Effects of π-Coordinated Transition-Metal Groups on Fluorene Acidities and Homolytic Bond Dissociation Enthalpies

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Received February 25, 1994®

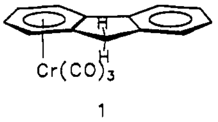
Summary: The pK_{HA} *values of the fluorene complexes* (η^6-*FlH*)*Cr*(*CO*)$_3$, (η^6-*FlH*)*Mn*(*CO*)$_3^+PF_6^-$, *and* (η^6-*FlH*)-*FeCp*$^+PF_6^-$ *were determined in DMSO solution to be 17.0, 5.7, and 14.6, respectively. When these* pK_{HA} *values were combined with the oxidation potentials of their conjugate bases, the homolytic bond dissociation enthalpies (BDEs) of the acidic C—H bond in the fluorene ligands were determined and shown to be unaffected by π-coordination.*

In earlier work from our laboratory the equilibrium acidities in DMSO solution of a variety of 2-, 3-, and 9-substituted fluorenes have been measured, and the relative effects of these substituents on the homolytic bond dissociation enthalpies (BDEs) of the acidic C—H bonds in these fluorenes have been assessed by combination of the pK_{HA} values with the oxidation potentials of their conjugate bases (eq 1).[1] The BDEs estimated in this way are empirically derived gas-phase BDEs.

$$\mathrm{BDE_{HA}} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{ox}}(\mathrm{A}^-) + 73.3\ \mathrm{kcal/mol} \qquad (1)$$

We have now extended these studies to three transition-metal groups π-coordinated to the fluorene ring. π-Coordination of $Cr(CO)_3$ to the benzene ring of benzoic acid or phenylacetic acid has been shown to cause increases in acidities in 50% aqueous ethanol of 0.9 and 0.6 pK_{HA} units, respectively. These effects are nearly identical with that of a p-NO_2 group.[2] Also, a Hammett plot of pK_{HA}s in 50% aqueous ethanol of phenols π-coordinated to $Cr(CO)_3$ has been shown to be comparable to that of a Hammett plot for uncomplexed phenols, but with a slope that is less than half as large.[3] Little or no quantitative information is available, however, that will allow a comparison of the relative effects of various transition-metal groups on the acidities and on BDEs of the acidic C—H bonds in a ligand.

Our objective in the present study was to obtain quantitative information concerning the effects of π-coordination of transition-metal complexes on the equilibrium acidities and BDEs of the acidic C—H bonds in the fluorene ligands of complexes **1**–**3**.



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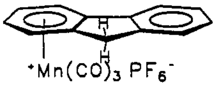

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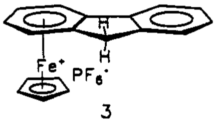

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The transition metals in $Cr(CO)_3$, $Mn(CO)_3^+$, and $Fe(C_5H_5)^+$ groups are isoelectronic, with 12 electrons around each metal. The fluorene ligand provides 6 more electrons to each metal to complete the 18-electron shell. Qualitative estimates, based on deprotonations with Et_3N and t-BuOK, have suggested that the conjugate base of **3** has a basicity similar to that of the fluorenide carbanion, whereas the conjugate base of **2** is about 10 orders of magnitude weaker.[6] Differences in the equilibrium acidities of these compounds in DMSO should provide a quantitative measure of their relative anion basicities. Also, combination of the pK_{HA} values obtained for **1**–**3** with the oxidation potentials of their conjugate bases, according to eq 1, should provide quantitative information concerning the BDEs of the acidic C—H bonds and the stability of the corresponding radicals.[4]

Complexes **1**–**3** were prepared according to literature procedures.[5–7] Deprotonation of **2** and **3** gave the corresponding conjugate bases, zwitterionic (η^6-Fl)Mn-$(CO)_3$ (**5**)[5] and (η^6-Fl)FeCp (**6**),[6] which were isolated in crystalline form. Both **5** and **6** are stable in DMSO; **5** is deep red, and **6** is dark blue. Deprotonation of complex **1** by $CH_3S(O)CH_2^-K^+$ produced its conjugate anion (η^6-Fl)$Cr(CO)_3^-$ (**4**). Anion **4** has been shown to undergo rapid haptotropic rearrangement to form (η^5-Fl)$Cr(CO)_3^-$ (**4′**).[6,7] From NMR experiments it was estimated that the time for this isomerization to reach equilibrium was about 5 min in DMSO-d_6 at room temperature, however, which is long enough for a reliable pK_{HA} measurement of **1**.

4 4′

The pK_{HA} values of **1**–**3** were measured in DMSO by an overlapping indicator method.[8] Since complexes **2** and **3** and their conjugate bases **5** and **6** could be isolated, **2** and **5** or **3** and **6** were mixed in DMSO in known concentrations and the mixtures were titrated with DMSO solutions of standard acids. The pK_{HA} of **1** was measured by adding a DMSO solution to a solution of $CH_3S(O)CH_2^-K^+$ to generate its conjugate base **4** and

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® Abstract published in *Advance ACS Abstracts,* June 15, 1994.

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0276-7333/94/2313-2920$04.50/0

Table 1. Equilibrium Acidities and Homolytic Bond Dissociation Enthalpies for the Acidic C—H Bonds in Substituted Fluorenes

group on Fl	pK_{HA}[a]	$E_{ox}(A^-)$[e]	BDE (kcal/mol)[f]	ref
9-H	22.6	−1.050	80	*g*
π-$Cr(CO)_3$ (**1**)	17.0[b]	−0.720	80	
π-$^+Mn(CO)_3$ (**2**)	5.7[c]	0.009	81	
π-^+FeCp (**3**)	14.6[d]	−0.565	80	
2-NO_2	17.0	−0.684	81	*g*
2-CN	18.2	−0.813	80	*g*
2-$PhSO_2$	18.1	−0.792	80	*g*
2-MeO	22.7	−1.056	80	*h*
2-Me	23.1	−1.08	80	*h*
9-Me_3N^+	17.8	−0.563	79	*i*
9-Ph_3P^+	6.6	−0.044	81	*i*

[a] pK_{HA} values were measured in DMSO by the method described earlier.[8] [b] A solution of **1** was added to a potassium dimsyl solution in DMSO to generate its conjugate base **4**. The mixture then was titrated at 570 nm with a solution of diethyl malonate (pK_{HA} = 16.4). Each run was completed within 5 min, and the average of three runs (17.0, 17.1, 17.0) was 17.0. [c] Solutions of **2** and its conjugate base **5** were mixed to give a concentration where the absorbance reading at 610 nm was between 1 and 0.1 Titration of the mixture was carried out at 610 nm by adding aliquots of a solution of $Ph_3P^+CH_2COPh(PF_6^-)$ (pK_{HA} = 6.0). The average of three runs (5.7, 5.7, 5.6) was 5.7. [d] Solutions of **3** and its conjugate base **6** were mixed in a concentration that gave an absorbance reading at 740 nm of between 1 and 0.1. Titration was carried out at 740 nm by adding aliquots of a solution of bis(methylsulfonyl)methane (pK_{HA} = 15.0). The average of three runs (14.6, 14.3, 14.7) was 14.6. [e] Irreversible oxidation potentials referenced to the ferrocene/ferrocenium couple in DMSO. [f] Calculated according to eq 1. [g] Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1992**, *114*, 9787. [h] Bordwell, F. G.; Cheng, J. P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867. [i] Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 968.

then titrating with a standard acid. Irreversible oxidation potentials of the anions, $E_{ox}(A^-)$ values, for **4**–**6** in DMSO were determined by cyclic voltammetry and referenced to ferrocene–ferrocenium couple. Despite the irreversibility of the oxidation potentials, it has been shown that BDEs estimated by eq 1 agree to within ±2 kcal/mol with the best known gas-phase data for the C—H bonds in 19 hydrocarbons and related heterocycles.[1]

Examination of Table 1 shows that the presence of the π-$Cr(CO)_3$ group has caused an acidity increase for the acidic hydrogen atom in the fluorenide ligand of 5.6 pK_{HA} units (7.7 kcal/mol). This large effect, which is due partially to the field/inductive effects of the three carbonyl groups, is as large as that for a 2-NO_2 group (Table 1), which agrees with the effects for a π-$Cr(CO)_3$ group observed on benzoic and phenylacetic acids.[2] The π-^+FeCp effect is somewhat larger (ΔpK_{HA} = 8.0 pK_{HA} units), indicating that the stabilizing effects on the anion of the field/inductive and polarizability effects of the positive charge are greater than the effects of the carbonyl groups in $Cr(CO)_3$. The acidifying effect of the π-^+FeCp group is somewhat larger than that of a Me_3N^+ group attached at the C-9 position of fluorene (ΔpK_{HA} = 5.1 units)[9] but much smaller than that of a 9-Ph_3P^+ group (ΔpK_{HA} = 16.3 units).[9] The effect of the π-$^+Mn(CO)_3$ group on the acidity of the fluorene ligand is even larger than that of the 9-Ph_3P^+ group (ΔpK_{HA} = 16.9 units), which is understandable because the $^+Mn(CO)_3$ group has not only large field/inductive and polarizability acidifying effects associated with the positive charge but also field/inductive effects associated with the carbonyl groups.

Examination of the BDEs in Table 1 reveals that the three transition-metal groups, like other electron-withdrawing groups, have little or no effect on the homolytic bond dissociation enthalpies of the acidic C—H bonds in fluorene. In other words, there is no evidence to indicate that these groups can stabilize a remotely situated carbon-centered radical.

Acknowledgment. This research was supported by the National Science Foundation.

OM940147X

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(9) Statistically corrected for the number of acidic hydrogen atoms.