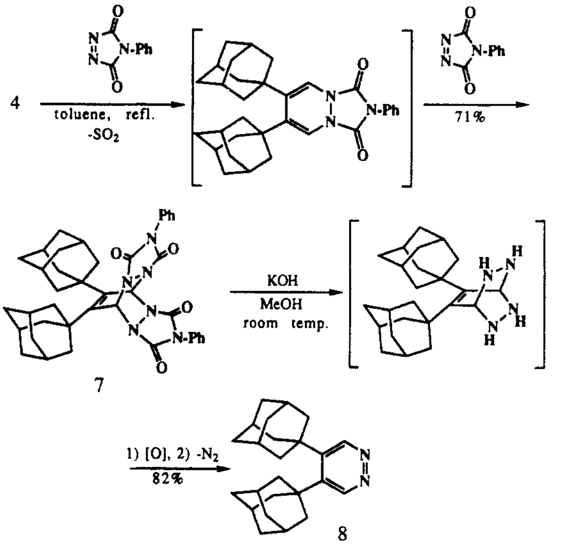
p-Toluenesulfonic acid catalyzed dehydration of **2** in refluxing benzene for 0.5 h produced the expected thiophene **3**[4,6] in 60% yield.[5a,c] Oxidation of **3** with *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 at room temperature gave the corresponding 1,1-dioxide **4**[4] in 75% yield.[5c]

The diels-Alder reaction of dioxide **4** with phenyl vinyl sulfone (3 equiv) in refluxing *o*-dichlorobenzene for 24 h afforded *o*-di-1-adamantylbenzene (**5**)[4,7,8] in 92% yield with cheletropic loss of sulfur dioxide and of benzenesulfonic acid from the initial adduct. Similarly, the reaction of **4** with dimethyl acetylenedicarboxylate (DMAD) in refluxing *o*-dichlorobenzene for 7 h furnishes dimethyl 4,5-di-1-admantylphthalate (**6**)[4,9] in 90% yield with extrusion of sulfur dioxide from the initial adduct.[10]

The reaction of **4** with excess 4-phenyl-1,2,4-triazoline-3,5-dione (7.5 equiv) in refluxing toluene affords the bis adduct (**7**)[4] in 72% yield. Treatment of **7** with KOH/MeOH at room temperature followed by air oxidation and nitrogen extrusion leads directly to 4,5-di-1-adamantylpyridazine (**8**)[4,11] in 82% yield.[12]



The two adamantyl substituents of **3**, **5**, and **8** are equivalent in the ^1H NMR spectra, which confirms that rotation about the bond from the aromatic ring to adamantyl is fast on the ^1H NMR time scale at room temperature. A similar conclusion is reached from ^{13}C NMR analysis.[13]

Treatment of **3** with $AlCl_3$ in CS_2 at room temperature for 6 days brings about quantitative isomerization to 2,4-di-1-adamantylthiophene.[14] Treatment of **5** under similar conditions results in exhaustive deadamantylation, although the use of benzene as the solvent gives 1-adamantylbenzene[15] in 41% yield.

Supplementary Material Available: Experimental details of the preparation of compounds **2–8** and spectroscopic data (^1H and ^{13}C NMR, IR, and UV) for these compounds (4 pages). Ordering information is given on any current masthead page.

---

(6) **3**: mp 198–199 °C; ^1H NMR ($CDCl_3$) (400 MHz) δ 1.76 (s, 12 H), 2.10 (br s, 6 H), 2.18 (d, J = 3 Hz, 12 H), 7.20 (s, 2 H, thiophene ring); ^{13}C NMR ($CDCl_3$) (100.6 MHz) δ 29.32 (d), 36.78 (t), 38.17 (s), 44.14 (t), 122.15 (d, C_2 and C_5 of thiophene ring), 152.20 (s, C_3 and C_4 of thiophene ring); UV (hexane) λ_{max} (ϵ) 237 (5350), 242 nm (5350).

(7) **5**: mp 184.5–185 °C; ^1H NMR ($CDCl_3$) (400 MHz) δ 1.74 (d, J = 12 Hz, 6 H), 1.80 (d, J = 12 Hz, 6 H), 2.13 (s, 6 H), 2.29 (s, 12 H), 7.13 (m, 2 H, benzene ring), 7.64 (m, 2 H, benzene ring); ^{13}C NMR ($CDCl_3$) (100.6 MHz) δ 29.71 (d), 36.84 (t), 40.95 (s), 44.59 (t), 125.47 (d), 128.66 (d), 150.39 (s); UV (hexane) λ_{max} (ϵ) 264 nm (145).

(8) The only known isomer is the para-substituted one: Rundel, W. *Chem. Ber.* **1966**, *99*, 2707–2708.

(9) **6**: mp 192–193 °C; ^1H NMR ($CDCl_3$) (400 MHz) δ 1.75 (d, J = 13 Hz, 6 H), 1.80 (d, J = 13 Hz, 6 H), 2.15 (br s, 6 H), 2.26 (d, J = 2 Hz, 12 H), 3.89 (s, 6 H, CO_2Me), 7.99 (s, 2 H, benzene ring); ^{13}C NMR ($CDCl_3$) (100.6 MHz) δ 29.41 (d), 36.54 (t), 41.39 (s), 44.15 (t), 52.45 (q, Me), 127.95 (s, C_1 and C_2), 129.73 (d, C_3 and C_6), 154.46 (s, C_4 and C_5), 168.53 (s, carbonyl).

(10) For Diels–Alder reactions of thiophene 1,1-dioxides, see: Rajappa, S. in *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon: New York, Vol. 4, Chapter 3.14.

(11) **8**: mp 257.5–258 °C; ^1H NMR ($CDCl_3$) (400 MHz) δ 1.75 (s, 12 H), 2.13 (s, 6 H), 2.21 (s, 12 H), 9.15 (s, 2 H, pyridazine ring); ^{13}C NMR ($CDCl_3$) (100.6 MHz) δ 29.03 (d), 36.34 (t), 39.84 (s), 43.34 (t), 147.77 (s, C_4 and C_5), 150.23 (d, C_3 and C_6).

(12) Nakayama, J.; Hirashima, A. *Heterocycles* **1989**, *29*, 1241–1242.

(13) Single-crystal structure analyses of **3** and **5** are under way by Professor F. Iwasaki of the University of Electro-Communications and will be reported elsewhere in detail. Preliminary results show that the two adamantyls of **5** are twisted with a torsion angle of 16.6° and an adamantyl–C_1–C_2 bond angle of 129.3° (bond angle adamantyl–C_2–C_3, 115.0°), and the C_1–C_2 bond is as long as 1.446 Å, while the C_4–C_5 bond is interestingly as short as 1.333 Å.

(14) Such isomerization was also observed with 3,4-di-*tert*-butylthiophene.[5c]

(15) Stetter, H.; Schwarz, M.; Hirschhorn, A. *Chem. Ber.* **1959**, *92*, 1629–1635.

Molecular Clefts. 3. The Crystal Structure of a Chiral Molecular Tweezer and Its Guest

Michael Harmata* and Charles L. Barnes

Department of Chemistry
University of Missouri—Columbia
Columbia, Missouri 65211

Received April 6, 1990

Host–guest chemistry constitutes an important area of research. Many intriguing, structurally diverse hosts have been devised and synthesized for the purpose of studying the nature of the binding interactions between host and guest and exploiting such interactions to some productive end (e.g., catalysis).[1] Molecular clefts represent a structural class of hosts that are currently of great interest, primarily due to the work of Rebek and co-workers.[2] A subset of this class of hosts comprises the molecular tweezers, currently being studied in detail by Zimmerman and co-workers.[3] In the course of our work on the development of analogues of Kagan's ether (**1**) as hosts, it became clear that it would, in principle, be possible to synthesize a new class of chiral molecular tweezers capable of binding to neutral aromatic systems.[4,5] In this paper we report the first example of a crystal structure of an unnatural chiral, but racemic, molecular tweezer and its guest.[6,7]

1

---

(1) For recent reviews, see: (a) Dugas, H. *Bioorganic* Chemistry—*A Chemical Approach to Enzyme Action*, 2nd ed.; Springer-Verlag: New York, 1989. (b) Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 362. (c) Pederson, C. J. *Ibid.* **1988**, *27*, 1021. (d) Cram, D. J. *Ibid.* **1988**, *27*, 1009. (e) Lehn, J.-M. *Ibid.* **1988**, *27*, 89. (f) *Host–Guest Complex Chemistry: Macrocycles*; Vögtle, F., Wever, E., Eds.; Springer-Verlag: New York, 1985. (g) *Synthesis of Macrocycles—The Design of Selective Complexing Agents*; Izatt, R. M., Christensen, J. J., Eds.; Progress in Macrocyclic Chemistry, Vol. 3; Wiley: New York, 1987.

(2) For a comprehensive review of the seminal contributions of Rebek and co-workers to the area of molecular clefts, see: Rebek, J., Jr. *Top. Curr. Chem.* **1988**, *149*, 190.

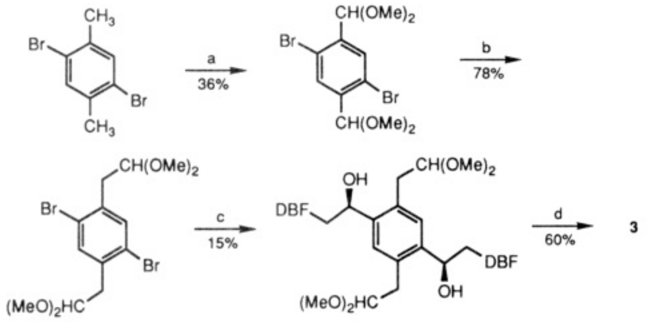
(3) (a) Zimmerman, S. C.; Mrksich, M.; Baloga, M. *J. Am. Chem. Soc.* **1989**, *111*, 8528. (b) Zimmerman, S. C.; Wu, W. *Ibid.* **1989**, *111*, 8054. (c) Zimmerman, S. C.; VanZyl, C. M.; Hamilton, G. S. *Ibid.* **1989**, *111*, 1373. (d) Zimmerman, S. C. *Tetrahedron Lett.* **1988**, 983. (e) Zimmerman, S. C.; VanZyl, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 7894.

(4) Wilcox and co-workers have made significant contributions in their studies of Troeger's base and its analogues. Troeger's base is structurally very similar to **1**. See: (a) Webb, T. H.; Wilcox, C. S. *J. Org. Chem.* **1990**, *55*, 363. (b) Adrian, J. C., Jr.; Wilcox, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 8055. (c) Sucholeiki, I.; Lynch, V.; Phan, L.; Wilcox, C. S. *J. Org. Chem.* **1988**, *53*, 98. (d) Wilcox, C. S.; Greer, L. M.; Lynch, V. *J. Am. Chem. Soc.* **1987**, *109*, 1865. (e) Larson, S. B.; Wilcox, C. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 224. (f) Wilcox, C. S.; Cowart, M. D. *Tetrahedron Lett.* **1986**, 5563. (g) Wilcox, C. S. *Ibid.* **1985**, 5749.

(5) (a) Harmatra, M.; Murray, T. *J. Org. Chem.* **1989**, *54*, 3761. (b) Harmata, M.; Barnes, C. L. *Tetrahedron Lett.* **1990**, 1825.

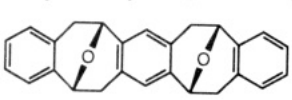
0002-7863/90/1512-5655$02.50/0

Scheme I[a]

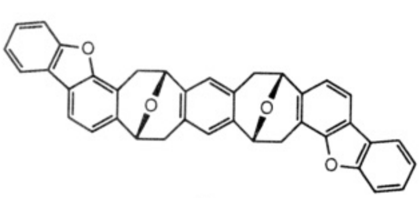


[a] (a) (1) CrO_3; (2) MeOH, H_2SO_4, reflux, 3.5 h. (b) (1) 1 N HCl, reflux 2.5 h; (2) $Ph_3PCHOMe$, THF, 25 °C; (3) MeOH, H_2SO_4, reflux, 12 h. (c) 4.3 equiv of *t*-BuLi, THF, −78 °C, then $DBFCH_2CHO$. (d) (1) cat. TsOH, CH_2Cl_2, −78 °C, 10 min, to 25 °C, 1 h; (2) $SnCl_4$, CH_2Cl_2, −78 °C, 30 min.

We recently reported the synthesis of **2** and found that while it served well as a clathrand, no evidence for a 1:1 binding interaction between **2** and various guests could be found, either in solution or the solid state.[5b] We therefore sought a tweezer with a deeper cleft and prepared **3** in exactly the same fashion as **2**, albeit in considerably lower yield (Scheme I).[8]



2



3

The tweezer **3** has proven recalcitrant to forming a crystal suitable for X-ray analysis. However, crystallization by slow evaporation of a ca. 1:1 mixture of **3** and trinitrobenzene (TNB) in chloroform/nitrobenzene produced crystals suitable for X-ray analysis. Not unexpectedly, the crystal proved to be that of a 1:1 complex in which the TNB was securely couched in the cleft of **3**. An ORTEP plot of the structure and space-filling model are shown in Figure 1.[9]

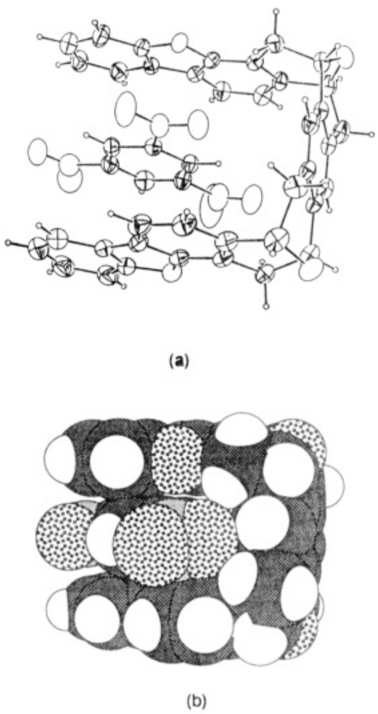


Figure 1. ORTEP plot (a) and space-filling model (b) of **3**–TNB.

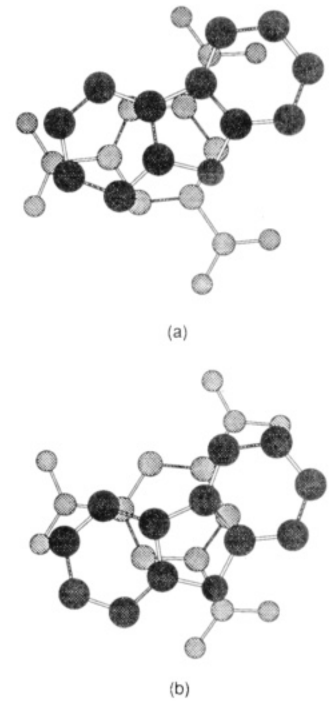


Figure 2. Top (a) and bottom (b) views of **3**–TNB.

Several aspects of the structure merit discussion. The distance between the least-squares planes of the dibenzofuran (DBF) units on **3** and the TNB is ca. 3.32 Å, as expected for a stacking interaction between two π systems.[10] The angles between each DBF unit and the central benzene ring of **3** are 89.3° and 89.4°, respectively. This figure differs dramatically from that obtained for **2** and suggests that conformational freedom provided by the carbon–carbon single bonds in **3** does not present a prohibitive energy barrier with respect to guest binding.[5b] Interestingly, the dibenzofuran chromophores are not both parallel to the TNB guest. This lack of symmetry can be seen more dramatically if the complex is viewed through the dibenzofuran rings as shown in Figure 2. Clearly, the orientations of the TNB and each DBF chromophore are quite different. The DBF ring shown in Figure 2b is 5.2° out of a parallel plane, with the DBF oxygen bending toward the proximal nitro group of the guest. This may result from an electrostatic attraction between the lone pair on the oxygen and the nitro group or repulsive interactions between the TNB and the back half of the DBF chromophore.

---

(6) The crystal structures of natural molecular tweezers, triostin A and echinomycin, and a guest, a DNA hexanucleotide, have been reported. See: (a) Wang, A. H. J.; Ughetto, G.; Quigley, G. J.; Hakoshima, T.; van der Marel, G. H.; van Boon, J. H.; Tich, A. *Science* **1984**, *225*, 1115. (b) Ughetto, G.; Wang, A. H. J.; Quigley, G. J.; van der Marel, G. H.; van Boon, J. H.; Rich, A. *Nucleic Acids Res.* **1985**, *13*, 2305.

(7) Crystal structures of related hosts or host–guest complexes have been reported. See: (a) Reference 3a. (b) Reference 4c. (c) Jazwinski, J.; Blacker, A. J.; Lehn, J.-M.; Cesario, M.; Guilheim, J.; Pascard, C. *Tetrahedron Lett.* **1987**, 6057. (d) Muehldorf, A. V.; Van Engen, D.; Warner, J. C.; Hamilton, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 6561.

(8) Details of the synthesis will be reported elsewhere.

(9) Enraf-Nonius CAD4 diffractometer; $C_{38}H_{26}O_4 \cdot C_6H_3N_3O_6$, MW = 759.74; space group *P*21/*C* (314); *a* = 11.694 (4) Å, *b* = 18.788 (4) Å, *c* = 15.796 (4) Å, β = 94.38 (2)°, *V* = 3460 (3) Å^3, *Z* = 4; D_{calcd} = 1.458 g/cm^3; radiation, Mo Kα (λ = 0.71073 Å); μ = 1.0 cm^{-1}; *F*(000) = 1576; temperature = 23 ± 1 °C; final *R* = 0.048 for 2783 observed reflections. In Figure 1a the thermal ellipsoids are drawn at the 50% probability level. The space-filling model in Figure 1b was produced by CHEM-3D using the crystal coordinates of **3**–TNB.

(10) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984; pp 134–140.

J. Am. Chem. Soc. **1990,** *112,* 5657-5658

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.

Acknowledgment. We are grateful to the National Science Foundation for partial support of the NMR (PCM-8115599) and MS (PCM-8811711 6) facilities at the University of Missouri—Columbia.

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.

---

(11) (a) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23. (b) Burley, S. K.; Petsko, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 7995. (c) Anelli, P. L.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, P. J. *Tetrahedron Lett.* **1988**, 1575 and references therein.

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 $H–Cr(CO)_2(L)(C_5R_5)$

Gabor Kiss, Kai Zhang, Shakti L. Mukerjee, and
Carl D. Hoff*

Department of Chemistry, University of Miami
Coral Gables, Florida 33124

Gerald C. Roper

Department of Chemistry, Dickinson College
Carlisle, Pennsylvania 17013

Received March 19, 1990

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.

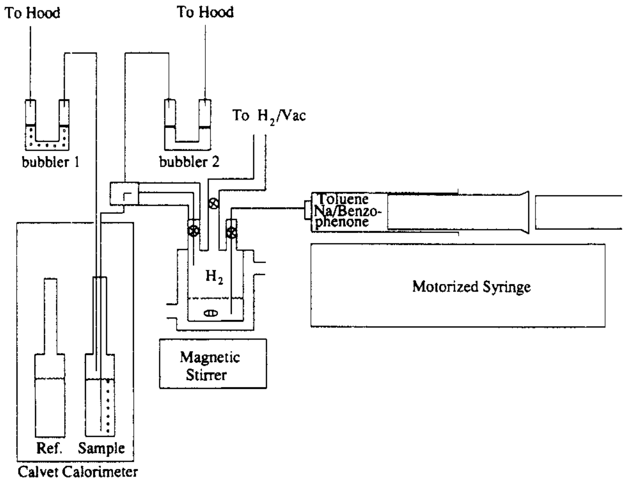


Figure 1. Schematic drawing of apparatus used to measure heats of reaction with H_2 gas.

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-

---

(1) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335. For a review, see: Blake, D. M. *Coord. Chem. Rev.* **1982**, *47*, 205.

(2) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.

(3) For leading references on the use of PAS in transition-metal chemistry, see: Yang, G. K.; Vaida, V.; Peters, K. S. *Polyhedron* **1988**, 1619.

(4) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711.

(5) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563.

(6) Jaeger, T. J.; Baird, M. C. *Organometallics* **1988**, *7*, 2074. For a review in this area, see: Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

(7) Goh, L. Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192.

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

(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.

0002-7863/90/1512-5657$02.50/0