9.4 Hz), 3.33 (1 H, s), 3.15 (1 H, dd, $J = 9.4$ and 4.4 Hz), 2.94–3.12 (2 H, m), 3.33–2.67 (3 H, m), 1.70–1.92 (1 H, m), 1.10–1.72 (8 H, m). MS calcd for $C_{22}H_{24}N_2O_4$ *m/e* 380.1736; found *m/e* 380.1737. It was identical in all respects except rotation and melting point with a sample of (−)-kopsine, which was kindly supplied by Prof. Manfred Hesse (Zurich).

Treatment of the α-Chloro Acid 19 with AgOAc. A suspension of **19**[8] (49 mg, 0.09 mmol) and AgOAc (50 mg, 0.3 mmol) in nitromethane (4 mL) was stirred at 25 °C in the dark for 24 h. The mixture was partitioned between dichloromethane (10 mL)/water (10 mL), and the organic layer was separated and dried (Na_2SO_4). The products were separated by PLC, eluting with EtOAc/CH_2Cl_2 (3:1) to give **23** (9.1 mg, 19%) and **24** (5 mg, 10%). The base-line material was treated with diazomethane in ether/THF (3 mL, 1:1) to give two compounds, which were separated by PLC, eluting with EtOAc/CH_2Cl_2 (1:3) to give the cyclobutane derivative **22** (11.4 mg, 25%) and the α,β-unsaturated ester **21** (9.1 mg, 20%). **22** was recrystallized from $CHCl_3$/pentane to give colorless cubes, mp 250–252 °C (dec) suitable for single-crystal X-ray structure determination. IR (CH_2Cl_2) 2920, 1730, 1694, 1599, and 1150 cm^{-1}. ^1H NMR δ 8.10 (2 H, d, $J = 9$ Hz), 6.82–7.16 (4 H, m), 6.99 (2 H, d, $J = 9$ Hz), 4.12–4.22 (1 H, m), 3.86 (3 H, s), 3.78 (1 H, s), 3.75 (3 H, s), 3.55 (1 H, s), 2.97 (1 H, dt, $J = 13$ and 4 Hz), 2.66–2.82 (1 H, m), 2.35 (1 H, d, $J = 13.9$ Hz), 2.17 (1 H, dd, $J = 13.9$ and 3 Hz), 1.83–2.02 (1 H, m), 1.1–1.8 (6 H, m). **23**: IR (CH_2Cl_2) 3540, 2940, 1680, and 1600 cm^{-1}. ^1H NMR δ 7.9 (2 H, d, $J = 9$ Hz), 7.1–7.2 (2 H, m), 6.94–7.02 (1 H, m), 6.92 (2 H, d, $J = 9$ Hz), 4.33 (1 H, s), 4.18–4.26 (1 H, m), 3.83 (3 H, s), 3.59 (1 H, s), 3.15 (1 H, d, $J = 17$ Hz), 2.88–2.98 (1 H, m), 2.60–2.76 (1 H, m), 2.28 (1 H, m), 1.85 (1 H, d, $J = 17$ Hz), 1.0–2.0 (10 H, m). MS calcd for $C_{26}H_{28}N_2O_5S$ *m/e* 480.1719; found *m/e* (EI) 480.1706. **24** IR (CH_2Cl_2) 2940 (m), 1750 (m), 1680 (s), and 1594 (m) cm^{-1}. ^1H NMR 7.84 (2 H, d, $J = 9$ Hz), 7.49 (1 H, d, $J = 8$ Hz), 6.96–7.21 (3 H, m), 6.86 (2 H, d, $J = 9$ Hz), 4.10–4.20 (1 H, m), 3.83 (3 H, s), 3.59–3.63 (1 H, m), 3.55 (1 H, s), 3.22 (1 H, d, $J = 17.8$ Hz), 2.61–2.78 (1 H, m), 1.98–2.12 (2 H, m), 1.77 (3 H, s), 1.67 (3 H, s), 1.1–1.9 (4 H, m). MS (EI *m/e* 463 (67), 292 (98), 171 (100).

Acknowledgment. The National Institutes of Health (GM 32718) are gratefully thanked for their financial support. Drs. James Schultz and Rudolf Waditschatka are thanked for their contributions to earlier efforts in this research. Dr. John Huffman is thanked for the single-crystal X-ray crystallographic structure determination of **22**.[11] Professor Manfred Hesse is thanked for the authentic sample of (−)-kopsine (**1**).

Supplementary Material Available: Crystal data, fractional coordinates, isotropic thermal parameters, anisotropic thermal parameters, bond distances, and bond angles for **22** (10 pages). Ordering information is given on any current masthead page.

Solution Homolytic Bond Dissociation Energies of Organotransition-Metal Hydrides

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Received August 4, 1988.
Revised Manuscript Received April 8, 1989

Abstract: The homolytic bond dissocation energies (BDEs) of the mononuclear metal carbonyl hydride complexes ($(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W), $(\eta^5\text{-}C_5Me_5)Mo(CO)_3H$, $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H$, $(\eta^5\text{-}C_5H_5)M(CO)_2H$ (M = Fe, Ru), $H_2Fe(CO)_4$, $Mn(CO)_4PPh_3H$, $Mn(CO)_5H$, $Re(CO)_5H$, and $Co(CO)_3LH$ (L = CO, PPh_3, $P(OPh)_3$) have been estimated in acetonitrile solution by the use of a thermochemical cycle that requires knowledge of the metal hydride pK_a and the oxidation potential of its conjugate base (anion). The BDE values obtained by this method fall in the range 50–67 kcal/mol. In most cases, these results agree well with literature data. Our data provide strong support for the common assumption that the M–H bond energies are greater for third-row and for second-row metals than for first-row metals, the difference being 5–11 kcal/mol. Effects of neither phosphine or phosphite substitution nor permethylation of the cyclopentadienyl ring on the M–H bond energies could be detected within the error limits of the method. The results are discussed in relation to previous M–H BDE estimates and metal hydride reactivity patterns.

Organotransition-metal hydride (M–H) complexes constitute an important class of compounds and have received considerable attention particularly because of their involvement in many stoichiometric and catalytic processes.[2] It is clear that the M–H bond strengths exert a major influence on the properties of metal hydride compounds, and a detailed knowledge of the factors that determine the M–H bond strengths would greatly aid in understanding reactivity patterns in many processes.[3] For example, the activation of alkane carbon–hydrogen bonds by coordinatively unsaturated transition-metal complexes is a process that is being vigorously pursued.[4] The formation of M–H and M–C bonds provides the driving force for such reactions, and the sum of the M–H and M–C bond dissociation energies must be on the order of 110 kcal/mol for the reaction to be thermodynamically feasible.[5]

Scheme I

	energy change	
$L_nM\text{-}H \rightarrow L_nM^{\bullet} + H^{\bullet}$	BDE	(1)
$L_nM\text{-}H \rightarrow L_nM^{-} + H^{+}$	$BDE - EA(L_nM^{\bullet}) + IP(H^{\bullet})$	(2)
$L_nM\text{-}H \rightarrow L_nM^{+} + H^{-}$	$BDE + IP(L_nM^{\bullet}) - EA(H^{\bullet})$	(3)

Three modes of cleavage of M–H bonds have been envisaged, as shown in Scheme I.[2a] The first reaction is a homolytic cleavage reaction for which the energy change is given by the homolytic bond dissociation energy (BDE) of the M–H bond. In reaction

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Scheme II

$$\begin{array}{llll}
 & & \Delta G^\circ & \\
\text{M-H(sol)} & \rightarrow \text{M}^-\text{(sol)} + \text{H}^+\text{(sol)} & 2.301RT\text{p}K_a & (4) \\
\text{M}^-\text{(sol)} & \rightarrow \text{M}^\bullet\text{(sol)} + e^- & FE^\circ_{\text{ox}}(\text{M}^-) & (5) \\
\text{H}^+\text{(sol)} & \rightarrow \text{H}^+\text{(aq)} & -\Delta G^\circ_{\text{tr}}(\text{H}^+) & (6) \\
\text{H}^+\text{(aq)} + e^- & \rightarrow 0.5\text{H}_2\text{(g)} & 0 & (7) \\
0.5\text{H}_2\text{(g)} & \rightarrow \text{H}^\bullet\text{(g)} & \Delta G^\circ_f(\text{H}^\bullet)_g & (8) \\
\text{H}^\bullet\text{(g)} & \rightarrow \text{H}^\bullet\text{(sol)} & \Delta G^\circ_{\text{sol}}(\text{H}^\bullet) & (9) \\
\text{M-H(sol)} & \rightarrow \text{M}^\bullet\text{(sol)} + \text{H}^\bullet\text{(sol)} & \text{BDE} & (10)
\end{array}$$

$$\text{BDE} = 2.301RT\text{p}K_a + FE^\circ_{\text{ox}}(\text{M}^-) - \Delta G^\circ_{\text{tr}}(\text{H}^+) + \Delta G^\circ_f(\text{H}^\bullet)_g + \Delta G^\circ_{\text{sol}}(\text{H}^\bullet) \quad (11)$$

2, the hydrogen is removed as a proton, and in solution the free-energy change of this reaction may be extracted from Brønsted acidity (pK_a) data when such are available. In reaction 3, the hydrogen is removed as a hydride ion. The energetics of reactions 2 and 3 furthermore are linked to the BDEs through the electron affinities (EAs) and ionization potentials (IPs) of $L_nM^\bullet$ and $H^\bullet$, as is also shown in Scheme I.

A considerable amount of Brønsted acidity data is available for a variety of metal hydrides,[2a,6] and such data have been used to distinguish between proton-transfer mechanisms and other viable alternatives in reactions of metal hydrides.[7] It is also of considerable importance to have quantitative information about solution homolytic bond dissociation energies of M-H bonds, eq 1. Such data are notably scarce.[8] A few estimates have appeared, and it is commonly believed that metals in the third and second transition series form stronger bonds to hydrogen than members of the first series.[2a,b] Calorimetric data for group 6 metal hydrides (Cr, Mo, W) support this view.[9] Some other circumstantial evidence, based on chemical reactivity, is also available in support of this notion.[2a,b,7b,10]

The scarcity of M-H BDE data may be attributed to the lack of generally suitable methods for their measurement. Calorimetric methodology has been applied in some instances, but frequently these methods depend on the use of metal-metal BDE estimates, which may be controversial themselves (for example, estimates of the Mn-Mn BDE in $Mn_2(CO)_{10}$ varies from 18.9 to 36.8 kcal/mol[11]), before M-H bond energies can be extracted.[9,11] Kinetic methods are useful for quantitative estimates only if decomposition proceeds by means of a homolytic cleavage pathway. However, other pathways may often be energetically more favorable. In order to avoid these complications, a different and widely applicable method, based on thermodynamic quantities, for the evaluation of M-H bond energies would be desirable.

In this paper, we report a number of M-H BDEs in acetonitrile solution, estimated by using a thermochemical cycle that requires knowledge of the M-H Brønsted acidity and the reversible oxidation potential of the corresponding M^- anion. The method is widely applicable and results in BDE values within about 1 kcal/mol of the most reliable literature values available.

Results and Discussion

Method. The method we use to estimate M-H BDEs involves a thermochemical cycle analogous to that employed recently by Bordwell[12] (after a modification of the cycle presented by Nicholas and Arnold[13]) for various C-H, O-H, and N-H BDEs in DMSO solution (Scheme II). The use of the method is not limited to DMSO, and for our study, we chose acetonitrile because this solvent is more commonly used in experimental organometallic chemistry and because a wide range of M-H pK_a values have been measured in acetonitrile.[6] Here, pK_a is the Brønsted acidity of the metal hydride in solution. $E^\circ_{\text{ox}}(\text{M}^-)$ is the reversible potential for the oxidation of the M^- anion versus the *hydrogen electrode in acetonitrile*. In order to refer the electrode potentials to the *standard hydrogen electrode* (SHE), the free energy of transfer of the proton from water to acetonitrile, $\Delta G^\circ_{\text{tr}}(\text{H}^+)$, is subtracted. For consistency, we have used values for these constants from a single source.[14]

The value for $\Delta G^\circ_{\text{sol}}(\text{H}^\bullet)$, the free energy of solvation of the hydrogen atom, is assumed to be equal to that of the hydrogen molecule,[15] found to be +5.12 kcal/mol based on reported ΔH° and ΔS° values.[17] A value for $\Delta G^\circ_f(\text{H}^\bullet)_g$ is taken as 48.58 kcal/mol.[18] With these constants, eq 11 leads to eq 12 for the

$$\text{BDE}_G = 1.37\text{p}K_a + 23.06E^\circ_{\text{ox}}(\text{M}^-) + 45.6 \quad (12)$$

calculation of BDE_G values (kcal/mol) at 298.15 K, where the subscript signifies that the values are free-energy BDEs. In order to enable comparison with values obtained by calorimetry and other methods, an entropy contribution, $T\Delta S^\circ$, must be included to convert to ΔH. The overall entropy change for the M-H bond homolysis is given by eq 13. Making the reasonable assumption that $S^\circ(\text{M-H})_{\text{sol}} = S^\circ(\text{M}^\bullet)_{\text{sol}}$,[19] the entropy change is given by eq 14 where $\Delta S^\circ_{\text{sol}}(\text{H}^\bullet)$ is the entropy of solvation of the hydrogen

$$\Delta S^\circ_{\text{hom}} = S^\circ(\text{M}^\bullet)_{\text{sol}} + S^\circ(\text{H}^\bullet)_{\text{sol}} - S^\circ(\text{M-H})_{\text{sol}} \quad (13)$$

$$\Delta S^\circ_{\text{hom}} = S^\circ(\text{H}^\bullet)_{\text{sol}} = S^\circ(\text{H}^\bullet)_g + \Delta S^\circ_{\text{sol}}(\text{H}^\bullet) \quad (14)$$

atom in acetonitrile, assumed to be equal to the entropy of solvation of the hydrogen molecule,[15] −11.9 eu.[17] Taking the entropy of formation of the hydrogen atom in the gas phase to be 27.4 eu,[18] $\Delta S^\circ_{\text{hom}} = 15.5$ eu and the total $T\Delta S^\circ$ contribution to the BDE equals 4.62 kcal/mol. Equation 15 gives the final expression that

$$\text{BDE} = 1.37\text{p}K_a + 23.06E^\circ_{\text{ox}}(\text{M}^-) + 50.3 \quad (15)$$

will provide the enthalpy-based BDEs. Once again, $E^\circ_{\text{ox}}(\text{M}^-)$ is the electrode potential referring to that of the hydrogen electrode in acetonitrile. Assumptions and approximations that give rise to the constant term, 50.3, in eq 15 have recently been applied by others.[12,20] We regard the most serious approximations to be those regarding the solvation energies of $H^\bullet$ and H^+ in acetonitrile. For example, the free energy of transfer of the proton from water to acetonitrile may be quite different from the corresponding value for transfer to acetonitrile/0.1 M Bu_4NPF_6, the medium used for

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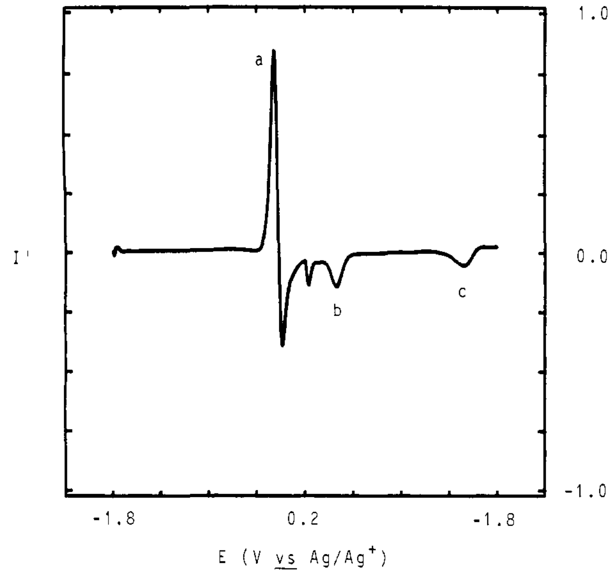

Figure 1. Derivative cyclic voltammogram of $PPN^+Mn(CO)_5^-$ (1.0 mM) in acetonitrile/$Bu_4N^+PF_6^-$ (0.1 M) at a Pt microelectrode (d = 0.4 mm) at 25 °C and a sweep rate, ν, of 1.0 V/s.

the electrochemical measurements. Furthermore, solvation properties of the electronically unsaturated $H^•$ atom may not be accurately described by the properties of the closed-shell H_2 molecule.

Electrochemical Measurements. The measurement of the oxidation potentials for the M^- anions were carried out either on the PPN^+ (PPN^+ = bis(triphenylphosphine)iminium, $(Ph_3P)_2N^+$) salts of the anions (M = $(\eta^5\text{-}C_5H_5)Cr(CO)_3$, $(\eta^5\text{-}C_5H_5)Mo(CO)_3$, $(\eta^5\text{-}C_5H_5)W(CO)_3$, $Mn(CO)_5$, $Mn(CO)_4PPh_3$, $Re(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, $HFe(CO)_4$, $Co(CO)_4$, $Co(CO)_3PPh_3$, $Co(CO)_3P(OPh)_3$) or on anions generated in situ from the bromide $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)Br$ or from the metal–metal bonded dimers M_2 (M = $(\eta^5\text{-}C_5Me_5)Mo(CO)_3$, $(\eta^5\text{-}C_5H_5)Ru(CO)_2$) by keeping the electrode rest potential negative enough to cause reduction of these precursors. The latter method was applied to the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W) and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ complexes as well, and the results were indistinguishable within experimental error from those obtained with the PPN^+ salts. Attempts to measure the oxidation potential of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2^-$ by either method were unsuccessful. Only a broad, featureless cyclic voltammetry wave from which no reliable data could be extracted was observed. This problem may be due to adsorption or to possible instability of the anion in the acetonitrile/0.1 M $Bu_4^+NPF_6^-$ medium that was used. The $(\eta^5\text{-}C_5Me_5)Fe(CO)_2^-$ anion may be expected to be more reactive (as a base or as a nucleophile) than the less electron rich but still strongly nucleophilic[24] $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ anion. The latter, as the PPN^+ salt, was found to undergo about 40–50% decomposition during the course of 10–15 min when dissolved in the electrolyte, as observed by a gradual decrease in the oxidation peak intensity in the cyclic voltammograms. No efforts were made at identifying the products of this decomposition.

Table I. Metal Anion Oxidation Potentials, Metal Radical Recombination Rate Constants, and Calculated Kinetic Potential Shifts

compound	$E_{ox}(M^-)^{a}$	$k_{dim}{}^{b}$	$E_{corr}{}^{c}$
$(\eta^5\text{-}C_5H_5)Cr(CO)_3^-$	-0.688^{d}		0.000
$(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$	−0.501	$3 \times 10^{9\,e}$	0.116
$(\eta^5\text{-}C_5Me_5)Mo(CO)_3^-$	-0.709^{f}	$1 \times 10^{9\,g}$	0.106
$(\eta^5\text{-}C_5H_5)W(CO)_3^-$	−0.491	$1.9 \times 10^{9\,h}$	0.112
$(\eta^5\text{-}C_5H_5)W(CO)_2PMe_3^-$	−1.225	$1 \times 10^{9\,g}$	0.106
$(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$	−1.352	$3.2 \times 10^{9\,i}$	0.117
$(\eta^5\text{-}C_5H_5)Ru(CO)_2^-$	−1.057	$3 \times 10^{9\,j}$	0.116
$Mn(CO)_5^-$	−0.555	$9.5 \times 10^{8\,k}$	0.106
$Mn(CO)_4PPh_3^-$	−0.870	$1 \times 10^{7\,l}$	0.067
$Re(CO)_5^-$	−0.690	$3.7 \times 10^{9\,k}$	0.118
$Co(CO)_4^-$	−0.271	$4.2 \times 10^{8\,m}$	0.099
$Co(CO)_3P(OPh)_3^-$	−0.489	$9 \times 10^{7\,n}$	0.086
$Co(CO)_3PPh_3^-$	−0.723	$1 \times 10^{7\,o}$	0.067
$HFe(CO)_4^-$	−0.403	$4 \times 10^{8\,p}$	0.099

[a] V versus ferrocene/ferricinium in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at 298 K and a voltage sweep rate, ν, of 1.00 V/s. $E_{ox}(M^-)$ values were determined as described in the text versus a Ag/Ag^+ reference electrode and subsequently converted to the ferrocene/ferricinium scale. Oxidation processes were chemically irreversible unless otherwise noted. [b] Rate constants ($M^{-1}\ s^{-1}$) for the dimerization of $M^•$ radicals in solution. [c] Kinetic potential shift to be added to $E_{ox}(M^-)$ in order to obtain the reversible electrode potential. Calculated according to ref 23. [d] Reversible process. [e] Acetonitrile, 293 K.[29] [f] Measured in dichloromethane (see Experimental Section). The difference in oxidation potentials between $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ and $(\eta^5\text{-}C_5Me_5)Mo(CO)_3^-$ is assumed to be the same in acetonitrile as in dichloromethane (0.208 V). [g] The value for k_{dim} is based on the reported 5×10^8–$5 \times 10^9\ M^{-1}\ s^{-1}$ estimate for $(\eta^5\text{-}C_5Me_5)Fe(CO)_2^•$ in cyclohexane.[62] [h] Cyclohexane, 295 K.[28] [i] Cyclohexane, 293 K.[63] [j] Not available but taken to be similar to Fe analogue. [k] n-Hexane, 295 K.[64] [l] n-Hexane, 298 K.[31b] [m] n-Hexane, 298 K.[65] [n] Value reported[65] for $Co(CO)_3P(n\text{-}Bu)_3$ in n-hexane, 298 K. See also ref 31a. [o] The relative rates within the $Co(CO)_3L$ series have been taken to be the same as within the $Mn(CO)_4L$ series; see ref 31. [p] It has been suggested that $HFe(CO)_4^•$, generated by oxidation of the anion[66a] or by photolysis of $Fe(CO)_5$ in the presence of CO and H_2 in pentane,[66b] undergoes dimerization to give unstable $H_2Fe_2(CO)_8$. The rate is here assumed to be similar to that for $Co(CO)_4^•$.

The metal anion oxidation potentials were determined by derivative cyclic voltammetry (DCV),[25] and the oxidation potentials (with the reversible ferrocene/ferricinium couple as the reference[22]) measured at 298 K and a voltage sweep rate, ν, of 1.00 V/s are listed in Table I. Figure 1 shows a DCV trace for the oxidation of $PPN^+Mn(CO)_5^-$. The cyclic voltammetry peak potential can be measured with high precision as the point where the rapidly descending DCV curve crosses the base line. The peak labeled c corresponds to the reduction of $Mn_2(CO)_{10}$,[26] verified by comparison with an authentic sample. The low ratio of the derivative peak current on the reverse scan (labeled b) relative to that for oxidation of the anion (a) indicates that the electrode-generated $Mn(CO)_5^•$ radical has a very short lifetime.[27] It is known[28] that many 17-electron organometallic radicals dimerize to form the corresponding metal–metal bonded species at rates approaching diffusion control. For example, $(\eta^5\text{-}C_5H_5)Mo(CO)_3^•$ undergoes dimerization with a rate constant of $(3 \pm 1) \times 10^9\ M^{-1}\ s^{-1}$ in acetonitrile at 293 K.[29] In THF, it was shown that the rate of dimerization was unaffected by the addition of $Bu_4N^+PF_6^-$,[29] a finding which is of importance for our electrochemical studies because $Bu_4N^+PF_6^-$ is used as the supporting electrolyte.

The presence of such rapid follow-up reactions that consume the electrode-generated species will cause a shift in the cyclic voltammetry peak potential away from the reversible potential. For an oxidation process, this shift will be in the cathodic direction.[23] For the accurate estimation of M–H BDE values, we need the reversible electrode potentials. Fortunately, when the dimerization rate constant and the bulk concentration of the

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(27) When *derivative* cyclic voltammetry is used, a small peak is to be expected during the reverse scan even in the event that the electrode-generated species undergoes "complete reaction" during the timescale of the measurement. This contrasts with the lack of a peak under these conditions during normal cyclic voltammetry experiments.

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Table II. Metal Hydride Brønsted Acidity and Bond Dissociation Data in Acetonitrile

entry	compd	$E_{ox}(M^-)$ vs $(H^+/H_2)_{AN}$	M–H pK_a[a]	M–H BDE, kcal/mol b	M–H BDE, kcal/mol lit. data
1	$(\eta^5\text{-}C_5H_5)Cr(CO)_3H$	−0.639	13.3	54	
2	$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$	−0.336	13.9	62	65 ± 6,[9] 66 ± 8,[37] 66 ± 1.5[38]
3	$(\eta^5\text{-}C_5Me_5)Mo(CO)_3H$	−0.554[d]	17.1	61	
4	$(\eta^5\text{-}C_5H_5)W(CO)_3H$	−0.330	16.1	65	80.7[9]
5	$(\eta^5\text{-}C_5H_5)W(CO)_2PMe_3H$	−1.070[d]	26.6	62	
6	$Mn(CO)_5H$	−0.400	14.1[c]	60	65,[2a] 51,[11] 63[21]
7	$Mn(CO)_4PPh_3H$	−0.754	20.4	61	
8	$Re(CO)_5H$	−0.523	21.1	67	
9	$(\eta^5\text{-}C_5H_5)Fe(CO)_2H$	−1.186	19.4	50	
10	$(\eta^5\text{-}C_5H_5)Ru(CO)_2H$	−0.892	20.2	57	
11	$Fe(CO)_4H_2$	−0.255[d]	11.4	60	<65[2a]
12	$Co(CO)_4H$	−0.123[d]	8.3	59	58[41]
13	$Co(CO)_3P(OPh)_3H$	−0.354	11.3	58	
14	$Co(CO)_3PPh_3H$	−0.607[d]	15.4	57	

[a] As reported by Norton and co-workers.[6] [b] This work. Calculated from eq 15 and data in Table I after correcting for kinetic potential shifts. [c] Kristjánsdóttir, S. S.; Norton, J. R. Unpublished work. [d] The kinetic potential shifts in these cases were based on estimated rate constants for dimerization and therefore are associated with a greater uncertainty in the estimated reversible potentials.

substrate (anion) are known, this kinetic potential shift may be calculated.[23] In the case of $(\eta^5\text{-}C_5H_5)Mo(CO)_3^\bullet$, with $c = 10^{-3}$ M and $k = 3 \times 10^9$ M^{-1} s^{-1}, the shift will be 0.116 V. It is worth noticing that an error in the estimated rate constant of a factor of 10 will only cause a 20-mV change in this correction term, corresponding to 0.5 kcal/mol in the BDE estimates. Although recombination rate constants for radicals other than $(\eta^5\text{-}C_5H_5)Mo(CO)_3^\bullet$ are not available in acetonitrile solution, data are in many cases available for other solvents. These data are used directly for the calculation of the respective potential shifts, shown in Table I. The errors that arise from doing so are expected to be small because the viscosities of the solvents that were used did not differ very much. No correction is needed for the oxidation potential of $(\eta^5\text{-}C_5H_5)Cr(CO)_3^-$ since this anion is reversibly oxidized as a consequence of the facile equilibrium between the radical and its dimer in solution.[30] For the substituted radicals $Co(CO)_3L^\bullet$ ($L = P(OPh)_3, PPh_3$), it has been necessary to make extrapolations based on recombination rates found in a series of manganese compounds.[31] The errors involved here are expected to be considerably less than an order of magnitude in k values. Reasonable estimates of dimerization rates also had to be made for the radicals $(\eta^5\text{-}C_5H_5)W(CO)_2PMe_3$ and $(\eta^5\text{-}C_5Me_5)Mo(CO)_3$.

Meyer and Pugh,[32] by the use of fast-scan (5000 V/s) cyclic voltammetry, observed reversible waves for the $Mn(CO)_5^-/Mn(CO)_5^\bullet$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-/(\eta^5\text{-}C_5H_5)Fe(CO)_2^\bullet$ couples. They reported potentials for these processes equal to −0.15 and −0.93 V versus the saturated calomel electrode (SCE). After applying the kinetic shift correction terms to our peak potentials (Table I) and converting to the SCE scale by the addition of 0.312 V, we obtain estimates for the reversible oxidation potentials for these processes of −0.137 and −0.924 V, respectively. The excellent agreement between our results and those reported[32] for the reversible potential measurements indicates that our kinetic shift corrections are appropriate.

The estimated maximum error in our electrode potentials, including that in the kinetic shift correction, is ±20 mV (0.5 kcal/mol). Most of the reported M–H pK_a estimates[6] are reported with an uncertainty of less than 0.2pK_a units (0.3 kcal/mol). Taking these uncertainties into account, our method should yield M–H BDE values with a relative accuracy of on the order of ±1 kcal/mol.

Metal–Hydrogen Bond Dissociation Energies. When combined with the known[6] acetonitrile pK_a values of the hydrides, the corrected oxidation potentials discussed above may be used in eq 15 to yield estimates of the metal–hydrogen BDEs. Table II lists the appropriate pK_a and calculated BDE values. Also included are previously reported M–H bond energies when such are available. Our BDEs range from 50 ($(\eta^5\text{-}C_5H_5)Fe(CO)_2H$) to 67 ($Re(CO)_5H$) kcal/mol, all within the 50–75 kcal/mol that have been proposed as "first approximation" values for M–H BDEs.[2a]

The data in Table II serve to confirm the notion that, for structurally similar compounds, third- and second-row metals form stronger bonds to hydrogen than first-row metals do. This appears to be the case in groups 6–8 for which we have data to compare. In group 6, entries 1 and 4 in Table II indicate that the W–H bond is stronger than the Cr–H bond by 11 kcal/mol. Group 7 metals, entries 6 and 8, differ by only 5 kcal/mol, whereas in group 8, entries 9 and 10, the difference is 7 kcal/mol between the first- and second-row members. Other values reported for third-row metals, but not included in Table II, are 73 kcal/mol for $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(C_6H_{11})H$[5] and 72 kcal/mol for $(\eta^5\text{-}C_5H_5)_2WH_2$.[33]

Based on our data, there appears to be no clear trend in M–H BDEs when passing through a row in the transition-metal series. Nor does there seem to be any correlation between BDEs and pK_a values alone or between BDEs and anion oxidation potentials. Clearly, the combined effect of the two factors must be taken into account.

It is of interest to compare the observed tendency for second- and third-row metals to form stronger M–H bonds with observations that have been made in the gas phase.[34] One might expect that relative gas-phase BDEs could differ from relative solution-phase BDEs due to differential solvation energies for first-, second-, and third-row metals. Such an effect could be of importance when comparing first- and second-row members, since these are quite different in size. For second- and third-row metals, the atomic radii are quite similar, and such an effect would therefore be expected to be of less importance when comparing second- and third-row BDE data. Interestingly, gas-phase BDE data for the ions $[M(CO)_6\text{–}H^+]$ (M = Cr, 58; Mo, 65; W, 64 kcal/mol[35])) are reasonably close to those estimated for the $(\eta^5\text{-}C_5H_5)M(CO)_3H$ series by us. In a more recent account,[36] a compilation of a number of gas-phase BDEs of "naked" $M^+\text{–}H$ ions indicates that there may not be any significant systematic differences between first- and second-row metal hydride BDEs.

Comparison with Calorimetric and Equilibrium Data. Inspection of Table II revelas that, in most cases where direct comparisons can be made, our values agree well with data obtained by other methods. This will be the focus of the discussion to follow.

Hoff and co-workers[9,37,38] have carried out direct (Cr) and indirect measurements of the heats of hydrogenation (ΔH_{hyd}) of group 6 dimers ($(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$, M = Cr, Mo, W) in the solid state (eq 16) and obtained results with exceptionally good internal consistency. The reactions were found to be slightly exothermic for M = Cr (ΔH_{hyd} = −3.3 kcal/mol) and W (−1.5 kcal/mol) but somewhat endothermic for M = Mo (+6.3 kcal/mol).[9] The M–H BDEs were extracted from these data employing eq 17, using previously measured M–M BDEs (32.5

$$(\eta^5\text{-}C_5H_5)_2M_2(CO)_6(s) + H_2(g) \rightarrow 2(\eta^5\text{-}C_5H_5)M(CO)_3H(s) \tag{16}$$

$$\Delta H_{hyd} = BDE_{M\text{-}M} + BDE_{H\text{-}H} - 2BDE_{M\text{-}H} \tag{17}$$

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[31] (a) In the $Mn(CO)_4L^\bullet$ series, relative recombination rates of 10, 9, and 1 were found for L = $P(n\text{-}Bu)_3$, $P(OPh)_3$, and PPh_3.[31b] (b) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 3748.

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[34] A recent review offers a tabulation of gas-phase measurements of M–H bond energies; see ref 4b.

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[36] Elkind, J. L.; Armentrout, P. B. *Inorg. Chem.* **1986**, *25*, 1080.

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kcal/mol for M = Mo[39] and 55.9 kcal/mol for M = W[40]).

Recent measurements of the solution monomer/dimer equilibrium of $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ indicated a Cr–Cr BDE of 14.8 kcal/mol in THF.[30b] Taking BDE_{H-H} as 104.2 kcal/mol[18] and $\Delta H_{hyd} = -3.3$ kcal, eq 17 predicts a BDE_{Cr-H} of 59.5 kcal/mol. Taking into account that the calorimetric data were obtained for the solid state and that the Cr–Cr and our Cr–H BDE estimates are solution-phase values, the agreement with our value of 54 kcal/mol is reasonably good.

The temperature dependence of the equilibrium constant for reaction 18 in *n*-heptane yielded a heat of hydrogenation, ΔH_{hyd}, of +3.2 kcal/mol.[41] Assuming a Co–Co bond strength of 14.5 kcal/mol,[42] this yielded a Co–H BDE of 59 kcal/mol. Again, an excellent agreement with our data is found.

$$Co_2(CO)_8(sol) + H_2(g) \rightleftarrows 2\ Co(CO)_4H(sol) \qquad (18)$$

Only for entry 4, $(\eta^5\text{-}C_5H_5)W(CO)_3H$, is there a significant difference between our energies and previously published M–H bond energies. Considering the successful application of our method in the corresponding Cr and Mo and other systems, we feel that this difference may indicate that the literature value is too high, possibly reflecting an overestimation of the W–W bond strength in the dimer (55.9 kcal/mol, obtained by mass spectrometry[40]). However, the discrepancy may also reflect the lack of solvation effects in the gas phase.

Substituent Effects on Metal–Hydrogen Bond Energies. It is of great importance to understand the effects that substituent changes will have on the M–H bond energies in structurally related complexes. We set out to determine the effects of CO substitution and permethylation of the cyclopentadienyl ring system in this respect.

Reliable acidity data in acetonitrile are available for complexes $(\eta^5\text{-}C_5H_5)W(CO_2)LH$ (L = CO, PMe_3), $Mn(CO)_4L$ (L = CO, PPh_3), and $Co(CO)_3LH$ (L = CO, $P(OPh)_3$, PPh_3).[6] We have observed that the substituted hydrido species are kinetically more stable toward air oxidation than the unsubstituted ones, both in solution and in the solid state. Our bond energy data (Table II) suggest that this stabilization is not due to a thermodynamic stabilization of the W–H, Mn–H, and Co–H bonds upon CO substitution.

It has been proposed that phosphine substitution might stabilize metal hydrides due to electronic factors but that this effect could be counteracted by the steric demands of the phosphine ligand and possibly by stabilization of the radical formed by hydrogen atom loss, the overall effect being that M–H BDEs would be quite insensitive to phosphine substitution.[7a] This analysis was used to explain why the rate of addition of M–H bonds across the vinylidene carbon–carbon double bond of $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2\text{-}(\mu\text{-}C{=}CH_2)$, a reaction believed to take place via initial hydrogen atom transfer,[7a] was only moderately influenced by ligand substitution at M: With compounds $(\eta^5\text{-}C_5H_5)Mo(CO)_2LH$ as hydrogen atom donors, the relative rates were found to be 13, 6.4, and 0.8 for L = CO, PMe_3, and PPh_3. We detect no effect of phosphine or phosphite substitution on M–H BDEs within experimental error.

Halpern and co-workers[43] in one case have observed spontaneous H$^\bullet$ transfer from $Mn(CO)_5H$ to $Mn(CO)_4LH$ (where L = $(p\text{-}CH_3OC_6H_4)_3P$), even though the reaction is not significantly exothermic, as will be explained in the following. In this study, $Mn(CO)_5^\bullet$ and $Mn(CO)_4L^\bullet$ were generated in a stoichiometric ratio of 1:1 (pseudo-first-order rate constant $k = 5.4 \times 10^{-4}\ s^{-1}$ at 75 °C) in the presence of a large excess of $Mn(CO)_5H$. Scheme III depicts the reactions that are of importance when describing the fate of these radicals.

Reaction 19 would be expected to be reversible under the reaction conditions,[44] the two Mn–H bond energies being similar; it does not matter here which one is the stronger. Reaction 20 will also be reversible, with k_{20} approaching the diffusion-controlled limit and k_{-20} being 0.16 s^{-1} using published activation parameters for the cleavage of the Mn–Mn bond in $Mn_2(CO)_8L_2$.[45] Reaction 21, the forward reaction approaching diffusion control and k_{-21} being measured to be $4.1 \times 10^{-5}\ s^{-1}$,[43] is essentially irreversible under the reaction conditions, and it was concluded[43] that $Mn_2(CO)_9L$ was not a major contributor to the generation of $Mn(CO)_4LH$. Since reaction 21 removes equal amounts of $Mn(CO)_5^\bullet$ and $Mn(CO)_4L^\bullet$ radicals from the system, it does not affect the $Mn(CO)_4LH/Mn(CO)_5H$ balance. The crucial point now is that reaction 22 serves to *irreversibly remove* $Mn(CO)_5^\bullet$ from the system (the reverse reaction will have a rate constant of $4.3 \times 10^{-7}\ s^{-1}$ by extrapolation, using activation parameters obtained from measurements at higher temperatures[46]). Each time $Mn_2(CO)_{10}$ is formed, in order to maintain the metal hydride mass balance in the system, one molecule of $Mn(CO)_4LH$ must be formed—and it does not matter whether the Mn–H BDE in $Mn(CO)_4LH$ is weaker or stronger than that of $Mn(CO)_5H$!

Scheme III

$$Mn(CO)_5H + Mn(CO)_4L^\bullet \underset{k_{-19}}{\overset{k_{19}}{\rightleftharpoons}} Mn(CO)_5^\bullet + Mn(CO)_4LH \qquad (19)$$

$$2Mn(CO)_4L^\bullet \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} Mn_2(CO)_8L_2 \qquad (20)$$

$$Mn(CO)_4L^\bullet + Mn(CO)_5^\bullet \underset{k_{-21}}{\overset{k_{21}}{\rightleftharpoons}} Mn_2(CO)_9L \qquad (21)$$

$$2Mn(CO)_5^\bullet \underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} Mn_2(CO)_{10} \qquad (22)$$

The pentamethylcyclopentadienyl ligand has found widespread applications in organometallic chemistry, in part because of its propensity to stabilize many complexes relative to their unsubstituted cyclopentadienyl counterparts.[47] The stabilization may be of a kinetic or thermodynamic nature and arise from steric and/or electronic factors. Hoff and co-workers[48] have reported that the hydrogenation of $(\eta^5\text{-}C_5R_5)_2Mo_2(CO)_6$ is more favorable by about 2 kcal/mol for R = Me than for R = H. This effect was attributed to increased steric repulsion (a weaker Mo–Mo bond) in the permethylated dimer, rather than to a difference in the respective Mo–H bond energies. Our data verify that the Mo–H bond strengths in the two corresponding molybdenum hydrides are practically identical (within experimental error; note that $(\eta^5\text{-}C_5Me_5)Mo(CO)_3^-$ oxidation was carried out in dichloromethane—see Experimental Section for details). Thus, permethylation does not lead to an inherently stronger Mo–H bond and therefore the increased thermal stability of $(\eta^5\text{-}C_5Me_5)\text{-}Mo(CO)_3H$ must be caused by other effects, whether steric or electronic in origin.

Metal Hydrides as Hydrogen-Atom-Transfer Reagents. Metal hydrides are well-established intermediates in the catalytic hydrogenation of alkenes.[8] Many isolable metal hydrides readily hydrogenate alkenes or dienes in a stoichiometric fashion. Although possible mechanisms for such reactions are diverse, a radical mechanism involving direct hydrogen atom transfer to the alkene is plausible, provided that the metal–hydrogen bond is sufficiently weak. In fact, considerable evidence has accumulated in support of such mechanisms during the stoichiometric hydrogenation of styrenes,[49] anthracenes,[49a,50] allenes,[51] and conjugated

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[44] See, for example, the recent observation that H$^\bullet$ transfer between $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_3^\bullet$ is rapid on the NMR timescale: Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563.

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dienes[51,52] by transition-metal hydrides. CIDNP effects have been observed in some cases.[49a,g,h,n,o,51,52]

Halpern[49p] suggested a method to estimate upper limits for M–H bond energies as follows: Sweany and Halpern[49a] in a classic study observed CIDNP effects during the hydrogenation of α-methylstyrene with $Mn(CO)_5H$. They concluded that the rate-limiting step was transfer of $H^{\bullet}$ from $Mn(CO)_5$ to the alkene, and from their data, ΔH° for this reaction has a maximum value of 19 kcal/mol. This then leads to an upper limit for the Mn–H bond energy of 65 kcal/mol. The same treatment on data from analogous reactions between metal hydrides and α-methylstyrene or styrene provides the following upper limits for some M–H bond strengths: $Co(CO)_4$–H,[49i] ≤63 kcal/mol; $(\eta^5\text{-}C_5H_5)Mo(CO)_3$–H,[49d] ≤65 kcal/mol; $(\eta^5\text{-}C_5H_5)W(CO)_3$–H,[49d] ≤67 kcal/mol. In all cases, our BDE values (Table II) are less than these maximum values.

The hydrides $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ (Fe–H BDE = 50 kcal/mol) and $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ (Cr–H BDE = 54 kcal/mol) are the ones that the present study indicates as having the weakest M–H bonds and as such would be the most reactive in $H^{\bullet}$-transfer reactions. Using a "radical clock" technique to probe the hydrogen-atom-transfer rates from metal hydrides to vinylcyclopropanes, Bullock and Samsel[55] found that the rate constant (22 °C) for $H^{\bullet}$ transfer from $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ to the 1-cyclopropyl-1-phenylethyl radical was ca. 10^9 M^{-1} s^{-1}, whereas $H^{\bullet}$ transfer from $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ was slower, 4×10^7 M^{-1} s^{-1}. On the basis of the ratios of ring-opened to rearranged products, $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ reacts slower than the Cr complex, and $(\eta^5\text{-}C_5H_5)W(CO)_3H$ reacts still slower. Iron compounds $(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_3)H$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ gave more ring-opened product than did $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, apparently in conflict with the substituent effects on the BDEs that we have found. However, the radical clock experiments were carried out at different temperatures. Furthermore, the kinetics would be sensitive to steric effects of bulky ligands in a way that does not affect our thermodynamic techniques.

Reliability of BDE Determined by Using the Thermochemical Cycle. The assumption that the solvation energy of the hydrogen atom is equal to that of the hydrogen molecule is the most serious source of uncertainty in the BDE values. At the present time, there is no way to evaluate how great an error this assumption introduces. For this reason, it is of interest to consider the relative accuracy of the BDE values determined by using the thermochemical cycle. When either the reversible potential can be measured directly or the observed potential can be corrected using a known rate for the reaction following charge transfer, the error introduced from the electrode potential measurement is no more than 10 mV. This corresponds to an uncertainty of about 0.2 kcal/mol and together with the error in the pK_a (0.3 kcal/mol) results in an uncertainty of about 0.5 kcal/mol in the BDE. When the rate of dimerization of the radical species is unknown, an order of magnitude error in the estimated rate constant corresponds to a 20-mV error in the estimated reversible potential and adds another 0.5 kcal/mol to the overall error. In general, we are confident that the values that we report in Table II are associated with a relative error of no more than 1 kcal/mol.

Because of the lower degree of uncertainty in the relative values of the BDE in Table II, we considered choosing a reliable BDE from the literature and adjusting our values to this standard. One possibility considered was the Co–H BDE[67] of $Co(CO)_4$–H, which has been reported to be equal to 58 kcal/mol.[42] Another possibility that we considered for a standard is the Mn–H BDE of $Mn(CO)_5$–H, which has recently been set at 63 kcal/mol[21] but not without approximations. Since in both cases our BDE values are close to the reported values, we decided not to make an empirical correction.

Experimental Section

The metal anion PPN^+ salts were prepared by metathesis of the corresponding sodium salts with PPN^+Cl^- in THF at ambient temperature, followed by recrystallization by slow cooling of saturated acetonitrile solutions. The preparation of most of these, and analogous salts, has been previously reported.[56] The salts, although somewhat air stable as solids, were stored under nitrogen in a Vacuum Atmospheres drybox.

Complexes $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$[57] and $(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_6$[58] were prepared according to published procedures. The bromide $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)Br$ was prepared by treating an ether solution of the hydride $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H$[59] with 2 equiv of CBr_4 for 10 min at ambient temperature. Recrystallization from dichloromethane/hexane gave the product (91% yield) as orange-red needles: mp 187–189 °C dec; ^1H NMR (100 MHz, $CDCl_3$) δ 1.72 (d, J = 9.8 Hz, 9 H), 5.29 (d, J = 2.4 Hz, 5 H)(trans isomer); δ 1.74 (d, J = 9.8 Hz, 9 H), 5.51 (s, 5 H) (cis isomer)[60] (cis:trans ratio 66:34); IR (ν_{CO},THF) 1953, 1864 cm^{-1}.

The electrochemical instrumentation, cells, data handling procedures, and electrodes have been previously described.[25a,61] All measurements were carried out in reagent-grade acetonitrile that had been distilled from P_2O_5 and passed through a column of active neutral alumina before use to remove water and protic impurities. Before the organometallic complexes were added, the electrolyte was freed of air by purging with argon. All measurements were carried out under a blanket of solvent-saturated argon at 25 ± 0.5 °C.

Repeated peak potential measurements by DCV on one solution were generally reproducible to ±3 mV or better, provided that care was taken to thoroughly clean the surface of the Pt working electrode between scans. If cleaning was not done, the DCV peaks would undergo broadening with concomitant current decrease, and the peak potentials would drift, indicative of adsorption problems. For the peak potential measurements on independently prepared solutions of the same compounds, the reproducibility was better than ±10 mV.

Oxidation of $(\eta^5\text{-}C_5Me_5)Mo(CO)_3^-$, generated in situ from the dimer,

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in acetonitrile resulted in a poorly defined, broad wave from which no useful oxidation potential data could be obtained. However, in dichloromethane, the oxidation process was well-defined. It was therefore necessary to use the dichloromethane data, and these have been converted to acetonitrile solution values by making the assumption that the oxidation potential difference between $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ and $(\eta^5\text{-}C_5Me_5)Mo(CO)_3^-$ is identical in the two solvents.

Acknowledgment. We gratefully acknowledge support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters. We thank Professors J. Halpern and J. R. Norton for many helpful comments and suggestions.

Evidence for Concert in the Vinylcyclopropane Rearrangement. A Reinvestigation of the Pyrolysis of *trans*-1-Methyl-2-(1-*tert*-butylethenyl)cyclopropane

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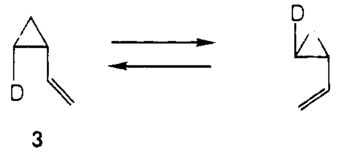
Abstract: Pyrolysis at 280 °C isomerizes *trans*-1-methyl-2-(1-*tert*-butylethenyl)cyclopropane to 1-*tert*-butyl-4-methylcyclopentene and 5,6,6-trimethyl-1,4-heptadiene in a 1:2 ratio. Monodeuteration of the exo methylene and optical activity studies of the rearrangement indicate that the cyclopentene is formed primarily (greater than 72%) through a suprafacial inversion pathway. Deuterium substitution on the trans-methyl group resulted in $k^H/k^{D_3} = 1.11$ with no change in the ratio of cyclopentene to diene, indicating no hydrogen transfer in the rate-determining step for formation of the diene. Dideuteration of the terminal methylene gave $k^H/k^{D_2} = 1.13$ for formation of cyclopentene and 1.03 for formation of diene. The equivalent isotope effects with *trans*-1-methyl-2-vinylcyclopropane are 1.17 and 1.05, respectively, all with an average deviation of 0.03. The isotope effect at the terminal methylene suggests substantial twisting of the methylene in the rate-determining transition state, suggesting that the 1,3-shift of carbon in the vinylcyclopropane rearrangement is concerted.

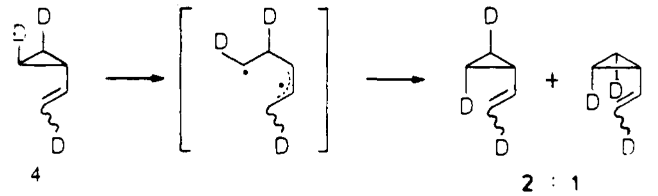
Since the thermal rearrangement of 2,2-dichlorovinylcyclopropane to 4,4-dichlorocyclopentene was first discovered in 1959,[1] many attempts have been made to elucidate the mechanism of this first-order and presumably unimolecular 1,3-sigmatropic shift. Wellington found that cyclopentene, **2**, comprised 96% of the pyrolysate from vinylcyclopropane, **1**, and was formed with log $k(1/s) = 13.5 - 49700/2.3RT$.[2] The rest of the product mixture consisted of dienes.

1 2

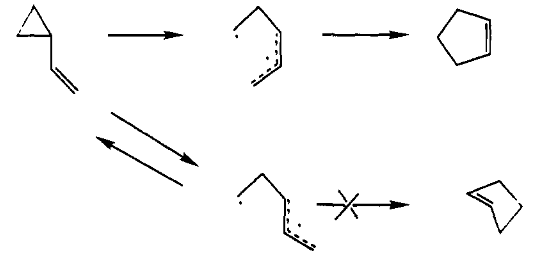
Geometric isomerization of *cis*-2-deuterio-1-vinylcyclopropane, **3**, occurs with log $k(1/s) = 14.5 - 48200/2.3RT$.[3] Further, if only cleavage to C1 occurs, as is expected because of formation of an allylic species, the geometric isomerization of 1-(*trans*-2-deuteriovinyl)-*trans*,*trans*-2,3-dideuteriocyclopropane, **4**, which gives a near statistical ratio of the *trans*- and *cis*-dideuterio isomers, appears to proceed via a randomized biradical intermediate.[4]



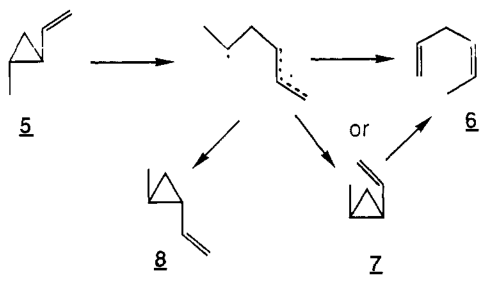
3



Scheme I



Scheme II



Substituents that are cis on the double bond of vinylcyclopropane have been found to decrease the rate of cyclopentene formation.[5] This suggests that for the 1,3 shift, the vinyl group is cisoid in the activated complex and that the cis methyl destabilizes this complex. This conclusion is not unreasonable because a transoid complex would give a *trans*-cyclopentene! (See Scheme I.)

A hydrogen shift to *cis*-hexa-1,4-diene, **6** (Scheme II), is responsible for ca. 93% of the product from pyrolysis of *trans*-2-methyl-1-vinylcyclopropane, **5**, and this diene is the exclusive product at lower temperatures when the corresponding cis isomer,

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