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Electrochemical and Structural Characterization of *cis*- and *trans*-[Cp(CO)Ru(μ-As(C_6H_5)$_2$)]$_2$, Isomers That Undergo Two-Electron-Transfer Oxidations[†]

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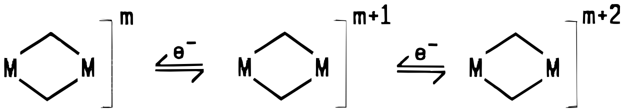
The structures and oxidations of the cis and trans isomers of the doubly bridged dinuclear species [Cp(CO)Ru(μ-AsPh$_2$)]$_2$ (Ph = C_6H_5) have been studied by X-ray crystallography, electrochemistry, and IR and NMR spectroscopies. Each complex oxidizes in a single two-electron voltammetric process, the $E_{1/2}$ values being −0.36 V for the cis isomer (**1**) and −0.30 V for the trans isomer (**2**) in CH_2Cl_2/0.1 M [NBu_4][PF_6] (referenced to ferrocene). These are apparently the first comparative redox potentials published for cis and trans isomers of bridged dinuclear organometallic complexes. Oxidation of **1** to $\mathbf{1}^{2+}$ was cleanly accomplished either by electrolysis or by oxidation of **1** by 2 equiv of ferrocenium, allowing isolation of the dication. The split carbonyl absorptions in the IR spectra of $\mathbf{1}^{2+}$ (ν_{CO} = 2032, 2050 cm^{-1}) are consistent with formation of a Ru−Ru bond in the oxidation reaction. The electrode reaction $\mathbf{1}/\mathbf{1}^+ + e^-$ is much slower than the reaction $\mathbf{1}^+/\mathbf{1}^{2+} + e^-$, implying that the metal−metal bond is formed in the former process. This conclusion is supported by the observation that the inner-sphere activation barrier, $\Delta G^\ddagger$, is about 8.5 kcal/mol, close to that (~10 kcal/mol) estimated for a one-electron oxidation involving formation and cleavage of a Ru−Ru bond. The electron-transfer (ET) activation barrier is higher in these Ru complexes than in analogous Fe complexes, which are known to undergo large ET-induced changes in metal−metal bond lengths, most likely because M−M bond strengths are larger when M = Ru than when M = Fe.

Introduction

The electron-transfer (ET) properties of several dinuclear complexes bridged by group 15 or group 16 moieties have been reported.[1,2] A number of such complexes can be prepared, or at least generated, having electron counts differing by two, e.g., $Fe_2(CO)_6(\mu\text{-}S_2)$ and the corresponding dianion.[3] The factors affecting both the ET stoichiometries (i.e., one or two ET steps between two-electron products) and energetics are not, however, well understood. The most basic question is whether or not a thermodynamically stable one-electron intermediate (charge = $m + 1$ in the drawing) is formed as the molecules transit between the outlying oxidation states, m and ($m + 2$):



Electrochemistry (cyclic voltammetry, CV, in particular) is a powerful method for probing these ET phenomena. Examples are known in which the overall two-electron process has the voltammetric characteristics of a single Nernstian two-electron wave, with $E_{1/2}{}^2 \ll E_{1/2}{}^1$,[4] a pair of unresolved one-electron waves ($E_{1/2}{}^2 \approx E_{1/2}{}^1$),[5] two well-separated one-electron waves ($E_{1/2}{}^2 \gg E_{1/2}{}^1$),[6,7] or an ECE process.[8] Although one expects that structural changes in the ET series, specifically changes in M−M bond length and M−bridging atom−M bond angles, will influence the values of $\Delta E_{1/2}(=E_{1/2}{}^2 - E_{1/2}{}^1)$ and the charge-transfer rates of the couples,[6,7,9,10] the relationships among these factors are still unclear.[5,7]

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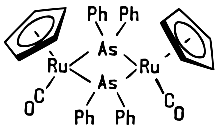
In an attempt to learn more about this problem, we have investigated the oxidation of *cis*-$[Cp(CO)Ru(\mu\text{-}AsPh_2)]_2$ (**1**) and (less extensively) its trans isomer, **2**.



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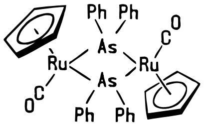

2

In contrast to their first-row analogue $[Cp(CO)Fe(\mu\text{-}PPh_2)]_2$, which undergoes two well-separated ($\Delta E_{1/2} \approx$ 350 mV) one-electron oxidations,[7] the two diruthenium complexes show single *two-electron* anodic waves that deviate from Nernstian behavior only at higher CV sweep rates. Although the dication $\mathbf{1}^{2+}$ proved isolable, X-ray quality crystals of it were not obtained. The crystal structures of the two neutral complexes were obtained, however, providing a rare comparison of the molecular structure of cis- and trans-isomers of a bridged dinuclear system. The dication was characterized by spectroscopic methods, and the couple $\mathbf{1}/\mathbf{1}^{2+}$ was shown to constitute a chemically reversible two-electron redox system, with the neutral-to-monocation ET being the rate-determining step.

Experimental Section

Materials. $[CpRu(CO)_2]_2$[11] and cyclo-$(C_6H_5As)_6$[12] were prepared according to literature procedures. Hydrocarbon solvents were distilled under nitrogen from sodium/benzophenone, while halogenated solvents were dried over molecular sieves.

Thermolysis of $[CpRu(CO)_2]_2$ with cyclo-$(C_6H_5As)_6$. A solution in a 40-mL heavy-wall Carius tube containing 0.308 g of $[CpRu(CO)_2]_2$ (0.695 mmol), 0.640 g of cyclo-$(C_6H_5As)_6$ (0.701 mmol), and 15 mL of toluene was degassed using three freeze−pump−thaw cycles and then flame sealed. The tube was placed inside an end-capped steel pipe with several small vents. (***Caution:*** Pressures within the tube may reach 10−20 atm at the maximum temperature. Ruptures occur in about 10% of the tubes prepared in this manner. Tubes can be most safely opened after cooling the contents in liquid nitrogen.) The tube was heated in an oven at 180 °C for 65 h and then slowly cooled to room temperature. The tube was opened, and its contents were filtered and washed with toluene. The solvent was removed from the filtrate to give a reddish tar. The tar was redissolved in a minimum volume of CH_2Cl_2 and then chromatographed on an alumina column. After an initial flush of the column with hexanes to remove excess cyclo-$(C_6H_5As)_6$, a gradient mixture of CH_2Cl_2 in hexanes was used to elute the column. The first major product fraction appeared as a yellow band with 20% CH_2Cl_2. ^1H NMR spectra showed the presence of two cyclopentadienyl compounds in this and subsequent bands that varied quanititatively, indicating the presence of two products. All fractions containing these two proton resonances were combined, and a second alumina column, eluted with 15% CH_2Cl_2 in hexanes, separated the mixture into two products, both yellow-orange. Both samples were recrystallized from acetone/hexanes. X-ray diffraction identified these compounds as the cis (**1**, 30% yield) and trans (**2**, 10%) isomers of $[Cp(CO)Ru(\mu\text{-}AsPh_2)]_2$. For **1**: IR ($CHCl_3$) ν_{CO} = 1958(s), 1925(m); UV/vis ($CHCl_3$, 4.4×10^{-5} M) bands observed at 205 (ϵ = 9773), 245 (26 704), and 330 nm (6477) (the 330-nm band tails off at 470 nm); ^1H NMR ($CDCl_3$) δ = 7.62 (dd, l0H), 7.35 (m, 10H), 4.59 (s, 10H); ^{13}C NMR ($CDCl_3$) δ = 207 (s), 145 (s), 138 (s), 134 (s), 131 (s), 127 (q), 82 (s); MS parent ion at m/z = 847 (isotope pattern for two Ru atoms). Elemental analysis: C, 50.67; H, 3.44; As, 16.9 (calcd C, 51.07, H, 3.57, As, 17.70) (Galbraith). For **2**: IR ($CHCl_3$) ν_{CO} = 1957(s); UV/vis ($CHCl_3$, 2.48×10^{-5} M) bands at 240 (ϵ = 23 790) and 337 nm (6250) (the 337-nm band tails off at 450 nm); ^1H NMR ($CDCl_3$) δ = 7.63 (dd, 10H), 7.32 (s, 16H), 4.52 (s, 10H); ^{13}C NMR ($CDCl_3$) δ = 141 (s), 139 (s), 134 (s), 133 (s), 129 (d), 127 (d), 83 (s). Elemental analysis: C, 50.85; H, 3.72; As, 16.8 (Galbraith).

[*cis*-$\{Cp(CO)Ru(\mu\text{-}AsPh_2)\}_2][PF_6]_2$. A CH_2Cl_2 solution containing 30 mg (35 μmol) of **1** and 23 mg (70 μmol) of ferrocenium hexafluorophosphate[13] was stirred at room temperature for 1 h. During this time, the color of the solution changed from the green of **1** to yellow-green, and a precipitate was deposited. After filtration, the solid was washed copiously with diethyl ether to remove ferrocene. Recrystallization from CH_3NO_2/ethyl ether at 243 K gave small yellow crystals of the desired dication (19 mg, 41%) (elemental analysis by Robertson Laboratories: C, calcd 38.02, found 36.80; H, calcd 2.64, found 2.52): ^1H NMR (CD_3NO_2) δ = 6.03 (s, Cp), 7.30−7.55 (m, Ph); IR (CH_2Cl_2) ν_{CO} = 2050, 2032 cm^{-1}; IR Nujol) ν_{CO} = 2043, 2023 cm^{-1}; PF_6^- at 850 cm^{-1}.

Electrochemistry. Measurements were conducted under an atmosphere of dinitrogen within a drybox, using solvents and procedures previously described.[14] The working electrodes were commercially available disks, except in the case of rotating platinum electrode scans, for which a homemade Pt bead mounted through soft glass was employed. A synchronous rotator (Sargent, 1800 rpm) was used in rotating electrode experiments. The disk diameters were nominally 1 mm, except for the larger (Beckman) electrode used for chronoamperometry experiments. The electrochemical area of the larger electrode was calibrated as 0.393 cm^2 using the oxidation of $K_4[Fe(CN)_6]$ in aqueous 2 M KCl.[15] Disk electrodes were polished with a series of diamond pastes, finishing with a particle size of 0.25 μm.

Potentials in the paper are quoted vs the ferrocene−ferrocenium couple, as recommended by IUPAC.[16] Ferrocene was added to the analyte solutions as an internal standard at an appropriate point in the experiment. Conversion to the aqueous SCE scale may be achieved by addition of 0.46 V for CH_2Cl_2 solutions and 0.40 V for DMF solutions. In all cases, the supporting electrolyte was 0.1 M $[NBu_4][PF_6]$. Digital simulations of CV scans were performed originally with a program for EE mechanisms written at the University of Vermont, based on the explicit finite difference method of Feldberg,[17] but later confined using DIGISIM (Bioanalytical Systems).

X-ray Structural Characterization. Crystallographic data for **1** and **2** are collected in Table 1. Both were found to possess 2/*m* Laue symmetry. For **1**, systematic absences in the diffraction data and the presence of two-fold rotational symmetry along an axis aligned with the crystallographic *b* axis indicated that the correct space group was *C*2/*c*. For **2**, systematic absences uniquely indentified the space group as *P*2$_1$/*c*. Empirical corrections for absorption was made using ψ-scan data. Both structures were solved by direct methods and refined with anisotropic parameters for all non-hydrogen

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Table 1. Crystallographic Data for *cis-* and *trans-*[CpRu(CO)As(C_6H_5)$_2$]$_2$

	cis	trans
(a) Crystal Parameters		
formula	$C_{36}H_{30}O_2As_2Ru_2$	$C_{36}H_{30}O_2As_2Ru_2$
crystal system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a, Å	9.443(3)	21.860(1)
b, Å	36.037(12)	15.544(3)
c, Å	9.663(2)	18.92(1)
b, deg	98.34(2)	96.98(4)
V, Å^3, Z	3253(2), 4	6380(5), 8
cryst dimens, mm	0.15 × 0.30 × 0.35	0.24 × 0.25 × 0.42
crystal color	orange	orange
D(calc), g cm^3	1.73	1.76
m(Mo Kα), cm^{-1}	49.74	50.72
temp, K	296	296
(b) Data Collection		
diffractometer	Nicolet R3	Nicolet R3
2θ scan range, deg	$4 \geq 2\theta \geq 50$	$4 \geq 2\theta \geq 50$
no. rflns colltd, indpt, obsvd	3108, 2878, 2057	12 075, 11 242, 6771
(c) Refinement		
$R(F)$, $R(wF)$ %[a]	3.40, 4.53	4.40, 5.16
$\Delta(\rho)$, e Å^{-3}	0.481	1.015
GOF	1.04	1.05

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

atoms. Hydrogen atoms were treated as idealized contributions. All computations used SHELXTL (ver. 4.2, G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Synthesis and Structures. The reaction of [CpRu(CO)$_2$]$_2$ with the homocycle cyclo-(AsC_6H_5)$_6$ in a sealed tube at 145 °C in toluene leads to a disproportionation of the phenylarsenido group to form diphenylarsenido-bridged and naked arsenic clusters. No naked arsenic clusters were isolable, but, from solution spectroscopic data and analogy to earlier work with cyclopentadienyl Fe[18] and Mo[19] carbonyl reactions under similar conditions, it is likely that these are tetrahedrane analogues of general formula [CpRu(CO)]$_m$As$_n$. The bridged diphenylarsenido complexes formed have been crystallographically characterized as the cis (**1**) and trans (**2**) isomers of [CpRu(CO)(μ-AsPh$_2$)]$_2$ (Figures 1 and 2). **1** and **2** are separable by column chromatography and are produced in a 3:1 ratio:

$$[\mathrm{CpRu(CO)_2}]_2 + \text{cyclo-}(\mathrm{AsC_6H_5})_6 \rightarrow [\mathrm{CpRu(CO)}\mu\text{-}\mathrm{As(C_6H_5)_2}]_2 + [\mathrm{CpRu(CO)}]_m\mathrm{As}_n$$
$$\text{cis } (\mathbf{1}) \text{ and trans } (\mathbf{2})$$

The cis isomer **1** crystallizes in the monoclinic space group $C2/c$; selected bond parameters are given in Table 2. There is a crystallographically imposed two-fold rotation axis located at the centroid of the Ru$_2$As$_2$ rhombus, which it generates and to which it is perpendicular. The average ruthenium−arsenic bond is 2.455 Å. The Ru$_2$As$_2$ framework is virtually planar; the angle formed by the two RuAs$_2$ planes in the rhombus is 179.3(1)°. Ruthenium exhibits a distorted octahedral environment if the Cp ring is viewed as occupying three coordination sites. The most acute angle found is at As−Ru−As(a), 75.2(1)°. A slightly distorted tetrahedral environment is seen at arsenic; the smallest angle found about arsenic is that between the two phenyl rings, C(16)−As−C(26) = 99.9(1)°. The phenyl rings about arsenic are situated such that those on the same side of the Ru$_2$As$_2$ plane as the Cp rings are rotated to fit the space available. The rings are contained in an approximate plane formed by the As and ipso C atoms. The other two phenyl rings are twisted so that they are essentially perpendicular to this plane.

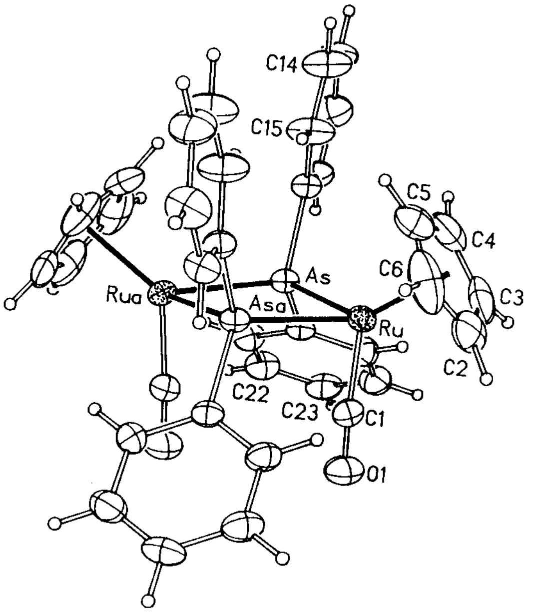

Figure 1. Molecular structure of *cis*-[CpRu(CO)(μ-AsPh$_2$)]$_2$ (**1**), with atoms represented as 40% thermal ellipsoids.

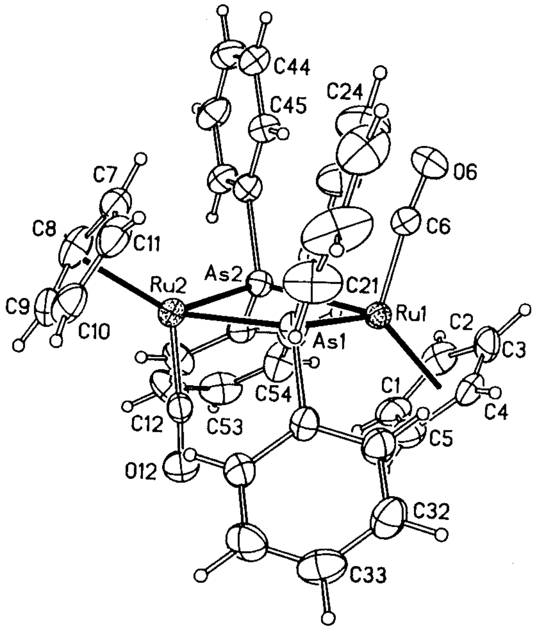

Figure 2. Molecular structure of *trans*-[CpRu(CO)(μ-AsPh$_2$)]$_2$ (**2**), with atoms represented as 40% thermal ellipsoids. One of two independent molecules is shown.

For the trans isomer **2**, two independent molecules crystallize in the monoclinic space group $P2_1/c$; selected bond parameters are given in Table 2. There are only minor deviations in the bond lengths and angles for the

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Table 2. Selected Bond Distances and Angles for *cis*- (1) and *trans*-[CpRu(CO)μ-As(C_6H_5)$_2$]$_2$ (2)

1		2		
			molecule A	molecule B
		(a) Bond Distances (Å)		
Ru–As	2.457(1)	Ru(1)–As(1)	2.485(1)	2.466(1)
Ru–As(a)	2.453(1)	Ru(1)–As(2)	2.478(1)	2.469(1)
		Ru(2)–As(1)	2.461(1)	2.457(1)
		Ru(2)–As(2)	2.459(1)	2.463(1)
Ru–CNT	1.897(8)	Ru(1)–CNT1	1.886(6)	1.894(7)
		Ru(2)–CNT2	1.900(7)	1.891(7)
Ru···Ru(a)	3.884(1)	Ru(1)···Ru(2)	3.872(1)	3.843(1)
		(b) Bond Angles (deg)		
As–Ru–As(a)	75.2(1)	As(1)–Ru(1)–As(2)	75.8(1)	74.3(1)
As–Ru–C(1)	88.5(2)	As(1)–Ru(1)–C(6)	96.9(3)	91.9(3)
AS(a)–Ru–C(1)	89.6(2)	As(2)–Ru(1)–C(6)	93.7(2)	100.6(3)
As–Ru–CNT	130.7(2)	As(1)–Ru(1)–CNT1	125.2(3)	129.6(2)
As(a)–Ru–CNT	127.3(2)	As(2)–Ru(1)–CNT1	128.2(2)	122.2(3)
CNT–Ru–C(1)	128.6(2)	CNT1–Ru(1)–C(6)	124.1(2)	124.9(2)
		As(1)–Ru(2)–As(2)	76.5(1)	74.6(1)
		As(1)–Ru(2)–C(12)	88.8(2)	85.1(3)
		As(2)–Ru(2)–C(12)	86.3(2)	89.7(3)
		As(1)–Ru(2)–CNT2	130.3(2)	132.7(2)
		As(2)–Ru(2)–CNT2	128.8(3)	129.8(3)
		CNT2–Ru(2)–C(12)	128.8(3)	127.4(3)
Ru–As–Ru(a)	104.5(1)	Ru(1)–As(1)–Ru(2)	103.1(1)	102.6(1)
C(16)–As–C(26)	99.9(1)	C(26)–As(1)–C(36)	96.4(2)	101.1(2)
		Ru(1)–As(2)–Ru(2)	103.3(1)	102.3(2)
		C(46)–As(2)–C(56)	97.3(2)	97.8(3)

two molecules. The average Ru–As bond is 2.467 Å, which is slightly longer than that found in **1**. Again, the Ru_2As_2 rhomboid is flat; the angle formed by the two $RuAs_2$ planes is 179.3(1)°. The local Ru atom geometry is again distorted octahedral, with the largest angles found about the Cp centroid–ruthenium vector, and the smallest angles found within the As–Ru–As portion of the rhombus. Arsenic again exhibits distorted tetrahedral geometry, with the phenyl–As–phenyl angle consistently being acute. The phenyl rings about arsenic in **2** are oriented in a slightly different manner from those of **1**. Each pair of phenyl rings lies tilted slightly in deference to the Cp ring located on that side of the Ru_2As_2 plane. The Ru···Ru distances in both **1** (3.884(1) Å) and **2** (av 3.858 Å) preclude direct metal–metal interactions.

The structures of **1** and **2** are the first published for iron triad metals in bridged dinuclear complexes of the type [CpM(CO)(μ-ER_2)]$_2$ and only the second for a related complex of any dinuclear cyclopentadienyl metal complex with bridging diorganoarsenido groups, the first being [CpMo(CO)$_2$(μ-$AsMe_2$)]$_2$.[20] Additionally, isomers **1** and **2** constitute only the second example of an isolated and crystallographically characterized set of cis–trans isomers for any bis-diorganopnictido-bridged structure of the very general formula [CpM$_n$(ER_2)]$_2$, the first being [CpCr(NO)N(CH_3)$_2$]$_2$.[21]

Conversion of **1** to **2**, or vice versa, by thermal means was not possible. Even after 72 h at 160 °C, there was no evidence for conversion of a toluene solution as monitored by ^1H NMR. However, it is possible to convert the cis isomer **1** to the trans isomer **2** irreversibly and in 90% yield after a 4-h exposure at room temperature with a low-pressure photochemical apparatus emitting at about 360–440 nm. The photochemical conversion of cis to trans may proceed via Ru–As bond breaking and inversion at Ru. The Mo–As bond breaking/Mo inversion scenario was proposed for the cis → trans photochemical process in [CpMo(CO)$_2$(μ-$AsMe_2$)]$_2$.[22] These results imply that **1** is the kinetic product, while **2** is the thermodynamically favored product.

Electrochemical Oxidation of 1: Two-Electron Stoichiometry. Complex **1** displays a single anodic wave (Figure 3) in CH_2Cl_2 or DMF with $E_{1/2}$ values (computed from average of E_{pa} and E_{pc}) of −0.36 and −0.30 V, respectively (Table 3). The oxidation was established as a chemically reversible two-electron process (eq 1) by cyclic voltammetry (CV), double-potential step chronoamperometry (CA), and bulk coulometry experiments.

$$\mathbf{1} \rightleftharpoons \mathbf{1}^{2+} + 2e^- \tag{1}$$

CV scans in CH_2Cl_2 at ambient temperatures gave a ratio of i_c/i_a of slightly above unity with scan rates as low as 0.05 V/s. CA gave a reverse-to-forward current ratio, i_{rev}/i_{fwd}, at the end of a 5-s step time, of 0.29, in agreement with expectations for formation of a stable electrode product.[23] The CV current function ($i_{pa}/\nu^{1/2}$)[24] was exactly twice that of equimolar decamethylferrocene.[25] CV peak separations, ΔE_p ($=E_{pa} - E_{pc}$), were about 40 mV, and the anodic peak breadth, δE_p ($=E_p - E_{p/2}$), was 34 mV, with $\nu = 0.05$ V/s. The two-electron nature of the process was finally confirmed by bulk coulometry, in which 2.1 F/equiv was released when **1** was electrolyzed to 99% completion at a Pt basket, with $E_{appl} = 0$ V at $T = 273$ K.

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(23) Theory for a completely reversible couple, 0.293 (Schwarz, W. M.; Shain, I. *J. Phys. Chem.* **1965**, *69*, 30); experiment for ferrocene under our conditions, 0.284.

(24) Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; p 683.

(25) This demonstrates that the oxidation of **1** is a two-electron process *if* the diffusion coefficients of **1** and decamethylferrocene are similar.

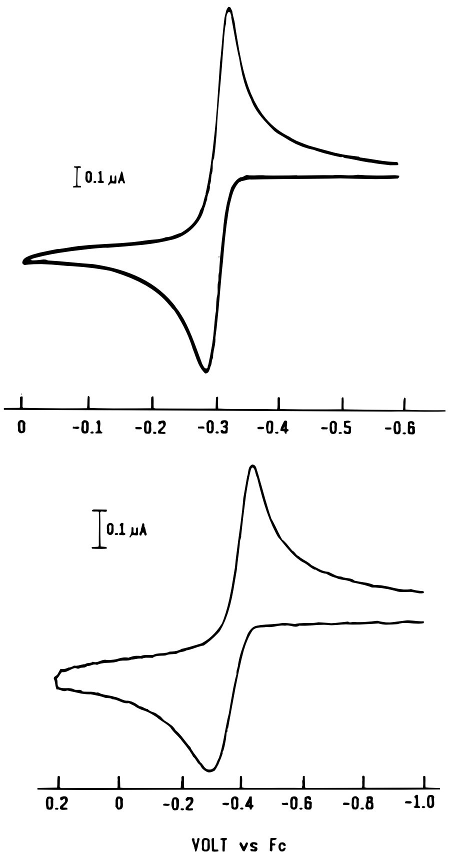


Figure 3. Cyclic voltammetry scans of 0.5 mM **1** in DMF/ 0.1 M $[NBu_4][PF_6]$ at 295 K: top, $\nu = 0.05$ V/s; bottom, $\nu = 1$ V/s.

Table 3. Electrochemical Potentials of 1 and 2 (Volts vs Fc)

complex	product	solvent	$E_{1/2}$	D_0 (cm²/s)
1	$\mathbf{1}^{2+}$	CH_2Cl_2	−0.36	*a*
1	$\mathbf{1}^{2+}$	DMF	−0.30	2.5×10^{-6}
$\mathbf{1}^{2+}$	**1**	DMF	−0.30	*a*
1	$\mathbf{1}^{2-\,b}$	DMF	-2.3^{b}	*a*
2	$\mathbf{2}^{2+}$	CH_2Cl_2	−0.30	8.7×10^{-6}

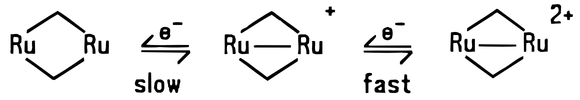
[a] Not measured. [b] Irreversible reduction wave of two-electron height; E_{pc} at $\nu = 0.1$ V/s given.

Solutions of $\mathbf{1}^{2+}$ generated coulometrically were stable in CH_2Cl_2, and the back-reduction of $\mathbf{1}^{2+}$ to **1** at $E_{appl} = -0.6$ V was efficient (2.1 F/equiv also found in the cathodic electrolysis of $\mathbf{1}^{2+}$). Only about 10% lower current was found in RPE voltammograms of **1** after the bulk oxidation/reduction cycle. Every indication, therefore, points to the adequacy of eq 1 as a description of this redox process.

It is worth noting that the diffusion coefficient (D_0) of $\mathbf{1}^{2+}$ is, apparently, substantially lower than that of **1**. This conclusion is indicated by the fact that a current plateau of 3.7 μA was measured for **1** prior to bulk electrolysis, but only 2.7 μA was observed for $\mathbf{1}^{2+}$ after the anodic reaction. Considerably reduced diffusion coefficients have been found previously for dications in CH_2Cl_2 compared to their neutral precursors.[14,26−29]

Complex **1** was also studied in DMF, a solvent superior to CH_2Cl_2 for quantitative fast voltammetry. Its oxidation was again described by the chemically reversible two-electron process of eq 1 [$E_{1/2} = -0.30$ V; $i_c/i_a = 1.05$ at $\nu = 0.05$ V/s; $i_{rev}/i_{fwd} = 0.29$ for 5-s CA step time; $D_o = 2.5 \times 10^{-6}$ cm²/s (from CA)]. The isolated dication (see below) also had $E_{1/2} = -0.30$ V in DMF.

In every published example of which we are aware, a two-electron wave for a bridged dinuclear complex has been ascribed to the making and breaking of a metal−metal bond accompanying the overall charge transfer(s).[30] The voltammetry is, therefore, interpreted in light of such a model; as the next section shows, the structural changes are likely apportioned between the two one-electron steps, with the major change occuring in the first electron transfer:



Deviations from Reversible Voltammetry: Use of Higher Scan Rates To Estimate Electron-Transfer Rate Constants for 1. The CV responses of **1** at higher scan rates are of interest because, under quasi-reversible charge-transfer conditions, some information may be extracted about the individual one-electron processes that make up the overall two-electron transfer.[14,27,30] ΔE_p values increased with increases in ν for either CH_2Cl_2 or DMF solutions of **1**. Anodic peak potentials (E_{pa}) also increased, and anodic current functions ($\chi_a = i_{pa}/\nu^{1/2}$) decreased at higher scan rates. No new peaks or other features were detected up to $\nu = 100$ V/s, nor were the voltammetric wave shapes affected by changes in concentration of **1** from 0.28 to 1.10 mM.

The two functions E_{pa}, and χ_a, though less widely employed as diagnostics than ΔE_p values, shed light on the ET reversibility of the electrode reaction. Figure 4 shows their values as the oxidation process goes from nearly Nernstian behavior (low ν) to one which displays irreversible charge-transfer kinetics (high ν). The current function is expected to decrease according to eq 2,

$$\chi_a(\text{irrev}) = 1.11(\alpha n_\alpha)^{1/2}\chi_a(\text{rev}) \qquad (2)$$

in which α is the charge-transfer coefficient, n_α is the number of electrons transfered in the rate-determining step, and χ(irrev) and χ(rev) are the current functions for electrode reactions in the irreversible and Nernstian limits, respectively. The limiting current function for **1** at high sweep rates is consistent with $\alpha = 0.4$ and $n_\alpha = 1$.

The shifts in anodic peak potentials at high ν also are consistent with $\alpha = 0.4$, $n_\alpha = 1$, as shown by the straight line in Figure 4 computed from eq 3:

$$d(E_p)/d(\log \nu) = 30\ \text{mV}/\alpha n_\alpha \qquad (3)$$

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(26) Edwin, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1990**, *112*, 7104.

(27) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

(28) In well-defined hydrodynamic circumstances (e.g., a rotating disk electrode), the relative values of the diffusion coefficients for the reduced and oxidized forms of the redox couple may be obtained from the plateau currents prior to and subsequent to, respectively, an anodic electrolysis. Quantitative comparisons are less certain when the (empirically shaped) Pt bead electrode is used.[29] A reasonable estimate is that the diffusion coefficient of $\mathbf{1}^{2+}$ is about one-half of that of **1** in CH_2Cl_2.

(29) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; John Wiley and Sons: New York, 1974; p 91.

(30) For leading citations, see refs 5, 6, 10, and 14.

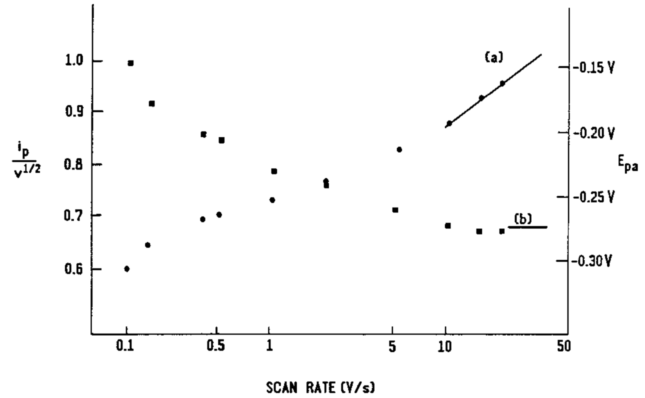

Figure 4. Anodic current function (■, left ordinate) and anodic peak potential (●, right ordinate) as a function of CV scan rate for **1** in DMF at 295 K. The current function is ratioed to the value at low sweep rates (the Nernstian limit). Line a gives the expected slope in the irreversible limit for a process with $\alpha = 0.4$, and line b gives the expected current function in the irreversible limit for $\alpha = 0.4$.

The data in Figure 4 tell us that the quasi-reversible charge-transfer regime lies at scan rates below 10 V/s for the oxidation of **1**, so we now turn to this scan rate region to estimate the quantitative electron transfer parameters of **1**.

Figure 5 shows a CV recorded at $\nu = 1$ V/s. The fact that the anodic peak height is less than the cathodic peak height means that the first charge-transfer step is rate limiting,[31] consistent with the dominant structural change occurring in the process **1**/**1**$^+$. In digital simulations, we set the value of $(E_{1/2}{}^2 - E_{1/2}{}^1)$ at -180 mV, based on the nearly Nernstian behavior of the couple[32] at slow sweep rates and the value of $k_s(2)$ at 0.1 cm/s, consistent with findings for related systems.[5a,7] In fact, the simulations have little sensitivity to the precise value of $k_s(2)$, since the value of $k_s(1)$ is rate limiting. Simulations such as those shown in Figure 5 were consistent with the values $k_s(1) = 0.007 \pm 0.002$ cm/s and $\alpha(1) = 0.42 \pm 0.05$. As a test of internal consistency, the α value agrees with that implied from the changes in current function and anodic peak potential with scan rate (Figure 4, vide ante).

Preparation of 1^{2+} by Chemical Oxidation. Oxidation of **1** using 2 equiv of ferrocenium hexafluorophosphate in CH_2Cl_2 gave a yellow-green solid which, when recrystallized from CH_3NO_2/diethyl ether, produced fine needles which analyzed as [**1**]$[PF_6]_2$. When this reaction was carried out in an NMR tube in CD_2Cl_2, the Cp ^1H resonances of **1** ($\delta = 4.63$) and $\mathbf{1}^{2+}$ ($\delta = 6.03$) were observed, without evidence of intermediates or side products. IR spectra of $\mathbf{1}^{2+}$ in CH_2Cl_2 gave a pair of CO stretches at 2050 and 2032 cm^{-1}, shifted an average of $+87$ cm^{-1}, from the single ν_{CO} of **1** at 1954 cm^{-1}. The split band in the dication is significant, since the implied vibronic coupling between the CO groups is consistent with the presence of a metal–metal bond in $\mathbf{1}^{2+}$.

The dication [**1**]$[PF_6]_2$ displayed the expected voltammetry in DMF, i.e., a single reduction wave at $E_{1/2} = -0.30$ V (cf. Figure 6).

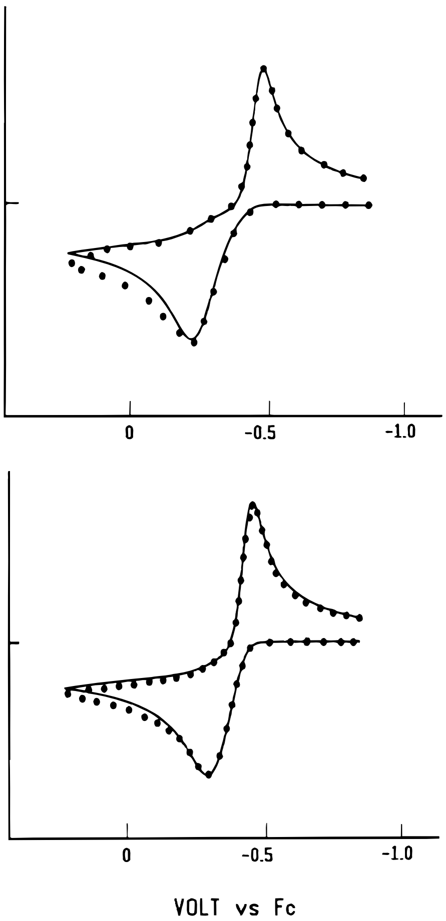

Figure 5. Fits between theory (solid lines) and experiment (dots) for the oxidation of 1.0 mM **1** in DMF at 298 K and (top) 10 V/s and (bottom) 1 V/s. Simulation parameters: $E_{1/2}{}^1 = -0.27$ V, $\alpha_1 = 0.42$, $k_S(1) = 0.007$ cm/s; $E_{1/2}{}^2 = -0.45$ V, $\alpha_2 = 0.50$, $k_S(2) = 0.1$ cm/s.

Electrochemical Properties of 2. The trans isomer **2** also undergoes a two-electron oxidation in CH_2Cl_2 to a persistent dication.[33] Its potential ($E_{1/2} = -0.30$ V) was 60 mV positive of that of the cis isomer **1** in the same medium. The dication $\mathbf{2}^{2+}$ did not appear to be as stable as $\mathbf{1}^{2+}$: about one-third of **2** was lost in a bulk coulometry experiment in which $\mathbf{2}^{2+}$ was generated at 273 K and then re-reduced back to neutral **2**.

Significance of Electron-Transfer Properties. The difference in $E_{1/2}$ values for the two isomers, although small (60 mV), shows that cis and trans isomers of dinuclear systems may have resolvable formal potentials. There is no evidence for interconversion of the two isomers in either of the higher oxidation states. Although worth noting, this observation may not be general for dinuclear bridged complexes, since the formation of a metal–metal bond in the dication may impart isomeric rigidity to the complexes that might be otherwise lacking.

Of, perhaps, greater interest is the contrast between the present diruthenium complexes and their diiron analogues having sulfido or phosphido bridges. Both $[Cp(CO)Fe(\mu\text{-}PPh_2]_2$ (**3**) and $[Cp(CO)Fe(\mu\text{-}SMe)]_2$ (**4**) may

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[31] Ryan, M. D. *J. Electrochem. Soc.* **1978**, *125*, 547. See also citations contained in ref 27.

[32] Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.

[33] In CV at $\nu = 0.05$ V/s, $i_c/i_a = 1.08$, $\Delta E_p = 34$ mV, $E_p - E_{p/2} = 28$ mV; double-potential step chronoamperometry, $i_{rev}/i_{fwd} = 0.27$ (5-s pulses); bulk coulometry, 1.9 F/equiv for 99% electrolysis (all data at Pt electrodes).

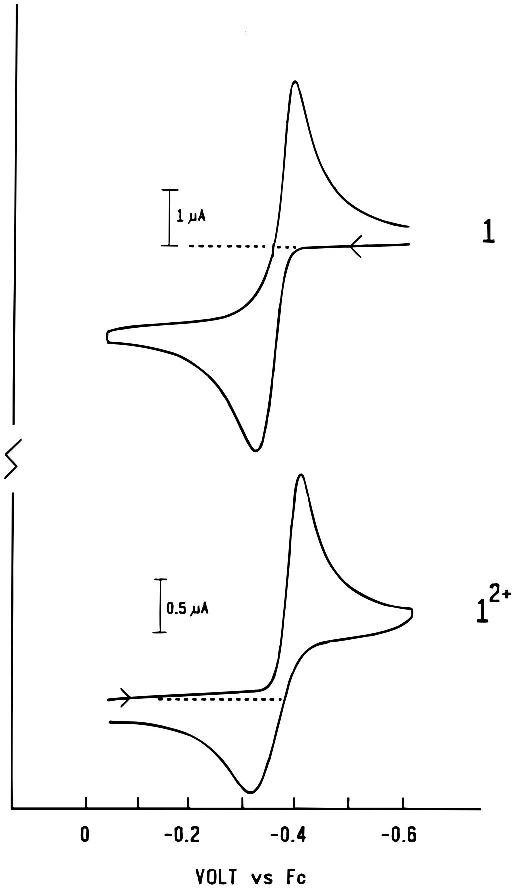
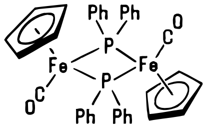


Figure 6. Cyclic voltammetric scans for **1** (top) and $\mathbf{1}^{2+}$ (bottom) in identical media (CH_2Cl_2/0.1 M $[NBu_4][PF_6]$) prior to (top) and after (bottom) exhaustive electrolysis ($E_{appl} = 0$ V) of a 1 mM solution of **1**. Scan rate, 0.2 V/s; $T = 273$ K.

be oxidized to dications, but their oxidations differ from those of **1** and **2** in (i) being well-separated one-electron processes and (ii) exhibiting fast electrode kinetics.[7]



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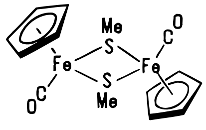

4

Factor i argues that the energy of the one-electron (monocation) intermediate is lowered more in the Ru_2 case than in the Fe_2 case, compared to the two outlying oxidation states. Factor ii, when contrasted with the slow:fast character of the two one-electron transfers $\mathbf{1}/\mathbf{1}^+$:$\mathbf{1}^+/\mathbf{1}^{2+}$, argues that the major part of the structural change in the diruthenium system comes in the first of these ET steps, in contrast to a more distributed set of structural changes in the diiron systems. Stated in another way, the M−M bond formation is more gradual in the sequence $Fe_2/Fe_2{}^+/Fe_2{}^{2+}$ than in the sequence $Ru_2/Ru_2{}^+/Ru_2{}^{2+}$, where M_2 stands for the dinuclear complexes under discussion.

The activation barrier to ET, $\Delta G^‡$, consists of inner-sphere and outer-sphere contributions, $\Delta G^‡{}_{IS}$ and $\Delta G^‡{}_{OS}$, respectively (eq 4). Furthermore, the inner-sphere barrier is one-fourth of the inner-sphere reorganizational energy, λ_{in} (eq 5).

$$\Delta G^‡ = \Delta G^‡{}_{IS} + \Delta G^‡{}_{OS} \tag{4}$$

$$\Delta G^‡{}_{IS} = \lambda_{in}/4 \tag{5}$$

In the limit that there is localized bond making and breaking in the ET transition state, the inner-sphere reorganizational energy is essentially equal to the bond enthalpy.[34] The latter may be estimated for a Ru−Ru bond of ≈2.8 Å from the work of Connor[35] as ≈20 kcal/mol. This suggests a value of $\Delta G^‡{}_{IS} \approx 5$ kcal/mol if the Ru−Ru bond is fully formed in the first one-electron transfer $\mathbf{1}/\mathbf{1}^+$. Using an estimate of 5 kcal/mol for $\Delta G^‡{}_{OS}$,[36] an overall value of ≈10 kcal/mol is predicted for a one-electron process involving *full* formation of a Ru−Ru single bond in the transition state. Given the uncertainties involved in these estimates, the observed value of 8.5 kcal/mol is respectably close to the prediction of this model.[37]

Conclusions

The cis and trans isomers of $[Cp(CO)Ru(\mu\text{-}AsPh_2)]_2$ have been prepared and characterized by X-ray crystallographic methods.

Both isomers display single anodic voltammetric waves of two-electron stoichiometry, the cis isomer being 60 mV easier to oxidize than the trans isomer. There is little previous literature on the question of whether cis and trans isomers of bridged dinuclear complexes have measureably different redox potentials.[38]

The dication of the cis isomer, $\mathbf{1}^{2+}$, has been isolated and characterized by NMR and IR spectroscopies. The presence of two CO stretches in the IR spectrum of 1^{2+} is evidence that the dication possesses the expected Ru−Ru bond.

The CV waves are essentially Nernstian at slow sweep rates but become quasi-reversible at higher scan rates. The wave shapes of the cis isomer are fit quantitatively by $E_{1/2}{}^1, = -0.27$ V vs Fc, $E_{1/2}{}^2 = -0.45$ V, $\alpha_1 = 0.42$, $\alpha_2 = 0.5$, $k_S(1) = 0.007$ cm/s, and $k_S(2) > 0.1$ cm/s.

The fact that the first oxidation is the rate-determining anodic process suggests that a major structural change occurs in electron transfer between the neutral and monocationic complexes. An activation barrier, $\Delta G^‡$, of 8.5 kcal/mol is consistent with the metal−metal bond being formed largely in this step.

The differences in electrode behavior between the present diruthenium complexes and their diiron analogues are explicable in terms of the presence of a stronger M−M bond in the one-electron intermediate formed upon oxidation of the diruthenium complexes.

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(34) (a) Saveant, J. M. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1994; Vol. 4, p 53. (b) Andrieux, C. P.; Robert, M.; Saveant, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9340 and references therein.

(35) Connor, J. A. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; John Wiley and Sons: Chichester, 1980; p 356.

(36) Weaver, M. J.; Gennett, T. *Chem. Phys. Lett.* **1985**, *113*, 213.

(37) From a value of 0.007 cm/s for $k_s(1)$ and an assumed preexponential term of 10^4, $\Delta G^‡ = 0.38$ eV (8.5 kcal/mol) at room temperature. For an introductory treatment of these concepts, see: Hale, J. M. In *Reactions of Molecules at Electrodes*; Hush, N. S. Ed.; Wiley-Interscience: London, 1971; p 229.

(38) The inorganic dinuclear complex $[(triphos)(H)Rh(\mu\text{-}Cl)]_2$ has been reported to display a single irreversible reduction wave for a 1:1 solution of trans:cis isomers: Bianchini, C.; Meli, A.; Laschi, F.; Ramirez, J. A.; Zanello, P.; Vacca, A. *Inorg. Chem.* **1988**, *27*, 4429.

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Supporting Information Available: Tables of atomic coordinates, complete bond distances and angles, and anisotropic thermal parameters for **1** and **2** (15 pages). Ordering information is given on any current masthead page.

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