elucidation of the anomeric specificity of this specific phosphatase helps in the design of stereochemically defined inhibitors for this enzyme, which may serve as antibiotics acting on lipopolysaccharide biosynthesis.[17]

(17) (a) Hammond, S. M.; Claesson, A.; Jannson, A. M.; Larsson, L. G.; Brian, G. P.; Town, C. M.; Ekstrom, B. *Nature* **1987**, *327*, 730. (b) Goldman, R.; Kohlbrenner, W.; Lartey, P.; Pernet, A. *Nature* **1987**, *329*, 162.

Involvement of 19-Electron Species in Oxidatively Induced Homolytic Metal–Carbon Bond Cleavage Reactions: Decomposition of 17-Electron Cyclopentadienylruthenium Methyl Cations

Torill Aase,[1a] Mats Tilset,*[,1a] and Vernon D. Parker[1b]

*Department of Chemistry, University of Oslo
P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway
Department of Chemistry and Biochemistry
Utah State University, Logan, Utah 84322-0300*

Despite the vigorous current interest in the chemistry of 17- and 19-electron organotransition-metal species,[2] little is known about the mode of decomposition of 17-electron complexes to even-electron products via substitution of one-electron donors by two-electron ligands.[3] The oxidation of transition-metal alkyls and other compounds containing σ-bound ligands has been observed to lead to solvent substitution in donor solvents.[4] Accumulated evidence suggests that 17e $\rightarrow$ 19e $\rightarrow$ 17e cycles are operational when entering and leaving ligands are both two-electron donors.[5] Oxidation of $(\eta^5\text{-}C_5H_5)Fe(CO)(L)R$ compounds induces catalytic CO insertion processes[6,7] believed to proceed by similar 17e $\rightarrow$ 19e $\rightarrow$ 17e sequences. The oxidative behavior of analogous ruthenium complexes remains less thoroughly studied, although decomposition products indicative of the formation of metal-centered radicals have been reported.[8] In this commu-

nication, we describe the results of an investigation of the oxidation of ruthenium methyl compounds $(\eta^5\text{-}C_5H_5)Ru(CO)(PR_3)CH_3$ [R = Cy (cyclohexyl) (**1a**), Ph (**1b**)]. Our data suggest that Ru–CH$_3$ bond homolysis may take place, *after prior solvent coordination to the cation radicals*, upon oxidation of **1a** and **1b**. We present (1) large solvent effects on the rate of decomposition, indicating that the reactions occur via 19-electron species; (2) quantitative kinetic and mechanistic data showing that cations **1**$^{\bullet+}$ react via competing processes that are of first and second order in **1**$^{\bullet+}$, and (3) kinetic isotope effects suggestive of agostic interactions in cations **1**$^{\bullet+}$.

The first half of the derivative cyclic voltammetry[9] (DCV) response for the oxidation of methyl compound **1a** (90:10 CH$_3$CN/CH$_2$Cl$_2$,[10] 0.1 M Bu$_4$N$^+$PF$_6^-$) is shown in Figure 1. Peak a (+0.19 V vs Ag/Ag$^+$) corresponds to the oxidation of **1a**, while peaks b (+0.64 V) and c (+1.33 V) arise from oxidation of decomposition products $(\eta^5\text{-}C_5H_5)Ru(PCy_3)(NCCH_3)_2^+$ (**2a**) and $(\eta^5\text{-}C_5H_5)Ru(CO)(PCy_3)(NCCH_3)^+$ (**3a**), respectively, verified by comparison with authentic samples. Oxidation of **1a** takes place at +0.11 V vs the ferrocene/ferricinium (FC) couple, consuming 1.1 ± 0.1 faraday/mol (constant–current coulometry with linear sweep voltammetry monitoring of substrate disappearance[11]). A 1:3 to 1:4 mixture of **2a** and **3a** was isolated after preparative-scale one-electron exhaustive electrolysis of **1a** (80% combined yield).

Reaction-order analysis by DCV[9b] showed **1a**$^{\bullet+}$ to decompose slowly, exhibiting first-order behavior at substrate concentrations ranging from 0.5 to 2.0 mM. The rate of disappearance of **1a**$^{\bullet+}$ was measured in the temperature range −20 to +20 °C, giving a first-order rate constant k (20 °C) = 0.26 ± 0.02 s^{-1}, $\Delta H^* = 10.6 \pm 0.3$ kcal/mol, and $\Delta S^* = -25 \pm 1$ eu. An inverse k_H/k_D isotope effect (0 °C) of 0.89 ± 0.02 was found when $(\eta^5\text{-}C_5H_5)Ru(CO)(PCy_3)CD_3$ (**1a**-d_3) was employed. Finally, a DCV analysis carried out in CH$_2$Cl$_2$/0.1 M Bu$_4$N$^+$PF$_6^-$ showed **1a**$^{\bullet+}$ to undergo no reaction on the time scale of the measurement (voltage sweep rate $v = 0.1$ V/s). Comparison with theoretical data for a first-order EC mechanism yields a factor of 50 as a *lower limit* for the rate enhancement upon changing the solvent from CH$_2$Cl$_2$ to CH$_3$CN. DCV reaction-order analysis indicated an apparent CH$_3$CN reaction order of 0.8 ± 0.05 in the concentration range 0–20% CH$_3$CN (by volume) in CH$_2$Cl$_2$.

Oxidation of **1a** with 1 equiv of $(\eta^5\text{-}C_5H_5)_2Fe^+PF_6^-$ (**4**) in CD$_3$CN yielded a 44:56 mixture of $(\eta^5\text{-}C_5H_5)Ru(PCy_3)(NCCD_3)_2^+$ (**2a**-d_6) and $(\eta^5\text{-}C_5H_5)Ru(CO)(PCy_3)(NCCD_3)^+$ (**3a**-d_3) (82% combined yield; ^{1}H NMR, internal standard). Methane was detected by ^{1}H NMR (δ 0.18) and GLC analysis (94 ± 8% yield). Mass spectrometry indicated a CH$_4$:CH$_3$D ratio of 93:7. Conversely, ferricinium oxidation of **1a**-d_3 in CH$_3$CN gave a 98:2 CH$_3$:CD$_4$ ratio.

Methyl compound **1b** underwent a one-electron (constant-current coulometry), chemically irreversible (DCV) oxidation at +0.32 V vs FC. Reaction-order analysis of the decomposition of **1b**$^{\bullet+}$ provided a strikingly different mechanistic picture from that observed for **1a**$^{\bullet+}$. In CH$_3$CN, the decomposition was second order in cation **1b**$^{\bullet+}$ in the concentration range 1–4 mM and approached first order at concentrations lower than 0.5 mM. For the second-order process, kinetic data acquired from −14 to +20 °C (2 mM) gave k (20 °C) = (1.2 ± 0.07) × 10^5 M^{-1} s^{-1}, $\Delta H^* = -0.7 \pm 0.2$ kcal/mol, and $\Delta S^* = -38 \pm 2$ eu. An inverse isotope effect of 0.87 ± 0.04 was observed. Under first-order conditions (0.25 mM), the kinetic parameters were k (20 °C) = 29 ± 2 s^{-1}, $\Delta H^* = 8.2 \pm 0.6$ kcal/mol, $\Delta S^* = -23 \pm 2$ eu, and $k_H/k_D = 0.85 \pm 0.08$.

Oxidation of **1b** under second-order conditions (one-electron constant-current electrolysis, 2.0 mM substrate in CH$_3$CN/0.1

(1) (a) University of Oslo. (b) Utah State University.
(2) For recent reviews of the chemistry of 17- and 19-electron complexes, see: (a) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (c) Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643. (d) *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*; Chanon, M., Julliard, M., Poite, J. C., Eds.; Kluwer Academic: Dordrecht, 1989. (e) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125. (f) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153.
(3) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285.
(4) (a) Chen, J. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 1450. (b) Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.
(5) For leading entries to the extensive literature covering ligand substitution in 17-electron complexes, see references quoted in the above reviews (refs 2a–f).
(6) (a) Magnuson, R. H.; Zulu, S.; T'sai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790. (c) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460. (d) Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* **1985**, *4*, 374. (e) Trogler, W. C.; Therien, M. *J. Am. Chem. Soc.* **1987**, *109*, 5127. (f) Golovin, M. N.; Meirowitz, R.; Rahman, M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 2285. (g) Liu, H.-Y.; Golovin, M. N.; Fertal, D. A.; Tracey, A.; Eriks, K.; Giering, W. P.; Prock, A. *Organometallics* **1989**, *8*, 1454.
(7) (a) Reger, D. L.; Mintz, E. *Organometallics* **1984**, *3*, 1759. (b) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940. (c) Reger, D. L.; Klaeren, S. A.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 181.
(8) Joseph, M. F.; Page, J. A.; Baird, M. C. *Organometallics* **1984**, *3*, 1749.

(9) (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem.* **1981**, *121*, 73. (b) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.
(10) CH$_2$Cl$_2$ was added as a cosolvent in order to increase the solubility of **1a**.
(11) (a) Bethell, D.; Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 895. (b) Tilset, M.; Bodner, G. S.; Senn, D. R.; Gladysz, J. A.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 7551.
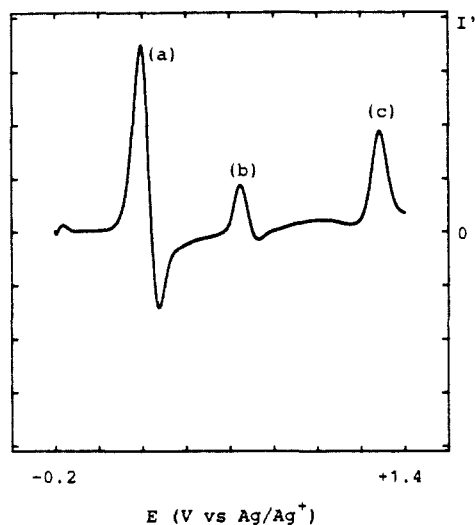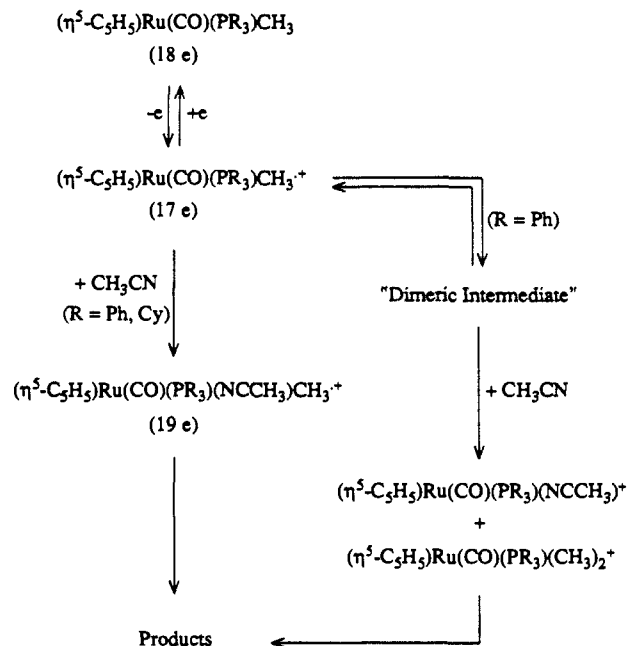
Figure 1. First half of derivative cyclic voltammogram for the oxidation of $(\eta^5\text{-}C_5H_5)Ru(CO)(PCy_3)CH_3$ (**1a**) (1.0 mM) in 90:10 CH_3CN/CH_2Cl_2, $Bu_4N^+PF_6^-$ (0.1 M), at a Pt microelectrode (d = 0.6 mm) at 16 °C and a voltage sweep rate ν = 0.1 V/s.

M $Bu_4N^+PF_6^-$) or first-order conditions (4^{12} in CD_3CN) proceeded to give high yields (electrolysis, 82% combined yield; oxidation with **4**, 88% by ^1H NMR with internal standard) of **2b** and **3b** in a remarkably constant ratio of $(46 \pm 3){:}(54 \pm 3)$. Methane was observed (^1H NMR) after oxidations with **4**. In an attempt at generating higher concentrations of $1b^{\bullet+}$, mimicking second-order conditions, oxidation of **1b** with $Fe(phen)_3^{3+}(PF_6^-)_3$ (E = 0.78 V vs FC; phen = 1,10-phenanthroline) in 96:4 CD_2Cl_2/CD_3CN at -40 °C led to the initial observation of **3b** and an intermediate that has been tentatively assigned the structure $trans\text{-}(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(CH_3)_2^+$ [^1H NMR δ 5.71 (s, 5 H), 1.14 (d, $J_{P\text{-}CH_3}$ = 8.1 Hz, 6 H)]. The decomposition of this intermediate resulted in the formation of acetone, but in quantities too small (GLC–MS; ^1H NMR: 15% based on available methyl in system) to represent a major decomposition pathway of this species. Oxidation of **1b**-d_3 similarly yielded $(CD_3)_2CO$.

The large solvent effect on the rate of decomposition of $1a^{\bullet+}$ (CH_2Cl_2 vs CH_3CN) and the near-first-order dependence of the rate on the concentration of CH_3CN suggest that the solvent CH_3CN plays an active role in the decomposition reaction, possibly interacting with $1a^{\bullet+}$ to form a 19-electron intermediate or transition state leading to the products. Ru–C homolysis at this stage would directly generate **3a**, whereas CO insertion[6] and/or substitution[5] at the 19-electron stage ultimately could lead to **2a**. The labeling experiments demonstrate that the eventual methyl radicals preferentially abstract hydrogen atoms from spectator ligands in the substrate.[13,14]

The apparent low, near-zero activation enthalpy and the highly

---

(12) A redox equilibrium between **4** and **1b** will provide equilibrium concentrations of $1b^{\bullet+}$ well below those required for limiting first-order decomposition of the cation, the equilibrium constant being K_{eq} = 3.2 × 10^{-6} (20 °C). A kinetic experiment (^1H NMR, CD_3CN, 20 °C, 1.0 equiv of **4**) verified that the decomposition was first order in $1b^{\bullet+}$, the observed rate constant for disappearance of **1b** (3 half-lives) found to be k_{obsd} = 1.2 × 10^{-4} s^{-1}. The ratio k_{obsd}/K_{eq} gives the rate constant for unimolecular decomposition of $1b^{\bullet+}$, 38 s^{-1}, in excellent agreement with the electrochemical results.

(13) Attempts at trapping methyl and acetyl radicals with $CBrCl_3$, which has been shown previously to act as an efficient trap,[3] led to the formation of the expected CH_3Br and CH_3COBr. However, we observed a considerable increase in the rate of consumption of substrate (^1H NMR, $CD_3CN/CBrCl_3$ 10:1, 1 equiv of **4**) and thus suspect the formation of these products to be due to a process not directly related to the possible formation of free radicals in the absence of this trap. On the time scale of these experiments, both **1a** and **4**, in separate solutions, were stable in the presence of $CBrCl_3$.

(14) A referee pointed out that if the methyl radicals do abstract H from spectator ligands, this should result in degradation of the reagents and products, which is hard to reconcile with the high isolated product yields. While we share this concern, we suggest that it could be possible for the intermediate resulting from H loss to abstract H (or D) from the solvent before subsequent degradation takes place.

---

negative activation entropy for the decomposition of $1b^{\bullet+}$ under second-order conditions are indicative of an exothermic pre-equilibrium dimerization followed by a rate-determining reaction step.[11b,15] Scheme I displays a reaction sequence consistent with these observations.

Inverse kinetic isotope effects are often associated with multistep mechanisms including inverse *equilibrium* isotope effects and have been observed frequently during the reductive elimination of alkanes from hydridoalkyl complexes.[16] In the case at hand, agostic[17] (M–H–C) interactions in $1^{\bullet+}$ cations could give rise to inverse isotope effects.[18a] Since in complexes with agostic hydrogens, H (rather than D) preferentially occupies the briding position,[17] agostic effects in $1^{\bullet+}$ could lead to a stabilization of the Ru–CH_3 bond relative to the Ru–CD_3 bond. The possible occurrence of agostic interactions in 17-electron metal alkyl cations has been suggested previously.[19]

Work in progress is aimed at gaining further understanding of the dynamics of oxidatively induced metal–alkyl cleavage reactions in these and related systems.

Supplementary Material Available: Description of preparation and spectroscopic and analytical data for compounds **1a**, **2a,b**, and **3a,b** (1 page). Ordering information is given on any current masthead page.

(15) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1986**, *108*, 6371 and references cited therein.

(16) (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (c) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897. (d) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502. (e) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.

(17) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(18) (a) An inverse secondary α-deuterium isotope effect normally requires a rehybridization from sp^2 to sp^3 in the transition state[18b] and apparently does not provide a rationale for the observed effects in this case. (b) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980.

(19) Asaro, M. F.; Cooper, S. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 5187.

Scheme I

$(\eta^5\text{-}C_5H_5)Ru(CO)(PR_3)CH_3$

(18 e)

$(\eta^5\text{-}C_5H_5)Ru(CO)(PR_3)CH_3^{\bullet+}$

(17 e)

(R = Ph)

+ CH_3CN
(R = Ph, Cy)

"Dimeric Intermediate"

$(\eta^5\text{-}C_5H_5)Ru(CO)(PR_3)(NCCH_3)CH_3^{\bullet+}$

(19 e)

+ CH_3CN

$(\eta^5\text{-}C_5H_5)Ru(CO)(PR_3)(NCCH_3)^+$

+

$(\eta^5\text{-}C_5H_5)Ru(CO)(PR_3)(CH_3)_2^+$

Products