Inorg. Chem. **1999,** *38,* 4135−4138 **4135**

Thermodynamic and Activation Parameters for Dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ into Paramagnetic Monomers from ^1H NMR Shift and Line Width Measurements

David C. Woska, Yaping Ni, and Bradford B. Wayland*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received March 30, 1999

^1H NMR spectra for solutions prepared by dissolution of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ in toluene in the temperature range 190−390 K are interpreted in terms of thermodynamic and kinetic parameters for dissociation of the diamagnetic dimers into the paramagnetic monomers $CpCr(CO)_3$ and $Cp^*Cr(CO)_3$. There is no evidence in this temperature range for thermally populated excited states or non-Curie magnetic behavior of the monomers making a significant contribution to the NMR. An expression for the temperature dependence of the NMR chemical shift at limiting fast interchange of monomer and dimer in terms of the ΔH° and ΔS° for dimer dissociation is applied in determining the thermodynamic parameters for Cr−Cr bond homolysis of $[CpCr(CO)_3]_2$ ($\Delta H_1^\circ = 15.3 \pm 0.6$ kcal mol^{-1}; $\Delta S_1^\circ = 39 \pm 2$ cal K^{-1} mol^{-1}) and $[Cp^*\ Cr(CO)_3]_2$ ($\Delta H_2^\circ = 14.2 \pm 0.4$ kcal mol^{-1}; $\Delta S_2^\circ = 47 \pm 2$ cal K^{-1} mol^{-1}). Rate constants and activation parameters have been evaluated from ^1H NMR line broadening in the region of slow dimer−monomer interchange for dissociation of $[CpCr(CO)_3]_2$ (k_1 (240 K) ≈ 59 s^{-1}; $\Delta H_1^\ddagger = 17 \pm 2$ kcal mol^{-1}; $\Delta S_1^\ddagger = 21 \pm 6$ cal K^{-1} mol^{-1}) and $[Cp^*Cr(CO)_3]_2$ (k_2 (240K) $\approx 1.4 \times 10^4$ s^{-1}; $\Delta H_2^\ddagger = 16 \pm 1$ kcal mol^{-1}; $\Delta S_2^\ddagger = 30 \pm 6$ cal K^{-1} mol^{-1}). Paramagnetic shifts also were used in deriving electron−proton coupling constants (A_H) for $CpCr(CO)_3$ (8.22×10^5 Hz) and $Cp^*Cr(CO)_3$ (1.33×10^6 Hz).

Introduction

Thermally and photolytically promoted reactions of metal−metal single bonded complexes often occur through M−M bond homolysis into more highly reactive metalloradicals ($M^\bullet$).[1−8] Recognition of the significance of metalloradicals in a wide variety of organometallic reactions has motivated the use of increased ligand steric demands to enhance reactivity by weakening and even precluding the formation of M−M bond.[6−8] Substitution of pentamethyl cyclopentadienide (Cp*) for cyclopentadienide (Cp) is commonly used as an approach for increasing ligand steric requirements that can enhance dissociation of M−M bonded complexes[2]. One of the most prominent examples is the dissociation of $[CpCr(CO)_3]_2$ (**1**) and $[Cp^*Cr(CO)_3]_2$ (**2**) into paramagnetic ($s = 1/2$) monomers $CpCr(CO)_3$ (**3**) and $Cp^*Cr(CO)_3$ (**4**) (eqs 1 and 2) where the Cp* derivative **2** is substantially more dissociated in solution than **1**.[2,3]

$$[CpCr(CO)_3]_2 \rightleftharpoons 2CpCr(CO)_3 \qquad (1)$$

$$[Cp^*Cr(CO)_3]_2 \rightleftharpoons 2Cp^*Cr(CO)_3 \qquad (2)$$

Our interest in the scope and thermodynamics of metalloradical reactions[9−13] has stimulated an effort to develop convenient methods to determine thermodynamic and activation parameters for bond homolysis processes.[14−16] This article reports on determining the thermodynamics (ΔH°, ΔS°) for dissociation of $[CpCr(CO)_3]_2$ (**1**) and $[Cp^*Cr(CO)_3]_2$ (**2**) by analysis of ^1H NMR shifts and the evaluation of activation parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$) for homolysis of **1** and **2** from ^1H NMR line broadening. The thermodynamic parameters determined from fast exchange averaged ^1H NMR for dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ are found to be in good agreement with values determined by alternate approaches[5,17] which contrast with prior interpretations of ^1H NMR studies for these systems.[17−19] Several prior kinetic studies provide estimates of rate constants for bond homolysis and metalloradical recombination events for reactions 1 and 2,[20,21] but this study of the ^1H NMR line broadening provides the first estimates of the activation parameters for the dissociation of **1** and **2**.

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10.1021/ic990342+ CCC: $18.00

Experimental Section

Materials. All manipulations of reagents were performed in an inert atmosphere box under argon. Deuterated toluene-d_8 (Aldrich) was degassed by employing three freeze−pump−thaw cycles and then dried by refluxing over sodium and benzophenone. $[Cp'Cr(CO)_3]_2$ ($Cp' =$ Cp or Cp*) compounds were synthesized and purified using the method described by Kubas.[7] The compounds were characterized by ^{1}H NMR and stored under argon in a freezer. Samples of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ were weighed and put into vacuum adapted NMR tubes, and toluene-d_8 solvent was vacuum transferred into the volumetric NMR tubes. The NMR sample tubes were degassed by three freeze−pump−thaw cycles, frozen in liquid nitrogen, and flame-sealed in vacuo.

Experimental Procedures. NMR experiments were performed on Bruker 500 MHz AMX-500 and 200 MHz AC-200 nuclear magnetic resonance spectrometers equipped with Bruker VT-1000 temperature control units. The temperature inside the NMR sample tube was calibrated (±0.1 K) using the difference in chemical shifts of ethylene glycol or methanol standards.[22] Samples were placed in the NMR spectrometer and the temperature was equilibrated for 45 min before spectra were acquired. Spectra were calibrated to the toluene-d_8 methyl resonance ($\delta(CH_3) = 2.09$ ppm; $T = 296$ K) and corrected for the temperature dependence of the toluene chemical shifts.[23] The chemical shift and line width for the cyclopentadienide proton resonances of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ were recorded at a series of temperatures in the range 190−390 K. The chemical shift (δ_{obs}) and the line width ($\Delta\nu_{1/2(obs)}$) of the Cp and Cp* proton resonances were found to change reversibly as the temperature was sequentially raised and lowered.

Results and Analysis

Thermodynamic Parameters for the Homolytic Dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ from ^{1}H NMR Chemical Shifts. Thermodynamic parameters for the dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ were obtained from analysis of the temperature dependence of the ^{1}H NMR chemical shifts (δ_{obs}) for the case of limiting fast exchange between a diamagnetic dimer (D) and a Curie paramagnetic monomer (M) ($D \rightleftharpoons 2M$). Equation 3 gives the relationship between the fast exchange averaged chemical shift (δ_{obs}) at temperature T in terms of the chemical shifts for the diamagnetic dimer (δ_D), Curie paramagnetic monomer (δ_M) ($\delta_M = C_M T^{-1} + \delta_m$; where δ_m is the chemical shift for M when $T^{-1} = 0$), the initial concentration of the dimer ($[D]_i$), and the thermodynamic parameters ($\Delta H°$, $\Delta S°$) for dissociation of D into 2M. The measured δ_{obs} values at a series of temperatures T are used to obtain the nonlinear least-squares best fit to eq 3 in terms of

$$\delta_{obs} = \left[\delta_D + \frac{\delta_D}{8[D]_i} e^{-\Delta H°/RT + \Delta S°/R} - \frac{\delta_D}{8[D]_i}\left(16[D]_i e^{-\Delta H°/RT+\Delta S°/R} + e^{-2(\Delta H°/RT+\Delta S°/R)}\right)^{1/2}\right] + \left[-\frac{e^{-\Delta H°/RT+\Delta S°/R}}{8[D]_i} + \frac{1}{8[D]_i}\left(16[D]_i e^{-\Delta H°/RT+\Delta S°/R} + e^{-2(\Delta H°/RT+\Delta S°/R)}\right)^{1/2}\right](C_M T^{-1} + \delta_m) \quad (3)$$

best fit values for $\Delta H°$, $\Delta S°$, and the slope of the paramagnetic shift (C_M). In this approach a single sample that is evaluated at a series of temperatures is used in deriving the thermodynamic parameters. This is a substantial simplification from the usual approach of using a series of concentrations to evaluate an equilibrium constant at each of a series of temperatures.

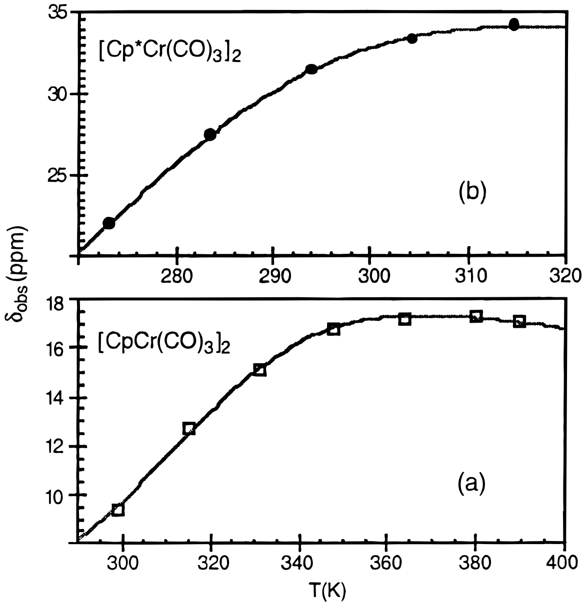

Figure 1. Observed ^{1}H NMR chemical shifts at a series of temperatures are given by the points. Solid lines are calculated from evaluation of eq 3 using the best fit values for $\Delta H°$, $\Delta S°$, and C_M. (a) Toluene-d_8 solution of $[CpCr(CO)_3]_2$ with an initial concentration of 4.71×10^{-3} M. ($\Delta H° = 15.3$ kcal mol^{-1}; $\Delta S° = 39$ cal K^{-1} mol^{-1}; $C_M = 5.10 \times 10^3$ ppm K). (b) Toluene-d_8 solution of $[Cp^*Cr(CO)_3]_2$ with an initial concentration of 3.10×10^{-3} M. ($\Delta H° = 14.2$ kcal mol^{-1}; $\Delta S° = 47$ cal K^{-1} mol^{-1}; $C_M = 10.8 \times 10^3$ ppm K).

Table 1. Thermodynamic and Activation Parameters for Dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ into Monomers

	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal K^{-1} mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
$[CpCr(CO)_3]_2$	15.3 ± 0.6	39 ± 2	17 ± 2	21 ± 6
$[Cp^*Cr(CO)_3]_2$	14.2 ± 0.4	47 ± 2	16 ± 1	30 ± 6

Thermodynamics for Dissociation of $[CpCr(CO)_3)]_2$. The temperature dependence of the observed chemical shift for the cyclopentadienide hydrogens is illustrated in Figure 1. The chemical shift increased from 4.16 ppm ($T < 230$ K) to a maximum of 17.4 ppm at 370 K and then decreased as the temperature was elevated further (Figure 1). At temperatures above 300 K, $[CpCr(CO)_3]_2$ (**1**) is in limiting fast exchange with the paramagnetic monomer, $CpCr(CO)_3$ (**3**), such that the observed shift is the mole fraction averaged positions of the NMR observable protons for **1** and **3** in equilibrium (eq 1).

Changes in the chemical shift (δ_{obs}) with temperature result from temperature dependencies for both the equilibrium constant for $[CpCr(CO)_3]_2$ dissociating into $CpCr(CO)_3$ and the paramagnetic shift for the monomer ($\delta_M = C_M T^{-1} + \delta_m$). A nonlinear least-squares best fit for δ_{obs} at a series of temperatures (T) to eq 3 gives $\Delta H^{\circ}_1([CpCr(CO)_3]_2) = 15.3 \pm 0.6$ kcal mol^{-1}; $\Delta S^{\circ}_1([CpCr(CO)_3]_2) = 39 \pm 2$ cal K^{-1} mol^{-1} and $C_M(CpCr(CO)_3) = 5100 \pm 60$ ppm K (Figure 1, Table 1). The slope of the contact shift for **3** was used to evaluate the electron−proton coupling constant for the cyclopentadienide hydrogens in $CpCr(CO)_3$ ($A_H(CpCr(CO)_3) = 8.22 \times 10^5$ Hz; $A_H = C_M(s(s+1))^{-1}(g_e\beta_e)^{-1}(3\gamma_H k)$).

Thermodynamics for Dissociation of $[Cp^*Cr(CO)_3]_2$. The chemical shift methodology was also applied in determining thermodynamic values for dissociation of pentamethyl cyclopentadienide chromium tricarbonyl dimer $[Cp^*Cr(CO)_3]_2$ (**2**)

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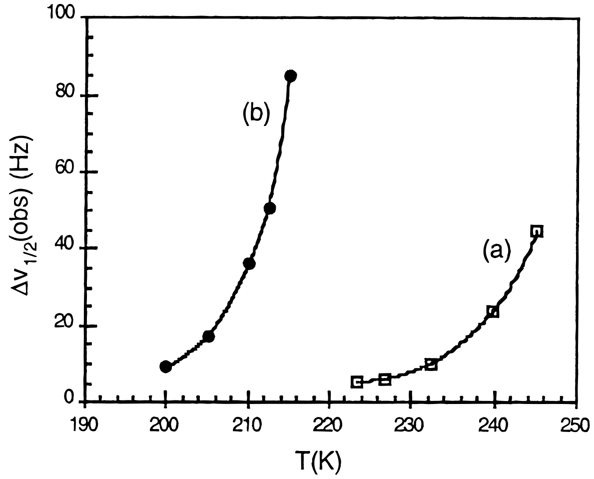

Figure 2. Temperature dependence of the observed ^{1}H NMR line width at half-maximum intensity $\Delta\nu_{1/2(\mathrm{obs})}$ for (a) the cyclopentadienide proton resonance of $[CpCr(CO)_3]_2$ and (b) the methyl resonance of $[Cp^*Cr(CO)_3]_2$ in toluene-d_8.

into paramagnetic monomers, $Cp^*Cr(CO)_3$ (**4**) (eq 2). The temperature dependence of δ_{obs} for **2** is illustrated in Figure 1. The nonlinear least-squares best fit for δ_{obs} at a series of temperatures to eq 3 gives $\Delta H_2^\circ([Cp^*Cr(CO)_3]_2) = 14.2 \pm 0.4$ kcal mol^{-1}; $\Delta S_2^\circ([Cp^*Cr(CO)_3]_2) = 47 \pm 2$ cal K^{-1} mol^{-1}; $C_M(Cp^*Cr(CO)_3) = 10\,800 \pm 80$ ppm K (Figure 1, Table 1). The slope of the paramagnetic shift for the methyl group in **4** yields $A_H(Cp^*Cr(CO)_3) = 1.33 \times 10^6$ Hz.

Paramagnetic shifts ($\delta_M = C_M T^{-1} + \delta_m$) for the cyclopentadienide hydrogens (5100 ppm K T^{-1}) of $CpCr(CO)_3$ and the pentamethyl cyclopentadienide hydrogens (10 800 ppm K T^{-1}) of $Cp^*Cr(CO)_3$ correspond to electron−proton coupling constants (A_H) of 8.22×10^5 and 1.33×10^6 Hz, respectively. Observation that the A_H for the Cp* methyl hydrogens is larger in magnitude and has the same sign as A_H for the Cp hydrogens suggests that the predominant contribution to the coupling is from direct overlap of the respective H_{1s} orbitals with the odd electron molecular orbital. EPR studies of $CpCr(CO)_3$ place the odd electron in an effectively degenerate e molecular orbital[24] where the d_{xy},d_{yz} character is appropriate for direct overlap with the Cp and Cp* ligand hydrogens.

Activation Parameters for the Dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ Determined by ^{1}H NMR Line Broadening. The ^{1}H NMR spectra for $[CpCr(CO)_3]_2$ (**1**) and $[Cp^*Cr(CO)_3]_2$ (**2**) in toluene-d_8 exhibit line broadening without large shifts of the cyclopentadienide hydrogen and methyl peaks as the temperature is increased from the limiting slow exchange regime. The observed line width at half-maximum intensity ($\Delta\nu_{1/2(\mathrm{obs})}$) for solutions of **1** and **2** are illustrated in Figure 2. The increase in line width as the temperature is elevated through the slow exchange regime is ascribed to the lifetime broadening that results from dissociation of diamagnetic dimers into the paramagnetic ($s = {}^1/_2$) monomers. The expression that describes this exchange case is given by eq 4 which reduces to $T_2^{-1} = \tau_d^{-1}$ for nuclei in paramagnetic species where the mean lifetime (τ_p) is long and the electron−nuclear coupling constant (A) is large such that $(A\tau_p/2)^2 \gg 1$.[25−30]

$$\pi\Delta\nu_{1/2(\mathrm{ex})} = T_2^{-1} = \tau_d^{-1}[(A\tau_p/2)^2][1 + (A\tau_p/2)^2]^{-1} \quad (4)$$

The apparent mean lifetime for the diamagnetic species (τ_d) that results from the observed T_2^{-1} yields the apparent rate constant ($\tau_d^{-1} = k_{\mathrm{app}}$) for bond homolysis events that produce paramagnetic species with efficient nuclear relaxation ($(A\tau_p/2)^2 \gg 1$).

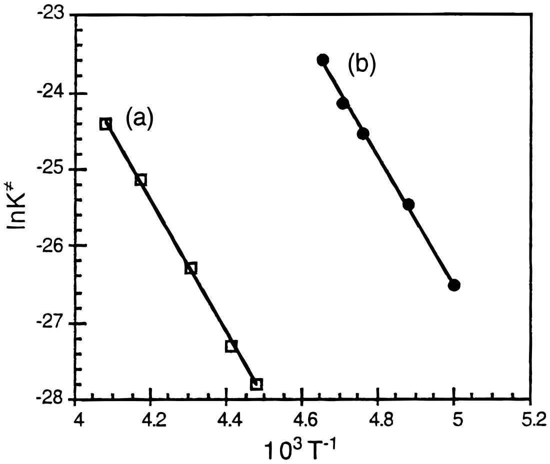

Figure 3. Determination of the apparent activation parameters for bond homolysis from ^{1}H NMR line broadening in toluene-d_8. (a) $[CpCr(CO)_3]_2$ ($\Delta H^\ddagger_{\mathrm{app}} = 17 \pm 2$ kcal mol^{-1}; $\Delta S^\ddagger_{\mathrm{app}} = 21 \pm 6$ cal K^{-1} mol^{-1}). (b) $[Cp^*Cr(CO)_3]_2$ ($\Delta H^\ddagger_{\mathrm{app}} = 16 \pm 1$ kcal mol^{-1}; $\Delta S^\ddagger_{\mathrm{app}} = 30 \pm 6$ cal K^{-1} mol^{-1}).

Bond homolysis that produces freely diffusing radicals in solution occurs through the intermediacy of solvent caged radical pairs ($M{-}M \rightleftharpoons \overline{M^{\bullet\bullet}M} \rightleftharpoons 2M^\bullet$). The activation parameters to produce freely diffusing radicals are said to be apparent values ($\Delta H^\ddagger_{\mathrm{app}}$, $\Delta S^\ddagger_{\mathrm{app}}$) because they are composites of activation values for the fundamental steps of radical pair formation and separation.[31−33] The predominant contribution to $\Delta H^\ddagger_{\mathrm{app}}$ is from the bond homolysis step that produces the radical pair. Apparent activation parameters for dissociation of **1** and **2** were obtained from the temperature dependence of $\Delta\nu_{1/2(\mathrm{ex})}$ and the use of transition state theory ($K^\ddagger_{\mathrm{app}} = k_{\mathrm{app}}(h/kT)$; $-RT\ln K^\ddagger_{\mathrm{pp}} = \Delta G^\ddagger_{\mathrm{app}} = \Delta H^\ddagger_{\mathrm{app}} - T\Delta S^\ddagger_{\mathrm{app}}$)[14,15] (Figure 3, Table 1). Using $\Delta\nu_{1/2(\mathrm{nat})} = 4.0$ Hz yields the apparent activation parameters for dissociation of $[CpCr(CO)_3]_2$ (**1**) ($\Delta H^\ddagger_{\mathrm{app}} = 17 \pm 2$ kcal mol^{-1}; $\Delta S^\ddagger_{\mathrm{app}} = 21 \pm 6$ cal K^{-1} mol^{-1}) and $[Cp^*Cr(CO)_3]_2$ (**2**) ($\Delta H^\ddagger_{\mathrm{app}} = 16 \pm 1$ kcal mol^{-1}; $\Delta S^\ddagger_{\mathrm{app}} = 30 \pm 6$ cal K^{-1} mol^{-1}). Uncertainty in the natural line width of ~0.5 Hz necessitates assigning relatively large error limits for the activation parameters.

Discussion

The thermodynamic values for dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ into the paramagnetic monomers determined from the temperature dependence of the interchange averaged ^{1}H NMR shifts by fitting to eq 3 are found to be in good agreement with values obtained by several other approaches[5,17] (Table 2) which contrasts with prior ^{1}H NMR studies.[34]

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Table 2. Comparison of Thermodynamic Parameters for the Dissociation of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ in Toluene Determined by Different Techniques

	ΔH° (kcal mol^{-1})	ΔS° (cal K^{-1} mol^{-1})	method	ref
$[Cp^*Cr(CO)_3]_2$	14.2	47	NMR	this work
	14.7	45	FTIR	17
	14	43	χ^a	17
$[CpCr(CO)_3]_2$	15.3	39	NMR	this work
	15.8	37	UV−vis	5
	14.7	35	FTIR	17

[a] χ = magnetic susceptibility.

The unusually large entropy of dissociation of $[CpCr(CO)_3]_2$ ($\Delta S_1^\circ = 39$ cal K^{-1} mol^{-1}) must have substantial contributions from inhibition of internal modes in the dimer relative to the monomer. An exceptionally long Cr−Cr distance in $[CpCr(CO)_3]_2$ (3.281 Å)[35] has been ascribed to severe steric crowding between the monomer fragments in the dimer and relief of sterically constrained motions must be the origin for the unusually large entropy change when the dimer dissociates. Additional internal modes for the methyl groups of Cp* and the increased steric demands of Cp* compared with Cp that restrict internal motions further, result in the even larger entropy gain associated with dissociation of $[Cp^*Cr(CO)_3]_2$ ($\Delta S_2^\circ = 47$ cal K^{-1} mol^{-1}). As previously pointed out,[17] the difference in the entropies for dissociation for **1** and **2** is primarily responsible for the larger dissociation of $[Cp^*Cr(CO)_3]_2$ compared to $[CpCr(CO)_3]_2$.

The lifetime broadening for the ^1H NMR of solutions of **1** and **2** observed as the temperature is elevated from 190 K through the relatively slow exchange regime is interpreted as resulting from the dynamics of dissociation of the diamagnetic dimers **1** and **2** into the paramagnetic monomers (eqs 1 and 2). Activation enthalpies for dissociation of $[CpCr(CO)_3]_2$ (**1**) and $[Cp^*Cr(CO)_3]_2$ (**2**) ($\Delta H_1^\ddagger = 17 \pm 2$ kcal mol^{-1}; $\Delta H_2^\ddagger = 16 \pm 1$ kcal mol^{-1}) are each about 2 kcal mol^{-1} larger than the enthalpy of dissociation of **1** and **2**, respectively, which is in the range frequently observed for homolysis processes in low-viscosity media.[36,37] The very large positive activation entropies ($\Delta S^\ddagger_{1\,\mathrm{app}} = 21 \pm 6$ cal K^{-1} mol^{-1}; $\Delta S^\ddagger_{2\,\mathrm{app}} = 30 \pm 6$ cal K^{-1} mol^{-1}) clearly indicate that dissociative processes for **1** and **2** are responsible for the line broadening. The entropy increases sequentially as the dimer dissociates to form the radical pair and then proceeds on to freely diffusing radicals, and thus $\Delta S^\ddagger$ for a homolysis process is invariably smaller than ΔS°. The $\Delta S^\ddagger$ values for bond homolysis processes are often about 0.5−0.7 that of ΔS° [14−16] which is in the range observed for the process assigned to the homolysis of **1** and **2** (Table 1).

The ^1H NMR spectra for solutions obtained by dissolution of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ in toluene thus can be interpreted in terms of the thermodynamic and activation parameters for the single process of dissociation of **1** and **2** into an equilibrium distribution with their respective paramagnetic monomers (eqs 1 and 2). Postulation of additional species, thermally excited states or non-Curie magnetic behavior are not warranted by the observed ^1H NMR in the temperature interval 190−390 K. In the high-temperature region (280−390 K) where rapid dimer−monomer interchange occurs, the exchange-averaged ^1H NMR shift (δ_{obs}) used in conjunction with eq 3 gives ΔH° and ΔS° for dissociation of **1** and **2**. In the slow interchange region at lower temperatures (190−250 K) the temperature dependence of the ^1H NMR line widths for **1** and **2** result from the rate of dissociation of the diamagnetic dimers to paramagnetic monomers and were used in evaluating the rate and activation parameters for homolysis of **1** and **2**. The successful application of NMR shift and line width measurements to evaluate thermodynamic and activation parameters for homolysis of $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ provides encouragement that these convenient and technically accessible approaches will find wide application in bond homolysis studies.

Acknowledgment. This research was supported by grants from the National Science Foundation and the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Grant DE-FG02-86ER-13615.

Supporting Information Available: Analysis of ^1H NMR shifts for thermodynamics of dimerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) Several prior studies to determine thermodynamics values for the dissociation of **1** and **2** by ^1H NMR shift measurements resulted in very high values ($\Delta H^\circ \sim 18-21$ kcal mol^{-1}; $\Delta S^\circ \sim 51-57$ cal K^{-1} mol^{-1})[17−19] compared to our ^1H NMR results and values obtained by using other techniques (Table 2). We believe that the expressions used in the prior analysis may be in error because reanalysis of the reported data for dissociation of **2** (ref 18) using eq 3 results in $\Delta H^\circ = 14.2$ kcal mol^{-1} and $\Delta S^\circ = 45$ cal K^{-1} mol^{-1} which is in good agreement with our results (Table 1). The expression previously used (refs 17−19) for the exchange averaged shift position (δ_{obs}) may not take into account that the dimer has twice the number of hydrogens as the monomer.

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