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## The Equilibrium between $[CpCr(CO)_3]_2$ and $CpCr(CO)_3$. The Thermodynamics of Cr-Cr Single Bond Cleavage

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There is NMR,[1] ESR,[2] and electrochemical[2] evidence for the reversible thermal dissociation of $[CpCr(CO)_3]_2$ in solution (reaction 1). We wish to report a quantitative study of this equi-

$$\underset{\mathbf{1}}{[CpCr(CO)_3]_2} \rightleftharpoons \underset{\mathbf{2}}{2CpCr(CO)_3} \qquad (1)$$

librium which demonstrates that the equilibrium concentration of radical **2** is much higher than previously supposed. We also report the first infrared spectrum of **2** in solution.

Solutions of **1** have a strong UV absorbance that is associated with the Cr-Cr bond [$\lambda_{max}$ = 450 nm, $^1(\sigma^2) \rightarrow {}^1(\sigma\sigma^*)$].[3,4] Upon dilution, this absorbance decreases more than expected from Beer's law behavior. If the diluted solution is reconcentrated, the original intensity of the 450-nm band is restored. Spectra recorded at different concentrations and scaled to adjust for concentration show an isosbestic point at 370 nm. These observations are consistent with a concentration dependent equilibrium between **1** and a species with no Cr-Cr bond.

The UV spectrum of **1** is temperature dependent. Increasing the temperature from -65 °C to +95 °C causes a reversible reduction in the intensity of the 450-nm band (Figure 1). This dramatic temperature dependence is consistent with the reversible formation of **2** (reaction 1). At temperatures below -35 °C, where the equilibrium is shifted entirely to **1**, the spectra have an isosbestic point at 456 nm (Figure 1 insert). The isosbestic behavior of **1** can be interpreted as a temperature dependent equilibrium between two rotational isomers with similar but not identical UV spectra (Figure 2).[1,5] $[CpMo(CO)_3]_2$, which is also known to be an equilibrium mixture of two rotomers,[6] exhibits similar isosbestic behavior (toluene solution, -35 °C to +45 °C, $\lambda_{max}$ = 390 nm, isosestic point = 400 nm). The spectra shown in Figure 1 can be fit to the equilibrium model of reaction 1 to give accurate values of $\Delta H$, $\Delta S$, $\epsilon_1$, and $\epsilon_2$ (Table I).[7] Experiments in THF give similar results.

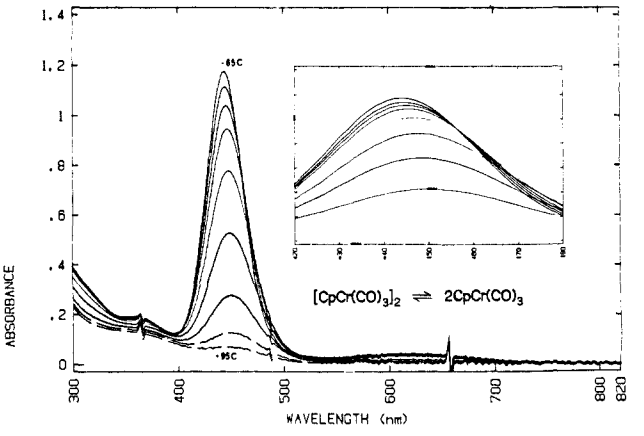


**Figure 1.** UV spectra of **1** in toluene (0.0020 M, 0.10 cm cell) from -65 °C to 95 °C (20 °C increments). Insert is -65 °C to 5 °C (10 °C increments). Spectra are corrected for the temperature dependence of the solvent density. The discontinuities at 360, 490, and 660 nm are artifacts.

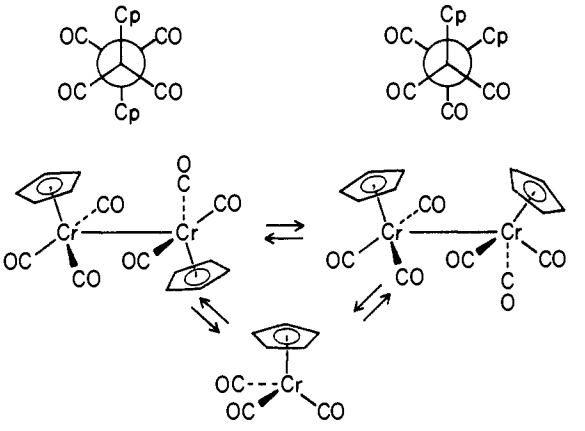

**Figure 2.** Equilibrium between anti dimer, gauche dimer, and monomer.

**Table I.** Thermodynamic Parameters[a] for the **1** ⇌ **2** Equilibrium

| method | solvent | $\Delta H$ | $\Delta S$ | $\Delta G_{300}$ |
|---|---|---|---|---|
| UV[b] | toluene | 15.8 (0.4) | 37.1 (1.4) | 4.6 |
| IR | toluene | | | 4.6 |
| UV[c] | THF | 14.8 (0.4) | 34.3 (1.3) | 4.5 |
| IR | THF | | | 4.7 |

[a] $\Delta H$ and $\Delta G$ in kcal mol$^{-1}$; $\Delta S$ in cal mol$^{-1}$ K$^{-1}$; figures in parentheses are esd's. [b] $\epsilon_1$ (456 nm) = 17 740 (960); $\epsilon_2$ (456 nm) = 328 (106). [c] $\epsilon_1$ (446 nm) = 18 600 (990); $\epsilon_2$ (446 nm) = 180 (150).

IR spectra of **1** in solution show direct evidence of **2**. The complex solution spectrum of **1** has been attributed to an equilibrium mixture of anti and gauche rotometers (Figure 2, Figure 3a).[5] However, the concentration dependence of the spectrum (Figure 3a,b) can only be accounted for by an additional *intermolecular* equilibrium (i.e., reaction 1). Subtracting an appropriately scaled spectrum of a concentrated sample from the spectrum of a less concentrated sample gives a spectrum of **2**, the species favored at lower concentration (Figure 3c). This spectrum can be compared with the spectrum of **2** produced by photolysis of $CpCr(CO)_3H$ in a CO matrix ($\nu_{CO}$ = 1986, 1910, 1902 cm$^{-1}$).[8] The subtraction factor SF used to obtain Figure 3c can be used to calculate the equilibrium constant of reaction 1.[9] This value

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(7) Starting with the definition of the equilibrium constant for reaction 1, $K_{eq} = [\mathbf{2}]^2/[\mathbf{1}]$, the following model was derived: absorbance = $\epsilon_1 l[\mathbf{1}] + \epsilon_2 l[\mathbf{2}]$; $[\mathbf{1}] = \{[Cr_{tot}] - [\mathbf{2}]\}/2$; $[\mathbf{2}] = \{-K_{eq} + (K_{eq}^2 + 8K_{eq}[Cr_{tot}])^{1/2}\}/4$; $K_{eq} = e^{-\Delta G/RT}$; $\Delta G = \Delta H - T\Delta S$; $[Cr_{tot}] = \{[Cr_{25}]/d_{25}\}\{d_0 + AT_c + BT_c^2 + CT_c^3\}$ where $\epsilon_1$, $\epsilon_2$ = extinction coefficients of **1** and **2** at the isosbestic frequency; $l$ = UV cell pathlength (cm); $[Cr_{tot}]$ = the total concentration of Cr atoms in solution; $T$, $T_c$ = temperature in K and °C; $[Cr_{25}]$ = Cr atom concentration of the starting solution at 25 °C; $d_0$, $d_{25}$ = solvent densities at 0 °C and 25 °C; $A$, $B$, $C$ = solvent thermal expansion coefficients. The data were least-squares fit to this model by using SAS/ETS software with Gauss-Newton minimization.
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(9) The conditions for obtaining a null of **1** in a spectral substraction are $[\mathbf{1}]_a - SF[\mathbf{1}]_b = 0$. [**1**] can be expressed as a function of $K_{eq}$ and $[Cr_{tot}]$: $[\mathbf{1}] = \{4[Cr_{tot}] + K_{eq} - (8[Cr_{tot}]K_{eq} + K_{eq}^2)^{1/2}\}/8$. Substitution of this equation into the spectra subtraction equation gives an equation of the form $f(K_{eq}, [Cr_{tot}]_a, [Cr_{tot}]_b, SF) = 0$. The value if $K_{eq}$ was determined by an iterative root finding program on a pocket calculator.

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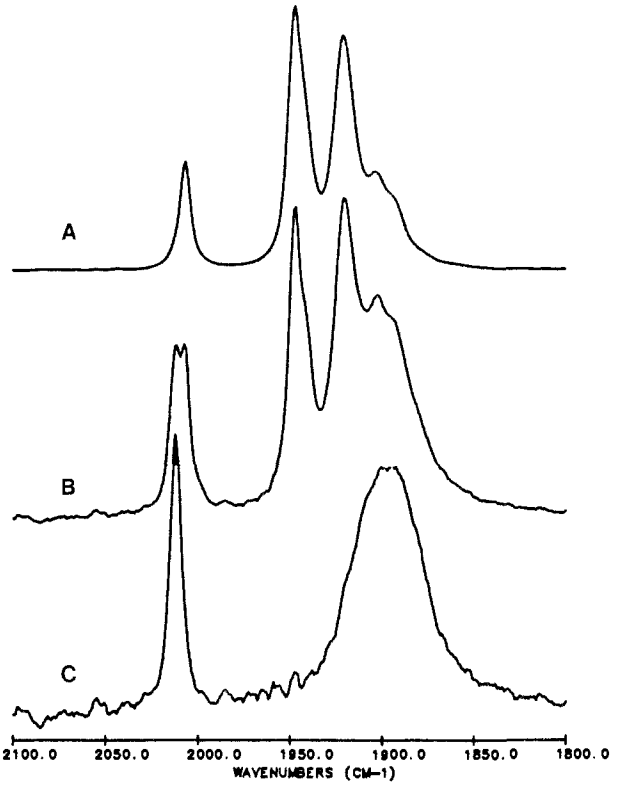


**Figure 3.** FTIR spectra of **1** in THF: (a) 0.005 M, (b) 0.0005 M, (c) subtraction B-(SF)A.

is in good agreement with the results of UV experiments, thus confirming our equilibrium model (Table I). As the temperature is increased, IR spectra show a shift in the equilibrium toward **2**. At 92 °C, the equilibrium is shifted almost entirely to **2**, and the IR spectrum resembles Figure 3c.

The thermodynamic parameters indicate an extremely weak Cr–Cr bond for **1**. The amount of radical **2** present in solutions of **1** at room temperature is much greater than previously estimated.[2] For example, a 0.01 M solution of **1** at 25 °C is about 10% dissociated to **2**. The large positive value of $\Delta S$ and its insensitivity to solvent (toluene versus THF) both argue against any direct participation of solvent in reaction 1. Similar values of $\Delta S$ have been reported for Fe–Fe bond cleavage in $[(allyl)Fe(CO)_3]_2$.[10] Upon the basis of the heat of hydrogenation of **1** and an estimate of the Cr–H bond strength, Hoff had previously estimated the enthalpy of reaction 1 to be 12.7 kcal/mol.[11] Considering the approximation use by Hoff, his estimate is in good agreement with our results.

Upon the basis of the known lability of 17-electron radicals,[12] solutions of **1**/**2** are expected to react readily with donor ligands. Indeed, the carbonyl ligands of **1** exchange with $^{13}CO$ at 25 °C and subatmospheric pressure! Reaction with $Me_3CNC$ yields the stable monomeric 17-electron complex $CpCr(CO)_2(CNCMe_3)$.[13]

**Registry No.** $[CpCr(CO)_3]_2$, 12194-12-6; $CpCr(CO)_3$, 12079-91-3; $CpCr(CO)_2(CNCMe_3)$, 112043-97-7; $Me_3CNC$, 7188-38-7.

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(13) *$CpCr(CO)_2(CNCMe_3)$*. A solution of $Me_3CNC$ (0.083 g, 1.00 mmol) in 25 mL of pentane was added dropwise to a rapidly stirred suspension of $[CpCr(CO)_3]_2$ (0.201 g, 0.50 mmol) in 75 mL of pentane over a period of 30 min. After having been stirred an additional 10 min, the mixture was filtered and cooled to −40 °C to give dark red-brown needles, 0.176 g (69%): IR (pentane solution, $cm^{-1}$) 2096 (w), 2071 (vw), 1938 (vs), 1842 (s); ESR (3-methylpentane, −80 °C) 2.0423. Anal. Calcd for $C_{12}H_{14}CrNO_2$: C, 56.25; H, 5.51; Cr, 20.3; N, 5.47. Found: C, 56.19; H, 5.46; Cr, 19.6; N, 5.63.

# DNA Strand Scission by (−)-Epicatechin and Procyanidin $B_2$

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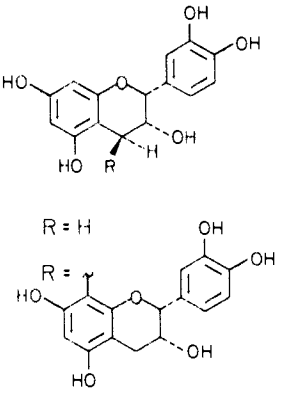
In recent years, considerable effort has been made to identify and characterize molecules capable of mediating nucleic acid strand scission. These include natural[1] and synthetically derived[2] products as well as known DNA binders that have been modified with adjuvants capable of "sequence-neutral" cleavage.[3] Interestingly, in spite of the natural origin of many of these species, we are unaware of any systematic effort to identify additional natural products that mediate nucleic acid strand scission. Reported herein is the identification of two plant-derived natural products that mediate DNA strand scission at micromolar concentrations.

(−)-Epicatechin (**1a**)[4] and (−)-epicatechin-[4β-8]-(−)-epicatechin (**1b**) (procyanidin $B_2$[5]) were isolated from an extract of *Celastrus*

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