

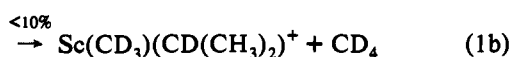
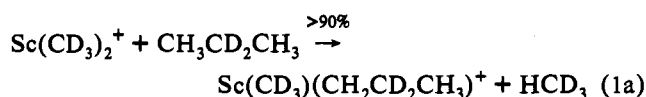
Trends in Sc<sup>+</sup>-Alkyl Bond Strengths

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Recent Fourier transform ion cyclotron resonance (FTICR) studies of the gas-phase  $\sigma$ -bond metathesis reactions of Sc(CH<sub>3</sub>)<sub>2</sub><sup>+</sup> with alkanes (C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and *n*-C<sub>4</sub>H<sub>10</sub>) demonstrate a preference for attack at *primary* rather than *secondary* C-H bonds,<sup>1</sup> reaction 1a rather than 1b. This occurs even though the substrate primary



bond is  $\sim 2.4$  kcal/mol stronger than the secondary bond.<sup>2</sup> In addition, the efficiencies of the reactions are observed to increase with the size of the alkane ( $\leq 0.02$ , 0.17, and 0.37 for C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and *n*-C<sub>4</sub>H<sub>10</sub>, respectively). *Ab initio* calculations on the analogous reaction with CH<sub>4</sub> indicate that the reaction proceeds via a four-center transition state. Consequently, the variations in the observed reactivities should be largely attributable to the differences in the corresponding metal-alkyl and alkyl-H bond strengths. In order to verify that this is the case, we examined the Sc<sup>+</sup>-R bond strengths, where R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, and *t*-C<sub>4</sub>H<sub>9</sub> (see Table 1 and Figure 1). While transition metal hydride and metal methyl cations have been well studied both experimentally<sup>3</sup> and theoretically,<sup>4-6</sup> information on the strengths of the bonds of larger ligands is sparse.<sup>7</sup> To our knowledge, this work represents the first systematic theoretical study of such metal-alkyl bond strengths.

Our results indicate that the observed selectivity has a clear thermodynamic origin and the Sc<sup>+</sup>-R bond strengths are consistent with two sometimes conflicting trends: (i) Bond strengths decrease as methyl > primary > secondary > tertiary. (ii) Bond strengths increase with the increasing size of the ligand. These two trends are in agreement with the observed increasing reactivity of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and *n*-C<sub>4</sub>H<sub>10</sub> and the observed selectivity for activating primary C-H bonds over secondary bonds. For C<sub>3</sub>H<sub>8</sub>, the Sc<sup>+</sup>-(*n*-C<sub>3</sub>H<sub>7</sub>) bond is 8.5 kcal/mol stronger than the Sc<sup>+</sup>-(*i*-C<sub>3</sub>H<sub>7</sub>) bond! As a result, reaction 1a is  $\sim 6$  kcal/mol more exothermic than 1b.

(1) Crellin, K. C.; Geribaldi, S.; Beauchamp, J. L. *Organometallics*, submitted.

(2) The use of isotopic labels in the experiments will have a negligible effect on the exothermicities of the metathesis reactions. Therefore, for clarity we only consider C-H bond strengths and not C-D bond strengths.

(3) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* 1990, 90, 629 and references therein.

(4) Schilling, J. B.; Goodard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* 1987, 109, 5573.

(5) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H.; Barnes, L. A. *J. Chem. Phys.* 1989, 91, 2399.

(6) (a) Ohanessian, G.; Goddard, W. A., III. *Acc. Chem. Res.* 1990, 23, 386. (b) Petterson, L. G. M.; Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Chem. Phys.* 1987, 87, 481.

(7) See, for example: Armentrout, P. B.; Clemmer, D. E. In *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; Kluwer: Netherlands, 1992; pp 321-356 and references therein.

Table 1. Calculated Dissociation Energies<sup>a</sup> for Sc<sup>+</sup>-Alkyl Bonds

	method	D <sub>0</sub>	ΔD <sub>0</sub>
Sc <sup>+</sup> -CH <sub>3</sub>	MCPF	44.9 <sup>b</sup>	0.0
	CCCI	47.2	0.0
	MRSDCI+Q	46.1	0.0
Sc <sup>+</sup> -C <sub>2</sub> H <sub>5</sub>	MCPF	40.2 <sup>c</sup>	-4.7
	CCCI	42.7	-4.5
	MRSDCI+Q	40.8	-5.3
Sc <sup>+</sup> -( <i>n</i> -C <sub>3</sub> H <sub>7</sub> )	MCPF	45.4	0.5
Sc <sup>+</sup> -( <i>i</i> -C <sub>3</sub> H <sub>7</sub> )	MCPF	36.9	-8.0
Sc <sup>+</sup> -( <i>t</i> -C <sub>4</sub> H <sub>9</sub> )	MCPF	34.5	-10.4

<sup>a</sup> In kilocalories/mole. <sup>b</sup> 50.5 kcal/mol using the extended basis set of ref 14. <sup>c</sup> 45.6 kcal/mol using the extended basis set of ref 14.

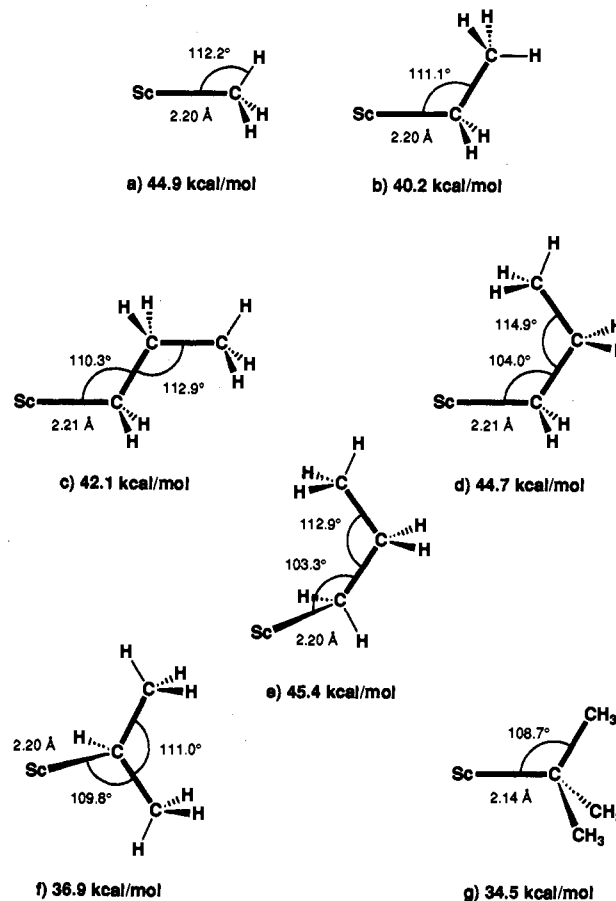


Figure 1. Geometries and MCPF Sc-alkyl<sup>+</sup> bond dissociation energies (in kcal/mol) for (a) Sc(CH<sub>3</sub>)<sup>+</sup>, (b) Sc(C<sub>2</sub>H<sub>5</sub>)<sup>+</sup>, (c-e) Sc(*n*-C<sub>3</sub>H<sub>7</sub>)<sup>+</sup>, (f) Sc(*i*-C<sub>3</sub>H<sub>7</sub>)<sup>+</sup>, and (g) Sc(*t*-C<sub>4</sub>H<sub>9</sub>)<sup>+</sup>.

We used a variety of *ab initio* methods to determine the Sc<sup>+</sup>-CH<sub>3</sub> and Sc<sup>+</sup>-C<sub>2</sub>H<sub>5</sub> bond strengths.<sup>8-12</sup> Table 1 summarizes all calculated energetics [geometries, along with the bond energies determined at the modified coupled pair functional (MCPF) level, are shown in Figure 1]. We find that the Sc<sup>+</sup>-C<sub>2</sub>H<sub>5</sub> bond is about 5 kcal/mol *weaker* than the Sc<sup>+</sup>-CH<sub>3</sub> bond. However, the

(8) Calculations were performed using (a) MOLECULE/SWEDEN, an electronic structure program system written by Almlöf, J., Bauschlicher, C. W., Jr., Blomberg, M. R. A., Chong, C. P., Heiberg, A., Langhoff, S. R., Malmqvist, P. A., Rendell, A. P., Roos, B. O., Siegbahn, P. E. M., and Taylor, P. R., and (b) GVB, a suite of electronic structure programs written at the California Institute of Technology under the supervision of Goddard, W. A., III (unpublished).

(9) Methods include the following. (a) Correlation-consistent configuration interaction (CCCI); see: Carter, E. A.; Goddard, W. A., III. *J. Chem. Phys.* 1988, 88, 3132. (b) Modified coupled pair functional (MCPF); see: Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* 1986, 84, 5606. (c) Multireference singles plus doubles CI including Davidson's correction (MRSDCI+Q). (d) Geometry optimizations were performed at the Hartree-Fock (HF) level.

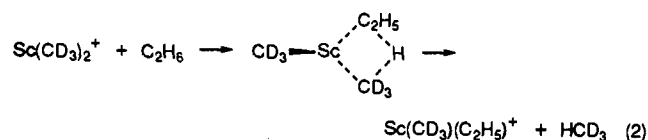
(10) An effective core potential was used to replace all but the valence and outer core 3s/3p electrons of Sc<sup>+</sup>; see: Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* 1985, 82, 299.

**Table 2.** Predicted Thermochemistry<sup>a</sup> for the  $\sigma$ -Bond Metathesis Reaction  $Sc(R)^+ + R'H \rightarrow Sc(R')^+ + RH$ 

R	R'				
	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>
CH <sub>3</sub>	0.0	1.0 <sup>b</sup>	-4.2	1.9	2.2
C <sub>2</sub> H <sub>5</sub>	-1.0 <sup>c</sup>	0.0	-5.2	0.9	1.2
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	4.2	5.2	0.0	6.1	6.4
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	-1.9	-0.9	-6.1	0.0	0.3
<i>t</i> -C <sub>3</sub> H <sub>9</sub>	-2.2	-1.2	-6.4	-0.3	0.0

<sup>a</sup> In kilocalories/mole. <sup>b</sup> 1.2 kcal/mol using the extended basis set of ref 14. <sup>c</sup> -1.2 kcal/mol using the extended basis set of ref 14.

C-H bond strength is also 3.7 kcal/mol weaker for C<sub>2</sub>H<sub>6</sub> than for CH<sub>4</sub> (101.0 and 104.7 kcal/mol, respectively).<sup>13</sup> Thus, a metathesis reaction of Sc(CH<sub>3</sub>)<sub>2</sub><sup>+</sup> with C<sub>2</sub>H<sub>6</sub> (reaction 2) should be nearly thermoneutral (endothermic by 1 kcal/mol, as shown in Table 2).<sup>14</sup>



Geometries and MCPF bond energies for the various configurations of ScC<sub>3</sub>H<sub>7</sub><sup>+</sup> are shown in Figure 1c-f. As noted, the bond of Sc<sup>+</sup>-(*n*-C<sub>3</sub>H<sub>7</sub>) is 8.5 kcal/mol stronger than that of Sc<sup>+</sup>-(*i*-C<sub>3</sub>H<sub>7</sub>). This is in contrast to the C-H bonds, which differ only by about 2.4 kcal/mol (101.0 kcal/mol for a primary bond and 98.6 kcal/mol for a secondary bond).<sup>13</sup> Thus, we find that activation of a primary C-H bond (reaction 1a) is *exothermic*

(11) (a) The Sc basis set was derived from the basis set of ref 10 by adding diffuse s ( $\alpha = 0.0106$ ) and d ( $\alpha = 0.0179$ ) functions and contracting the basis to (4s3p3d). To this, an f function ( $\alpha = 0.51$ ) was added. (b) The carbon basis set was (11s7p/5s3p) from Huzinaga and Sakai: Huzinaga, S.; Sakai, Y. *J. Chem. Phys.* 1969, 50, 1371. (c) The hydrogen basis set was (6s/3s) from Dunning: Dunning, T. H. *J. Chem. Phys.* 1971, 55, 855. (d) A single set of polarization functions was added to the carbon ( $\alpha_d = 0.550$ ) and hydrogen ( $\alpha_p = 0.727$ ) basis sets from Dunning: Dunning, T. H. *J. Chem. Phys.* 1989, 90, 1007.

(12) The zero-point correction was estimated as 0.7 kcal/mol for R = CH<sub>3</sub>, 0.5 kcal/mol for R = C<sub>2</sub>H<sub>5</sub> and C<sub>3</sub>H<sub>7</sub>, and 0.4 kcal/mol for R = C<sub>4</sub>H<sub>9</sub>.

(13) (a) Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* 1992, 96, 9847. (b) For a review, see: Berkowitz, J.; Ellison, G. B.; Gutman, D. *Annu. Rev. Phys. Chem.*, in press.

(14) The MCPF bond strength for Sc<sup>+</sup>-CH<sub>3</sub> ( $D_0 = 44.9$  kcal/mol) is smaller than both the experimental value [ $\sim 57.5 \pm 3$  kcal/mol at 0 K from Sunderlin et al. (Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* 1987, 109, 78)] and the current best theoretical estimate ( $D_0 = 52.4$  kcal/mol from ref 5). Using a more extended basis set [Sc, (4s3p3d2f); C, (6s4p3d1f); H, (3s2p)], the Sc<sup>+</sup>-CH<sub>3</sub> bond energy (MCPF level) increases to  $D_0 = 50.5$  kcal/mol while the Sc<sup>+</sup>-C<sub>2</sub>H<sub>5</sub> bond energy increases to 45.6 kcal/mol. The difference between the Sc<sup>+</sup>-CH<sub>3</sub> and Sc<sup>+</sup>-C<sub>2</sub>H<sub>5</sub> bond energies changes by only 0.2 kcal/mol, suggesting that the smaller basis set is sufficient for obtaining accurate ( $\pm 1$  kcal/mol) relative bond strengths.

by 4 kcal/mol whereas activation of a secondary C-H bond (reaction 1b) is *endothermic* by 2 kcal/mol. This dramatic difference in the thermochemistry provides an explanation for the >90% selectivity of primary C-H bond activation over secondary C-H bond activation observed experimentally.<sup>1</sup>

The results for R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, and *t*-C<sub>4</sub>H<sub>9</sub> suggest that the Sc<sup>+</sup>-R bond strengths decrease as methyl > primary > secondary > tertiary, correlating with the electron affinities of the radicals. This is appropriate, as Mulliken populations indicate that charge is transferred from the metal to the ligand. This total charge transfer is approximately the same for all ligands (0.17 electron for R = CH<sub>3</sub> and 0.16 electron for R = C<sub>2</sub>H<sub>5</sub>); however, the resulting negative charge on the  $\alpha$ -carbon varies extensively (-0.70 for R = CH<sub>3</sub> and -0.63 for R = C<sub>2</sub>H<sub>5</sub>). This negative charge leads to an electrostatic attraction between the ligand and the cationic metal, which is consistent with the above trend in bond energies.

The results for R = C<sub>2</sub>H<sub>5</sub> and *n*-C<sub>3</sub>H<sub>7</sub> suggest that the Sc<sup>+</sup>-R bond strengths increase with the size of the ligand. This trend is related to the polarizability of the ligand and the ability of the ligand to solvate the ion. As a result, there is an increase of 5.2 kcal/mol in the bond strength between Sc<sup>+</sup>-C<sub>2</sub>H<sub>5</sub> and Sc<sup>+</sup>-(*n*-C<sub>3</sub>H<sub>7</sub>). The energy of Sc<sup>+</sup>-(*n*-C<sub>3</sub>H<sub>7</sub>), in particular, depends dramatically on the configuration of the ligand. Principally, these differences arise from the electrostatic interaction between Sc<sup>+</sup> and the  $\beta$ -methyl of the *n*-propyl ligand. The most stable configuration of Sc<sup>+</sup>-(*n*-C<sub>3</sub>H<sub>7</sub>) is the gauche conformer (Figure 1e), in which the  $\beta$ -methyl coordinates to the metal. This is 3.3 kcal/mol more stable than the trans conformer (Figure 1c), indicating the relative strength of this interaction. Indeed, the second most stable configuration involves an *eclipsed* 1,2-C-C bond of the propyl ligand (Figure 1d). This configuration is only 0.5 kcal/mol higher in energy than the gauche conformer as the cost of eclipsing the C-C bond is offset by the more favorable ion induced dipole interaction with the  $\beta$ -methyl group.

In summary, the observed chemistry of reaction 1 can be readily explained by the trends in the pertinent Sc<sup>+</sup>-alkyl bond strengths. These trends are strongly dependent on the cationic and electropositive nature of the metal.

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