Oxidatively Induced Reductive Eliminations. Kinetics and Mechanism of the Elimination of Ethane from the 17-Electron Cation Radical of $Cp^*Rh(PPh_3)(CH_3)_2$

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The dimethylrhodium compound $Cp^*Rh(PPh_3)(CH_3)_2$ (1; $Cp^* = \eta^5\text{-}C_5Me_5$) undergoes an overall 2-electron oxidation at 0.04 V vs the ferrocene/ferrocenium (Fc) couple in 9:1 acetonitrile/dichloromethane, 0.1 M $Bu_4N^+PF_6^-$. The oxidation results in the intramolecular reductive elimination of ethane and yields $Cp^*Rh(PPh_3)(NCMe)_2{}^{2+}$ (2) as the Rh-containing product. A mechanistic and kinetic investigation of the reaction by derivative cyclic voltammetry (DCV) showed the reductive elimination to be a first-order reaction with respect to $1^{\bullet+}$. Very small solvent effects (acetonitrile, acetone, THF, dichloromethane) on the reaction rate indicated the nonintervention of 19-electron species in the reductive elimination. The DCV analysis provided kinetic parameters $k(20\ °C) = 96 \pm 3\ s^{-1}$, $\Delta H^{\ddagger} = 53.1 \pm 0.8$ kJ/mol, and $\Delta S^{\ddagger} = -25.9 \pm 3.3$ J/(K·mol) in acetonitrile. The data are interpreted in terms of a direct, concerted elimination of ethane from the 17-electron cation radical $1^{\bullet+}$. It is estimated that the rate of reductive elimination has been increased by a factor of at least 3×10^9 due to the oxidation of 1 to $1^{\bullet+}$. In dichloromethane, the intramolecular elimination of ethane was initiated by an overall 1-electron process. The major product in this case was $Cp^*Rh(PPh_3)(CH_3)X^+$ (X most likely is coordinated dichloromethane or the counterion PF_6^-) as a result of a secondary intermolecular methyl-transfer process. The methyl transfer was mimicked by a quantitative (^1H NMR) reaction between 1 and 2 which yielded $Cp^*Rh(PPh_3)(NCMe)CH_3{}^+$ (3).

Introduction

Reductive elimination reactions constitute a fundamental reaction type in organotransition-metal chemistry.[1] Oxidatively induced reductive elimination reactions are commonly encountered, a phenomenon that may be rationalized by the simple argument that an increase in the oxidation state of a metal center should enhance its tendency to undergo reductive elimination. The oxidative activation may be achieved by the addition of electrophiles like H^+ or halogens at electron-rich metal centers, as well as by the oxidative addition of symmetrical or unsymmetrical reagents X–Y at unsaturated metal centers. However, in this paper we will be specifically concerned with *oxidative activation by electron transfer*.

The importance of odd-electron species in the reactions of organotransition-metal species has been widely appreciated during the last decade.[2] Accumulated evidence has established that much of the behavior of odd-electron complexes may be described in terms of 17/19-electron interconversions. When compared with their 18-electron counterparts, the 17-electron species frequently are significantly activated toward reactions such as ligand substitution, CO insertion, and structural and geometrical isomerizations.[2-5] The involvement of 19-electron intermediates is commonly invoked in these reactions.

The 1-electron oxidation of organotransition-metal complexes containing σ-bonded ligands may result in a variety of reactions that all represent different modes of reductive elimination. The deprotonation of 17-electron metal hydride cation radicals,[6] generated by the oxidation

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[4] For key references to CO insertion chemistry in 17/19 electron complexes, see the reviews in ref 2 and: (a) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* 1982, *104*, 5790. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* 1983, *2*, 460. (c) Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* 1985, *4*, 374. (d) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* 1986, *108*, 1940. (e) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* 1987, *109*, 5127. (f) Golovin, M. N.; Meirowitz, R.; Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* 1987, *6*, 2285. (g) Donovan, B. T.; Geiger, W. E. *Organometallics* 1990, *9*, 865. (h) Tracey, A. A.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* 1990, *9*, 1399. (i) Prock, A.; Giering, W. P.; Greene, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. C.; Wilson, M.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* 1991, *10*, 3479.

[5] For some recent examples of electron-transfer induced isomerizations, see: (a) Bond, A. M.; Colton, R.; Kevekordes, J. E. *Inorg. Chem.* 1986, *25*, 749. (b) Vallat, A.; Person, M.; Roullier, L.; Laviron, E. *Inorg. Chem.* 1987, *26*, 332. (c) Rieke, R. D.; Kojima, H.; Saji, T.; Rechberger, P.; Öfele, K. *Organometallics* 1988, *7*, 749. (d) Bond, A. M.; Colton, R.; Mann, T. F. *Organometallics* 1988, *7*, 2224. (e) Kuchynka, D. J.; Kochi, J. K. *Organometallics* 1989, *8*, 677. (f) Bond, A. M.; Colton, R.; Feldberg, S. W.; Mahon, P. J.; Whyte, T. *Organometallics* 1991, *10*, 3320.

[6] (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* 1980, *102*, 208. (b) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* 1990, *112*, 2618. (c) Ryan, O. B.; Tilset, M.; Parker, V. D. *Organometallics* 1991, *10*, 298. (d) Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* 1991, *113*, 9554. (e) Westerberg, D. E.; Rhodes, L. F.; Edwin, J.; Geiger, W. E.; Caulton, K. G. *Inorg. Chem.* 1991, *30*, 1107.

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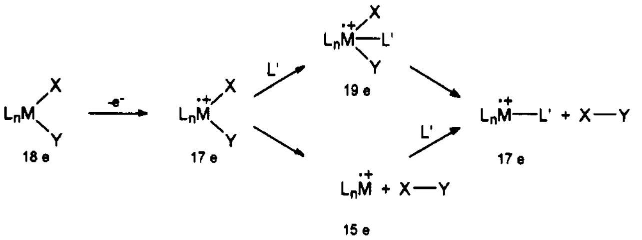
Scheme I



of stable 18-electron hydrides, represents a formal 2-electron reduction of the metal. Metal alkyls and other complexes can undergo homolysis, which involves a formal 1-electron reduction of the metal.[7] Homolysis reactions may involve 19-electron intermediates.[7f,g] Finally, the "normal" type of reductive elimination in which two σ-bonded ligands X and Y are eliminated as X–Y may also result.[8] A particularly interesting system was provided by Kochi and co-workers in their investigation of the reactivity of *cis*-(bpy)$_2$FeEt$_2$.[8d] The neutral compound underwent β-elimination yielding ethene and ethane. On the other hand, the isolable cation radical yielded products derived from Fe–C homolysis reactions, whereas the unstable dication underwent smooth reductive elimination producing *n*-butane.

A plethora of mechanisms are available for reductive elimination reactions in even-electron systems.[1] When 17-electron systems are considered, one fundamental question that may be posed is whether 19-electron intermediates are involved or not. If reductive elimination from a 17-electron species were to proceed directly, a highly unsaturated 15-electron product would result. This unsaturated product presumably could be avoided by prior ligand coordination to yield a 19-electron intermediate, because reductive elimination from a 19-electron complex would produce a less unsaturated, and presumably more stable, 17-electron product (Scheme I). Assuming that product stability is reflected in the energy of the transition state for the reductive elimination, 17/19-electron conversions certainly deserve to be considered for this reaction type. We note that Kochi has suggested that initial solvent ligation takes place in the elimination of biaryls from Ar$_2$NiL$_2$ complexes, initiated by 1-electron oxidation to the 15-electron cation radicals.[8b] In this case, the formation of a 13-electron (!) product is averted by prior ligand coordination. To our knowledge, the possible assistance by external ligands in oxidatively induced reductive elimination reactions has not been previously explored by detailed kinetic and mechanistic analyses.

In this paper, we describe the details of a study of the mechanism of the reductive elimination of ethane from the cation radical of Cp*Rh(PPh$_3$)(CH$_3$)$_2$ (1; Cp* = η^5-C$_5$Me$_5$). In particular, the possible intervention of 19-electron intermediates has been addressed. During the investigation of this process, we discovered an unexpected comproportionation reaction of 1 and the product formed from the 2-electron oxidation of 1 in acetonitrile, Cp*Rh(PPh$_3$)(NCMe)$_2$$^{2+}$. Details about this reaction, which quantitatively produces Cp*Rh(PPh$_3$)(NCMe)CH$_3$$^+$ and bears direct relevance on the oxidation chemistry of 1 in dichloromethane, are also presented.

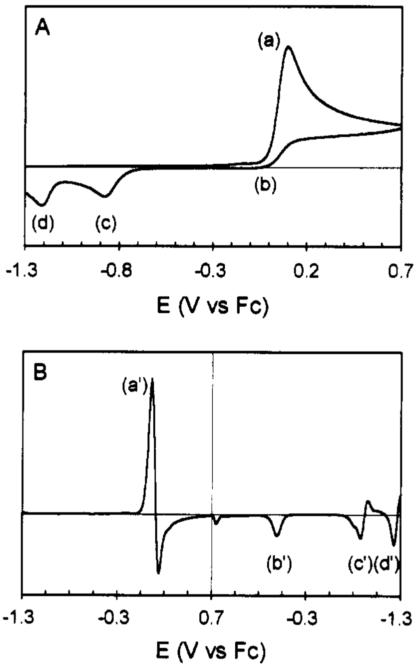


Figure 1. Cyclic voltammogram (A) and derivative cyclic voltammogram (B) for the oxidation of Cp*Rh(PPh$_3$)(CH$_3$)$_2$ (1.0 mM) in 9:1 acetonitrile/dichloromethane, 0.1 M Bu$_4$N$^+$PF$_6$$^-$ at a Pt disk microelectrode (d = 0.6 mm) at 20 °C and a voltage sweep rate v = 1.0 V/s.

Results and Discussion

Electrochemical Oxidation of Cp*Rh(PPh$_3$)(CH$_3$)$_2$ (1). The initial electrochemical analysis was carried out in 9:1 acetonitrile/dichloromethane with 0.1 M Bu$_4$N$^+$PF$_6$$^-$ as the supporting electrolyte. The role of the dichloromethane was to improve substrate solubility. Figure 1A shows a cyclic voltammogram for the oxidation of 1 (20 °C, 0.6 mm diameter Pt disk microelectrode, voltage sweep rate v = 1.0 V/s). Peak a corresponds to the oxidation of 1. The absence of a matching peak for the reduction of 1$^{\cdot+}$ to 1 at position b indicates that 1$^{\cdot+}$ is rapidly consumed by a follow-up reaction on the cyclic voltammetry time scale. Peaks c and d arise from a product formed during the follow-up reaction of 1$^{\cdot+}$ and will be discussed later. Figure 1B depicts a derivative cyclic voltammetry[9] (DCV) trace for the same process. The cyclic voltammetry peak potential in this case is represented by the point at which the rapidly descending DCV curve crosses the base line after the derivative peak a′. Although it is not so obvious in the voltammograms recorded at v = 1 V/s, the DCV curve is free of the double-layer charging current that makes the base line ill-defined during fast-scan cyclic voltammetry experiments, especially during the reverse

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[8] (a) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* 1975, *97*, 7262. (b) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* 1978, *100*, 1634. (c) Almemark, M.; Åkermark, B. *J. Chem. Soc., Chem. Commun.* 1978, 66. (d) Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* 1982, *1*, 155. (e) Ishikawa, K.; Fukuzumi, S.; Tanaka, T. *Inorg. Chem.* 1988, *28*, 1661. (f) Burk, M. J.; Tumas, W.; Ward, M. D.; Wheeler, D. R. *J. Am. Chem. Soc.* 1990, *112*, 6133.

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scan. This significantly enhances the ease with which voltammetric techniques may be applied to study the kinetics of electrode reactions.[10]

At the higher voltage sweep rate $v = 50$ V/s, the oxidation process appeared to be near-reversible in the chemical and in the Nernstian sense. The cyclic voltammetry peak current was 90% of the intensity that was measured for the 1-electron oxidation of an equimolar solution of ferrocene under identical conditions. The separation between the anodic and cathodic cyclic voltammetry peak potentials as well as the derivative current peak width at half-height were nearly identical to the corresponding values for ferrocene. The chemical reversibility was manifested by a near-unity cathodic to anodic derivative peak–current ratio. This constrasts the situation in Figure 1, in which the cathodic to anodic peak–current ratio and derivative peak–current ratio are clearly less than unity at $v = 1.0$ V/s. The oxidation potential for **1**, taken to be the midpoint between the oxidation and reduction waves at 50 V/s, was located at 0.04 V vs the ferrocene/ferrocenium couple (Fc).

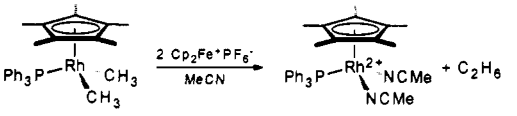
Constant-current coulometry experiments (9:1 acetonitrile/dichloromethane, 0.1 M $Bu_4N^+PF_6^-$) in which the substrate disappearance was monitored by DCV required the passage of 1.8 faraday/mol of charge for complete consumption of the substrate, in reasonable agreement with an overall 2-electron, rather than a 1-electron, process on this time scale (5–10 min). When the coulometry experiment was performed in dichloromethane/0.2 M $Bu_4N^+PF_6^-$, 1.8 faraday/mol of charge was again consumed.

A preparative-scale electrolysis in acetonitrile, followed by workup of the reaction mixture (see Experimental Section for details), led to an inseparable product mixture which by ^1H NMR spectroscopy consisted mostly of $Cp^*Rh(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$. A description of the independent synthesis and characterization of this compound follows in the next paragraph.

Chemical Oxidation of $Cp^*Rh(PPh_3)(CH_3)_2$ in Acetonitrile. Synthesis and Characterization of $Cp^*Rh(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (2(PF_6^-)$_2$). When a suspension of **1** in acetonitrile-d_3 was treated with 1 equiv of $Cp_2Fe^+PF_6^-$, the immediately acquired ^1H NMR spectrum revealed that only 50% of the substrate had been consumed and showed the presence of a product that, in addition to the rather noninformative phenyl signals, gave rise to a Cp* resonance at δ 1.46 (d, $J = 3.9$ Hz) along with a singlet at δ 0.85 indicative of the formation of ethane. When 2 equiv of $Cp_2Fe^+PF_6^-$ was added, complete substrate conversion occurred, and the same product signals were observed. The product yield of the Cp* containing species was found to be greater than 95% (^1H NMR) when hexamethylbenzene was added as an internal standard for product quantification. When the reaction was carried out in acetonitrile, followed by isolation of the product and analysis by ^1H NMR spectroscopy, the product displayed signals at δ 1.46 (d, $J = 3.9$ Hz, 15 H) and 2.14 (s, 6 H). The latter gradually disappeared as a result of exchange with the solvent. This information suggests that the identity of the product was $Cp^*Rh(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (**2**(PF_6^-)$_2$). Further support for this formulation was provided by the independent, high-yield synthesis of **2**(PF_6^-)$_2$ by iodide abstraction from $Cp^*Rh(PPh_3)I_2$ with 2 equiv of $AgPF_6$ in acetonitrile (see Experimental Section).[11]

Analysis of the volatiles from the ferrocenium oxidation of **1** by GLC and mass spectrometry verified that ethane had been produced. There was no indication of methane production, which would be expected from a metal–carbon homolysis reaction. Judging from the ^1H NMR spectrum (and considering that the ethane would be distributed in the gas phase and in solution in the sealed tube), the ethane yield was essentially quantitative. The oxidation of a mixture of **1** and $Cp^*Rh(PPh_3)(CD_3)_2$ (**1**-d_6) resulted in the formation of C_2H_6 and C_2D_6, with less than 10% of the $C_2H_3D_3$ crossover product. The reductive elimination reaction clearly takes place intramolecularly.

The electrochemical behavior of **2** was briefly investigated by DCV. Two chemically irreversible reduction waves were observed at −0.90 and −1.20 V vs Fc, respectively. The positions of these two waves correspond to the two product peaks c′ and d′ in Figure 1B. Thus, seeding a solution of **1** with **2**(PF_6^-)$_2$ led to an increase in the intensities of the product peaks c′ and d′. This establishes that the first observable product from the electrochemical oxidation of **1** is indeed **2** (eq 1), which also results from the chemical oxidation of **1** in acetonitrile.



1 **2** (1)

Chemical Oxidation of $Cp^*Rh(PPh_3)(CH_3)_2$ in Dichloromethane-d_2. The oxidation of **1** with $Cp_2Fe^+PF_6^-$ in dichloromethane required the consumption of only 1 equiv of the oxidant. When the reaction was carried out in dichloromethane-d_2, the immediately recorded ^1H NMR spectrum revealed the presence of ethane and methane (ca. 6:1), and the major organometallic product displayed resonances at δ 1.04 (dd, $J = 6.7$, 1.8 Hz, 3 H) and 1.35 (d, $J = 2.6$ Hz, 15 H). Signals due to a minor product were observed at δ 0.78 (dd) and 1.41 (d). The relative amounts of the two products appeared to roughly match the relative amounts of ethane and methane. The intensities of the ethane signal and the methyl signal from the major product were nearly identical. The major product underwent complete decomposition within 3 h in the sealed NMR tube at ambient temperature. The ^1H NMR spectroscopic data for the minor product closely resembled those of $Cp^*Rh(PPh_3)(I)CH_3$ (δ 0.87, 1.43), which suggests that the product may be the chloro complex $Cp^*Rh(PPh_3)(Cl)CH_3$. The addition of acetonitrile to a freshly prepared solution containing the mixture of the two products led to the formation of $Cp^*Rh(PPh_3)(NCMe)CH_3^+$ (**3**) from the major product, while the minor product remained unchanged. From this, we propose that the major product from the oxidation is a species Cp*Rh-

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[10] For some recent examples of the use of DCV in organic and organometallic chemistry, see ref 6b–d, 7f–g, and: (a) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1986**, *108*, 6371. (b) Tilset, M.; Bodner, G. S.; Senn, D. R.; Gladysz, J. A.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 7551. (c) Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4968. (d) Tanko, J. M.; Drumright, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 5362. (e) Parker, V. D.; Chao, Y.; Reitstöen, B. *J. Am. Chem. Soc.* **1991**, *113*, 2336. (f) Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1991**, *113*, 6954. (g) Tilset, M. In *Energetics of Organometallic Species*; Simões, J. A. M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; p 109.

[11] While this work was in progress, it was reported that a closely related complex $Cp^*Rh(PMe_3)(NCMe)_2^{2+}(CF_3SO_3^-)_2$ was obtained by treatment of $Cp^*Rh(PMe_3)Cl_2$ with 2 equiv of $Ag(OSO_2CF_3)$ followed by anion displacement with acetonitrile: Stang, P. J.; Huang, Y.-H.; Arif, A. M. *Organometallics* **1992**, *11*, 231.

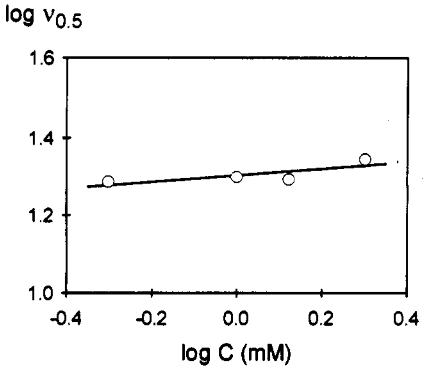

Figure 2. Reaction-order plot of log $v_{0.5}$ vs log [**1**] based on a DCV analysis of the oxidation of **1**. Experimental conditions are as in the caption to Figure 1.

$(PPh_3)(CH_3)X^+$ where the identity of X is uncertain but may be weakly bound counterion PF_6^- [12a] or dichloromethane,[12b–d] or adventitious traces of water. The independent synthesis and characterization of **3** will be discussed later.

The presence of ethane and methane was verified by a GLC analysis of the volatiles of the reaction in dichloromethane. A crossover experiment in which **1** and **1**-d_6 were oxidized together again generated little or no $C_2H_3D_3$, in accord with an *intra*molecular elimination of ethane.

Kinetics of the Reductive Elimination from $1^{\bullet+}$. Derivative cyclic voltammetry has been established as a powerful tool for the investigation of the mechanisms and kinetics of organic and organometallic electrode reactions.[10] The parameter of interest for the discussion to follow is $v_{0.5}$, defined as the voltage sweep rate which for defined experimental conditions causes the cathodic (peak b′ in Figure 1B) to anodic (peak a′) derivative peak current ratio to be equal to 0.5. The time lag between the detection of peaks a′ and b′ correlates with the half-life of the electrode-generated intermediate. The parameter $v_{0.5}$ provides valuable kinetic information since it is directly proportional to the rate constant for the follow-up reaction[9] and may be obtained under different experimental conditions. Provided that the separation between the scan reversal potential (E_{switch}) and the reversible electrode potential for the oxidation of **1** (E_{rev}) in a series of experiments is maintained at a constant value, DCV may be used in a reaction-order analysis[9b] to establish the rate law for the follow-up reaction. When the overall rate law and reaction stoichiometry is known, the kinetic parameters for the reaction are evaluated by comparison of the DCV data with theoretical data obtained by digital simulation.

Figure 2 shows a reaction-order plot of log $v_{0.5}$ vs log [**1**] in the substrate concentration range 0.5–2.0 mM. The pertinent experimental data are included in Table I. The measurements were performed at 20 °C with $E_{\mathrm{switch}} - E_{\mathrm{rev}} = 200$ mV. The near-zero (0.08) slope of the curve demonstrates that the half-life for consumption of electrode-generated $1^{\bullet+}$ is independent of the substrate concentration; i.e., the reaction consuming $1^{\bullet+}$ is a first-order process. The results of variable-temperature measurements are depicted in Figure 3, which is an Arrhenius-type plot of ln ($v_{0.5}/T$) vs $1/T$.[9] Repeated runs on independently prepared solutions resulted in highly reproducible $v_{0.5}$ vs T data. Linear regression based on data from three independent runs yielded the activation energy for the reaction of $1^{\bullet+}$, $E_a = 55.2 \pm 0.9$ kJ/mol (uncertainty given as one standard deviation).

Table I. DCV Reaction-Order Data for Reductive Elimination of Ethane from $Cp^*Rh(PPh_3)(CH_3)_2^{\bullet+}$ at 20 °C[a]

	$v_{0.5}$ (V/s)			
[**1**] (mM)[b]	9:1 CH_3CN/ CH_2Cl_2[c]	acetone[c]	THF[d]	CH_2Cl_2[d]
0.50	19.3	16.2[e]	11.8[e]	15–20[f]
1.00	19.9	17.3	11.2	18
1.33	19.7	18.9	11.8	17
2.00	22.1	20.4	11.2	14

[a] $E_{\mathrm{sw}} - E_{\mathrm{rev}} = 200$ mV. [b] Concentration of **1**. [c] 0.1 M $Bu_4N^+PF_6^-$. [d] 0.2 M $Bu_4N^+PF_6^-$. [e] 0.66 mM. [f] Uncertainty due to severe adsorption.

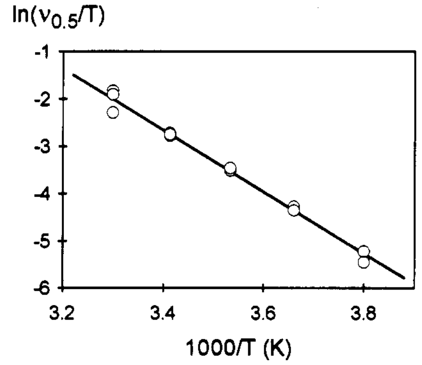

Figure 3. Arrhenius-type plot of ln ($v_{0.5}/T$) vs $1000/T$ for the reaction of $1^{\bullet+}$ at 1.0 mM substrate. Experimental conditions are as in the caption to Figure 1.

The information at hand from DCV, coulometry, and observed products is in agreement with an ECE mechanism in which the chemical reaction is a first-order elimination of ethane from $1^{\bullet+}$. The $v_{0.5}$ values may be compared with theoretical data for this mechanism, and this yields the kinetic parameters $k(20\ °C) = 96 \pm 3\ s^{-1}$, $\Delta H^{\ddagger} = 51.1 \pm 0.9$ kJ/mol, and $\Delta S^{\ddagger} = -25.9 \pm 3.4$ J/(K·mol). The ease of elimination from $1^{\bullet+}$ may be contrasted with the extremely slow thermal decomposition of **1** to unidentified products even at 92 °C in benzene-d_6 ($t_{1/2}$ ca. 72 h by ^1H NMR). By extrapolation to 92 °C, the rate of reaction of $1^{\bullet+}$ is $k(92\ °C) = 8350\ s^{-1}$ and *the rate enhancement toward reductive elimination due to the 1-electron oxidation amounts to at least a factor of 3×10^9!*

The kinetics of the oxidatively induced reductive elimination from the deuterated substrate **1**-d_6 were also investigated by DCV. The observed $v_{0.5}$ values were identical, within experimental uncertainties, to those found for **1**. Therefore, the secondary kinetic isotope effect k_H/k_D was not significantly different from unity.

Solvent and Electrolyte Effects on the Kinetics of the Reductive Elimination Reaction. In order to probe the possible intervention of solvent acetonitrile as a stoichiometric reactant in the reductive elimination process, the kinetics of the reaction were investigated in the normally poorly coordinating solvent dichloromethane. We have previously measured rate enhancements as high as 2000[7g] for the oxidatively induced cleavage of metal–

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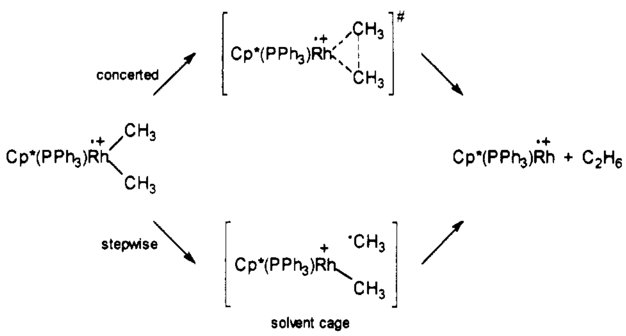
[12] (a) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. (b) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89. (c) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (d) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349. (e) Song, L.; Trogler, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 3355. (f) Darensbourg, M.; Borman, C. *Inorg. Chem.* **1976**, *15*, 3121. (g) Darensbourg, M. Y. *Progr. Inorg. Chem.* **1985**, *33*, 221. (h) Kochi, J. K.; Bockman, T. M. *Adv. Organomet. Chem.* **1991**, *33*, 51.

carbon bonds when the solvent is changed from dichloromethane to acetonitrile.

DCV reaction-order data for the oxidation of 1 in acetone/0.1 M $Bu_4N^+PF_6^-$, THF/0.2 M $Bu_4N^+PF_6^-$, and dichloromethane/0.2 M $Bu_4N^+PF_6^-$ are included in Table I. The electrochemical response was not as good in dichloromethane as in the other solvents, repeated DCV scans leading to somewhat irreproducible results that may be attributed to fouling of the electrode surface caused by adsorption. The problem was particularly noticeable at low substrate concentrations and lower temperatures. However, for all solvents the data unambiguously indicate that the reaction of $1^{\bullet+}$ is a first-order process. Most importantly, solvent effects on the reaction rate at 20 °C are very small, considering the differences in donor capabilities of the solvents. Relative rates (taken as the average of the data listed for each solvent in Table I) are k_{rel} = 1.0 for 9:1 acetonitrile/dichloromethane, 0.9 for acetone, 0.6 for THF, and 0.8 for dichloromethane. High-quality variable-temperature data could not be obtained in dichloromethane due to the poor response at lower temperatures (although qualitatively, the $v_{0.5}$ vs T dependence appeared to follow the trend seen in acetonitrile). Variable-temperature data were obtained for acetone/0.1 M $Bu_4N^+PF_6^-$, resulting in E_a = 46.4 ± 3.0 kJ/mol, and for THF/0.2 M $Bu_4N^+PF_6^-$, yielding E_a = 49.8 ± 1.8 kJ/mol. These values are similar to the acetonitrile value (53.1 kJ/mol), and again, the solvent effects are seen to be rather modest. From this, we conclude that the direct involvement of acetonitrile (or any other solvent) in a stoichiometric fashion before or during the rate-determining step of the reductive elimination of ethane is unlikely.

The PF_6^- anion is usually considered to be a poorly coordinating ligand.[12a] However, close ion pairing has been reported to affect the kinetics of halide-induced disproportionation reactions of 17-electron cations $M(CO)_3(PCy_3)_2^{\bullet+}$ (M = Fe, Ru, Os) in dichloromethane.[12e] In order to probe the possible involvement of the counterion in the reductive elimination reaction, measurements were performed in which the supporting electrolyte concentration was varied between 0.1 and 0.2 M in dichloromethane. The rate for the reaction of $1^{\bullet+}$ was insensitive to this change in the electrolyte concentration. In view of the recent results from Song and Trogler[12e] we believe that close ion pairing is likely to exist between $1^{\bullet+}$ and PF_6^- and maybe even more so between the putative 15-electron intermediate $Cp^*Ph(PPh_3)^{\bullet+}$ (vide infra) and PF_6^-. In THF, ion pair dissociation constants between 17-electron cations[12e] and PF_6^- are comparable with those of 18-electron cations[12f] with this counterion. It is not clear whether the ion pairing between $1^{\bullet+}$ and PF_6^- will result from a purely electrostatic effect or if a more intimate contact (i.e., direct coordination) will exist. In any event, the ion-pairing interaction is certain to be weakened or eliminated in acetonitrile.[12g,h] The result is that the reductive elimination from $1^{\bullet+}$ may occur from a strongly (contact) ion-paired species in dichloromethane, as opposed to from a relatively free ion (or solvent-separated ion pair) in acetonitrile. The observed lack of dependence of the reaction rate on the electrolyte concentration and on the nature of the solvent (the latter will affect the concentration of free PF_6^-) probably implies that the PF_6^- counterion does not actively assist the reductive elimination reaction. However, a fortuitous cancellation of effects from ion pairing and other sources cannot be rigorously ruled out.

Scheme II



Discussion of the Mechanism of the Reductive Elimination of Ethane from $1^{\bullet+}$. The transformation of $1^{\bullet+}$ to 2 and ethane embodies several steps: reductive elimination of ethane, two acetonitrile ligations, and a 1-electron oxidation. A direct oxidation of $1^{\bullet+}$ to 1^{2+} is unlikely in view of the general idea that direct 2-electron oxidation processes are expected to take place only if a structural change (which may include solvent coordination) occurs to render the second oxidation more facile than the first.[13] The reaction of $1^{\bullet+}$ with external ligands (acetonitrile or PF_6^-) before or during the rate-limiting step has been rendered unlikely on the basis of the available experimental results. The data for the reductive elimination reaction therefore indicate that *the reductive elimination proceeds directly from the 17-electron cation radical, generating a 15-electron intermediate.* This intermediate undergoes rapid, double acetonitrile coordination and oxidation to yield the observed product 2. In our view it is probable that the second oxidation occurs after the *second* acetonitrile addition. The oxidation potential of the electron rich 19-electron intermediate $Cp^*Rh(PPh_3)(NCMe)_2^{\bullet+}$ of course is the same as the reduction potential of 2, −0.90 V vs Fc, and obviously this intermediate will be spontaneously oxidized under conditions that cause the oxidation of 1.

For the primary reductive elimination step an ambiguous situation still persists. The reaction may be a concerted process, or it may occur stepwise by homolysis, followed by an S_H2 methyl radical abstraction within the solvent cage. These alternatives are shown in Scheme II. An analogous problem has been previously discussed in order to explain product distributions arising from oxidation of *cis*-$(bpy)_2CoR_2^{2+}$ [8e] and Cp_2MR_2[8f] (M = Ti, Zr) complexes. In $1^{\bullet+}$, the mutual disposition of the methyl groups is clearly such as to facilitate both processes.

For the reactions that were performed in acetonitrile, the absence of methane among the detected products may be taken as evidence against the stepwise process. However, this is by no means conclusive, since an efficient in-cage reaction would also suppress methane formation. The most informative piece of evidence that allows a distinction to be made is the negative entropy of activation

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(13) (a) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107. (b) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558.

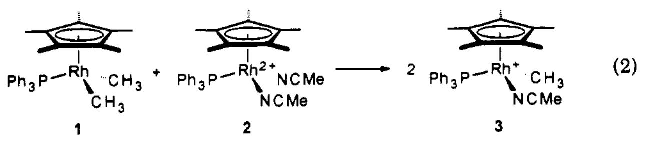
(14) (a) Mancuso and Halpern have investigated the kinetics of thermal M–C homolysis reactions in M–CHMePh complexes (M = $CpFe(CO)_2$, $CpRu(CO)_2$, $CpMo(CO)_3$, $CpW(CO)_3$) in hydrocarbon solvents and reported positive $\Delta S^{\ddagger}$ values in the range 21–80 J/(K·mol): Mancuso, C.; Halpern, J. *J. Organomet. Chem.* **1992**, *428*, C8. (b) For solvent-assisted homolysis reactions, i.e. *associative* reactions, $\Delta S^{\ddagger}$ values of ca. -100 J/(K·mol) have been estimated.[7f]

of −25.9 J/(K·mol). The negative ΔS^* appears not consistent with the dissociative nature of a homolysis reaction.[14] On the other hand, the ΔS^* value is readily reconciled with the somewhat ordered transition state that would be expected for a concerted reaction.

The generation of methane when the oxidation was performed in dichloromethane suggests that at least a minor part of the reaction takes place by homolysis to give the methyl radical. Still, the kinetics indicate that the homolysis pathway cannot be the predominant mode of reaction. This implies that the concerted reaction is the most important reaction even in this solvent, while the methane-generating Rh–C homolysis is a minor, competing reaction. The branching point for the ethane and methane-producing reactions therefore must be at the substrate cation radical, rather than at the solvent cage in the mechanism of Scheme II.

It is interesting to note that, in spite of the occurrence of an intramolecular elimination of ethane (as established by the labeling experiment) from $1^{\bullet+}$ in dichloromethane, a methyl-containing product is formed in this reaction. This indicates that a rapid reaction occurs between the immediately formed reductive elimination product Cp*Rh-$(PPh_3)^{\bullet+}$ (or possibly a solvent adduct or a counterion adduct or ion pair) and 1 or $1^{\bullet+}$, leading to methyl transfer between two metal centers. If 1 is involved, it must be assumed that a 1-electron oxidation accompanies this reaction. The secondary reaction of Cp*Rh$(PPh_3)^{\bullet+}$ takes place after the rate-limiting ethane elimination, and the exact mechanism therefore cannot be established from the kinetic data. The feasibility of a methyl-transfer process will be demonstrated with a strikingly similar transformation in the next paragraph. The overall result of this reaction sequence is a 1-electron oxidation, in agreement with experimental data for the homogeneous oxidation. The coulometry measurements in dichloromethane were in better agreement with an overall 2-electron process; the apparent discrepancy may be explained in terms of dilution effects that disfavor the second-order methyl-transfer reaction. Homogeneous oxidations were typically performed at 20–50 mM concentrations of the substrate, whereas coulometry measurements were run on 1–2 mM solutions.

Formation of Cp*Rh(PPh$_3$)(NCMe)CH$_3^+$ by the Comproportionation of Cp*Rh(PPh$_3$)(CH$_3$)$_2$ and Cp*Rh(PPh$_3$)(NCMe)$^{2+}$. When the mixture of 1 and 2 that resulted from the oxidation of 1 with 1 equiv of $Cp_2Fe^+PF_6^-$ in acetonitrile-d_3 was left for several hours at ambient temperature, it was observed that the ^{1}H NMR resonances attributed to 1 and 2 gradually disappeared, with the concomitant appearance of new signals at δ 1.38 (d, J = 2.9 Hz, 15 H) and 0.71 (dd, J = 2.2, 6.2 Hz, 3 H). The spectroscopic data suggest that the new product is Cp*Rh(PPh$_3$)(NCMe)CH$_3^+$ (3, eq 2). The transformation took place quantitatively, as shown when a 1:1 mixture of 1 and 2, along with hexamethylbenzene as an internal standard, was allowed to react in 4:1 dichloromethane-d_2/acetonitrile-d_3 in a sealed NMR tube. The coordinated acetonitrile ligands in 2 underwent exchange with the solvent at a rate much greater than the rate of the reaction between 1 and 2. A smooth reaction between 1 and 2 was also observed to take place in dichloromethane-d_2, despite the fact that $2(PF_6^-)_2$ is hardly soluble in this solvent. The good solubility of the product $3(PF_6^-)$ facilitates the reaction.



1 + 2 ⟶ 2 3 (2)

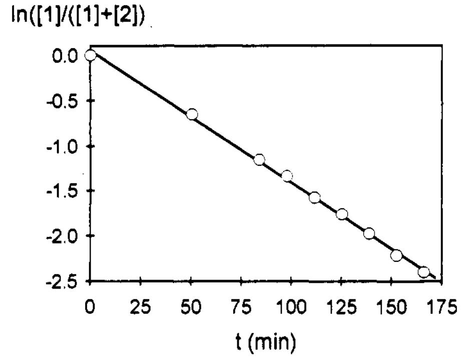


Figure 4. Plot of kinetic data for the reaction between 1 and 2 in 4:1 acetonitrile-d_3/dichloromethane-d_2 at 39.2 °C, as monitored by ^{1}H NMR spectroscopy, according to a pseudo-first-order reaction scheme.

The identity of 3 was verified by the independent synthesis of $3(PF_6^-)$. Treatment of Cp*Rh(PPh$_3$)(I)CH$_3$ with 1 equiv of AgPF$_6$ in acetonitrile led to the formation of $3(PF_6^-)$, which was isolated in 75% yield and characterized spectroscopically and by elemental analysis.

Kinetics of the Comproportionation of 1 and 2. Due to the limited solubility of $2(PF_6^-)_2$ in dichloromethane, and of 1 in acetonitrile, the kinetics were investigated in a 4:1 mixture of acetonitrile-d_3 and dichloromethane-d_2, which allowed for sufficient amounts of both reactants to dissolve and their concentrations to be monitored by ^{1}H NMR spectroscopy. Hexamethylbenzene was employed as an internal standard for quantification purposes in a kinetic run in which the reaction of equimolar amounts of 1 and $2(PF_6^-)_2$ was monitored for about 3–4 half-lives. The reaction was found to be quantitative (>95%) within the experimental uncertainties, whether measured by the Cp* or the Rh–CH$_3$ signal intensities. As a consequence of this, further experiments were performed without the internal standard. Assuming a quantitative transformation, the conversion of 1 could be readily determined by measuring the [1]/([1] + [3]) ratio from the intensities of the fully separated Rh–CH$_3$ resonances.

Figure 4 shows a plot of ln ([1]/([1] + [3])) vs t for a run performed at 39.2 °C. A straight line is obtained for this experiment which was monitored until 91% conversion, or almost 4 half-lives. This observation signals a first-order rate law, i.e. [1] and [2] cannot *both* enter into the rate law. Repeated runs always gave rise to good first-order plots. In spite of this, the rate constants that were extracted from separate runs were rather irreproducible. Qualitatively, however, the reaction rate appeared to increase with increasing concentrations of 2 at constant concentrations of 1, suggesting a rate law $-d[1]/dt = -d[2]/dt = k[2]$. Activation parameters obtained from variable-temperature runs were useless due to the irreproducible rate measurements.

Addition of 1–2 equiv of PPh$_3$ to the 1:1 mixture of 1 and $2(PF_6^-)_2$ had no significant effect on the rate of methyl transfer when taking into account the variation in observed rates in its absence.

When a mechanism for the methyl migration reaction is proposed, it must be taken into account that the rate law appears to be first-order with respect to **2** and zero-order with respect to **1** and that acetonitrile exchange occurs at rates much faster than methyl migration. The first point rules out a direct reaction between **1** and **2** as well as a reversible dissociation of acetonitrile from **2** followed by rate-determining capture of the resulting unsaturated intermediate with **1**, since these reaction sequences would lead to overall second-order kinetics. The observed fast exchange of acetonitrile rules out rate-determining dissociation of one acetonitrile ligand, assuming that a dissociative exchange mechanism is operative. However, if the rapid ligand exchange occurs via a concerted (associative) process, then the reaction between **1** and **2** may well include a rate-determining acetonitrile dissociation. Alternative mechanisms that are consistent with the observed kinetics include rate-determining PPh_3 loss, as well as reversible dissociation of one acetonitrile followed by rate-limiting expulsion of the second. These alternatives would generate formally 16-electron ($Cp^*Rh(NCMe)_2{}^{2+}$) and 14-electron ($Cp^*Rh(PPh_3)^{2+}$) intermediates, respectively. Either of these intermediates, which may be ion-paired with the PF_6^- counterion, would then be required to selectively react with **1** in a fast step in order to account for the first-order kinetics. Formation of a Rh–Rh dative bond[15] and/or bridging methyl ligands between this intermediate and **1** could then be the key step to initiate the methyl migration from one metal center to the other.[16] We note here that the combination of $Cp^*Rh(PPh_3)^{2+}$ and **1** leads to a species of the same composition as the reaction between $Cp^*Rh(PPh_3)^{\bullet+}$ and $\mathbf{1}^{\bullet+}$, which was considered to be a possible product-forming reaction during the oxidation of **1** with $Cp_2Fe^+PF_6^-$ in dichloromethane. The mechanisms of the two reactions may be intimately related.

As a final word of caution, we want to emphasize that the suggested mechanisms for the comproportionation reaction necessarily remains speculative as long as the source of the irreproducibility in the kinetic runs is not identified.

Concluding Remarks. We have established that the oxidatively induced reductive elimination from $Cp^*Rh(PPh_3)(CH_3)_2$ proceeds directly from the cation radical, most likely by a concerted expulsion of ethane, producing an unobserved, highly unsaturated 15-electron primary product. The reaction is not assisted by solvent coordination, and therefore, 19-electron intermediates appear not to be involved in the reductive elimination. The formation of different products under different reaction conditions reflects that the fate of the reactive intermediate $Cp^*Rh(PPh_3)^{\bullet+}$ strongly depends on the identities of other species that are present in solution. Work is in progress to establish whether the unassisted reductive elimination is a fairly general mechanism or if the mechanistic variations that are prevalent in 18/16-electron systems will also complicate matters in the realm of odd-electron species.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile was distilled from P_2O_5, and acetonitrile-d_3, dichloromethane, and dichloromethane-d_2 were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. P.a. grade acetone was used as received. The electrochemical instrumentation, cells, data handling procedures, and electrodes have been previously described.[17] Acetonitrile/dichloromethane (9:1) containing 0.1 M $Bu_4N^+PF_6^-$ was used as the solvent for electrochemical experiments unless otherwise mentioned and was passed through a column of active neutral alumina before use to remove water and protic impurities. The electrolyte was freed of air by purging with purified argon, and all measurements and electrolyses were carried out under a blanket of solvent-saturated argon. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian XL-300 or Varian Gemini-200 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standards. Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany. Methane and ethane analyses were performed on a Varian 3400 gas chromatograph operating at 50 °C, using a 30 m × 0.54 mm GS Q capillary column.

The compounds $Cp^*Rh(PPh_3)I_2$,[18a] $Cp^*Rh(PPh_3)Cl_2$,[18a] and $Cp_2Fe^+PF_6^-$ [18b] were prepared according to published procedures. Other chemicals were used as received from commercial suppliers.

$Cp^*Rh(PPh_3)(CH_3)_2$ (1). This modification of a previously reported procedure[18a] was found to give significantly improved yields of the product. A solution of CH_3MgI (2.5 mL of a 1 M solution in ether, 2.5 mmol) was added slowly to a stirred solution of $Cp^*Rh(PPh_3)I_2$ (500 mg, 0.663 mmol) in benzene (3 mL). The reaction mixture gradually turned yellow and was stirred for 15 h at ambient temperature. The solution was transferred through a double-ended needle onto a rapidly stirred saturated aqueous ammonium chloride solution (5 mL) held at 0 °C. The resulting mixture was stirred vigorously to ensure complete hydrolysis of the excess Grignard reagent. The organic phase was separated and washed with water (10 mL). The aqueous phase was washed with ether (3 × 5 mL) and the combined organic extracts were dried ($MgSO_4$) for 15 min. The solution was filtered, and the solvents were removed in vacuo. The resulting solid was purified by column chromatography (silica gel, toluene) under N_2. The yellow product was recrystallized from benzene/heptane (2/1) by slowly removing the benzene by rotary evaporation to give yellow crystals (288 mg, 82%). ^1H NMR (200 MHz, chloroform-d): δ −0.19 (dd, J = 2.5, 4.7 Hz, 6 H), 1.40 (d, J = 1.7 Hz, 15 H), 7.30 (m, 15 H).

$Cp^*Rh(PPh_3)(CH_3)I$. Improved yields of the product were obtained by the following modification of a previously reported procedure.[18a] A solution of CH_3MgI (3.5 mL of a 1 M solution in ether, 3.5 mmol) was added slowly to a stirred solution of $Cp^*Rh(PPh_3)Cl_2$ (500 mg, 0.875 mmol) in benzene (3 mL). The resulting reddish-brown homogeneous solution was stirred for 30 min and then worked up following the same procedure as that described for $Cp^*Rh(PPh_3)(CH_3)_2$. The product was obtained as reddish-brown crystals (332 mg, 60%). ^1H NMR (200 MHz,

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[15] (a) Antonelli, D. M.; Cowie, M. *Organometallics* **1990**, *9*, 1818. (b) Antonelli, D. M.; Cowie, M. *Organometallics* **1991**, *10*, 2550. (c) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620.

[16] Methyl transfers between metal centers in mononuclear and dinuclear complexes are well documented. For some references, see: (a) Rice, G. W.; Tobias, R. S. *J. Organomet. Chem.* **1975**, *86*, C37. (b) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255. (c) Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4766. (d) Bryndza, H. E.; Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 4948. (e) Arnold, D. P.; Bennett, M. A.; McLaughlin, G. M.; Robertson, G. B.; Whittaker, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, *32*. (f) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturo, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451. (g) Okeya, S.; Meanwell, N. J.; Taylor, B. F.; Isobe, K.; Vázquez de Miguel, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1453. (h) Krause, M. J.; Bergman, R. G. *Organometallics* **1986**, *5*, 2097. (i) Baxter, S. M.; Ferguson, G. S.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4231. (j) Baxter, S. M.; Wolczanski, P. T. *Organometallics* **1990**, *9*, 2498.

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[18] (a) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) Lyatifov, I. R.; Solodovnikov, S. P.; Babin, V. N.; Materikova, R. B. *Z. Naturforsch., B* **1979**, *34B*, 863.

chloroform-*d*): δ 0.87 (dd, J = 2.3, 6.6 Hz, 3 H), 1.43 (d, J = 2.6 Hz, 15 H), 7.3–7.6 (m, 15 H). Some $Cp^*Rh(PPh_3)(CH_3)_2$ (54 mg, 12%) was also isolated.

$Cp^*Rh(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (2(PF$_6^-$)$_2$). $Cp^*Rh(PPh_3)I_2$ (300 mg, 0.398 mmol) and $Ag^+PF_6^-$ (201 mg, 0.795 mmol) were dissolved in acetonitrile. The reaction mixture was stirred for 5 min and filtered through Celite. The solution was concentrated in vacuo, and the product (285 mg, 82%) was obtained by the addition of ether: yellow crystals, mp 185–190 °C slow dec; ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 1.46 (d, J = 3.9 Hz, 15 H), 2.14 (s, 6 H), 7.4–7.7 (m, 15 H); ^{13}C{^{1}H} NMR (75 MHz, dichloromethane-d_2) δ 9.8, 106.2 (d), 118.3, 128.2 (d), 130.5 (d), 133.4, 134.9 (d). Anal. Calcd for $C_{32}H_{36}F_{12}N_2P_3Rh$: C, 44.05; H, 4.16; N, 3.21. Found: C, 44.24; H, 4.21; N, 3.18. No acetonitrile (ν_{CN}) absorptions could be detected by IR spectroscopy.

$Cp^*Rh(PPh_3)(NCMe)(CH_3)^+PF_6^-$ (3(PF$_6^-$)). A mixture of $Cp^*Rh(PPh_3)(CH_3)I$ (200 mg, 0.311 mmol) and $Ag^+PF_6^-$ (78.7 mg, 0.311 mmol) was dissolved in acetonitrile. The solution was stirred for 5 min, during which AgI(s) precipitated. The solution was filtered through Celite and concentrated by vacuum transfer. Slow addition of ether caused the precipitation of the product (164 mg, 75%): orange crystals, mp 164–166 °C dec; ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 0.71 (dd, J = 2.2, 6.2 Hz, 3 H), 1.38 (d, J = 2.9 Hz, 15 H), 1.96 (s, 3 H), 7.46 (m, 15 H); ^{13}C{^{1}H} NMR (75 MHz, dichloromethane-d_2) δ 2.2 (dd), 9.0, 9.4 (d), 101.2, 129.1, 131.4, 134.1. Anal. Calcd for $C_{31}H_{36}F_6NP_2Rh$: C, 53.08; H, 5.17; N, 2.00. Found: C, 53.66; H, 5.20; N, 3.14. The acetonitrile ν_{CN} absorption was not observed by IR spectroscopy.

Quantitative Analysis of the Ferrocenium Oxidation of $Cp^*Rh(PPh_3)(CH_3)_2$ in Acetonitrile-d_3. A mixture of 1 (8.0 mg, 0.015 mmol) and hexamethylbenzene (1.5 mg, 0.009 mmol) was dissolved in ether (1 mL) and distributed equally into two NMR tubes equipped with ground-glass joints. The solvent was removed from both tubes by careful vacuum transfer at −20 °C. $Cp_2Fe^+PF_6^-$ (5.0 mg, 0.015 mmol) was added to one tube, and acetonitrile-d_3 (0.5 mL) was added to both tubes by vacuum transfer. The tubes were sealed under vacuum. The ^{1}H NMR spectrum of the solution to which $Cp_2Fe^+PF_6^-$ had been added revealed the presence of Cp_2Fe (δ 4.15), 2, and ethane (δ 0.85). Comparison of the integrated signal intensities with those for the substrate in the tube without oxidizing agent revealed that the substrate conversion was 86%, and the yield of 2 based on consumed 1 was at least 95%. After 15 h, a partial reaction between 1 and 2 was indicated by the reduces signal intensities due to 1 and 2 and the emergence of signals arising from 3.

Quantitative Analysis of the Reaction between $Cp^*Rh(PPh_3)(CH_3)_2$ and $Cp^*Rh(PPh_3)(NCMe)_2^{2+}$ in Acetonitrile-d_3. A mixture of 1 (2.5 mg, 0.0047 mmol), 2(PF$_6^-$)$_2$ (4.1 mg, 0.0047 mmol), and hexamethylbenzene (0.3 mg, 0.0016 mmol) was added to an NMR tube equipped with a ground-glass joint. Acetonitrile-d_3 (0.57 mL) and dichloromethane-d_2 (0.14 mL) were added by syringe in the drybox, and the tube was sealed under vacuum. Immediate recording of an ^{1}H NMR spectrum at ambient temperature revealed the presence of only traces of the product 3. The hexamethylbenzene internal standard allowed for determination of the yield of 3 as time progressed, and it was established that all the methyl groups (>95%) initially available in 1 could be accounted for in the product 3.

Kinetics of the Reaction between $Cp^*Rh(PPh_3)(CH_3)_2$ and $Cp^*Rh(PPh_3)(NCMe)_2^{2+}$ Monitored by ^{1}H NMR Spectroscopy. In order to ensure identical substrate concentrations and solvent compositions for all the kinetic runs, the following procedure was employed for sample preparation. In the drybox, $Cp^*Rh(PPh_3)(CH_3)_2$ (17.5 mg, 0.030 mmol) and $Cp^*Rh(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (28.8 mg, 0.030 mmol) were dissolved in a mixture of acetonitrile-d_3 (4 mL) and dichloromethane-d_2 (1 mL). The solution was portioned into seven NMR tubes that were equipped with ground-glass joints. The tubes were attached to the vacuum-line via adapters, cooled in a dry ice/acetone bath, evacuated, and sealed. The tubes were stored in a cold room at −20 °C until the start of each kinetic run. No substrate consumption was observed to take place at this temperature. However, exchange of coordinated acetonitrile with solvent acetonitrile-d_3 was observed to be complete at the time when the first ^{1}H NMR spectrum was recorded. Kinetic runs were performed by inserting the tubes into the preheated spectrometer probe. Because it was established that the reaction was quantitative, it was decided that the addition of an internal standard for quantification purposes was not necessary. The progress of the reaction was followed by monitoring the decay of the intensity of the Rh–CH$_3$ resonance of 1 relative to the combined Rh–CH$_3$ resonance intensities of 1 and the product 3. Straight lines, indicative of first-order reactions, were obtained when ln ([1]/([1] + [3])) was plotted vs time at temperatures in the range 29–62 °C, but repeated runs under apparently identical conditions led to poor reproducibility.

A similar procedure was employed for the investigation of the reaction of 1 with 2 in the presence of PPh_3, and of 1 with excess 2. The former experiment demonstrated that, within the experimental uncertainties, there was no dependence of the reaction rate on the presence of PPh_3, while the latter demonstrated a significant increase in the rate of disappearance of 1 with increasing concentrations of 2. Plots of ln ([1]/([1] + [3])) vs time in all cases were linear.

Reaction between $Cp^*Rh(PPh_3)(CH_3)_2$ and $Cp^*Rh(PPh_3)(NCMe)_2^{2+}$ in Dichloromethane-d_2. An NMR tube that was equipped with a ground-glass joint was loaded with $Cp^*Rh(PPh_3)(CH_3)_2$ (2.5 mg, 0.005 mmol) and $Cp^*Rh(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (4.1 mg, 0.005 mmol). Dichloromethane-d_2 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The tube, containing the solution of $Cp^*Rh(PPh_3)(CH_3)_2$ and insoluble $Cp^*Rh(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$, was heated at 30 °C for 17 h. Inspection of the ^{1}H NMR spectrum at this time revealed that the reaction had gone to completion, and $Cp^*Rh(PPh_3)(NCMe)CH_3^+$ (3) was the only observable product: δ 0.76 (dd, J = 2.2, 6.2 Hz, 3 H), 1.40 (d, J = 2.9 Hz, 15 H), 1.96 (s, 3 H), 7.3–7.5 (m, 15 H).

Stoichiometry of the Reaction between 1 and $Cp_2Fe^+PF_6^-$ in Dichloromethane. The stoichiometry of the reaction was established by the "ferrocenium titration" technique that we described recently.[6d] A solution of 1 (18.0 mg, 0.0339 mmol) in dichloromethane (2.0 mL) was added by slow addition with a syringe to a vigorously stirred mixture of $Cp_2Fe^+PF_6^-$ (10.1 mg, 0.0305 mmol) in dichloromethane (2 mL). The oxidant only partially dissolved in the solvent. A 1.0-mL volume of the substrate solution was added at once, and then smaller portions of 0.1 mL each were added. The green color caused by the presence of unreacted (blue) ferrocenium appeared to recede at the addition of 1.4–1.6 mL of substrate solution. However, due to the intense color of the mixture, there was no abrupt color change. The solution was checked by TLC (alumina/hexane), which revealed that no 1 appeared to be present. Only when 1.7 mL substrate had been added to the oxidant did the TLC analysis show unreacted substrate in the reaction mixture. This corresponds to the consumption of 1.06 mol of ferrocenium/mol of 1.

Ferrocenium Oxidation of 1 in Dichloromethane-d_2. An NMR tube equipped with a ground-glass joint was loaded with 1 (5.3 mg, 0.0100 mmol) and $Cp_2Fe^+PF_6^-$ (3.5 mg, 0.0106 mmol). Dichloromethane-d_2 (0.5 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The ^{1}H NMR spectrum revealed the presence of ethane and methane (ca 6:1) at δ 0.85 and 0.19, respectively. The major organometallic product displayed resonances at δ 1.04 (dd, J = 6.7, 1.8 Hz, 3 H) and 1.35 (d, J = 2.6 Hz, 15 H). Signals due to a minor product were observed at δ 0.78 (dd, 3 H, unresolved J) and 1.41 (d, J = 2.7 Hz, 3 H). The substrate consumption was complete. The relative amounts of the two products appeared to match the relative amounts of ethane and methane, and the relative intensities of the ethane (δ 0.85) and methyl (δ 1.04) signals were near 1:1. The major product underwent complete decomposition in less than 3 h in the sealed NMR tube at ambient temperature leading to an ill-defined, broadened NMR spectrum.

In another experiment, the reaction between 1 (5.3 mg, 0.0100 mmol) and $Cp_2Fe^+PF_6^-$ (3.5 mg, 0.0106 mmol) was performed in dichloromethane-d_2 (0.6 mL) in a 5-mL round-bottom flask. When the reaction was judged complete, acetonitrile (2 μL) was added. This caused the orange solution to turn yellow immediately. The ^{1}H NMR spectrum showed that instead of the major product that was observed in the absence of acetonitrile, signals were present that matched those of $Cp^*Rh(PPh_3)(NCMe)CH_3^+$ (3). The minor product was still present.

Analysis of the Volatiles from the Ferrocenium Oxidation of 1 in Acetonitrile and Dichloromethane. The experiments were performed in the same fashion for both solvents. A 5-mL round-bottom flask was loaded with 1 (10.0 mg, 0.019 mmol) and $Cp_2Fe^+PF_6^-$ (12.5 mg, 0.038 mmol). The flask was attached to the vacuum line via a vacuum adapter, the solvent (1 mL) was added by vacuum transfer, the vessel was closed, and the reaction mixture was stirred until the reaction appeared complete. The volatiles were transferred to another flask by vacuum transfer and analyzed by GLC. Only ethane was observed for the reaction in acetonitrile, its identity authenticated by mass spectrometry. The dichloromethane reaction revealed the presence of ethane and methane in a 6:1 to 10:1 ratio.

The volatiles from a crossover experiment in which 1 and 1-d_6 (10 mg of each, 0.038 mmol combined) were oxidized with $Cp_2Fe^+PF_6^-$ (25 mg, 0.076 mmol) in 1 mL of solvent were analyzed by attaching the closed reaction vessel directly to the mass spectrometer. The volatiles were observed to contain C_2H_6 and C_2D_6, and less than 10% $C_2H_3D_3$, regardless of the solvent used (acetonitrile or dichloromethane).

Constant-Current Coulometry and Preparative Electrolysis Experiments. The constant-current electrolyses were performed in an H-shaped cell, the compartments of which were separated by a medium-frit glass junction. A platinum-gauze working electrode was used. Solutions of 1 (1–2 mM) in 20 mL of 9:1 acetonitrile/dichloromethane with 0.1 M $Bu_4N^+PF_6^-$ as the supporting electrolyte were electrolyzed with a constant current of 10 mA, while the consumption of the substrate was monitored by DCV. Three separate measurements indicated the consumption of 1.8 ± 0.2 faraday/mol of charge. In dichloromethane/0.2 M $Bu_4N^+PF_6^-$, 1.8 ± 0.1 faraday/mol was measured.

A constant-current electrolysis was similarly done in acetonitrile/0.05 M $Me_4N^+BF_4^-$. The solution from the anode compartment was concentrated by vacuum transfer, and the solid residue was extracted with dichloromethane (10 mL). The extract was filtered, and the solvent was removed in vacuo. The ^{1}H NMR spectrum revealed that the product consisted mostly of $2(BF_4^-)_2$; the yield of impure product was ca. 50%. The modest yield most likely reflects the poor solubility of the product in dichloromethane.

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