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Electrooxidation of Dirhodium(II) Tetracarboxylate–Nitrogenous Base Adducts[1]

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The electrochemical oxidation of six tetrakis(carboxylato)dirhodium(II) dimers (where the identity of the carboxylate was pivalate, butyrate, acetate, benzoate, methoxyacetate, and chloroacetate) dissolved in 1,2-dichloroethane containing tetra-*n*-butylammonium perchlorate as the supporting electrolyte was investigated at a Pt-button electrode. Midpoint potentials ranged from 1.55 to 1.21 V vs. the saturated calomel electrode and depended upon the identity of the carboxylate. The complexation of the dimers by selected substituted pyridines was studied in situ. At substoichiometric levels of base, separate processes were observed for oxidation of the mono- and diadducts. Complexation produced cathodic shifts in potential. The magnitude of the potential shift was a function of carboxylate structure as well as the number and identity of the axial ligand. The results obtained were discussed in the context of the Kawamura and Nakatsuji model of Rh–Rh bonding.

Introduction

During the last two decades, binuclear rhodium(II) compounds have been the subject of intensive research.[2] Much of the effort in this area has focused on dirhodium tetracarboxylate complexes because of their intriguing chemical reactivity and, in part, their ease of preparation. Teyssie and co-workers have shown that dirhodium(II) carboxylates catalyze the decomposition of diazo esters,[3] as well as the oxidation of cycloalkenes.[4] These complexes have been listed as the preferred catalytic reagents for these reactions.[5] Bear and co-workers[6] have reported that $Rh_2(carboxylate)_4$ compounds were potent inhibitors of Ehrlich ascites, L1210 ascites, and P388 tumors in mice. They have shown that the antitumor activity of these compounds parallels their toxicity. Interestingly, the singly oxidized complex displays greater antitumor activity than the neutral complex.

The affinity of dirhodium carboxylates to form either mono- or diadducts with Lewis bases has been well established.[2] A great number of compounds having the general formula $Rh_2(carboxylate)_4(B)_2$ have been synthesized and characterized crystallographically. A generalized structure is shown in Figure 1. The Rh–Rh single-bond distance varies from 2.371 to 2.486 Å and is a function of the identity both of the carboxylate and of the axial ligand(s). Crystallographic investigations on $Rh_2(carboxylate)_4(nitrogenous\ base)_2$ complexes indicated that the Rh–Rh bond length varies as much as 0.067 Å. A linear relationship between the Rh–Rh bond length and the Lewis basicity of the axial ligand has been observed.[7]

Electrochemical studies on the redox reactions of dirhodium tetracarboxylates have appeared only recently.[6c,8-13] Wilson and Taube studied the aqueous oxidation of $Rh_2(OAc)_4$ with ceric ion potentiometrically.[8] They found that the dimeric Rh(II) complex could be reversibly oxidized in a single electron transfer. The potential of the oxidation was dependent upon the pH of the medium. Das et al.[11] investigated the electrooxidation and -reduction reactions of several $Rh_2(carboxylate)_4$ complexes in a number of solvents. They observed that the midpoint potentials depended upon the identity of both the carboxylate and the solvent. Carboxylates possessing electron-withdrawing substituents were more difficult to oxidize. A linear relationship between the oxidation potentials and the Taft polar substituent constants was observed. These workers also found that the potential for electrooxidation of a given $Rh_2(carboxylate)_4$ complex was inversely related to the solvent's donor ability. Drago and co-workers[12] investigated the electrooxidation of a select group of 1:1 and 1:2 $Rh_2(but)_4$–Lewis base adducts dissolved in dichloromethane. They observed that the 1:2 adducts were more easily oxidized that the corresponding 1:1 adducts.

The impetus for the work presented herein was provided by the findings of Kawamura and co-workers.[13] On the basis of the results of EPR and electronic spectral measurements, Kawamura and Nakatsuji have constructed a model to describe the intermetallic bonding present in $Rh_2(carboxylate)_4$ complexes. Their model takes into account the relative energy level of the d_{z^2} MO in the monoadduct and the orbital energy splitting between the σ and σ^* MO's in the diadduct. They have described the wave function for the d_{z^2} MO as the d_{z^2} AO with normalized antiphase contaminants of the combination of the four oxygen lone pairs expanding toward the metal atom, i.e.

$$Y_{z^2} = C_{Rh}d_{z^2} - C_Ln_L - C_On_O \qquad (1)$$

This description suggests that an increase of σ donor strength in the axial ligand will induce an upward shift of the energy of the d_{z^2} MO, an increase in C_L and a decrease in C_{Rh}. Also, for a given axial ligand, changes in the identity of the carboxylate structure will result in significantly larger changes in C_L as compared to C_{Rh}. This prediction was made because changes in the carboxylate structure (e.g. addition of an electron-withdrawing group) will modify the orbital energy separation between n_L and the d_{z^2} MO. Our hypothesis was that these predictions, previously substantiated by spectral

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(1) Abbreviations: MO = molecular orbital; AO = atomic orbital; SCE = saturated calomel electrode; B = Lewis base molecule; TBAP = tetra-*n*-butylammonium perchlorate; $EtCl_2$ = 1,2-dichloroethane; OAc = acetate; but = butyrate.

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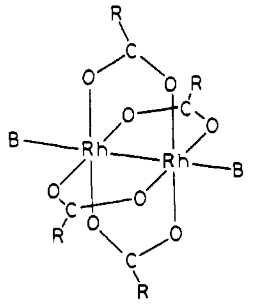

Figure 1. Generalized structure of dirhodium tetracarboxylate axially coordinated by two Lewis base molecules.

measurements,[13] would also be demonstrated in the electrochemistry of these complexes. As electrooxidation of Rh_2(carboxylate)$_4$(B)$_2$ adducts resulted in the removal of an electron from a σ MO, the oxidation potentials should be a direct function of the identity of the axial ligand and of the carboxylate structure. To test this hypothesis, we synthesized six different Rh_2(carboxylate)$_4$ complexes and reacted these in situ with seven different nitrogenous bases. A detailed electrochemical analysis of the resultant adducts was undertaken. The results obtained were evaluated in the context of the Kawamura and Nakatsuji model of Rh–Rh bonding.

Experimental Section

Chemicals. The Rh_2(but)$_4$ used in this study was the generous gift of Professor John L. Bear of the University of Houston. All other Rh complexes were synthesized by carboxylate substitution of Rh_2(OAc)$_4$ utilizing standard literature methods.[14-17] Rh_2(OAc)$_4$ was used as received from Strem Chemical Co. Completeness of the carboxylate substitution reaction was verified by ^{1}H NMR spectroscopy.

The solvent, $EtCl_2$, was purchases as reagent grade from Scientific Products. Prior to use, this material was extracted with an equal volume of concentrated H_2SO_4, washed with a 5% solution of KOH, and dried over anhydrous $MgSO_4$. This extract was then fractionally distilled over P_2O_5 under an atmosphere of N_2 and stored in the dark under activated 3A molecular sieves. The supporting electrolyte TBAP was purchased from Aldrich Chemicals. This material was recrystallized from absolute ethanol, dried in vacuo at 100 °C for 24 h, and stored in an evacuated desiccator. Pyridine was purchased from Mallinckrodt as reagent grade. This ligand was first treated with NaOH pellets, fractionally distilled from CaO under N_2, and then stored at 0 °C. All other axial ligands were used, as received, from Aldrich Chemicals. Aliquots of ligands were delivered to solutions of Rh_2(carboxylate)$_4$ via Hamilton microliter syringes.

Instrumentation. Cyclic voltammetric and differential-pulse voltammetric experiments were performed with an EG&G Princeton Applied Research Model 174A polarographic analyzer utilizing a Pt-button working electrode, a Pt-wire counterelectrode, and a saturated calomel reference electrode. This instrument was modified to allow the user to select the pulse direction independently of the potential sweep direction. Differential-pulse voltammograms were obtained with the following instrumental settings: pulse interval 0.5 s; pulse amplitude 25 mV; potential sweep rate 10 mV/s. Data were recorded on a Houston Omnigraphic 2000 X-Y recorder.

Aqueous contamination of the nonaqueous solution from the reference electrode fill solution was minimized by isolating the reference electrode via a porous glass frit. All solutions were deoxygenated by passing a stream of solvent-saturated prepurified N_2 into the solution for at least 10 min prior to recording voltammetric data. To maintain an O_2-free environment, the solution was blanketed with solvent-saturated N_2 during all experiments. All potentials reported herein were referenced to the SCE, were measured at 23 ± 1 °C, and were uncorrected for liquid-junction potentials. The uncertainty in each potential reported herein is ±10 mV.

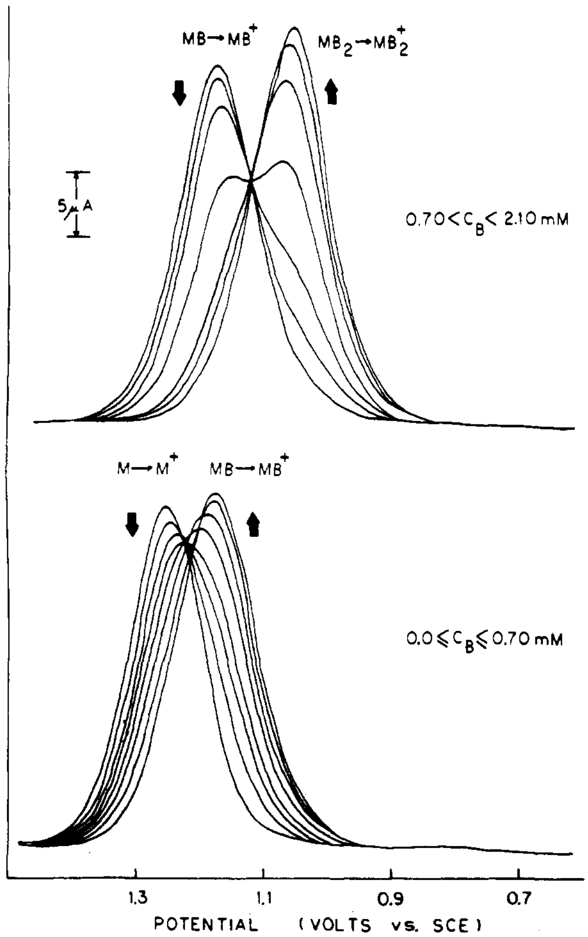

Figure 2. Differential-pulse voltammograms taken during the titration of a 1.43 mM solution of Rh_2(but)$_4$ with 4-cyanopyridine. The lower trace was obtained over the 4-cyanopyridine concentration range 0.0–0.70 mM. The upper trace was obtained over the range 0.70–2.10 mM.

Results

Voltammetric experiments on a 0.991 mM solution of Rh_2(but)$_4$ dissolved in $EtCl_2$ containing 0.1 M TBAP yields only one oxidation process within the potential range 0.0–2.0 V. Analysis of the cyclic voltammograms obtained as a function of potential sweep rate indicated the following: (1) the midpoint potential was 1.26 V vs. SCE and was invariant over all potential sweep rates investigated; (2) $i_{p,a}$ was proportional to the square root of the potential sweep rate; (3) the ratio of the peak currents ($i_{p,c}/i_{p,a}$) was essentially unity and independent of potential sweep rate; (4) the potential difference between $E_{p,a}$ and $E_{p,c}$ was ~70 mV and increased with increasing potential sweep rate. Analysis of the differential-pulse voltammograms obtained in the manner described by Birke[18] yielded a $E_{p(+)} - E_{p(-)}$ value of 21 ± 1 mV for a pulse amplitude of 25 mV. Taken collectively, these data indicated that the electrooxidation process was best described as a quasi-reversible, single-electron-transfer process.

Voltammetric analyses of the six different Rh_2(carboxylate)$_4$ complexes investigated produced identical electron-transfer mechanisms. The midpoint potentials for each complex are listed in Table I.

Addition of an excess of Lewis base to solution results in the generation of a new electron-transfer process. Analysis of the peak shape, peak currents, and peak potentials as a

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Table I. Midpoint Potentials for Electrooxidation of $Rh_2(carboxylate)_4$ Complexes in $EtCl_2$ Containing 0.1 M TBAP

carboxylate	pK_a[a]	$4\sigma^*$[b]	$E_{1/2}$, V
pivalate	4.79	−1.20	1.21
butyrate	4.62	−0.40	1.24
acetate	4.57	0.00	1.23
benzoate	3.79	0.40	1.29
methoxyacetate	3.31	2.08	1.37
chloroacetate	2.68	4.20	1.55

[a] Values taken from: Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1976; p 144. [b] Values taken from from: Taft, R. W., Jr. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956.

function of potential sweep rate indicated that there was no change in the rate of heterogeneous electron transfer upon complexation. At substoichiometric levels of base, three distinct electron-transfer processes are observed. Figure 2 depicts the differential-pulse voltammograms obtained during the course of the titration of $Rh_2(but)_4$ with 4-cyanopyridine. The oxidation process observed at $E_p = 1.26$ V decreases in magnitude (Δi) with increasing base concentration. A second oxidation process, located at $E_p = 1.18$ V, first increased and then decreased in magnitude as the 4-cyanopyridine concentration was increased to 2 equiv (with respect to the concentration of $Rh_2(but)_4$). At 4-cyanopyridine concentrations greater that 0.8 equiv, a third process was observed at $E_p = 1.05$ V. The potentials for all three electrode reactions were invariant with changes in base concentration. This indicated that an equivalent number of base molecules were coordinated to both the electrode reactant and product. The peak currents measured for each process were very dependent upon the concentration of base present in solution. Figure 3 depicts the plot of corrected peak current vs. the molar ratio of 4-cyanopyridine to $Rh_2(but)_4$. For this base, the potential difference between the oxidation process at $E_p = 1.18$ V was just 75 mV cathodic of the peak potential for the oxidation of the uncomplexed Rh complex. The measured peak currents were corrected for overlap via an iterative curve-fitting program written in BASIC-E. The algorithm used assumed that the peak width at half-current and the peak potentials remained constant throughout the titration. These assumptions were empirically verified in each case. This data analysis method

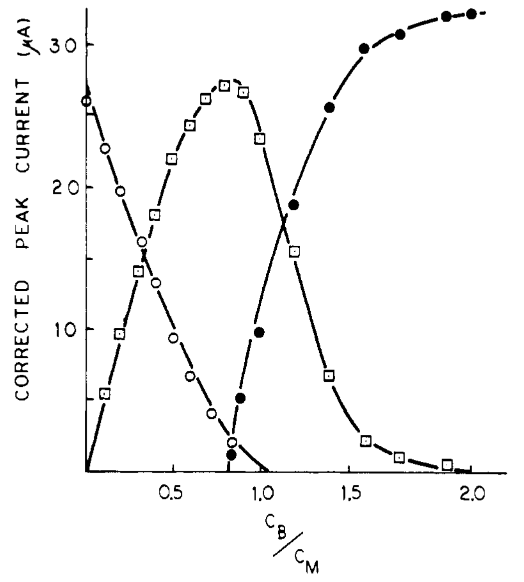

Figure 3. Plot of the differential-pulse peak current corrected for background vs. the molar ratio of 4-cyanopyridine to $Rh_2(but)_4$ (see Figure 2). Open circles denote peak currents at $E_p = 1.25$ V; squares denote peak currents at $E_p = 1.18$ V; closed circles denote peak currents at $E_p = 1.05$ V.

clearly indicated that the electron transfer at $E_p = 1.18$ V was due to the oxidation of the monoadduct and that the electron transfer at $E_p = 1.05$ V was due to the oxidation of the diadduct.

Titration experiments were performed in the manner described on six different $Rh_2(carboxylate)_4$ complexes with at least seven substituted pyridines. The electron-transfer mechanism remained constant throughout the entire series. The midpoint potentials for oxidation of the monoadducts formed in situ are listed in Table II; peak potentials for oxidation of the diadducts formed in situ are listed in Table III.

Discussion

For the entire series of carboxylates and nitrogenous bases studied, complexation produced adducts that were easier to oxidize. This manifests the preferential stabilization of the mixed-valence cation, $[Rh_2(carboxylate)_4(B)_{1\,or\,2}]^+$, over the

Table II. Midpoint Potentials for Electrooxidation of $Rh_2(carboxylate)_4(B)$ Complexes in $EtCl_2$ Containing 0.1 M TBAP

		carboxylate					
base	pK_{BH^+}[a]	pivalate	butyrate	acetate	benzoate	methoxy-acetate	chloro-acetate
3,5-dichloropyridine	0.67	1.13	1.16	1.19	1.26	1.33	1.54
3-cyanopyridine	1.45	1.11	1.18	1.17	1.26	1.34	1.52
3-bromopyridine	2.84	1.08	1.14	1.16	1.20	1.33	1.49
3-acetylpyridine	3.18	1.08	1.14	1.13	1.22	1.32	1.48
pyridine	5.28	1.02	1.09	1.10	1.18	1.29	1.46
4-methylpyridine	5.98	1.01	1.06	0.99	1.16	1.27	1.43
3,4-dimethylpyridine	6.46	1.00	1.06	1.08	1.16	1.25	1.42

[a] Values taken from: Schoefield, K. A. "Hetero-Aromatic Nitrogen Compounds"; Plenum Press: New York, 1967; p 146.

Table III. Midpoint Potentials for Electrooxidation of $Rh_2(carboxylate)_4(B)_2$ Complexes in $EtCl_2$ Containing 0.1 M TBAP

		carboxylate					
base	pK_{BH^+}[a]	pivalate	butyrate	acetate	benzoate	methoxy-acetate	chloro-acetate
3,5-dichloropyridine	0.67	1.03	1.08	1.15	1.20	1.30	1.45
3-cyanopyridine	1.45	0.99	1.07	1.09	1.17	1.27	1.41
3-bromopyridine	2.84	0.89	0.97	1.03	1.09	1.22	1.35
3-acetylpyridine	3.18	0.88	0.98	1.00	1.06	1.19	1.31
pyridine	5.28	0.80	0.88	0.94	1.01	1.09	1.23
4-methylpyridine	5.98	0.77	0.83	0.88	0.96	1.08	1.17
3,4-dimethylpyridine	6.46	0.73	0.72	0.86	0.91	1.03	1.13

[a] Values taken from: Schoefield, K. A. "Hetero-Aromatic Nitrogen Compounds"; Plenum Press: New York, 1967; p 146.

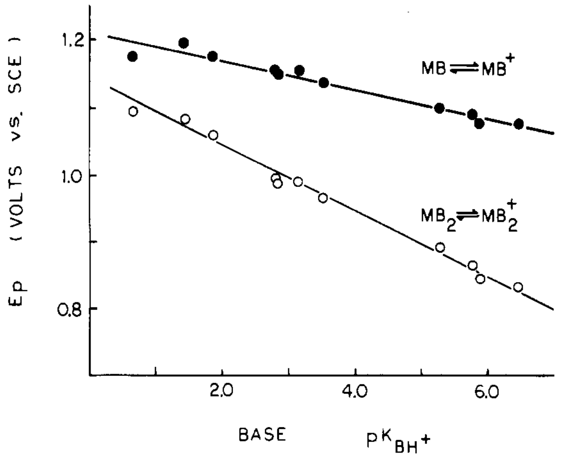

Figure 4. Plot of the peak potential measured for electrooxidation of $Rh_2(but)_4(B)$ (closed circles) and $Rh_2(but)_4(B)_2$ (open circles) vs. the pK_{BH^+} of the nitrogen donor atom of the axial ligand.

neutral species. A similar stabilization of the oxidized species was observed by Das et al.[11] in solvents of strong coordinating ability. Drago and co-workers[12] have measured the stepwise formation of pyridine to $Rh_2(but)_4$ in benzene ($\log K_1 = 8.20$; $\log K_2 = 4.38$). The oxidation potentials are proportional to the ratio of the formation constants for the cation (K^+) over that of the neutral dimer (K). Assuming that the values of K_1 and K_2 measured by Drago in benzene are within 1 order of magnitude of the values one would obtain in $EtCl_2$, then the estimated formation constants for stepwise addition of pyridine to $[Rh_2(but)_4]^+$ are $\log K^+_1 = 11$ and $\log K^+_2 = 8$.

The extent of cation stabilization by adduct formation was found to be a function of the number and identity of the pyridines bound to the Rh center. Figure 4 depicts a plot of the peak potentials observed for each coordinated $Rh_2(but)_4$-substituted pyridine complex studied against the pK_{BH^+} value for the axial base. The parameter pK_{BH^+} is used here as a measure of the σ donor ability of the nitrogen lone pair on the base. For both the mono- and diadducts, linear relationships were observed. The change in peak potential per unit pK_{BH^+} was −25 mV for the monoadducts and −53 mV for the diadducts investigated. As pK_{BH^+} increased, the σ donor strength of the nitrogenous base increased, inducing an upward shift in the energy of the d_{z^2} MO. This was manifest in a cathodic shift in the oxidation potentials. *The twofold increase in the slope reflects the additive effect of complexation on the energy level of the highest occupied MO.*

Inspection of the potential data in Table I showed a direct relationship between the degree of carboxylate ionization (as measured by pK_a) and the ease of dimer oxidation. When stronger acids were used as equatorial ligands, the resultant dimers were more difficult to oxidize. Similarly, carboxylates with electron-donating substituents were oxidized at less positive potentials. A linear free energy relationship between the midpoint potential for oxidation of each dimer and the Taft polar substituent parameter was constructed and depicted in Figure 5. A straight line with a slope of 0.063 ± 0.004 V was observed. Das et al.[11] have previously investigated the effect of substituents on the dimer dissolved in CH_2Cl_2 and measured a slope of 0.064 ± 0.004 V. Interestingly, when the oxidation potentials for the mono- and diadducts were plotted against the Taft polar substituent parameter, linear relationships are also observed, but with significantly larger slopes.

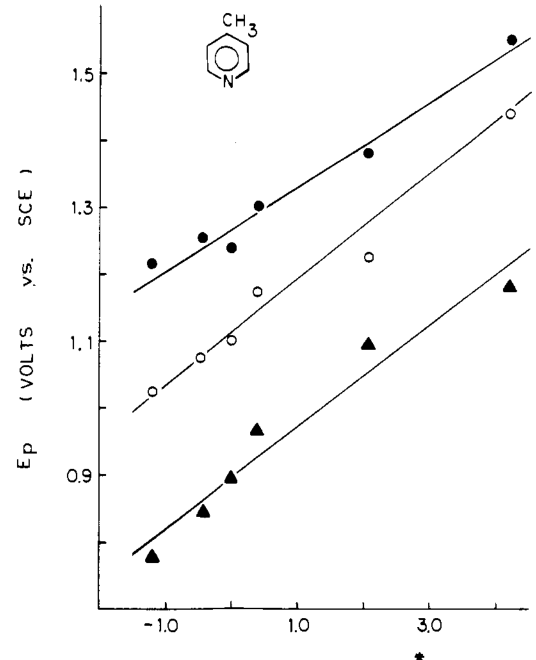

Figure 5. Plot of the peak potential measured for electrooxidation of various $Rh_2(carboxylate)_4$ complexes vs. the Taft polar substituent constant, σ^*. Closed circles denote the potentials for electrooxidation of the uncomplexed dimer, open circles denote the potentials of the monoadducts, and triangles denote the potentials of the diadducts formed by the reaction of the dimer with 4-methylpyridine.

Figure 5 also depicts the traces observed when the oxidation potentials for the mono- and diadducts of 4-methylpyridine were plotted against $4\sigma^*$. Slopes of 0.083 and 0.076 V were obtained for the mono- and diadducts, respectively. Similar results were obtained for all seven substituted ligands investigated. The slopes ranged from 0.075 to 0.083 V with a mean and standard deviation of 0.078 ± 0.003 V. Thus, for the entire series of dimers investigated, axial ligation resulted in an increased sensitivity to the electronic characteristics of the bridging ligand. As the electron-withdrawing ability of the carboxylate substituent increased, the orbital energy separation between n_L (see eq 1) and the d_{z^2} MO decreased, resulting in an apparent increase in the carboxylate substituent-effect sensitivity.

In summary, complexation of the dimer by substituted pyridines resulted in a cathodic shift in potential for electrooxidation. For a given carboxylate, changes in the identity of the axial ligand produced potentials shifts of up to 360 mV. Changes in the structure of the carboxylate produced potential shifts of up to 340 mV when the axial positions on the dimer were vacant and 460 mV when the axial positions of the dimer were occupied by a given ligand. These observations are in accord with expectations based upon the model of Rh–Rh interactions put forth by Kawamura and Nakatsuji.[13]

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