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Parameter Scale for Substituent Effects in Cyclopentadienyl Complexes Based on Gas-Phase Electron-Transfer Equilibrium Studies of Ruthenocene Derivatives

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Gas-phase electron-transfer equilibrium (ETE) studies have been used to obtain the free energies of ionization at 350 K for a number of ruthenocene derivatives of general formula LL′Ru, where L and L′ are derivatives of the η^5-cyclopentadienyl ligand (Cp). Equilibrium constants were determined by using Fourier transform ion cyclotron resonance mass spectrometry. Various metallocene and organic reference compounds have been used to establish the free energies of ionization ($\Delta G_i°$), and the derived values cover a range from ~135 to 195 kcal mol^{-1}. A parameter scale (γ) for Cp substituent effects is derived from the data by assigning anchor parameters to Cp and η^5-pentamethylcyclopentadienyl (Cp*). The ETE results suggest that L = fluorenyl does not stabilize the oxidation of Cp*RuL to the extent that L = Cp* does, with the effect of L = Flu being ~65% of the Cp* effect. The consistency of the calculated free energies of ionization based on the assumption of ligand additivity is within ~3 kcal mol^{-1}. The potential usefulness of the γ parameters in correlation and prediction of Cp substituent effects in organometallic reactivity and catalysis is considered.

The variation of reactivity at metal centers is often strongly influenced by the nature of ancillary ligands, and modification of η^5-cyclopentadienyl (Cp) ancillary ligands has been used extensively to modify reactivity in organometallic chemistry.[1] In some cases, Cp substituent effects have been attributed to ancillary ligand/substrate steric interactions that inhibit the formation of key transition states.[1] The substitution of C_5Me_5 (Cp*) for Cp is certainly one of the best known methods for increasing steric congestion at a metal center.[1] In other cases, electronic effects of Cp substituents are considered to be dominant. For example, the changes in the electronic properties of metallocenes when Cp* replaces Cp are well documented.[2] In these ways, modifications of ancillary Cp ligands can be used to increase the stability of reactive metal complexes and alter their catalytic properties.

Variation of oxidation–reduction energetics with changes in substituents is a useful method for assessing electronic effects since the influences of steric effects are negligible when the structural changes that accompany oxidation or reduction are small. Thus, electrochemistry[3] and photoelectron spectroscopy[4] (PES) have been used to characterize electronic Cp substituent effects in metallocenes and related compounds. The applicability of these methods can be somewhat limited by experimental factors such as electrochemical irreversibility of redox couples and the vertical nature of PES transitions.[5]

We have previously demonstrated the usefulness of electron-transfer equilibrium (ETE) techniques in the study of the thermodynamics of gas-phase metal-centered redox reactions.[6,7] Free energies for the oxidation or reduction of neutral metal complexes in the gas phase can be derived from Fourier transform mass spectrometric (FTMS) studies[8] between room temperature and ~500 K. For example, in an earlier study[6] the free energy of ionization of ruthenocene (eq 1, $\Delta G_i° = 164.6$ kcal mol^{-1}) was

$$Cp_2Ru \rightleftharpoons Cp_2Ru^+ + e^- \qquad (1)$$

determined at 350 K, thus providing thermal ionization energetics for the solvent-free $Cp_2Ru^{+/0}$ couple. The solution electrochemistry of the one-electron oxidation of ruthenocene is irreversible under most conditions,[9] but Mann and co-workers recently reported[9b] a reversible potential in CH_2Cl_2 containing a very weakly coordinating electrolyte. Most other ruthenocene derivatives also display irreversible electrochemical oxidations with more common electrolyte/solvent combinations, one known exception being the decamethylruthenocene couple $Cp^*_2Ru^{+/0}$, which is reversible in methylene chloride.[9] The differential solvation energies derived from the gas-phase data and the reversible electrochemical potentials will be discussed below.

Given the absence of reversible electrochemical data for most ruthenocenes, we initiated a FTMS ETE investigation of the gas-phase ionization energetics of a number of

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(1) Examples of the modification of organometallic reactivity by altering Cp ancillary ligands can be found for different types of compounds and reactions in many texts and compilations, e.g.: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987. (b) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982. A useful recent review of cyclopentadienyl derivatives with bulky substituents: Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291.

(2) (a) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. (b) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

(3) Kotz, J. C. In *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum Press: New York, 1986.

(4) Green, J. C. *Struct. Bonding* **1986**, *43*, 37.

(5) Rabalais, J. W. *Principles of Ultraviolet Photoelectron Spectroscopy*; Wiley-Interscience: New York, 1977.

(6) Ryan, M. F.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1992**, *114*, 8611.

(7) (a) 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. (b) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1990**, *29*, 2779. (c) Richardson, D. E. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; NATO ASI Series C; Kluwer: Dordrecht, The Netherlands, 1992; Vol. 367. (d) Sharpe, P.; Richardson, D. E. *Coord. Chem. Rev.* **1989**, *93*, 59.

(8) For reviews of the ion cyclotron resonance technique, 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. *TrAC, Trends Anal. Chem.* (*Pars. Ed.*) **1986**, *5*, 44.

(9) (a) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130 and references therein. (b) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687.

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Table I. Free Energies of Ionization and Other Data

compd[a]					
LL′Ru	no.	$\Delta G_i°$(expt)[b]	$E_{1/2}$[c]	XPS[d]	$\Delta G_i°$(eq 3)[b]
(Cp)(Cp)Ru	1	164.6 ± 2.0	0.80 (1.03)[e]	280.7 (7.15)[f]	164.6
(Cp)(Cp*)Ru	2	152.3 ± 2.0	0.54[e]	280.2	151.6
(TTFMH)(Cp*)Ru	3	192 ± 5	1.78[g]		192
(TTFMOSi)(Cp*)Ru	4	171.7 ± 2.0	1.55[g]		171.7
(C_5Cl_5)(Cp*)Ru	5	165.4 ± 2.0	1.30[e]	280.8	165.4
(NO_2Cp)(Cp*)Ru	6	161.9 ± 2.0			161.9
(TMSCp)(TMSCp)Ru	7	158.4 ± 2.0			160.2
(Ind)(Ind)Ru	8	151.0 ± 2.0			153.9
(TMSCp)(Cp*)Ru	9	151.3 ± 2.0			149.4
(Ind)(Cp*)Ru	10	149.4 ± 2.0	0.43[e]	280.1	146.3
(Flu)(Cp*)Ru	11	143.1 ± 2.0	0.34[e]	279.6	143.1
(Cp*)(Cp*)Ru	12	137.9 ± 2.0	0.42[e,h]	279.9	138.6

[a] Ligand abbreviations in Table II. [b] Units are kcal mol^{-1}. [c] Units are V. All $E_{1/2}$ values are for LL′$Ru^{+/0}$ couples, are referenced versus SCE in CH_2Cl_2, and are irreversible unless otherwise noted. [d] Values for 3d binding energies of ruthenocenes taken from ref 9a. Units are eV. [e] Reference 9a except for value in parentheses for Cp_2Ru (ref 9b, a reversible potential vs Ag/AgCl in CH_2Cl_2). [f] Vertical ionization energy from ref 4. [g] Reference 21b. [h] Reversible.

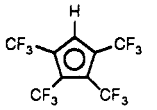
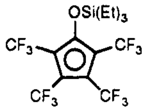
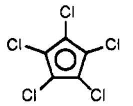
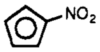
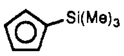
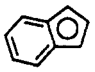
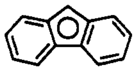
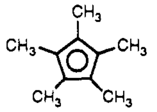
ruthenocene derivatives LL′Ru that were expected to have $\Delta G_i°$ values greater than or less than that of Cp_2Ru. The observed $\Delta G_i°$ values fall in a range that is covered by various metal and organic reference compounds; therefore, the ETE studies provide accurate measures of the relative and absolute ionization free energies for the new compounds. The ETE data are used to develop a new Cp substituent parameter scale that might be useful in correlating and interpreting the electronic effects of Cp modifications on other types of reactivity. In the course of this work, it was observed that the electronic effect of the fluorenyl group based on the present ETE results differed significantly from that implied by previous XPS and electrochemical studies.[9]

Results

Figure 1 is an electron-transfer equilibrium ladder displaying all reactions studied in this work. Values adjacent to the double arrows represent derived $\Delta G_{et}°$ values for a particular reaction. All $\Delta G_i°$ quantities derived in this work lie adjacent to the compounds in Figure 1 and are summarized in Table I. Compound abbreviations are in Table I, and ligand abbreviations are given in Table II.

The ruthenocene derivatives examined exhibit a wide range of free energy of ionization values (spanning >2 eV). Various organic compounds[10,11] and metallocenes[6] were used as reference compounds to measure equilibrium constants for ETE reactions. Aniline and benzene derivatives have IP values that are anchored to *N*,*N*-dimethylaniline (DMA) and benzene ($\Delta H_i°$ = 164.9 and 213.3 kcal/mol, respectively).[12] The $\Delta G_i°$ values for metallocene reference compounds were previously determined from ETE studies involving aniline derivatives.[5] The $\Delta G_i°$ value for 1 was reported previously[6] and is used here as reference for other observed ETE reactions. Thus, the organometallic reference compounds are also ultimately anchored to DMA and benzene. Specific assumptions made regarding the reference compounds are discussed elsewhere.[6]

Table II. Ligand γ* and γ Parameters

ligand	abbrev	γ*(L)	γ(L)
	TTFMH	2.76	3.10
	TTFMOSi	1.31	1.55
	C_5Cl_5	0.91	1.06
	NO_2Cp	0.67	0.79
	Cp	0[a]	0[a]
	TMSCp	−0.07	−0.17
	Ind	−0.20	−0.41
	Flu	−0.64	−0.65
	Cp*	−1[a]	−1[a]

[a] By definition.

In several cases, compounds were brought to equilibrium with more than one reference compound or another metallocene as a check on the internal consistency of the ladder. In general, the consistency is good. For example, 1 and 5 were both brought to equilibrium with *N*,*N*-dimethylaniline and each other (Figure 1), and it can be seen that the expected difference in the $\Delta G_i°$ values for 1 and 5 is obtained. Unfortunately, it was not always possible to do such cross-checks, since many of the organometallics had to be introduced on a heated solids probe, thereby restricting reference compounds to those sufficiently volatile for introduction via a leak valve (see Experimental Section).

For the ruthenocene complexes, errors in $\Delta G_i°$ values are reported at ±2 kcal mol^{-1} for values derived from ETE. Errors originate from two sources in the experiments (error limits of the reference compounds and error limits from measured K_{eq} values). Most of the IP data for organic reference compounds reported in the literature[10-12] have error limits of ±1 kcal mol^{-1}, although some reference compounds have experimental errors as high as ±2 kcal mol^{-1}. An additional uncertainty of ±0.5 kcal mol^{-1} is

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(10) (a) Lias, S. G.; Jackson, J. A.; Argenian, H.; Liebman, J. F. *J. Org. Chem.* **1985**, *50*, 333. (b) Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 6027.

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(12) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G., Eds.; *Gas-Phase Ion and Neutral Thermochemistry*; American Institute of Physics: New York, 1988.

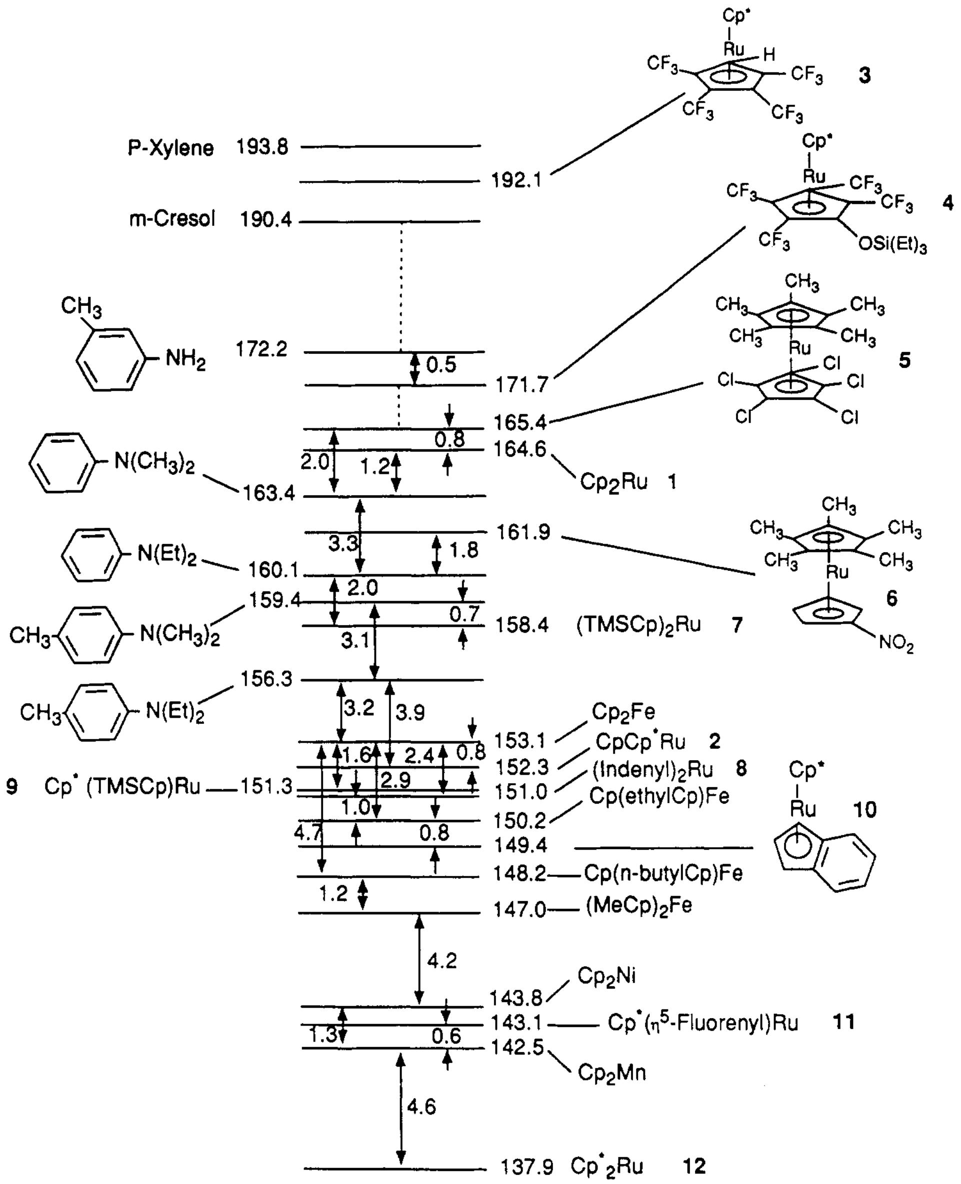

Figure 1. Electron-transfer equilibrium ladder for several ruthenocene derivatives for the process $M^+ + R = M + R^+$. Values adjacent to arrows denote $\Delta G_{et}°$ at $T = 350$ K for individual ETE couples. Ruthenocene $\Delta G_i°$ values (kcal mol^{-1}) are anchored to $\Delta G_i°$(DMA). The $\Delta G_i°$ value for **3** is a bracketed value.

assigned for each individual electron-transfer equilibrium reaction resulting from errors in the measured partial pressures of the neutral gases. (An error in the corrected partial pressures of the neutral gases as large as 30% would only result in a 0.2 kcal mol^{-1} error in $\Delta G_{et}°$.) Errors in the measured ion intensities are not expected to exceed 10%. Considering all possible sources of error, a ±2 kcal mol^{-1} range is assigned for the $\Delta G_i°$ values of ruthenocenes in this work.

Definitive ETE for Cp*(TTFMH)Ru (**3**) could not be established with either *m*-cresol or *p*-xylene. Therefore, a bracketed value for $\Delta G_i°$ of **3** is reported with a ±5 kcal mol^{-1} error. The reaction rate of 3^+ with *m*-cresol was slow and may explain why equilibrium was not attained ($k_f = 4.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 3^+ + *m*-cresol → *m*-cresol$^+$ + **3**). Cp*(η^5-$C_5(CF_3)_4OSiEt_3$)Ru (**4**) was observed to attain electron-transfer equilibrium with *m*-toluidine. The rate constant for the forward electron-transfer reaction (**4** + *m*-toluidine$^+$ → *m*-toluidine + 4^+) is 4.8×10^{-10} cm^3 molecule^{-1} s^{-1}.

Discussion

The experimentally derived values of $\Delta G_i°$ in Table I follow the generally expected trend, with ruthenocenes bearing halogen substituents ($-CF_3$ and $-Cl$) having ionization energies greater than that of Cp_2Ru. At the other extreme, $(C_5Me_5)_2Ru$ has the lowest $\Delta G_i°$ value determined in this work.

Comparisons to Electrochemical Data. As seen in the plot in Figure 2, the estimated potentials for the typically irreversible electrode redox processes (Table I) are not strongly correlated with the gas-phase ETE results, but an overall trend with slope ~1 is apparent. It is probable that in many cases the electrochemical potentials are poor estimates of the true one-electron LL'Ru$^{+/0}$ electrode potentials due to the irreversible nature of the oxidations in solution. However, it is also possible that the poor correlation arises from unpredictable differential solvation energetics[13] for the various couples.

The difference between the reversible $E_{1/2}$ values for $Cp_2Ru^{+/0}$ and $Cp_2Fe^{+/0}$ determined in CH_2Cl_2 by cyclic

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[13] (a) Richardson, D. E. *Inorg. Chem.* **1990**, *29*, 3213. (b) Sharpe, P.; Richardson, D. E. *J. Am. Chem. Soc.* **1991**, *113*, 8339. (c) Krishtalik, L. I.; Alpatova, N. M.; Ovsyannikova, E. V. *Electrochim. Acta* **1991**, *36*, 435.

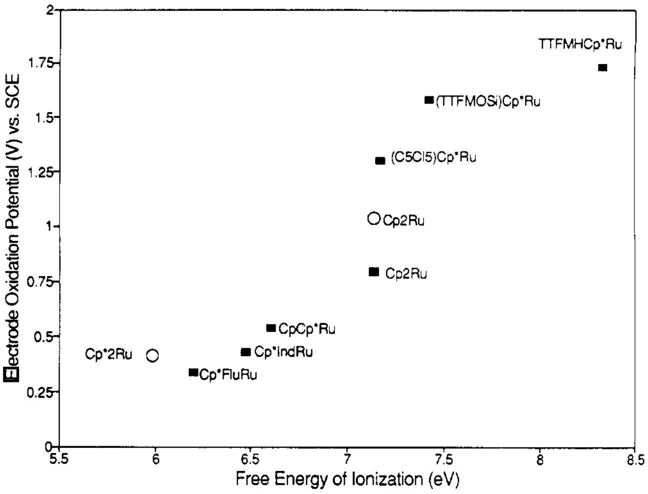

Figure 2. Plot of $E_{1/2}$ versus $\Delta G_i°$ values for several ruthenocene derivatives. Filled squares indicate irreversible $E_{1/2}$ values and circles denote $E_{1/2}$ values which are reversible. The reversible potential for ruthenocene was measured in CH_2Cl_2 versus Ag/AgCl.[9b] All other electrochemical data were taken from ref 9a and 21b.

voltammetry[9b] (0.56 V) can be compared to the difference between the gas-phase $\Delta G_i°$ values[6] (0.50 eV), and the comparison leads to the conclusion that the absolute value of the differential solvation energy[13] for the $Cp_2Ru^{+/0}$ couple is only ~1.4 kcal mol^{-1} lower than that of the $Cp_2Fe^{+/0}$ couple. Given that experimental error in the relative gas-phase values could be on the order of 1.5–2.0 kcal mol^{-1}, the reduction of solvation energy in the ruthenocene case may not be significant, but it is noteworthy that the same difference (1.4 kcal mol^{-1}) is deduced from the data for $Cp_2Os^{+/0}$.[6,9b] The slightly larger dimensions[14] of ruthenocene compared to ferrocene can account for the somewhat less negative differential solvation energy, essentially since Cp_2Ru^+ would have a larger Born radius and therefore would be less stabilized by solvation than Cp_2Fe^+ (making the electrode potential somewhat more positive for ruthenocene than would be the case if its solvation energetics were the same as those of ferrocene).

A value of $\Delta\Delta G_{solv}° = -38$ kcal mol^{-1} has been estimated[6] for the $Cp_2Fe^{+/0}$ couple in acetonitrile ($E_{1/2} = 0.31$ V vs SCE), and the somewhat higher potential for the ferrocene couple in CH_2Cl_2 (0.47 V vs Ag/AgCl[9b]) suggests that $\Delta\Delta G_{solv}°(Cp_2Fe^{+/0}) \approx -35$ kcal mol^{-1} in the latter solvent. Thus, $\Delta\Delta G_{solv}°(Cp_2Ru^{+/0}) \approx -34$ kcal mol^{-1} in CH_2Cl_2. The change in $\Delta\Delta G_{solv}°$ for the ferrocene couple deduced for going from acetonitrile to CH_2Cl_2 is on the order of that expected on the basis of a Born equation analysis,[6] but comparisons of electrochemical potentials measured in nonaqueous solution with aqueous reference electrodes must be considered only approximate. In comparisons of gas-phase and solution redox thermodynamics, it is preferred to reference energetics of couples to a common standard, and ferrocene is an excellent choice for most oxidation/ionization studies.

In the case of $Cp^*_2Ru^{+/0}$, a reversible electrochemical response is also observed in methylene chloride. From the reported $E_{1/2}$ value (Table I), a differential solvation free energy can be deduced for the couple and is estimated as −20 kcal mol^{-1}. The smaller value of $-\Delta\Delta G_{solv}°$ for the decamethyl complex in comparison to $Cp_2Ru^{+/0}$ (ca. −34 kcal mol^{-1}) is expected because of the larger average radius of the Cp* complex, and the effective Born thermochemical radius is ~7.3 Å in methylene chloride. This value can be compared to an average radius estimate from the crystal structure of decamethylruthenocene (~5 Å)[15] and suggests that solvation of decamethylmetallocene redox couples are not reasonably modeled by the conducting charged sphere ideal of the Born model. In contrast, solvation energetics of the parent metallocene $Cp_2M^{+/0}$ couples seem to be well-modeled by the Born approach.[6,7,13] In the case of metal acetylacetonate complexes ($ML_3^{0/-}$ couples), the effective thermochemical radius is smaller than the crystallographic radius.[7,13]

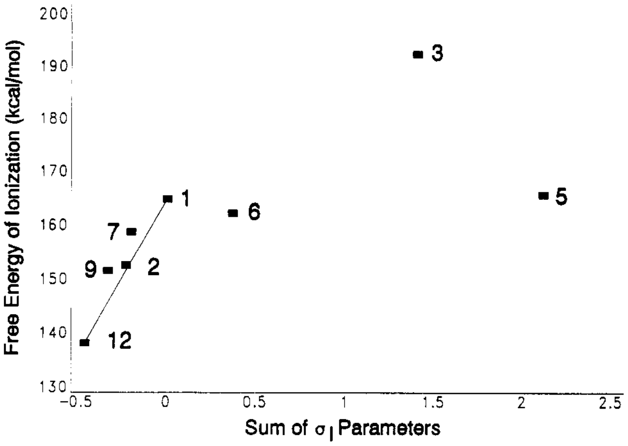

Figure 3. Correlation of $\Delta G_i°$ values for several ruthenocene compounds with Taft σ_I parameters. The best-fit line is drawn for $\Delta G_i°$ vs $\sum\sigma_I$ for methylated ruthenocene derivatives only (1, 2, 12). Compound numbers are defined in Table I.

Attempted Correlation with Taft σ_I Parameters. We have reported[6] the correlation of free energies of ionization in alkylferrocenes with Taft σ_I parameters,[16] and Levitt and Levitt[17] have previously correlated PES ionization energies for chromium arenes, $(C_6H_5R)Cr(CO)_3$, with the same parameters.

An attempt to correlate several of the ruthenocene complexes with alkyl Taft σ_I parameters is shown in Figure 3. A correlation with the entire series of ruthenocene complexes was not possible because σ_I parameters do not exist for all substituents studied (i.e. $OSiEt_3$ or fused-ring systems). The poor correlation of $\Delta G_i°$ values with σ_I values (Figure 3) shows that these parameters are not useful for predicting Cp ligand effects in the ruthenocene derivative ionizations. The methylated compounds (**1**, **2**, **12**) yield a linear fit of $\Delta G_i°$ vs σ_I, but compounds with electron-withdrawing groups (**3**, **5**, **6**) do not increase the ionization energies to the extent predicted by the σ_I parameters.

Experimental data suggest that the published values of σ_I for TMS (−0.10 or −0.11) may be too large.[18] The correlation of σ_I with $\Delta G_i°$ for compounds **7** and **9** indicates that the predicted $\Delta G_i°$ values for both compounds are consistently lower than the experimental ETE value by ~5 kcal mol^{-1}. A recent note by Gassman and co-workers on the core binding energies of several trimethylsilyl organometallics reports that the TMS group is 1.25 times

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[14] Seiler, P.; Dunitz, J. D. *Acta Crystallogr.* **1980**, *B36*, 2946.

[15] (a) Liles, D. C.; Shaver, A.; Singleton, E.; Wiege, M. B. *J. Organomet. Chem.* **1985**, *282*, C33. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levedis, D. C. *Organometallics* **1986**, *5*, 2321.

[16] Levitt, L. S.; Widing, H. F. *Prog. Phys. Org. Chem.* **1976**, *12*, 119.

[17] Levitt, L. S.; Levitt, B. W. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1907.

[18] (a) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley-Interscience: New York, 1975. (b) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119. (c) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1986**, *18*, 1.

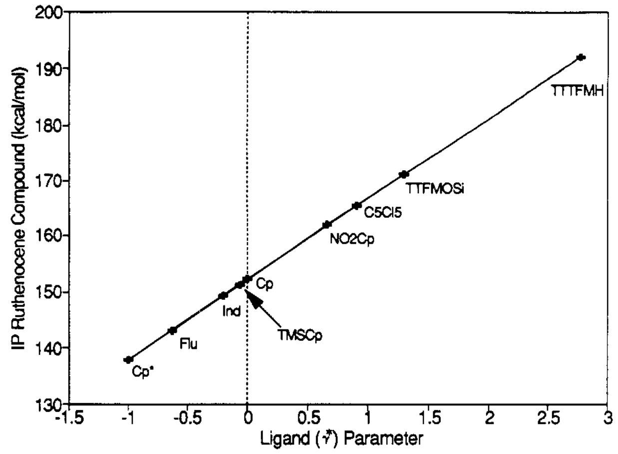

Figure 4. Plot of $\Delta G_i°$ versus γ^* ligand parameters derived from the equation $\Delta G_i°(Cp^*Ru–L) = 14.4\gamma^* + \Delta G_i°(CpCp^*Ru)$ (see text).

more electron donating than a methyl group.[19] Hence, a σ_I value of −0.06 for TMS would predict $\Delta G_i°$ values for **7** and **9** in better agreement with the experimental $\Delta G_i°$ values and would be more consistent with the data of Gassman and co-workers.[19]

The predicted $\Delta G_i°$ value for **5** based on the slope for the methylated compounds (line in Figure 3) is 120 kcal mol^{-1} greater than the determined ETE value. Thus, although $|\sigma_I|$ for chloride (0.47) is approximately 1 order of magnitude larger than $|\sigma_I|$ for methyl (−0.046), $\Delta G_i°(5) \approx \Delta G_i°(1)$. These results are similar to those of Levitt and Levitt,[17] who found that substituting a Cl for a ring H in $(C_6H_6)Cr(CO)_3$ leads to only a small increase (0.1 eV) in the ionization energy. They attribute the small net effect of a Cl to resonance donation into the ring, which partially compensates for the positive inductive effect. It is also notable that the observed substituent effects for Cl (**5**) and CF_3 (**3**) in the ruthenocenes are reversed from what would be predicted by the σ_I parameters (Figure 3). The observed shift in ionization free energy accompanying replacement of H atoms in Cp by CF_3 groups (compare **1** and **3**) is also much smaller than predicted by the Taft parameters, but the attenuation of the effect is less than that observed for Cl. The larger effect of CF_3 compared to Cl is again consistent with a model of lone-pair resonances donation by Cl (but not by CF_3). Such effects are well-known from studies of organic substituent effects.[18]

New Parameter Scale for Cyclopentadienyl Substituents. Given the absence of parameters appropriate for many of the substituents in the ruthenocene derivatives **1**–**12** (particularly for fused-ring ligands Flu and Ind) and the lack of general correlation with σ_I parameters noted above, we have chosen to develop a new parameter scale for cyclopentadienyl derivatives in which an overall parameter is deduced for the ligand rather than the individual ring substituents. The desired parameters relate specifically to the stabilization or destabilization of oxidation in the ruthenocene derivatives. It is expected that the parameters might correlate with the general tendency of the ligands to promote processes that involve positive charge buildup at a metal center in a metal Cp complex.

To establish the new Cp ligand parameters (γ values), the scale was anchored to Cp itself (γ(Cp) = 0) and C_5Me_5 (γ(Cp*) = −1.00). Two approaches have been used to assign parameters to the remaining ligands. The first of these uses only the data for the Cp*RuL complexes, where L denotes the ligands for which the parameters, γ^*(L), are to be deduced. Equation 2 was used to obtain the γ^*

$$\begin{aligned}\Delta G_i(Cp^*RuL) &= a^*[\gamma^*(L)] + \Delta G_i(CpCp^*Ru)\\ &= 14.4[\gamma^*(L)] + 152.3 \text{ (kcal mol}^{-1}) \end{aligned} \quad (2)$$

parameters. The value of the "sensitivity parameter" a^* (=14.4 kcal mol^{-1}) is fixed by the anchored values of γ^* for Cp and Cp* (0 and −1, respectively), and a plot of eq 2 is shown in Figure 4. All of the data points necessarily lie on the line because the $\Delta G_i°$ values are used to deduce the appropriate parameters. Those ligands to the right of the vertical dashed line in Figure 4 destabilize the oxidation of Cp*RuL relative to L = Cp. The γ^* values obtained from eq 2 are summarized in Table II.

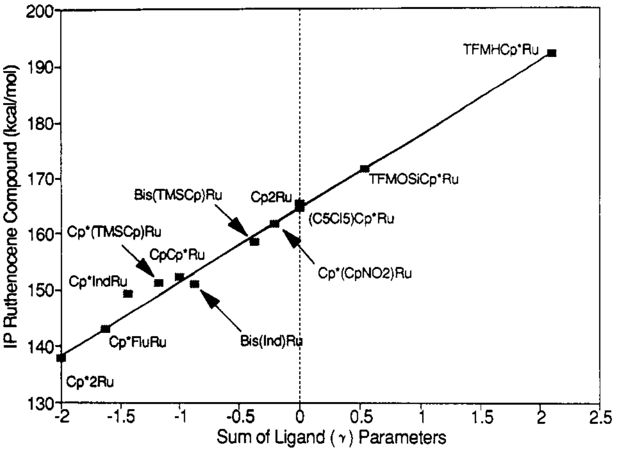

Figure 5. Plot of $\Delta G_i°$ versus γ ligand parameters derived from the equation $\Delta G_i°(L_1–Ru–L_2) = 13.0[\gamma(L_1) + \gamma(L_2)] + \Delta G_i°(Cp_2Ru)$ (see text).

A second approach for deducing ligand parameters also makes use of data for homoleptic compounds in this study (L_2Ru). Incorporating all the gas-phase data requires a ligand additivity assumption as expressed in eq 3.

$$\Delta G_i°(LL'Ru) = a(\gamma(L) + \gamma(L')) + \Delta G_i°(Cp_2Ru) \quad (3)$$

Equation 3 assumes direct ligand parameter additivity is a valid approach (i.e., the effect of L is independent of the effect of L′). The best-fit value of a (=13.0 kcal mol^{-1}) is derived from experimental values of $\Delta G_i°$ for Cp^*_2Ru, Cp*CpRu, and Cp_2Ru. The experimental $\Delta G_i°$ values (Table I) were then used to derive best-fit γ values for the various Cp derivatives in this work according to eq 3. In many cases the γ values are established by a single $\Delta G_i°$ value, since the ligand appears in a single compound only. In other cases, mixed-ligand (L ≠ L′) and homoleptic (L = L′) compounds could be used to refine the parameters.

The resulting γ parameters are summarized in Table II, and the correlation of the experimental $\Delta G_i°$ values with the γ(L) + γ(L′) sum is shown in Figure 5. From the correlation in Figure 5 and the comparisons of predicted to experimental $\Delta G_i°$ values in Table II, it is apparent that the assumption of ligand additivity is approximately upheld. Predicted values of $\Delta G_i°$ are typically within ~2–3 kcal mol^{-1} of the experimental values. Of course, the additivity assumption has not been tested for those ligands that appear in a single compound only.

Comparison of Fluorenyl and Pentamethylcyclopentadienyl Ligands. On the basis of electrochemical data and core (Ru 3d) photoelectron spectroscopy, Winter and Gassman[9a] have suggested that the fluorenyl ligand (Flu) is more "electron donating" than pentamethyl-

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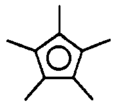
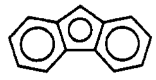
[19] Gassman, P. G.; Deck, P. A.; Winter, C. H.; Dobbs, D. A.; Cao, D. H. *Organometallics* **1992**, *11*, 959.



Cp*



Flu

cyclopentadienyl (Cp*). Comparison of $\Delta G_i°$ values for $Cp*_2Ru$ (1) and (Cp*)(Flu)Ru (11) in Table I are clearly not consistent with the trends in electrochemical potentials (Figure 2) and XPS energies (Figure 6) noted by these workers. With respect to adiabatic ionization in the gas phase, L = Flu clearly does not stabilize Cp*RuL toward oxidation to the extent that L = Cp* does. The electrochemical potentials may follow a different trend due to differences in solvation energetics for the Flu vs Cp* complexes or because the irreversible electrochemistry for Cp*(Flu)Ru does not yield a good estimate for the true thermodynamic potential. We have no explanation for the difference in order of "electron donating" effect as obtained from core XPS and ETE studies. It is clear from Figure 6 that the general correlation of XPS binding energies and $\Delta G_i°$ values breaks down for Cp* and fluorenyl, but the amount of data that can be compared is not extensive. We have not determined the entropies of ionization for these two complexes, but substantial differences could in principle reverse the order of $\Delta H_i°$ values and bring the two experimental trends into accord. However, there is no obvious reason for a large difference in the entropies of ionization.[6] In any case, the adiabatic ionization energetics from ETE studies probably reflect the Flu vs Cp* ligand electronic effect that would be expected in chemical reactivity of complexes with these ancillary ligands.

Conclusions

Gas-phase electron-transfer equilibria have been used to determine free energies of ionization of various ruthenocene derivatives at 350 K. The results provide an accurate direct measure of intrinsic Cp substituent effects on ruthenocene derivative oxidations. The irreversible electrochemical potentials and Ru 3d core binding energies reported earlier are roughly correlated with the gas-phase $\Delta G_i°$ values, but the correlation is poor in some cases. In particular, the ETE results suggest that L = fluorenyl does not stabilize the oxidation of Cp*RuL to the extent that Cp* does, with the effect of L = Flu being ~65% of the Cp* effect.

A Cp ancillary ligand parameter set has been defined for the ligands investigated here. The parameters, termed γ or γ^* depending on the derivation used, should provide the basis for correlating and predicting electronic effects of Cp derivative ancillary ligands on the physical and chemical properties of other organometallic compounds. Such parameters may provide insight into the electronic effects of various Cp ligands on the activity and selectivity of homogeneous organometallic catalysts bearing these ancillary ligands. For example, gas-phase ion/molecule studies of $L_2Zr-CH_3^+$ cations are presently underway to assess the influence of various Cp derivative ancillary ligands L on the reactivity of these species in fundamental processes such as hydrogenolysis, alkene insertion, and C–H activation.

Finally, it should be emphasized that the γ parameters have been derived here from gas-phase experiments and therefore represent intrinsic electronic effects in the absence of solvent perturbations. In attempts to use the parameters to correlate condensed-phase data, proper care should be taken in assessing the modifications of the trends by solvent and any structural differences between various complexes (e.g., η^5 vs η^3 coordination).

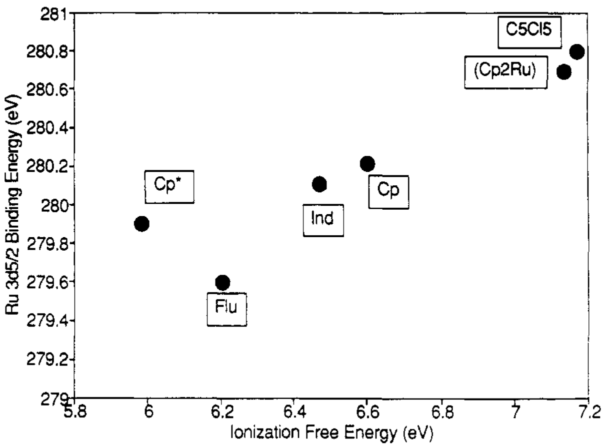


Figure 6. Plot of Ru $3d_{5/2}$ binding energies from ref 9a versus ETE $\Delta G_i°$ values for several Cp*Ru–L derivatives and ruthenocene.

Experimental Section

Electron-Transfer Equilibrium Measurements. Electron-transfer equilibrium studies were performed by using a Fourier transform ion cyclotron resonances mass spectrometer equipped with a 3-T superconducting magnet and an Ionspec data system. Details of the FTICR-MS experiment have been described previously;[7] thus, only a brief summary of the experimental procedures will be given. Ruthenocene derivatives were sublimed from a solids insertion probe to give partial pressures in the 1×10^{-7}–1×10^{-6} Torr range. For several of the ruthenocene derivatives (3–6) additional heating of the solids probe (to ~340 K) was necessary to generate partial pressures of the neutrals in the 1×10^{-7} Torr regime. Reference compounds were admitted to the high-vacuum region through a precision leak valve. Molecular ions were generated by electron impact with beam voltages adjusted in the range of 10–14 eV to generate ion signals in good yield and minimize production of unwanted fragment ions. Equilibrium was established for the ruthenocene derivative and the reference compound when the product ion intensities reached a constant ratio. Electron-transfer equilibrium was usually established with ~1 s reaction time and was monitored for a further 5–10 s. During the charge-transfer reaction time, the ions undergo hundreds of ion/molecule collisions, thus promoting thermalization of all product ions produced in electronically, vibrationally, or rotationally excited states. Approach to equilibrium was observed from endoergic and exoergic directions to insure reproducibility of observed ETE reactions. Endoergic electron transfer was observed by ion ejecting the thermodynamically unfavorable cation from the analyzer cell subsequent to electron impact of the parent neutral and monitoring the change in ion intensities for ~10 s.

The usual equations were used to determine K_{eq} from partial pressure and ion intensity ratios.[6,7] The operating cell temperature was determined to be 350 K with an Omega RTD thin film detector, and this temperature was used in $\Delta G_{et}°$ calculations. When absolute ETE was not observed (as demonstrated by compound 3), charge-transfer bracketing was used.

Pressures were measured directly by using a Fil-Tech nude ion gauge with a Granville-Phillips ion gauge controller. Partial pressures were corrected for systematic errors and ionization sensitivities by calibrating the ion gauge with a Baratron capacitance manometer in the 1×10^{-5} Torr range. Pressure calibrations for the ruthenocene derivatives varied only slightly within the series of compounds studied. A more complete discussion of pressure calibrations for ETE studies has been given elsewhere.[20]

Ruthenocene Derivatives and Reference Compounds. Compounds 2, 5, 10, 11, and 12 were prepared by using (η^5-pentamethylcyclopentadienyl)ruthenium(III) chloride oligomer, $(Cp*RuCl_2)_x$, as described by Gassman and Winter.[9] All compounds were obtained in yields of approximately 40% and

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[20] Bruce, J. E.; Eyler, J. R. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 727.

characterized by ^{1}H NMR (CD_3Cl) and mass spectrometry. Resublimation of (η^5-pentamethylcyclopentadienyl)(η^5-fluorenyl)ruthenium(II) was necessary prior to mass spectral studies to remove trace impurities of unreacted fluorene. Ruthenocene and anhydrous ruthenium(III) chloride were purchased from Aldrich Chemicals and used without further purification.

(η^5-Tetrakis(trifluoromethyl)cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (3). To [(η^5-C_5Me_5)Ru(MeCN)$_3$]O_3SCF_3[21] (0.10 g, 0.20 mmol) in THF (2 mL) was added dropwise a solution of [$C_5(CF_3)_4H$]Me_4N[22] (0.081 g, 0.20 mmol) in THF (2 mL). The reaction mixture immediately turned colorless from orange upon the addition. After the mixture was stirred for 1 h, the volatiles were removed in vacuo, affording a colorless solid. Extraction into pentane (10 mL), filtration, and slow solvent concentration followed by cooling (−20 °C) yielded the product as colorless crystals (106 mg, 94%). ^{1}H NMR (THF-d_8): δ 1.90 (s, 15 H), 5.58 (s, 1 H). ^{19}F NMR (relative to $CFCl_3$): δ −56.5 (m, 6 F), −53.9 (m, 6 F). ^{13}C NMR: δ 124.8 (q, J_{CF} = 270 Hz, CF_3), 124.75 (q, J_{CF} = 270 Hz, CF_3), 82.0 (overlapping q, J_{CF} = 41 Hz, *C*–CF_3), 94.2 (*C*–CH_3), 76.0 (J_{CF} = 3.8 Hz, *C*–H), 10.5. Anal. Calcd for $C_{19}H_{16}F_{12}Ru$: C, 39.80; H, 2.81; F, 39.76. Found: C, 39.88; H, 2.79; F, 38.22.

(η^5-Tetrakis(trifluoromethyl)((triethylsilyl)oxy)cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (4). To a THF solution (4 mL) of [(η^5-C_5Me_5)Ru(MeCN)$_3$]O_3SCF_3 (0.474 g, 0.93 mmol) was added a THF solution (4 mL) of [$C_5(CF_3)_4OSiEt_3$]Me_4N[23] (0.505 g, 0.93 mmol), and an immediate colorless precipitate of $Me_4NO_3SCF_3$ formed. After it was stirred for 30 min, the reaction mixture was cooled to −30 °C for 1 h. The mixture was then filtered and the resulting solution concentrated to a greenish residue, which was charged into a sublimation apparatus (cold finger 0 °C) and heated to 85 °C (0.005 Torr) for 12 h to afford the title complex as a colorless sublimate (0.562 g, 86%). ^{19}F NMR (THF-d_8): δ −51.4 (m, 6 F), −52.2 (m, 6 F). ^{13}C NMR (THF-d_8): δ 5.45 (Si$CH_2$$CH_3$), 6.65 ($SiCH_2$*CH*$_3$), 10.3 ($C_5Me_5$ *CH*$_3$), 93.9 (C_5Me_5 *C*), 120.0 (*C*–$OSiEt_3$), 124.8 (*C*F_3), 125.1 (*C*F_3). ^{29}Si NMR: δ +28.81. Anal. Calcd for $C_{25}H_{30}F_{12}OSiRu$: C, 42.67; H, 4.30. Found: C, 42.58; H, 4.33.

(η^5-Pentamethylcyclopentadienyl)(η^5-nitrocyclopentadienyl)ruthenium(II) (6). Cp*$CpNO_2$Ru was synthesized from [(η^5-C_5Me_5)Ru(MeCN)$_3$]O_3SCF_3 and Tl($CpNO_2$) in the same manner described for 3 and 4 above.

Bis(η^5-(trimethylsilyl)cyclopentadienyl)ruthenium(II) (7). The synthesis is patterned after the method of Pertici.[24] (Trimethylsilyl)cyclopentadiene (2 g, 14.6 mmol) was added to a stirred mixture of 7.4 g of zinc dust and 0.73 g of $RuCl_3 \cdot xH_2O$. After it was stirred for 4 h, the reaction mixture was filtered and solvent evaporated from the filtrate. The residue was extracted with 70 mL of boiling hexane. The extract was evaporated and the residue recrystallized from $(Me_3Si)_2O$ at −78 °C. The crude product thus obtained was further purified by preparative-scale TLC (silica/hexane) to give 0.17 g of off-white crystals. ^{1}H NMR ($CDCl_3$): δ 4.60, 4.42 (AA′XX′ pattern, apparent $J_{AX} + J_{A'X'}$ = 3.1 Hz), 0.13 (Si*CH*$_3$). ^{13}C NMR: δ 76.10 (C_{ipso}), 74.59 (J_{Si-C} = 6 Hz, C_2), 72.80 (C_3), −0.13 (Si*CH*$_3$). Anal. Calcd for $C_{16}H_{26}RuSi_2$: C, 51.2; H, 6.9. Found: C, 51.1; H, 6.9.

Bis(η^5-indenyl)ruthenium(II) (8). Compound 8 was prepared by the method of Samuel[25] and purified by repeated TLC (hexane/silica). ^{1}H NMR ($CDCl_3$): δ 6.64, 6.49, 4.86 ($H_{1,3}$), 4.60 (H_2).

(η^5-(Trimethylsilyl)cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (9). *n*-Butyllithium (3 mL of a 2.5 M solution in hexane) was added with stirring to $Me_3SiC_5H_5$ (1.04 g, 7.6 mmol) in 40 mL of THF. After 2.5 h, 1.0 g of $(Cp^*RuCl_2)_x$ was added. After this mixture was refluxed for 12 h, the tetrahydrofuran was removed under vacuum and the residue extracted with 250 mL of boiling hexane. The extract was concentrated and then chromatographed on a 6 in. × 1 in. alumina column. Hexane eluted the crude product as oily crystals that were further purified by preparative TLC (silica, hexane). The yield was 0.29 g (24%). ^{1}H NMR ($CDCl_3$): δ 4.21, 4.08 (ring C*H*), 1.92 (Cp*CH*$_3$), 0.13 (Si*CH*$_3$). ^{13}C NMR: δ 84.60 (Me*C*), 75.94, 75.19 (ring *C*H), 71.97 (Me_3Si*C*), 12.23 (*C*H_3Cp), −0.52 (Si*C*H_3). Anal. Calcd for $C_{18}H_{28}RuSi$: C, 57.9; H, 7.5. Found: C, 57.6; H, 7.3.

Organic reference compounds and ferrocene were purchased from Aldrich Chemicals. Ethylferrocene, manganocene, and nickelocene were purchased from Strem Chemicals. All ETE reference compounds were used without further purification.

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