Thermodynamic and Kinetic Study of Oxidative Addition/Reductive Elimination of H_2 and D_2 to Fulvalene$Cr_2(CO)_6$: Evidence for Relatively Strong Metal−Metal Bonds in Fulvalenedimetals

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Hydrogen adds reversibly to the chromium−chromium bond of $FvCr_2(CO)_6$ yielding $FvCr_2(CO)_6(H)_2$ (Fv = fulvalene). Equilibrium data for this process have been measured in toluene and deuteriobenzene in the temperature range 50−80 °C and pressures up to 72 atm H_2 [$\Delta H° = -1.0(0.4)$ kcal/mol, $\Delta S° = -14.0(2.0)$ cal/mol deg]. These data are used to estimate the enthalpy [16.5 (2.0) kcal/mol] and entropy (11 cal/mol deg) for breaking the Cr−Cr bond in $FvCr_2(CO)_6$. A theoretical calculation of the isodesmic process $FvCr_2(CO)_6(H)_2 + [\eta^5\text{-}C_5H_5Cr(CO)_3]_2 \rightarrow FvCr_2(CO)_6 + 2\ \eta^5\text{-}C_5H_5Cr(CO)_3H$ predicts it to have an enthalpy of −1.74 kcal/mol, very close to the experimental value of −2 kcal/mol. Thus, and assuming that the individual Cr−H bonds in $FvCr_2(CO)_6(H)_2$ and $\eta^5\text{-}C_5H_5Cr(CO)_3H$ are equal, these results lead to the conclusion that the metal−metal bond in the fulvalene system is 2 ± 2 kcal/mol stronger than that in $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, despite the greater Cr−Cr bond length in the former. This result is also in accord with the measured enthalpy of reaction $[FvCr_2(CO)_6]^{2-}(Na^+)_2 + [\eta^5\text{-}C_5H_5Cr(CO)_3]_2 \rightarrow FvCr_2(CO)_6 + 2\ [\eta^5\text{-}C_5H_5Cr(CO)_3]^-Na^+$, $\Delta H = -2.4(0.4)$ kcal/mol. Deuterium was found to add to $FvCr_2(CO)_6$ with a normal equilibrium isotope effect: $K_{eq}(H_2)/K_{eq}(D_2) = 1.45(0.10)$. A kinetic study of reductive elimination of H_2 in the temperature range 45−75 °C shows that it obeys first-order kinetics: [$k_{-1}^{45.5} = 1.0 \times 10^{-5}\ s^{-1}$, $\Delta H^‡ = 27.8(2.0)$ kcal/mol, $\Delta S^‡ = 5.6(3.0)$ cal/mol deg]. Similarly, the oxidative addition reaction reveals first-order behavior in both $FvCr_2(CO)_6$ and H_2 [$\Delta H^‡ = 26.8(2.5)$ kcal/mol, $\Delta S^‡ = -19.6\ (6.0)$ cal/mol deg]. The obtained combined kinetic data are in reasonable agreement with the measured equilibrium constant. The rate of hydrogenation under 60 atm of H_2 is not retarded by addition of 15 atm of CO, arguing against a transition state involving CO loss. Studies of the rate of oxidative addition/reductive elimination of D_2 suggest a late transition state for the former which involves cleavage of the D−D (H−H) bond. Substitution of ^{12}CO in $FvCr_2(^{12}CO)_6$ by ^{13}CO occurs 1−2 orders of magnitude faster than does hydrogenation [$k_1^{43.7} = 5.6 \times 10^{-6}\ s^{-1}\ atm^{-1}$, $\Delta H^‡ = 16.7(1.5)$ kcal/mol, $\Delta S^‡ = -30.0(4.0)$ cal/mol deg] but is much slower than in analogous complexes $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ (R = H, Me). The crystal structure of $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ is reported.

Introduction

The fulvalene (Fv) ligand[1] and its oligocyclopentadienyl analogues[2] constitute attractive scaffolds on which to assemble two or more strongly bound metals in order to elicit novel reactivity and enforce unusual structural features. Two key aspects of the fulvalene dimetallic frame have been emphasized in this endeavor, namely, the anticipated electronic communication between the directly linked cyclopentadienyls (Cps) and the presumed strain induced on metal−metal bond formation. The latter is impeded by the prohibitive distance between the Cp centroids (∼4 Å) in planar fulvalene and made possible only by deplanarization of the π system. The resulting "strain" has led to the expectation of relatively weak Fv(M−M) bonds compared to those in CpM−MCp.[1] On the other hand, MO arguments indicating a stabilizing interaction between the M−M electrons and the Fv LUMO[1,3] would argue against this notion. The available literature is inconclusive in this respect.[1,4,5]

In this connection, $FvCr_2(CO)_6$ is of particular interest: it has the longest CpCr−CrCp bond known, 3.471(1) Å, and acts as a hydrogenation catalyst,[5] strongly suggestive of the presence of a labile M−M bond capable of adding H_2 and donating it to an acceptor (by whatever mechanism). However, unlike its Cp analogues $[CpCr(CO)_3]_2$[6] and $[Cp^*Cr(CO)_3]_2$[7] which have

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(1) For the fulvalene concept, see: (a) Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146. (b) McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, 493.

(2) (a) Boese, R.; Bräunlich, G.; Gotteland, J.-P.; Hwang, J.-T.; Troll, C.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 995. (b) de Azevedo, C. G.; Boese, R.; Newman, D. A.; Vollhardt, K. P. C. *Organometallics* **1995**, *14*, 4980. (c) Boese, R.; Myrabo, R.; Newman, D. A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 549.

(3) (a) Sharp, P. R.; Raymond, K. N.; Smart, J. C.; McKinney, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 753. (b) Lichtenberger, D. L.; Gruhn, N. E.; Rempe, M. E.; Geiger, W. E.; Chin, T. T. *Inorg. Chim. Acta* **1995**, *240*, 623.

(4) See, inter alia: (a) Boese, R.; Cammack, J. K.; Matzger, A. J.; Pflug, K.; Tolman, W. B.; Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 6757 and references therein. (b) Chin, T. T.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 5002 and references therein. (c) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4074, 4084, and references therein.

(5) McGovern, P. A., Vollhardt, K. P. C. *Chem. Commun.* **1996**, 1593.

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shorter intermetallic distances and "visibly" dissociate to the corresponding 17e monomers, it requires bulky ligand substitution to reveal (NMR) equilibration with the corresponding biradicals.[8] In this vein, the direct reaction of H_2 with $FvCr_2(CO)_6$ and, more generally, its Mo and W relatives (eq 1) has never been observed. On the other hand, the reverse process,

$$FvM_2(CO)_6 + H_2 \rightleftharpoons FvM_2(CO)_6(H)_2 \qquad (1)$$

H_2 elimination from $FvM_2(CO)_6(H)_2$, occurs rapidly with Cr,[5,8a] more slowly with Mo,[9] and very sluggishly with W,[1a] possibly through radical or ionic[10] intermediates under the conditions employed, although detailed mechanistic studies are lacking.

In light of these observations and the lack of quantitative thermodynamic and kinetic data the present study was initiated, focusing on the reaction of $FvCr_2(CO)_6$ with H_2. It expands on previous work on the thermochemistry of the $[CpM(CO)_3]_2$ (M = Cr, Mo, W) relatives of the corresponding Fv complexes, which has yielded heats of H_2 activation and M−M and M−H bond strengths.[11] In a broader context, dinuclear H_2 addition/elimination is of fundamental phenomenological importance,[12] provides a model for H_2 absorption and evolution on surfaces,[13] and may be relevant in homogeneous catalysis other than hydrogenation, such as hydroformylation. The latter features perhaps the best example of oxidative addition of H_2 to a dinuclear complex (eq 2), a transformation that exhibits aspects that may have some general significance. The mechanism of

$$Co_2(CO)_8 + H_2 \rightleftarrows 2\ H\text{-}Co(CO)_4 \qquad (2)$$

this process has yet to be completely elucidated, despite prolonged efforts. Reductive elimination of hydrogen is inhibited by CO as shown by Ungvary and Marko,[14] but catalyzed by the presence of the $^{\bullet}Co(CO)_4$ radical as reported by Wegman and Brown.[15] Oxidative addition can be catalyzed by complexes formed by disproportionation in the presence of added donor ligands (eq 3).[16]

$$3Co_2(CO)_8 + 2nL \rightleftarrows 2[L_nCo]^{2+} + 4Co(CO)_4^- \qquad (3)$$
$$L = py, H_2O, THF$$

This paper reports investigations of the thermodynamics and kinetics of the reaction of $FvCr_2(CO)_6$ with H_2, D_2, and ^{13}CO, and of $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ with $[C_5R_5Cr(CO)_3]_2$. Work on the corresponding molybdenum and tungsten complexes is in progress and will be reported later.[17]

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or in a Vacuum Atmospheres glovebox. Solvents were purified by distillation from sodium/benzophenone under argon into flame dried glassware. Hydrogen (5.0), deuterium (99.5% isotopic purity), and ^{13}CO (99.5% isotopic purity) from Matheson Gas or Liquid Carbonic were used as obtained. The chromium complexes $FvCr_2(CO)_6$, $[FvCr_2(CO)_6]^{2-}(Na^+)_2$, $[C_5H_5Cr(CO)_3]_2$, and $[C_5Me_5Cr(CO)_3]_2$ were prepared and purified by standard literature procedures.[5,8,18] Equilibrium measurements were made on a Perkin-Elmer 2000 FTIR spectrometer in a high-pressure cell obtained from Harrick Scientific, and calorimetric measurements were carried out in stainless steel cells using a Setaram 60 Calvet calorimeter as described in detail elsewhere.[19] Experimental errors represent 95% confidence limits.

Equilibrium Measurements for the Binding of H_2 and D_2 to $FvCr_2(CO)_6$. The high-pressure cell was filled in the glovebox with 25 mL of a solution of $FvCr_2(CO)_6$ in toluene ($c \approx 3$ mg/mL) under a slight argon pressure. Following equilibration at the given temperature and running of an initial FTIR spectrum, the cell was pressured up with H_2 or D_2. The equilibrium was studied in the pressure and temperature range of 1−72 atm and 50−80 °C, respectively. The extent of binding was monitored by following the increase in the peak intensity at 2008 cm^{-1} due to the dihydrido complex $FvCr_2(CO)_6(H)_2$.[5,8] Pressure readings were corrected for the vapor pressure of the solvent.

Kinetics of Binding of H_2 and D_2 to $FvCr_2(CO)_6$. The high-pressure cell was filled in the glovebox with 25 mL of a solution of $FvCr_2(CO)_6$ in benzene (H_2) or deuteriobenzene (D_2) ($c \approx 3$ mg/mL) under a slight argon pressure. Following equilibration at 75 °C and running of an initial FTIR spectrum, the cell was pressured up with, on average, 60 atm of H_2 or D_2. The rate of binding was established by measuring the time dependence of the increase in the peak intensity at 2008 cm^{-1}. Pressure readings were corrected for the vapor pressure of the solvent.

Kinetics of Reductive Elimination of H_2 from $FvCr_2(CO)_6(H)_2$. The high-pressure cell was filled in the glovebox with 25 mL of a solution of $FvCr_2(CO)_6$ in benzene ($c \approx 3$ mg/mL) under a slight argon pressure. Following equilibration at the given temperature and running of an initial FTIR spectrum, the cell was pressured up with 60 atm H_2. After reaching equilibrium (hours to days depending on the temperature), the H_2 was released and the decrease in the peak intensity at 2008 cm^{-1} monitored as a function of time. Pressure readings were corrected for the vapor pressure of the solvent.

Kinetics of Substitution of CO by ^{13}CO in $FvCr_2(CO)_6$. The high-pressure cell was filled in the glovebox with 25 mL of a solution of $FvCr_2(CO)_6$ in benzene ($c \approx 3$ mg/mL) under a slight argon pressure. Following equilibration at the given temperature and running of an initial FTIR spectrum, the cell was pressured up with on average 4.8 atm of ^{13}CO. The rate of substitution was studied at 43.7, 52.5, and 60.6 °C by monitoring the decrease in the peak intensity at 2018 cm^{-1} due to $FvCr_2(CO)_6$ as a function of time. Pressure readings were corrected for the vapor pressure of the solvent.

Substitution of CO by ^{13}CO in $FvCr_2(CO)_6$ in the Presence of $FvCr_2(CO)_6(H)_2$. The high-pressure cell was filled in the glovebox with 25 mL of a solution of $FvCr_2(CO)_6$ in benzene ($c \approx 3$ mg/mL) under a slight argon pressure. Following equilibration and running of an initial FTIR spectrum, the cell was pressured up with 60 atm of H_2.

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(6) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

(7) Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907.

(8) (a) Kovács, I.; Baird, M. C. *Organometallics* **1996**, *15*, 3588. (b) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 5469.

(9) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280.

(10) See: Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. *Organometallics*, **1996**, *15*, 2360 and references therein.

(11) (a) Landrum, J. T.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 215. (b) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357. (c) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657. (d) Ju, T. D.; Lang, R. F.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 5328.

(12) (a) Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370. (b) Sevin, A.; Hengtai, Y.; Chaquin, P. *J. Organomet. Chem.* **1984**, *262*, 391. (c) Halpern, J. *Inorg. Chim. Acta* **1982**, *62*, 31. (d) Hay, P. J. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 4.

(13) See, inter alia: (a) Mamaev, V. M.; Gloriozov, I. P.; Simonyan, V. V.; Zernova, E. V.; Prisajnuk, A. V.; Ustynyuk, Y. A. *Mendeleev Commun.* **1997**, 246. (b) Koelle, U. *New. J. Chem.* **1992**, *16*, 157. (c) Nakatsuji, H.; Hada, M.; Yonezawa, T. *J. Am. Chem. Soc.* **1987**, *109*, 1902. (d) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(14) Ungváry, F.; Marko, L. *J. Organomet. Chem.* **1969**, *20*, 205.

(15) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

(16) Sisak, A.; Ungváry, F.; Marko, L. *Organometalllics* **1983**, *2*, 1244.

(17) Bauer, A.; Capps, K. B.; Hoff, C. D.; Vollhardt, K. P. C., work in progress.

(18) (a) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82. (b) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239.

(19) (a) Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179. (b) Gonzalez, A. A.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4295.

After about 90 min, an IR spectrum was taken showing formation of approximately 5−10% $FvCr_2(CO)_6(H)_2$. H_2 was released and the cell was immediately pressured up with 4.4 atm of ^{13}CO. The rate of substitution was studied at 59.4 °C by monitoring the decrease in the peak intensity at 2018 cm^{-1} as a function of time. Pressure readings were corrected for the vapor pressure of the solvent.

Crystal Structure of $[FvCr_2(CO)_6]^{2-}(Na^+)_2 \cdot 5THF$. A yellow, blade-shaped single crystal, 0.30 × 0.17 × 0.10 mm,[3] of $[FvCr_2(CO)_6]^{2-}(Na^+)_2 \cdot 5THF$ was mounted on a glass fiber using Paratone N Hydrocarbon oil and used for the collection of intensity data on a Siemens SMART[20] diffractometer. The unit cell parameters were obtained from a least-squares refinement of 3536 reflections with $I > 3\sigma(I)$ in the range $3.00° < 2\theta < 45.00°$. Area detector frames were collected at 229 K by the ω scan technique (0.3°) with an exposure time of 10 s per frame using monochromated Mo Kα ($\lambda = 0.710\,69$ Å) radiation. A total of 4584 reflections were collected, of which 3226 were unique ($R_{int} = 0.048$). The frame data were integrated using the program SAINT.[21] The intensities were corrected for Lorentz and polarization effects and an empirical absorption correction ($T_{max} = 0.866\,40$, $T_{min} = 0.722\,46$) was applied. The structure was solved by direct methods (SIR92[22]) and refined by full-matrix least-squares calculations against F^2. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included but not refined. The refinement based upon 2484 unique reflections with $I > 3\sigma(I)$ and 227 variable parameters converged with agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_c| = 0.061$ and $R_w = [(\sum\omega(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.069$ [$w = 4F_o^2/\sigma^2(F_o^2)$]. The standard deviation of an observation of unit weight was 1.96, and the maximum shift-to-error ratio was 0.1. The maximum and minimum residual electron density on the final difference Fourier map was 0.70 and − 1.44 e Å^{-3}, respectively. The scattering factors used were taken from Cromer and Waber,[23] anomalous dispersion and mass attenuation coefficients from Creagh and Hubbel.[24] All calculations were performed using the TeXsan[25] crystallographic software package of Molecular Structure Corporation. $[FvCr_2(CO)_6]^{2-}(Na^+)_2 \cdot 5THF$ ($C_{36}H_{48}O_{11}Cr_2Na_2$, $F_w = 806.74$ g/mol) crystallizes from THF/heptane with 5 equiv of lattice THF in the triclinic space group $P\bar{1}$[No. 2] with $a = 7.9746(4)$ Å, $b = 11.3146(7)$ Å, $c = 11.4817(7)$ Å, $\alpha = 82.618(1)°$, $\beta = 77.093(2)°$, $\gamma = 73.733(1)°$, $V = 966.98$ Å^3; $Z = 2$, $D_{calcd} = 1.509$ g cm^{-3}, μ(Mo Kα) = 6.49 cm^{-1}.

Enthalpy of Reaction of $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ with $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ (R = H, Me). The enthalpy of reaction was measured using a two chamber mixing cell at 30 °C in the Calvet calorimeter. Typically, the Calvet cell was taken into a glovebox and the inner chamber loaded with 1.6 mL of a solution of $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ in tetrahydrofuran ($c \approx 0.015$ g/mL). The inner chamber was sealed with a stainless steel cap, on top of which the solid chromium complex $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ (≈0.01 g) was placed. After equilibration for about 90 min, the reaction was initiated by inverting the calorimeter. Continuous rotation of the latter throughout the course of the reaction ensured good mixing. For R = H, the enthalpy of reaction was found to be +2.2 ± 0.3 kcal/mol (average of four experiments) and for R = Me, +10.5 ± 0.3 kcal/mol (average of three experiments). The product solutions exhibited the expected quantitative FTIR spectra.

Results

Equilibrium Studies of the Reaction of H_2 and D_2 with $FvCr_2(CO)_6$. Using the high-pressure reactor/FTIR cell described in detail elsewhere,[19] we found clear signs of establishment of the equilibrium in eq 4 in the temperature range 50−80 °C.

$$FvCr_2(CO)_6 + H_2 \xrightleftharpoons[k_{-1}]{k_1} FvCr_2(CO)_6(H)_2 \qquad (4)$$

When the cell was left for days at various pressures (up to 72 atm), there was a slow decrease of the band assigned to $FvCr_2(CO)_6$ at 2018 cm^{-1} and the emergence of the peak due to $FvCr_2(CO)_6(H)_2$ at 2008 cm^{-1}, as well as other spectral changes as shown in Figure 1 of the Supporting Information. These changes were found to be fully reversible, simply by increasing or decreasing the hydrogen pressure at a fixed temperature and allowing for the slow establishment of the new equilibrium position. Computer subtraction of the spectrum of $FvCr_2(CO)_6$ leaves the simple spectrum of $FvCr_2(CO)_6(H)_2$ (Figure 2 of the Supporting Information) with peaks at 2008 (vs), 1936 (sh), and 1929 (vs) cm^{-1}, in exact agreement with the literature.[5,8] Quantitative analysis of the spectral data yields $K_{eq} = 4.7(0.3) \times 10^{-3}$ atm^{-1} for the equilibrium constant at 55 °C. Temperature dependent studies showed that, while the rate of approach to equilibrium depends strongly on temperature (see discussion of kinetics below), the equilibrium itself is nearly independent of it. A small decrease in K_{eq} with increasing temperature was observed in the range 50−80 °C, $\Delta H° = -1.0 \pm 0.4$ kcal/mol and $\Delta S° = -14.0 \pm 2.0$ cal/mol deg. Deuterium was found to bind more weakly than hydrogen: $K_{eq} = (3.3 \pm 0.3) \times 10^{-3}$ atm^{-1} at 55 °C, yielding a normal equilibrium isotope effect $K_{eq}(H_2)/K_{eq}(D_2) = 1.45 \pm 0.10$.

Kinetics of Oxidative Addition/Reductive Elimination of H_2 and D_2. The rates of oxidative addition/reductive elimination of hydrogen and deuterium were studied by either addition or release of gas pressure to the thermostated reactor system. The entire apparatus was shaken vigorously to facilitate gas uptake by solvent, and periodically during the course of the reaction to ensure gas saturation. The rate of transformation was monitored by the change in the bands at 2018 and 2008 cm^{-1} due to $FvCr_2(CO)_6$ and $FvCr_2(CO)_6(H)_2$, respectively. Typical spectra are shown in Figure 3 of the Supporting Information. An isosbestic point at 2015 cm^{-1} was clearly maintained throughout the entire process. All reactions were studied under pseudo-first-order conditions of constant gas pressure in the cell. All kinetic and equilibrium data are based on H_2 gas pressure. Conversion of these data to values based on the concentration of H_2 in solution is readily accomplished using published solubilities and enthalpies and entropies of solution of hydrogen in toluene.[26] Plots of $\ln[A - A^\infty]$ versus time gave straight lines for up to five half-lives as shown in Figure 4 of the Supporting Information. The value of k_{obs} for oxidative addition was always found to be larger than that for reductive elimination of hydrogen. The reaction shown in eq 4 is pseudo-first order in the forward direction and first order in reverse, and approach to equilibrium is expected to obey first-order kinetics[27] in either direction, as illustrated in eq 5.

$$k_{obs} = k_1[H_2] + k_{-1} = \{K_{eq}[H_2] + 1\}k_{-1} \cong \{0.0045^{-1}[H_2] + 1\}k_{-1} \qquad (5)$$

Using the average value of 0.0045 atm^{-1} for K_{eq} in this temperature range leads to calculated values of k_{obs} equal to

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(20) *SMART Area Detection Software Package*; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(21) *SAX Area Detector Integration Program*, V4.024; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(22) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(23) Cromer, D. T.; Waber, *J. T.* In *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2A.

(24) Creagh, D. C.; Hubbell, J. H. in *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C., Table 4.2.6.8, p 219.

(25) *TeXsan Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1992.

(26) Battino, R. *IUPAC Solubility Data Series*; Pergamon Press: Oxford, 1982.

(27) Capellos, C.; Bielski, B. H. J. *Kinetic Systems*; Krieger Publishing Company: Huntington, NY, 1980.

$1.0045k_{-1}$ for reductive elimination at 1 atm versus a value of $1.3015k_{-1}$ for oxidative addition at 67 atm. The predicted ratio of the rates of 1.30 is close to the observed ratio of 1.21 for the data shown in Figure 4 of the Supporting Information. Due to the small value of K_{eq}, data for reductive elimination can be used to calculate k_{-1} directly [45.5 °C, 1.0×10^{-5} s^{-1}; 54.5 °C, 4.0×10^{-5} s^{-1}; 63.0 °C, 1.1×10^{-4} s^{-1}; 73.6 °C, 3.9×10^{-4} s^{-1}]. Figure 5 of the Supporting Information shows a plot of k_{-1} versus temperature, from which the activation parameters of reductive elimination [$\Delta H^{\ddagger} = 27.8 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = 5.6 \pm 4.0$ cal/mol deg] can be derived. Activation parameters for oxidative addition [$\Delta H^{\ddagger} = 26.8 \pm 2.5$ kcal/mol, $\Delta S^{\ddagger} = -19.6 \pm 6.0$ cal/mol deg] are obtained readily from these numbers by using the equilibrium data discussed above. This provides more accurate values, because the direct measurement of k_1 for oxidative addition relies on determining the *difference* between the slopes depicted in Figure 4 of the Supporting Information. Kinetic studies for reductive elimination of D_2 from $FvCr_2(CO)_6(D)_2$ reveal that it is faster: $k_{-1}(D_2)/k_{-1}(H_2) = 1.10 \pm 0.05$.

The effect of added carbon monoxide on the rate of approach to equilibrium from either side of eq 4 was investigated. Application of 15 atm of CO had no noticeable effect on either reaction. Addition of the free radical $[C_5Me_5Cr(CO)_3]^{\bullet}$ (which reacts rapidly with H_2 forming $C_5Me_5Cr(CO)_3H$) was not found to catalyze the approach to equilibrium. The reaction with hydrogen is clean without side or decomposition products over periods ranging from days to weeks, under pressure of H_2 at temperatures up to 90° C.

Kinetics of ^{13}CO Substitution. The rate of substitution by ^{13}CO was investigated by following the decrease in intensity of the band at 2018 cm^{-1} due to $FvCr_2(^{12}CO)_6$ (eq 6).

$$FvCr_2(^{12}CO)_6 + {}^{13}CO \rightleftharpoons FvCr_2(^{12}CO)_5(^{13}CO) + {}^{12}CO \quad (6)$$

The reaction obeyed the expected first-order kinetics in both metal complex and ^{13}CO. It was studied under pseudo-first-order conditions of constant ^{13}CO pressure, and values for k_1 at 43.7, 52.5, and 60.6 °C of 5.4×10^{-6}, 9.8×10^{-6}, and 2.2×10^{-5} s^{-1} atm^{-1}, respectively, yielded the activation parameters of $\Delta H^{\ddagger} = 16.7 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -30.0 \pm 4.0$ cal/mol deg.

One of these experiments was performed with a sample that contained a small amount of $FvCr_2(CO)_6(H)_2$. Surprisingly, the rate of ^{13}CO substitution was significantly higher. This effect was confirmed by pretreatment of pure solutions of $FvCr_2(CO)_6$ with hydrogen, until approximately 5−10% $FvCr_2(CO)_6(H)_2$, had been generated, and then replacing H_2 by ^{13}CO. Again, the rate of ^{13}CO incorporation was much (about 50 times) faster than that for samples which did not contain the dihydride.

Preparation and Crystal Structure of $[FvCr_2(CO)_6]^{2-}(Na^+)_2$. Reaction of $FvCr_2(CO)_6$ with Na/Hg in THF[5] provided $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ in nearly quantitative yield. Single crystals suitable for X-ray crystallography were obtained by layering a filtered THF solution with heptane. The structure of the dianion is shown in Figure 1. Crystal data can be found in the Experimental Section and structural details in the Supporting Information. Selected bond lengths and angles are in the figure caption.

As in the case of $[FvW_2(CO)_6]^{2-}$ $[Et_4N^+]_2$,[1a] the molecule adopts the anti configuration of a completely (co)planar Fv ligand (both the "twist" and "bend" angles[1b] are zero). Unlike the former, however, the sodium ions are ligated by oxygens from the carbonyls and THF molecules. The average Cr−CO bond length, 1.800 Å, is noticeably shorter than that in $FvCr_2(CO)_6$, 1.863 Å,[5] as a consequence of increased Cr−CO d → π* back-bonding in the dianion. The average Cr−C(Cp) ring distance in the latter is 2.214 Å, slightly greater than that in the Cr−Cr bonded neutral system (2.189 Å). The trends observed compare well to those in the analogous FvW_2 pair[1a] and are also evident in the couples $Cp_2Mo_2(CO)_6$[28a]/$CpMo(CO)_3^-$ [28b] and $Cp_2Cr_2(CO)_6/CpCr(CO)_3^-$.[29] Finally, and as in the W relatives,[1a] the Cp−Cp bridge of the Fv moiety lengthens somewhat on going from the neutral (1.433 Å) to the charged complex (1.480 Å), a phenomenon attributable to a number of factors, including removal of the bridging Cr−Cr bond and charge repulsion.

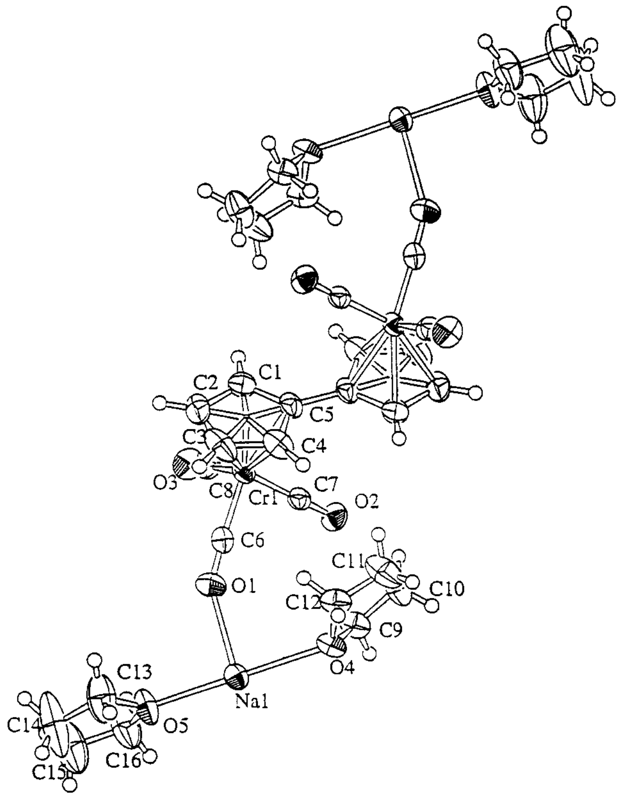

Figure 1. ORTEP view of $[FvCr_2(CO)_6^{2-}(Na^+)_2{\cdot}5THF$ (unit cell) in the crystal, showing the 50% probability thermal ellipsoids (one molecule of THF_{solv} has been omitted for clarity). Selected bond lengths (Å) and angles (deg): Cr(1)−C(1), 2.203(7); Cr(1)−C(2), 2.205(7); Cr(1)−C(3), 2.207(6); Cr(1)−C(4), 2.217(6); Cr(1)−C(5), 2.232(6); Cr(1)−C(6), 1.804(6); Cr(1)−C(7), 1.803(7); Cr(1)−C(8), 1.794(6); Na(1)−O(1), 2.473(5); O(1)−C(6), 1.180(7); C(5)−C(5)′, 1.48(1); C(1)−Cr(1)−C(2), 37.1(3); C(1)−Cr(1)−C(3), 61.3(3); C(6)−Cr(1)−C(7), 88.3(3); C(2)−C(1)−C(5), 109.4(7); C(1)−C(2)−C(3), 107.8(7); C(2)−C(3)−C(4), 108.7(6); C(3)−C(4)−C(5), 107.1(7); C(1)−C(5)−C(4), 106.9(6); C(1)−C(5)−C(5)′, 127.5(8).

Enthalpy of Reaction of $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ with $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$. Reduction of the metal−metal bonded dimers by $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ (eq 7) was rapid and quantitative in THF solution as investigated by FTIR spectroscopy.

$$[FvCr_2(CO)_6]^{2-}(Na^+)_2 + [C_5R_5Cr(CO)_3]_2 \rightleftharpoons FvCr_2(CO)_6 + 2[C_5R_5Cr(CO)_3]^-Na^+ \quad (7)$$

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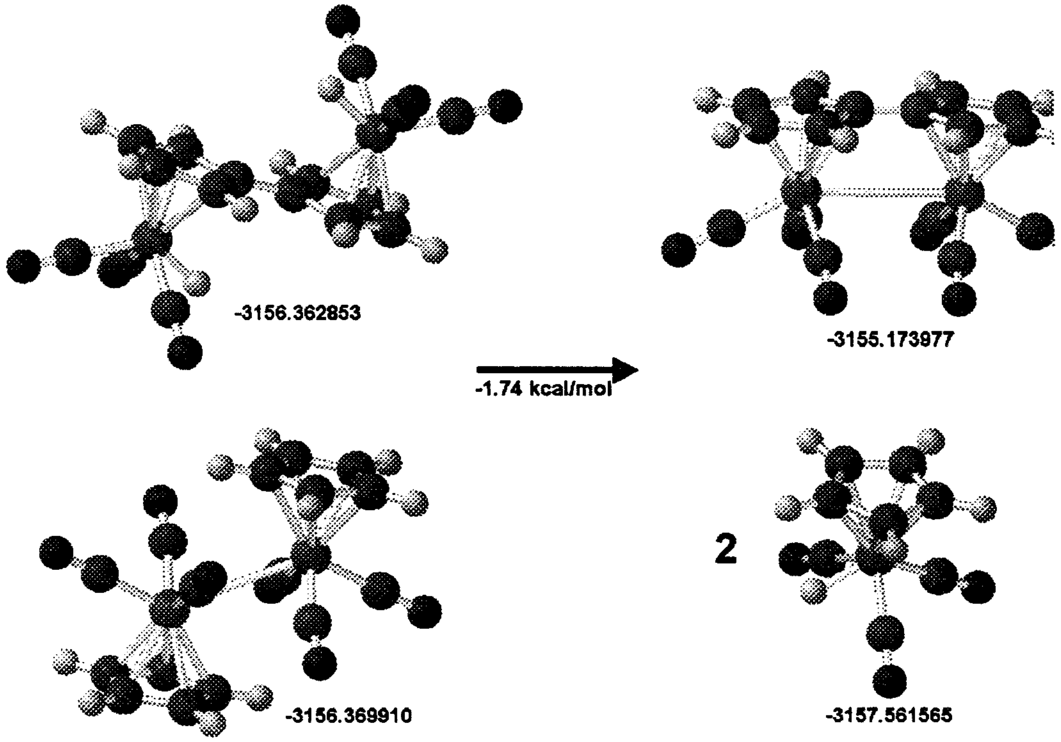
(28) (a) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086. (b) Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, *16*, 920.

(29) Feld, R.; Hellner, E.; Klopsch, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1978**, *442*, 173.

Scheme 1



The enthalpies of these reactions were measured on the solids, and then corrected for enthalpies of solution. The enthalpies of reaction of the solid dimers with a THF solution of $[FvCr_2(CO)_6]^{2-}(Na^+)_2$ were +2.2 ± 0.3 kcal/mol for R = H and +10.5 ± 0.3 kcal/mol for R = Me. Using data for the enthalpies of solution of 4.6 and 5.9 kcal/mol for the respective metal−metal bonded complexes leads to calculated enthalpies of reaction (eq 7) of −2.4 (R = H) and +4.6 kcal/mol (R = Me) with all species in solution (THF).

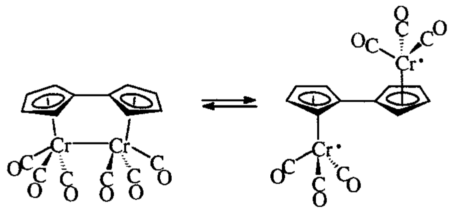
A Theoretical Estimate of the Comparative Cr−Cr Bond Strengths in $FvCr_2(CO)_6$ and $Cp_2Cr_2(CO)_6$. To arrive at a computational estimate of the relative strengths of the metal−metal bonds in $FvCr_2(CO)_6$ and $Cp_2Cr_2(CO)_6$, the enthalpy of the isodesmic reaction in Scheme 1 was calculated at the B3LYP/6-311G* level using Gaussian 94.[31] The optimized geometries of the structures (see also Supporting Information) are depicted in Scheme 1, in addition to their energies in Hartrees. The computed enthalpy of the hydrogenation of the CpCr dimer by the $FvCr_2$ dihydride is −1.74 kcal/mol. Given the reasonable assumption of similar metal−hydride bond strengths (vide infra), it is tempting to associate this energy difference primarily with the greater strength of the Cr−Cr bond in the fulvalene complex, a notion reinforced by the experimental data (Scheme 1).

Discussion

A primary goal of this work was to determine the chromium−chromium bond strength in $FvCr_2(CO)_6$ and compare it to values for the complexes $[C_5R_5Cr(CO)_3]_2$ (R = H, Me). The enthalpies and entropies of dissociation in solution for these complexes (eq 8) had been determined earlier by a combination of thermodynamic and equilibrium studies.[11,32]

$$[C_5R_5(CO)_3Cr{-}Cr(CO)_3C_5R_5] \rightleftarrows 2\,{}^{\bullet}Cr(CO)_3C_5R_5 \tag{8}$$

Direct measurement of the enthalpy and entropy of the reaction in eq 9 is precluded, because the diradical form of the fulvalene dimetal cannot be observed as a stable species.[5,8]



(9)

However, a second approach is successful−determination of the enthalpy of hydrogenation of eq 4: −1 kcal/mol. This value is to be compared with that obtained on $Cp_2Cr_2(CO)_6$: −3 kcal/mol,[11] allowing an experimental estimate of the enthalpy of Scheme 1, −2 kcal/mol, in remarkable agreement with the calculated value of −1.74 kcal/mol.

It is reasonable to assume that the metal−hydrogen bond strengths in the fulvalene hydrides are comparable to those of their cyclopentadienyl analogues. For example, the difference in Cr−H bond strengths of $CpCr(CO)_3H$ and $C_5Me_5Cr(CO)_3H$ is less than 1 kcal/mol.[11,33] Thus, it is expected that the substituent effect of the appended $CpCr(CO)_3$ unit on its

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(30) (a) Kiss, G.; Nolan, S. P.; Hoff, C. D. *Inorg. Chim. Acta* **1994**, *227*, 285. (b) The electrochemical potentials for oxidation and reduction of fulvalene complexes have been determined, but since they are irreversible they cannot be used to generate thermochemical data: Moulton, R.; Weidman, T W.; Vollhardt, K. P. C.; Bard, A.. J. *Inorg. Chem.* **1986**, *25*, 1846.

(31) Revision B.1; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lahm, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. R.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y., Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkely, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*, Gaussian, Inc.; Pittsburgh, PA, 1995.

(32) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643.

neighbor will be negligible. It is instructive to recall that this substituent effect affects the pK_a values of $FvW_2(CO)_6(H)_2$ by only 2−3 units relative to that of $CpW(CO)_3H$,[1a] and that these differences are reflected to a much lesser degree in bond strength data, since the enthalpies of reduction versus those of protonation tend to cancel. For example, the ΔpK_a $CpCr(CO)_3H/C_5Me_5Cr(CO)_3H$ is 3 units. Therefore, the results point to a Cr−Cr bond in $FvCr_2(CO)_6$ that is estimated to be stronger than that in $Cp_2Cr_2(CO)_6$ by 2 ± 2 kcal/mol, even though it is longer by nearly 0.2 Å. While experimental error does not allow definite conclusion that the Cr−Cr bond is stronger for the fulvalene system, it can safely be stated that the bond is not weaker compared to the analogous cyclopentadienyl systems. Additional experimental support is derived from the measurement of the enthalpies of reduction of $FvCr_2(CO)_6$ with sodium, which is intermediate between those of the dimeric cyclopentadienyl and pentamethylcyclopentadienyl complexes. The relatively unfavorable enthalpy of reduction of $[C_5Me_5Cr(CO)_3]_2$ is attributed to the destabilizing influence of the relatively more electron donating pentamethylcyclopentadienyl ligand on the resulting anion. As is always the case with ionic complexes, the role of ion pairing in the thermochemistry is difficult to sort out and can be expected to play a role.

At any rate, the finding of no reduction in the Fv(Cr−Cr) bond strength is clearly at odds with one of the original tenets of FvM_2 chemistry,[1] namely, that strain would weaken (and hence activate) M−M bonds. It lends support for the proposal that there are strong electronic effects, notably the interaction of the M−M bond with the π system, which strongly influence the behavior of the system, as observed spectroscopically and in its chemistry. In short, the FvM_2 core is best viewed as a delocalized framework. Work on the corresponding molybdenum and tungsten derivatives is planned to determine whether this "fulvalene effect" is present for the heavier metals as well.

The relatively small negative entropy (−14 cal/mol deg) of the H_2 addition as shown in eq 4 is also noteworthy. Its value can be compared to that observed[19] for eq 10, −25 cal/mol deg.

$$(PCy_3)_2Cr(CO)_3 + H_2 \rightleftarrows (PCy_3)_2Cr(CO)_3(H_2) \qquad (10)$$

The difference is most reasonably ascribed to the relative rigidity of the metal−metal bonded fulvalene frame, considerably attenuated once the compound is converted to the freely rotating dihydride. This contrasts with the relatively favorable dissociation of the dimers in eq 8 which is ascribed to the increased translational entropy for the two particle system produced. Breaking the chromium−chromium bond of the fulvalene dimer as shown in eq 9 is not expected to have such a favorable entropy associated with it. Considering that the measured value differs from that reasonably expected for an unconstrained system (~25 cal/mol deg)[19a] by about 11 cal/mol deg, suggests the latter value for the entropy of formation of the diradical in eq 9. This estimate is reasonable considering general estimates of the expected increased rotational freedom associated with eq 9.[34] A comparison of the data is given in Table 1.

Table 1. Cr−Cr Bond Lengths and Thermodynamic Data for Homolytic Bond Cleavage in Selected Chromium Complexes

complex	d(Cr−Cr) (Å)	ΔH (kcal/mol)	ΔS (cal/mol deg)	ΔG°(298 K) (kcal/mol)
$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$	3.281(1)	14.7	35	4.3
$[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$	3.310(1)	14.7	45	1.3
$FvCr_2(CO)_6$	3.471(1)	16.5	11	13.2

The observed normal isotope effect for binding of H_2 in preference to D_2 contrasts with the inverse effect observed for the molecular hydrogen complex in eq 10.[19] The latter could be attributed in large part to the increased number of vibrational bands associated with molecular hydrogen complexes. Such vibrational coupling would not be expected for the dinuclear dihydrides and is clearly not observed.

The kinetic study of both oxidative addition and reductive elimination provides information regarding possible mechanisms. The following summarizes the observations described in more detail in the Results section:

1. Oxidative addition/reductive elimination is much slower than that for the species $[C_5R_5Cr(CO)_3]_2$ which show minor (R = H) and extensive (R = Me) dissociation to radicals in solution.

2. The reactions are first order in metal complex and hydrogen, clean, and reversible, and the solutions provide no indication of decomposition over a period of weeks. The rate of reaction is influenced neither by application of 15 atm CO nor by the presence of 5−10 mol % $[C_5Me_5Cr(CO)_3]$.

3. Thermodynamic parameters ($\Delta H° = -1.0$ kcal/mol, $\Delta S° = -14.0$ cal/mol deg) combined with activation energies for k_{-1} ($\Delta H^{\ddagger} = 27.8$ kcal/mol, $\Delta S^{\ddagger} = 5.6$ cal/mol deg) provide activation parameters for k_1 ($\Delta H^{\ddagger} = 26.8$ kcal/mol, $\Delta S^{\ddagger} = -19.6$ cal/mol deg). The estimate for the chromium−chromium bond strength in $FvCr_2(CO)_6$ is 16.5 ± 2.0 kcal/mol.

4. The value of $k_{-1}(H_2)/k_{-1}(D_2) = 0.91$, when combined with $K_{eq}(H_2)/K_{eq}(D_2) = 1.45$, furnishes $k_1(H_2)/k_1(D_2) = 1.32$.

5. Substitution of ^{13}CO is first order in metal complex and ^{13}CO, and occur 1−2 orders of magnitude faster than does reaction with H_2. The activation parameters for substitution are $\Delta H^{\ddagger} = 16.7$ kcal/mol, $\Delta S^{\ddagger} = -30.0$ cal/mol deg. Addition of $FvCr_2(CO)_6(H)_2$ to $FvCr_2(CO)_6$ increases the rate of ^{13}CO substitution in $FvCr_2(CO)_6$.

Among the number of plausible mechanisms, some may be ruled out or are unlikely. For example, dissociation of CO to generate a coordinatively unsaturated species which then reacts with H_2 (or ^{13}CO) is shown in eq 11. This pathway is rendered

$$FvCr_2(CO)_6 \xrightarrow{-CO} FvCr_2(CO)_5 \xrightarrow{H_2} FvCr_2(CO)_5(H)_2 \xrightarrow{+CO} \text{product} \qquad (11)$$

unlikely by the high negative entropies associated with the reaction of both H_2 and ^{13}CO and the fact that the rate of H_2 oxidative addition was not inhibited by external CO pressure.

Formation of (zwitter)ionic complexes[5,10] that somehow catalyze hydrogenation, as shown for cobalt in eq 2, is unlikely since aromatic solvents were used, but it remains a possibility for diene hydrogenation in THF.[5] A radical chain mechanism is discounted on the basis of the highly reproducible nature of the reaction with hydrogen—such mechanisms are notoriously irreproducible—and the lack of influence of added $[C_5Me_5Cr(CO)_3]^{\bullet}$. The strictly first-order mechanism over 4−5 half-lives argues against bimolecular mechanisms involving two $FvCr_2(CO)_6$ molecules or their derivatives.

A mechanism reasonably consistent with the experimental data is depicted in Scheme 2, ignoring syn−anti rotation which is expected to be fast.[4b] It assumes a fast preequilibrium of $FvCr_2(CO)_6$ with its biradical isomer which undergoes fast

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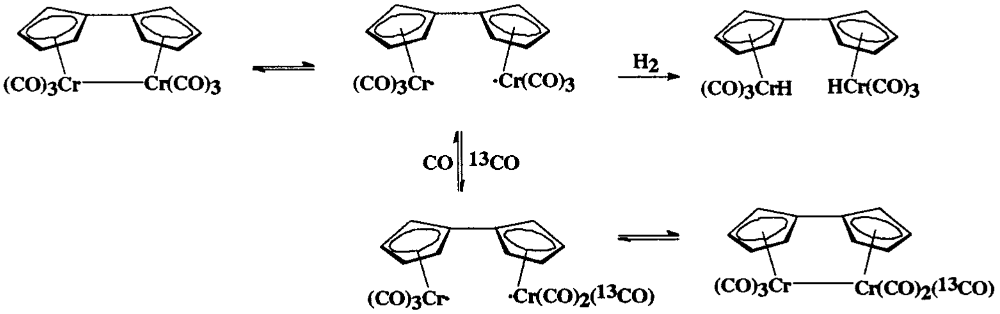
(33) See also: (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711; **1990**, *112*, 2843. (b) Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493.

(34) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

Scheme 2

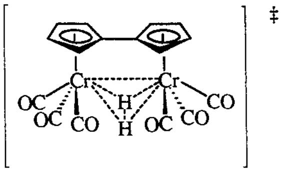


associative ^{13}CO exchange, as observed for $CpCr(CO)_3^{\bullet}$ [32,35] and $(C_5Me_5)Cr(CO)_3^{\bullet}$,[36] or H_2 activation, perhaps as in $(C_5Me_5)Cr(CO)_3^{\bullet}$.[11c] The fact that the enthalpy of activation of ^{13}CO incorporation is only 0.2 ± 2 kcal/mol higher than our estimate of the enthalpy of cleaving the Cr−Cr bond is consistent with this picture. The entropy of activation of −30.0 cal/mol deg is also in agreement with associative substitution and is more negative compared to the H_2 reaction (−19.6 cal/mol deg), in keeping with a smaller loss of translational entropy for hydrogen versus carbon monoxide.[19]

Reaction with H_2 is envisaged to proceed by a similar associative mechanism, now with a greater activation energy, because the strong H−H bond is broken. The observed barrier to this process is larger by 10 kcal/mol than the Cr−Cr bond strength. The exact structure of the transition state, intentionally loosely depicted as **A** to encompass several options,[37] is a matter of speculation which, in its simplest variant, could have as a starting point an initial dihydrogen complex[19,38] which would then be activated toward oxidative addition. It may be noted that the enthalpy of activation for oxidative addition in the Kubas complex (eq 12) is on the order of 10 kcal/mol.[39] Thus, complete

$$(PCy_3)_2W(CO)_3(H_2) \rightleftharpoons (PCy_3)_2W(CO)_3(H)_2 \qquad (12)$$

cleavage of the H−H bond in $FvCr_2$ may occur either at one metal center and be followed by rapid H transfer[12d,30a,40] to give the final dihydride, or may involve both metals simultaneously,[12] or any variant thereof. An attractive alternative, namely the direct oxidative addition to the diradical[12d] (or, indeed even the metal−metal bonded species)[12a] cannot be ruled out, nor can a direct attack pathway with simultaneous ring slippage.[1,4a] Whatever the details of **A** may be, the kinetic parameters as well as the kinetic isotope effect require it to feature significant Cr−Cr *and* H−H bond elongation. Recent results on the rate of reaction of the $C_5Me_5Cr(CO)_3$ radical with H_2 show an enthalpy of activation of 0 ± 1 kcal/mol.[36] This is presumably due to better alignment of the two chromium radicals in the $[C_5Me_5(CO)_3Cr(\mu\text{-}H_2)Cr(CO)_3C_5Me_5]$ transition state which may be free to assume a range of configurations including linear. For the fulvalene system, the transition state may be spatially confined to a trapezoidal configuration. Such a conclusion may be speculative, but it highlights the (unknown)role that radical orientation may play on the trajectory of oxidative addition of hydrogen to a diradical system.



A

Finally, while CO had no apparent influence on the rate of hydrogenation of $FvCr_2(CO)_6$, the presence of the dihydrido complex $FvCr_2(CO)_6(H)_2$ caused a rate increase of ^{13}CO substitution signaling a change in mechanism. One can envision this change to be caused by reversible H atom or proton transfer from the hydride species to the Cr−Cr bond generating a somewhat more substitutionally labile radical or cationic species. This hypothesis may be readily tested and will be the subject of future work which will also encompass the thermochemistry of oligocyclopentadienyls.

Conclusions

The primary goal of this work was to determine the role of the fulvalene ligand in the kinetics and thermodynamics of metal complex reactivity. A number of interesting effects were noted, most significantly that the fulvalene ligand stabilizes the associated Cr−Cr bond with respect to both enthalpy and entropy. Thus, despite a longer Cr−Cr bond in the solid phase, the enthalpy of dissociation of $FvCr_2(CO)_6$ is equal to or slighltly higher than those of its cyclopentadienyl analogues. This finding is attributed to the special electronic characteristics of the fulvalene ligand. Entropy also disfavors bond rupture in comparison, since the resulting radicals are not free to dissociate. The equilibrium data for hydrogenation provide an estimate of ∼11 cal/mol deg for this quantity, compared to 45 cal/mol deg for $[C_5Me_5Cr(CO)_3]_2$. This effect is probably the dominant reason for the failure to detect significant concentrations of the biradical species in solution. To show the same free energy change upon dissociation, the chromium−chromium bond in the fulvalene derivative would have to have an estimated bond dissociation enthalpy of only 6 kcal/mol.

The observed kinetics of oxidative addition/reductive elimination of hydrogen provides a first view of hydrogen activation in fulvalene systems. The most important observation is that there is an additional barrier of approximately 10 kcal/mol above

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(35) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965.

(36) Capps, K. B.; Bauer, A.; Kiss, G.; Hoff, C. D. *J. Organomet. Chem.*, submitted for publication.

(37) Hoffmann, R.; Minkin, V. I.; Carpenter, B. K. *Bull. Soc. Chim. Fr.* **1996**, *133*, 117.

(38) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577. (b) Morris, R. H. *Can. J. Chem.* **1996**, *74*, 1907. (c) See also, inter alia: Jang, M.; Duckett, S. B.; Eisenberg, R. *Organometallics* **1996**, *15*, 2863 and references therein.

(39) B. Zhang, K.; Gonzalez, A. A.; Hoff, C. D. *J. Am. Chem. Soc.* **1989**, *111*, 3627; Gonzales, A. A.; Zhang, K.; Mukerjee, S. L.; Kubas, G. K.; Khalsa, G. R. K.; Hoff, C. D. *ACS Symp. Ser.* **1990**, *428*, 133.

(40) See, inter alia: (a) Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681. (b) Protasiewicz, J. D.; Theopold, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 5559. (c) Creutz, C. *Adv. Chem. Ser.* **1997**, *253*, 151. (d) Branchadell, V.; Dedieu, A. *New. J. Chem.* **1988**, *12*, 443.

that of ^{13}CO substitution and also of our estimate of the metal–metal bond strength. This barrier apparantly does not exist for reaction of two moles of the nontethered $C_5Me_5(CO)_3Cr$ radical. This may be due to nonoptimal interaction between hydrogen and the fulvalenedimetal diradical which is forced by steric demands in the tethered system. Further experimental and theoretical work on this topic is currently underway in our laboratories.

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Supporting Information Available: Supplementary Figures 1–5 and complete information on data collection, atomic coordinates, thermal parameters, structural tables for $FvCr_2(CO)_6{}^{2-}(Na^+)_2{\cdot}5THF$, and optimized calculated geometries of the molecules in Scheme 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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