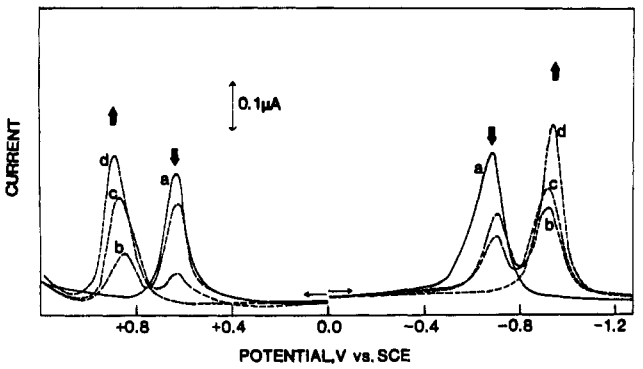

Figure 3. Differential pulse polarograms of 1.09×10^{-3} M (TPP)Fe(C_6H_5) and (TPP)Fe(C_6H_5)(NO) in PhCN with 0.1 M TBA(PF_6) (scan rate 0.005 V/s, modulation amplitude 25 mV). Total NO pressure: (a) 0 mm; (b) 29 mm; (c) 48 mm; (d) 72 mm.

electron transfer. This wave was still present (but in reduced currents) under an NO pressure of 29 mm (Figure 1b). The currents for this process further decreased with increase of NO pressure, and the wave totally disappeared under an NO pressure of 72 mm (Figure 1c), where a new reversible process was present (at $E_{1/2} = 0.86$ V). At this point, the spectrum of the solution was monitored and indicated complete conversion of (TPP)Fe(C_6H_5) to (TPP)Fe(C_6H_5)(NO). The spectrum of this latter species is given in Figure 2a and agrees with similar spectra in the literature.[9] Thus, the electrode reaction at 0.86 V can be written as

$$(TPP)Fe(C_6H_5)(NO) \rightleftarrows [(TPP)Fe(C_6H_5)(NO)]^+ + e^- \quad (1)$$

The oxidation-reduction of (TPP)Fe(C_6H_5)(NO) is less reversible at high NO pressures, and some decomposition of the oxidation product occurs. The initial (TPP)Fe(C_6H_5)(NO) is still oxidized to [(TPP)Fe(C_6H_5(NO)]$^+$ at $E_{1/2} = 0.86$ V, but this species rapidly reacts with excess NO to yield a mixture of [(TPP)Fe(C_6H_5)(NO)]$^+$ and [(TPP)Fe$(NO)_2$]$^+$ in solution. Both singly oxidized species are then reduced on the reverse potential sweep, giving cathodic peaks at $E_{pc} = 0.82$ and 0.72 V,[10] respectively. This is illustrated in Figure 1d (for oxidation under 171 mm NO pressure), and the overall oxidation-reduction mechanism at high NO concentrations is shown in Scheme I.

Scheme I

$$(P)Fe^{II}(R)(NO) \underset{E_{pa} = 0.92\text{ V},\ E_{pc} = 0.82\text{ V}}{\overset{-e^-}{\rightleftharpoons}} [(P)Fe(R)(NO)]^+ \xrightarrow[-R]{NO}$$

$$[(P)Fe(NO)_2]^+ \underset{E_{pc} = 0.72\text{ V}}{\overset{+e^-}{\rightleftharpoons}} (P)Fe^{II}(NO)_2$$

Addition of NO to (TPP)Fe(C_6H_5) and (TPP)Fe(C_6H_5)(NO) was also monitored by differential pulse polarography. This technique was previously used[2] to identify (TPP)Fe$(NO)_2$ and is useful to differentiate reduction waves due to the porphyrin moiety from the reduction of free NO, which yields significant currents at NO pressures higher than 100 mm. This is shown in Figure 3, which records differential pulse polarograms of (TPP)Fe(C_6H_5) as a function of NO pressure. As seen in this figure, quantitative conversion of (TPP)Fe(C_6H_5) to (TPP)Fe(C_6H_5)(NO) occurs at an NO pressure of 72 mm. This latter compound is reduced at -0.92 V. No evidence of intermediates was found under our experimental conditions, although at higher concentrations of NO, bis(nitrosyl) adducts were present.

Similar electrochemistry was also observed for addition of NO to (OEP)Fe(C_6H_5) although, in this case, conversion to (OEP)Fe(C_6H_5)(NO) required greater than 200 mm NO pressure. Formation of (OEP)Fe(C_6H_5)(NO) was ascertained under electrochemical conditions by comparing the UV-visible spectrum of the solution with that already reported.[9,11] The six-coordinate (OEP)Fe(C_6H_5)(NO) is oxidized at 0.73 V and reduced at -1.16 V. The shapes of the cyclic voltammograms and differential pulse polarograms indicate a reversible oxidation to yield [(OEP)Fe(C_6H_5)(NO)]$^+$ and a quasi-reversible reduction to yield [(OEP)Fe(C_6H_5)(NO)]$^-$.

It is significant to note that the reversible oxidations of (TPP)Fe(C_6H_5)(NO) and (OEP)Fe(C_6H_5)(NO) involve neutral compounds formally characterized as Fe(II). Thus, it appears that the effect of an NO molecule in stabilizing the iron(II) porphyrin oxidation state is greater than that of the σ-bonded phenyl group, which produces Fe(III) species. Finally, potentials for oxidation and reduction of (P)Fe(C_6H_5)(NO) and (P)Fe(NO) are separated by only 40-110 mV, again indicating the strong effect of the NO group in determining oxidation-reduction potentials.

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(10) (TPP)Fe$(NO)_2$ and (TPP)Fe(NO) are oxidized at the same potential (see ref 2). However, under >170 mm NO gas, the predominant species was found to be the bis(nitrosyl) complex.

(11) (OEP)Fe(C_6H_5) (1.31×10^{-3}) reacted under 180 mm NO gas to yield the new (OEP)Fe(C_6H_5)(NO) species, which had the following absorbance maxima (λ, nm ($10^{-3}\epsilon$)): 360 (50), 430 (140), 550 (27), 575 (sh). (TPP)Fe(C_6H_5) (1.09×10^{-3} M) reacted under 72 mm NO gas to yield (TPP)Fe(C_6H_5)(NO) (λ, nm ($10^{-3}\epsilon$)): 370 (sh), 445 (16), 515 (sh), 560 (27), 600 (sh), 690 (sh).

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Electrochemical Generation of New Dinuclear Ruthenium Acetamidate Complexes

Sir:

Recently we reported the synthesis and electrochemical properties of a new class of diruthenium(II,III) dimers.[1] The initial reported compound, $Ru_2(HNOCCF_3)_4Cl$, has the same cage structure as that of the *N*-phenylacetamidato-bridged dirhodium(II,II) dimer[2] $Rh_2(PhNOCCH_3)_4$ but differs from the well-studied dirhodium[3,4] and diruthenium[5] carboxylates in that the bridging ligands contain mixed oxygen and nitrogen donor atoms rather than all oxygen donor groups.

The electrochemistry of $Ru_2(HNOCCF_3)_4Cl$ has been carried out in several solvents with, and without, excess chloride ions as supporting electrolyte[1] and is quite similar to that

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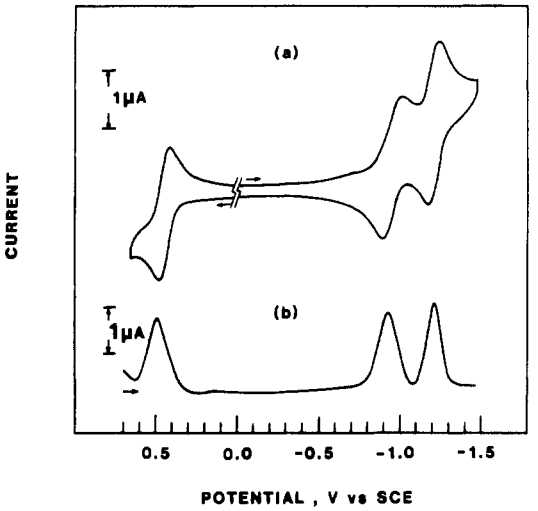

Figure 1. (a) Cyclic voltammogram (at v = 50 mV/s) and (b) differential pulse voltammogram (at v = 4 mV/s) of 1 mM $Ru_2(HNOCCH_3)_4Cl$ in Me_2SO containing 0.1 M LiCl.

reported for the diruthenium carboxylate $Ru_2(O_2CC_3H_7)_4Cl$.[1,5] A similarity in electrochemistry has also been reported between trifluoroacetamidate- and acetate-bridged dimers of rhodium(II).[6] In contrast, large negative shifts in potential (up to 1.02 V) are observed for the first oxidation (Rh(II,II) → Rh(II,III)) upon going from the acetate to the acetamidate complexes of dirhodium(II,II).[7] In addition, a second reversible oxidation generating a metastable dirhodium(III,III) species is also observed for the $Rh_2(HNOCCH_3)_4$ complex at a potential of 1.41 V in CH_3CN, 0.1 M TBAP. This suggests the possibility for electrochemical generation and isolation of diruthenium(III,III) dimers from diruthenium(II,III) complexes containing acetamidate bridging ligands, especially since the generation of both dirhodium(III,III)[7] and dirhenium(III,III)[8,9] complexes is possible. This indeed is the case as we wish to report here.

The diruthenium(II,III) acetamidate $Ru_2(HNOCCH_3)_4Cl$ was synthesized and purified in a manner similar to that reported for $Ru_2(HNOCCF_3)_4Cl$.[1] The molecular weight of the cation was found to be 435 by use of LC/MS. Elemental analyses for C, H, N, and Cl were all in good agreement with the indicated formula. The $Ru_2(HNOCCH_3)_4Cl$ complex is EPR active and gives an axial spectrum with $g_\perp$ = 4.23 and $g_\parallel$ = 1.98 at 77 K in dimethyl sulfoxide (Me_2SO), which is similar to that of both the trifluoroacetamidato[1] and the carboxylato[5] diruthenium complexes. The solid-state effective magnetic moment of the complex at 295.9 K is 3.07 μ_B per ruthenium atom and is indicative of three unpaired electrons in the diruthenium(II,III) complex. The bond order of the complex is 2.5.

Figure 1 shows the cyclic voltammogram and differential pulse voltammogram of $Ru_2(HNOCCH_3)_4Cl$ in Me_2SO containing 0.1 M lithium chloride (LiCl) as supporting electrolyte. One oxidation (at $E_{1/2}$ = +0.47 V) and two reductions (at $E_{1/2}$ = −0.96 and −1.22 V) are observed between +0.80 and −1.50 V vs. SCE. The separation between anodic and cathodic peaks is larger than 59 mV, indicating sluggish (quasi-reversible) electron-transfer kinetics, which thus prohibits use of peak separations for evaluating the number of electrons transferred in each step. Controlled-potential coulometry was therefore carried out after each reaction and showed the addition, or

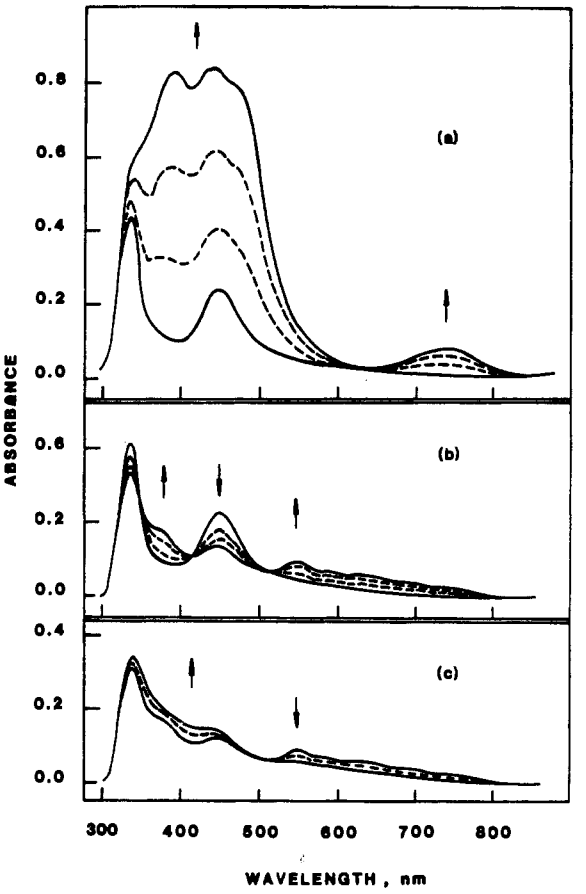

Figure 2. Thin-layer spectra recorded during coulometric oxidation and reduction of $Ru_2(HNOCCH_3)_4Cl$ in Me_2SO, 0.1 M LiCl: (a) first oxidation product, E_{app} = +0.63 V; (b) first reduction, E_{app} = −1.10 V; (c) second reduction, E_{app} = −1.45 V. Solid lines represent the initial and final spectra, and the dashed lines represent the intermediate.

abstraction, of 1.0 ± 0.1 electrons in each of the three steps, which are represented by eq 1–3. Bound counterions or

$$[Ru_2(HNOCCH_3)_4]^+ \rightleftarrows [Ru_2(HNOCCH_3)_4]^{2+} + e^- \quad (1)$$

$$[Ru_2(HNOCCH_3)_4]^+ + e^- \rightleftarrows Ru_2(HNOCCH_3)_4 \quad (2)$$

$$Ru_2(HNOCCH_3)_4 + e^- \rightleftarrows [Ru_2(HNOCCH_3)_4]^- \quad (3)$$

solvent molecules are not shown in the above equations, but one or more solvated forms of each oxidation state couple certainly exist in solution.

Figure 2 illustrates thin-layer spectra obtained during the stepwise addition or abstraction of each electron. The first oxidation gives rise to large absorbance changes in the visible region (see Figure 2a). The original spectrum may be reversibly regenerated upon going to potentials more negative than +0.4 V, and the overall reaction may be assigned as due to the metal-centered oxidation:

$$Ru(II,III) \rightleftarrows Ru(III,III) \quad (4)$$

This reaction occurs at 0.47 V in Me_2SO, which is well within the electrochemical potential range of Me_2SO. This oxidation has not been reported for any diruthenium complex and would correspond to an increase in bond order from 2.5 to 3.0 upon abstraction of one electron. To our knowledge a diruthenium triple-bonded system has never been reported.

Reaction 1 (and reaction 4) is also observed in other solvent, supporting electrolyte combinations. In Me_2SO or CH_3CN

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containing (TBA)Cl the oxidation is reversible and well-defined. However, in Me_2SO containing perchlorate supporting electrolytes (such as TBAP, $LiClO_4$, or $NaClO_4$) the oxidation becomes complicated due to the presence of equilibria involving different forms of bound solvent molecules or counterions. The oxidation process or processes also occur at a more positive potential ($\geq$0.55 V), thus suggesting that, in the presence of excess LiCl, Cl^- ion is the ligand predominantly bound to the original and/or oxidized species.

Substantial spectral changes are also observed during the first reduction (Figure 2b), which is also reversible. Similar to reaction 4, this reaction is also postulated to be metal centered and would correspond to the reaction

$$Ru(II,III) \rightleftarrows Ru(II,II) \quad (5)$$

A similar reaction of Ru(II,III) is observed for $Ru_2(HNOCCF_3)_4Cl$ and $Ru_2(O_2CC_3H_7)_4Cl$ in bonding solvents such as Me_2SO or CH_3OH with TBAP, but in nonbonding solvents the reactions are more complicated and several equilibria involving solvent molecules, Cl^-, and/or ClO_4^- appear to exist.[1]

It is significant to note that the well-defined oxidation/reduction peaks for reaction 2 have been negatively shifted by 750 mV from that for the well-defined reduction of $Ru_2(HNOCCF_3)_4Cl$ in the same solvent system. The direction and magnitude of this shift is consistent with the replacement of four CF_3 groups by four CH_3 groups in the bridging ligand.[6,7] In addition, the 750-mV negative shift of potential may be compared with a 1.0-V shift observed between dirhodium carboxylates and dirhodium acetamidates.[7]

The thin-layer spectra after the second reduction (reaction 3) are shown in Figure 2c. Although this reduction is reversible on the cyclic voltammetric time scale (Figure 1), it is not fully reversible on the spectroelectrochemical time scale. The reversibility for this reduction is dependent on the cation of the supporting electrolyte and increases in the order $Li^+ > Na^+ > (C_4H_9)_4N^+$. In addition, the potential for the reduction shifts negatively as the cation is changed from Li^+ to Na^+ to $(C_4H_9)_4N^+$. This is not unexpected and relates to an ion-pairing phenomenon similar to that observed for organic radicals, where the charge is localized on a single reduction site.[10] In addition, for the specific case of $Ru_2(HNOCCH_3)_4$ reduction in Me_2SO containing LiCl, very little spectral changes are observed in the visible region, thus suggesting the possibility of a ligand-centered reaction. The spectral data do not, however, rule out the formation of a diruthenium(II,I) complex for this reaction.

On the basis of the above results, it appears that three and possibly four diruthenium complexes with differing bond orders may be generated under the same solution conditions. The original Ru(II, III) compound has a bond order of 2.5, while the singly oxidized and singly reduced compounds have bond orders of 3.0 and 2.0, respectively. The exact nature of the doubly reduced species is open to question, but if this reaction involves the orbitals of the ruthenium ions, the bond order of the reduced product would be 1.5. Attempts are now under way to isolate the oxidized and reduced dimers for structural and physicochemical characterization. This should greatly add to our understanding of metal–metal-bonded systems with variable bond order.

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