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Additivity of Fluorine Substituent Effects in Ruthenocene Ionization Energetics

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Summary: Free energies of ionization ($\Delta G_i°$) in the gas phase have been determined for the seven fluorine-substituted ruthenocenes with formulas (η^5-C_5Me_5)(η^5-$C_5H_{5-n}F_n$)Ru (n = 1−5) and (η^5-C_5H_5)(η^5-C_5F_5)Ru. In (η^5-C_5Me_5)(η^5-$C_5H_{5-n}F_n$)Ru (n = 1−5), each additional fluorine was found to increase the ionization free energy by 3.7 ± 0.5 kcal mol^{-1}, and the $\Delta G_i°$ difference between the two possible isomers for n = 2 and n = 3 was found to be ≤ 1 kcal mol^{-1}. Therefore, the intrinsic effect of each fluorine substituent on ionization energy is approximately additive.

The syntheses of the fluorine-substituted ruthenocenes (η^5-C_5Me_5)(η^5-C_5F_5)Ru (**1**)[1] and (η^5-C_5H_5)(η^5-C_5F_5)Ru (**2**)[2] were recently published by Hughes and co-workers. Relatively little is known about the nature of fluorine substituent effects in metallocene chemistry since **1** and **2** were the first two η^5-C_5F_5 complexes to be reported. The electrochemistry and gas-phase ionization free energy ($\Delta G_i°$) of **1** were investigated,[3] and it was concluded that fluorine is not an unusual substituent compared to the other halogens. A γ parameter value[4,5] of 1.5 was obtained for the η^5-C_5F_5 ligand, indicating that five fluorine substituents raised the ionization free energy compared to η^5-C_5H_5 (Cp).

The effect of individual fluorine Cp substituents on oxidation energetics is not known, and it is not known if the effects for multiple fluorine substitution are additive. Because the net effect of a fluorine substitutent is an unusual combination of strong σ withdrawing effect and significant π donation to the ring,[6] we felt that substituent additivity could not necessarily be assumed. Furthermore, it is not known if *ligand* additivity can be assumed for η^5-C_5F_5 and any Cp derivative L in (η^5-C_5F_5)(L)$M^{0/+}$ metallocene ionization energetics, as has proven to be the case for a few other ruthenocenes LL′$Ru^{0/+}$ (errors in predicted values ≤ 3 kcal mol^{-1}).[4]

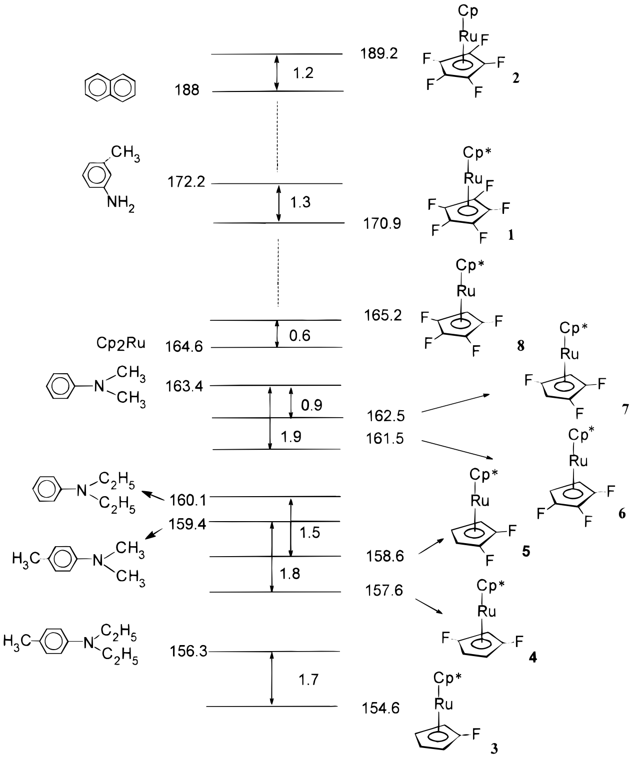

Figure 1. Free energy ladder. Reference compounds are on the left. $\Delta G_{et}°$ and $\Delta G_i°$ values at 350 K are shown in kcal mol^{-1}.

In the present work, the free energies of ionization ($\Delta G_i°$) in the gas phase have been determined for the seven fluorine-substituted ruthenocenes with formulas (η^5-C_5Me_5)(η^5-$C_5H_{5-n}F_n$)Ru (n = 1−5) and (η^5-C_5H_5)(η^5-C_5F_5)Ru. The results address the questions of ligand and substituent additivity for these novel metallocenes.

Experimental Section

The preparation of the compounds of general formula (η^5-C_5Me_5)(η^5-$C_5H_{5-n}F_n$)Ru (n = 1−4) will be reported elsewhere.[7] The synthetic method used closely follows that used to prepare (η^5-C_5Me_5)(η^5-C_5F_5)Ru (**1**) and (η^5-C_5H_5)(η^5-C_5F_5)Ru (**2**).[8]

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(1) Curnow, O. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1992**, *114*, 5895.

(2) Hughes, R. P.; Zheng, X.; Ostrander, R. L.; Rheingold, A. L. *Organometallics* **1994**, *13*, 1567.

(3) Richardson, D. E.; Ryan, M. F.; Geiger, W. E.; Chin, T. T.; Hughes, R. P.; Curnow, O. J. *Organometallics* **1993**, *12*, 613.

(4) Ryan, M. F.; Siedle, A. R.; Burk, M. J.; Richardson, D. E. *Organometallics* **1992**, *11*, 4231. The γ parameters for the electronic effects of Cp derivatives as ligands are based on their effect on the ionization free energy of LL′Ru complexes, where L is the ligand of interest and L′ is either L or another Cp ligand with a known γ parameter. The scale is anchored to $\gamma = 0$ for Cp and $\gamma = -1.0$ for C_5Me_5, and a negative value of γ therefore indicates that the ligand decreases the ionization free energy of ruthenocene derivatives relative to Cp.

(5) Richardson, D. E. In *Organometallic Ion Chemistry*; Freiser, B., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996.

(6) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(7) Hughes, R. P., Zheng, X.; Morse, C. A. Manuscript in preparation.

(8) Compounds were judged analytically pure by NMR and mass spectrometry.

(9) For reviews of FTICR-MS, see: (a) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316. (b) Gross, M. L.; Rempel, D. L. *Science* **1984**, *226*, 261. (c) Eyler, J. R.; Baykut, G. *Trends Anal. Chem.* **1986**, *5*, 44.

(10) (a) Ryan, M. F.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1992**, *114*, 8611. (b) Sharpe, P.; Richardson, D. E. *Inorg. Chem.* **1990**, *29*, 2776. (c) Richardson, D. E.; Christ, C. S.; Sharpe, P.; Ryan, M. F.; Eyler, J. R. In *Bond Energetics in Organometallic Compounds;* Marks, T. J., Ed.; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990.

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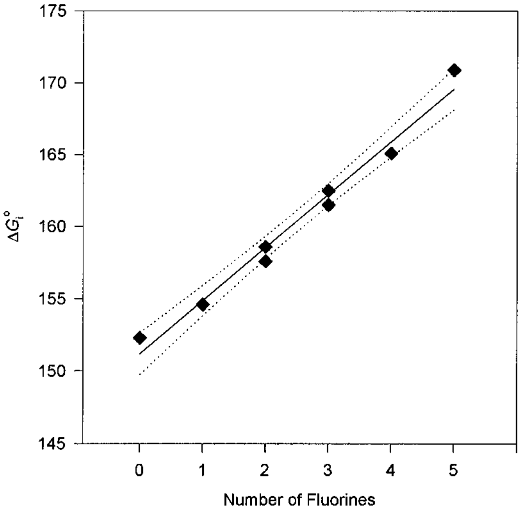

Figure 2. Plot of $\Delta G_{i,350}°$ vs number of fluorines. The solid line is the linear regression, and dotted lines are 95% confidence intervals.

Table 1. Free Energies of Ionization and Derived γ(L) Values

ligand	$\Delta G_i°(L(C_5Me_5)Ru)$/ kcal mol^{-1}	γ(L)
η^5-C_5H_5	152.3	0 (defined)
η^5-C_5H_4F	154.6	0.23
η^5-1,3-$C_5H_3F_2$	157.6	0.46
η^5-1,2-$C_5H_3F_2$	158.6	0.54
η^5-1,2,3-$C_5H_2F_3$	161.5	0.76
η^5-1,2,4-$C_5H_2F_3$	162.5	0.84
η^5-C_5HF_4	165.2	1.0
η^5-C_5F_5	170.8	1.5 (1.7 ± 0.2)[a]

[a] See text.

Fourier transform mass spectrometry[9] was used to investigate the thermal electron-transfer equilibrium, ETE,[10] reactions of compounds **1**−**8** (compound abbreviations in Figure 1) with several organic reference compounds. The general reaction of eq 1 was studied, and equilibrium constants and

$$LL'Ru + R^+ = R + LL'Ru^+ \qquad (1)$$

reaction free energies, $\Delta G_{et}°$, were determined at 350 K as previously described for various reference compounds R. Previously reported $\Delta H_i°$ values and estimates of $\Delta S_i°$ for the reference compounds have been used to derive $\Delta G_{i,350}°$(R) values at 350 K. Pressures for neutrals were obtained directly from the N_2-calibrated ion-gauge reading and are likely to be low for both the metallocenes and the reference compounds. However, the assumption was made that the reference compounds and the metallocenes have similar ion gauge sensitivities and system factors so the equilibrium constants, which depend on the pressure ratios, could be obtained with acceptable accuracy. Previous pressure calibration studies in our laboratory have shown that the assumption is approximately true for the reference compounds and nonfluorinated metallocenes if the pumping speed in the main chamber is reduced substantially, as we did in this work. Thus, the relative ionization free energies are estimated to be accurate within ±0.5 kcal mol^{-1}. Due to the pressure errors, we estimate that the absolute errors are ±1.5 kcal mol^{-1}. Note that an unusually large pressure ratio error of 5/1 would lead to an error of ±1.1 kcal mol^{-1} in $\Delta G_{et}°$ at 350 K.

Results and Discussion

The measured $\Delta G_{et}°$ values for the ETE reactions of **1**−**8** with various reference compounds are shown in Figure 1 as a free energy ladder. The derived values of $\Delta G_{i,350}°$ are shown next to the compounds in the ladder. The value obtained in this work for **1** agrees within ±0.1 kcal mol^{-1} with that reported earlier.[3]

A plot of $\Delta G_{i,350}°$ vs the number of fluorines, n, in $(\eta^5$-$C_5Me_5)(\eta^5$-$C_5H_{5-n}F_n)Ru$ ($n = 0-5$) is shown in Figure 2. The points form a good straight line with slope = 3.7 ± 0.5 kcal mol^{-1} n^{-1} (95% confidence interval) and $r^2 = 0.96$. We conclude that fluorine substituent effects are essentially additive, with each additional fluorine raising the ionization energy by ~3.7 kcal mol^{-1}.

Equation 2 can be used to derive the γ parameters for Cp derivatives in ruthenocenes by setting $\gamma(C_5Me_5)$

$$\Delta G_i°(LL'Ru) = [13.0(\gamma(L) + \gamma(L')) + 164.6] \text{ kcal mol}^{-1} \qquad (2)$$

= −1.0 and using the derived values for $\Delta G_i°$ (**1**, **3**−**8**) in Figure 1. The senstivity factor of 13.0 kcal mol^{-1} is the previously determined[4] value for M = Ru, while 164.6 kcal mol^{-1} is the $\Delta G_i°$ value for L = L′ = Cp (for which γ is defined as zero). Derived γ values for the fluorinated Cp derivatives are given in Table 1 along with Cp for comparison. Although the overall trend is clearly additive with respect to F substituent effects, we do note some small but reproducible deviations from additivity. For $n = 2$ and 3, two structural isomers are available and appear to have significantly different $\Delta G_i°$ values. No particular trend is noted with respect to the isomer structures. In addition, the jump from $n = 4$ to 5 (5.7 kcal mol^{-1}) is larger than the rest but is just inside the 95% confidence interval (see Figure 2). This larger jump may represent a "perfluoro" effect,[11] but the effect is small and may be accounted for by experimental error.

From the data for **2**, eq 2 with $\gamma(Cp) = 0$ yields $\gamma(\eta^5$-$C_5F_5) = 1.9$ for η^5-C_5F_5 with Cp rather than C_5Me_5 as the other ligand (which leads to $\gamma(\eta^5$-$C_5F_5) = 1.5$). It is tempting to suggest that ligand effects are not additive and that the electron-rich C_5Me_5 ligand may reduce the ionization energy-raising effect of η^5-C_5F_5 more effectively than Cp itself. However, the number of systematically studied compounds with respect to ligand additivity is small, and the poorest additivity observed[4] previously (L = indenyl) also has a large range on its value of γ (−0.4 ± 0.2). Therefore, we simply suggest a range of $\gamma(C_5F_5) = 1.7 \pm 0.2$ based on the two η^5-C_5F_5 metallocenes studied to date and do not conclude that η^5-C_5F_5 is unusual with respect to additivity.

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(11) Rabalais, J. W. *Principles of Ultraviolet Photoelectron Spectroscopy*; Wiley: New York, 1977; pp 323−327.