

amples that indicate that indium trialkyls can be employed in cross-coupling. Thus, we reveal the new organoindium characteristic of high alkylating power with triad efficiency, derived from a relatively strong Lewis acid nature and weak In-alkyl bond, which will be extensively available for organic synthesis in future.¹⁵

Supplementary Material Available: Spectral data of the cross-coupling products (2 pages). Ordering information is given on any current masthead page.

(14) Most of the following articles reported the addition of organoindium compounds to unsaturated bonds: (a) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1940**, *62*, 2353. (b) Clark, H. C.; Pickard, A. L. *J. Organomet. Chem.* **1967**, *8*, 427. (c) Tada, H.; Yasuda, K.; Okawara, R. *Inorg. Nucl. Chem. Lett.* **1971**, *28*, 21. (d) Maeda, T.; Tada, H.; Yasuda, K.; Okawara, R. *J. Organomet. Chem.* **1971**, *27*, 13. (e) Dolzine, T. W.; Oliver, J. P. *J. Organomet. Chem.* **1974**, *78*, 165. (f) Chao, L. C.; Riecke, R. D. *J. Org. Chem.* **1975**, *40*, 2253. (g) Araki, S.; Ito, H.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291. (h) Nomura, R.; Fujii, S.; Matsuda, H. *Inorg. Chem.* **1990**, *29*, 4586. (i) Araki, S.; Shimizu, T.; Johar, P. S.; Jin, S.-T.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2538.

(15) One of the reviewers of this article has suggested the use of indium trialkyls in a one-pot procedure without the isolation of them. Our preliminary attempts indicated indium trialkyls generated in situ from indium trichloride and 1.5 equiv of Grignard reagents showed similar reactivities. We should state in addition that the indium trialkyls possess a stability almost equal to the corresponding aluminum alkyls.

One-Electron Oxidation of Cyclopentadienylchromium Carbonyl Hydrides: Thermodynamics of Oxidative Activation of Metal-Hydrogen Bonds toward Homolytic and Heterolytic Cleavage

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Received September 25, 1991

Organotransition-metal hydrides play a crucial role in important catalytic and stoichiometric processes.¹ The energetics of metal-hydrogen bond cleavage reactions have been extensively investigated,² often with great difficulty due to the lack of generally suitable methods. In organic chemistry, thermochemical cycles incorporating electrode potential data have gained widespread use for the extraction of otherwise inaccessible thermochemical data.^{3,4} We have applied this methodology for the estimation of metal-hydrogen bond dissociation energies (BDEs)^{5a,b} and metal hydride cation radical acidities^{5c-e} in solution. A number of metal hydrides were activated toward deprotonation by 20 pK_a units or more as

(1) (a) *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH Publishers: New York, 1991. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) (a) Kristjānsdóttir, S. S.; Norton, J. R. In ref 1a, and references cited. (b) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.*, in press. (c) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888. (d) Kristjānsdóttir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983. (e) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (f) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (g) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(3) (a) Breslow, R.; Balasubramanian, K. *J. Am. Chem. Soc.* **1969**, *91*, 5182. (b) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973**, *95*, 411.

(4) For some leading references, see: (a) Arnett, E. M.; Venimadhavan, S. *J. Am. Chem. Soc.* **1991**, *113*, 6967. (b) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635. (c) Griller, D.; Simões, J. A. M.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872. (d) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792. (e) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(5) (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711; **1990**, *112*, 2843. (b) Parker, V. D.; Handoo, K.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493. (c) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (d) Ryan, O. B.; Tilset, M.; Parker, V. D. *Organometallics* **1991**, *10*, 298. (e) Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 9554.

Table I. Metal Anion, Radical, and Hydride Oxidation Potentials^a

metal center (M)	$E_{ox}(M^-)^b$	$E_{ox}(M^*)^c$	$E_{ox}(M-H)^c$
CpCr(CO) ₂ (P(OMe) ₃)	-1.11	-0.21	+0.28
CpCr(CO) ₂ (PPh ₃)	-1.29	-0.29	+0.12
CpCr(CO) ₂ (PEt ₃)	-1.51	-0.37	+0.00
Cp*Cr(CO) ₃	-0.83	+0.19 ^d	+0.55

^aVolts vs Fc, determined by derivative cyclic voltammetry.¹³ See Figure 1 caption for experimental conditions. ^bReversible potentials, taken as the midpoints between anodic and cathodic waves. ^cPeak potentials for irreversible waves. ^dSomewhat broadened wave, perhaps reflecting a slow heterogeneous electron-transfer rate.

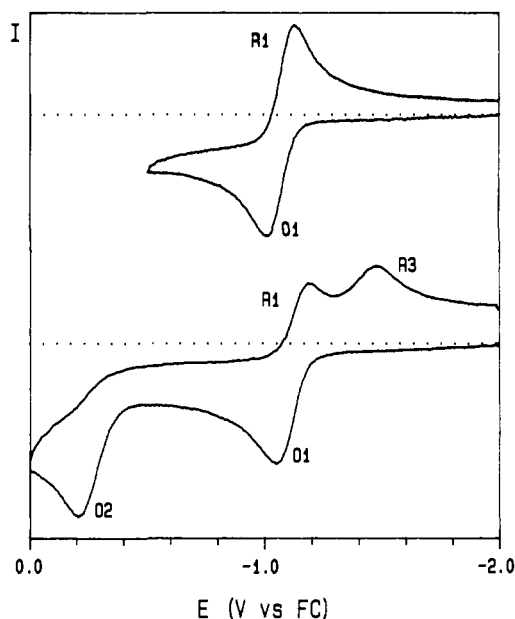
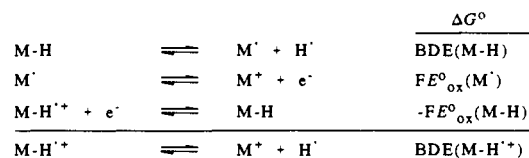


Figure 1. Cyclic voltammograms for the oxidation of CpCr(CO)₂(P(OMe)₃)Et₄N⁺ (1.0 mM) in acetonitrile/0.1 M Bu₄N⁺PF₆⁻ at a Pt disk electrode ($d = 0.6$ mm) at 25 °C and a voltage sweep rate $\nu = 1.0$ V/s.

Scheme I



$$BDE(M-H^{•+}) = BDE(M-H) + F[E_{ox}^\circ(M^*) - E_{ox}^\circ(M-H)] \quad (1)$$

a result of a 1e oxidation.^{5c,d} In this communication, we present the first estimates of M-H BDEs in metal hydride cation radicals and a comparison of the magnitudes of M-H activation toward homolytic and heterolytic cleavage resulting from 1e oxidation processes.

The thermochemical cycle in Scheme I, analogous to one devised for the estimation of BDEs in organic cation radicals,^{4c} may be used to determine M-H BDEs of metal hydride cation radicals. BDE(M-H) and BDE(M-H^{•+}) represent the BDEs of the neutral hydride and its cation radical, and $E_{ox}(M-H)$ and $E_{ox}(M^*)$ represent the oxidation potentials of the hydride and the corresponding 17e radical.^{6a,7}

Rapid radical dimerizations⁸ usually preclude the determination of $E_{ox}(M^*)$. However, the hydrides CpCr(CO)₂(PR₃)H (R = OMe, **1a**; Ph, **1b**; Et, **1c**) and Cp*Cr(CO)₃H (**1d**)⁹ represent cases

(6) (a) The resulting BDE(M-H) - BDE(M-H^{•+}) difference translates to enthalpy values since entropy changes may be safely assumed to cancel.^{6b} (b) Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311.

(7) This method may be used to estimate the magnitude of BDE(M-X) - BDE(M-X^{•+}) for any σ -bonded ligand X.

(8) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187 and references cited therein.

Table II. Chromium Hydride pK_a and BDE Data in Acetonitrile

metal hydride (M-H)	BDE(M-H) ^{a,b}	pK_a (M-H) ^c	$\Delta(pK_a) = pK_a$ (M-H) - pK_a (M-H ⁺) ^d	$\Delta(\text{BDE}) = \text{BDE}(\text{M-H}) - \text{BDE}(\text{M-H}^+)$ ^{b,e}
CpCr(CO) ₂ (P(OMe) ₃)H	62.7	21.1	23.5	11
CpCr(CO) ₂ (PPh ₃)H	59.8	21.8 ^f	23.9	10
CpCr(CO) ₂ (PEt ₃)H	59.9	25.8	25.5	9
Cp*Cr(CO) ₃ H	62.3	16.1	23.3	8

^a From ref 10. ^b In kilocalories/mole. ^c $pK_a(\text{M-H}) = (\text{BDE}(\text{M-H}) - F E_{\text{ox}}^{\circ}(\text{M}^-) - 59.5)/2.301 RT$ (ref 5b) unless otherwise noted. ^d $pK_a(\text{M-H}) - pK_a(\text{M-H}^+) = F(E_{\text{ox}}^{\circ}(\text{M-H}) - E_{\text{ox}}^{\circ}(\text{M}^-))/2.301 RT$ (ref 5c). ^e From eq 1. ^f From equilibrium measurements (ref 5b).

for which the corresponding radicals CpCr(CO)₂(PR₃)[•] (**2a-c**) and Cp*Cr(CO)₃[•] (**2d**) are stable enough for their oxidation potentials to be measured.¹⁰ In conjunction with the pertinent Cr-H BDEs which have been calorimetrically determined,¹¹ the oxidation potentials for CpCr(CO)₂(PR₃)⁻ (**3a-d**) and Cp*Cr(CO)₃⁻ (**3d**) give access to the respective Cr-H pK_a values.^{5a,b}

Figure 1 shows cyclic voltammograms for the oxidation of **3a**-Et₄N.¹² The reversible oxidation of **3a** is observed at -1.11 V (taken as the midpoint between the anodic (O1) and cathodic (R1) waves) vs the ferrocene/ferricinium (Fc) couple. An irreversible wave (O2) of the same intensity as O1 is observed at -0.21 V vs Fc. A product resulting from the reaction of the species generated at O2 is observed as reduction wave R3 at -1.48 V vs Fc and is assumed to be CpCr(CO)₂(P(OMe)₃)(NCMe)⁺ (**4a**). The disappearance of **3a** and the appearance of **4a** were monitored during a constant-current coulometry experiment, and it was revealed that R3 did not emerge until **3a** had been completely oxidized to **2a**. The **3a/2a** couple vanished after the passage of 2 faraday/mol, generating a solution of **4a** (IR (dichloromethane) ν_{CO} 2000, 1930 cm⁻¹).

The metal anion, radical, and hydride oxidation potentials are summarized in Table I. Table II lists the BDE and calculated pK_a values for the neutral metal hydrides and the BDE and pK_a changes caused by their oxidation.

The $\Delta(pK_a)$ estimates represent minimum numbers due to the kinetic potential shifts caused by the irreversible nature of the M-H oxidation waves.¹⁴ The activation of the Cr-H bonds toward heterolysis, $-\Delta\Delta G_{\text{het}} = 2.3RT\Delta(pK_a)$, amounts to at least 32-35 kcal/mol.¹⁵ The irreversibility of the M[•] and M-H oxidation waves introduces some uncertainty into the 8-11 kcal/mol estimates for the homolytic activation, $-\Delta\Delta G_{\text{hom}} = \Delta(\text{BDE})$, but these potential shifts will cancel in part. Despite these uncertainties, the data leave little doubt that the activation toward heterolysis by far exceeds the homolytic activation. In fact, the equations (Table II, footnotes c and d) that lead to $\Delta\Delta G_{\text{het}}$ and $\Delta\Delta G_{\text{hom}}$ may be combined and rearranged to give $(\Delta\Delta G_{\text{het}} - \Delta\Delta G_{\text{hom}}) = F(E_{\text{ox}}^{\circ}(\text{M}^-) - E_{\text{ox}}^{\circ}(\text{M}^{\bullet}))$, which implies that the heterolytic activation will be greater than the homolytic activation if $E_{\text{ox}}^{\circ}(\text{M}^{\bullet}) > E_{\text{ox}}^{\circ}(\text{M}^-)$. This condition should be fulfilled unless significant structural changes occur when the anion is oxidized to the radical.¹⁶

(9) Cp = $\eta^5\text{-C}_5\text{H}_5$; Cp* = $\eta^5\text{-C}_5\text{Me}_5$.

(10) (a) Goh, L.-Y.; D'Aniello, M. J., Jr.; Slater, S.; Muettterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192. (b) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563. (c) Jaeger, T. J.; Baird, M. C. *Organometallics* **1988**, *7*, 2074. (d) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965. (e) O'Callaghan, K. A. E.; Brown, S. J.; Page, J. A.; Baird, M. C.; Richards, T. C.; Geiger, W. E. *Organometallics* **1991**, *10*, 3119.

(11) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D. *J. Am. Chem. Soc.* **1990**, *112*, 5657.

(12) Et₄N⁺ (**3a-c**) or (Ph₃P)₂N⁺ (**3d**) salts were prepared by treating **1a-d** with *t*-BuOK in THF, followed by cation exchange. IR (ν_{CO}) and elemental analysis data are given in the supplementary material.

(13) (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 73. (b) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

(14) Characteristics of the oxidation wave for **1a** are representative: $E_p - E_{p/2} = 76$ mV at $\nu = 1.0$ V/s (cf. 68 mV for ferrocene); no observable return wave for $\nu < 100$ V/s.

(15) The pK_a differences are comparable with those reported for other metal hydrides^{5c,d} and also fall in the range estimated for neutral/cation radical acidities in many organic systems.^{4a,d}

It has been discussed previously whether metal hydride cation radicals react via initial H⁺ or H[•] transfer,^{5c,17,18} the former being supported by experimental evidence in most cases. The data presented here provide a quantitative and sound rationale for the observed behavior.

Acknowledgment. We gratefully acknowledge support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters, and from the Norwegian Council for Science and the Humanities, NAVF. We thank Professor Jack Norton for kindly providing preprints of refs 2a and 2b and Professor Kenneth G. Caulton for helpful discussions.

Supplementary Material Available: IR (ν_{CO}) and elemental analysis data for compounds **3a**-Et₄N, **3b**-Et₄N, **3c**-Et₄N, and **3d**-(Ph₃P)₂N (1 page). Ordering information is given on any current masthead page.

(16) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558.

(17) (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208. (b) Detty, M. R.; Jones, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 5666. (c) Westenberg, D. E.; Rhodes, L. F.; Edwin, J.; Geiger, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1107.

(18) H[•] transfer has been reported from Sn, Ge, and Si hydride cations to the tetracyanoethylene radical anion: Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

Functionalization of the β -Lactam Ring: Diastereoselective Azide Transfer and N-O Bond Reduction on C₄-Substituted N-Hydroxy β -Lactams in One Step

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While investigating new methods for the synthesis of the carbacephem class of β -lactam antibiotics,¹ we serendipitously discovered a fascinating transformation on N-hydroxy β -lactams which effected simultaneous azide transfer to the C₃ position diastereoselectively with cleavage of the N-hydroxy bond.

This conversion was effected during attempted diazotization² of racemic β -keto ester **2** (Scheme I). Compound **2** was obtained

(1) (a) Zmijewski, M. J.; Briggs, B. S.; Thompson, A. R.; Wright, I. G. *Tetrahedron Lett.* **1991**, *32*, 1621. (b) Bodurow, C. C.; Boyer, B. D.; Brennan, J.; Bunnell, C. A.; Burks, J. E.; Carr, M. A.; Doecke, C. W.; Eckrich, T. M.; Fisher, J. W.; Gardner, J. P.; Graves, B. J.; Hines, P.; Hoying, R. C.; Jackson, B. G.; Kinnick, M. D.; Kochert, C. D.; Lewis, J. S.; Luke, W. D.; Moore, L. L.; Morin, J. M., Jr.; Nist, R. L.; Prather, D. E.; Sparks, D. L.; Vladuchick, W. C. *Tetrahedron Lett.* **1989**, *30*, 2321. (c) Hirata, T.; Matsukuma, I.; Mochida, K.; Sato, K. American Society for Microbiology, Program and Abstracts of the 27th Interscience Conference on Antimicrobial Agents and Chemotherapy, New York, October 1987, Abstract No. 1187. (d) Gray, G.; Ramotar, K.; Krulicki, W.; Louie, T. J. *Ibid.* Abstract No. 1200. (e) Quay, J. F.; Coleman, D. L.; Finch, L. S.; Indelicato, J. M.; Pasini, C. E.; Shouffer, J. R.; Sullivan, H. R.; Turner, J. C. *Ibid.* Abstract No. 1205.

(2) Regitz, M.; Maas, G. *Diazo Compounds: Properties and Synthesis*; Academic Press: New York, 1986; Chapter 13.