It has been found that a number of aromatic systems interact not by face to face stacking but by edge to face stacking. Such interactions not only are significant in the solid state but appear to have an important role in determining the tertiary structures of proteins and may play a role in molecular recognition in biological systems.[7d,11] The crystal structure of 3–TNB suggests that such an interaction may be taking place. A single hydrogen on TNB is pointing almost directly at the centroid of the benzene ring of 3 at a distance of ca. 3.22 Å (5.58 Å, centroid to centroid). This represents a nearly ideal distance for a favorable interaction between the positively charged hydrogen of the TNB ring and the benzene ring of 3.[11]

In summary, we have reported the first crystal structure of an unnatural chiral molecular tweezer (3) and its guest, trinitrobenzene. Both electron donor–acceptor stacking and edge–face interactions appear to be involved in stabilizing the complex. Further synthetic and binding studies, including enantiomer recognition, will be reported in due course.

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Supplementary Material Available: Tables of positional parameters, thermal parameters, interatomic distances, interatomic angles, dihedral angles, and least-squares planes for 3–TNB (13 pages); listing of observed and calculated structure factors for 3–TNB (10 pages). Ordering information is given on any current masthead page.

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Heat of Reaction of the $Cr(CO)_3(C_5Me_5)$ Radical with H_2 and Related Reactions. Relative and Absolute Bond Strengths in the Complexes $H-Cr(CO)_2(L)(C_5R_5)$

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In spite of the importance of bond strength data to understanding catalytic reactions of hydrogen, there are few available M–H single bond dissociation energies for transition-metal complexes in solution. Average M–H bond strength estimates based on reactions in which dihydrogen undergoes oxidative addition such as that shown in eq 1 have been made for several complexes.[1]

$$(PPh_3)_2Ir(CO)(Cl) + H_2 \rightarrow (PPh_3)_2Ir(CO)(Cl)(H)_2 \quad (1)$$

Determination of single M–H bond strengths, however, requires that the product radicals be stable on the time scale of the measurement. Since M–H bond strengths are typically on the order of 60 kcal/mol,[2] kinetic methods for determination of pure dissociative homolytic reactions of the M–H bond are limited in scope. Pulsed laser photoacoustic calorimetry[3] gives a second approach provided the quantum yields are known and the reactions are clean. Recently, electrochemical data has been combined with pK_a measurements in thermochemical cycles to generate M–H bond strengths[4] in solution. To date, calorimetric data involving organometallic radicals has not been reported, owing to the fact that there are few stable organometallic free radicals that react with hydrogen.

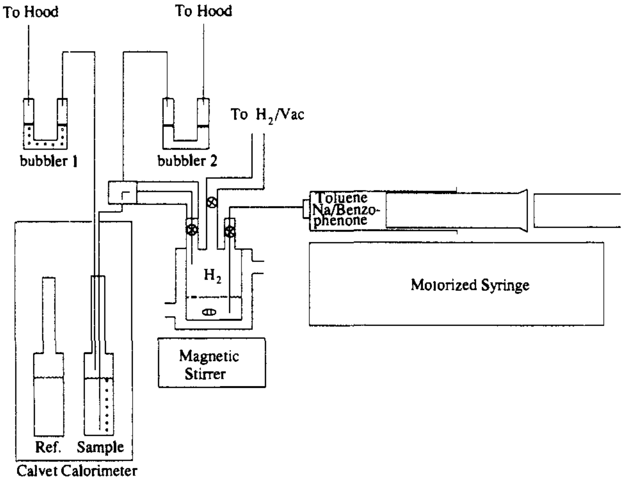

Figure 1. Schematic drawing of apparatus used to measure heats of reaction with H_2 gas.

Table I. Metal–Hydrogen Bond Dissociation Energies[a]

complex	M–H BDE, kcal/mol
$H-Cr(CO)_2(PPh_3)(C_5H_5)$	59.8
$H-Cr(CO)_2(PEt_3)(C_5H_5)$	59.9
$H-Cr(CO)_3(C_5H_5)$	61.5
$H-Cr(CO)_3(C_5Me_5)$	62.3
$H-Cr(CO)_2(P(OMe)_3)(C_5H_5)$	62.7

[a] Relative errors are on the order of ±0.2 kcal/mol. Absolute errors are on the order of ±1 kcal/mol.

Baird and co-workers have recently synthesized and obtained X-ray structural data for the stable $17e^-$ radical $Cr(CO)_2(PPh_3)(C_5H_5)$.[5] The complexes $[Cr(CO)_3(C_5Me_5)]_2$[6] and $[Cr(CO)_2(P(OMe)_3)(C_5H_5)]_2$[7] are metal–metal-bonded dimers in the solid state but dissociate to radicals in solution. McLain[8] has reported equilibrium data for the parent dimer $[Cr(CO)_3(C_5H_5)]_2$, which exists in equilibrium with the radical as shown in eq 2.

$$[Cr(CO)_3(C_5H_5)]_2 \rightleftharpoons 2\,{}^{\bullet}Cr(CO)_3(C_5H_5) \quad (2)$$

These observations pave the way for development of the thermochemistry of organochromium radicals. In this paper we report the first direct calorimetric measurements of relative and absolute metal–hydrogen bond strengths for transition-metal complexes in solution.

Solutions of the ${}^{\bullet}Cr(CO)_3(C_5Me_5)$ radical (which contain small amounts of the dimer[9] react with hydrogen, as shown in eq 3.

$${}^{\bullet}Cr(CO)_3(C_5Me_5) + \tfrac{1}{2}H_2 \rightarrow H-Cr(CO)_3(C_5Me_5) \quad (3)$$

Measurement of the enthalpy of this reaction presented several difficulties; however, reliable data was obtained by using the calorimetric cell shown in Figure 1. A solution of sodium ben-

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(9) (a) Equilibrium data[9b] for the reaction $[Cr(CO)_3(C_5Me_5)]_2 \rightleftharpoons 2\,{}^{\bullet}Cr(CO)_3(C_5Me_5)$ was used to correct observed heats of reaction to those based on 100% radical concentration. This correction was small, on the order of 0.6 ± 0.1 kcal/mol for most concentrations. (b) Kiss, G.; Roper, G. C.; Hoff, C. D., unpublished results.

zophenone ketyl in toluene was used to drive purged, thermostated H_2 gas saturated with toluene vapor through the Calvet cell. The enthalpy of reaction 3, −10.2 ± 1.0 kcal/mol, can be used to calculate the solution-phase Cr–H bond strength in this complex of 62.3 ± 1.0 kcal/mol.

Relative Cr–H bond strengths in solution can be determined to within ±0.2 kcal/mol by solution calorimetric measurement of radical/hydride reactions.[10] For example, reaction 4 is rapid at room temperature. The enthalpy of reaction 4, −2.5 ± 0.2

$$^{\bullet}Cr(CO)_3(C_5Me_5) + H{-}Cr(CO)_2(PPh_3)(C_5H_5) \rightarrow HCr(CO)_3(C_5Me_5) + {}^{\bullet}Cr(CO)_2(PPh_3)(C_5H_5) \quad (4)$$

kcal/mol, is a direct measure of the difference in solution-phase bond strengths between the two complexes and leads to a Cr–H bond strength of 59.8 kcal/mol for the PPh_3-substituted complex. In analogous fashion, the Cr–H bond strength estimates for the PEt_3, CO, and $P(OMe)_3$ complexes shown in Table I have been determined.

The value for the $H{-}Cr(CO)_3(C_5H_5)$ bond strength is in agreement with our earlier work[11] on the heat of hydrogenation of the Cr–Cr dimer shown in eq 5. At that time, no accurate

$$[Cr(CO)_3(C_5H_5)]_2(s) + H_2(g) \rightarrow 2\,H{-}Cr(CO)_3(C_5H_5)(s) \quad (5)$$

value was available for the Cr–Cr bond strength. Use of the recent value[8] of 14.8 kcal/mol for the Cr–Cr bond strength and $\Delta H_{rxn} = -3 \pm 1$ kcal/mol[11] leads to a Cr–H bond strength estimate of 61 kcal/mol, in agreement with the present work. These data are also in agreement with the work of Tilset and Parker based on electrochemical and pK_a data.[12]

The Cr–H bond strengths shown in Table I represent some of the first data to demonstrate the role of ligand substituents on single M–X bond strengths in solution. The range of values is on the order of 3 kcal/mol. In view of the fact that radical/hydride transfer reactions are rapid, as discussed below, this data may be useful in understanding concurrent reactions with several metal species present. The lowest value, 59.8 kcal/mol, is close to the estimated limit for thermodynamic stability for M–H complexes of 56 kcal/mol.[13]

In view of the importance of hydrogen atom transfer in catalytic reactions, we have studied the kinetics of reaction 4 using stopped-flow techniques. The hydride abstraction is first order in both reactants: rate = $k[^{\bullet}Cr(CO)_3(C_5Me_5)][H{-}Cr(CO)_2(PPh_3)(C_5H_5)]$, with values for the second-order rate constant k = 1040, 910, and 768 $M^{-1}\,s^{-1}$ at 35, 25, and 15 °C, respectively. The low enthalpy of activation ($\Delta H^{\ddagger} = 2.1 \pm 0.2$ kcal/mol) and high negative entropy of activation ($\Delta S^{\ddagger} = -38.2 \pm 3.8$ cal $mol^{-1}\,deg^{-1}$) are consistent with direct H atom transfer through a Cr···H···Cr′ intermediate. Additional work is in progress to map out the thermodynamic and kinetic factors controlling stability in these and related hydride/radical reactions.

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(10) In studies of the radical/hydride reactions, a large excess of one reagent was used to drive the equilibrium quantitatively to products. Enthalpies of reaction based on the use of hydride as limiting reagent were in agreement with those done with radical as limiting reagent.

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(12) (a) Bond-strength estimates based on electrochemical data have recently been corrected by 8.0 kcal/mol.[12b] The reported bond strength for $H{-}Cr(CO)_3(C_5H_5)$ of 54 ± 1.0 kcal/mol[4] would then be 62 ± 1.0 kcal/mol, in agreement with our value of 61.5 kcal/mol. (b) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.

(13) For the reaction $2M^{\bullet} + H_2 \rightarrow 2M{-}H$, entropic factors (on the order of 8 kcal/mol at room temperature) will favor loss of H_2. If the M–H bond strength = 56 kcal/mol, the free energy of H_2 addition will be 0 at room temperature. Metal complexes with bond strengths lower than this will be thermodynamically unstable with respect to loss of H_2.

Stannadesulfurization of a Bis(dimethyldithiocarbamato)tungsten(II) Complex: Formation of a Coordinated $Me_2NCCNMe_2$ Complex

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Reactions leading to C–C bond formation may often be effected via organometallic intermediates.[1] Many C–S bond-cleavage reactions are likewise metal assisted.[2] We now report the exhaustive desulfurization of two bis(dithiocarbamato) ligands $[\eta^2\text{-}S_2CNMe_2]^-$ at a tungsten center with concomitant production of the coordinated alkyne $\mu^2\text{-}Me_2NC{\equiv}CNMe_2$ by a reaction involving both these processes.

Numerous metal complexes containing a terminally coordinated stannylene ligand SnX_2 are known but, with the exception of a single Sc(III) and several Cr(0), Mo(0), and W(0) complexes, there are no reports of such derivatives of an early transition metal in a higher oxidation state.[3]

Yellow plates of $[W(CO)_2(\eta^2\text{-}S_2CNMe_2)_2(SnR_2)]$ [R = $CH(SiMe_3)_2$] (**1**) were obtained from $[W(CO)_3(\eta^2\text{-}S_2CNMe_2)_2]$[4] and an equimolar portion of SnR_2[5] in benzene at ambient temperature. Spectroscopic data for **1**[6] are consistent with the illustrated monocapped trigonal prismatic structure, having a cis arrangement of the CO's and a plane of symmetry bisecting the SnR_2 unit and one $[\eta^2\text{-}S_2CNMe_2]^-$ ligand but containing the other. Surprisingly the ligand arrangement in **1** was stereochemically rigid (−80 to +60 °C, ^1H NMR), an unusual feature for a seven-coordinate metal complex,[7] attributed to the bulky SnR_2 moiety. The SnR_2 unit was readily (24–72 h) displaced by a nucleophile L; e.g., reaction with Ph_2C_2 yielded $[W(CO)(\eta^2\text{-}PhC{\equiv}CPh)(\eta^2\text{-}S_2CNMe_2)_2]$.[8]

Thermolysis of $[W(CO)_2(\eta^2\text{-}S_2CNMe_2)_2(SnR_2)]$ (**1**) in benzene for 4 h generated $[SnR_2(\mu\text{-}S)]_n$ (**2**)[9] and emerald crystals of $[\{W(\eta^2\text{-}SCNMe_2)(\eta^2\text{-}S_2CNMe_2)\}\{W(S)(\eta^2\text{-}S_2SnR_2)\}(\mu\text{-}$

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(6) $[W(CO)_2(\eta^2\text{-}S_2CNMe_2)_2(SnR_2)]$ (**1**) (75%, after column chromatography on a Florisil support and elution with $n\text{-}C_6H_{14}$): IR (Nujol) ν(CO) 1984 (s) and 1887 (s), ν(C–N) 1504 (m), ρ(Si–C–Si) 841 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.57 and 3.56 (s, 3 H each, NCH_3), 3.18 (s, 6 H, NCH_3), 0.50 [s, 2 H, $C(H)Si_2$], 0.19 [br s, 36 H, $Si(CH_3)_3$]; ^{13}C NMR (C_6D_6) δ 223.9 ($^1J_{WC}$ 134 Hz, CO), 210.4 and 205.4 ($S_2CN<$), 45.3, 44.7, and 38.1 (NCH_3), 18.1 [$C(H)Si_2$], 5.3 and 4.9 [$Si(CH_3)_3$]; ^{119}Sn NMR (C_6D_6) δ 188.3. Mass spectrum (FAB), m/z (assign) 862 $(M - 2CO)^+$. Anal. Calcd for $C_{22}H_{50}N_2O_2S_4Si_4SnW$: C, 28.8; H, 5.50; N, 3.05. Found: C, 28.6; H, 4.96; N, 2.81.

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(9) $[SnR_2(\mu\text{-}S)]_n$ (**2**): IR (Nujol) ρ(Si–C–Si) 841 (s) cm^{-1}; ^1H NMR (C_7D_8) δ 1.13 [s, $C(H)Si_2$], 0.32 [s, $Si(CH_3)_3$]; ^{13}C NMR (C_7D_8) δ 4.6 [$Si(CH_3)_3$], $C(H)Si_2$ carbon signal was obscured by solvent resonances; ^{119}Sn NMR (C_7D_8) δ 121.4.

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