)(chloro)(acetonitrile)bis(η^4-cyclooctadiene)diruthenium(II), $[(C_8H_{12})_2Ru_2Cl_3(Cl)(CH_3CN)]$*

In this synthesis the starting material is the Ru(II) polymer, $[(C_8H_{12})RuCl_2]_n$, which was prepared according to the literature procedure [17]. In a typical reaction, 1.0 g of the Ru(II) polymer was reacted with naphthalene (2.0 g, 15.6 mmol) and Zn dust (10.0 g, 153.0 mmol) in 20.0 ml of freshly distilled THF. The reaction mixture was refluxed for 12 h after which the solvent was removed under reduced pressure. The yellow product that remained was then extracted into 40.0 ml of pentane and the solution transferred to a second Schlenk flask via a cannula, one end of which was covered with filter paper. Removal of the solvent under reduced pressure resulted in the formation of a brown–yellow powder that was then redissolved in 10.0 ml of acetonitrile, followed by the addition of 4.0 ml of a 1.0 M HCl/diethyl ether solution. After stirring for 12 h at room temperature, a yellow precipitate was obtained following the addition of 15 ml of diethyl ether. The product was isolated by filtration, rinsed with an additional 5.0 ml aliquot of ether, and isolated in 26.4% yield (566 mg) based on the use of 1.0 g of the Ru(II)(COD) polymer. ^{1}H and ^{13}C spectra showed the product to be identical to that obtained using the (COT)Ru(0)(COD) starting material, again with no evidence of any free or complexed naphthalene.

3.3. *Electrochemistry*

The redox properties of the complexes were determined using cyclic voltammetry and a cell consisting of a platinum working electrode, a platinum counter electrode and an Ag/AgCl reference electrode. To 10.0 ml of a 0.1 M solution of $[NBu_4][PF_6]$ in nitromethane was added 1.0 ml of a 9.74 mmol solution of the chloro-bridged ruthenium(II) complex, also in nitromethane. In order to ensure that no oxygen was present, the solution was purged with N_2 for 8 min. Initially a potential of 0.1 V was applied, and the cyclic voltammogram recorded by applying a positive potential and scanned linearly out to 1.25 V.

3.4. *X-ray crystal structure determination*

$C_{18}H_{27}Cl_4NRu_2$, $M=601.3$, monoclinic, space group $C2/c$, $a=21.258(6)$, $b=7.179(2)$, $c=27.068(7)$ Å, $\beta=93.18(2)°$, $V=4124(2)$ Å^3, $Z=8$, λ(Mo Kα)$=0.71073$ Å, $F(000)=2384$, $T=295$ K, $\rho=1.937$ Mg m^{-3}.

3.5. *Data collection, structure solution and refinement*

Crystals suitable for crystallographic work were obtained following crystallization from a nitromethane/diethyl ether solution. A regularly shaped yellow crystal having approximate dimensions 0.12×0.08×0.40 mm was selected and mounted on the end of a glass fiber in a random orientation. Monoclinic symmetry was suggested on the basis of the interaxial angles and axial rotation photographs. Refined cell parameters were determined from the setting angles of 39 reflections with $10<2\theta<25°$. Data collection was carried out at ambient temperature using the ω-scan technique in bisecting geometry on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation. Scan rate variable, 3–15° min^{-1}; scan range, 1.2° in ω. Three standards measured every 97 data showed only minor variations in intensity (<3.0%) over the period of data collection. A total of 2794 reflections $(+h, +k, +l;\ h_{max}=22,\ k_{max}=7,\ l_{max}=28)$ with $3.5<2\theta<45°$ was obtained and corrected for Lorentz and polarization effects. Absorption corrections were applied empirically on the basis of azimuthal scans of seven strong reflections spanning a range of 2θ values (minimum and maximum transmission, 0.320 and 0.346, respectively). Equivalent reflections were merged leading to 2711 unique reflections ($R_{int}=1.41\%$).

3.6. Crystal structure solution and refinement

Structure solution and refinement was carried out using the SHELXTL-PLUS (PC version) collection of crystallographic software [18]. Assignment to the *C*2/*c* space group was made following examination of the systematically absent reflections ($h+k=2n+1$, h, 0, l, $l=2n+1$). The structure was solved using direct methods and standard difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically using scattering factors that included terms for anomalous dispersion [19]. Hydrogen atoms were included in idealized positions with fixed isotropic $U=0.08$ Å^2. Refinement was based on F using weights of the form $w^{-1}=[\sigma^2(F)+0.0008(F^2)]$. The maximum shift/$\sigma$ for the final cycle was 0.001 with minimum and maximum residual electron densities of 0.43 and −0.52 e Å^{-3}. One intense low-angle reflection (2 0 0) appeared to suffer from some form of extinction and was therefore omitted during the final stages of refinement. Convergence to conventional R values of $R=0.0368$ and $R_w=0.0394$ with a goodness-of-fit of 0.95 was obtained for 226 variable parameters and 2710 reflections with $I>0\sigma(I)$.

4. Supplementary material

Lists of anisotropic thermal parameters, H atom coordinates, as well as observed and calculated structure factors are available from author L.C.P. upon request.

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