

Electrochemical Characterization of a Rhodium(II) Dimer with *N*-Phenylacetamido Bridging Ligands

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Received May 20, 1983

The redox reactions of dimeric $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ were investigated in nonaqueous media. Two reversible one-electron oxidation steps were obtained in solvents with large anodic potential limits $[(\text{CH}_3)_2\text{CO}, \text{CH}_2\text{Cl}_2, \text{CH}_3\text{CN}, \text{ and PrCN}]$ while in Me_2SO , a solvent with a smaller anodic limit, only a single reversible oxidation was observed. The first oxidation occurred at 0.55 V vs. SCE in methylene chloride and is at a potential much lower than that reported for any other dinuclear rhodium(II) carboxylate in the same solvent. The solvent effects of $E_{1/2}$ on the electrode reactions of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ were compared with those for $\text{Rh}_2(\text{O}_2\text{C}_2\text{H}_5)_4$ and $\text{Rh}_2(\text{HNOCCF}_3)_4$. The electronic absorption spectra of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ and $[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$ are reported and are quite different from those of $\text{Rh}_2(\text{O}_2\text{CR})_4$ and $\text{Rh}_2(\text{HNOCCF}_3)_4$. The spectrum of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ is characterized by four transitions in the visible region.

Introduction

Dinuclear rhodium(II) complexes of the type $\text{Rh}_2(\text{O}_2\text{CR})_4$ and $\text{Rh}_2(\text{O}_2\text{CR})_4(\text{L})_2$ have proven to be unique and interesting systems for probing the electronic structure and chemistry of these orbitally complex small metal clusters. The Rh-Rh bond distance,¹⁻⁴ the electronic spectra,⁵⁻⁷ and the electrochemistry⁸⁻¹⁰ of $\text{Rh}_2(\text{O}_2\text{CR})_4$ and $\text{Rh}_2(\text{O}_2\text{CR})_4(\text{L})_2$ have been investigated with respect to the σ -donor and π -acceptor characteristics of the axial ligands, L, and the inductive effects of the substituents, R, on the carboxylato bridge. These studies have resulted in considerable disagreement concerning the nature of the metal-metal,¹¹⁻¹⁴ and metal-ligand^{8,9,11-15} interactions. One area for which there are many unanswered questions is the role of the bridging moiety in the overall bonding scheme and the constraints the bridge places on the Rh^{4+} ion. Until recently, there were very few examples of dinuclear rhodium(II) complexes with bridging ligands containing different kinds of donor atoms.¹⁶⁻¹⁸ For this reason, little is known about the effects of heterodonor atom bridging groups on the Rh-Rh interaction or about how these types of ligands alter the molecular structure and chemical reactivity of the dirhodium(II) complex.

Recently, the synthesis of a new class of rhodium(II) complexes was reported.¹⁹⁻²¹ These compounds, $\text{Rh}_2(\text{RNOCR})_4$,

have a structure similar to the well-studied rhodium carboxylates,¹⁻¹⁵ $\text{Rh}_2(\text{O}_2\text{CR})_4$ (Figure 1a), but have mixed oxygen and nitrogen donor atoms in place of the two oxygen donors of the carboxylato bridging ligands. In the first reported synthesis of these compounds, it was shown that $\text{Rh}_2(\text{HNOCCF}_3)_4$ (Figure 1b) could be electrochemically oxidized to form $[\text{Rh}_2(\text{HNOCCF}_3)_4]^+$ in a number of solvents at a potential between +0.90 and +1.08 V vs. SCE. This is not the case for the corresponding trifluoroacetato-bridged complex $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$, which was not oxidized in the potential range of most solvents normally used for electrochemical investigations (up to ~ 1.8 V vs. SCE).²⁰ Thus, replacing four of the eight oxygens in $\text{Rh}_2(\text{O}_2\text{CR})_4$ by NH groups lowered the oxidation potential of the complex by at least 700 mV.

The oxidation potential of the amidate ligand complexes is quite sensitive to the substituents on both the amide carbon and the nitrogen atoms. The structure of one such substituted complex, $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$, is shown in Figure 1c. Two geometric isomers of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ were isolated, and it was shown that the electronic spectra and electrochemistry of these complexes are dramatically different from those of any other known dirhodium(II) compound.²¹ Each of these isomers undergoes two reversible one-electron transfer oxidation steps. The first oxidation occurred at a much lower potential than that reported for any known dinuclear rhodium(II) carboxylate. The second oxidation step had never been observed before for dirhodium(II) complexes. The visible spectra of the neutral and cationic complexes are also considerably different from those observed for dinuclear rhodium(II) complexes involving other types of bridging ions. In this paper we present a detailed study of one of the totally substituted isomers.

Experimental Section

Chemicals. The $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ dimers were synthesized by heating 1 g of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ and 30 g of *N*-phenylacetamide at 150 °C for 48 h. Excess *N*-phenylacetamide was then removed by sublimation, 30 g of fresh *N*-phenylacetamide added to the reaction mixture, and the heating process continued for another 48 h. Excess *N*-phenylacetamide was again removed by sublimation, producing a mixture of organic impurities and several different rhodium complexes. This mixture was separated by using high-performance liquid chromatography with a CN-bonded phase column and methanol eluent. Two isomers of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ have been isolated in low yield from the reaction of tetrakis(μ -acetato)dirhodium(II) and *N*-phenylacetamide.²¹ The ¹³C NMR spectra indicate that one of the isomers is the 3,1 complex shown in Figure 2.²¹ Because of the difficulty involved in obtaining a sufficient amount of this 3,1 isomer for a complete study, results for oxidation of this complex are not presented in this paper. The other isomer, which is produced in a

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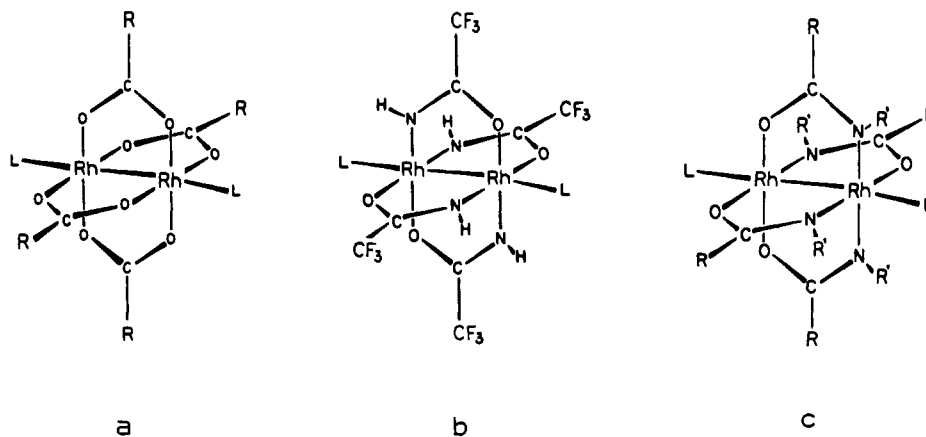


Figure 1. Structure of (a) $\text{Rh}_2(\text{O}_2\text{CR})_4$, (b) $\text{Rh}_2(\text{HNOCCF}_3)_4$, and (c) $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ (where $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$). Two donor ligands are shown bound to each complex.

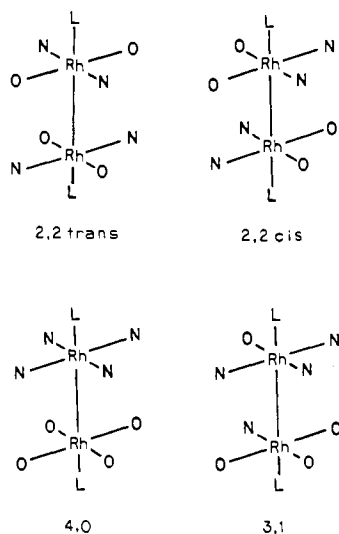


Figure 2. Isomers of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$.

considerably higher yield, is one of the remaining isomers in which the bridging ligands are magnetically equivalent. At this time we have not determined the molecular structure of this complex. However the major product of the reaction involving trifluoroacetamide is the 2,2-cis product in Figure 2 and is the likely candidate in this case.

Solvents utilized were methylene chloride (CH_2Cl_2), acetone ($(\text{C}_2\text{H}_5)_2\text{CO}$), acetonitrile (CH_3CN), butyronitrile (PrCN), pyridine (py), and dimethyl sulfoxide (Me_2SO); these were of reagent grade. CH_2Cl_2 was distilled over P_2O_5 . All other solvents were dried and stored over 4-Å molecular sieves before use. Tetrabutylammonium perchlorate (TBAP) was utilized as a supporting electrolyte and was 0.1 M throughout. The TBAP was recrystallized from an ethyl acetate/ether mixture and dried under reduced pressure.

Instrumentation. Polarographic and cyclic voltammetric measurements were made on an EG&G Princeton Applied Research (PAR) Model 174 polarographic analyzer or an EC Model 225 voltammetric analyzer utilizing a three-electrode system. The working electrode consisted of either a platinum button electrode or a dropping mercury electrode (DME). A commercial saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire was used as the counter electrode. The reference electrode was separated from the bulk of the solution by a bridge containing the same solvent and supporting electrolyte. $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ concentrations were between 10^{-4} and 10^{-3} M. Potentials were measured vs. a saturated calomel electrode as well as with respect to the ferrocenium/ferrocene (Fc^+/Fc) couple in order to correct for differences in liquid junction potential between different solvents. Cyclic voltammetric scan rates were between 0.02 and 3.0 V/s. For controlled-potential coulometry, a Princeton Applied Research Model 173 potentiostat was used. Current-time curves were recorded on a PAR Model 179 integrator. Large coiled platinum wires served as both the anode and cathode, which were separated by means of a fritted glass disk. A Cary 14

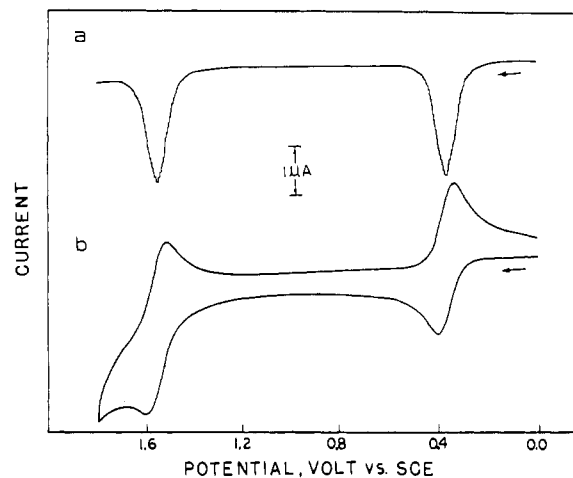


Figure 3. (a) Differential pulse voltammogram (modulation amplitude = 25 mV, scan rate = 5 mV/s) and (b) cyclic voltammogram (scan rate = 0.1 V/s) for the oxidation of 1.0 mM $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ in acetone, 0.1 M TBAP.

spectrophotometer or a Tracor Northern 1710 optical spectrometer/multichannel analyzer was used to obtain electronic absorption spectra. ESR spectra were measured on an IBM Model 100D ESR spectrometer.

Results and Discussion

Electron Transfer Reactions of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$. Figure 3 illustrates a typical cyclic voltammogram and differential pulse voltammogram for the oxidation of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ in acetone-0.1 M TBAP. As seen in this figure, two reversible processes occur at 0.39 and 1.59 V vs. SCE. The currents observed by differential pulse voltammetry (Figure 3a) or by cyclic voltammetry (Figure 3b) for the two steps are of equal height, indicating an identical number of electrons in each step. In addition $E_{pa} - E_{pc} = 60 \pm 5$ mV at low scan rates ($v < 100$ mV/s), and $i_p/v^{1/2}$ from the cyclic voltammograms was constant for the two processes, indicating that one electron is reversibly transferred in each step. Similar cyclic voltammograms were obtained in solvents with large anodic potential limits [CH_2Cl_2 , CH_3CN , and PrCN], while in Me_2SO , a solvent with a smaller anodic limit, only a single process was observed. These half-wave potentials are listed in Table I, which also includes potentials relative to the Fc^+/Fc couple in each solvent.

Confirmation of the overall number of electrons transferred in each step was obtained by controlled potential electrolysis. Controlled potential oxidations of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ were carried out at potentials 200 mV more anodic than the first half-wave potential and showed a one electron/dimer oxidation

Table I. Half-Wave Potentials (V vs. SCE or Fe³⁺/Fe) for the Oxidation of Rh₂(C₆H₅NOCCH₃)₄ in Different Solvents Containing 0.1 M TBAP

no.	solvent	DN ^a	Rh ₂ L ₄ ⇌ [Rh ₂ L ₄] ⁺			[Rh ₂ L ₄] ⁺ ⇌ [Rh ₂ L ₄] ²⁺		
			E _{pa} - E _{pc} , mV	E _{1/2} (vs. SCE)	E _{1/2} (vs. Fe ³⁺ /Fe)	E _{pa} - E _{pc} , mV	E _{1/2} (vs. SCE)	E _{1/2} (vs. Fe ³⁺ /Fe)
1	CH ₂ Cl ₂	0.0	60	0.55 ^b	+0.05	60	1.65	1.15 ^b
2	CH ₃ CN	14.1	60	0.34	-0.06	60	1.54	1.14
3	PrCN	16.6	60	0.35	-0.12	60	1.57	1.10
4	(CH ₃) ₂ CO	17.0	60	0.39	-0.11	60	1.59	1.09
5	Me ₂ SO	29.8	60	0.40	-0.06			

^a Reference 25. ^b Potentials reported are for freshly prepared solutions. Exposure to air or aging of solutions produced a shift of potentials towards negative values.

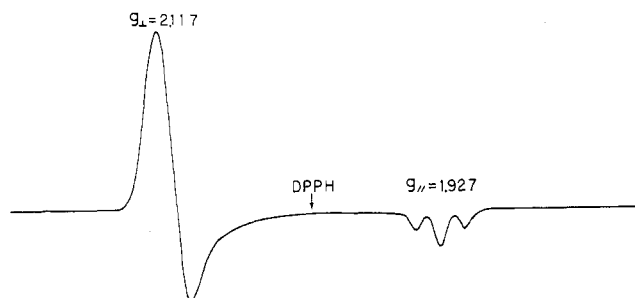
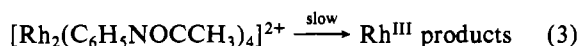
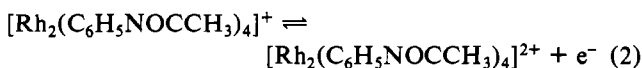
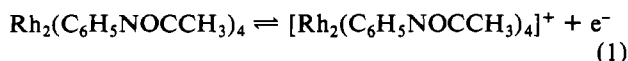


Figure 4. ESR spectrum at -196 °C of electrochemically generated [Rh₂(C₆H₅NOCCH₃)₄]⁺ in acetone-0.1 M TBAP. The electrolysis was carried out at 0.75 V.

as the color changed from blue or green to purple. The first oxidation was totally reversible, as evidenced by the fact that rereduction could be accomplished at 0.0 V with the addition of one electron/dimer, producing the original blue or green color. Reversibility of the second step, however, was not obtained on the longer time scale of bulk electrolysis. In this case, 2 faradays could be abstracted from the complex by directly stepping the potential to 1.7 V to produce a yellow solution. Cyclic voltammetry of this oxidized solution showed no evidence of dimers and gave only an ill-defined reduction peak at about 0.0 V.

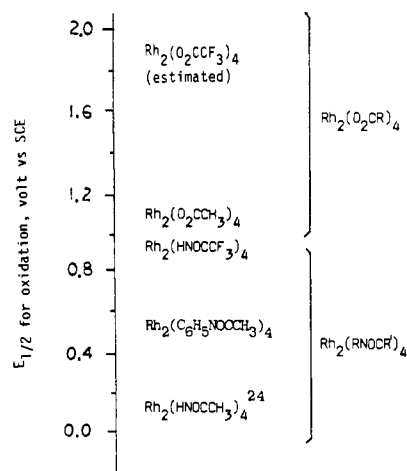
The products of the first and second oxidation were investigated by ESR spectroscopy. Before electrolysis no ESR signal was observed. After electrolysis at 0.75 V, the ESR signal shown in Figure 4 was obtained. This spectrum, which was taken at -196 °C in acetone, has an axial symmetrical character with $g_{\perp} = 1.927$ and $g_{\parallel} = 2.117$, which may be compared with the values of $g_{\parallel} = 1.996$ and $g_{\perp} = 2.148$ for [Rh₂(O₂CR)₄(PPh₃)₂]⁺.^{22,23} For ¹⁰³Rh (100% natural abundance), I is equal to 1/2. Due to the interaction between the electron and two nuclei of the rhodium ions, a hyperfine splitting with a 1:2:1 triplet is predicted. As seen in Figure 4 this is observed at $g_{\parallel} = 1.927$. Finally, after controlled potential oxidation at potentials anodic of the second peak, no ESR signal was observed.

On the basis of coulometric, voltammetric, and ESR data, the following reactions may be assigned:



Reactions 1, 2, and 3 are written without coordinated solvent molecules, although, as will be discussed below, a strong in-

Scheme I



teraction does exist in strongly bonding solvents. Both reactions 1 and 2 are reversible on the voltammetric time scale of seconds to milliseconds, but decomposition occurs on the longer time scale needed for controlled potential electrolysis (20–30 min).

In an earlier paper we compared the electrochemistry of Rh₂(O₂CCF₃)₄, Rh₂(O₂CCH₃)₄, and Rh₂(HNOCCF₃)₄ in a variety of solvents.²⁰ By comparing the oxidation potentials of Rh₂(HNOCCF₃) and Rh₂(O₂CCF₃)₄ we were able to establish that the substitution of HN for O in the complexing ligand results in a lowering of the E^{ox}_{1/2} by at least 700 mV. This lowering is intrinsic to the donor properties of the nitrogen vs. oxygen atoms since all other substituents are the same. The lowering of the potential from ~1.1 V for Rh₂(HNOCCF₃)₄ to 0.55 V for Rh₂(C₆H₅NOCCH₃)₄ in CH₂Cl₂ is a result of a change in the substituents both on the amide carbon and on the nitrogen atoms. Since the electrochemistry of Rh₂(HNOCCH₃)₄ is very similar to that of Rh₂(O₂CCH₃)₄²⁰ it appears that with respect to "tuning" the redox potentials of the dirhodium(II) center, the lower limit of the carboxylato bridged system is about the same (1.1 V) as the upper limit of the amidato complexes. This is illustrated in Scheme I, which lists the potentials for several representative Rh₂(O₂CR)₄ and Rh₂(RNOCr)₄ complexes in CH₂Cl₂.

By varying the substituents on the bridging moiety we know that we can tune the oxidation potential from ~1.0 V to greater than 1.7 V for the dirhodium(II) tetracarboxylates. It now appears with the proper choice of an amidato substituent the dirhodium(II) system can be tuned from 0.15²⁴ to 1.0 V vs. SCE.

The appearance of the second one-electron oxidation process for Rh₂(C₆H₅NOCCH₃)₄ is intriguing from the standpoint of future studies. This oxidation is reversible on the time scale of the cyclic voltammetric experiment and shows that a di-

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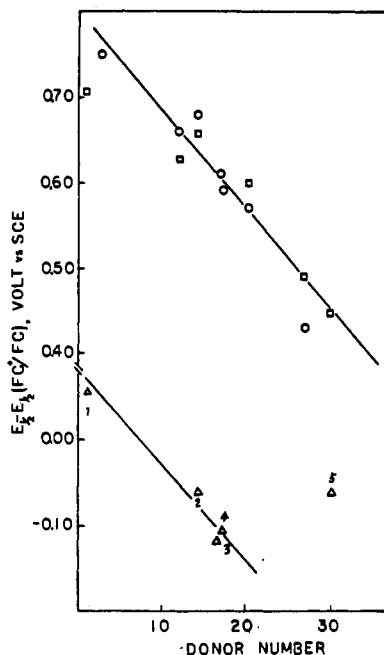
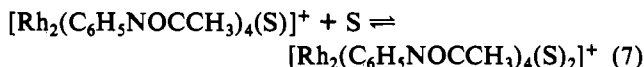
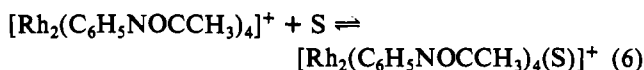
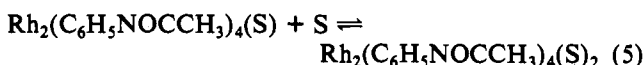
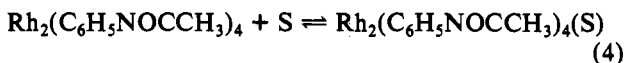


Figure 5. Plot of $E_{1/2}$ vs. donor number for the first oxidation of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ (Δ), $\text{Rh}_2(\text{HNOCCF}_3)_4$ (O), and $\text{Rh}_2(\text{O}_2\text{C}-\text{C}_2\text{H}_5)_4$ (\square). Data for the last two compounds were taken from ref 20 and 9, respectively; numbers for $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ correspond to the solvents given in Table I.

rhodium(III,III) dimer with a reasonable stability is produced. This also presents the possibility that a dirhodium(III,III) dimer could be isolated if one has the correct amide substituent and axial ligands.

Solvent Effects on Electrode Reactions. Either $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ or $[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$ may be complexed with solvent molecules as shown in eq 4–7. Redox potentials



for oxidation in solvents where S is axially complexed will be shifted anodically or cathodically from the values measured for reactions 1 and 2 depending on which oxidation state of the dimer is more greatly stabilized by solvent binding. Generally, strong σ donor solvents stabilize the higher charged species in the redox couple,²⁵ as was observed for the reactions of $\text{Rh}_2(\text{O}_2\text{CCR})_4$ in various solvents.⁹ In this study, five solvents were utilized that varied from nonbonding CH_2Cl_2 (DN = 0.0) to strongly bonding Me_2SO (DN = 29.8). Figure 5 shows a plot of half-wave potentials vs. donor number for the oxidations of $\text{Rh}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$,⁹ $\text{Rh}_2(\text{HNOCCF}_3)_4$,²⁰ and $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$. It is interesting to note from Figure 5 that an almost identical solvent effect (the slope of $E_{1/2}$ vs. DN) is observed for $\text{Rh}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ and $\text{Rh}_2(\text{HNOCCF}_3)_4$. This was explained by the stronger solvent-binding ability of the mixed oxidation state dimer over that of the neutral Rh^{II} complexes.²⁰ A similar trend is observed for the oxidation potential of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ in all the solvents studied

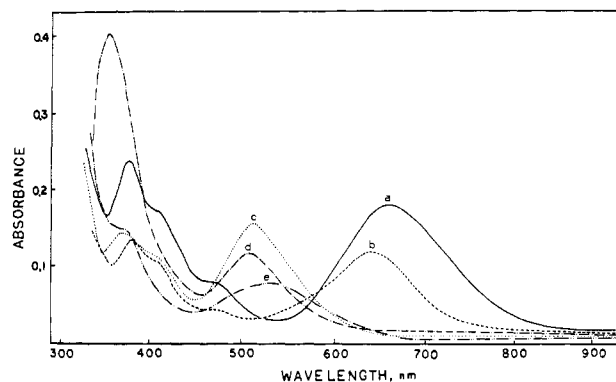


Figure 6. Electronic absorption spectra for 2.7×10^{-4} M $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ in different solvents: (a) CH_2Cl_2 , (b) $(\text{CH}_3)_2\text{CO}$, (c) CH_3CN , (d) py; (e) Me_2SO .

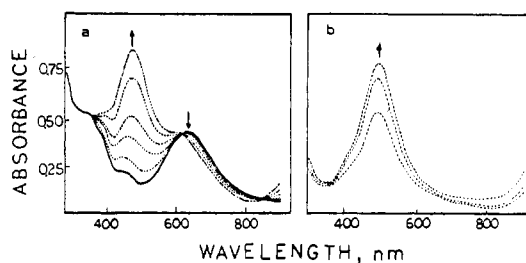


Figure 7. UV-visible spectra for a 2.0×10^{-3} M solution of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ in acetone at various times of electrolysis: (a) between 0 and 2 min; (b) between 2 and 20 min.

Table II. UV-Visible Spectra for $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ and $[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$ in Selected Solvents Containing 0.1 M TBAP

no. ^a	solvent	λ_{max} of major peaks, nm ($\epsilon \times 10^{-3}$, $\text{M}^{-1} \text{cm}^{-1}$)	
		$\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$	$[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$
1	CH_2Cl_2	375 (0.44), 420 sh, 470 sh, 668 (0.34)	~350, 420 sh, 513 (2.6)
4	acetone	378 (0.48), 410 sh, 642 (0.44)	~325, 510 (3.3)
2	CH_3CN	323 (0.50), 370 sh, 513 (0.38)	
5	Me_2SO	333 (1.12), 370 sh, 530 (0.29)	
	py	358 (1.48), 508 (0.43)	

^a Numbers correspond to solvents given in Table I.

except Me_2SO . In this latter solvent, $E_{1/2}$ is considerably more positive than expected from comparisons to carboxylate systems. This result alone does not justify a lengthy discussion. One point, however, should be made at this time. From the $E_{1/2}$ values of the amidate-bridged dimers, it is obvious that the energy of the HOMO and other metal-centered molecular orbitals are increased substantially over those for the corresponding carboxylate species. Therefore, the amidate complexes should be weaker σ acceptors and better π donors with respect to axial adduct interactions. There is strong evidence that the dinuclear rhodium(II) carboxylates are at best weak π bonders. This situation could be different for the amidate complexes in that π bonding becomes significant with π acid ligands such as Me_2SO .

Electronic Absorption Spectra of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ and $[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$. The UV-vis spectra of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ in several selected solvents are shown in Figure 6, and a summary of the maximum wavelengths and molar absorptivities is listed in Table II. The longer wavelength band of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ occurs at 668 nm in CH_2Cl_2 (Figure 6a) and 642 nm in acetone (Figure 6b). This peak is shifted to 508–513 nm when the solvent is CH_3CN , Me_2SO , or py

(25) Gutman, V. "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978.

(Figure 6c-e).

Spectra obtained during the first oxidation step of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ are shown in Figure 7. Figure 7a shows the visible spectrum after very short time intervals of oxidation while Figure 7b shows the progressive oxidation to the final product, $[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$. Table II also gives the visible spectral characterization of the oxidized complex in CH_2Cl_2 and acetone. The visible spectra of virtually all previously studied dirhodium(II) complexes are characterized by two bands in the visible region. These bands have been assigned to $\text{Rh-Rh } \pi^* \rightarrow \text{Rh-Rh } \sigma^*$ and $\text{Rh-Rh } \pi^* \rightarrow \text{Rh-O } \sigma^*$ transitions by theoretical¹² and experimental methods.^{5,6} The energy of the lower energy band ($\pi^* \rightarrow \sigma^*$) is very sensitive to the nature of the axial ligand whereas the higher energy band ($\pi^* \rightarrow \text{Rh-O } \sigma^*$) is relatively insensitive to the axial ligand. The visible spectrum of $\text{Rh}_2(\text{HNOCCF}_3)_4$ also shows these two bands but shifted to higher energy than the corresponding carboxylato-bridged complexes.²⁰

There are some questions with regard to assignment of the visible bands when the tetracarboxylato dimer is bound axially to a strong σ donor such as PR_3 . Recent theoretical and experimental results^{7,15,22,23} strongly suggest that the HOMO is an orbital of $\text{Rh-Rh } \sigma$, $\text{Rh-P } \sigma^*$ character and not δ^* as has been previously proposed for the H_2O adduct.¹² By the use of this orbital description, the lowest energy transitions predicted are $\text{Rh-Rh } \sigma$, $\text{Rh-P } \sigma^* \rightarrow \text{Rh-O } \sigma^*$ and $\text{Rh-Rh } \sigma$, $\text{Rh-P } \sigma^* \rightarrow \text{Rh-Rh } \sigma^*$, $\text{Rh-P } \sigma^*$, with the former transition being lowest in energy.

The spectrum observed for $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ is different from that of $\text{Rh}_2(\text{O}_2\text{CR})_4$ and $\text{Rh}_2(\text{HNOCCF}_3)_4$. Four, rather than two, transitions are observed in the visible region. They are similar, however, in that the lowest energy band at 668 nm in CH_2Cl_2 is quite sensitive to the nature of the axial ligand. This indicates that this transition involves a Rh-Rh orbital of σ symmetry that interacts most strongly with the

axial donor. Considering the various molecular orbital patterns that have resulted from the different theoretical approaches, it is easy to visualize a pattern where the $\text{Rh-Rh } \pi^*$, δ^* , and σ orbitals are quite close in energy. Also, with a heterodonor atom bridging group containing both Rh-O and Rh-N bonds, the equatorial symmetry is different from that of the carboxylato complexes. Therefore, it is not surprising that more than two bands appear in the visible region.

The visible spectrum of the cation, $[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$, in CH_2Cl_2 is characterized by an unusually strong absorbance at 513 nm. A similar strong band is observed for the trifluoroacetamido-bridged cation, $[\text{Rh}_2(\text{HNOCCF}_3)_4]^+$, at 449 nm.²⁰ This transition, with a molar extinction coefficient of $\sim 10^3$, is not observed for the carboxylato-bridged complexes, and more experimental and theoretical information is needed for assignment of this band. A good possibility, however, is that it involves a nitrogen to metal charge transfer. We are in the process of investigating a series of partially substituted amidato complexes that should shed light on this problem.

In summary, we have shown in this study that the electrochemical oxidation of $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ is quite different from that of dinuclear rhodium(II) carboxylates. Two reversible oxidations are observed. One corresponds to the formation of a formal $\text{Rh}^{\text{II,III}}$ complex and occurs at a potential considerably lower than has been observed for dirhodium carboxylates, while the second oxidation corresponds to the formation of a metastable rhodium(III,III) dimer.

Acknowledgment. Support from the Robert A. Welch Foundation (J.L.B. E-916, K.M.K. E-680) is gratefully acknowledged.

Registry No. Rh_2L_4 , 88477-03-6; $[\text{Rh}_2\text{L}_4]^+$, 88477-04-7; $[\text{Rh}_2\text{L}_4]^{2+}$, 88477-05-8; $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$, 15956-28-2; Rh, 7440-16-6.