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Gas-Phase and Solution Studies of the Oxidation of the First Perfluorocyclopentadienyl Complex, $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5F_5)]$

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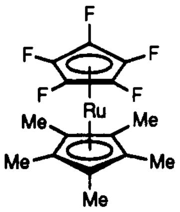
Summary: The oxidation of the title compound (1) has been investigated in solution (electrochemistry in various solvents) and the gas phase (by using the electron-transfer equilibrium method). The C_5F_5 ligand is compared in its electronic effect to other known cyclopentadienyl ligands.

The preparation of the first metallocene complex of the pentafluorocyclopentadienyl ligand, $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5F_5)]$ (1), was reported recently.[1] Given the novelty of the C_5F_5 ligand, it is of interest to consider its effect on the oxidation thermochemistry of 1 relative to that of a large number of ruthenocene derivatives that have been investigated in solution[2] and the gas phase.[3] We report here the solution redox chemistry of 1 (studied by using cyclic voltammetry) and the gas-phase ionization free energy of 1 (to 1^+) ($\Delta G_i°$, studied by using Fourier transform ion cyclotron resonance mass spectrometry).



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Gas-Phase Ionization Energetics. Fourier transform mass spectrometry[4] was used to investigate the thermal electron-transfer equilibrium[5] (ETE) reactions of 1 with several organic reference compounds. The general reaction of eq 1 was studied, and equilibrium constants and reaction

$$1 + R^+ = R + 1^+ \qquad (1)$$

free energies ($\Delta G_{et}°$) were determined as previously described[3,5] 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.[5a] The measured $\Delta G_{et}°$ values for ETE reactions of 1 with reference compounds azulene ($\Delta G_i° = 167.8 \pm 1.5$ kcal mol^{-1}) and *m*-toluidine (172.2 ± 1.5 kcal mol^{-1}) are $+2.6$ and -1.0 kcal mol^{-1}, respectively, yielding an average value of $\Delta G_i°$ for 1 of 170.8 ± 1.5 kcal mol^{-1}.

Comparison of C_5F_5 to Other C_5H_5 Derivatives. Ryan et al.[3] recently reported a new parameter scale (γ parameters) for the electronic effects of Cp derivatives as ligands 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 indicates that the ligand decreases the ionization free energy of ruthenocene derivatives relative to Cp. Equation 2 can be

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

used to derive the appropriate γ parameter for C_5F_5 by setting $\gamma(Cp^*) = -1.0$ and using the above value for $\Delta G_i°(1)$. The value of $\gamma(C_5F_5) = 1.5$ obtained from eq 2 is compared to a number of other Cp derivatives in Table I. Initially, it might be surprising to find that the highly electronegative F leads to a $\gamma(C_5F_5)$ value comparable to that for C_5Cl_5 ($\gamma = 1.06$) and a value much smaller than that estimated for $C_5(CF_3)H$ ($\gamma \approx 3$). The effect on the free energy of ionization of $[Ru(C_5X_5)Cp^*]$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) when X = Cl is replaced with F amounts to an increase of only ~1 kcal mol^{-1} per F. This effect can be compared to the ionization energetics of substituted benzenes, C_6X_6, where F substitution for Cl increases the ionization energy by ~3.5 kcal mol^{-1} per F.[6] A "perfluoro" effect has been well characterized in the photoelectron spectroscopy of perfluorinated aromatic compounds, where the ionization energies of ring σ electrons are more strongly affected than those of the π electrons as a result of the π resonance interactions.[7]

The nature of F substituent effects can be described by classical electrostatic parameterization schemes. Param-

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Table I. Ligand and Substituent Parameters for Selected Cyclopentadienyl Derivatives

L	$\gamma(L)^a$	substituent	$\sigma_\alpha{}^b$	$\sigma_F{}^b$	$\sigma_{R^+}{}^b$	$\Delta G_i°[Ru(L)Cp^*]^c$	E_{pa} vs Fc^e
C_5F_5	1.5	F	0.13	0.44	−0.25	170.8	1.07
C_5Cl_5	1.06	Cl	−0.43	0.45	−0.17	165.4	1.11^f
$C_5H_4NO_2$	0.79	NO_2	−0.26	0.65	0	161.9	0.7
$C_5(CF_3)_4H$	~3	CF_3	−0.25	0.44	0	~192	1.3
C_5H_5	0^d	H	0^d	0^d	0^d	152.3	0.35
C_5Me_5	-1.00^d	Me	−0.35	0	−0.08	137.9	0.15^g

[a] From ref 3 except for C_5F_5 (this work). [b] Substituent parameters from ref 7. [c] Free energy of ionization at 350 K in kcal mol^{-1}. [d] By definition. [e] Anodic peak potentials (in V) in $CH_2Cl_2/0.10$ M NBu_4PF_6 at ambient temperature. The reference potential is $E_{1/2}(Fc^{+/0})$. [f] Quasi-reversible with $E_{1/2} = 1.03$ V vs Fc. [g] Reversible with $E_{1/2} = 0.09$ V vs Fc.

eters appropriate for fitting gas-phase data have been described by Taft and co-workers, and they include σ_α (polarizability), σ_F (field effects), and σ_{R^+} (π resonance effects on aromatic rings).[8] The published parameters for several substituents are given in Table I. A negative value for the particular parameter indicates that this effect would stabilize the buildup of positive charge and, in the present case, contribute to a lowering of the ionization energy of LL′Ru. The field effects of Cl and F are essentially equal in this particular parameterization scheme (Table I), so only σ_α and σ_{R^+} will contribute to the difference between Cl and F as substituents. Compared to Cl, F is expected to increase the ionization energy as a consequence of its lower polarizability, but the π resonance effect of F compensates substantially in the case of the ruthenocene derivatives here with the net result that the ionization energies of 1 and [Ru(C_5Cl_5)Cp*] are similar.

Electrochemistry. Cyclic voltammetry (CV) experiments were conducted at Pt electrodes with an electrolyte system of $CH_2Cl_2/0.1$ M Bu_4NPF_6 at ambient temperatures over the scan rate range of $0.02 < v < 50$ V/s. Ferrocene (Fc) was used as a 1e$^-$ Nernstian internal standard, and all potentials are referenced to the $Fc^{+/0}$ couple. Peak potentials for the oxidation of 1 at different CV scan rates were referenced to those of Fc in order to minimize ohmic errors.

Complex 1 exhibits a diffusion-controlled, irreversible, two-electron oxidation for which $E_{pa} = +1.07$ V vs Fc when $v = 0.2$ V/s. No cathodic waves were observed out to the solvent limit of −2.4 V. At a Pt-disk electrode, the peak current function for this wave, 10.0 μA/mM(V/s)$^{1/2}$, was about twice that of equimolar ferrocene (4.3 μA/mM(V/s)$^{1/2}$) under identical conditions (Figure 1). Since the diffusion coefficients of 1 and Fc are expected to be similar, the comparative current functions are strongly suggestive of a 2e$^-$ oxidation for 1.

The anodic peak potential of an irreversible wave is predicted to shift positively by $30/\alpha n$ mV per decade increase in v.[9] Taking $n = 2$ and assuming $\alpha \approx 0.5$, the observed shift of 35 mV is consistent with expectations for an irreversible system.

Bulk electrolysis of 1 under nitrogen with $E_{appl} = +1.2$ V consumed 2.2 faradays/equiv as the solution went from colorless to light yellow. Voltammetric scans after electrolysis showed cathodic waves for electrolysis products at $E_{pc} = -0.16$ and -0.96 V. After subsequent reduction of the electrolysis solution at $E_{appl} = -0.3$ V, several other waves arising from apparent decomposition products were observed, but 1 was not regenerated.

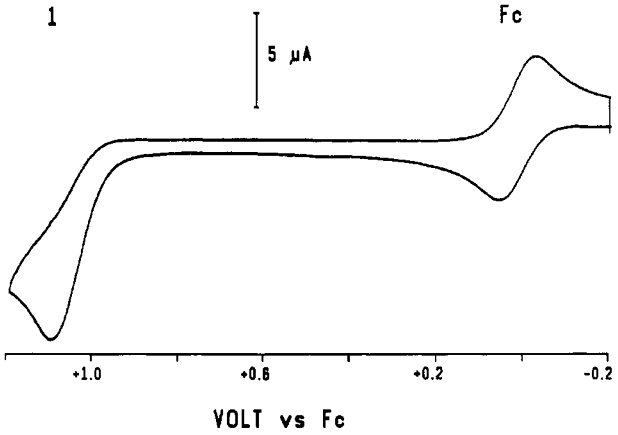

Figure 1. Cyclic voltammogram of an equimolar mixture of ferrocene and 1 in $CH_2Cl_2/0.1$ M Bu_4NPF_6 at a Pt electrode. Conditions: ambient temperature, $v = 0.20$ V/s, concentration 0.71 mM.

All electrochemical results are consistent with the oxidation of 1 being an irreversible 2e$^-$ process in $CH_2Cl_2/0.1$ M Bu_4NPF_6. Similar observations have been made for other ruthenocene derivatives.[2] Mann and co-workers have shown that the oxidation of Cp_2Ru is a reversible 1e$^-$ process when the poorly nucleophilic ion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate is used as the anion of the supporting electrolyte.[2a] It is unlikely, therefore, that the electron-transfer reactions of ruthenocenes are inherently slow and very likely that the irreversibility of these processes is due to rapid follow-up reactions of the initial monocation with the anions present in most supporting electrolytes. If the rates of such reactions are similar for a set of substituted ruthenocene cations, their electrochemical potentials (e.g., E_{pa} or $E_{1/2}$ values) will be displaced an approximately constant amount from their $E°$ values. This apparently accounts for the overall correlation of E_{pa} values for substituted ruthenocenes with the Ru 3d binding energies[2b] and the gas-phase free energies of ionization of the complexes.[3]

Values of E_{pa} vs Fc for several ruthenocene derivatives are given in Table I for comparison to gas-phase $\Delta G_i°$ values. As expected from the gas-phase results, the E_{pa} values for 1 and [Ru(C_5Cl_5)Cp*] (2) are close to the same value.[10] The differential solvation energy[5,11] for the $1^{+/0}$ couple would be expected to be somewhat larger than that of $2^{+/0}$ because of the smaller size of the former, and this is consistent with the smaller difference between the solution potentials (~1 kcal mol^{-1}) compared to the

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(10) We have investigated the electrochemistry of [Ru(C_5Cl_5)Cp*] in CH_2Cl_2/NBu_4PF_6 and find that the +/0 redox couple is quasi-reversible with an $E_{1/2}$ value of 1.03 V vs Fc ($E_{pa} = 1.11$ V). Potentials measured in this work for other [RuCp*L] couples are also given in Table I. In general, our results are in agreement with the potentials *relative to Fc* reported in ref 2b (within ~100 mV).

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difference between the gas-phase potentials (~5 kcal mol^{-1}). Variations in solvation energetics account for part of the scatter in plots correlating $\Delta G_i°$ values and electrochemical potentials for ruthenocene derivatives.[3]

Conclusions. It is clear that the η^5-C_5F_5 ligand is quite comparable to other Cp derivatives with moderately electron-withdrawing substituents in its electronic properties. This result is consistent with the findings of Paprott and Seppelt,[12] who observed a small perfluorination effect on the acidity of C_5F_5H. They estimated the acidity of C_5F_5H to be greater than that of cyclopentadiene (pK_a = 15.5) but less than that of CF_3CH_2OH (pK_a = 12.8).[12] Comparison of the present data to our earlier ETE studies of ruthenocene derivatives indicates that the F substituent is similar in electronic effect to Cl as a substituent. Although η^5-C_5F_5 complexes have proven to be elusive until recently, the ligand does not lead to any particularly unexpected effects in the redox chemistry of the ruthenocene complex 1.

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