a singlet at 7.09 ppm (2 H).

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Registry No. **1**, 100681-67-2; **2**, 87830-08-8; **6**, 796-62-3; **7**, 789-54-8; 2,4,6-*t*-$Bu_3C_6H_2OH$, 732-26-3; 2,4-*t*-Bu_2-4-MeC_6H_2OH, 128-37-0; PCl_3, 7719-12-2; $Na_2Fe(CO)_4$, 14878-31-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, H coordinates and thermal parameters, and observed and calculated structure factor tables for compound 1 (19 pages). Ordering information is given on any current masthead page.

The Determination of the Mn–Mn Bond Strength in $Mn_2(CO)_{10}$ Using Pulsed Time-Resolved Photoacoustic Calorimetry

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Summary: The enthalpy of reaction for the photodissociation of $Mn_2(CO)_{10}$ in several solvents has been measured by pulsed time-resolved photoacoustic calorimetry. Using known quantum yield measurements for Mn–Mn homolysis and Mn–CO ligand dissociation, the Mn–Mn bond strength is determined to be 38.0 ± 5 kcal/mol.

Crucial to the development of metal cluster chemistry is a knowledge of the metal–metal and metal–ligand bond strengths in at least a few transition-metal cluster complexes. The difficulties in obtaining such information are illustrated with the example of the metal–metal bond strength in $Mn_2(CO)_{10}$, the first unsupported metal bond to be characterized.[1] The dissociation energy for the metal–metal bond has been obtained from thermochemical measurements (16 kcal/mol,[2] 22.5 kcal/mol,[3] and 34 ± 13 kcal/mol[4]), electron-impact mass spectroscopic data[5–9] (values ranging from 19 to 28 kcal/mol), kinetic measurements in solution[10–12] (36.8 kcal/mol), and recently a combination of ICR and photoelectron spectroscopy[13] (41 ± 9 kcal/mol$^-$). This disturbing scatter of values points to the difficulty of obtaining specific bond energies in transition-metal complexes.

The metal–ligand bond dissociation energy in $Mn(CO)_5L$ complexes has been investigated,[3,14] but the absolute Mn–L bond energies are based on the value estimated from *D*(Mn–Mn) in $Mn_2(CO)_{10}$ and are, therefore, themselves only as reliable as this estimate.

Scheme I

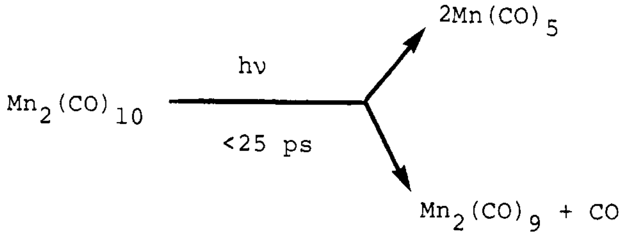

Table I. Enthalpies of Reaction in Various Solvents[a]

solv	ΔH_r,[b] kcal/mol
hexane (C_6H_{14})	14.0
cyclohexane (C_6H_{12})	13.6
THF	11.9
acetonitrile (CH_3CN)	11.5

[a] Photolysis of $Mn_2(CO)_{10}$ solutions (OD < 0.4) at room temperature with 337-nm excitation. [b] Errors are ±1.0 kcal/mol.

In this communication, we report an estimate of the *D*(Mn–Mn) in $Mn_2(CO)_{10}$ in solution obtained by using pulsed time-resolved photoacoustic calorimetry. This is a method whereby reaction enthalpies for ground-state reactants forming stable or transient photoproducts are measured. In this experiment, a fraction of the energy absorbed by the sample from an incident light beam is ultimately released as heat. Local thermal expansion generates pressure waves which can be detected by a transducer. An in-depth analysis of the theory and experiment has been reported.[15]

Quantitative interpretation of the heat deposition measured in this experiment requires a knowledge of the mechanism and kinetics of the photochemical reaction under study. Fortunately, the photochemistry of $Mn_2(CO)_{10}$ is one of the best studied among transition-metal cluster carbonyls.[16] Kinetic experiments in several laboratories[17–19] are consistent with the mechanism outlined in Scheme I. Picosecond flash photolysis experiments performed in our laboratory[17] showed that photolysis of $Mn_2(CO)_{10}$ leads to the formation of $Mn(CO)_5$ and $Mn_2(CO)_9$ within 25 ps of excitation. Quantum yield measurements for the dissociation of $Mn_2(CO)_{10}$ are available, yet the literature values are varied.

In the study reported herein, the enthalpy of reactions ΔH_r of the above photoprocess were measured[20,21] in a variety of solvents at room temperature and are listed in Table I. Simply, ΔH_r is determined by comparison of the integrated photoacoustic waveform obtained from photolysis of $Mn_2(CO)_{10}$ to that obtained from photolysis of a standard, i.e., ferrocene, with known photophysical and

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[1] Dahl, L. F.; Ishishi, E.; Rundle, R. E. *J. Chem. Phys.* **1957**, *26*, 1750.

[2] Connor, J. A. "Transition Metal Clusters"; Johnson, B., Ed.; Wiley: New York, 1900; Chapter 5.

[3] Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

[4] Cotton, F. A.; Monchamp, R. R. *J. Chem. Soc.* **1960**, 533.

[5] Bidinosti, D. R.; McIntyre, N. S. *J. Chem. Soc., Chem. Commun.* **1966**, 555.

[6] Bidinosti, D. R.; McIntyre, N. S. *Can. J. Chem.* **1970**, *48*, 593.

[7] Svec, H. J.; Junk, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 2836.

[8] Svec, H. J.; Junk, G. H. *Inorg. Chem.* **1967**, *7*, 1688.

[9] Junk, G. H.; Svec, J. H. *J. Chem. Soc. A* **1970**, 2102.

[10] Hopgood, D.; Poe, A. J. *J. Chem. Soc., Chem. Commun.* **1966**, 831.

[11] Poe, A. J. *ACS Symp. Ser.* **1981**, *No. 155*, 135.

[12] Marcomini, A.; Poe, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6952.

[13] Martinho Simoes, J. A.; Schultz, J. C.; Beauchamp, J. L. *Organometallics*, in press.

[14] Stevens, A. E. Ph.D. Thesis, California Institute of Technology, 1981.

[15] (a) Rothberg, L. J.; Simon, J.; Bernstein, M.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 3464. (b) Rudzki, J.; Goodman, J. L.; Peters, K. *J. Am. Chem. Soc.* **1985**, *107*, 7849.

[16] (a) Hughey, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49. (b) Smith, G. P., private communicaton.

[17] Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536.

[18] Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249.

[19] Meyer, T. J. *Chem. Rev.*, in press, and references therein.

[20] Freshly sublimed $Mn_2(CO)_{10}$ was dissolved in deoxygenated spectrograde solvents. Samples were degassed with argon for 10 min and then maintained under an argon atmosphere during the experiment. Photolysis was initiated by a nitrogen laser (5 ns, 337 nm, ≤20 μJ, 2-mm diameter). Sample absorbances did not change during photolysis, suggesting that no decomposition occurred at these low fluence levels.

[21] On the time scale of the laser experiment (≃1 μs), both recombination processes, $2Mn(CO)_5 \rightarrow Mn_2(CO)_{10}$ and $Mn_2(CO)_9 + CO \rightarrow Mn(CO)_{10}$, are slow and consequently do not contribute to the overall enthalpy of reaction.[18,25]

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photochemical properties. The enthalpy of reaction can be related to D(Mn–Mn) by

$$\Delta H_r = \phi_{-M}[D(\mathrm{Mn{-}Mn}) + 2\Delta H_{\mathrm{coord}}(\mathrm{Mn(CO)_5})] + \phi_{-\mathrm{CO}}[D(\mathrm{Mn{-}CO}) + \Delta H_{\mathrm{coord}}(\mathrm{Mn_2(CO)_9})]$$

where ϕ_{-M} is the quantum yield for Mn–Mn bond cleavage, ϕ_{-CO} is the quantum yield for Mn–CO bond cleavage, D(Mn–CO) is the bond enthalpy of the Mn–CO bond, D(Mn–Mn) is the enthalpy of the metal–metal bond, $\Delta H_{coord}(Mn(CO)_5)$ is the coordination energy of the Mn(CO)$_5$ fragment, and $\Delta H_{coord}(Mn_2(CO)_9)$ is the coordination energy of the $Mn_2(CO)_9$ fragment. Recent reports place the Mn–CO bond enthalpy at 36 ± 2 kcal/mol.[16]

As the present experiments are performed in solution, the enthalpy of coordination to the solvent of the photoproducts must be considered. Reliable estimates for these values are not available. For the solvents employed, $\Delta H_{coord}(Mn(CO)_5)$ is expected to be small and therefore should contribute little to the overall enthalpy of reaction. However, $\Delta H_{coord}[Mn_2(CO)_9]$ should be more substantial, perhaps ranging from 5 to 25 kcal/mol. However, the small quantum yield, 0.1, for CO dissociation[22,24] suggests that the contribution to ΔH_r from the ligand loss pathway, $\phi_{-CO}[D(Mn–CO) + \Delta H_{coord}Mn_2(CO)_9]$ leads to values ranging from 1.1 to 3.1 kcal/mol. This conclusion is supported by the small range in ΔH_r values observed for both weakly and strongly coordinating solvents.

With use of the enthalpies of reaction reported herein, the literature quantum yields,[22] a value of 36 kcal/mol for D(Mn–CO), and a range of 5–15 kcal/mol for ΔH_{coord}-$[Mn_2(CO)_9]$ in hexane, the value obtained for D(Mn–Mn) is 38.0 ± 5 kcal/mol in hydrocarbon solvents. The indicated errors is D(Mn–Mn) come only from the precision of the ΔH_r measurement and do not reflect errors in other values used in the calculation.

The determination of the D(Mn–Mn) is dependent on accurate photochemical quantum yields. The quantum yields of 0.3 and 0.1 for the homolysis and ligand loss, respectively, yield a reasonable value for D(Mn–Mn).[22-24] Total quantum yield measurements reporting a higher value[26] are inconsistent with our results. Were the total quantum yield greater than 0.6, values of less than 20 kcal/mol would be calculated for D(Mn–Mn) from our measurements. Such a low value for the metal bond dissociation energy is inconsistent with chemical evidence,[27] and we therefore favor the lower literature values.

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Registry No. $Mn_2(CO)_{10}$, 10170-69-1; CO, 630-08-0; Mn, 7439-96-5.

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(22) The quantum yields for photodissociation,[23] ϕ_{-M} = 0.3, and the quantum yields for decarbonylation,[24] ϕ_{-CO} = 0.1, have been determined in a number of solvents. The yields appear relatively insensitive to solvent, and consequently the values chosen are average values.

(23) (a) Fox, A.; Poe, A. *J. Am. Chem. Soc.* **1980**, *102*, 2498. (b) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1974**, *97*, 2065. (c) Hallock, S. A.; Wojcicki, A. *J. Organomet. Chem.* **1979**, *182*, 521.

(24) (a) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (b) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q.; Pitts, R. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1189.

(25) Church, S. P.; Hermann, H.; Grevels, F. H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

(26) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095.

(27) Covill, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2499.

Stereospecific Synthesis of the *B*-(*Z*)-1-Alkenyl-9-borabicyclo[3.3.1]nonanes Not Available via Hydroboration

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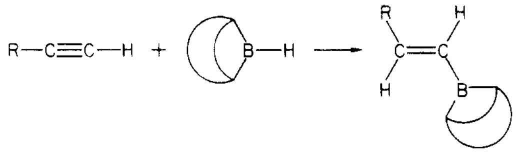
Summary: The reaction of (*Z*)-1-lithio-1-alkenes with *B*-methoxy-9-borabicyclo[3.3.1]nonane proceeds to form lithium (*Z*)-1-alkenyl-*B*-methoxy-9-borabicyclo[3.3.1]nonanes. Treatment of the "ate" complexes with boron trifluoride–diethyl etherate affords the unknown *B*-(*Z*)-1-alkenyl-9-borabicyclo[3.3.1]nonanes in good yields. These undergo smooth reaction with benzaldehyde and methyl vinyl ketone, providing the corresponding allylic alcohols and 4-alkenyl-2-butanones, respectively, with the corresponding stereochemistry.

The *B*-(*E*)-1-alkenyl-9-borabicyclo[3.3.1]nonanes (*B*-(*E*)-1-alkenyl-9-BBN) exhibit exceptional stereospecific reactivity, not exhibited by other boron derivatives.[2] These *B*-(*E*)-1-alkenyl-9-BBN reagents are readily prepared via the regio- and stereospecific monohydroboration of 1-alkynes with 9-BBN in high yields (eq 1).[3] Unfortunately, the lack of a convenient procedure for the clean preparation of the corresponding stereoisomeric *B*-(*Z*)-1-alkenyl-9-BBN derivatives has severely limited the general application of syntheses based on these derivatives.



(1)

In the past, two routes have been investigated for the stereospecific synthesis of the *B*-(*Z*)-1-alkenyl-9-BBN reagents. The first effort involves hydroboration of 1-halo-1-alkynes with 9-BBN, followed by treatment with *tert*-butyllithium.[4] Unfortunately, this procedure afforded a mixture of two products due to indiscriminate migration of both the hydride and the cyclooctyl ring.

In the second effort, the controlled catalytic hydrogenation of *B*-1-alkynyl-9-BBN reagents under a variety of experimental conditions resulted in a complex mixture of products containing the desired alkenylborane in <50% yields.[5]

In view of the fact that alkyl-[6] and *B*-1-alkynyl-9-BBN[7] reagents are readily prepared via reaction of the corresponding lithium reagents with *B*-methoxy-9-BBN, it seemed possible that a similar reaction using (*Z*)-1-

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(2) (a) Jacob, P., III; Brown, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 7832. (b) *J. Org. Chem.* **1977**, *42*, 579. (c) Brown, H. C.; Molander, G. A. *Ibid.* **1981**, *46*, 645. (d) Molander, G. A.; Singaram, B.; Brown, H. C. *Ibid.* **1984**, *49*, 5024.

(3) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96.

(4) Campbell, J. B., Jr.; Molander, G. A. *J. Organomet. Chem.* **1978**, *156*, 71.

(5) Molander, G. A. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1979.

(6) Kramer, G. W.; Brown, H. C. *J. Oganomet. Chem.* **1974**, *73*, 1.

(7) Brown, H. C.; Sinclair, J. A. *J. Organomet. Chem.* **1977**, *131*, 163.

0276-7333/86/2305-0816$01.50/0