J|A|C|S
COMMUNICATIONS

Published on Web 03/12/2008

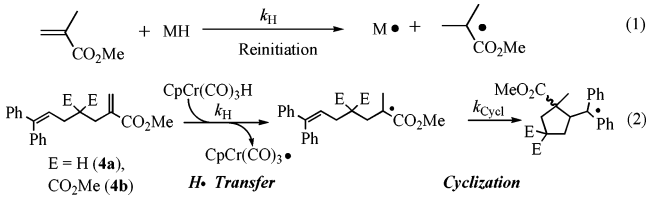
Unusually Weak Metal−Hydrogen Bonds in $HV(CO)_4(P-P)$ and Their Effectiveness as H• Donors

Jongwook Choi, Mary E. Pulling, Deborah M. Smith, and Jack R. Norton*

Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027

Received November 19, 2007; E-mail: jrn11@columbia.edu

The transfer of H• from a transition metal to an olefin is a key step in some hydrogenations and hydroformylations,[1] in the reinitiation step of chain transfer catalysis (eq 1),[2] and in our Cr-catalyzed radical cyclization (eq 2).[3] Increasing the rate of such an



H• transfer can presumably be accomplished by decreasing the strength of the M−H bond. While most such bonds lie between 60 and 80 kcal/mol,[4] there is evidence suggesting that V−H bonds are weaker: $HV(CO)_4$(dppm) and related vanadium hydrides convert dienes into allyl ligands at ≤0 °C.[5] Calculations by Landis and co-workers on the hypothetical VH_5 say that it has the weakest M−H bond dissociation energy (42.8 kcal/mol) of any "valency-saturated" neutral hydride complex MH_n of the 27 first-, second-, and third-row metals considered.[6] (Landis and co-workers define a "valency-saturated" compound as one that forms the maximum number of bonds involving s and d orbitals from the available valence electrons.[6])

We have therefore investigated the V−H bonds in the seven-coordinate complexes $HV(CO)_4(P-P)$ (P−P = $Ph_2P(CH_2)_nPPh_2$, with n = 1 (dppm) in **1a**, n = 2 (dppe) in **1b**, n = 3 (dppp) in **1c**, and n = 4 (dppb) in **1d**).[7] (We expected the high coordination number to decrease the bond strength further.) We have found that these V−H bonds are indeed weak and that they are excellent donors of H• to double bonds.

The Bond Dissociation Enthalpies (BDE values) for the V−H bonds in $HV(CO)_4(P-P)$ (**1a**−**1d**) have been determined from their pK_a values in CH_3CN and the $E°(M^-/M•)$ values of their conjugate bases in the same solvent (eq 3).[8]

$$\text{BDE (M−H)} = 1.37\ \text{p}K_a + 23.06\ E°(M^-/M•) + 59.5\ \text{(kcal/mol)} \quad (3)$$

Cyclic voltammetry of $[Et_4N][V(CO)_4(P-P)]$ (**2**) has given the $E°$ values straightforwardly, as the metalloradicals $•V(CO)_4(P-P)$ (**3**) produced by the one-electron oxidation of these anions are stable[9] and the oxidations are therefore reversible. That reversibility is demonstrated by the peak-to-peak separation, which is close to 60 mV for all four anions **2** and is illustrated for **2b** in Figure 1.

Direct measurement of the pK_a values of the hydrides **1** in CH_3CN proved impossible in view of the insolubility of $HV(CO)_4$-(dppp) (**1c**) and $HV(CO)_4$(dppb) (**1d**) in that solvent. We estimated the pK_a values of the hydrides **1** in CH_3CN from that (17.0)[10,11] of $Cp^*Cr(CO)_3H$ in the same solvent by measuring K_{eq} for the proton transfer in eq 4 by ^1H NMR in CD_2Cl_2.[12] The resulting estimates

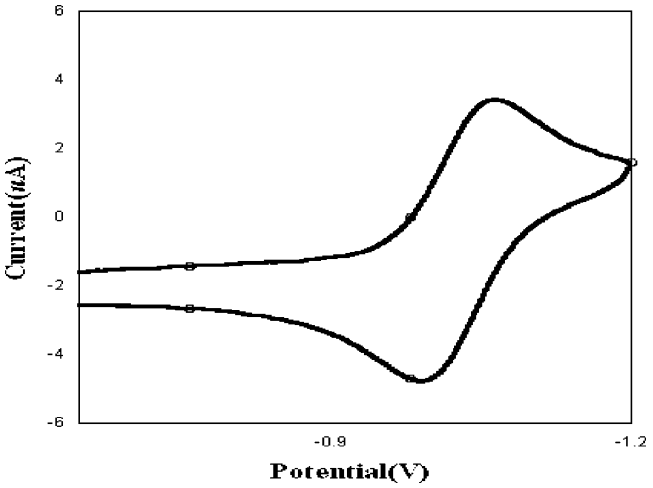


Figure 1. Cyclic voltammogram of 1 mM $[Et_4N][V(CO)_4(dppe)]$ in acetonitrile/0.1 M n-Bu_4NPF_6 with a scan rate of 50 mV/s.

for CH_3CN pK_a values were 18.7(1) for **1a**, 17.4(1) for **1b**, 17.1(1) for **1c**, and 16.7(1) for **1d**.

$$\text{HV(CO)}_4\text{(P-P)} + [\text{Et}_4\text{N}][(\eta^5\text{-C}_5\text{Me}_5)\text{Cr(CO)}_3] \underset{CD_2Cl_2}{\overset{K_{eq}}{\rightleftharpoons}} [\text{Et}_4\text{N}][\text{V(CO)}_4\text{(P-P)}] + (\eta^5\text{-C}_5\text{Me}_5)\text{Cr(CO)}_3\text{H} \quad (4)$$

In order to check the validity of these estimates, we determined the CH_3CN pK_a values of $HV(CO)_4$(dppm) (**1a**) and $HV(CO)_4$(dppe) (**1b**) with Et_3N and $PhCH_2NH_2$, respectively. If we take the pK_a of Et_3NH^+ in CH_3CN as 18.82 and that of $PhCH_2NH_3^+$ as 16.91 (their values on the unified scale recently published for CH_3CN[11]), we obtain pK_a values of 18.8(1) for **1a** and 17.6(2) for **1b**. These results agree satisfactorily with the indirect pK_a values from K_{eq} measurements in CD_2Cl_2.

It is clear from Table 1 that the pK_a of **1a**−**d** decreases as the natural bite angle[13] of the P−P ligand increases. Presumably the six-coordinate anion arising from deprotonation prefers an octahedral geometry, with angles close to 90°. In the Cambridge Structural Database[14] the average dppm bite angle in metal complexes is 71.3°, with a maximum value of 76.2°, implying that a dppm ligand cannot achieve a P−M−P angle close to the optimal value of 90°. With increasing bite angle, the strain imposed by deprotonation decreases and the pK_a decreases.[15]

The $E°$ and pK_a values for **1** imply not only BDE values from eq 3 but also free energies of V−H bond dissociation ($\Delta G°$(H•)) from eq 5;[8d] both are given in Table 1 for **1a**−**d**. Mayer has noted that $\Delta S°$(M−H) is not always equal to $\Delta S°$(M•), as assumed in the derivation of eq 3, and has suggested that the free energies be used instead of BDE values in assessing the thermodynamics of H• transfer.[16]

$$\Delta G°_{\text{H•}} = 1.37\text{p}K_a + 23.06E° + 54.9\ \text{(kcal/mol)} \quad (5)$$

10.1021/ja710455c CCC: $40.75

Table 1. Values of E° for $[Et_4N][V(CO)_4(P-P)]$ (**2**) and Values of pK_a, BDE, and $\Delta G^\circ(H\bullet)$ for $HV(CO)_4(P-P)$ (**1**); Natural Bite Angles for P−P

P–P	E° [a] (V)	pK_a [b]	V–H BDE (kcal/mol)	$\Delta G^\circ(H^\bullet)$ (kcal/mol)	natural P–M–P bite angle[c] (deg)
dppm	−1.18 (1)	18.7(1)	57.9	53.3	
dppe	−1.12 (1)	17.4(1)	57.5	52.9	78.1
dppp	−1.17 (1)	17.1(1)	56.0	51.4	86.2
dppb	−1.19 (1)	16.7(1)	54.9	50.3	98.6

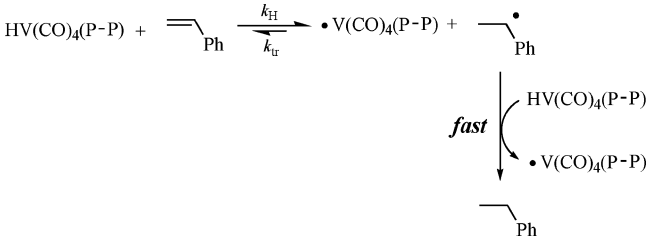
[a] Relative to ferrocene. [b] Estimated in MeCN from measurements in CD_2Cl_2. [c] Natural bite angle by molecular modeling.[13]

Table 2. Rate Constants k_H for H• Transfer from **1a**−**d** and $CpCr(CO)_3H$ to Styrene at 285 K in C_6D_6

	M–H BDE (kcal/mol)	k_H ($M^{-1}\,s^{-1}$) $\times 10^{-3}$	relative rate
$HV(CO)_4$(dppm) (**1a**)	57.9	≥17 (1)	20.0
$HV(CO)_4$(dppe) (**1b**)	57.5	≥9.0 (5)	10.6
$HV(CO)_4$(dppp) (**1c**)	56.0	7.0 (1)	8.2
$HV(CO)_4$(dppb) (**1d**)	54.9	5.7 (4)	6.7
(η^5-C_5H_5)$Cr(CO)_3H$	62.2[a]	0.85 (20)[b]	1

[a] Recalculated from the data in ref 8d on the basis of the unified pK_a scale in ref 11. See ref 28. [b] Obtained by extrapolation from the data in ref 24b.

Scheme 1



To our knowledge the results in Table 1 are the first *solution* measurements of V−H bond strengths[4,17] and imply that the bonds in **1** are significantly weaker than the M−H bonds in other neutral hydride complexes. No stable neutral hydride with an M−H BDE < 57.1 kcal/mol (the BDE of $CpFe(CO)_2H$) is listed in a recent compilation.[4,18]

The BDE and $\Delta G^\circ(H\bullet)$ values in Table 1 confirm that the V−H bonds of the vanadium hydrides **1** are substantially weaker than the Cr−H bond in $CpCr(CO)_3H$ (Table 2).[19] The BDE and $\Delta G^\circ(H\bullet)$ values for the hydrides **1** are low enough[20−22] to call into question the *thermodynamic* stability of **1** with regard to loss of H_2 (eq 6).[23] The stability of the hydrides **1** at room temperature is probably the result of a *kinetic* barrier to hydrogen evolution.

$$2\,HV(CO)_4P{-}P \rightleftharpoons H_2 + 2\,{\bullet}V(CO)_4P{-}P \qquad (6)$$

The V−H bonds in **1** do transfer H• more rapidly than does $CpCr(CO)_3H$.[24] The rate constants k_H for H• transfer to styrene (Scheme 1) can be determined by observing the hydrogenation of styrene by the vanadium hydrides **1**.[25] The extent of back transfer (rate constant k_{tr}) can, as we have shown in other studies on such reactions,[24b,26] be established by treating styrene with **1**-d_1. With **1c**-d_1 and **1d**-d_1, ^{2}H NMR shows deuterium incorporation only into the product (ethylbenzene) and not into recovered styrene; k_H is thus rate determining, and can be computed from eqs 7 and 8. With **1a**-d_1 and **1b**-d_1 a small amount (∼10%) of H/D exchange is observed, so the k_H in Table 2 (obtained from eqs 7 and 8) is a lower limit.

$$-\frac{d[\mathbf{1}]}{dt} = k_{obs}[\mathbf{1}] \qquad (7)$$

$$k_{obs} = 2k_H[\text{Styrene}] \qquad (8)$$

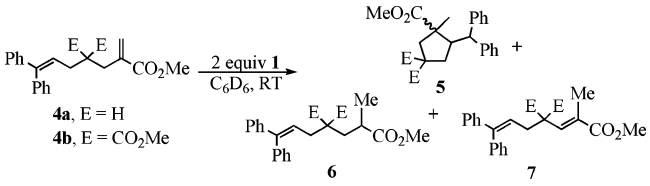
The resulting k_H values for **1** (Table 2) are 7 to 20 times faster than k_H to styrene from $CpCr(CO)_3H$. These ratios, however, are considerably smaller than the ones we would expect if the differences in k_H were entirely the result of the differences in BDE between V−H and Cr−H. If we compare **1b** with $CpCr(CO)_3H$ and assume an α of unity in the Polanyi equation (eq 9),[27] the ratio of k_H(**1b**) to k_H(CpCr) will be 4020. Steric effects (the bulk of the chelating phosphine ligands in the hydrides **1**, and crowding within their seven-coordinate structures) presumably decrease the rate of H• transfer from vanadium.

$$\log k \propto \beta + \alpha(\Delta H) \qquad (9)$$

The relative value of the rate constants *within the vanadium series* in Table 2 is *opposite* that predicted from the V−H bond strengths; i.e., k_H *decreases* in the order **1a**(dppm) > **1b**(dppe) > **1c**(dppp) > **1d**(dppb). Again, steric effects (the increasing size of the chelate ligands from dppm through dppb) are presumably responsible. Such effects are also apparent in the influence of olefin structure on the value of k_H from a given M−H (substituents on the carbon to which the H• is being transferred decrease k_H substantially).[26]

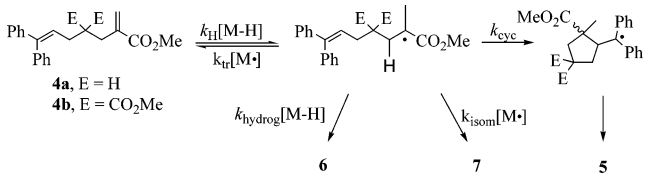
The vanadium hydrides **1** also effect the radical cyclization of dienes **4(a,b)** more rapidly, and under milder conditions, than does $CpCr(CO)_3H$. With 2 equiv of the Cr hydride the cyclizations of **4(a,b)** did not go to completion. Under the same conditions 2 equiv of **1b** (0.034 M) converted **4a** (0.017 M) to **5a** in 77% yield, along with 13% of the hydrogenation product **6a** and 10% of the isomerization product **7a** (Scheme 2). Similar results were obtained with **1c** and **1d**, whereas **1a** gave 56% **5a** (and 35% of the hydrogenation product **6a**) after a shorter reaction time. (See Supporting Information for details.)

Scheme 2



The higher yield of the hydrogenation product **6a** obtained with **1a** reflects the faster rate at which H• is transferred from that hydride. Presumably k_{hydrog} (Scheme 3) for **1a** increases along with k_H.

Scheme 3



Similar reactions between **4b** and 2 equiv of **1a**, **1b**, **1c**, or **1d** gave quantitative yields of the cyclization product **5b**, reflecting the faster cyclization (larger rate constant k_{cycl}) resulting from the Thorpe−Ingold effect when E = CO_2Me.[3,29]

With $CpCr(CO)_3H$ we were able to make the cyclizations of **4(a,b)** catalytic by performing them under hydrogen pressure, which regenerates the hydride from Cr• as in eq 10.[3]

$$2\ CpCr(CO)_3H \rightleftharpoons H_2 + 2\ CpCr(CO)_3\bullet \qquad (10)$$

However, when we treated **4a** or **4b** with a catalytic amount of **1(a**, **b**, **c**, or **d)** under 80 psi of H_2 at 50 °C, little or no **5** was formed. Apparently the reaction in eq 6 does not proceed at an appreciable rate in *either* direction under ordinary conditions.

Acknowledgment. This work has been supported by DOE Grant DE-FG02-97ER14807. The authors are grateful to Prof. J. Ellis for a generous donation of $[Et_4N][V(CO)_6]$, to Prof. Ellis and Prof. C. D. Hoff for helpful discussions, and to the reviewers for useful comments.

Supporting Information Available: Synthetic details, kinetic procedures and data, and details of pK_a measurements and electrochemistry. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575−584. (b) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55−66.
(2) (a) Gridnev, A. A.; Ittel, S. D. *Chem. Rev.* **2001**, *101*, 3611−3659. (b) Heuts, J. P. A.; Roberts, G. E.; Biasutti, J. D. *Aust. J. Chem.* **2002**, *55*, 381−398.
(3) Smith, D. M.; Pulling, M. E.; Norton, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 770−771.
(4) Tilset, M. Organometallic Electrochemistry: Thermodynamics of Metal-Ligand Bonding. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: 2007; Vol. 1, pp 279−305. $TpCr(CO)_3H$ is listed with a BDE of 51.4 kcal/mol, although it has not been isolated. Its pK_a has been estimated from its extensive deprotonation in CH_3CN even when no base is added.
(5) (a) Franke, U.; Weiss, E. *J. Organomet. Chem.* **1978**, *152*, C19−C23. (b) Franke, U.; Weiss, E. *J. Organomet. Chem.* **1980**, *193*, 329−337.
(6) Uddin, J.; Morales, C. M.; Maynard, J. H.; Landis, C. R. *Organometallics* **2006**, *25*, 5566−5581.
(7) (a) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 131−136. (b) Puttfarcken, U.; Rehder, D. *J. Organomet. Chem.* **1978**, *157*, 321−325.
(8) (a) Breslow, R.; Balasubramanian, K. *J. Am. Chem. Soc.* **1969**, *91*, 5182−5183. (b) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973**, *95*, 411−418. (c) Bordwell, F. G.; Cheng, J. P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229−1231. (d) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−6717 and **1990**, *112*, 2843. (e) Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493−7498.
(9) Ihmels, K.; Rehder, D. *J. Organomet. Chem.* **1981**, *218*, C54−C56.
(10) With $PhCH_2NH_2$ in CH_3CN (taking the pK_a of $PhCH_2NH_3^+$ as 16.91, its value on the unified scale recently published (ref 11) for CH_3CN) we found the pK_a of $Cp^*Cr(CO)_3H$ to be 17.0(1). The somewhat smaller number (16.1) given by Tilset (Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740−2741) was obtained from the calorimetrically determined Cr−H bond strength and the measured $E°$.
(11) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019−1028.
(12) The *relative* pK_a of two hydride complexes should be similar in H_2O, CH_3CN, or CH_2Cl_2. (a) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581−582. (b) Kristjánsdóttir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; Chapter 9.
(13) (a) Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.* **1990**, *30*, 299−304. (b) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998**, 25−27. (c) Dierkes, P.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519−1529.
(14) CSD version 5.28 (November 2006).
(15) Angelici and co-workers proposed a similar explanation for the fact that *cis*-$Mo(CO)_2(dppm)_2$ is more basic than its dppe and dppp analogues. Sowa, J. R., Jr.; Bonanno, J. B.; Zanotti, V.; Angelici, R. J. *Inorg. Chem.* **1992**, *31*, 1370−1375.
(16) Mader, E. A.; Davidson, E. R.; Mayer, J. M. *J. Am. Chem. Soc.* **2007**, *129*, 5153−5166.
(17) The dissociation energy of V−H in the gas phase has been measured by guided ion beam mass spectrometry; the BDE obtained was 49.0(16) kcal/mol. (a) Chen, Y.; Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1993**, *98*, 4929−4936. (b) Armentrout, P. B.; Kickel, B. L. Gas Phase Thermochemistry of Transition Metal Ligand Systems: Reassessment of Values and Periodic Trends. In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Boston, 1996; pp 1−45.
(18) Smaller values of $\Delta G°(H^\bullet)$ have been reported for two *cationic* hydride complexes: (a) 52.6 kcal/mol for $Ni(Ph_2PCH{=}CHPPh_2)_2^+$, in Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; DuBois, D. L. *Organometallics* **2001**, *20*, 1832−1839. (b) 49.9 kcal/mol for the paramagnetic $[HCo(dppe)_2]^+$, in Ciancanelli, R.; Noll, B. C.; DuBois, D. L.; DuBois, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 2984−2992.
(19) The *relative* BDE values of our M−H bonds have an uncertainty, derived from the variation in pK_a and $E°$ results over repeated measurements of ±0.3 kcal/mol.
(20) The *absolute* uncertainty in such BDE values is problematic, involving (a) the difference in $\Delta S°$ between **1** and **2** (see text above eq 5). (b) the uncertainty in the free energy of solvation of H• ($\Delta G°_f(H\bullet)$ in CH_3CN has been estimated as 51.8 kcal/mol).[21] (c) the *absolute* accuracy of the unified CH_3CN scale we have used (ref 11). Comparison of such BDE values with those from calorimetry[22] and considerations of internal consistency suggest that the absolute uncertainty of our BDE values is a little over 1 kcal/mol. For a detailed discussion of these issues, see Choi, Jongwook. Ph.D. Thesis, Columbia University, 2007.
(21) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287−294.
(22) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657−5658.
(23) It has been suggested[22] that M−H bonds weaker than 56 kcal/mol are thermodynamically unstable at room temperature with respect to H_2 evolution. This estimate is based on the observed ΔS for the binding of H_2 to $L_2M(CO)_3$ (M = Cr, Mo): Gonzalez, A. A.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4295−4297.
(24) (a) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886−6898. (b) Tang, L.; Papish, E. T.; Abramo, G. P.; Norton, J. R.; Baik, M.; Friesner, R. A.; Rappé, A. *J. Am. Chem. Soc.* **2003**, *125*, 10093−10102, and **2006**, *128*, 11314.
(25) The hydrogenation of styrene (both stoichiometric and catalytic) by a dinuclear vanadium hydride $V_2(\mu\text{-}H)_2$ has been reported: Aharonian, G.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 5008−5010.
(26) Choi, J.; Tang, L.; Norton, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 234−240.
(27) See reference 71 in Gardner, K. A.; Kuehnert, L. L.; Mayer, J. M. *Inorg. Chem.* **1997**, *36*, 2069−2078.
(28) If we use the pK_a value of pyridinium H^+ (12.53) from the new unified CH_3CN scale,[11] the pK_a of $CpCr(CO)_3H$ becomes 13.55. Using this pK_a in eq 3 gives the Cr−H BDE in $CpCr(CO)_3H$ as 62.2 kcal/mol, which we have shown for consistency in place of the previously published values of 62 kcal/mol (thermodynamic cycle)[8d] and 61.5 (calorimetric).[22]
(29) Kaneti, J.; Kirby, A. J.; Koedjikov, A. H.; Pojarlieff, I. G. *Org. Biomol. Chem.* **2004**, *2*, 1098−1103.

JA710455C