4888 *Organometallics* **1996,** *15,* 4888−4890

Hydride Abstraction Reactivity of Haloruthenoceniums and Haloosmoceniums

Agnes N. Xu, Daniel B. Studebaker, and T. David Westmoreland*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459

Received July 29, 1996[⊗]

Summary: $[Cp_2RuCl]PF_6$ reacts with benzylruthenocene in acetonitrile with a 1:1 stoichiometry to produce Cp_2Ru and phenylruthenocenyl methylium cation. Similar hydride abstraction reactivity has also been observed with diruthenocenylmethane, ethylruthenocene, and benzylferrocene. The complexes $[Cp_2MX]^+$ (M = Ru, Os; X = Cl, Br, I) also react with leuco crystal violet and leuco malachite green to give the corresponding carbenium ions but do not exhibit any detectable reactivity with triphenylmethane, cycloheptatriene, or xanthene. On the basis of these observations, the pK_R^+ values for the $[Cp_2MX]^+$ species are estimated to be between +4.7 and +6.9.

High oxidation state metal oxo complexes have been employed as versatile and convenient electron acceptors for many organic and inorganic oxidations.[1] The wide range of formal redox potentials and variety of mechanistic pathways available to such complexes provide a basis for their broad reactivity. Three distinct mechanistic possibilities have been identified for the initial step of oxidations by metal oxo complexes resulting in net oxygen transfer:[2,3] direct oxygen atom transfer, hydride abstraction followed by hydroxide transfer, and hydrogen atom abstraction followed by hydroxyl transfer. High-valent metal halide species, while commonly employed as outer-sphere oxidants, have not been as extensively investigated as metal oxo species. In particular, the possibility of multiple reactivity pathways paralleling those of metal oxo complexes has not been fully established. The halometallocenium species $[Cp_2MX]^+$ (M = Ru, Os; X = Cl, Br, I) have been shown to undergo self-exchange or net chemical reactions with metallocenes[4−7] as shown in eq 1:

$$[Cp_2MX]^+ + Cp_2M' \rightarrow Cp_2M + [Cp_2M'X]^+ \quad (1)$$

Equation 1 corresponds to the net transfer of X^+, a species that is isoelectronic with oxygen atom.

We[8] and others[9] have noted the ability of haloruthenoceniums to abstract hydride from the electron-rich methylene C−H bond in diruthenocenylmethane, eq 2,

$$[Cp_2RuX]^+ + CpRu(C_5H_4)CH_2(C_5H_4)RuCp \rightarrow Cp_2Ru + [CpRu(C_5H_4)CH(C_5H_4)RuCp]^+ + H^+ + X^- \quad (2)$$

or from ferrocenylruthenocenylmethane.[10] These results suggest that multiple mechanistic pathways paralleling those observed for metal oxo complexes may be available to high-valent metal halides as well.

We report herein the ability of the complexes $[Cp_2MX]^+$ (M = Ru, Os; X = Cl, Br, I) to abstract hydride from a variety electron-rich C−H bonds. We have further characterized the hydride abstraction reactivity in these systems by determining the approximate pK_R^+ values for the halometalloceniums.

Experimental Section

Synthesis. All materials were obtained from commercial sources and used as received unless otherwise indicated. $[Cp_2MX]PF_6$ (M = Ru, Os; X = Cl, Br, I),[4] $[CpRu(C_5H_4)COOH]$,[11] and $[CpRu(C_5H_4CH_2Ph)]$[12] were prepared according to literature methods.

$[CpRu(C_5H_4)CO(C_5H_4)RuCp]$. Diruthenocenyl ketone was previously prepared by the reaction of lithioruthenocene with *N*,*N*-dimethylcarbamoyl chloride.[9] In an alternative synthetic approach, the compound was prepared by Friedel−Crafts acylation of ruthenocene by ruthenocenyl chloride. PCl_5 (0.93 g) was added to 1.0638 g of $CpRu(C_5H_4)COOH$ in 15 mL of distilled toluene under an atmosphere of nitrogen. The solution was shaken for 15 min, during which it turned from yellow to red. The solvent was then removed under vacuum and 1.0010 g of ruthenocene in 50 mL of dichloromethane was added. The resulting solution was added dropwise over 30 min to 0.53 g of $AlCl_3$ in 50 mL of dichloromethane under nitrogen. After addition was complete, the mixture was heated at reflux for 30 min then quenched with deoxygenated water. The organic layer was separated and dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. The light brown residue was applied to an alumina column and was eluted under pressure with 30% ethyl acetate/hexanes; 0.5214 g of yellow crystals was obtained (55% based on $CpRu(C_5H_4COOH)$). Anal. Calcd for $C_{21}H_{18}ORu_2$: C, 51.63; H, 3.71; Found: C, 51.22; H, 3.71. The ^1H NMR in CD_3CN exhibits slightly different chemical shifts from

---

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

[1] (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds;* Academic: New York, 1981. (b) Mijs, W. J.; de Jonge, C. R. H. I., Eds.; *Organic Synthesis by Oxidation With Metal Compounds;* Plenum: New York, 1986. (c) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds;* Wiley Interscience: New York, 1988.

[2] Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C−228C.

[3] Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401−1449.

[4] Smith, T. P.; Iverson, D. J.; Droege, M. W.; Kwan, K. S.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2882−2884.

[5] (a) Kirchner, K.; Dodgen, H. W.; Hunt, J. P.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 604−605. (b) Kirchner, K.; Dodgen, H. W.; Hunt, J. P.; Wherland, S. *Inorg. Chem.* **1990**, *29*, 2381−2385. (c) Kirchner, K.; Han, L. F.; Dodgen, Hunt, J. P.; Wherland, S. *Inorg. Chem.* **1990**, *29*, 2556−4559. (d) Anderson, K. A.; Kirchner, K.; Dodgen, H. W.; Hunt, J. P.; Wherland, S. *Inorg. Chem.* **1992**, *31*, 2605−2608.

[6] Watanabe, M.; Sano, H. *Chem. Lett.* **1991**, 555−558.

[7] Shea, T. M.; Deraniyagala, S. P.; Studebaker, D. B.; Westmoreland, T. D. *Inorg. Chem.*, in press.

[8] Studebaker, D. B.; Westmoreland, T. D. *Abstracts of Papers*, 204th National Meeting of the American Chemical Society, Washington DC; American Chemical Society: Washington DC, 1992; INOR 444.

[9] Watanabe, M.; Motoyama, I.; Sano, H. *Inorg. Chim. Acta* **1994**, *225*, 103−109.

[10] Watanabe, M.; Iwamoto, T.; Nakashima, S.; Sadai, H.; Motoyama, I.; Sano, H. *J. Organomet. Chem.* **1993**, *448*, 167−174.

[11] Rausch, M. D.; Fischer, E. O.; Grubert, H. *J. Am. Chem. Soc.* **1960**, *82*, 76−82.

[12] Mark, V.; Rausch, M. D. *Inorg. Chem.* **1964**, *3*, 1067−1069.

S0276-7333(96)00624-3 CCC: $12.00

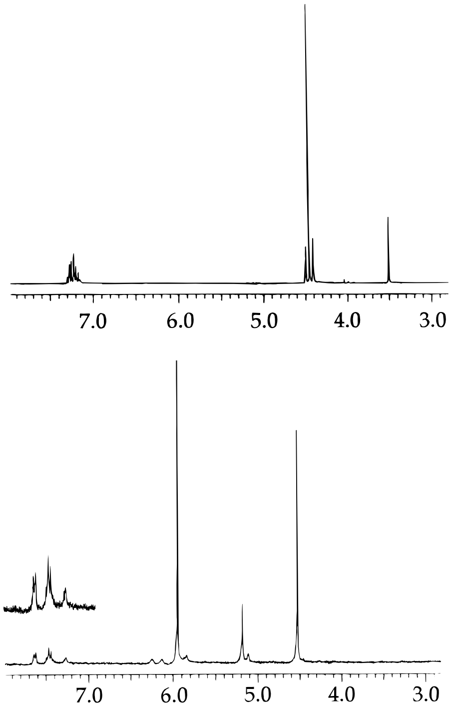

Figure 1. ^{1}H NMR spectra of (top) benzylruthenocene and (bottom) a mixture of benzylruthenocene with 2.0 equiv of $[Cp_2RuCl]^+$ after 20 min at 25 °C.

those obtained previously[9] in $CDCl_3$: δ 4.52 (s, 10H); 4.66 (s, 4H); 5.19 (s, 4H). The CO stretching frequency in KBr was at 1625 cm^{-1}.

The synthesis of diruthenocenylmethane from diruthenocenylketone paralleled the previously published procedure.[9] $CpRu(C_5H_4)CO(C_5H_4)RuCp$ (0.4010 g) was added to 100 mL of ether under a nitrogen atmosphere. The solution was cooled in an ice bath and 0.11 g of $AlCl_3$ was added, followed by 0.2 g of $LiAlH_4$. The system was then stirred at room temperature for 2.5 h and at reflux for an additional 3.75 h. The reaction was quenched with ice/water and the organic layer dried over $MgSO_4$. Rotary evaporation of the solution gave 0.1083 g (28%) of white diruthenocenylmethane. ^{1}H NMR in CD_3CN: δ 3.08 (s, 2H); 4.39 (t, 4H); 4.45 (s, 10H); 4.50 (t, 4H). The ^{1}H and ^{13}C NMR assignments in $CDCl_3$ have been previously reported and all other properties of our sample agree with the published values.[9]

Reactions. All ^{1}H NMR spectra were acquired using a Varian Gemini 300 MHz spectrometer. Chemical shifts were referenced to the solvent (CD_3CN, $\delta = 1.93$ ppm). Hydride abstraction reactions were performed by placing weighed amounts of $[Cp_2MX]PF_6$ and the reductant into a standard NMR tube. CD_3CN (0.75 mL) was added, and the contents were thoroughly mixed. The NMR spectrum of each mixture was monitored periodically until no further change was detected (2−20 min, depending on the reactants). Integrations of the ^{1}H NMR peaks were used to estimate the relative concentrations of the species present at equilibrium.

Results

Hydride Abstraction from Alkyl Metallocenes.

In Figure 1 are shown ^{1}H NMR spectra of the reaction of $[Cp_2RuCl]PF_6$ with benzylruthenocene at 25 °C. Figure 1 (top) gives the spectrum of benzylruthenocene[12] in CD_3CN. Of particular note is the methylene resonance which occurs at 3.49 ppm (2H). Also clearly apparent are the resonances for the unsubstituted Cp ring (4.45 ppm, 5H) and for the benzyl-substituted Cp ring (4.41 ppm, 2H; 4.50 ppm, 2H). The phenyl resonances appear as a multiplet centered at 7.22 ppm (5H). On addition of a 2-fold excess of $[Cp_2RuCl]PF_6$, the spectrum shown in Figure 1 (bottom) appears within minutes and after 20 min remains unchanged for at least 12 h. The spectrum is dominated by the resonances for $[Cp_2RuCl]^+$ (5.95 ppm) and Cp_2Ru (4.52 ppm). All resonances due to benzylruthenocene are absent but have been replaced by a new set. These resonances are identical to those obtained by treating benzylruthenocene with trityl cation and have been assigned to the phenylruthenocenyl methylium cation, $[CpRu(C_5H_4CHPh)]^+$. The peak at 7.28 ppm corresponds to the carbenium proton, and the chemical shift is consistent with those of similar previously reported carbeniums.[9,13] The resonance for the unsubstituted Cp ring occurs at 5.19 ppm and those of the substituted ring at 5.12, 5.85, 6.14, and 6.25 ppm. The phenyl resonances comprise the multiplet with two main features centered at 7.45 and 7.63 ppm.

The net reaction which the NMR results suggest is

$$CpRu(C_5H_4CH_2Ph) + [Cp_2RuCl]^+ \rightarrow [CpRu(C_5H_4CHPh)]^+ + Cp_2Ru + H^+ + X^- \quad (3)$$

This reaction corresponds to the net abstraction of H^- from the methylene group of benzylruthenocene ultimately yielding the net two-electron reduction of $[Cp_2RuCl]^+$ to give the indicated products. The NMR spectral results in Figure 1 give direct evidence for each of the ruthenium-containing products and the stoichiometry, as determined from NMR integrations, is 1:1 $[CpRu(C_5H_4CHPh)]^+$: $[Cp_2RuCl]^+$, consistent with eq 3.

The hydride abstraction reaction seems to be fairly general for electron-rich C−H bonds and has also been observed for other alkylmetallocenes, including ruthenocenylferrocenylmethane,[10] ethylruthenocene, and benzylferrocene,[14] as well as for some wholly organic hydride donors as described below. Metallocene stabilized carbenium ions are known,[15] and metallocenyl substituents are generally recognized as good electron-donating groups.[16] For example, the Hammett σ_p value for ferrocenyl is estimated to be −0.18.[17] It seems reasonable that reaction 3 and related reactions are driven by the thermodynamic stability of the product carbenium.

Hydride Abstraction from Triphenylmethanes.

In order to more fully characterize the hydride-abstracting reactivity of the metalloceniums, we have examined their reactions with a variety of organic hydride donors, particularly with derivatives of triphenylmethane. It is known[18] that the relative stabilities of the product

---

[13] Boev, V. J. *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 555−559; *Zh. Obshch. Khim.* **1987**, *57*, 633−639.

[14] Studebaker, D. B.; Westmoreland, T. D., unpublished results.

[15] (a) Lupan, S.; Kapon, M.; Cais, M.; Herbstein, F. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1025−1027. (b) Rybinskaya, M. I.; Kreindlin, A. Z.; Fadeeva, S. S. *J. Organomet. Chem.* **1988**, *358*, 363−374. (c) Yanovsky, A. I.; Struchkov, Y. T.; Kreindlin, A. Z.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *369*, 125−130. (d) Rybinskaya, M. I.; Kreindlin, A. Z.; Struchkov, Y. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1989**, *359*, 233−243.

[16] Rosenblum, M. *Chemistry of the Iron Group Metallocenes;* Wiley-Interscience: New York, 1965; Part 1.

[17] Nesmeyahov, A. N.; Perevalova, E. G.; Gubin, S. P.; Grandberg, K. I.; Kozlovsky, A. G. *Tetrahedron. Lett.* **1966**, 2381−2387.

[18] March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1985; pp 165−172.

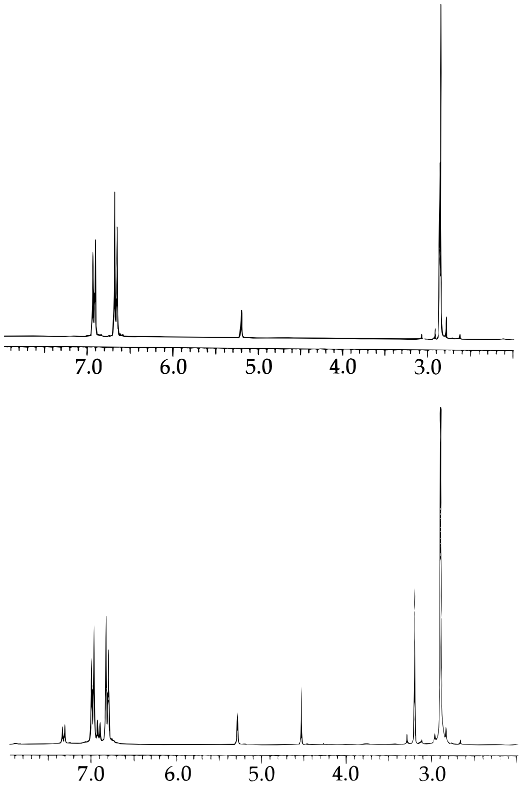

Figure 2. ^{1}H NMR spectra of (top) leuco crystal violet and (bottom) a mixture of leuco crystal violet with 0.04 equiv of $[Cp_2RuCl]^+$ after 15 min at 25 °C.

carbeniums are related to the quantity $pK_R{}^+$, defined by eq 4. The $pK_R{}^+$ of a species has been shown to be

$$ROH + H^+ \rightleftharpoons R^+ + H_2O \qquad pK_R{}^+ = -\log K_{eq} \qquad (4)$$

proportional to the heterolytic gas phase dissociation energy of RH to R^+ and H^- and is thus a measure of hydride-donating ability.[19]

In Figure 2 is shown the reaction of excess leuco crystal violet, $HC(C_6H_4N(CH_3)_2)_3$, with $[Cp_2RuCl]^+$ at 25 °C. Figure 2 (top) gives the spectrum of leuco crystal violet in CD_3CN.[20] Addition of a substoichiometric amount[21] of $[Cp_2RuCl]PF_6$ leads to an immediate change from colorless to deep violet, characteristic of the crystal violet carbenium ion, $[C(C_6H_4N(CH_3)_2)_3]^+$. The ^{1}H NMR spectrum of the mixture is shown in Figure 2 (bottom), in which no $[Cp_2RuCl]^+$ resonance is evident, only that from Cp_2Ru. In addition, new resonances that correspond to those of an authentic sample of crystal violet carbenium are evident.[22] The results in Figure 2 clearly indicate that $[Cp_2RuCl]^+$ is thermodynamically capable of reaction with leuco crystal violet to give net hydride abstraction.[23]

Table 1. $pK_R{}^+$ Values for Hydride Abstractors, R^+, and Halometallroceniums[a]

R^+	$pK_R{}^+$
crystal violet	+9.36
malachite green	+6.92
$[Cp_2MX]^+$ (M = Ru, Os; X = Cl, Br, I)	~6
tropylium cation	+4.7
xanthenyl cation	−0.85
trityl cation	−6.6

[a] $pK_R{}^+$ values for the organic species are from refs 24 and 25.

In Table 1 are listed several commercially available organic hydride donors and their measured $pK_R{}^+$ values. All of the halometallroceniums examined ($[Cp_2MX]^+$; M = Ru, Os; X = Cl, Br, I) yield carbenium ions with leuco crystal violet and leuco malachite green. With cycloheptatriene, xanthene, and triphenylmethane, however, none of the corresponding carbenium ions were detected by ^{1}H NMR after 12 h, nor was any ruthenocene or osmocene detected. On the basis of these results, we have placed the halometallroceniums on the scale as shown, with $pK_R{}^+$ values between +4.7 and +6.9.

Although all the halometallroceniums seem to be thermodynamically similar in their hydride-abstracting ability, we have noted qualitatively that reactions of chlorometallroceniums seem to reach completion faster than those of the corresponding iodometallroceniums, with bromometallocenium intermediate. Furthermore, the ruthenoceniums react faster than the corresponding osmoceniums. All reactions are, however, complete within 20 min. The ruthenoceniums are better two-electron oxidants than the corresponding osmoceniums.[4]

The results described above provide evidence for a general oxidative reactivity pathway for $[Cp_2MX]^+$ complexes, in addition to the previously reported coupled two-electron/atom transfer pathway.[4−7] The thermodynamic results indicate that $[Cp_2MX]^+$ is relatively weak hydride abstractor. It is not yet clear whether hydride abstraction occurs via direct attack by the halide or by the formation of a metal hydride, followed by reductive elimination of HX. Studies are currently underway to address these details more fully.

Acknowledgment. Mr. T. M. Shea is gratefully acknowledged for providing $[Cp_2RuCl]PF_6$. The donors of the Petroleum Research Fund, administered through the American Chemical Society, are acknowledged for support. D.B.S. also acknowledges support from the Howard Hughes Medical Institute and a DuPont College Science grant.

OM9606247

---

(19) Cheng, J. P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2655−2660.

(20) 2.84 ppm, $HC(C_6H_4N(C\mathit{H}_3)_2)_3$; 5.20 ppm, $\mathit{H}C(C_6H_4N(CH_3)_2)_3$; 6.67 and 6.92 ppm, $HC(C_6\mathit{H}_4N(CH_3)_2)_3$.

(21) Addition of stoichiometric or excess $[Cp_2RuCl]^+$ is complicated over time by the oxidation of chloride by the metallocenium,[7] e.g., $[Cp_2RuCl]^+ + 2Cl^- \rightarrow Cp_2Ru + Cl_3{}^-$. These side reactions did not interfere on the time scale of Figures 1 and 2.

(22) 3.19 ppm, $[C(C_6H_4N(C\mathit{H}_3)_2)_3]^+$; 6.90 and 7.31 ppm, $[C(C_6\mathit{H}_4N(CH_3)_2)_3]^+$.

(23) The stoichiometry of this reaction is difficult to reproduce but usually gives more crystal violet carbenium than ruthenocene. The ratios are very sensitive to O_2 and to the purity of the materials and have not been sufficiently reproducible in our hands for a stoichiometry to be reported with confidence. The initial reaction is most likely a 1:1 reaction based on the alkylmetallocene results . At any rate, it is clear that the ultimate products are those obtained by net hydride abstraction and that the metallocenium is thermodynamically competent to carry out the reaction.

(24) Diffenbach, R. A.; Sano, K.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 4747−4749.

(25) (a) Hisatome, M.; Yamakawa, K. *Tetrahedron* **1971**, *27*, 2101−2110. (b) Ceccon, A.; Giacometti, G.; Venzo, A.; Paolucci, D.; Benozzi, D. *J. Organomet. Chem.* **1980**, *185*, 231−239.