# **ORGANOMETALLICS**

# Homogeneous Catalysis and Selectivity in Electrochemistry

Michael Michman,\* Lina Appelbaum,<sup>†</sup> Jenny Gun, Alexander D. Modestov,<sup>‡</sup> and Ovadia Lev

The Institute of Chemistry, The Hebrew University, Campus Safra, 91904 Jerusalem, Israel

**ABSTRACT:** The relationship between homogeneous catalysis and electrochemistry is examined in light of two examples based on our work concerning (a) catalyst activation, regarding selective electrochemical C–H oxidation with  $Ru^{III}/Ru^{IV}$  mediation, and (b) catalyst suppression, regarding controlling selectivity in electrochemical aromatic chlorination. The first example (a) deals with the role of catalysis at the working electrode. The electrochemical (EC) oxidation of specific hydrocarbons such as tetralin and indane is performed using tris(acetonitrile)ruthenium trichloride (Ru(CH,CN),CL) as a mediator. The role of this me



trichloride  $(Ru(CH_3CN)_3Cl_3)$  as a mediator. The role of this mediator in the oxidation of tetralin has been reported. This homogeneous C–H activation by electron transfer (ET) is accompanied by the redox transitions of the mediator in the course of the catalytic oxidation, and these are the main points of interest here. Additional studies with a rotating ring disk electrode (RRDE) provided a follow-up of creation and recovery of Ru<sup>III</sup>/Ru<sup>II</sup> and Ru<sup>III</sup>/Ru<sup>IV</sup> species in the process. Using electrochemistry linked with electrospray ionization mass spectrometry (EC/ESI-MS) gave additional information on the structure of the reduced and oxidized forms of  $Ru(CH_3CN)_3Cl_3$  and the effect of water in the solvent on their lifetimes. The second example (b) of electrochlorination has been reported elsewhere and is brought up as complementary remarks. Aromatic electrophilic chlorination of 1,4-dimethoxy-2-tertbutylbenzene is autocatalyzed and unselective. The EC procedure provides a simple means to inhibit the catalytic runaway reaction. This example shows how the counter electrode affects catalysis and selectivity.

# INTRODUCTION

Homogeneous catalysis in organometallic chemistry deals with aspects of structural interactions, steric control, ligand exchange, addition-elimination steps, and (not least) redox reactions and electron transfer (ET). A recent review covered these reactions from the perspective of catalytic C-H activation.<sup>1</sup> The specialized methods and procedures of electrochemistry are largely concerned with the last two categories. Organometallic homogeneous catalysis in electrochemical reactions is aimed at the control of ET and selectivity. Recent advances were featured in a special issue of Chemical Reviews,<sup>2</sup> and the possibilities in this discipline are far from exhausted. The ET process is anything but simple, as detailed in a status report by a leading team,<sup>3</sup> yet the attraction of ET as a clean and manageable method, in comparison with the employment of hazardous oxidation reagents, is clear. Catalysis in electrochemistry is often concerned with solid electrode materials and modification or adsorption of catalysts on the electrode and, in many respects, emulates heterogeneous catalysis. Homogeneous catalysis of electrochemical reactions in solution is intricate, even if the working electrode is considered as inert. Unlike chemically homogeneous catalysts that act throughout the entire solution, electrochemical reactions and primary electron transfers take place at the electrode surface and are confined within the solution to the narrow domain of the capacitor-like double layer. The reactions are further regulated within the Nernst diffusion layer, by diffusion-controlled concentrations of reactants that are very different from those in bulk solution.<sup>4</sup> In addition to this solution regimen, electrochemical reactions often involve mediators and electrogenerated reagents as intermediates.<sup>5</sup> Electrochemical catalysis *in solution* may therefore be considered as a "hybrid" case between heterogeneous and homogeneous catalysis. A critical analysis by Savéant et al. described electrocatalysis and turnover values for several systems where the catalyst is a defined solution component rather than a modified electrode.<sup>6</sup> Jutand et al. have elucidated the mechanisms for many catalytic cycles using EC techniques.<sup>7</sup>

Our intent is to consider experimental aspects of the relationship between homogeneous catalysis and electrochemistry as they are reflected in two of our works and in further results. Both examples were chosen as representative illustrations of this relationship. The first case deals with an electrogenerated ruthenium mediator based on Ru- $(CH_3CN)_3Cl_3$ , for selective C–H activation.<sup>8</sup> The second case describes selectivity in an aromatic chlorination where inhibition of autocatalysis is affected by the counter electrode.<sup>9</sup>

Catalysis by ruthenium compounds is a considerably large subject.<sup>10</sup> We studied electrochemistry with RuCl<sub>3</sub> in acetonitrile solutions, where the actual identity of the catalyst is not always clear.<sup>11</sup> Indeed, Duff and Heath found that RuCl<sub>3</sub> is strongly solvated in acetonitrile to give several complexes, including Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>.<sup>12</sup> Reduction of RuCl<sub>3</sub> in acetonitrile with Zn, for example, yields Ru(CH<sub>3</sub>CN)<sub>6</sub>X<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup>, OTf <sup>-</sup>).<sup>13</sup> Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> was also selectively obtained by controlled heating in acetonitrile.<sup>14</sup> Reduction of RuCl<sub>3</sub> in

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acetonitrile with hydrogen yields a mixture of at least four ruthenium acetonitrile compounds, among these Ru- $(CH_3CN)_4Cl_2$ , Ru $(CH_3CN)_3Cl_3$ , and Ru $(CH_3CN)_2Cl_4$ . Screening by cyclic voltammetry (CV) proved effective in following the solvation of RuCl<sub>3</sub> in acetonitrile and for detection of these various complexes and observing the specific catalytic reactivity of Ru $(CH_3CN)_3Cl_3$ , which Ru $(CH_3CN)_4Cl_2$  and Ru $(CH_3CN)_2Cl_4$  do not possess.

### RESULTS AND DISCUSSION

Selective Electrochemical Oxidation with a Ru(III)/ Ru(IV) Catalyst. Tris(acetonitrile)ruthenium trichloride (Ru-(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>) is in fact a precatalyst. When oxidized, it acts as an electrogenerated mediator for the oxidation of cyclohexene, methylcyclohexene, indane, tetralin, and intermediates such as 1-tetralol. This selectivity toward these hydrocarbons is due to their oxidation potentials being only slightly higher than that of the mediator, as observed with cyclic voltammetry. Preparative electrolysis of tetralin and indane shows that subsequent reactions of the oxidized hydrocarbon are consistent with oxidation at the benzyl position. Tetralin yields 1-tetralol, 1tetralone, 1-dehydrotetralin, and 1-acetamidotetralin, whereas indane gives 1-indanol, 1-indanone, and 1-indene.

Three reaction zones can be defined for  $Ru(CH_3CN)_3Cl_3$ , as illustrated in Scheme 1 for the oxidation of tetralin: reversible



electrogenerated mediation (red), reaction with hydrocarbons (black), and loss of the oxidized ruthenium complex through reaction with water or reduction to the nonreactive Ru- $(CH_3CN)_4Cl_2$  (blue). Different experimental methods are suitable for inspecting each of these zones. The primary Ru<sup>III</sup>/ Ru<sup>IV</sup> step and subsequent electron transfers (ET) can be followed using fast CV and rotating ring disk electrode (RRDE) tests. The hydrocarbons and the products of their organic reactions, which voltammetry cannot detect, have been established by electrolysis and product studies. Accumulation of  $Ru(CH_3CN)_4Cl_2$  can be monitored by collecting CV data for the solution during electrolysis. Further insight into both the ET and the ruthenium complexes involved is given by combined electrochemistry-electrospray ionization mass spectroscopy (EC/ESI-MS),<sup>15</sup> which also shows the destruction of oxidized Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> by water in the course of catalysis.

**Cyclic Voltammetry (CV) and Electrolysis.** Cyclic voltammetry scans are sensitive to the mediator and the primary ET step. The reaction of  $Ru(CH_3CN)_3Cl_3$  with tetralin has been described previously in detail.<sup>8</sup> Here, Figure 1 shows CV scans for indane oxidation in the range -0.3 to +1.8 V, with the baseline of the solution scanned to 2.2 V (dotted line). The voltammetry trace for  $Ru(CH_3CN)_3Cl_3$  alone in solution (black line) shows two reversible redox conversions. The conversion



**Figure 1.** Cyclic voltammetry of 0.1 mM  $Ru(CH_3CN)_3Cl_3$  (black), oxidation of 1 mM indane alone (violet), and catalyzed oxidation of 1 mM (green) and 2 mM (red) indane. The solution background is shown by a dotted line. Conditions: acetonitrile solution with 1.0 M TBAP; scan rate 20 mV s<sup>-1</sup>; Pt electrode vs SCE; anode Pt tip ~1 mm<sup>2</sup>; counter electrode Pt plate 1 cm<sup>2</sup>.

between the Ru<sup>II</sup> and Ru<sup>III</sup> states occurs at ~0.0–0.1 V, while the conversion between the Ru<sup>III</sup> and Ru<sup>IV</sup> states occurs at ~1.7 V (vs SCE). Both of these redox steps are single-electron transfers. A bias in the shape of the Ru<sup>III</sup>/Ru<sup>IV</sup> transition at 1.7 V is noted, especially at high scan rates above 20 mV/s.

The hydrocarbons of interest all have oxidation potentials of around 1.85 V. The short trace for indane is shown at 1.82–1.84 V (violet, Figure 1). The oxidation potential for indane is about 130 mV higher than that for  $Ru(CH_3CN)_3Cl_3$ . When indane is present, the  $Ru^{III}/Ru^{IV}$  transition shows a catalytic oxidation current at 1.6 V (1 mM indane (green) and 2 mM indane (red); Figure 1). The catalytic traces show the expected sigmoidal shape, Nernstian narrowing of the return curve, and the absence of reduction current.<sup>16a</sup> At the same time the  $Ru^{II}/Ru^{III}$  step remains unaffected by the presence of indane, and this step can be regarded as an internal standard.

Electrolysis at the catalysis potential yields 1-indanol, 1indanone, and 1-indene, identified by GC-MS using the GC retention times and the mass spectral details. For prolonged electrolysis carbon counter electrodes are better than Pt, since Pt gets passivated. Acetonitrile used for these tests had a water content of up to 0.03% ( $17 \times 10^{-3}$  M). This is the source of oxygen in the hydrocarbon products. However, water is destructive to the catalyst, as shown below, and increasing the concentration of water or the electrolysis time is counterproductive.

We have not studied indane further, as behavior analogous to that observed previously for tetralin electrolysis is evident. All subsequent experiments described below refer to reactions with tetralin.

Voltammetry with Rotating Ring Disk Electrode (RRDE). The catalytic step (red, Scheme 1) was examined with reference to the oxidation of tetralin.

Unlike CV, RRDE, termed hydrodynamic voltammetry,<sup>17</sup> is a fast-flow system, conducted under fast movement of the solution. Fast rotation causes the solution to encounter the central disk in fast vertical flow and be driven sideways in a radial course to the ring. The ring response depends on the collection efficiency of the ring. Potentials of the central disk and of the surrounding ring are operated independently by a double potentiostat.

In the present example the disk electrode was scanned from -0.05 to 2.5 V to record the current-potential traces shown in

Figure 1. The ring electrode was kept at 1.5 V in order to oxidize any  $Ru^{II}$  or reduce any  $Ru^{IV}$  compounds produced on the disk. At 1.5 V it is indifferent to tetralin. Experiments were run with rotation frequencies of 700, 1500, 2000, and 2500 rpm. The results for 700 rpm are shown in Figure 2. The



Figure 2. RRDE tests at 700 rpm: (red) 0.1 mM,  $Ru(CH_3CN)_3Cl_3$ alone (disk bright red, ring thin dark red); (blue)  $Ru(CH_3CN)_3Cl_3$  0.1 mM + tetralin 0.5 mM. (disk dark blue, ring light blue); (gray) 0.5 mM tetralin alone (oxidized on the disk above 2.1 V; ring current remains unchanged, a straight line). Conditions: Pt electrodes in acetonitrile with 1.0 M TBAP; potential sweep of disk from -0.05 to +2.5 V; ring potential fixed at 1.5 V (Ag/AgCl/KCl (3 M) reference).

responses of the disk scans from -0.05 to +2.5 V are the traces starting from the bottom left and increasing toward the right, whereas the ring responses are the traces starting from the top left and decreasing toward the right. Disc currents are marked on the left-side ordinate and ring currents on the right-side ordinate.

Figure 2 shows disk scans at 700 rpm with a constant ring potential of 1.5 V, with the gray line indicating 0.5 mM tetralin alone, the red line indicating 0.1 mM Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> alone, and the blue line indicating 0.1 mM Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> with added 0.5 mM tetralin. Tetralin is inert until it is oxidized irreversibly on the disk at potentials above 2 V; as the ring is at a lower potential, there is no reaction of tetralin at the ring. The disk scan for the solution of Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> alone shows the low-potential transition (Ru<sup>III</sup> to Ru<sup>III</sup>) from 0.0 to 0.15 V and the high-potential transities. With potentials up to 0.15 V on

the disk,  $Ru^{II}$  that reaches the ring is oxidized to  $Ru^{III}$  on the ring. At 1.75 V  $Ru^{III}$  that is oxidized to  $Ru^{IV}$  on the disk is reduced to  $Ru^{III}$  on the ring. These are reversible singleelectron transfers (eq 1); therefore, equal current intensities are observed on the ring as well.

$$\begin{bmatrix} \operatorname{Ru}(\operatorname{CH}_{3}\operatorname{CH})_{3}\operatorname{Cl}_{3} \end{bmatrix}^{-}$$

$$\stackrel{-e^{-}}{\underset{+e^{-}}{\rightleftharpoons}} \operatorname{Ru}(\operatorname{CH}_{3}\operatorname{CN})_{3}\operatorname{Cl}_{3}$$

$$\stackrel{-e^{-}}{\underset{+e^{-}}{\xleftarrow}} [\operatorname{Ru}(\operatorname{CH}_{3}\operatorname{CH})_{3}\operatorname{Cl}_{3}]^{+}$$
(1)

When the solution contains both  $Ru(CH_3CN)_3Cl_3$  and tetralin, the disk and the ring current intensities at 0.0–0.15 V remain unchanged, whereas at 1.75 V the disk current surges, showing a catalytic current shape. Concurrently, the ring current at 1.75 V falls off. Less  $Ru^{IV}$  reaches the ring because some is consumed by tetralin. This takes place at ~250 mV below the oxidation potential of tetralin itself.

The collection efficiency of the ring (ring/disk current intensities) for this specific RRDE electrode set was determined by using standard reversible reactions (see the Experimental Section) and found to be 0.236. It is important to note that for a single ET process the collection efficiency does not depend on rotation rate (see p 87 of ref 4).

When Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> is tested alone, the collection efficiency for the oxidation from Ru<sup>II</sup> to Ru<sup>III</sup> around 0.0 V is within 0.230  $\pm$  0.005 at all rotation rates, which is consistent with a reversible single-electron transfer. At 1.75 V, where Ru<sup>III</sup> is recovered on the ring from the oxidized Ru<sup>IV</sup>, the collection efficiency is only 0.210  $\pm$  0.005 at all rotation rates, which means 90–95% recovery. This small loss of Ru<sup>IV</sup> may be due to reaction with water (~17 × 10<sup>-3</sup> M in the solvent) or with acetonitrile, forming Ru(CH<sub>3</sub>CN)<sub>4</sub>Cl<sub>2</sub> (blue trace in Scheme 1). This loss is slow in comparison with the reaction with tetralin and is not easily detected by CV analysis but is clearly observed by EC/ESI-MS, which allows for more time (see below).

In the presence of tetralin, the collection efficiency around 0.0 V remains unaffected, 0.230  $\pm$  0.005, and thus the Ru<sup>III/II</sup> transition is indifferent to tetralin and can be considered as an internal standard for both the disk and the ring measurements. However, at 1.75 V (Ru<sup>III</sup> recovery from Ru<sup>IV</sup>), the collection



**Figure 3.** Plot of the ratio  $i_d/\omega^{1/2}C$  versus log  $\omega$  (rad s<sup>-1</sup>) for rotation rates  $\omega$  of (left to right) 700, 1500, 2000, and 2500 rpm: (white  $\bigcirc$ ) [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>] alone, C = 0.1 mM; (blue  $\diamondsuit$ ) [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>] alone, C = 1.0 mM; (red  $\bigtriangleup$ ) [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>] 1.0 mM + 0.5 mM tetralin; (blue  $\square$ ) [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>] 0.1 mM + 1.0 mM tetralin. C = concentration of Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>.



Figure 4. EC-ESI-MS study of the reduction of  $Ru(CH_3CN)_3Cl_3$  (a) trace of current potential scan in the EC cell, of 1 mM  $Ru(CH_3CN)_3Cl_3$  in 50 mM lithium triflate/CH<sub>3</sub>CN from 0.1 to -0.8 V and back; (b) intensities of all ions obtained at 0.1 V; (c) intensities of all ions obtained at -0.8 V.

efficiency falls dramatically to 0.136 (0.65 intensity) at 2500 rpm and to 0.11 (0.52 intensity) at 700 rpm (Figure 2). This current deficiency therefore indicates that some of the oxidized  $Ru^{IV}$  has been regenerated to  $Ru^{III}$  by reaction with tetralin even before reaching the ring electrode.

The following summary of runs at different rotation rates is illustrative. Tests that were run at different rotation rates gave the same pattern, but the intensities of the response for catalysis were smaller at higher rotation rates. The current obtained on the disk depends not only on concentration but also in a complex way on factors of mass transport in solution, on convection, and on viscosity. Altogether, for the single-electron transfers the disk current ( $i_d$ ) is given by the Levich equation:

$$i_d = 0.62 n F D^{2/3} \nu^{-1/6} \omega^{1/2} C$$

where  $\omega$  is given in rad s<sup>-1</sup> and  $\nu$  is the kinematic viscosity and D the diffusion coefficient (both in cm<sup>2</sup> s<sup>-1</sup>).

It is possible to extricate the effect of catalytic current in the following way. The plot of  $i_d/\omega^{1/2}C$  against log  $\omega$ , where *C* is the concentration of [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>], is shown in Figure 3. The term  $i_d/\omega^{1/2}C$  is the current output in terms of electrons/ mole per mass transport. It remains unchanged between 700 and 2500 rpm (73.3–262 rad s<sup>-1</sup>), when Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> alone is present, whether C = 0.1 or 1.0 mM, reflecting a single electron transfer process.

When C = 1.0 mM and 0.5 mM tetralin is added (red  $\triangle$ , Figure 3), a slight increase is seen at  $\omega = 700$  rpm. The ruthenium compound is in excess and only a small part of it interacts with tetralin. However, when tetralin is in excess (C = 0.1 mM, tetralin 1.0 mM) the value increases at all rotation rates, and most dramatically at 700 rpm, showing a 3.5-fold increase. This reflects the current produced in excess due to catalysis: i.e., to recovery and repeated use of the mediator Ru<sup>IV</sup> (red arrows in Scheme 1). Slower rotation rates that slow the

mass transport to the disk and prolong contact are a critical factor for turnover frequency (TOF).

Electrochemistry Linked with Electrospray Ionization Mass Spectrometry, EC/ESI-MS. CV and RRDE tests show reversible reduction and oxidation of  $Ru(CH_3CN)_3Cl_3$  within the time scale of the experiments, implying preservation of the coordination sphere (eq 1). Whereas reduction of Ru-(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> is reversible and is not involved in catalysis, the situation is less clear for the oxidized complex in the course of catalytic oxidation.

Direct spray ionization MS detects ionized forms of  $Ru(CH_3CN)_3Cl_3$ . The cluster  $[Ru_2(CH_3CN)_6Cl_6Na]^+$  was detected (*m*/*z* 683–685,  $[M + Na]^+$ ) along with ions at *m*/*z* 642 and 602, consistent with the loss of one and two CH<sub>3</sub>CN units from this cluster, respectively.<sup>8</sup>

The combined EC/ESI-MS follows the redox cycle of  $Ru(CH_3CN)_3Cl_3$  and can be used to detect the associated molecular products. A radial thin-layer flow-through cell with three electrodes is used for the EC step. The product stream is introduced into the mass spectrometer at atmospheric pressure. The transfer times from the electrochemical cell to the ionization port are 1–70 s and are controlled by the flow rates. This time scale for detection in EC/ESI-MS is long compared with the time scale of RRDE, which is <50 ms.<sup>4</sup> Survival of products or secondary reactions may therefore become important factors in the interpretation of EC/ESI-MS data. The observed clusters are compared with calculated MS clusters determined using the "Sheffield ChemPuter Isotope Pattern Calculator".<sup>18</sup>

Reduction of  $Ru(CH_3CN)_3CI_3$ . The Ru<sup>II/III</sup> transition (eq 1, left) is used as a test case. The cell potential is scanned from 0.1 to -0.8 V (vs Ag/AgNO<sub>3</sub>), and the forward and reverse voltammetry traces are shown in Figure 4a. The mass spectra collected at 0.1 V and at -0.8 V are shown in Figures 4b,c, respectively. The prominent ion cluster observed at 0.1 V



**Figure 5.** (top) Decay and rise of intensity of cluster m/z 661–675 in the course of the potential sweep between 0.1 V and -0.8 V at 1 mV/s. Proposed assignments are m/z 669 [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>]<sub>2</sub>Li<sup>+</sup> or m/z 668{[Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>][Ru(CH<sub>3</sub>CN)<sub>4</sub>Cl<sub>2</sub>]}<sup>+</sup>. (bottom) Intensity of the ion m/z 880, increase and decay, along the same potential scan between 0.1 V and -0.80 V. The proposed structure for this cluster is [RuCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>Li]<sub>2</sub>Li<sup>+</sup> with attached CF<sub>3</sub>SO<sub>3</sub>Li and CH<sub>3</sub>CN. The insets show the clusters in detail.

occurs at m/z 660–670, whereas at -0.8 V, after reduction, the prominent ion cluster is at m/z 880.

In the course of the potential scans (1 mV/s) between 0.1 V and -0.8 V and back to 0.1 V, mass spectra were recorded continuously at a rate of 8–12 spectra per minute, at selected m/z ranges, to follow the ion output. The cluster at m/z 668–669 that is the dominant species between 0.0 and 1.4 V (vs Ag/AgNO<sub>3</sub>) decays below 0.0 V.

Figure 5 shows the decay and rise in abundance of m/z 668–669 that is accompanied by a corresponding rise and decay of the m/z 880 species during the potential scan.

The cluster at m/z 668–669 is assigned as a Ru<sup>III</sup> state. This cluster can be interpreted as [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>][Ru-(CH<sub>3</sub>CN)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> (m/z 668) or as [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>)<sub>2</sub>Li]<sup>+</sup> (m/z 669) in analogy to [(Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>)<sub>2</sub>Na]<sup>+</sup> mentioned above. The ion proposed for the cluster at m/z 880 is [[Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>Li]<sub>2</sub>Li<sup>+</sup>, CH<sub>3</sub>CN, CF<sub>3</sub>SO<sub>3</sub>Li], which is a Ru<sup>II</sup> state. The insets in Figure 5 show the clusters in detail. These assignments for the m/z 669 and 880 clusters reflect preservation of the ligand arrangement of Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>][Ru(CH<sub>3</sub>CN)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> (m/z 668) cannot be ruled out. Indeed, the presence of the compound Ru-(CH<sub>3</sub>CN)<sub>4</sub>Cl<sub>2</sub> in the solution is discussed below.

The reduction can be written as in eq 2.

$$2[\operatorname{Ru}(\operatorname{CH}_{3}\operatorname{CN})_{3}\operatorname{Cl}_{3}] + 2e^{-} + 3\operatorname{Li}^{+}$$
  
$$\approx [\operatorname{Ru}(\operatorname{CH}_{3}\operatorname{CN})_{3}\operatorname{Cl}_{3}\operatorname{Li}]_{2} + \operatorname{Li}^{+}$$
(2)

The reduction step appears to be reversible with preservation of the acetonitrile complex structure.

Oxidation of  $Ru(CH_3CN)_3CI_3$ . Figure 6a traces the intensities of the cluster at m/z 668–669 and the clusters at m/z 331–346 (derived from the monomer  $[Ru(CH_3CN)_3Cl_3Li]^+$ ), in the course of a potential sweep from 0.8 to 1.8 V and back to 0.8 V, at 1 mV/s. The intensities of these clusters decrease at the oxidation potential of  $Ru(CH_3CN)_3Cl_3$ . No new cluster signifying ruthenium oxidation is observed in the high-potential range: namely, no oxidized form appropriate for the spray ionization route survived the transfer to the MS analyzer. Only when the experiment was repeated with a *very dry* acetonitrile solution were new clusters observed. For these tests, acetonitrile was dried over molecular sieves and the electrolyte salts were vacuum-treated before use. In the very dry solvent, new clusters of ruthenium complexes appeared in the electrospray when the cell potential was 1.4 V and disappeared when potentials rose above 1.8 V, with the maximum intensity obtained under 1.5 V. These clusters correspond to oxidation of the ruthenium complex. Ion intensities and the corresponding cluster structure consistent with the observed m/z values are shown in Figure 6b.

It should be noted that potentials of 1.5 V for these EC/ESI-MS measurements roughly correspond to 1.8 V (vs Ag/AgCl) in CV and RRDE experiments. In Figure 6, 1.5 V corresponds to the range in which the catalytic reaction is the most intense. The absence of observable oxidized ions in the EC/ESI-MS measurements in standard acetonitrile (water content ~0.03%  $H_2O$ , 17 × 10<sup>-3</sup> M), implies a reaction of the Ru<sup>IV</sup> state with water. In the RRDE tests, the Ru<sup>IV</sup> complex formed on the disk survives transfer to the ring with only partial loss of about 5– 10%. Detection in RRDE experiments occurs on a time scale that is 3–4 orders of magnitude faster than detection in EC/ ESI-MS, and during the transfer time of the EC/ESI-MS experiment, reactions with water can completely consume the oxidized ions (blue route, Scheme 1).

Catalyzed Oxidation of Tetralin with Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> as a Mediator. Potential sweep tests (Figure 7, top left) for the catalyzed oxidation of tetralin, with 0.1 mM Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> and excess tetralin (2 mM), must be run in standard acetonitrile (~0.03% H\_2O, 17  $\times$  10<sup>-3</sup> M) to provide oxygen to tetralin (black route, Scheme 1). Under these conditions, no oxidized ruthenium clusters are detected, as explained in the preceding paragraph. With tetralin the catalytic process consumes the oxidized clusters even more quickly. However, another tracer is observed here. In the absence of tetralin, a cluster at m/z 330– 340 corresponding to a Ru<sup>III</sup> state, [Ru(CH<sub>3</sub>CN)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>, is observed in dry as well as in standard acetonitrile at potentials between 1.4 and 2.0 V (Figure 7, bottom left). In the presence of tetralin  $[Ru(CH_3CN)_4Cl_2]^+$  is detected, but its intensity is strikingly deficient within the potential range of the catalytic reaction (Figure 7, bottom right). Above 1.65 V, outside the range of the catalytic reaction, where the noncatalyzed



**Figure 6.** Oxidation of Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> in specially dried acetonitrile: (a) ion intensities of the m/z 668.5 cluster (left) and intensities of the overlapping clusters of m/z 330–350 (right); Ion intensities of oxidized forms and corresponding experimental isotopic patterns. The potential was swept between 0.8 and 1.8 V. (c) m/z 850–864 for {[Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>][Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)]} + 2CH<sub>3</sub>CN (left), m/z 850–880 for {[Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>][Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>][Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>]]<sup>+</sup> + 2CH<sub>3</sub>CN + CF<sub>3</sub>SO<sub>3</sub>Li (middle), and m/z 560–580 for [Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub>]<sup>+</sup> + 2CH<sub>3</sub>CN + CF<sub>3</sub>SO<sub>3</sub>Li (right).

oxidation of tetralin takes over,  $[Ru(CH_3CN)_4Cl_2]^+$  is again observed with significant intensity (Figure 7, bottom right). Higher potentials are destructive to the ruthenium acetonitrile complexes, and above 2.2 V the MS signals for these complexes decline sharply (Figure 7, bottom right).

These observations in the course of the catalyzed reaction with tetralin are remarkable.  $[Ru(CH_3CN)_4Cl_2]^+$  is possibly formed by nucleophilic attack of  $CH_3CN$  (present in large excess) on the oxidized and charged  $[Ru(CH_3CN)_3Cl_3]^+$  rather than the neutral  $Ru(CH_3CN)_3Cl_3$ . Indeed, gradual accumulation of  $Ru(CH_3CN)_4Cl_2$  during electrolysis has been recorded in our earlier work. The much faster reaction of tetralin in the mediated ET depletes the solution of

 $[Ru(CH_3CN)_3Cl_3]^+$ , hence the declining intensity of  $[Ru-(CH_3CN)_4Cl_2]^+$  in the catalytic range.

EC/ESI-MS was initially intended to follow structural features of the different oxidation states, yet it also exposes the competition among water, acetonitrile, and hydrocarbon in the reaction with  $[Ru(CH_3CN)_3Cl_3]^+$  (blue and black routes, Scheme 1).

**Controlling Selectivity with the Counter Electrode.** In contrast to the notion of catalyst activation on the working electrode, a case of aromatic electrophilic chlorination shows that occasionally simply *removing* the catalyst can increase selectivity.

Article



**Figure 7.** (top left) CV scan from 1.0 to 2.0 V and back of 0.1 mM Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> in 50 mM CF<sub>3</sub>SO<sub>3</sub>Li in standard CH<sub>3</sub>CN. (bottom left) Ion intensity of m/z 330–350. (bottom right) Ion intensity of m/z 330–350, during scan from 0.8 to 2.5 V of 0.1 mM Ru(CH<sub>3</sub>CN)<sub>3</sub>Cl<sub>3</sub> in presence of 2 mM tetralin. (top right) Corresponding experimental isotopic pattern, which fits [Ru(CH<sub>3</sub>CN)<sub>4</sub>Cl<sub>2</sub>].



Figure 8. Reaction profile for chlorination of 2-*tert*-butyl-1,4-dimethoxybenzene (1): (a) chlorination with  $Cl_{2j}$  (b) anodic chlorination. Products: 2-*tert*-butyl-6-chloro-1,4-dimethoxybenzene (2); 2-*tert*-butyl-5-chloro-1,4-dimethoxybenzene (3); 2,5-dichloro-1,4-dimethoxybenzene (4); 2-*tert*-butyl-3,6-dichloro-1,4-dimethoxybenzene (5). Compounds also formed in small amounts: 3-chloro-1,4-dimethoxybenzene (6); 2,3,5-trichloro-1,4-dimethoxybenzene (7); 2-*tert*-butyl-3,5,6-trichloro-1,4-dimethoxybenzene (8). Reproduced with permission from ref 9.

C–H bond activation by halogenation is well known. Indeed, transition metals have been used to gain selectivity in electrochemical chlorination or bromination, as in the chlorination of benzoquinoline aided by  $PdCl_2$ .<sup>19</sup> In this reaction  $PdCl_2$  does not act as a mediator but as a directing or protecting group in a proper reactive manifold that is frequently observed with palladium compounds.<sup>20</sup>

1,4-Dimethoxy-2-*tert*-butylbenzene is very reactive toward electrophilic aromatic substitution, in this case chlorination. The reaction with chlorine is autocatalyzed by the released protons, and the reaction accelerates as the pH falls significantly. Seven products are obtained from the chlorination reaction, some of which are chlorinated with greater ease than the starting material and others correspond to loss of the *tert*-butyl group.

Electrochemistry plays a double role in this chlorination reaction. The first role is the production of chlorine in situ from harmless materials in a controlled manner, instead of using free chlorine with the demanding technicalities and hazards involved. The second role is that of the counter electrode; in an undivided cell, protons are reduced on the cathode and the solution pH is kept at  $\sim$ 7. With the catalyst removed from the solution, selectivity is obtained. A detailed report<sup>9</sup> is not reiterated here, but in fact this electrochemical procedure in an undivided cell yielded just two monochlorinated products and the *tert*-butyl group is preserved, even at 80% completion of the reaction (Figure 8). The possibility of such simple complementary control using a counter electrode is an exclusive asset of the electrochemical method.

#### CONCLUSION

The two examples illustrate various parameters concerning links of electrochemistry with homogeneous catalysis. The parts played by the working electrode and the counter electrode, as concerns catalysis, are illustrated with two very different cases.

 $Ru(CH_3CN)_3Cl_3$  is in a sense an artless example, being molded in solution of  $RuCl_3$  in  $CH_3CN$  with no other especially tailored ligand attached.  $RuCl_3$  is known to catalyze oxidations similar to those of cyclohexene and cyclohexanol, when the transition metal is supported by strong oxidizers such as NaOCl<sup>21</sup> and NaIO<sub>4</sub><sup>22</sup> possibly involving RuO<sub>2</sub>/RuO<sub>4</sub> intermediates, in nonpolar solvent or in phase transfer. Replacing use of such reagents by electrode activation enables identification of active ruthenium species in solution and follow-up of the catalyzed oxidation, as delineated in Scheme 1. Several techniques such as CV, constant-potential electrolysis, RRDE, and ECSI-MS provide different perspectives of the time scale and material transport regime, oxidation states, and background reactions. That reduced and oxidized ruthenium complexes retain their basic coordination sphere is probably also due to the solvent and main ligand being the same. Evidence for  $RuO_2/RuO_4$  is not observed in this system.

The intimate details of contact between the ruthenium mediator and hydrocarbon are not known. Possibly, the aromatic HOMO level of tetralin or indane can act as a nucleophile toward  $[Ru(CH_3CN)_3Cl_3]^+$ . A consequent tetralin (or indane) cation radical is expected to be located on the aromatic ring, but the radical, after loss of proton, is positioned at the benzyl carbon, as are the final products. Such C–H activation is in a way indirect if oxidized Ru<sup>IV</sup> does not attack the actual CH bond that is eventually activated but initially triggers the adjacent aromatic segment or the double bond in cyclohexene.

In contrast, the case of chlorination focuses on the role of the counter electrode. Whereas the working electrode activates the chlorination process, the counter electrode suppresses the secondary effect of autocatalysis. This double operation is a special feature of electrochemistry.

#### EXPERIMENTAL SECTION

**Materials.** Solvents were degassed, and all procedures were carried out under Ar. Commercially dry acetonitrile used routinely contained up to ~0.03% ( $17 \times 10^{-3}$  M) water and was used as received unless additional drying was specified. This drying was carried out by prolonged storage over molecular sieves A. Lithium trifluoromethane-sulfonate (LiOTf) was used as supplied. RuCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> (1) was prepared as in ref 8.

**Instrumentation and Methods.** The electrode potential was controlled with a potentiostat/galvanostat. Cyclic voltammetry was performed under Ar in an undivided three-electrode cell with a Pt working electrode  $(1.7 \text{ mm}^2)$  and a Pt counter electrode  $(0.5 \text{ cm}^2)$  vs Ag/AgBF<sub>4</sub> (0.1 M in acetonitrile). Constant-potential electrolysis was carried out under Ar in an undivided three-electrode cell with a Pt working electrode  $(2 \text{ cm}^2)$  and a counter electrode of Pt or graphite vs Ag/AgCl (3 M in KCl). Reported potentials are related to the SCE for CV (Figure 1) and to Ag/AgCl (3 M in KCl) for electrolysis and RRDE tests (Figure 2). Potentials for the EC/ESI-MS experiments are given relative to a Ag/AgNO<sub>3</sub> (0.1 M in acetonitrile) reference electrode. Potential values of -0.25 and 1.45 V (vs Ag/AgNO<sub>3</sub>) correspond to 0.14 and 1.85 V (vs Ag/AgCl). The electrolytes were tetrabutylammonium perchlorate (TBAP) for CV and RRDE, LiClO<sub>4</sub> for electrolysis, and LiOTf for EC/ESI-MS.

Catalyzed electrolysis of indane was done under Ar in acetonitrile with LiClO<sub>4</sub> as the electrolyte. To the resulting solution was added water, followed by extraction with CDCl<sub>3</sub>. This same procedure was followed for electrolyzed solutions and for control solutions. Analysis was by GC-MS (injector 250 °C, split 1:50, temperature gradient 60 °C/min for 3 min, then 10 °C/min to 330 °C). The column was fused silica (Rxi-SSil MS) 30 m × 0.25 mm. First mass was at *m*/*z* 40. The solution after electrolysis was compared with the control, as well as with 1-indanol and 1-indanone.

A sample electrolysis is as follows. A 20 mL CH<sub>3</sub>CN solution was prepared of 2.1 mg (0.003 mM) of  $Ru(CH_3CN)_3Cl_3$ , 40 mg (0.34 mM) of indane, and 0.2 mL of H<sub>2</sub>O, doped with benzonitrile as a marker. A 10 mL portion was kept as the control solution, and 10 mL

was electrolyzed at a potential halfway up the catalytic current, at 1.9–2.1 V,  $\sim$ 1.2 mA, 2 h ( $\sim$ 8.5 C) in an undivided cell, with a Pt-wire anode and a graphite cathode (vs Ag/AgCl in 3 M KCl). A Pt cathode could not be used due to passivation.

GC-MS identified products (retention time/min (m/z), compound): 8:06 (118), indane; 8:18 (116), indene; 11:25 (134), 1-indanol (m/z (intensity) 134 (18), 133 (100), 115 (46), 105 (16), 91 (16); 12:00 (132)), 1-indanone <math>(m/z (intensity) 132 (100), 104 (60), 103 (48), 102 (9), 78 (95), 77 (25), 50 (20)).

A peak at 15.77 (167) for *N*-cyclohexylpyrrolidone was found from the processed graphite cathode. It was absent when the cathode was replaced.

RRDE was carried out under Ar with a double potentiostat using a Pt electrode with disk radius 4.57 mm  $(r_1)$ , ring internal radius 4.927 mm  $(r_2)$ , and outer radius 5.38 mm  $(r_3)$ . The disk-ring distance was 0.357 mm, and the ring width was 0.45 mm.

The collection efficiency *n* of the electrode  $(n = -i_r/i_d (i_r \text{ sign} \text{ opposite from } i_d))$  was determined for a 5 mM solution of 1,4-dimethoxy-2,5-ditertbutylbenzene, which is a reversible oxidation, and was found to be 0.236 ± 0.003 for rotation rates in the range of 700–2500 rpm.

RRDE tests were run at 700, 1500, 2000, and 2500 rpm. The ratio of ring current to disk current is constant at 0.235  $\pm$  0.005 for these rotation rates and is close to the collection efficiency with the standard.

Electrospray ionization mass spectrometry was carried out on a quadrupole ion trap mass spectrometer. The details of the online concentric coaxial EC cell and experimental setup have been described elsewhere.<sup>23</sup> Briefly, the working electrode is a Pt disk of 1.6 mm diameter placed at the bottom of the cell. Compartments with counter and reference electrodes were separated from the main flow of electrolyte by tube filters. The spray ionization was operated in the positive ion mode with a spray voltage of 2.0 kV (once at 3 kV), a capillary voltage of 25 V, and a source temperature of 120 °C. A syringe pump drove the solution through the outer tube to the electrode surface. The analyte jet contacts the surface of the working electrode through the outer tube of the double coaxial system, and the products of electrode reactions were transferred to the MS through the inner tube. The inner tube had an inner diameter of 125  $\mu$ m and an outer diameter of 1.6 mm and was 15 cm long. The reagent flow rate was set to 3  $\mu$ L min<sup>-1</sup>. With the help of auxiliary acetonitrile, the sample stream was delivered to the electrospray interface. The acetonitrile flow in the auxiliary tubing was 30  $\mu$ L min<sup>-1</sup> for potential sweep experiments.

Mass spectra were obtained by scanning the mass analyzer from m/z 50 to 2000 with five total micro scans. The maximum injection time into the ion trap was 50 ms. The analyzer was operated at a background pressure of  $2 \times 10^{-5}$  Torr.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*M.M.: e-mail, michman@mail.huji.ac.il; fax, 972 (0)35245559; tel, 972 (0)547482388.

#### **Present Addresses**

<sup>†</sup>Makhteshim Chemical Works Ltd., Saadia Mallal 3, 84100 Beer Sheva, Israel. E-mail: linaapelbaum@gmail.com; Lina. Apelbaum@adama.com.

<sup>‡</sup>Russian Academy of Sciences, A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Leninski Prospect 31, 119991 Moscow, Russia. E-mail: modestov@elchem.ac.ru.

#### Notes

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