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Oxidatively Induced Reductive Eliminations. A Mechanistic Study of the Oxidation Chemistry of $CnRhMe_3$ (Cn = 1,4,7-Trimethyl-1,4,7-triazacyclononane)

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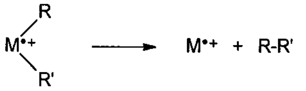
The trimethylrhodium(III) complex $CnRhMe_3$ (**1**, Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) undergoes a nearly reversible one-electron oxidation at $E° = -0.15$ V vs Cp_2Fe/Cp_2Fe^+ (cyclic voltammetry, 1.0 V/s) in acetonitrile/0.1 M Bu_4NPF_6. Preparative electrolysis as well as homogeneous oxidations with substituted ferricinium salts gives a mixture of $CnRhMe_2(NCMe)^+$ (**2**) and $CnRhMe(NCMe)_2^{2+}$ (**3**), the **2**:**3** ratio being independent of the nature of the oxidant. In addition, the reactions yielded ethane, mostly by intramolecular elimination. An investigation of the kinetics of the reaction of $\mathbf{1}^{\bullet+}$ by derivative cyclic voltammetry revealed a unimolecular reaction ($\Delta H^{\ddagger} = 57.0 \pm 0.9$ kJ/mol, $\Delta S^{\ddagger} = -35.4 \pm 3.0$ J/(K·mol), $k(20\ °C) = 5.9\ s^{-1}$) with negligible solvent effects (MeCN vs CH_2Cl_2). It is proposed that $\mathbf{1}^{\bullet+}$ eliminates ethane to generate the formally 15-electron $CnRhMe^{\bullet+}$ in the rate-determining step. The final Rh-containing products are likely formed from this species and $\mathbf{1}^{\bullet+}$.

Introduction

The electron-transfer oxidation of organotransition metal complexes containing σ-bonded ligands is frequently observed to induce reductive elimination, defined in a broad sense as summarized in eqs 1−3. Metal hydrides are activated toward deprotonation and typically react according to eq 1,[2] whereas homolysis[3] (eq 2) and apparently concerted reductive eliminations[4] according to eq 3 are found for compounds containing σ-bonded hydrocarbyl groups.

$$M^{\bullet+}\text{—}R \longrightarrow M^{\bullet} + R^{+} \qquad \text{two-electron, one-ligand reductive elimination} \qquad (1)$$

$$M^{\bullet+}\text{—}R \longrightarrow M^{+} + R^{\bullet} \qquad \text{one-electron, one-ligand reductive elimination} \qquad (2)$$



$$M^{\bullet+}(R)(R') \longrightarrow M^{\bullet+} + R\text{-}R' \qquad \text{two-electron, two-ligand reductive elimination} \qquad (3)$$

A detailed investigation of the kinetics and mechanisms for the reductive elimination from the cation radical of $Cp^*Rh(PPh_3)Me_2$ revealed a first-order process that gave intramolecular ethane formation and (for MeCN solvent) $Cp^*Rh(PPh_3)(NCMe)_2^{2+}$ by an ECE mechanism.[4f] The rate of this reaction was rather insensitive to the identity of the solvent, suggesting that 15-electron $Cp^*Rh(PPh_3)^{\bullet+}$ was the initially formed organometallic product. Rapid capture of two solvent molecules and reoxidation gave $Cp^*Rh(PPh_3)(NCMe)^{2+}$. Similar behavior resulted from the oxidation of the 16-electron complex $Ru(CO)(P^tBu_2Me)_2(CCPh)_2$,[4g] indicating that this behavior may have some generality.

In this contribution, we will describe the oxidation chemistry of $CnRhMe_3$ (where Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane). Although intramolecular elimination is again the result, it will be seen that this system differs from $Cp^*Rh(PPh_3)Me_2$ in interesting ways. Recent publications by Flood and coworkers[5] have focused on the organometallic chemistry of the CnRh moiety. The Cn ligand is bonded to the metal through three "hard",[6] poorly polarizable N atoms, devoid of π-backbonding capabilities. This is in contrast with more conventional ligands like Cp, CO, PR_3, etc., which are relatively "soft", polarizable, and capable of accepting electron density from the metal by backbonding. It is hoped that the relatively hard Rh center that results from the coordination of the Cn ligand will significantly alter the chemistry of coordinated hydrocarbon ligands when compared to the behavior of related Rh complexes that are ligated by softer ligands.[5a] Although it is not clear whether the effects arise from the altered hardness of the metal, several reports indicate important reactivity differences between

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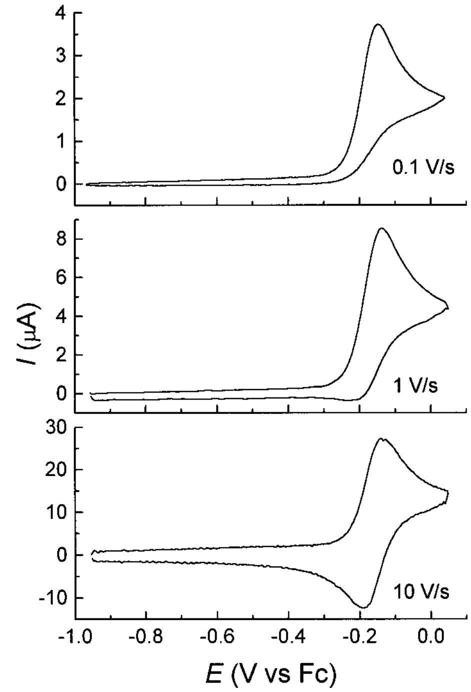

Figure 1. Cyclic voltammograms for the oxidation of $\mathrm{CnRhMe_3}$ at voltage sweep rates $\nu = 0.1$, 1.0, and 10 V/s. Experimental conditions: 2.0 mM substrate in acetonitrile/0.1 M $\mathrm{Bu_4N^+PF_6^-}$, 20 °C, $d =$ 1.0 mm Pt disk electrode.

CnRh and related CpRh and TpRh complexes. For example, Rh(III) complexes $\mathrm{CnRh(PR_3)(H)Me^+}$ (R = Me, OMe) are isolable and thermally stable at ambient temperature and only slowly eliminate methane at 50 °C,[5d] whereas analogous Rh(III) complexes $\mathrm{Cp^*Rh(PMe_3)(H)Me}$,[7a] Tp′Rh(CO)(H)Me,[7b] and Tp′Rh(CNtBu)(H)Me[7c] readily eliminate methane at considerably lower temperatures.

Results

Cyclic Voltammetry Analysis of the Oxidation of 1. Figure 1 shows cyclic voltammograms for the oxidation of **1** (1.0 mM in acetonitrile/0.1 M $\mathrm{Bu_4N^+PF_6^-}$, $T = 20$ °C, 0.6 mm diameter Pt disk electrode). At a relatively fast voltage scan rate $\nu = 10$ V/s (bottom), essentially full chemical reversibility is seen, as evidenced by the near unity ratio of the cathodic to anodic peak currents. At the intermediate rate $\nu = 1.0$ V/s, partial reversibility is seen, and at the slowest scan rate $\nu = 0.1$ V/s, the electrode-generated $\mathbf{1}^{\bullet+}$ has sufficient time to undergo essentially complete reaction on the experimental time scale. At $\nu < 10$ V/s, the peak-to-peak separations and the peak currents were near those for ferrocene. In the scan rate range $\nu = 0.5{-}10$ V/s, a linear dependence of i_p vs $\nu^{1/2}$ was seen. Taken together, these observations are in accord with an essentially Nernstian one-electron transfer at $E° = -0.15$ V vs $\mathrm{Cp_2Fe/Cp_2Fe^+}$ (Fc) accompanied by a moderately fast (on the CV time scale) follow-up chemical reaction.[8] Cyclic voltammograms were also monitored when the return (negative-going) scan was taken to more negative potentials in order to attempt the detection of cationic products that might be reducible. No waves attributable to such species were observed before the solvent/electrolyte discharge limit.

Coulometry and Preparative Electrolysis of 1. Constant-potential coulometry was performed at $E = +0.12$ V vs $E°(\mathbf{1})$ on 1.7−5.0 mM solutions of **1** in acetonitrile/0.05 M $\mathrm{Me_4N^+BF_4^-}$. The measurements yielded $n_{\mathrm{obs}} = 1.12(3)$ F/mol, in quite good agreement with the value of 1 anticipated for a one-electron process. ^{1}H NMR spectra of the concentrated anolyte after electrolysis (see Experimental Section for details) revealed the presence of $\mathrm{CnRh(NCMe)Me_2^+}$ (**2**) and $\mathrm{CnRh(NCMe)_2Me^{2+}}$ (**3**) in a 1:0.33 ratio (eq 4). The charge consumption and the **2**:**3** ratio were independent of the substrate concentration in the range 1.7−5 mM. (Details about the preparation and identification of **2** and **3** are given later.) The electrolyses were furthermore performed at different potentials, $E = -0.04$, +0.12, and +0.33 V vs $E°(\mathbf{1})$, corresponding to positions before, shortly after, and well after the cyclic voltammetry oxidation peak. The charge consumption and the product ratio were again independent of the applied electrode potential. The 1:0.33 ratio would require the passage of 1.25 F/mol of charge, assuming that only neutral organic products are formed. Despite the minor discrepancy between the coulometric n value and that predicted from the observed product ratio, these data taken together are indicative of a somewhat greater than 1 F/mol process.

$$\mathrm{CnRhMe_3} \xrightarrow[\text{(Cp}_2\text{Fe}^+\text{ or electrode)}]{\text{-e}^-\text{, MeCN}} \underset{\text{major}}{\mathrm{CnRh(NCMe)Me_2^+}} + \underset{\text{minor}}{\mathrm{CnRh(NCMe)_2Me^{2+}}} \qquad (4)$$

Preparation and Characterization of $\mathbf{CnRh(NCMe)Me_2^+(BF_4^-)}$ ($\mathbf{2(BF_4^-)}$) and $\mathbf{CnRh(NCMe)_2Me^{2+}(BF_4^-)_2}$ ($\mathbf{3(BF_4^-)_2}$). The compounds $\mathbf{2}(\mathrm{BF_4^-})$ and $\mathbf{3}(\mathrm{BF_4^-})_2$ were prepared in good yields by treating $\mathrm{CnRhMe_3}$ with 1 and 2 equiv, respectively, of $\mathrm{HBF_4{\cdot}Et_2O}$ in acetonitrile (eqs 5 and 6). The ^{1}H NMR spectroscopic characteristics of **2** and **3** in acetonitrile-d_3 were similar, but not identical, to those[5a] of $\mathrm{CnRhMe_2(BF_4)}$ and $\mathrm{CnRhMe(BF_4)_2}$ in dmso-d_6 (in which these species presumably exist as $\mathrm{CnRhMe_2(dmso\text{-}d_6)^+(BF_4^-)}$ and $\mathrm{CnRhMe(dmso\text{-}d_6)_2^{2+}(BF_4^-)_2}$, respectively). In acetonitrile-d_3, the Rh-methyl groups for **1** appear as a doublet at δ −0.50 ($J_{\mathrm{Rh-CH_3}} = 2.5$ Hz). For **2**, the Rh-methyl appears as a doublet at δ 0.32 ($J = 2.2$ Hz), and the coordinated MeCN ligand gives rise to a doublet at δ 2.27 ($J_{\mathrm{Rh-NCMe}} = 0.5$ Hz). For **3**, a further downfield shift to δ 1.53 is observed for the Rh-methyl ($J_{\mathrm{Rh-CH_3}} = 2.2$ Hz), while a MeCN doublet is found at δ 2.44 ($J_{\mathrm{Rh-NCMe}} = 0.4$ Hz). The trend toward lower fields with increasing positive charge at the complex is as might be expected. There was no sign of exchange of the coordinated acetonitrile in **2** or **3** with solvent acetonitrile-d_3, even after 5−7 days at 20 °C. Elemental analysis data and complete ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data for both species are given in the Experimental Section.

$$\mathrm{CnRhMe_3} \xrightarrow{\mathrm{HBF_4{\cdot}Et_2O}} \mathrm{CnRhMe_2(NCMe)^+(BF_4^-)} \qquad (5)$$

$$\mathrm{CnRhMe_3} \xrightarrow[\mathrm{MeCN}]{\mathrm{2HBF_4{\cdot}Et_2O}} \mathrm{CnRhMe(NCMe)_2^{+2}(BF_4^-)_2} \qquad (6)$$

Chemical Oxidation of 1. $\mathrm{CnRhMe_3}$ was oxidized in acetonitrile-d_3 solution using the $\mathrm{BF_4^-}$ salts of $\mathrm{Cp_2Fe^+}$, $\mathrm{^{Me}Cp_2Fe^+}$ ($E_{\mathrm{ox}} = -0.10$ V vs Fc[9]), and $\mathrm{^{Ac}CpCpFe^+}$ ($E_{\mathrm{ox}} = +0.25$ V vs Fc[10]) as oxidizing agents. A solution of the oxidant (4.3−4.4 mM) was added to a solution of **1** (5.0 mM) in acetonitrile. The quantities of the oxidants were adjusted so as to ensure incomplete substrate oxidation. This way, complications that might arise from overoxidation or from the presence of unconsumed paramagnetic oxidant in the ^{1}H NMR spectra were avoided. The only detectable Rh-containing products were again **2** and **3**. The yields of **2** and **3**, as determined by ^{1}H NMR

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[9] $^{\mathrm{Me}}$Cp = (η^5-$\mathrm{C_5H_4Me}$); $^{\mathrm{Ac}}$Cp = (η^5-$\mathrm{C_5H_4COMe}$).

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spectroscopy ($\mathrm{PPN^+BF_4^-}$ as internal standard), were 43 and 26% with ${}^{\mathrm{Me}}\mathrm{Cp_2Fe^+}$ as the oxidant (mass balance for Rh, 91%), 50 and 25% with $\mathrm{Cp_2Fe^+}$ (100% mass balance), and 43 and 17% with ${}^{\mathrm{Ac}}\mathrm{CpCpFe^+}$ (78% mass balance). The "yields" of the neutral ferrocenes could not be evaluated by NMR because they were prone to removal by sublimation during the workup procedure. However, the weighed amount of oxidant that was added corresponds almost perfectly with the charge balance of **2** and **3** (see Experimental Section) for the oxidants ${}^{\mathrm{Me}}\mathrm{Cp_2Fe^+BF_4^-}$ and $\mathrm{Cp_2Fe^+BF_4^-}$, but less well for ${}^{\mathrm{Ac}}\mathrm{CpCpFe^+BF_4^-}$. Considering the less-than-perfect mass balance, particularly for the strongest oxidizing agent (which conceivably might cause undesired side reactions or overoxidation), we conclude that the yields of **2** and **3** are rather insensitive to the identity of the oxidizing agent.

Reactions that were performed in sealed NMR tubes led to the formation of ethane, as indicated by a singlet at δ 0.85. Oxidations with the $\mathrm{BF_4^-}$ salts of $\mathrm{Cp_2Fe^+}$, ${}^{\mathrm{Me}}\mathrm{Cp_2Fe^+}$, and ${}^{\mathrm{Ac}}\mathrm{CpCpFe^+}$ were also performed in a closed vessel, sealed with vacuum stopcocks. The volatiles were analyzed by GC−MS. Thus, all experiments led to the formation of ethane and traces of methane (ca. 1%), regardless of the identity of the oxidizing agent.

Isotope Labeling and Crossover Experiments. A series of labeling experiments were designed to probe the details of the ethane formation. The mass spectrum of the ethane generated during the oxidation of a 1:1 mixture of $\mathrm{CnRh(CH_3)_3}$ (**1**) and $\mathrm{CnRh(CD_3)_3}$ (**1**-d_9) revealed that mostly $\mathrm{CH_3CH_3}$ and $\mathrm{CD_3CD_3}$ were formed; 4−10% of the crossover product $\mathrm{CH_3CD_3}$ was detected in different experiments. This establishes that the reductive elimination that generates ethane takes place almost exclusively in an intramolecular fashion. Since the major Rh-containing product, $\mathrm{CnRhMe_2(NCMe)^+}$, contains *two* methyl groups, this must mean that *methyl group migration, necessary to account for the dimethylrhodium product observed, must occur after the elimination of ethane*. Consequently, the two methyl groups in the major product $\mathrm{CnRhMe_2(MeCN)^+}$ must originate from two different Rh centers. An MS analysis of the scrambled product in the crossover experiment will, therefore, be uninformative. Experiments to be described in the following were designed to probe at what stage the methyl scrambling did occur.

Methyl group transfer frequently occurs between 18-electron metal centers.[4f,11] For example, when $\mathrm{Cp^*Rh(PPh_3)Me_2}$ and $\mathrm{Cp^*Rh(PPh_3)(NCMe)_2{}^{2+}(PF_6^-)_2}$ were mixed, quantitative comproportionation yielding $\mathrm{Cp^*Rh(PPh_3)(NCMe)Me^+PF_6^-}$ was seen after several hours.[4f] The dication $\mathrm{Cp^*Rh(PPh_3)(NCMe)_2{}^{2+}}$ was, however, the exclusive Rh-containing product obtained from the electron-transfer-induced reductive elimination of ethane from $\mathrm{Cp^*Rh(PPh_3)Me_2}$. Given the fact that methyl migration occurred in that system, we deemed it necessary to check whether the monocation $\mathrm{CnRh(NCMe)Me_2{}^+}$ might originate in primary production of $\mathrm{CnRh(NCMe)_2Me^{2+}}$, followed by rapid comproportionation with the substrate $\mathrm{CnRhMe_3}$. However, when the product mixture of an incomplete homogeneous oxidation, containing $\mathrm{CnRh(NCMe)_2Me^{2+}(BF_4^-)_2}$, $\mathrm{CnRh(NCMe)Me_2{}^+BF_4^-}$, and $\mathrm{CnRhMe_3}$ in acetonitrile-d_3, was monitored by ^{1}H NMR spectroscopy over time, no further reaction occurred during a period of 44 h. This establishes that the eventual methyl transfer between these 18-electron species is much too slow to be involved in the electron-transfer-induced reactions (eq 7). The methyl migration that ultimately yields $\mathrm{CnRh(NCMe)Me_2{}^+}$ must, therefore, occur from some transient intermediate en route to the final products $\mathrm{CnRh(NCMe)Me_2{}^+}$ and $\mathrm{CnRh(NCMe)_2Me^{2+}}$.

$$\mathrm{CnRhMe_3 + CnRh(NCMe)_2Me^{2+}} \overset{\text{MeCN}}{\nrightarrow} \mathrm{2\,CnRh(NCMe)Me_2{}^+} \qquad (7)$$

The isotopic purity of **1**-d_9 was checked by the ^{1}H NMR spectrum of **1**-d_9, and we estimate the complex to be better than 99% deuterated at the Rh-methyl groups. The crossover product formation (4−10% $\mathrm{CH_3CD_3}$) discussed in the previous paragraph is, therefore, a significant source of information regarding the reaction mechanism. Two fundamentally different scenarios may lead to $\mathrm{CH_3CD_3}$. One possibility is that it is formed in a minor intermolecular reaction that competes with the intramolecular reaction of $\mathbf{1}^{\bullet+}$. The other possibility is that some methyl scrambling occurs in **1** or $\mathbf{1}^{\bullet+}$ before the elimination of ethane takes place. A mass spectrometry experiment was designed to further illuminate these possibilities.

First, the chemical ionization ($\mathrm{NH_3}$) mass spectra of **1** and **1**-d_9 were obtained. For **1**, a well-defined peak at *m/z* 321 ($\mathrm{M^+ - CH_3 + NH_3}$) was seen. Correspondingly, a peak at *m/z* 327 ($\mathrm{M^+ - CD_3 + NH_3}$) was observed for **1**-d_9; significantly, no signal was found at *m/z* 324, which would be indicative of **1**-d_6 ($\mathrm{M^+ - CD_3 + NH_3}$) or **1**-$d_3$ ($\mathrm{M^+ - CH_3 + NH_3}$).

Next, a 1:1 mixture of **1** and **1**-d_9 was oxidized with an equimolar amount of $\mathrm{Cp_2Fe^+BF_4^-}$ in acetonitrile. Unreacted substrate was isolated from the reaction mixture (see Experimental Section for details) and subjected to the same CIMS analysis. In addition to the peaks seen for **1** and **1**-d_9 alone (see above), the mass spectrum of the mixture showed a rather diagnostic peak at *m/z* 324 which could arise from **1**-d_3 and/or **1**-d_6. In an important control experiment, the mass spectrum of a 1:1 mixture of **1** and **1**-d_9 was obtained. This spectrum displayed peaks at *m/z* 321 and 327 but not at *m/z* 324. The latter findings establish that methyl group scrambling does not occur during the MS analysis. Therefore, the scrambling found in the unoxidized substrate of the **1**:**1**-d_9 mixture shows that partial scrambling occurs as a consequence of the oxidation process. The crossover ($\mathrm{CH_3CD_3}$) ethane may, therefore, arise from intramolecular elimination from the partially scrambled substrate. On this basis, we propose that all ethane elimination occurs in an intramolecular fashion.

Voltammetric Investigation of the Kinetics and Mechanism of the Reaction of $\mathbf{1}^{\bullet+}$. The kinetics and mechanism of the oxidatively induced reaction of $\mathbf{1}^{\bullet+}$ were probed by derivative cyclic voltammetry (DCV).[12] The application of DCV in organometallic chemistry has been previously described in detail, [2e,4f,13] so only a brief description of the technique will be given here. In a DCV analysis of the mechanisms of electrode reactions, the voltage sweep rate ν is adjusted to ν_c, at which the reverse to forward derivative peak current ratio $I'_{\mathrm{r}}/I'_{\mathrm{f}}$ equals a constant value c. The separation between the CV switching potential, E_{switch}, and the reversible electrode potential for the process under investigation, E_{rev}, is fixed for a measurement series (500 mV for the present work, empirically chosen to give access to partially reversible voltammograms over a wide temperature range). The value of ν_c will increase with increasing rate of disappearance of the electrode-generated

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(11) For further examples, see ref 16 in ref 4f.

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Table 1. Rate Constants for the Reactions of $\mathbf{1}^{\bullet+}$ in Acetonitrile/0.1 M $Bu_4N^+PF_6^-$

run 1			run 2		
T (°C)	$\nu_{0.5}$ (V s^{-1})	k (s^{-1})	T (°C)	$\nu_{0.5}$ (V s^{-1})	k (s^{-1})
			−15	0.281	0.393
−5	0.497	0.955	−5	0.820	1.103
0	0.823	1.552	0	1.235	1.631
5	1.359	2.516	5	2.282	2.960
15	3.394	6.066	15	5.338	6.683
25	8.324	14.38	25	12.893	15.60
35	18.851	31.51	35	30.267	35.43

species. For $I'_r/I'_f = 0.5$, one obtains $\nu_{0.5}$, which correlates inversely with the half-life of the electrode-generated species and directly with the rate constant for its disappearance. Measurements of ν_c under different experimental conditions provide information about the reaction order of the homogeneous reaction with respect to the substrate redox couple, activation energies, etc. When the rate law and the stoichiometry of the reaction have been established, a comparison of ν_c data with theoretical working curves can provide the rate constants for the reactions.

A DCV reaction order analysis in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ established that $\nu_{0.5}$ was independent of the substrate concentration in the range 0.5−2.0 mM, implying a first-order reaction with respect to $\mathbf{1}^{\bullet+}$. (One might say, in simple terms, that these measurements entail establishing the half-lives of $\mathbf{1}^{\bullet+}$ over this 4-fold range of concentrations). When the solvent/electrolyte was changed to dichloromethane/0.2 M $Bu_4N^+PF_6^-$, it became clear that the voltammetric response was less well-behaved due to adsorption at the electrode, but we conservatively estimate that the $\nu_{0.5}$ values changed less than 20% when compared to the acetonitrile data. From this, we conclude that there is no appreciable solvent effect on the rate of the reaction of $\mathbf{1}^{\bullet+}$.

Variable-temperature DCV measurements of $\nu_{0.5}$ and $\nu_{0.6}$ in the temperature range from −15 to 35 °C were performed in acetonitrile. Assuming as a first approximation (but vide infra) a purely one-electron oxidation of **1** with clean first-order reaction of $\mathbf{1}^{\bullet+}$ (an EC mechanism), the measured ν data were converted to first-order rate constants by comparison with theoretical data. Data for two variable-temperature measurement series are summarized in Table 1. The Eyring equation was used to extract the kinetic parameters for the reaction. These were (uncertainties given as one standard deviation from the regression analysis) $\Delta H^{\ddagger} = 57.0 \pm 0.9$ kJ/mol, $\Delta S^{\ddagger} = -31.2 \pm 3.0$ J/(K·mol), and $k(20\ °C) = 9.8\ s^{-1}$. (A minor adjustment to the $\Delta S^{\ddagger}$ and k values will be introduced in the Discussion section.)

Discussion

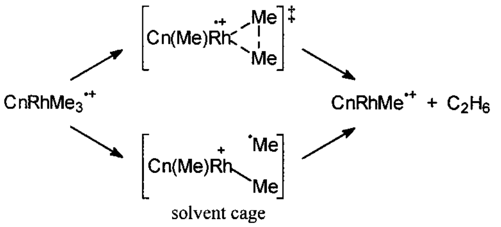
Summary of Important Experimental Results. When a mechanism is postulated for the oxidatively induced reaction of **1**, the following observations must be taken into account and explained: (a) The rate of reaction of $\mathbf{1}^{\bullet+}$ follows first-order kinetics, and solvent effects are small. (b) Ethane is the only significant organic product and is generated by a mechanism that is at least 90% intramolecular. (c) By chemical as well as electrochemical oxidation, somewhat more than 1 F/mol of charge is required for complete consumption of **1**. (d) The product ratio (monocation **2** vs dication **3**) is independent of the electrode potential, the identity of the oxidizing agent, and the order of mixing of reactants for the homogeneous oxidation with $Cp_2Fe^+BF_4^-$. (e) Methyl scrambling in unconsumed substrate suggests that the 4−10% crossover product CH_3CD_3 may be caused by methyl scrambling *before* elimination rather than by a competing intermolecular elimination pathway.

Rate-Limiting Reductive Elimination. Through the experimental findings, it has been established that, after the one-electron oxidation (eq 8), intramolecular elimination of ethane occurs in the rate-determining step (eq 9) to yield the apparently 15-electron product $CnRhMe^{\bullet+}$. One may ask whether the

$$CnRhMe_3 \rightleftharpoons CnRhMe_3^{\bullet+} + e^- \qquad (8)$$

$$CnRhMe_3^{\bullet+} \xrightarrow{k} CnRhMe^{\bullet+} + C_2H_6 \qquad (9)$$

reductive elimination occurs in a one-step, concerted reaction (eq 10, top path) or by a stepwise, homolytic S_H2 pathway (eq 10, bottom), which must occur mostly within a solvent cage to explain the highly intramolecular nature of the reaction. The



(10)

crossover product alone could be taken as evidence for “leakage” from the solvent cage in a two-step process. However, the extremely low yield of methane—a product expected from hydrogen atom abstraction from the solvent after cage leakage—argues against a stepwise mechanism. Furthermore, the somewhat negative entropy of activation of −28 J/(K·mol) is in better agreement with a somewhat ordered transition state of a concerted reaction than with a dissociative homolytic process. (An analogous ambiguity was discussed in our previous paper[4f] on the oxidation of $Cp^*Rh(PPh_3)Me_2$.)

Any consideration of what happens after the rate-determining step must necessarily be based, in part, on educated speculation. A variety of mechanistic possibilities are conceivable. However, a rather simple picture can serve to explain all experimental results.

The highly unsaturated species $CnRhMe^{\bullet+}$ probably coordinates a solvent molecule to yield a less unsaturated 17-electron species $CnRhMe(NCMe)^{\bullet+}$ (eq 11). Alternatively, the coun-

$$CnRhMe^{\bullet+} + MeCN \xrightarrow{\text{rapid}} CnRhMe(NCMe)^{\bullet+} \qquad (11)$$

terion[14] may coordinate at the metal center. (The proposed solvent or counterion coordination, while not proven, will have no profound effect on the major features of the later steps of the mechanism to be proposed.)

Disregarding, for a moment, the formation of the monocationic product **2**, the coordination of a *second* solvent molecule to yield 19-electron $CnRhMe(NCMe)_2^{\bullet+}$ at first sight might provide an attractive, direct route to the dicationic product **3** through a simple one-electron oxidation. Despite the fact that the interconversion between 17- and 19-electron species (the latter often quite strong reducing agents) via ligand association/dissociation is well documented,[15] we consider this scenario unlikely in this particular case. We find that the dication **3**

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(14) (a) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

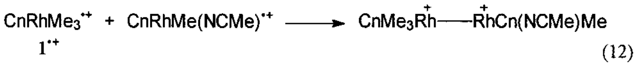
(15) For some pertinent reviews, see: (a) *Organometallic Radical Processes*; Trogler, W. C. Ed.; Elsevier: Amsterdam, 1990. (b) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (c) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: Weinheim, Germany, 1995.

cannot be electrochemically reduced before solvent/electrolyte reduction commences. This shows that the immediate reduction product of **3**, the 19-electron species CnRhMe(NCMe)$_2^{\bullet+}$, is energetically rather inaccessible. Quantitative data are not at hand, but we conclude that the 19-electron adduct is likely to be so high in energy that it cannot exist in concentrations sufficiently high to render it a kinetically competent intermediate. Another argument against an outer-sphere oxidation of CnRhMe(NCMe)$_2^{\bullet+}$ or its 17-electron precursor CnRhMe(NCMe)$^{\bullet+}$ is the independence of the **2**:**3** ratio on the reaction conditions.

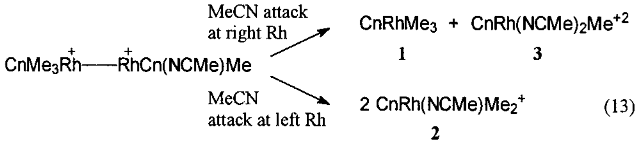
The fact that the **2**:**3** ratio does not depend on the electrode potential during exhaustive electrolysis experiments can be readily understood: the lifetime of **1**$^{\bullet+}$ is about 0.1 s at ambient temperature. Under the experimental conditions of vigorous stirring, the cation can be efficiently removed from the electrode surface before the homogeneous reaction occurs to any significant extent. Thus, the homogeneous chemistry—including the production and consumption of any reactive intermediates—will take place in the bulk solution, and the outcome should be electrode potential independent (as long as the final products are not electroactive).

The observation that the **2**:**3** product ratio is independent of the identity of the oxidant or of the order of mixing the reactants is particularly intriguing and, at first, not so readily understood. The fact that the doubly oxidized, dicationic product **3** is *not produced in greater quantities* when a stronger oxidant is used, or when an excess oxidizing agent is present during most of the reaction (such as when a solution of **1** was added slowly to a solution of the Cp$_2$Fe$^+$ oxidant), is a strong indication that dication formation is not the result of two successive outer-sphere electron transfer processes. Rather, it can be argued that a common intermediate lies at the branching point of two reaction channels and that the branching ratio does *not* depend on the oxidant. A consistent view can be provided when a doubly charged, dinuclear species is invoked as this key intermediate.

The substrate cation radical CnRhMe$_3^{\bullet+}$ and the proposed acetonitrile adduct CnRhMe(NCMe)$^{\bullet+}$ are 17-electron species and can attain a closed-shell (18-electron) configuration through radical—radical coupling processes. A dimerization of CnRhMe$_3^{\bullet+}$ itself is ruled out because second-order kinetics should result. Dimerizations of the reductive elimination “product” CnRhMe$^{\bullet+}$ or its acetonitrile adduct CnRhMe(NCMe)$^{\bullet+}$ cannot be ruled out but will be unlikely if they are generated in low steady-state concentrations. On the other hand, the half-life of CnRhMe$_3^{\bullet+}$ is known through the kinetics measurements to be on the order of 0.1 s at ambient temperature, and this species should have ample time to react, even with quite short-lived intermediates in second-order processes. Many organometallic radicals undergo rapid dimerization reactions,[16] including some cationic species.[17] We propose, at this point, that a dinuclear species is formed by a radical—radical coupling of CnRhMe$_3^{\bullet+}$ and CnRhMe(NCMe)$^{\bullet+}$. The dimer may possess a metal—metal bond, as suggested for simplicity in eq 12, or (perhaps more likely for steric reasons) it may be supported by methyl bridges. Solvent attack at the rightmost Rh center of the dimer (eq 13, top path) will lead to dication formation and regeneration of a substrate molecule. The combined dimerization and heterolysis according to this pathway may be viewed as an inner-sphere electron transfer. Alternatively, acetonitrile attack at the left Rh center accompanied by a methyl group transfer from the left to the right and metal—metal bond rupture would yield two molecules of the monocationic product (eq 13, lower path). The branching ratio starting from the dinuclear intermediate should be independent of the exact reaction conditions, and thus a rather constant **2**:**3** product ratio should result.



$$\underset{\mathbf{1}^{\cdot+}}{\mathrm{CnRhMe_3^{\cdot+}}} + \mathrm{CnRhMe(NCMe)^{\cdot+}} \longrightarrow \mathrm{CnMe_3\overset{+}{Rh}—\overset{+}{Rh}Cn(NCMe)Me} \qquad (12)$$



(13)

The proposed dinuclear intermediate also serves to rationalize the observed methyl scrambling in unconsumed substrate during the oxidation of the **1**:**1**-d_9 mixture. First, methyl groups might migrate between the Rh centers in the dinuclear intermediate. Reaction 13 will then regenerate **1** in which methyl scrambling has occurred. Alternatively, methyl migration between the two centers may also occur as a consequence of possible reversible dimer formation: after methyl exchange between the left and right Rh centers in the dinuclear species, dimer dissociation would generate **1**$^{\bullet+}$ with scrambled methyl. A simple electron exchange with unscrambled, neutral **1** will finally give scrambled **1**.

In order to account for a 1:0.33 ratio of **2** and **3**, as found by exhaustive constant-potential electrolysis, the branching must be such that 40% of the dinuclear intermediate reacts according to eq 13, upper path (each dinuclear unit gives *one* molecule of **3**), and 60% according to eq 13, lower path (each dinuclear unit gives *two* molecules of **2**). If this is taken into consideration, a small adjustment of the kinetic parameters obtained by the electrochemical analysis is needed. All the k values that were determined (the original determinations in the Results section were based on the *unimolecular* reaction of **1**$^{\bullet+}$ according to eq 9) must be multiplied by 0.6 to take into account the fact that, of the cation radicals that are consumed according to eq 9, 60% will cause the consumption of another cation radical according to eq 13. This will have no effect on $\Delta H^{\ddagger}$, whereas $\Delta S^{\ddagger}$ will be slightly more negative. The kinetic parameters will then be $\Delta H^{\ddagger} = 57.0 \pm 0.9$ kJ/mol, $\Delta S^{\ddagger} = -35.4 \pm 3.0$ J/(K·mol) and $k(20\ ^\circ\mathrm{C}) = 5.9\ \mathrm{s}^{-1}$. The adjustment has no influence on the conclusions based on the past discussion.

Concluding Remarks. The initial one-electron oxidation of CnRhMe$_3$ triggers the largely intramolecular reductive elimination of ethane. This is another example showing that apparently uncomplicated intramolecular reductive eliminations of hydrocarbons can be initiated by single-electron transfer events, as described by us previously.[4f−h] However, in the present work, the situation is more complicated than what immediately meets the eye because of the methyl scrambling that occurs before the rate-limiting elimination, and by the presence of mono- as well as dicationic organometallic products. The overall results emphasize the need to closely scrutinize the mechanism of formation of minor products, as well as the major ones. It is only when this is done that it is possible to understand in detail these fundamentally important reaction types.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum line, Schlenk, syringe,

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(16) (a) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187. (b) Scott, S. L.; Espenson, J. H.; Zhu, Z. L. *J. Am. Chem. Soc.* **1993**, *115*, 1789. (c) Richards, T. C.; Geiger, W. E.; Baird, M. C. *Organometallics* **1994**, *13*, 4494. (d) Peters, J.; George, M. W.; Turner, J. J. *Organometallics* **1995**, *14*, 1503. (e) Barbini, D. C.; Tanner, P. S.; Francone, T. D.; Furst, K. B.; Jones, W. E., Jr. *Inorg. Chem.* **1996**, *35*, 4017.

(17) See ref 13a and ref 15 cited therein.

or drybox techniques. Acetonitrile was distilled from P_2O_5, and acetonitrile-d_3, dichloromethane, and dichloromethane-d_2 were distilled from CaH_2. Acetonitrile and dichloromethane containing the supporting electrolyte were passed through a column of active neutral alumina prior to use to remove water and protic impurities before electrochemical measurements. The electrolyte was freed of air by purging with purified solvent-saturated argon, and all measurements and electrolyses were carried out under a blanket of argon.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Advance DXP 200 or 300 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standards. IR spectra were obtained on a Nicolet Magna-IR 550 FT-IR spectrometer. GLC analyses were done on a Hewlett Packard 5710A gas chromatograph using a 30 m × 0.54 mm Megabore GS-Q capillary column. Melting points were measured on an Electrothermal digital melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

Electrochemical measurements were performed with an EG&G-PAR Model 273 potentiostat/galvanostat driven by an external HP 3314A sweep generator. The signals were fed to a Nicolet 310 digital oscilloscope and processed by an on-line personal computer. The working electrodes were Pt disk electrodes ($d = 0.4-1.0$ mm), the counter electrode was a Pt wire, and the Ag wire reference electrode assembly was filled with acetonitrile/0.01 M $AgNO_3$/0.1 M $Bu_4N^+PF_6^-$. The reference electrode was calibrated against Cp_2Fe, which is also used as the reference in this work. The positive-feedback *iR* compensation circuitry of the potentiostat was employed; the separation of anodic and cathodic peak for the Cp_2Fe oxidation was 59−61 mV in acetonitrile.

Mass spectroscopic analysis was performed on a Fisons VG ProSpec-Q mass spectrometer. The GC−MS analysis was performed with a Fisons GC 8000 gas chomatograph (5 m × 0.25 mm Chrompack CP-SIL fused silica column) interfaced to the same mass spectrometer.

The compounds $Cp_2Fe^+PF_6^-$, $Cp_2Fe^+BF_4^-$, $^{Me}Cp_2Fe^+BF_4^-$, and $^{Ac}CpCpFe^+BF_4^-$ were prepared from the appropriately substituted ferrocene and $AgPF_6$ or $AgBF_4$.[10] A modification[18] of the literature procedure[5a] was used for preparing $CnRhMe_3$. In the modified procedure, $CnRhCl_3$ is more conveniently methylated, and improved yields result when using Me_2Mg instead of halide-free MeLi in THF. The same applies to $CnRhMe_3$-d_9.

$CnRhMe_2(NCMe)^+BF_4^-$ (2(BF_4^-)). The procedure is a modification of that used for preparing $CnRhMe_2BF_4$ in dichloromethane.[5a] A solution of $HBF_4{\cdot}Et_2O$ (51 mg, 0.31 mmol) in acetonitrile (1 mL) was added dropwise to a stirred solution of $CnRhMe_3$ (100 mg, 0.31 mmol) in acetonitrile/dichloromethane (2:1, 6 mL) at −14 °C. The mixture was stirred for 5 min before being slowly warmed to ambient temperature. After 1.5 h, the solvent was removed by vacuum transfer. The oily residue was washed with benzene (2 mL) to remove unreacted starting material, dissolved in dichloromethane (10 mL), and filtered through Celite. The product was recrystallized from dichloromethane/ether to give yellow crystals (108 mg, 81%): mp 158−161 °C; ^{1}H NMR (200 MHz, acetonitrile-d_3) δ 0.32 (d, $J = 2.2$ Hz, 6 H, Rh*Me*), 2.27 (d, $J = 0.5$ Hz, 3 H, *Me*CN), 2.39 (d, $J = 1.5$ Hz, 3 H, N*Me*), 2.69 (s, 6 H, N*Me*), 2.76 (apparent s, 8 H, N*CH$_2$*), 2.91 (br m, 4 H, N*CH$_2$*); ^{13}C{^{1}H} NMR (50 MHz, DMSO-d_6) δ 1.0 (d, $J_{Rh-Me} = 28$ Hz, Rh*Me*), 3.1 (*Me*CN), 48.3 (2 N*Me*), 50.1 (1 N*Me*), 54.9 (N*C*H$_2$), 57.5 (N*C*H$_2$), 61.8 (N*C*H$_2$); IR (MeCN) ν_{CN} 2290 (w) cm^{-1}. Anal. Calcd for $C_{13}H_{30}BF_4N_4Rh$: C, 36.13; H, 7.00; N, 12.97. Found: C, 36.29; H, 6.92; N, 13.05.

$CnRhMe(NCMe)_2^{2+}(BF_4^-)_2$ (3(BF_4^-)$_2$). The procedure is a modification of that used for preparing $CnRhMe(BF_4)_2$ in dichloromethane.[5a] A solution of $HBF_4{\cdot}Et_2O$ (30 mg, 0.185 mmol) in acetonitrile (1 mL) was added dropwise to a stirred suspension of $CnRhMe_3$ (29.6 mg, 0.093 mmol) in acetonitrile (4 mL) at −48 °C. The mixture was stirred for 5 min, whereupon the cooling bath was removed and stirring was continued until all starting material had dissolved (ca. 10 min). The solvent was removed by vacuum transfer, and the residue was washed with dichloromethane (2 × 2 mL) and recrystallized from acetonitrile/THF to yield the product as white crystals (149 mg, 56%): mp 253 °C (beginning of slow dec); ^{1}H NMR (200 MHz, acetonitrile-d_3) δ 1.53 (d, $J = 2.2$ Hz, 3 H, Rh*Me*), 2.44 (d, $J = 0.4$ Hz, 6 H, *Me*CN), 2.67 (d, $J = 1.2$ Hz, 6 H, N*Me*), 2.96 (s, 3 H, N*Me*), 3.0−3.15 (m, 12 H, N*CH$_2$*); ^{13}C{^{1}H} NMR (50 MHz, acetonitrile-d_3) δ 4.8 (*Me*CN), 8.5 (d, $J_{Rh-Me} = 21$ Hz, Rh*Me*), 49.7, 53.2, 56.2, 62.1, 65.1, 126.9 (Me*CN*); IR (MeCN) ν_{CN} 2328 (m), 2301 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{30}B_2F_8N_5Rh$: C, 30.86; H, 5.55; N, 12.85. Found: C, 31.55; H, 5.57; N, 12.78.

Oxidation of $CnRhMe_3$ with $Cp_2Fe^+BF_4^-$, $^{Me}Cp_2Fe^+BF_4^-$, and $^{Ac}CpCpFe^+BF_4^-$. (i) Gas Analysis. A solution of **1** (51.1 mg, 0.16 mmol) was prepared in acetonitrile (32 mL). The solution was evenly distributed into four Schlenk flasks equipped with rubber septa. Each of the oxidizing agents $^{Me}Cp_2Fe^+BF_4^-$ (10.3 mg, 34.2 μmol), $Cp_2Fe^+BF_4^-$ (9.6 mg, 35.2 μmol), and $^{Ac}CpCpFe^+BF_4^-$ (11.0 mg, 34.9 μmol) was dissolved in acetonitrile (8 mL). The oxidizing solutions were added dropwise to the solutions of **1** with stirring. The reactions were complete within seconds, and the gas phase was imediately analyzed by GLC. In all cases, the ethane:methane ratio was greater than 98.5:1.5.

(ii) Quantitative Yields by NMR. A solution of **1** (25.2 mg, 78.9 μmol) and $PPN^+BF_4^-$ (3.9 mg, 6.2 μmol, internal standard) was prepared in acetonitrile (32 mL). The solution was distributed equally (i.e., 19.7 μmol in each) into four round-bottom flasks with magnetic stirbars. Each of the oxidizing agents $^{Me}Cp_2Fe^+BF_4^-$ (5.7 mg, 18.9 μmol), $Cp_2Fe^+BF_4^-$ (5.2 mg, 19.1 μmol), and $^{Ac}CpCpFe^+BF_4^-$ (6.0 mg, 19.1 μmol) was dissolved in acetonitrile (8 mL). The oxidizing solutions were added dropwise to the solutions of **1** with stirring, whereupon the reactions took place immediately. The solvents were removed in vacuo. The residues were dissolved in acetonitrile-d_3, and the ^{1}H NMR spectra were recorded. The yields of **2** and **3** and the overall mass balance for Rh were determined from their integrated Rh*Me* signals as well as the CnRh*Me*$_3$ signal for the unoxidized solution relative to $PPN^+BF_4^-$. The results were as follows:

(a) $^{Me}Cp_2Fe^+BF_4^-$ Oxidant. The yields were 43% **2**, 26% **3**, and 22% **1** remaining (91% mass balance). By charge balance (charge consumed = % yield of **2** + 2 × % yield of **3**), these yields correspond to the consumption of 18.7 μmol of oxidant.

(b) $Cp_2Fe^+BF_4^-$ Oxidant. The yields were 50% **2**, 25% **3**, and 25% **1** remaining (100% mass balance). By charge balance, these yields correspond to the consumption of 19.7 μmol of oxidant.

(c) $^{Ac}CpCpFe^+BF_4^-$ Oxidant. The yields were 43% **2**, 17% **3**, and 18% **1** remaining (71% mass balance). By charge balance, these yields correspond to the consumption of 15.2 μmol of oxidant. The discrepancy between this number and the actual quantity of oxidant added may be traced to the rather poor mass balance.

$Cp_2Fe^+PF_6^-$ Oxidation of $CnRhMe_3$. Concentration Effects. An acetonitrile/dichloromethane (1:4) solution was used in order to fully dissolve both reactants before mixing.

(a) Gradual Addition of Oxidant to 1. $Cp_2Fe^+PF_6^-$ (10.0 mg, 29.8 μmol) was dissolved in 0.5 mL of an acetonitrile/dichloromethane (1:4) mixture and added dropwise to a solution of **1** (10.0 mg, 31.3 μmol) in the same solvent mixture (2 mL) under vigorous stirring.

(b) Gradual Addition of 1 to the Oxidant. A solution of **1** (10.0 mg, 31.3 μmol) in an acetonitrile/dichloromethane (1:4) mixture (0.5 mL) was added dropwise to a solution of $Cp_2Fe^+PF_6^-$ (10.0 mg, 29.8 μmol) in the same solvent mixture (2 mL) under vigorous stirring.

The solvents were removed in vacuo, and the residues were dissolved in acetonitrile-d_3 and filtered through Celite. ^{1}H NMR spectra were recorded. The **2**:**3** product ratio was 62:38 for experiment a and 61:39 for experiment b.

Constant-Potential Coulometry and Electrolysis of 1. These experiments were conducted in an H-shaped cell, the two 20-mL compartments of which were separated by a medium-porosity sintered glass filter. A platinum gauze working electrode was used. Stirring was effected by a vigorous argon flush through the solution in the working electrode compartment. The solvent/electrolyte was acetonitrile/0.05 $Me_4N^+BF_4^-$ (this electrolyte was chosen because of the relatively limited solubility even in acetonitrile, facilitating analysis of the electrolysis products by ^{1}H NMR spectroscopy without complete removal of the electrolyte).

Constant-potential coulometry was conducted on 1.7, 3.4, and 5.0 mM solutions of **1** at 20 °C at an electrode potential of +0.12 V vs

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(18) Flood, T. C. Private communication.

$E°$(**1**). Exhaustive electrolyses yielded n_{ox} = 1.12(3) F/mol. The solution in the working compartment was withdrawn with a pipet, the solvent was concentrated to about one-third of the original volume, and the solution was filtered through a glass wool plug. The remaining solvent was removed in vacuo. The solid was triturated with ca. 0.5 mL of acetonitrile-d_3. The **2**:**3** ratio was determined from the integrated Rh*Me* signals in the ^{1}H NMR spectra and are given in the Results section.

The same procedure was applied to the constant-potential electrolysis when **1** was oxidized at −0.04, +0.12, and +0.33 V vs $E°$(**1**). For this series, n_{ox} = 1.10(2). Product distributions are given in the Results section.

Homogeneous Oxidation of a Mixture of CnRhMe$_3$ (1) and CnRh(CD$_3$)$_3$ (1-d_3). Gas Analysis. A mixture of **1** (3.3 mg, 10 μmol) and **1**-d_9 (3.4 mg, 10 μmol) was dissolved in acetonitrile (2.5 mL) and kept in a round-bottom flask equipped with a rubber septum. A solution of $Cp_2Fe^+BF_4^-$ (7.2 mg, 25.9 μmol) in acetonitrile (0.75 mL) was added with a syringe. An aliquot of the gas phase above the reaction mixture was immediately withdrawn by syringe and injected into the GC−MS instrument. Signals due to the isotopomers CH_3CH_3 and CD_3CD_3 dominated the spectrum, whereas signals due to CH_3CD_3 were present to a lesser extent (4−10% for repeated experiments).

Mass Spectrometry Analysis of Recovered 1 after Incomplete Oxidation of a Mixture of CnRhMe$_3$ (1) and CnRh(CD$_3$)$_3$ (1-d_3). The solution obtained in the crossover experiment described above was evaporated to dryness and held under vacuum to remove the ferrocene by sublimation. A ^{1}H NMR spectrum of a small sample of the solid revealed the presence of **1**, **2**, and **3**, as seen in other oxidation experiments. The remaining **1** (and isotopomers) was separated from the ionic product by extraction with ether. The ether solution was evaporated to dryness, and the solid residue was subjected to a mass spectrometry analysis (chemical ionization with NH_3) that revealed the presence of isotopomers of **1**, as described in the Results section.

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