Synthesis and Characterization of a Ruthenocene Carboxylate Containing Ruthenium(II) Complex

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Summary: Reaction of [$Ru_2(\mu\text{-}O_2CRc)_4(MeOH)_2$]($PF_6$) (Rc = ruthenocenyl) with 1,2-bis(diphenylphosphino)ethane (dppe) results in a "dimer disassembly" that produces the bimetallic [Ru(η^2-O_2CRc)(dppe)$_2$](PF_6), whose structure has been confirmed by X-ray diffraction. The electrochemical properties have been investigated using cyclic and Osteryoung square-wave voltammetry.

Introduction

The use of metallocenecarboxylates as *ligands* is relatively sparse in the literature, and the vast majority of those used are ferrocenemonocarboxylates and -dicarboxylates.[1] Of these, only a handful have been bound to ruthenium centers.[2,3] This is unfortunate, as they can offer a facile way of introducing a second metal center (in an organometallic environment) to a "traditional" (Werner-type) coordination complex to form a bimetallic (or multimetallic) metal−organometallic system (MOMS).[4,5] The first structurally characterized complex containing a *ruthenocene*carboxylate, [$Ru_2(\mu\text{-}O_2CRc)_4$(1-proponal)$_2$]($PF_6$) (Rc = ruthenocenyl) was recently reported in our laboratory and contains four bridging (μ) ruthenocenecarboxylates surrounding a mixed-valent diruthenium core in the popular paddle-wheel arrangement.[3b]

In a parallel study we employed a "dimer disassembly" process which involved reacting various bis(diphenylphosphines) with the tetrakis(ferrocenecarboxylato)diruthenium(II,III) analogue [$Ru_2(\mu\text{-}O_2CFc)_4$(alcohol)$_2$]($PF_6$) to form heterobimetallic complexes of the form [Ru(η^2-O_2CFc)(dpp)$_2$](PF_6) (where dpp = a bis(diphenylphosphine) and Fc = ferrocenyl) that contained an η^2-bound ferrocenecarboxylate.[3a] In this paper we have shown that we can extend our previous synthetic method and wish to report the preparation, structural characterization, and electrochemical properties of the first η^2-bound ruthenocenecarboxylate-containing complex, [Ru(η^2-O_2CRc)(dppe)$_2$](PF_6) (**1**).

Results and Discussion

The synthesis of **1** was carried out in a fashion similar to previous syntheses of ferrocenecarboxylate-containing bis(diphosphine) ruthenium(II) complexes via a "dimer disassembly" of [$Ru_2(\mu\text{-}O_2CRc)_4(MeOH)_2$]($PF_6$) through the reaction with dppe.[3] In the current case the solubility of [$Ru_2(\mu\text{-}O_2CRc)_4(MeOH)_2$]($PF_6$) was somewhat less than for its ferrocenecarboxylate analogue, and the yields of **1** suffered as a consequence (35−40% versus 70−75% for [Ru(η^2-O_2CFc)(dppe)$_2$](PF_6)).

The infrared spectrum of **1** shows the characteristic symmetric (ν_{sym}) and asymmetric (ν_{asym}) carboxylate stretching frequencies at 1436 and 1481 cm^{-1}, respectively, with $\Delta\nu$ = 45 cm^{-1}, indicative of an η^2 binding mode. There are also C−H stretching modes at 2928 cm^{-1} (alkane) and 3061 cm^{-1} (phenyl and Cp ring) and a very strong P−F stretching mode at 839 cm^{-1} due to the PF_6^- counterion.[6]

The NMR spectra for **1** in $CDCl_3$ can be assigned in a fashion similar to that for [Ru(η^2-O_2CFc)(dppe)$_2$](PF_6).[3a] The ^{31}P spectrum shows a doublet of triplets (at 58.49 and 51.94 ppm) for the two pairs of equivalent dppe phosphorus atoms, consistent with an A_2X_2 splitting pattern. (This can be compared to 57.66 and 51.35 ppm for [Ru(η^2-O_2CFc)(dppe)$_2$](PF_6).) The PF_6^- counterion displays a septet at −143.25 ppm due to the P−F coupling with J(PF) = 711 Hz. The ^{1}H NMR shows the dppe phenyl ring protons (40) in the range 6.7−8.2 ppm and the methylene protons between 1.3 and 2.8 ppm. The ruthenocenyl Cp ring protons display chemical shifts upfield of the phenyl ring protons due to the shielding effect of the metal electrons. The multiplet signals for the protons on the bound Cp ring are in the range of 4.6−5.2 ppm, whereas the protons on the unbound Cp ring are seen as a singlet at 4.07 ppm.

We were successful in obtaining crystals of **1** from methanol that were suitable for X-ray analysis. The complex crystallizes in the triclinic space group $P\bar{1}$ and

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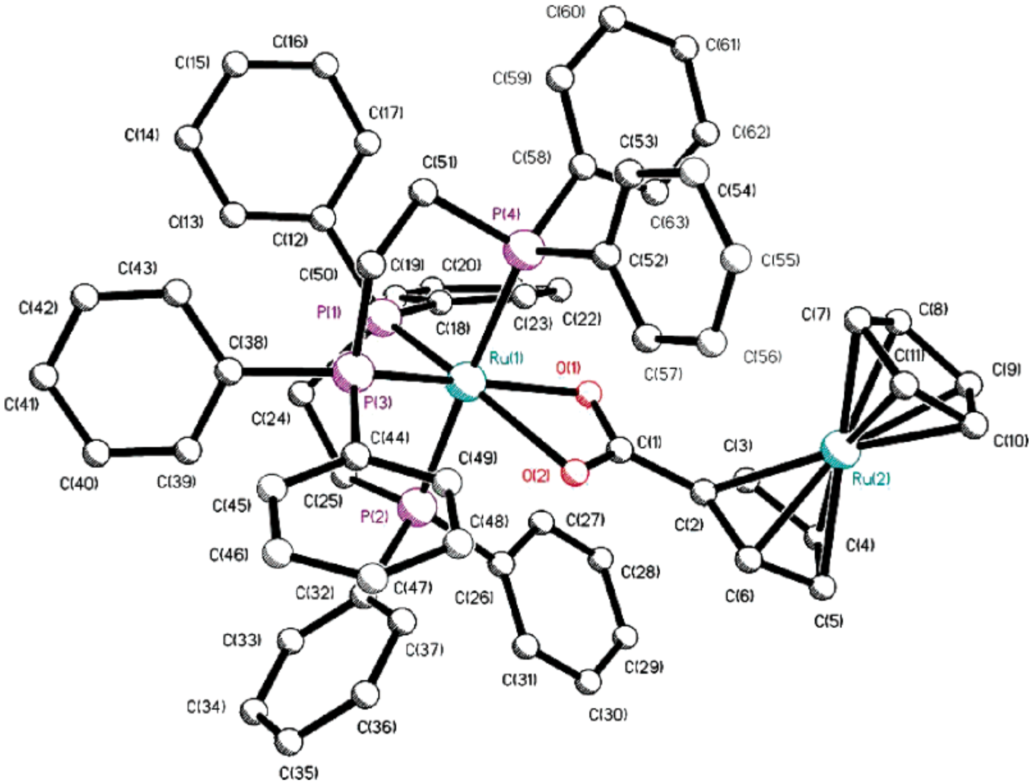

Figure 1. Molecular structure of $[Ru(\eta^2\text{-}O_2CRc)(dppe)_2]^+$ ($\mathbf{1}^+$). The molecules of solvation and the PF_6^- counterion were omitted for clarity.

Table 1. Crystal Data and Structure Refinement Details for 1

compd·(solvate)	$C_{63.75}H_{64}F_6O_{4.75}P_5Ru_2$
formula wt	1377.20
temp, K	296(2)
wavelength, Å	1.5418
cryst syst	triclinic
space group	$P\bar{1}$
cryst dimens, mm	0.32 × 0.25 × 0.17
a, Å	15.261(3)
b, Å	17.243(3)
c, Å	13.343(3)
α, deg	105.91(1)
β, deg	104.01(2)
γ, deg	67.47(1)
V, Å^3	3082(1)
Z	2
d_{calcd}, g cm^{-3}	1.48
abs coeff, mm^{-1}	5.757
F(000)	1403
max 2θ, deg	128.2
index ranges	$0 \le h \le 17$, $-18 \le k \le 20$, $-15 \le l \le 15$
no. of rflns	10 575
no. of indep rflns	10 113
no. of data/restraints/params	10113/382/720
goodness of fit on F^2	0.988
final R indices ($I > 2\sigma(I)$)	$R_F = 0.0650$, $R_w = 0.1698$
largest diff peak and hole, e Å^{-3}	1.949 and −1.156

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1

Ru(1)−O(1)	2.154(7)	Ru(1)−O(2)	2.233(7)
Ru(1)−P(1)	2.302(3)	Ru(1)−P(3)	2.312(3)
Ru(1)−P(2)	2.375(2)	Ru(1)−P(4)	2.394(2)
Ru(2)−C(2)	2.183(9)	Ru(2)−C(3)	2.19(1)
Ru(2)−C(4)	2.17(1)	Ru(2)−C(7)	2.18(1)
P(1)−C(12)	1.82(1)	P(1)−C(18)	1.85(1)
P(1)−C(24)	1.836(9)	P(2)−C(25)	1.85(1)
P(2)−C(26)	1.84(1)	P(2)−C(32)	1.82(1)
C(24)−C(25)	1.52(1)	P(3)−C(38)	1.84(1)
P(3)−C(44)	1.85(1)	P(3)−C(50)	1.838(9)
P(4)−C(51)	1.83(1)	P(4)−C(52)	1.85(1)
P(4)−C(58)	1.82(1)	C(50)−C(51)	1.52(1)
O(1)−C(1)	1.28(1)	O(2)−C(1)	1.25(1)
C(1)−C(2)	1.47(1)		
O(1)−Ru(1)−O(2)	59.8(3)	P(1)−Ru(1)−P(2)	82.63(9)
P(3)−Ru(1)−P(4)	82.97(9)	Ru(1)−O(1)−C(1)	91.8(6)
Ru(1)−O(2)−C(1)	88.9(6)	C(1)−C(2)−Ru(2)	127.9(7)
O(1)−C(1)−C(2)	118.5(9)	O(2)−C(1)−C(2)	122(1)
P(1)−Ru(1)−P(3)	94.2(1)	P(1)−Ru(1)−P(4)	98.4(1)
P(2)−Ru(1)−P(4)	178.0(1)	O(1)−Ru(1)−P(3)	163.8(2)
O(2)−Ru(1)−P(1)	156.0(2)	P(2)−Ru(1)−P(3)	98.72
O(1)−Ru(1)−P(1)	101.0(2)	O(1)−Ru(1)−P(2)	88.8(2)
O(1)−Ru(1)−P(4)	89.2(2)	O(2)−Ru(1)−P(2)	82.8(2)
O(2)−Ru(1)−P(3)	106.7(2)	O(2)−Ru(1)−P(4)	95.6(2)
O(1)−C(1)−C(2)	118.5(9)	O(2)−C(1)−C(2)	122(1)
C(3)−C(2)−C(1)	125.6(9)	C(6)−C(2)−C(1)	125(1)

has 0.75 molecules of methanol and 2 molecules of water present as solvates. The water molecules are apparently left over from the $[Ru_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2](PF_6)$ used to prepare the $[Ru_2(\mu\text{-}O_2CRc)_4(MeOH)_2](PF_6)$ starting material. The structure of **1** is depicted in Figure 1. Relevant crystallographic data are given in Table 1, with selected bond lengths and angles listed in Table 2.

The bond lengths and angles in **1** are similar to those seen in the ferrocenyl analogue $[Ru(\eta^2\text{-}O_2CFc)(dppe)_2](PF_6)$,[3a] with Ru−P bonds (trans to O) for **1** being 2.302−2.312 Å (compared to 2.299−2.309 Å), distinctly shorter than the Ru−P bonds (trans to P), which are 2.375−2.394 Å for **1** (compared to 2.370−2.389 Å for the ferrocenyl derivative). This clearly illustrates the greater trans influence of the phosphines. The binding of the ruthenocenecarboxylate is close to but not quite symmetric, with the two Ru−O bonds being 2.154(7) and 2.233(7) Å (a difference of 0.079 Å, and the values are not within error of each other). This is slightly less symmetric than in $[Ru(\eta^2\text{-}O_2CFc)(dppe)_2](PF_6)$, which

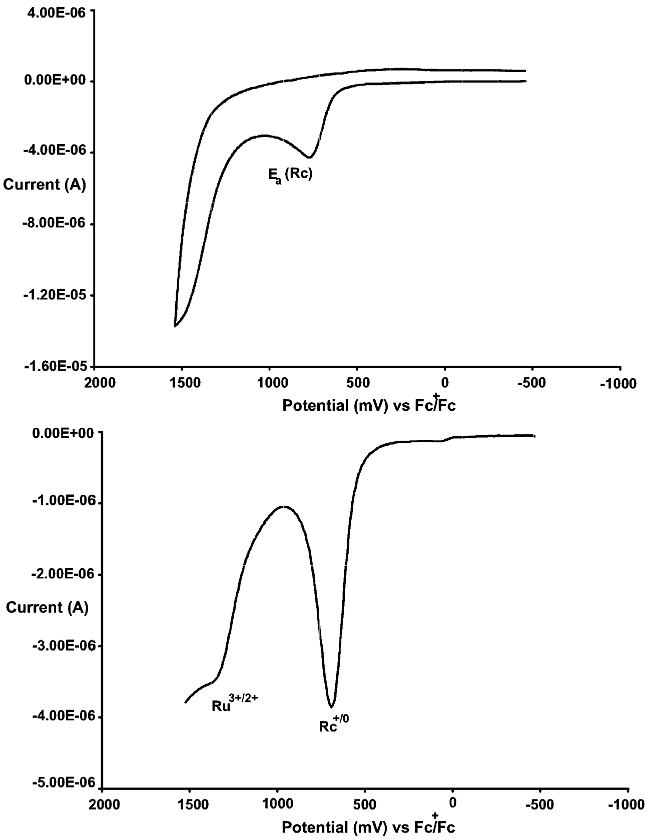

Figure 2. Cyclic voltammogram (top) and Osteryoung square-wave voltammogram (bottom) of **1**.

has Ru−O bonds of 2.161(2) and 2.211(2) Å (a difference of 0.050 Å, also not within error of each other). The O−Ru−O bite angle in **1** is 59.8(3)°, and the two P−Ru−P bite angles are 82.63(9) and 82.97(9)°, essentially identical with those in [Ru(η^2-O_2CFc)(dppe)$_2$](PF_6). Also, due to the larger size of Ru vs Fe, the average Ru−Cp(carbon) distance in **1**, 2.18 Å, is longer than the same average distance, 2.04 Å, in any of the ferrocenyl analogues studied earlier.[3a]

Cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) was carried out on **1** in 1,2-dichloroethane which contained 0.100 M tetrabutylammonium hexafluorophosphate (TBAH). For ease of solubility and for comparison purposes to the previously synthesized ferrocenyl derivatives, we used 1,2-dichloroethane (or dichloromethane).

The cyclic voltammogram (Figure 2, top) reveals an irreversible one-step two-electron (from coulometry) ruthenocenyl-based oxidation with an anodic potential, $E_a = 0.752$ V vs Fc^+/Fc, at a scan rate of 100 mV s^{-1}. A second, poorly resolved oxidation (presumably the other ruthenium center) is seen just before the solvent cutoff at ~1.45 V. The OSWV (Figure 2, bottom) reveals somewhat more detail. Two oxidations are clearly observed. The first, as with the CV, is the two-electron ruthenocenyl oxidation with $E_{1/2} = 0.644$ V vs Fc^+/Fc. The second appears as a shoulder on the solvent cutoff at $E_{1/2} = 1.35$ V vs Fc^+/Fc and corresponds to the one-electron oxidation of the “inorganic” ruthenium center ($Ru^{2+/3+}$). The latter process is at the same potential as that seen for the ruthenium center in the ferrocenyl analogue, [Ru(η^2-O_2CFc)(dppe)$_2$](PF_6).[3a] The value of 0.644 V for the ruthenocenyl-centered process in **1** compares well with the value of 0.600 V vs Fc^+/Fc (0.907 V vs SCE) measured by Kuwana et al. for $CpRuCOC_6H_5$ in the modestly coordinating acetonitrile/0.2 M $LiClO_4$ solvent system.[7]

It has been reported that ruthenocene and its derivatives, as opposed to their ferrocene analogues, usually undergo an irreversible one-step, two-electron oxidation process in most solvents and most electrolyte systems.[7−10] Two reasons (see eqs 1 and 2) have been postulated for

$$2Cp_2Ru^+ \rightarrow [Cp_2Ru]_2^{\,2+} \rightarrow Cp_2Ru + Cp_2Ru^{2+} \quad (1)$$

$$2Cp_2Ru^+ \rightarrow Cp_2Ru + Cp_2Ru^{2+} \quad (2)$$

$$Cp_2Ru^{2+} + X^- \rightarrow [Cp_2RuX]^+$$

$$X^- = \text{weakly coordinating anion}$$

this controversial behavior: (1) a rapid dimerization of the ruthenocenium (Cp_2Ru^+) species that is generated followed by disproportionation and (2) the direct disproportionation of Cp_2Ru^+ in the presence of even weakly coordinating ligands (anions from the electrolyte). Cp_2Ru has a larger ring−ring separation than Cp_2Fe and, hence, would be more prone to dimerization or nucleophilic attack by an anion.

Gale et al. were able to see a quasi-reversible one-electron oxidation in molten salts,[11] and Mann and coworkers were able to generate similar one-electron quasi-reversibility in the noncoordinating solvent dichloromethane using the essentially noncoordinating electrolyte tetrabutylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TBA^+TFPB^-).[12]

One way of preventing any potential dimerization from occurring is to introduce steric hindrance around the metal. This has been done successfully in the past by completely methylating the Cp rings to form the permethylated Cp^*_2Ru species, and again a quasi-reversible one-electron oxidation is observed.[13] In the case of complex **1** the steric hindrance imposed by the surrounding phenyl rings on the two dppe coligands does not appear sufficient to prevent any dimerization from occurring, certainly at modest scan rates. (Figure 1 shows the −(C_5H_4)RuCp group to be reasonably well exposed). It should be noted, however, that at very high scan rates (~20−40 V s^{-1}, which is the limit of our instrumentation) a weak return cathodic wave appears visible at 0.520 V and a very small amount of the −(C_5H_4)RuCp$^+$ moeity may be being rereduced. Whether this is due to the limited steric hindrance attenuating any possible dimerization or simply the scan rate having “caught up to” the intrinsic limiting rate of the dimerization in this complex will require further investigation.

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Summary

We have prepared the first complex containing a η^2-bound ruthenocenecarboxylate as ligand. The structure of [Ru(η^2-O_2CRc)(dppe)$_2$](PF$_6$)$\cdot$2$H_2O$$\cdot$0.75 CH_3OH has been confirmed by X-ray diffraction. Electrochemical measurements reveal an irreversible one-step two-electron oxidation of the ruthenocenyl centered "organometallic" ruthenium, followed by an irreversible one-step one-electron oxidation of the "inorganic" ruthenium center.

Experimental Section

All manipulations were carried out under an atmosphere of argon. All reagents were obtained from commercial sources and used as received, unless otherwise noted. Dichloromethane and 1,2-dichloroethane were distilled under nitrogen over CaH_2. [Ru$_2$(μ-O_2CRc)$_4$(MeOH)$_2$](PF$_6$) was prepared according to the procedure of Cooke et al.[3b]

^{1}H and ^{31}P NMR data were recorded on a Bruker Aspect 300 MHz NMR spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as a reference for ^{1}H data and 85% H_3PO_4 as the reference for the ^{31}P spectra. Infrared spectra were recorded on a Bio-Rad FTS-175 FTIR spectrophotometer as KBr disks. Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) were performed in 1,2-dichloroethane or dichloromethane using a BAS CV-50 voltammetric analyzer. The cell setup and conditions have been described elsewhere.[3a] The ferrocenium/ferrocene couple was used as an internal reference and found to have $E_{1/2} = 440$ mV vs Ag/AgCl ($\Delta E =$ 65 mV, scan rate 100 mV s^{-1}). Elemental analysis was performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada. X-ray data (vide infra) were collected at the DalX X-ray facility, Dalhousie University, Halifax, Canada.

[Ru$_2$(η^2-O_2CRc)(dppe)$_2$](PF$_6$)$\cdot$2$H_2O$$\cdot$0.75MeOH (1). [Ru$_2$($\mu$-$O_2$CRc)$_4$(MeOH)$_2$](PF$_6$) (0.080 g, 0.053 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe; 0.086 g, 0.22 mmol) were dissolved in 150 mL of methanol and refluxed for 12 h. The solution turned from yellow-green to bright yellow. After the reflux was complete, ammonium hexafluorophosphate (0.009 g, 0.055 mmol) was added to the solution, which was then reduced in volume under vacuum to 20−30 mL and cooled to −10 °C overnight. A yellow crystalline solid was collected and dried in vacuo. Yield: 0.052 g, 0.039 mmol (37%). Anal. Calcd for $Ru_2C_{63.75}H_{64}O_{4.75}P_5F_6$: C, 55.60; H, 4.68; P, 11.25; Ru, 14.7. Found: C, 55.88; H, 4.59; P, 10.93; Ru, 14.7. IR (cm^{-1}): 3427 (w), 3061 (w), 2928 (w), 1509 (s), 1481 (m), 1436 (s), 1400 (m), 1188 (w), 1099 (s), 1023 (m), 1002 (m), 839 (s), 746 (m), 697 (s), 557 (m), 528 (m), 457 (m). ^{1}H NMR (in $CDCl_3$; δ/ppm) 8.2−6.7 (multiplet, 40 phenyl protons); 2.8, 2.3, 2.1, 1.27 (multiplet, eight methylene protons); 4.76−4.64 (multplet, four bound Cp ring protons); 4.07 (singlet, five unbound Cp ring protons). ^{31}P NMR (in $CDCl_3$; δ/ppm): 58.49 (triplet, 2P), 51.94 (triplet, 2P), −143.25 (septet, 1P).

Crystallographic Analysis for 1. Crystals of complex **1** suitable for X-ray diffraction were grown by slow evaporation from methanol. Many of the experimental details are similar to those outlined previously[3a] and will not be mentioned here. A yellow crystal with approximate dimensions of 0.30 × 0.25 × 0.20 mm^3 was mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Rigaku AFC5R diffractometer equipped with a rotating anode generator. Cu Kα radiation was used. No decay correction was applied. The structure was solved by direct methods by SHELX97[14] and expanded using Fourier techniques.[15] The final cycle of full-matrix least-squares refinement was based on the observed reflections ($I > 3.00\sigma(I)$) and the variable parameters converged with unweighted (R1) and weighted agreement factors (wR2). All calculations were performed using the teXsan software package from Molecular Structure Corporation.[16]

The non-hydrogen atoms were refined anisotropically; however, the solvent molecules were refined isotropically. Hydrogen atoms were included but not refined. The hydrogen atoms of the solvent water molecules could not be accurately located and were not included in the final structure. All of the solvent molecules were quite mobile, resulting in their having large atomic displacement parameters. The occupancies of each of the solvent molecules were checked by refining different occupation factors and seeing which gave the best statistical results. Further crystallographic details are summarized in Table 1.

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Supporting Information Available: A crystallographic information file (CIF) for complex **1**. This information is available free of charge via the Internet at http://pubs.acs.org.

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