ICl(aq) and I⁻. Hence, the absence of a hydrolysis path in the previous study[8] is verified.

Conclusion

The hydrolysis of iodine monochloride in water is 5–6 orders of magnitude faster than that of Cl_2 and I_2. The difference is attributed to the dipole moment and polarizability of ICl and to the ease of valence shell expansion of iodine. This leads to the formation of ICl molecular complexes with H_2O, OH⁻, and buffers.

We propose that both ICl and H_2OICl exist in aqueous solution and that the reaction with ICl to form molecular complexes is diffusion controlled. Hydroxide ion has a dual role in the hydrolysis of ICl(aq). It can directly attack ICl to give HOICl⁻, and it can deprotonate H_2OICl to give HOICl⁻. The HOICl⁻ intermediate rapidly loses Cl⁻ to give HOI.

Organo-f-Element Thermochemistry. Absolute Metal–Ligand Bond Disruption Enthalpies in Bis(pentamethylcyclopentadienyl)samarium Hydrocarbyl, Hydride, Dialkylamide, Alkoxide, Halide, Thiolate, and Phosphide Complexes. Implications for Organolanthanide Bonding and Reactivity

### Steven P. Nolan, David Stern, and Tobin J. Marks*

Contribution from the Department of Chemistry, Northwestern Univeristy, Evanston, Illinois 60201-3113. Received February 8, 1989

Abstract: Absolute samarium–ligand bond disruption enthalpies in the series $Cp'_2Sm–R/X$ ($Cp' = \eta^5$-$(CH_3)_5C_5$) have been measured by iodinolytic and alcoholytic isoperibol titration calorimetry of $Cp'_2Sm/(Cp'_2Sm–I)_n$, $(Cp'_2Sm–O^tBu)_2/Cp'_2Sm–R/X$ ensembles in toluene. Derived $D(Cp'_2Sm–R/X)$ values in toluene solution are as follows (kcal/mol, R/X): 47.0 (1.5), $CH(SiMe_3)_2$; 45.0 (1.5), η^3-C_3H_5; 93.2, CCPh; 54.2 (3.0), H; 48.2 (1.8), NMe_2; 82.4 (3.5), O^tBu; 81.3 (1.0), $OCH(^tBu)_2$; 97.1 (3.0), Cl; 83.6 (1.5), Br; 69.4 (2.4), I; 73.4 (2.4), S^nPr; 32.6 (2.0), PEt_2. $D(Cp'_2Sm–THF)$ and $D(Cp'_2Sm(THF)–THF)$ values were also determined in toluene and are 7.3 (0.4) and 4.9 (1.0) kcal/mol, respectively, while $D(Cp'_2Sm(THF)–I)$ was found to be 72.7 (2.9) kcal/mol. The observed $D(Sm–halogen)$ parameters are close to the D_1 values of the corresponding samarium trihalides. Important trends in $D(Cp'_2Sm–R/X)$ include a relatively small value of $D(Sm–H) – D(Sm–alkyl)$, a large value of $D(Sm–I) – D(Sm–alkyl)$, and generally strong bonds to group 15 and group 16 ligands. A variety of Sm-centered ligand transposition and oxidative addition/reductive elimination processes are analyzed in light of the present data. The formation of strong Sm–heteroelement bonds makes an important contribution to the driving force. Hydrocarbon functionalization via dinuclear Sm(II) → Sm(III) oxidative addition processes is only expected to be exothermic in special cases.

Recent developments in organometallic thermochemistry have demonstrated the considerable insight into bonding and reaction chemistry that metal–ligand bond disruption enthalpy (eq 1 for

$$D(L_nM–R) = \Delta H_f°(L_nM) + \Delta H_f°(R^\bullet) – \Delta H_f°(L_nM–R) \quad (1)$$

$$L_n = \text{ancillary ligands}$$

$$L_nM–R \rightarrow L_nM + R^\bullet \quad (2)$$
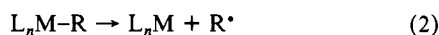
the adiabatic, homolytic process of eq 2) information can provide.[1,2] In the solution phase, *relative* metal–ligand bond enthalpies have been obtained by equilibration or various calorimetric techniques[1,2] and have shed considerable light on bonding patterns and the

driving forces for important reactions. *Absolute* metal–ligand bond enthalpies provide, in addition, an absolute quantitation of the energetics of eq 2 and a means of comparing bond enthalpies for different M and L_nM centers. Relative metal–ligand enthalpies can be placed on an approximately absolute scale by judicious choice of a reference ("anchor") point, such as the corresponding $D_1(MX_n)$ datum for an L_nMR/L_nMX series.[3,4] However, this approximation assumes aspects of transferability that may not always be general and certainly warrants further scrutiny. Direct measurements of absolute metal–ligand bond enthalpies have included kinetic,[2c,h,5] photoacoustic,[2j,6] laser pyrolytic,[7] two-electron

(1) Marks, T. J., Ed. Metal–Ligand Bonding Energetics in Organotransition Metal Compounds. *Polyhedron Symposium-in-Print* **1988**, 7.

(2) For some leading references, see also: (a) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal–Carbon Bond*; Harley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 43–90. (b) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71–110. (c) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238–244. (d) Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1983**, *47*, 204–238. (e) Mansson, M. *Pure Appl. Chem.* **1983**, *55*, 417–426. (f) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79–88. (g) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41–59. (h) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41–48. (i) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456. (j) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergram, R. G.; Yang, G. K.; Peters, K. G. *J. Am. Chem. Soc.* **1987**, *109*, 3143–3145, and references therein. (k) Dias, A. R.; Salema, M. S.; Martinho-Simoes, J. A. *J. Organomet. Chem.* **1981**, *222*, 69–78.

(3) (a) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715. (b) Dias, A. R.; Simoes, J. A. M. In ref 1, pp 1531–1544. (c) Lappert, M. F.; Patil, D.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830–831.
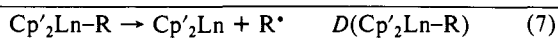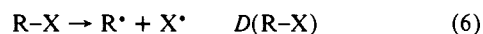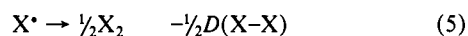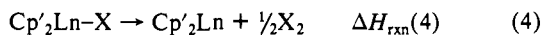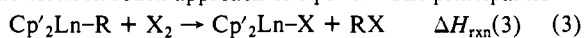
(4) (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832. (b) Sonnenberger, D. C.; Morss, L. R.; Marks, T. J. *Organometallics* **1985**, *4*, 352–355. (c) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275–7280, and ref 4. (d) Lin, Z. Ph.D. Thesis, Northwestern University, Evanston, IL, December 1988, Appendix A ($D(Th–S^nPr) = 105$ (5) kcal/mol).

(5) (a) Halpern, J. In ref 1, pp 1483–1490. (b) Hay, B. P.; Finke, R. G. In ref 1, pp 1469–1481. (c) Koenig, T. W.; Hay, B. P.; Finke, R. G. In ref 1, pp 1499–1516. (d) Wayland, B. B. In ref 1, pp 1545–1555. (e) Geno, M. K.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1052–1053.
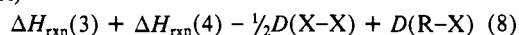
(6) (a) Yang, G. K.; Vaida, V.; Peters, K. S. In ref 1, pp 1619–1622. (b) Rothberg, L. J.; Simon, J. D.; Bernstein, M.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 3464–3470.

Organo-f-element Thermochemistry

J. Am. Chem. Soc., Vol. 111, No. 20, 1989 7845

redox,[2d,j,8] and one-electron redox approaches.[9] Each technique has intrinsic strengths and limitations, which indicate that none is likely to have universal applicability.

In the present contribution, we focus on determining absolute and relative metal–ligand bond disruption enthalpies in an archetypical bis(pentamethylcyclopentadienyl) organolanthanide[10] series—that of samarium.[11] Such Cp'_2Ln/Cp'_2LnR complexes exhibit a rich and distinctive organometallic/catalytic chemistry featuring many fascinating reaction patterns.[9b,10,12–15] The redox characteristics of the Ln = Sm system offer, in addition, the opportunity to determine absolute Cp'_2Ln–R bond enthalpies via the one-electron redox approach of eq 3–8. The principal issues

$$Cp'_2Ln-R + X_2 \rightarrow Cp'_2Ln-X + RX \qquad \Delta H_{rxn}(3) \qquad (3)$$

$$Cp'_2Ln-X \rightarrow Cp'_2Ln + \tfrac{1}{2}X_2 \qquad \Delta H_{rxn}(4) \qquad (4)$$

$$X^\bullet \rightarrow \tfrac{1}{2}X_2 \qquad -\tfrac{1}{2}D(X-X) \qquad (5)$$

$$R-X \rightarrow R^\bullet + X^\bullet \qquad D(R-X) \qquad (6)$$

$$Cp'_2Ln-R \rightarrow Cp'_2Ln + R^\bullet \qquad D(Cp'_2Ln-R) \qquad (7)$$

$$D(Cp'_2Ln-R) =$$
$$\Delta H_{rxn}(3) + \Delta H_{rxn}(4) - \tfrac{1}{2}D(X-X) + D(R-X) \quad (8)$$

addressed herein include the magnitudes of D for important metal–ligand bonds, ancillary ligand effects, and the transferability of bond enthalpies from one metal environment to another, as well as insights into unusual known and hypothetical Sm-centered transformations. In the process, we also report the synthesis and characterization of a number of new organosamarium complexes.

Experimental Section

General Considerations. Manipulations of organolanthanide complexes were carried out under an atmosphere of argon using standard high-vacuum techniques, or in a Vacuum/Atmospheres glovebox. Solvents used were predried and freshly distilled from Na/K alloy. The toluene

used in the calorimetric measurements was additionally stored over Na/K alloy and vacuum transferred immediately prior to use. ^{1}H NMR spectra were recorded on a JEOL FX-90 (FT, 90-MHz) or on a Varian XL-400 (FT, 400-MHz) spectrometer. Infrared spectra were recorded on Nujol mulls sandwiched between KBr plates by use of a Perkin-Elmer Model 283 spectrophotometer. They were calibrated with polystyrene film. Metal analyses were performed by direct EDTA complexometric titration.[16] Cryoscopic molecular weight determinations were carried out in benzene solution using a modified Knauer type 24.00 instrument calibrated with Cp'_2ThMe_2. Elemental analyses were carried out at Dornis and Kolbe Microanalytical Laboratory, Mulheim, West Germany.

Syntheses. All organolanthanide compounds are exceedingly air- and moisture-sensitive. The following organosamarium complexes were synthesized by using reported synthetic procedures: Cp'_2Sm[13b,c] (1), $Cp'_2Sm(THF)_2$[17] (5), $(Cp'_2SmH)_2$[15b] (7), $Cp'_2SmCH(SiMe_3)_2$[15b] (8), $[Cp' = \eta^5-(CH_3)_5C_5]$. Diethylphosphine (Strem) was dried over a small piece of sodium, subsequently stored over freshly activated Davison 4-A molecular sieves, and subjected to several freeze–pump–thaw degassing cycles. Dimethylamine (Matheson) was condensed into a storage tube containing sodium pieces, then freeze–pump–thaw degassed, stored over Davison 4-A molecular sieves, and delivered from a calibrated gas bulb. N-Amyl chloride (Aldrich) and n-butyl bromide (Aldrich) were dried over successive portions of activated molecular sieves, freeze–pump–thaw degassed, and vacuum distilled prior to use. Phenylacetylene (Aldrich) was dried over successive portions of molecular sieves, subjected to a series of freeze–pump–thaw degassing cycles, and vacuum distilled immediately prior to use. The reagent $^tBu_2CHOH$ was prepared[18] from di-tert-butyl ketone (Aldrich) and vacuum sublimed prior to use. Also subjected to vacuum sublimation prior to use were the reagents tert-butyl alcohol (sublimed from molecular sieves) and iodine.

$Cp'_2Sm(\eta^3-C_3H_5)$ (9). Compound 9 was prepared in a matter analogous to the reported lanthanum and neodymium allyl complexes.[15b] A 50-mL flask was charged with 0.600 g (0.711 mmol) of $(Cp'_2SmH)_2$ (7). Next, 40 mL of pentane was vacuum transferred into the flask at −78 °C. At this temperature, an excess of purified propylene was condensed into the reaction vessel. The solution was then allowed to stir at 0 °C for 8 h. All volatiles were next removed in vacuo, and 30 mL of pentane was used to extract 9. After filtration, the flask containing the orange-brown solution was slowly cooled with a dry ice/acetone slurry. Compound 9 was isolated as reddish-brown crystals by cold filtration: 0.510 g, 78.9% yield; IR (Nujol, cm^{-1}) 2900 (s), 2735 (w), 1543 (m), 1565 (s), 1380 (s), 1300 (w), 1250 (w), 1240 (m), 1020 (m), 805 (w), 772 (s), 727 (s), 672 (m), 592 (s); ^{1}H NMR (400 MHz, C_6D_6) δ 15.55 (s, 2 H, line width (lw) = 48 Hz), 7.19 (s, 1 H, lw = 24 Hz), 3.39 (s, 2 H, lw = 48 Hz), 1.20 (s, 15 H, lw = 48 Hz), 0.96 (s, 15 H, lw = 48 Hz). Anal. Calcd for $C_{23}H_{35}Sm$: C, 59.68; H, 7.76. Found: C, 59.80; H, 7.64.

Cp'_2SmNMe_2 (10). A 25-mL flask was charged with compound 7 (0.793 g, 0.94 mmol). While maintaining the flask at −78 °C, 15 mL of pentane was condensed onto the orange solid. Dimethylamine (485 Torr, 24 °C, 0.898 mmol) was then admitted to the flask. During the stirring of this suspension at −78 °C, the pressure in the flask began to rise (H$_2$ evolution) as the solid dissolved. The reaction mixture was stirred at this temperature for 15 min, then slowly warmed to 0 °C, and stirred an additional 15 min. The clear, bright reddish-orange solution was then filtered at room temperature, reduced in volume to 7 mL, and slowly cooled to −78 °C. Crystallization in this manner, followed by cold filtration afforded orange microcrystals of 10: 0.952 g, 60% isolated yield; IR (Nujol, cm^{-1}) 2920 (vs), 2720 (s), 1452 (s), 1378 (s), 1305 (w), 1253 (m), 1240 (m), 1156 (m), 1139 (m), 1018 (m), 925 (m), 858 (s), 824 (m), 754 (w), 720 (w), 682 (w), 660 (w), 630 (w), 610 (w), 577 (m), 465 (w); ^{1}H NMR (400 MHz, C_6D_6) δ 0.41 (s, 30 H, lw = 6 Hz), −7.35 (s, 6 H, lw = 46 Hz). Anal. Calcd for $C_{22}H_{36}NSm$: Sm, 32.3. Found: Sm, 31.8. The Nd analogue is monomeric by cryoscopy in benzene.[19]

$(Cp'_2SmO^tBu)_2$ (3). In the glovebox, 0.250 g (0.296 mmol) of 7 was loaded into a 25-mL flask fitted with a Teflon valve sidearm. At −78 °C, 25 mL of toluene was condensed onto the solid, then under an argon flush, a solution of tert-butyl alcohol (2.98 mL of a 0.1992 M solution in toluene; 0.296 mmol) was syringed onto the suspension. Gas (H$_2$) evolution was evident immediately upon addition of the alcohol. The orange-yellow solution was stirred for 15 min at −78 °C and then an additional 15 minutes at room temperature to ensure completion of the reaction. The solvent was then removed in vacuo, the resulting solids were extracted with pentane (10 mL), and the filtrate volume was re-

(7) Smith, G. P. In ref 1, pp 1605–1608.

(8) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. In ref 1, pp 1429–1440.

(9) (a) Schock, L. E.; Seyam, A. M.; Marks, T. J. In ref 1, pp 1517–1530. (b) Marks, T. J.; Gagné, M. R.; Nolan, S. P.; Schock, L. E.; Seyam, A. M.; Stern, D. *Pure Appl. Chem.*, in press.

(10) For leading references, see: (a) Forsberg, J. H.; Moeller, T. In *Gmelin Handbook of Inorganic Chemistry*; Moeller, T., Kmerke, Y., Schleitzer-Rust, E., Eds.; Springer: Berlin, 1983; pp 137–303. (b) Schumann, H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalá, I., Eds.; D. Reidel: Dordrecht, Holland, 1985; Chapter 1. (c) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131–177. (d) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (e) Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Chapter 50. (f) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, Chapter 21. (g) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51–107.

(11) Communicated in part: Nolan, S. P.; Stern, D.; Marks, T. J. *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA; American Chemical Society: Washington, DC, 1988; INOR 378.

(12) (a) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853–5855. (b) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915–917. (c) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 941–942. (d) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Green, J. C.; Hohl, D.; Rosch, N. *J. Chem. Soc., Chem. Commun.* **1986**, 405–407. (e) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49–C52.

(13) (a) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432, and references therein. (b) Evans, W. J. *Polyhedron* **1987**, *6*, 803–835. (c) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 3928–3936. (d) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272. (e) Evans, W. J.; Bloom, I.; Hunter, W. G.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403.

(14) (a) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1986**, *5*, 598–601. (b) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1987**, *6*, 1356–1358.

(15) (a) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200–202. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (c) Jeske, C.; Schock, L. E.; Mauermann, H.; Sweptston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118. (e) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109.

(16) Quiang, C.; Ye, C.; Lu, H.; Li, Y.; Zhou, J.; Tsutsui, M. *J. Organomet. Chem.* **1983**, *247*, 151–170.

(17) Evans, W. J.; Grate, J. W.; Chei, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

(18) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051–7064.

(19) Hedden, D.; Marks, T. J., unpublished results.

duced to ca. 3 mL. Overnight cooling at −78 °C followed by cold filtration yielded 95 mg (35% isolated yield) of orange-yellow microcrystalline compound: IR (Nujol, cm^{-1}) 2920 (vs), 2735 (w), 1890 (w), 1732 (w), 1672 (w), 1460 (s), 1380 (s), 1357 (m), 1260 (w), 1220 (m), 1195 (s), 1020 (m), 980 (s), 918 (w), 805 (w), 775 (m), 722 (w), 600 (w), 500 (m), 470 (m); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 5.00 (sa, 9 H, lw = 7 Hz), 0.55 (s, 30 H, lw = 7 Hz). Anal. Calcd for C$_{48}$H$_{78}$O$_2$Sm$_2$: Sm, 30.4; MW, 987.84. Found: Sm, 30.2; MW, 990 (cryoscopic in benzene).

Cp′$_2$SmOCH^{t}Bu$_2$ (15). Compound **15** was prepared in a manner similar to (Cp′$_2$SmO^{t}Bu)$_2$ by using 0.210 g (0.249 mmol) of **7** and ^{t}Bu$_2$CHOH^{18} (2.49 mL of a 0.200 M solution in toluene; 0.249 mmol). Crystallization of the product from cold pentane followed by cold filtration afforded 0.172 g (62% isolated yield) of a yellowish, microcrystalline solid: IR (Nujol, cm^{-1}) 2722 (m), 1560 (w), 1158 (m), 950 (w), 755 (m), 715 (m), 642 (s); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 8.14 (s, 1 H, lw = 16 Hz), 0.67 (s, 15 H, lw = 6 Hz), 0.61 (s, 15 H, lw = 6 Hz), 0.44 (s, 18 H, lw = 12 Hz). Anal. Calcd for C$_{29}$H$_{49}$OSm: Sm, 26.6; MW, 564.06. Found: Sm, 26.3; MW, 605 (cryoscopic in benzene).

(Cp′$_2$SmCl)$_3$ (12). A 25-mL flask fitted with a Teflon sidearm was charged with 0.275 g (0.326 mmol) of **7**. On the vacuum line, 15 mL of toluene was condensed onto the solid. While the flask was maintained at −78 °C, n-amyl chloride (2.95 mL of a 0.211 M solution in toluene) was added under an argon flush. The reaction mixture was briefly stirred at this temperature and was then allowed to warm to room temperature over a period of 45 min. At ca. −20 °C, the solution turned to a reddish-rust color. The solvent was then removed in vacuo, the solid residue slurried in pentane (10 mL), and the solution filtered. The product was washed with pentane (2 × 5 mL) and dried under vacuum to yield 0.215 g (72.1% isolated yield) of a maroon microcrystalline compound: IR (Nujol, cm^{-1}) 1270 (m), 1150 (br), 1025 (s), 732 (s); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 0.38 (s, 30 H, lw = 7 Hz). Anal. Calcd for C$_{60}$H$_{90}$Cl$_3$Sm$_3$: Sm, 33.0. Found: Sm, 32.6.

(Cp′$_2$SmBr)$_n$ (13). Compound **13** was synthesized in an analogous manner to **12** by using 0.275 g (0.326 mmol) of **7** and n-butyl bromide (3.47 mL of a 0.876 M solution in toluene; 0.652 mmol). The reddish-rust compound was collected by filtration: 0.262 g, 80% isolated yield; IR (Nujol, cm^{-1}) 1270 (m), 1090 (w), 1025 (s), 735 (s); ^{1}H NMR (400 MHz, CD$_6$Cl$_2$) δ 0.43 (s, 30 H, lw = 8 Hz). Anal. Calcd for C$_{20}$H$_{30}$BrSm: Sm, 30.0. Found: Sm, 29.6. This compound was insufficiently soluble for cryoscopy.

(Cp′$_2$SmI)$_n$ (2). By use of the same synthetic procedure as in the samarium chloride **12**, 0.275 g (0.326 mmol) of **7** and a solution of I$_2$ in toluene (0.0608 M, 5.36 mL) were reacted. Gas evolution was clearly evident during the addition, and the reaction appeared to proceed more rapidly than for the other halogenation reactions. The reaction yielded 0.198 g (57% isolated yield) of a purplish compound: IR (Nujol, cm^{-1}) 1265 (s), 1100 (w), 1025 (s), 805 (s); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 0.52 (s, 30 H, lw = 13 Hz). Anal. Calcd for C$_{20}$H$_{30}$ISm: Sm, 27.4. Found: Sm, 27.3. This compound was insufficiently soluble for cryoscopy.

[Cp′$_2$SmS(^{n}Pr)]$_2$ (4). A 50-mL flask fitted with a Teflon sidearm valve was charged with 0.200 g (0.237 mmol) of **7**. After the addition of pentane (20 mL) to the flask, the suspension was stirred at −78 °C while a solution of 1-propanethiol (2.61 mL of a 0.1816 M solution in toluene) was syringed into the reaction vessel under an argon flush. The reaction was stirred at this temperature for 15 min and then warmed to room temperature, where it was allowed to stir an additional 25 min. The orange solution was then cold filtered at 0 °C and the residue twice washed with 5 mL of cold pentane to yield 0.160 g (68% isolated yield) of a powdery orange solid: IR (Nujol, cm^{-1}) 2900 (s), 1460 (s), 1380 (s), 1262 (m), 1230 (m), 1090 (m), 1020 (m, br), 815 (w), 800 (m), 724 (w); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.77 (s, 30 H, lw = 13 Hz), −4.56 (t, 3 H, $^3J_{HH}$ = 6.4 Hz), −9.55 (s, 3 H, lw = 23 Hz), −10.41 (s, 2 H, lw = 20 Hz). Anal. Calcd for C$_{46}$H$_{74}$S$_2$Sm$_2$: C, 55.69; H, 7.52; MW, 992.02. Found: C, 55.56; H, 7.57; MW, 970 (cryoscopic in benzene).

Cp′$_2$SmPEt$_2$ (14). This complex was synthesized in a manner similar to the thiolate (**4**) by using 0.400 g (0.474 mmol) of **7** and 4.66 mL of a 0.2035 M solution of diethylphosphine (0.474 mmol) in toluene. Upon slow cooling, a brown microcrystalline precipitate formed and 0.300 g (62% isolated yield) of **14** was collected by cold filtration: IR (Nujol, cm^{-1}) 2930 (vs), 2880 (vs), 1460 (s), 1375 (s), 1300 (w), 1258 (m), 1090 (m, br), 1018 (m, br), 800 (m), 720 (w), 603 (w); ^{1}H NMR (400 MHz, toluene-d$_8$) δ 1.32 (s, 30 H, lw = 29 Hz), 0.04 (s, 4 H, lw = 5 Hz), −0.29 (s, 6 H, lw = 6 Hz). Anal. Calcd for C$_{24}$H$_{40}$PSm: Sm, 29.5. Found: Sm, 29.3. We assume this complex to be monomeric on the basis of results for the related complex (MeC$_5$H$_4$)$_2$SmPPh$_2$.^{27b}

(Cp′$_2$SmCCPh)$_2$ (11). A 25-mL flask with a Teflon valve sidearm was charged with 0.431 g (0.74 mmol) of **8**. On the vacuum line, 15 mL of pentane was condensed onto the solid. Under a flush of argon, 82 μL (0.74 mmol) of phenylacetylene was then syringed into the suspension.

The reaction flask was then allowed to warm to 0 °C over a period of 20 min, during which time a reddish-brown solid precipitated from solution. The reaction was stirred at this temperature for an additional 20 min and then 30 min more at room temperature to ensure completion of the reaction. The solvent was next removed in vacuo and the residue dissolved in 15 mL of warm (50 °C) toluene, slowly cooled to −15 °C, and cold filtered. This workup yielded 0.30 g (77% isolated yield) of brick-red Cp′$_2$SmCCPh (**10**): IR (Nujol, cm^{-1}) 2900 (vs), 1592 (w), 1510 (w), 1460 (s), 1379 (s), 1300 (w), 1262 (m), 1152 (w), 1100 (m, br), 1020 (s), 801 (m), 758 (m), 690 (m), 622 (w), 590 (w); ^{1}H NMR (400 MHz, toluene-d$_8$) δ 5.26 (t, 2 H, J_{HH} = 7.4 Hz), 3.87 (t, 8 H, J_{HH} = 6.0 Hz), 2.12 (s, 2 H), 1.36 (s, 30 H). Anal. Calcd for C$_{96}$H$_{130}$Sm$_2$: Sm, 28.8; MW, 1043.88. Found: Sm, 28.4; MW, 1004 (cryoscopic in benzene).

Calorimetric Measurements. All calorimetric measurements were performed with a Tronac Model 450 isoperibol titration calorimeter, which was extensively modified to permit the study of exceedingly air- and moisture-sensitive materials. The system has been described elsewhere.^{3a,20} In a typical experiment, glass ampules were charged in the glovebox with carefully weighed amounts of organosamarium complex. The ampules were then sealed with Ultra Torr fittings, removed from the glovebox, and inserted into the calorimeter reaction Dewar. The reaction Dewar, solvent bulb, and titrant bulb were then fixed to the calorimeter. The entire system, which is connected to a high-vacuum line, was then subjected to a series of evacuation and argon back-fill cycles to ensure that no oxygen or water was present in the system. The toluene was then introduced into the reaction vessel from an attached storage bulb and stirring was initiated. The reaction vessel and attached titrant storage bulb components of the system were then lowered into a 25 °C constant-temperature (±0.001 °C) bath and the system was allowed to equilibrate thermally. With the system now resting under an argon blanket and having equilibrated at 25 °C, a series of electrical/thermal calibrations was performed. The organosamarium complexes were then allowed to dissolve in the toluene by sequentially breaking each ampule with a metal anvil attached to the stirrer. This allowed the measurement of heats of solution of the organosamarium complexes. The motor-driven, titrant-filled buret was then activated and the enthalpies of reaction for a series of titrations were recorded until the organosamarium species in solution had been completely expended. The knowledge of the buret delivery rate (calibrated) and of the titrant molarity allows internal verification of the reaction stoichiometry. Such an analysis also tests for the presence of trace contaminants. The detection of sharp end points for each titration involving the present organosamarium compounds additionally verifies the rapid reaction kinetics observed during NMR titration experiments (vide infra). A second series of electrical/thermal calibrations was performed after reaching the end of the titration reaction sequence, and the average of the two sets of calibrations was used to calculate the chemical heat evolved during each individual titration. Enthalpies of reaction reported are the average of 20–30 individual titrations. Uncertainties reported for ΔH_{soln} and ΔH_{rxn} are 95% confidence limits (3σ),^{21} and uncertainties in derived D(Sm–R/X) values include these uncertainties plus reported uncertainties in literature parameters used to calculate D(Sm–R/X).

^{1}H NMR Titration Experiments. Prior to every calorimetric experiment, a known amount of the organosamarium complex of interest was weighed into a Wilmad screw-capped NMR tube fitted with a septum, and C$_6$D$_6$ was subsequently added. This solution was titrated with standard solutions of the titrant of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The titrations were monitored by ^{1}H NMR and the reactions were found to be rapid, clean, and quantitative, a condition necessary for accurate and meaningful calorimetric results. These criteria were satisfied for all organosamarium reactions investigated.

Results

We begin this section with a discussion of anaerobic Cp′$_2$Sm isoperibol calorimetry relevant to establishing absolute samarium–ligand enthalpies (cf. eq 3–8) for several Cp′$_2$Sm–X thermodynamic anchor points. These data and the results of correlated Cp′$_2$Sm–R/X calorimetry then establish absolute D(Cp′$_2$Sm–R/X) values for a varied series of R/X ligands. This approach deliberately incorporates a number of internal self-consistency checks. We also report the synthesis and characterization of several new types of Cp′$_2$LnR/X complexes where R/X = dialkylamide, alkylthiolate, and dialkylphosphide.

(20) Schock, L. E.; Marks, T. J., manuscript in preparation.
(21) Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I. *Experiments in Physical Chemistry*, 3rd ed.; McGraw-Hill: New York, 1974; pp 27–58.

Table I. Enthalpy of Solution, Enthalpies of Reaction of Cp'_2Sm (1) and $Cp'_2Sm(THF)_2$ (5) with Various Titrants in Toluene, and Derived Absolute Sm–X Bond Disruption Enthalpies

compound	$\Delta H_{soln}{}^a$	titrant	$-\Delta H_{rxn}{}^{a,b}$	$D(Sm-R/X)^{a,b}$	R/X
Cp'_2Sm (1)	4.7 (0.2)	I_2	102.4 (2.4)	69.4 (2.4)	I
		$^tBuOO^tBu$	127.3 (2.5)	82.4 (3.5)	O^tBu
		$^nPrSS^nPr$	72.9 (1.2)	73.4 (2.4)	S^nPr
		THF (1)^c	7.3 (0.4)	7.3 (0.4)	THF (1)
		THF (2)^c	4.9 (1.0)	4.9 (1.0)	THF (2)
$Cp'_2Sm(THF)_2$ (5)^d	4.1 (0.3)	I_2	105.4 (1.5)	72.7 (2.9)	I

^{a} Per mole of titrant (in kcal/mol). ^{b} Values in parentheses are 95% confidence limits (3σ). ^{c} Numbers in parentheses refer to the first and second equivalent of THF added to complex 1. ^{d} Reaction product is $Cp'_2Sm(THF)I$ (6).

Table II. Enthalpies of Solution, Enthalpies of Reaction of $Cp'_2Sm–R/X$ Compounds with Various Titrants in Toluene, and Derived Sm–R/X Bond Disruption Enthalpies

compound	$\Delta H_{soln}{}^a$	titrant	$-\Delta H_{rxn}{}^{a,b}$	$D(Sm-R/X)^{a,b}$	R/X
$(Cp'_2Sm-H)_2$ (7)	5.5 (0.3)	I_2	104.8 (1.5)	52.4 (2.0)	H
		^tBuOH	24.6 (0.5)	56.8 (3.0)	H
$Cp'_2Sm-CH(SiMe_3)_2$ (8)	3.4 (0.2)	I_2	40.5 (0.9)	46.0 (1.8)	$CH(SiMe_3)_2$
		^tBuOH	25.2 (0.6)	48.2 (1.5)	$CH(SiMe_3)_2$
$Cp'_2Sm-\eta^3-C_3H_5$ (9)	3.2 (0.2)	^tBuOH	21.8 (1.0)	45.0 (1.5)	$\eta^3-C_3H_5$
$Cp'_2Sm-NMe_2$ (10)	3.0 (0.2)	^tBuOH	24.6 (0.5)	48.2 (1.8)	NMe_2
$(Cp'_2Sm-CCPh)_2$ (11)	3.3 (0.4)	I_2	17.7 (0.4)	93.2^c	CCPh

^{a} Per mole of titrant (in kcal/mol). ^{b} Quantities in parentheses are 95% confidence limits (3σ, see text). ^{c} $D(PhCC-I)$ estimated by using eq 21. Confidence limit not estimated.

$(Me_5C_5)_2Sm$ Calorimetry. Thermodynamic Anchor Points.
Cp'_2Sm (1) reacts rapidly and quantitatively with I_2 in toluene as shown in eq 9 to yield iodo complex 2. From this reaction

$$Cp'_2Sm + I_2 \rightarrow 1/n(Cp'_2SmI)_n \qquad (9)$$
$$\quad 1 \qquad\qquad\qquad 2$$
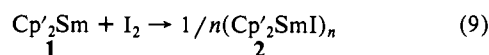
enthalpy and the known BDE for I_2,[22] an absolute $D(Cp'_2Sm-I)$ in this compound of 69.4 (2.4) kcal/mol is derived. The molecularity of complex 2 in solution is unknown since it is insufficiently soluble for cryoscopy. Judging from crystallographic results for related lanthanide $(Cp'_2LnX)_n$ complexes where X = halide,[13c,23] 2 is likely a dimer (e.g., A) or trimer (e.g., B) in the
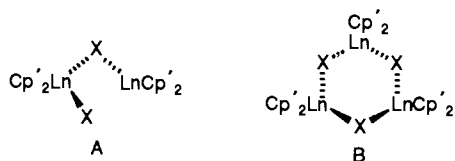
solid state. Several lines of argument (vide infra) strongly suggest that measured $D(Cp'_2Sm-R/X)$ values are not greatly affected by association. The reactions in eq 10 and 11 can similarly be

$$2Cp'_2Sm + {}^tBuOO^tBu \rightarrow (Cp'_2SmO^tBu)_2 \qquad (10)$$
$$\quad 1 \qquad\qquad\qquad\qquad 3$$

$$2Cp'_2Sm + {}^nPrSS^nPr \rightarrow (Cp'_2SmS^nPr)_2 \qquad (11)$$
$$\quad 1 \qquad\qquad\qquad\qquad 4$$
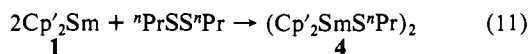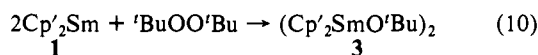
used, in combination with tabulated $D(RO-OR)$[24] and $D(RS-SR)$[25] data, to calculate $D(Cp'_2Sm-O^tBu)$ and $D(Cp'_2Sm-S^nPr)$ values of 82.4 (3.5) and 73.4 (2.0) kcal/mol, respectively (Table I). This $D(Cp'_2Sm-alkoxide)$ value is identical, within experimental error, to that obtained for a related *monomeric* Cp'_2Sm- alkoxide (vide infra). Compounds 3 and 4 were characterized by standard spectroscopic/analytical techniques (see Experimental Section for details); both are found to be dimeric in benzene solution by cryoscopy.
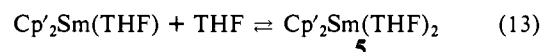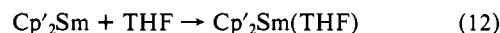
The utility of $Cp'_2Sm(THF)_2$ (5) as a convenient synthetic precursor[13] prompted the calorimetry of eq 12 and 13. A sharp,

$$Cp'_2Sm + THF \rightarrow Cp'_2Sm(THF) \qquad (12)$$

$$Cp'_2Sm(THF) + THF \rightleftharpoons Cp'_2Sm(THF)_2 \qquad (13)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad 5$$

stoichiometrically correct end point is observed in the heat versus equivalents titrant plot for eq 12, and a bond disruption enthalpy of 7.3 (0.4) kcal/mol is derived (Table I). In contrast, the titration plot for eq 13 evidences considerable curvature, and data analysis via a standard iterative numerical procedure[26] yields $D(Cp'_2Sm-(THF)-THF) \approx 4.9$ (1.0) kcal/mol. At these concentration levels, pure $Cp'_2Sm(THF)_2$ is approximately 50% dissociated in toluene.

Titration of complex 5 with I_2 (eq 14) yields the known, monomeric iodo complex 6.[27] From these calorimetric data and the above information on eq 13, a $D(Cp'_2Sm(THF)-I)$ value of 72.7

$$Cp'_2Sm(THF)_2 + \tfrac{1}{2}I_2 \rightarrow Cp'_2Sm(THF)I + THF \qquad (14)$$
$$\quad 5 \qquad\qquad\qquad\qquad\qquad 6$$
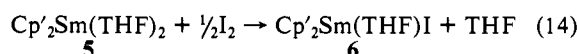
(2.9) kcal/mol is derived (Table I). This result is rather close to the aforementioned value of 69.4 (2.4) kcal/mol for $(Cp'_2SmI)_n$ and argues further that $D(Sm-I)$ is relatively insensitive to bridging interactions and ancillary ligation (it varies by less than 5% in these two compounds).

Calorimetry of $(Me_5C_5)_2Sm-R$ Complexes (R = Hydrocarbyl, Hydride, Dialkylamide). The complexes Cp'_2SmR were synthesized as described in the literature (R = H (7),[15b] $CH(SiMe_3)_2$ (8)[15b]) or by the routes shown in eq 15–17. Synthetic details and

$$(Cp'_2SmH)_2 + \text{[allyl]} \longrightarrow 2Cp'_2Sm(\eta^3-C_3H_5) + 2\text{[propene]} \qquad (15)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad 9$$

$$(Cp'_2SmH)_2 + 2HNMe_2 \rightarrow 2Cp'_2SmNMe_2 + H_2 \qquad (16)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad 10$$

$$Cp'_2SmCH(SiMe_3)_2 + HC{\equiv}CPh \rightarrow$$
$$\tfrac{1}{2}(Cp'_2SmC{\equiv}CPh)_2 + H_2C(SiMe_3)_2 \qquad (17)$$
$$\qquad\qquad\quad 11$$

characterization data are given in the Experimental Section.

(22) (a) Bond enthalpy estimates are calculated by using accepted values for all auxiliary data.[22b–d] (b) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Cleveland, OH, 1981; pp 231–241, and references cited. (c) McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532. (d) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976; p 309.

(23) Rausch, M. D.; Moriarity, K. J.; Atwood, J. L.; Weeks, J. A.; Hunter, W. E.; Brittain, H. G. *Organometallics* **1986**, *5*, 1281–1283.

(24) Baker, G.; Littlefair, L. H.; Shaw, R. *J. Chem. Soc.* **1965**, 6970–6972.
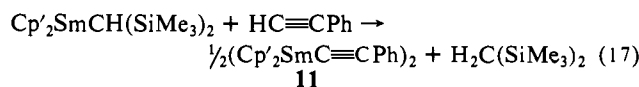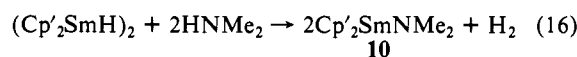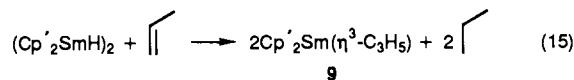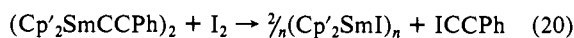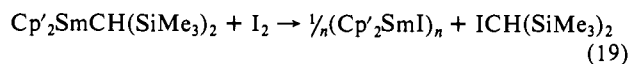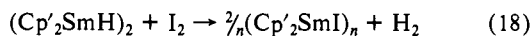
(25) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23–35.

(26) (a) Christensen, J. J.; Izatt, R. M.; Hansen, L. D.; Partridge, J. A. *J. Phys. Chem.* **1966**, *70*, 2003–2010. (b) Eatough, D. J.; Lewis, E. A.; Hansen, L. D. In *Analytical Solution Calorimetry*; Grime, K. J., Ed.; Wiley: New York, 1985; Chapter 5.

(27) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Paterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614–3619.
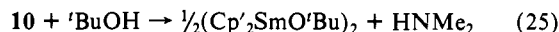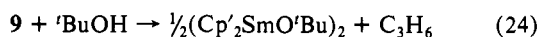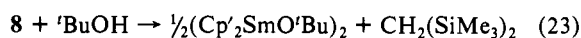
7848 *J. Am. Chem. Soc., Vol. 111, No. 20, 1989*

Nolan et al.

Compound **11** is found to be dimeric in benzene solution (cf. $(Cp_2ErC\equiv C—CMe_3)_2$[28a] and $[(MeC_5H_4)_2SmC\equiv CMe]_2$[28b]), while the neodymium analogue of **10** is known to be monomeric.[19] As monitored by NMR titrations, the reaction of **7, 8,** and **11** with I_2 under calorimetric conditions proceeds rapidly and cleanly, as shown in eq 18–20. Experimental calorimetry data for these

$$(Cp'_2SmH)_2 + I_2 \rightarrow \tfrac{2}{n}(Cp'_2SmI)_n + H_2 \qquad (18)$$

$$Cp'_2SmCH(SiMe_3)_2 + I_2 \rightarrow \tfrac{1}{n}(Cp'_2SmI)_n + ICH(SiMe_3)_2 \qquad (19)$$

$$(Cp'_2SmCCPh)_2 + I_2 \rightarrow \tfrac{2}{n}(Cp'_2SmI)_n + ICCPh \qquad (20)$$

iodinolysis titrations are reported in Table II with 95% confidence limits.[21] For the derivation of D(Sm–R), requisite D(R–I) data are taken from the literature,[22,29] and the reported experimental uncertainties in these data are incorporated in our calculations. In the case of R = CCPh, D(R–I) has not been reported. It was estimated from existing D(R–H) data[22c] by using the proportionality of eq 21.

$$D(R–I)/D(R–H) \approx D(Ph–I)/D(Ph–H) \qquad (21)$$

The other Cp'_2SmR complexes in this series were judged unsuitable for calorimetric investigation using the iodinolysis procedure either because of sluggish reactivity or lack of the proper D(R–I) information. We previously used alcoholysis reactions in calorimetric investigations of organoactinide complexes.[4] The reactivity of the organosamarium complexes **7–10** with *tert*-butyl alcohol was examined by NMR and found to be rapid and quantitative and therefore acceptable for calorimetry (eq 22–25).

$$7 + {}^tBuOH \rightarrow \tfrac{1}{2}(Cp'_2SmO^tBu)_2 + H_2 \qquad (22)$$

$$8 + {}^tBuOH \rightarrow \tfrac{1}{2}(Cp'_2SmO^tBu)_2 + CH_2(SiMe_3)_2 \qquad (23)$$

$$9 + {}^tBuOH \rightarrow \tfrac{1}{2}(Cp'_2SmO^tBu)_2 + C_3H_6 \qquad (24)$$

$$10 + {}^tBuOH \rightarrow \tfrac{1}{2}(Cp'_2SmO^tBu)_2 + HNMe_2 \qquad (25)$$

The absolute D(Cp'_2Sm–I) and D(Cp'_2Sm–O^tBu) parameters obtained from Cp'_2Sm calorimetry (vide supra) can be combined with the analysis of eq 18–25 and appropriate auxiliary data[22,30] to afford absolute Sm–R bond disruption enthalpy data for a broad range of ligands (Table II). It can be seen that the agreement in D(Cp'_2Sm–H) and D[Cp'_2Sm–CH(SiMe$_3$)$_2$] values obtained from iodinolytic and alcoholytic calorimetry (eq 18 and 19, 22 and 23; Table II) evidences good internal consistency. In subsequent discussion, the averages of the two determinations will be used for D(Cp'_2Sm–H) and D[Cp'_2Sm–CH(SiMe$_3$)$_2$].

Calorimetry of $(Cp'_2Sm$–H)$_2$ (7) with Alkyl Halides, Thiols, Phosphines, and Alcohols. The calorimetric titration of hydride **7** with *n*-amyl chloride and *n*-butyl bromide proceeds as shown in eq 26 and 27. Compound **12** has been reported previously.[13c]

$$\tfrac{1}{2}(Cp'_2SmH)_2 + n\text{-}C_5H_{11}Cl \rightarrow \tfrac{1}{3}(Cp'_2SmCl)_3 + C_5H_{12} \qquad (26)$$
$$\mathbf{12}$$

$$\tfrac{n}{2}(Cp'_2SmH)_2 + n\text{-}C_4H_9Br \rightarrow \tfrac{1}{n}(Cp'_2SmBr)_n + C_4H_{10} \qquad (27)$$
$$\mathbf{13}$$

Derived D(Sm–Cl) and D(Sm–Br) values for compounds **12** and **13** are 97.1 (3.0) and 83.6 (1.5) kcal/mol, respectively (Table III). 1-Propanethiol rapidly reacts with **6** affording **4** (eq 28). A

$$\tfrac{1}{2}(Cp'_2SmH) + HS^nPr \rightarrow \tfrac{1}{2}(Cp'_2SmS^nPr)_2 + H_2 \qquad (28)$$
$$\mathbf{4}$$

Table III. Enthalpies of Reactions of $(Cp'_2Sm$–H$)_2$ (**7**) with Various Titrants in Toluene and Derived Sm–R/X Bond Disruption Enthalpies

compound	titrant	$-\Delta H_{rxn}{}^{a,b}$	$D(\text{Sm–R/X})^{a,c}$	R/X
$(Cp'_2SmH)_2$ (**7**)	$n\text{-}C_5H_{11}Cl$	59.9 (1.2)	97.1 (3.0)	Cl
	$n\text{-}C_4H_9Br$	59.4 (1.0)	83.6 (1.5)	Br
	HS^{n}Pr	28.4 (1.0)	70.6 (2.4)	S^{n}Pr
	HPEt$_2$	5.4 (0.4)	32.6 (2.0)	PEt$_2$
	HOCH^{t}Bu$_2$	23.5 (0.8)	81.3 (1.0)	OCH^{t}Bu$_2$

^{a} In kcal/mol. ^{b} Per mole of titrant. Values in parentheses are 95% confidence limits (3σ). ^{c} Based on a D(Sm–H) = 54.2 kcal/mol, the average BDE obtained from alcoholysis and iodinolysis.

$D(Cp'_2Sm$–S$^nPr)$ value of 70.6 (2.4) kcal/mol is calculated[22,29] from the enthalpy of reaction 28. The result of this determination agrees well with the absolute $D(Cp'_2Sm$–S$^nPr)$ value determined from eq 11 (73.4 (2.4) kcal/mol). The samarium hydride **7** also undergoes reaction with HPEt$_2$ in toluene solution to yield Cp'_2SmPEt_2 (**14**) (eq 29), from which a $D(Cp'_2Sm$–PEt$_2)$ value

$$\tfrac{1}{2}(Cp'_2SmH)_2 + HPEt_2 \rightarrow Cp'_2SmPEt_2 + H_2 \qquad (29)$$
$$\mathbf{14}$$
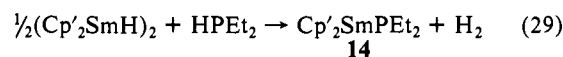
of 32.6 (2.0) kcal/mol is calculated.[22,29] We assume **14** to be monomeric based upon results for $(MeC_5H_4)_2SmPPh_2$.[28b] Titration of **7** with the bulky alcohol $^tBu_2CHOH$ was performed in order to examine the effect on $D(Cp'_2Sm$–OR) of an anticipated monomeric structure (eq 30). Cryoscopic measurements on

$$\tfrac{1}{2}(Cp'_2SmH)_2 + {}^tBu_2CHOH \rightarrow Cp'_2SmOCH^tBu_2 + H_2 \qquad (30)$$
$$\mathbf{15}$$
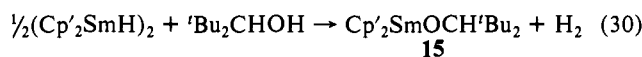
complex **15** confirm the monomeric[31] character in benzene solution (see Experimental Section for details). The derived $D(Cp'_2Sm$–OR) value in **15** is 81.3 (1.0) kcal/mol,[30] in close agreement with that found for dimeric **3**, 82.4 (3.5) kcal/mol.

Discussion

The present data provide absolute quantitation of $D(Cp'_2Sm$–R/X) values for the particular compounds studied. In comparing such data for different R and X groups it is implicitly/pragmatically assumed[3a,49] that differential R/R'/X-based exothermic or endothermic Cp'_2Sm reorganization effects (eq 7) are not energetically significant compared to other trends. While this assumption is supported by a very large body of organosamarium structural data,[10,13] further scrutiny is certainly warranted. Nevertheless, any perturbations introduced in derived D-$(Cp'_2Sm$–R/X) parameters by such effects are of course intrinsic characteristics of the actual coordination environment and as such are implicitly taken into account in subsequent analyses of known or hypothetical transformations of the type Cp'_2Sm–R $\rightarrow$ Cp'_2Sm–R' (vide infra).

Ancillary Ligand Effects and Trends in $D(Cp'_2Sm$–R/X) Values. The thermochemical results reported here provide the first detailed overview of solution-phase organolanthanide bond disruption enthalpies[32–34] for a range of interesting ligands. In regard to halogen ligands, it is found that the absolute value of $D(Cp'_2Sm$–I) in **2** is 69.2 (2.4) kcal/mol (72.7 (2.9) kcal/mol in Cp'_2Sm-(THF)(I)). This result is in close agreement with the reported value for D_1(SmI$_3$) of 68 (5) kcal/mol.[35] Interestingly, a recent thermochemical investigation of the Cp''_3U/Cp''_3U–R/X system[9a]

(28) (a) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119. (b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709–714.

(29) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, second ed., Chapman and Hall: London, 1986; Appendix Table 1.2.

(30) D(RO–H) taken from: Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(31) For a related monomeric complex, see: Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191–195.

(32) For gas-phase lanthanide ion-molecule studies, see: (a) Buckner, S. W.; Freiser, B. S. In ref 1, pp 1583–1603, and references therein. (b) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1988**, *110*, 4434–4435, and references therein.

(33) For earlier combustion studies on LnCp$_3$ complexes, see: Devyatykh, C. G.; Rabinovich, I. B.; Tel'noi, V. I.; Borisov, G. K.; Zyazina, L. F. *Dokl. Akad. Nauk. SSSR* **1974**, *217*, 673–674.

(34) For earlier mass spectrometric appearance potential data on YbCp$_2$ and YbCp$_3$, see: Thomas, J. L.; Hayes, R. G. *J. Organomet. Chem.* **1970**, *23*, 487–494.

(35) (a) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper and Row: New York, 1978; pp 824–850. (b) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, L.; Bailey, S. M.; Schumm, R. H.; Churney, K. L. *NBS Tech. Note (U.S.)* **1971**, No. 270–278. (c) Feher, R. C. *Los Alamos Sci. Lab [Rep.]* LA-3164 **1965**.

Table IV. Bond Disruption Enthalpies for Cp'$_2$Sm-X and SmX$_3$ Compounds (in kcal/mol)

X	D(Cp'$_2$Sm-X)[a]	D_1(SmX$_3$)[b]
Cl	97.1 (3.0)	102 (5)
Br	83.6 (1.5)	86 (5)
I	69.4 (2.4)	68 (5)
I	72.7 (2.9)[c]	68 (5)

[a] This work. [b] Taken from ref 34. [c] Value obtained from titration of Cp'$_2$Sm(THF)$_2$ with I$_2$ yielding Cp'$_2$Sm(THF)(I) (6).

(Cp'' = η^5-Me$_3$SiC$_5$H$_4$) also revealed agreement between D-(Cp''$_3$U-I) (62.4 (1.4) kcal/mol) and D_1(UI$_4$) (66 (8) kcal/mol).[39] It would thus appear that Cp'/Cp''/I ancillary ligation has a similar influence on D(M-I) in these organo-f-element systems. To test further the generality of these trends, D(Cp'$_2$Sm-Cl) in 12 and D(Cp'$_2$Sm-Br) in 13 were also determined in the present study and were found to be 97.1 (3.0) and 83.6 (1.5) kcal/mol, respectively. These results can be compared to the first bond disruption enthalpies in the corresponding samarium trihalides, D_1(SmCl$_3$) = 102 (5) kcal/mol[35] and D_1(SmBr$_3$) = 86 (5)[35] kcal/mol. Thus, the small sensitivity of D(Sm^{III}-halogen) to ancillary ligation, i.e., transferability of D(Sm^{III}-halogen) from one environment to another, appears to be rather general for the halogens. These results are summarized in Table IV and argue, along with previous results,[3a,9a,35,36] that D(metal-halogen) data are reasonably reliable thermodynamic anchor points for thermochemical studies of early-transition-metal and f-element organometallic compounds.

Further parallels between the Cp''$_3$U and Cp'$_2$Sm series are seen in the thermochemistry of Lewis base coordination. Thus, the THF bond enthalpy in Cp''$_3$U(THF) was previously found to be 9.8 (0.2) kcal/mol.[9a] This result can be compared to D-(Cp'$_2$Sm-THF) and D(Cp'$_2$Sm(THF)-THF) values in the organolanthanide system of 7.3 (0.4) and 4.9 (1.0) kcal/mol, respectively. The same organouranium thermochemical study found that D(Cp''$_3$U-CO) = 10.3 (0.2) kcal/mol. A priori extrapolation to the 4f system[37] suggests a roughly comparable (perhaps slightly lower) value for D(Cp'$_2$Sm-CO). Indeed, such species are likely precursors to the reductively coupled, oxygenate products observed in Cp'$_2$Sm/Cp'$_2$Sm(THF)$_2$/CO reaction chemistry.[38]

Reference to Tables I-III indicates that D(Cp'$_2$Sm-R/X) values are large, but not unexpectedly so. Thus, the metal-halogen bond disruption enthalpies are comparable to those of U(IV)[9a,39] (vide supra and D_1(UBr$_4$) = 75 (2) kcal/mol; D_1(UCl$_4$) = 100 (4) kcal/mol) and significantly lower than those of Zr(IV)[35] (e.g., D_1(ZrCl$_4$) = 116 (5) kcal/mol) and Th(IV)[39] (e.g., D_1(ThCl$_4$) = 133 (8) kcal/mol). Part of the explanation for these differences no doubt resides in the Sm(III) → Sm(II) reduction implied by eq 2 and the energetic accessibility of the divalent samarium oxidation state.[40] Continuing this trend, D(Cp'$_2$Sm-OR) values of 82.4 (3.5) (R = ^{t}Bu) and 81.3 (1.0) (R = CH^{t}Bu$_2$) kcal/mol found in the present investigation are large, but somewhat lower than comparable values for Cp$_2$Zr(OR)$_2$ of 103.2 (2.5) kcal/mol (R = CH$_2$CF$_3$, average, anchored to D_1(ZrCl$_4$))[3a] and for
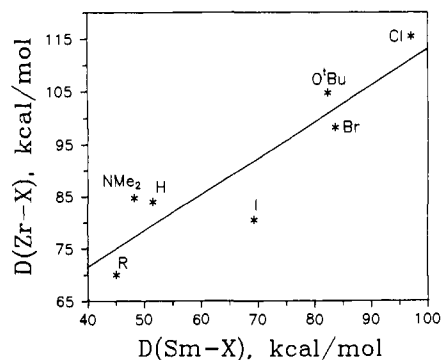

Figure 1. Comparison of measured D(Cp'$_2$Sm-R/X) data to those of the corresponding Cp'$_2$Zr(R/X)-R/X series (ref 3a, anchored to D_1(ZrCl$_4$); average of D[Cp'$_2$Zr(R/X)-R/X] and D[Cp'$_2$Zr(Cl,I)-R/X]). For Sm, R = CH(SiMe$_3$)$_2$, while for Zr, R = CH$_3$.
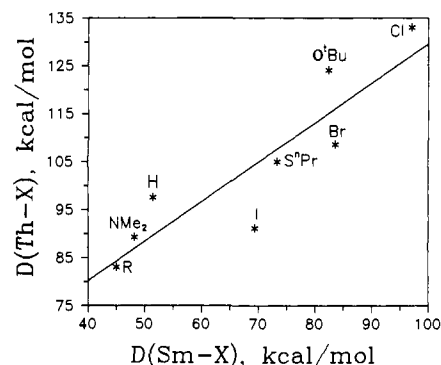

Figure 2. Comparison of measured D(Cp'$_2$Sm-R/X) data to those of the corresponding Cp'$_2$Th(R/X)-R/X series (ref 4a,d; using an approximate thermodynamic anchor). For Sm, R = CH(SiMe$_3$)$_2$ while for Th, R = Me. The X = H and S^{n}Pr data for Th are averages of D[Cp'$_2$Th(X)-X] and D[Cp'$_2$Th(O^{t}Bu)-X] data, and the X = halide data are from D_1-(ThX$_4$) (ref 38).
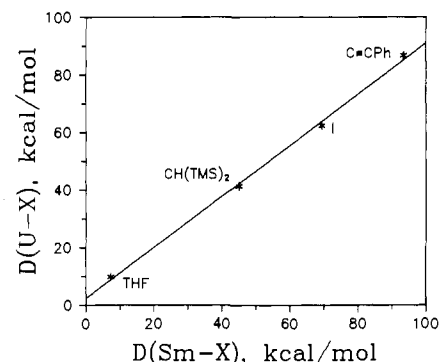

Figure 3. Comparison of measured D(Cp'$_2$Sm-R/X) and D(Cp'$_2$Sm-L) data to those of the corresponding D(Cp''$_2$U-R/X) and D(Cp''$_3$U-L) data of ref 9a. The D(Sm-THF) value is the average of the two quantitatives reported in Table I.

Cp'$_2$Th(OR)$_2$ of 124 kcal/mol (R = ^{t}Bu, anchored approximately to Th(OR)$_4$ and ZrCl$_4$).[4a] The rather large D(Cp'$_2$Sm-S^{n}Pr) value of 73.4 (2.4) kcal/mol is only slightly smaller than the corresponding alkoxide parameter, paralleling the thiolate/alkoxide trend observed for thorium.[4a,d] The difference between D-(Cp'$_2$Sm-NMe$_2$) and D(Cp'$_2$Sm-PEt$_2$) is significantly greater. Where comparable ligands are available, the data trends for the present organosamarium series parallel rather closely those for group 4[3a] and actinides.[4] These parallels are represented graphically in Figures 1-3. It can be seen that despite differences in steric environments, proportionalities exist in the D(Sm-R), D(Th-R), and D(Zr-R) data, which imply strong similarities in metal-ligand bonding among these 4d, 4f, and 5f systems, and dissimilarities (vide infra) with respect to representative middle- and late-transition-element complexes.

(36) Recent thermochemical results in the Cp'$_2$TiCl/Cp'$_2$TiR/Cp'$_2$TiCl$_2$/Cp'$_2$TiR$_2$ series (R = Me, Ph) further support this contention: Dias, A. R.; Salema, M. S.; Simoes, J. A. M.; Pattiasina, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1988**, *346*, C4-C6.

(37) While the π-donor character of the Cp''$_3$U center is likely to be greater,[37a-c] lanthanide carbonyls have been observed in cryogenic matrices[37d,e] and on oxide surfaces.[37f] (a) Tatsumi, K.; Nakamura, A. *J. Organomet. Chem.* **1984**, *272*, 141-154. (b) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1984**, *23*, 1633-1634. (c) Brennan, J. G.; Andersen, R. A.; Robbins, J. L. *J. Am. Chem. Soc.* **1986**, *109*, 335-336. (d) Hauge, R. H.; Gransden, S. E.; Margrave, J. L. *J. Chem. Soc., Dalton Trans.* **1979**, 745-748. (e) Sheline, R. K.; Slater, J. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 309-313. (f) Baltanas, M. A.; Stiles, A. B.; Katzer, J. R. *J. Catal.* **1984**, *88*, 516-518.

(38) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728-3730.

(39) Calculated from thermodynamic data given by: Morss, L. R. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Chapter 17.

(40) (a) Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1985**, *89*, 3317-3319. (b) Morss, L. R. *Chem. Rev.* **1976**, *76*, 827-841.

In regard to hydrocarbyl ligands, it can be seen that D-($Cp'_2Sm-CCPh$) in **11**, 93.2 kcal/mol, is approximately what would be expected on the basis of the corresponding value of 86.7 kcal/mol in Cp''_3UCCPh (Figure 3).[9a] This pattern suggests that the bridging nature of the μ-alkynyl bonding in **11** has not greatly affected the metal–alkynyl bond strength. We report elsewhere[41] that the quantity $D(Lu-H) - D(Lu-alkyl)$ increases by ca. 5–8 kcal/mol when the hydride and saturated alkyl ligands both occupy bridging rather than terminal positions. It is more difficult to assess the present $D[Cp'_2Sm-CH(SiMe_3)_2]$ value of 47.1 (1.5) kcal/mol since we have not previously measured bond disruption enthalpies involving this ligand, and the crystal structures of $Cp'_2LnCH(SiMe_3)_2/Me_2Si(Me_4C_5)_2LnCH(SiMe_3)_2$ complexes evidence both severe intramolecular nonbonded repulsions and bridging/"agostic" interactions involving the α-C–H bond and one Si–Me group (e.g., C).[15b,c,41,42] In comparison, $D(Cp''_3U-$
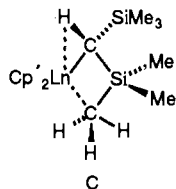
CH₂SiMe₃) = 39.3 (2.3) kcal/mol[9a] and $D[Cp'_2Th-(CH_2SiMe_3)-CH_2SiMe_3]$ = 80.0 (3.1) kcal/mol (the latter based on a more approximate anchor point).[4a] The observed value $D(Cp'_2Sm-H) - D[Cp'_2Sm-CH(SiMe_3)_2]$ = 6 (3) kcal/mol can be compared to corresponding $D(M-H) - D(M-alkyl)$ values of $D[Cp'_2Th(H)-H]$(average) $- D[Cp'_2Th(CH_2SiMe_3)-CH_2SiMe_3]$ = 17.5 (3.8) kcal/mol[4a] and $- D[Cp'_2Th(Me)-Me]$ = 16.5 (1.5) kcal/mol,[4a] $D[Cp'_2Zr(H)-H] - D[Cp'_2Zr(Me)-Me]$ = 10.4 (2.0) kcal/mol,[3a] $D(Cp'_2Sc-H) - D(Cp'Sc-CH_2CH_2CH_2C_5Me_4)$ = 18.0 (6) kcal/mol,[43] $D(Cp'_2Hf(H)-H) - D(Cp'Hf(H)-$ $CH_2CH_2CH_2C_5Me_4)$ = 23.0 (6) kcal/mol,[43] and $D[Cp'_2U(O-Si^tBuMe_2)-H] - D[Cp'_2U(OSi^tBuMe_2)-Me]$ = 6.4 (1.9) kcal/mol. As pointed out previously,[3a,4,9b,44] relatively small $D(M-H) - D(M-alkyl)$ values are generally to be expected for early transition and f-element systems and reflect, among other factors, the electropositive character of these metals. It seems unlikely that the agostic interactions contribute greater than ca. 5–10 kcal/mol to $D[Cp'_2Sm-CH(SiMe_3)_2]$.[45,46] The quantity $D(M-I) - D(M-alkyl)$ is another characteristic index of metal–ligand bonding, and trends in the parameter can be understood on the basis of electronegativity arguments.[3a,9a] For actinides and early transition metals, $D(M-I) - D(M-alkyl)$ is typically large, and the present $D(Cp'_2Sm-I) - D[Cp'_2Sm-CH(SiMe_3)_2]$ value of 22 kcal/mol can be compared to thorium- and uranium-based D-$(M-I) - D(M-Me)$ values of ca. 17[4a,9a] and 18[9a] kcal/mol, respectively. Clearly, the same trends obtains for the organosamarium system.

To our knowledge, the present value for $D[Cp'_2Sm-(\eta^3-C_3H_5)]$ of 45.0 (1.5) kcal/mol is the first bond disruption enthalpy measured for a d- or f-element π-allyl. The derived D is comparable to that for what appears to be a relatively strong metal–alkyl bond ($Cp'_2Sm-CH(SiMe_3)_2$), but significantly less than

(41) (a) Stern, D.; Sabat, M.; Marks, T. J. *Abstracts of Papers*, 194th National Meeting of the American Chemical Society, New Orleans, LA; American Chemical Society: Washington, DC, 1987; INOR 480. (b) Stern, D.; Sabat, M.; Marks, T. J., manuscript in preparation.

(42) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495–2502.

(43) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. In ref 1, pp 1409–1428.

(44) Bruno, J. W.; Duttera, M. R.; Fendrick, C. M.; Smith, G. M.; Marks, T. J. *Inorg. Chim. Acta* **1984**, *94*, 271–277.

(45) (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124, and references therein. (b) Yang, G. K.; Peters, K. S.; Vaida, J. *Chem. Phys. Lett.* **1986**, *125*, 566–570.

(46) In solution ¹H NMR studies, all of the Si–Me groups are typically magnetically equivalent down to ca. –85 °C.
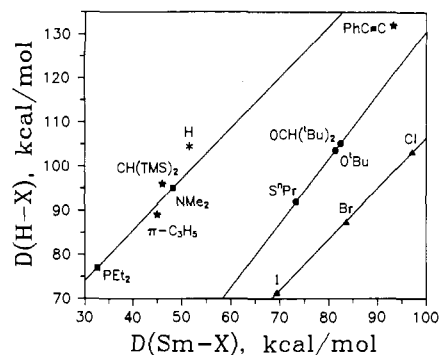

Figure 4. Correlations between $D(H-X)$ values and the corresponding $D(Cp'_2Sm-R/X)$ values measured in this study. Ligands of the same general type are denoted by separate symbols and the lines represent least-squares fits to the data points.

that for a very strong metal–alkynyl bond ($Cp'_2Sm-CCPh$).

In comparison to typical middle- and late-transition-element metal–ligand bonds,[1,2] the present organolanthanide parameters adhere well to patterns previously found for Th,[4] U,[4,9a] Zr,[3a] and Hf.[3a] Thus, very large $D(M-halogen)$ and $D(M-alkoxide)$ values relative to $D(M-alkyl)$ are generally typical of these electropositive metals and generally atypical of middle and late transition elements. Important factors are likely electronegativity,[3a,44,47] orbital repulsion,[48] and π-bonding (e.g., D) effects. As we noted pre-
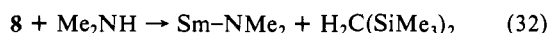
$$M-OR \leftrightarrow M^-=O^+R$$
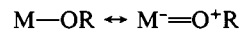
viously,[3a,9b] such patterns are particularly evident in plots[49] of $D(H-X)$ versus $D(M-X)$ data (for a wide range of X ligands), and early transition elements exhibiting considerable scatter from linearity. As can be seen in Figure 4, the present organosamarium data exhibit similar behavior, with the halogens and alkoxides skewed far to the right of the hydrocarbyl, hydride, amide line.

Thermochemistry of Samarium-Centered Transformations. The present bond enthalpy data provide an opportunity to analyze the thermodynamics of a variety of interesting samarium-centered reactions. We begin with a series of ligand transposition processes, which should be reasonably general for all Cp'_2Ln-R/X systems, and then proceed to redox chemistry, which should be more specific to samarium. In the discussion that follows, we shall take D-$[Cp'_2Sm-CH(SiMe_3)_2]$ in **8** to be typical of a samarium alkyl, realizing it may be somewhat larger than typical (vide supra). Bond enthalpies in organic fragments are taken from standard sources and it is assumed that the effects of metal substituents largely attenuate within two σ bonds.[22] Estimated ΔH values for various reactions have maximum uncertainties on the order of ± 5 kcal/mol.
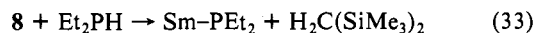
Cleavage reactions of metal–carbon σ bonds are an important class of transformations in organometallic chemistry. As can be seen in eq 31–36, the samarium-to-heteroatom bond-forming
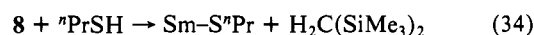
$$Sm-CH(SiMe_3)_2 + {}^tBu_2CHOH \rightarrow$$
$$\mathbf{8}$$

$$Sm-OCH^tBu_2 + H_2C(SiMe_3)_2 \quad (31)$$

$$\Delta H_{found} \approx -25 \text{ kcal/mol of Sm}$$

$$\mathbf{8} + Me_2NH \rightarrow Sm-NMe_2 + H_2C(SiMe_3)_2 \quad (32)$$

$$\Delta H_{calcd} \approx -7 \text{ kcal/mol of Sm}$$

$$\mathbf{8} + Et_2PH \rightarrow Sm-PEt_2 + H_2C(SiMe_3)_2 \quad (33)$$

$$\Delta H_{calcd} \approx -7 \text{ kcal/mol of Sm}$$

$$\mathbf{8} + {}^nPrSH \rightarrow Sm-S^nPr + H_2C(SiMe_3)_2 \quad (34)$$

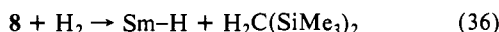$$\Delta H_{calcd} \approx -50 \text{ kcal/mol of Sm}$$

(47) Labinger, J. A.; Bercaw, J. R. *Organometallics* **1988**, *7*, 926–928.

(48) Ziegler, T.; Tschinke, V.; Versluis, L.; Baerends, N. J.; Ranenck, W. In ref 1, pp 1625–1637.

(49) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456. These authors also pointed out such effects in our published D(Th–OR) and D(Th–NR'₂) parameters.

$$8 + HCCPh \rightarrow Sm\text{-}CCPh + H_2C(SiMe_3)_2 \quad (35)$$
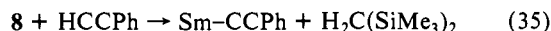
$$\Delta H_{calcd} \approx -18 \text{ kcal/mol of Sm}$$

$$8 + H_2 \rightarrow Sm\text{-}H + H_2C(SiMe_3)_2 \quad (36)$$

$$\Delta H_{calcd} \approx 0 \text{ kcal/mol of Sm}$$

reactions are all exothermic. Particularly noteworthy are those involving the group 16 elements, where the strong Sm-O and Sm-S bonds ensure a large exothermicity. The C-H functionalizing metathesis reaction[10d,15b-d,28] of eq 35 is also estimated to be rather exothermic; however, since phenylacetylide complex 11 is dimeric, it is likely to be entropically unfavorable since four particles form three particles ($T\Delta S \approx +5$–10 kcal/2 mol of Sm at room temperature[50]). The hydrogenolysis of eq 36 is calculated to be approximately thermoneutral, reflecting the rather small value of $D(Sm\text{-}H) - D(Sm\text{-}alkyl)$ (vide supra). Several of the corresponding protonolytic reactions of $(Cp'_2SmH)_2$ (7) have been characterized experimentally (eq 37, X = S^{n}Pr, PEt$_2$, OCH^{t}Bu$_2$,

$$\underset{7}{Sm\text{-}H} + HX \rightarrow Sm\text{-}X + H_2 \quad (37)$$
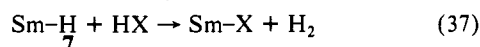
Table III) and have been found to be exothermic (especially for the group 16 elements). Equation 38 shows that dialkylamide

$$7 + HNMe_2 \rightarrow Sm\text{-}NMe_2 + H_2 \quad (38)$$

$$\Delta H_{calcd} \approx -3 \text{ kcal/mol of Sm}$$

formation from the hydride is nearly thermoneutral, however it should enjoy a favorable entropic contribution (3 particles → 4 particles). The major thermodynamic contributors to eq 39 are the great strengths of the Sm-CCPh and H-H bonds.

$$7 + HCCPh \rightarrow Sm\text{-}CCPh + H_2 \quad (39)$$

$$\Delta H_{calcd} \approx -11 \text{ kcal/mol of Sm}$$

The very favorable kinetics for olefin insertion processes within Cp'$_2$Ln-R coordination spheres[10d,15] prompts an examination of the thermodynamics of analogue reactions for the present samarium system using ethylene as the model olefin (eq 40–45).
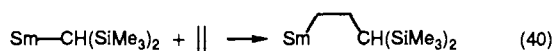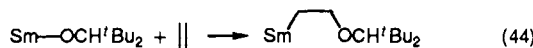

$$\Delta H_{calcd} \approx -24 \text{ kcal/mol of Sm} \quad (40)$$
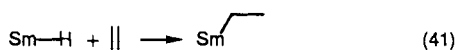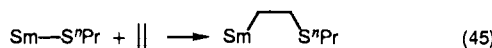

$$\Delta H_{calcd} \approx -32 \text{ kcal/mol of Sm} \quad (41)$$
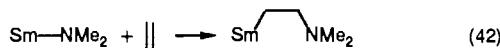
$$\Delta H_{calcd} \approx 0 \text{ kcal/mol of Sm} \quad (42)$$
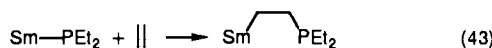
$$\Delta H_{calcd} \approx +2 \text{ kcal/mol of Sm} \quad (43)$$

$$\Delta H_{calcd} \approx +13 \text{ kcal/mol of Sm} \quad (44)$$
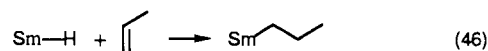

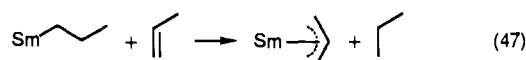$$\Delta H_{calcd} \approx +12 \text{ kcal/mol of Sm} \quad (45)$$

Since most of these reactions involve an overall net reduction in the number of particles (and presumably in translational entropy[50]), they are expected to be entropically unfavorable. Equation 40 models the propagation step for the coordinative polymerization of ethylene and is estimated to be rather exothermic, as expected[3a,4] (and is also thermodynamically metal-independent[4a]). While such

reactions have not been observed for Cp'$_2$LnCH(SiMe$_3$)$_2$ systems at 1 atm pressure, 25 °C (presumably for steric reasons), the related, less hindered Me$_2$Si(C$_5$H$_4$)(Me$_4$C$_5$)LnCH(SiMe$_3$)$_2$ complexes do initiate the polymerization of ethylene.[41] Equation 41 describes the reverse of β-H elimination and is predicted to be quite exothermic, in accord with general experimental observations.[10d,15a-d] The exothermicity appears to be slightly greater than estimated for most actinide (ca. -20 kcal/mol;[4a] ca. -30 to -35 kcal/mol with alkoxide ancillary ligands[4c]) and group 4 (ca. -13 kcal/mol[3a]) systems, possibly reflecting the relatively large D-(Sm-alkyl) value used in the calculations (vide supra), differential steric effects, and/or the lower electronegativity of samarium in this environment.[3a,9b] Equations 42 and 43 predict that ethylene insertion in lanthanide–group 15 bonds should be approximately thermoneutral. Since subsequent ethylene insertion events are expected to be highly exothermic, it is not surprising that Cp'$_2$NdNMe$_2$ initiates the polymerization of ethylene.[19] Furthermore, the coupling of insertion processes as in eq 42 with amide-forming protonolysis processes as in eq 32 closes a cycle for the organolanthanide-catalyzed hydroamination of olefins. The details of this chemistry are discussed elsewhere.[9a,15e] Olefin insertion into Sm-PEt$_2$ bonds appears to be only slightly unfavorable enthalpically (eq 43), while that involving Sm-OR and Sm-SR bonds is considerably more endothermic (eq 44 and 45). As shown elsewhere for group 4, insertion processes corresponding to eq 40–45 but involving acetylenes are anticipated to be more exothermic by ca. 30 kcal/mol or more.[3a]

In addition to the aforementioned, simple olefin insertion processes, organolanthanides also undergo more elaborate allylic C-H functionalization reactions with olefins.[15a-d] A facile example is shown in eq 46 and 47 (see Experimental Section for details)

$$\Delta H_{calcd} \approx -29 \text{ kcal/mol of Sm} \quad (46)$$
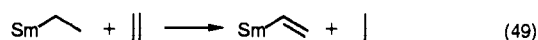

$$\Delta H_{calcd} \approx -10 \text{ kcal/mol of Sm} \quad (47)$$
$$\text{overall} \quad \Delta H_{calcd} \approx -39 \text{ kcal/mol of Sm}$$

and is readily understandable in light of the present thermodynamic information. Important contributors to the driving force are the weakness of the allylic propylene C-H bond, the strength of the Sm-(η^3-allyl) bond, and the exothermicity of hydrogenating 1 mol of propylene. In principle, reaction sequences as in eq 48 and 49 also appear to be feasible.
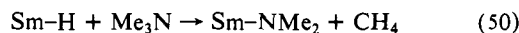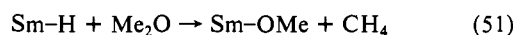

$$\Delta H_{calcd} = -32 \text{ kcal/mol of Sm} \quad (48)$$

$$\Delta H_{calcd} \approx +12 \text{ kcal/mol of Sm} \quad (49)$$
$$\text{overall} \quad \Delta H_{calcd} = -20 \text{ kcal/mol of Sm}$$

Hydride-mediated cleavage/demethylation reactions are also predicted to be exothermic (eq 50 and 51), especially when strong lanthanide–heteroatom bonds are formed. Reactions similar to eq 51 have been reported for $(Cp'_2LuH)_2$.[51]

$$Sm\text{-}H + Me_3N \rightarrow Sm\text{-}NMe_2 + CH_4 \quad (50)$$

$$\Delta H_{calcd} \approx -22 \text{ kcal/mol of Sm}$$

$$Sm\text{-}H + Me_2O \rightarrow Sm\text{-}OMe + CH_4 \quad (51)$$

$$\Delta H_{calcd} \approx -48 \text{ kcal/mol of Sm}$$

(50) (a) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805–6807. (b) Page, M. I. In *The Chemistry of Enzyme Action*; Page, M. I., Ed., Elsevier: New York, 1984; pp 1–54. (c) Page, M. I.; Jencks, W. F. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678–1683.

(51) (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276–277. (b) Such scission reactions are also predicted to be exothermic for lanthanide alkyls. Cp'$_2$Sm(THF)CH$_3$ is reported[13a] to undergo reaction with Et$_2$O to yield Cp'$_2$Sm(THF)OEt.

The accessibility of both divalent and trivalent samarium oxidation states prompts examination of several unusual, binuclear oxidative addition/reductive elimination and reductive coupling processes. The addition of dihydrogen to compound **1** (eq 52)

$$2Cp'_2Sm + H_2 \rightarrow (Cp'_2Sm-H)_2 \qquad (52)$$
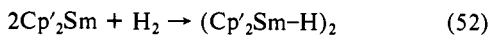
$$\Delta H_{calcd} \approx -5 \text{ kcal/mol of Sm}$$

is predicted to be slightly exothermic, but is probably slightly endergonic on the basis of unfavorable entropic characteristics. To our knowledge, neither the forward nor reverse reaction has been reported. Curiously, by ^{1}H NMR, we observe no indication of reaction of Cp'$_2$Sm with H$_2$ (1 atm pressure) over the course of days at room temperature, while thermolysis of (Cp'$_2$Sm-H)$_2$ results in a mixture of unidentified products. It is not clear whether such reactions may be hindered by a large kinetic barrier.

Dinuclear, samarium-centered oxidative addition processes also suggest a novel route for hydrocarbon activation (eq 53). Such

$$2Cp'_2Sm + RH \rightarrow Cp'_2SmR + \tfrac{1}{2}(Cp'_2SmH)_2 \qquad (53)$$
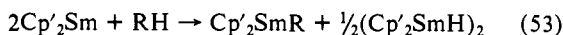
$$\Delta H \approx D(R-H) - D(Cp'_2Sm-R) - D(Cp'_2Sm-H) \qquad (54)$$

a pathway represents a significant departure from more conventional (for f elements) four-centered heterolytic mechanisms.[10d,15,52] From eq 54, it can be seen that the exothermicity depends crucially on the quantity $D(R-H) - D(Cp'_2Sm-R)$. Estimations using measured $D(Cp'_2Sm-R)$ parameters or assuming $D(Cp'_2Sm-R) \approx D[Cp'_2Sm-CH(SiMe_3)_2]$ argue that many alkane and arene functionalization processes are endothermic (hence, the elimination processes should be exothermic) owing to the large values of $D(R-H)$ (eq 55–57). Propylene does not, however, fall into this

$$2Sm + PhH \rightarrow Sm-Ph + Sm-H \qquad (55)$$
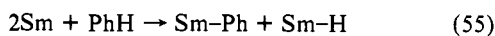
$$\Delta H_{calcd} \approx +10 \text{ kcal/mol of PhH}$$

$$2Sm + CH_4 \rightarrow Sm-CH_3 + Sm-H \qquad (56)$$

$$\Delta H_{calcd} \approx +3 \text{ kcal/mol of CH}_4$$

$$2Sm + HCCPh \rightarrow Sm-CCPh + Sm-H \qquad (57)$$
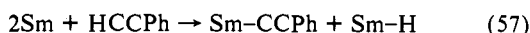
$$\Delta H_{calcd} \approx -15 \text{ kcal/mol of HCCPh}$$

category, and C–H activation is predicted to be exothermic (eq 58). Furthermore, follow-up reaction of the samarium hydride
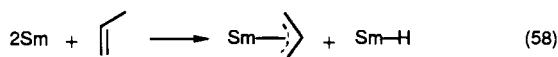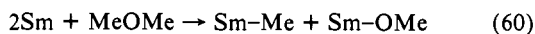

$$\Delta H_{calcd} \approx -12 \text{ kcal/mol of } \text{(propylene)} \qquad (58)$$

product with additional propylene should further increase the exothermicity of propylene activation (eq 46 and 47). Experimentally, we find by ^{1}H NMR in C$_6$D$_{12}$ that Cp'$_2$Sm undergoes rapid reaction with excess propylene to yield Cp'$_2$Sm(η^3-C$_3$H$_5$)[53] and propane as the only detectable products.

In contrast to the aforementioned hydrocarbon activation processes, the great majority of oxidative addition sequences forming lanthanide–heteroatom bonds should be highly exothermic (e.g., eq 59–61). Variants of eq 59 have been reported.[14]

$$2Sm + MeCl \rightarrow Sm-Me + Sm-Cl \qquad (59)$$

$$\Delta H_{calcd} \approx -59 \text{ kcal/mol of MeCl}$$

$$2Sm + MeOMe \rightarrow Sm-Me + Sm-OMe \qquad (60)$$

$$\Delta H_{calcd} \approx -45 \text{ kcal/mol of MeOMe}$$
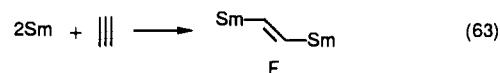
$$2Sm + Me_2S \rightarrow Sm-Me + Sm-SMe \qquad (61)$$

$$\Delta H_{calcd} \approx -41 \text{ kcal/mol of Me}_2\text{S}$$

Dinuclear addition processes to olefins and, by extension, to acetylenes are also predicted to be highly exothermic (eq 62 and 63) assuming $D(Sm-C) \approx D[Cp'_2SmCH(SiMe_3)_2]$, $D(C-C) \approx$
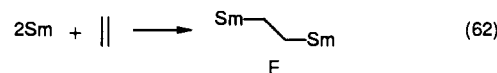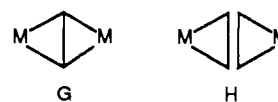

$$\Delta H_{calcd} = -35 \text{ kcal/mol of } \text{(ethylene)} \qquad (62)$$

$$\Delta H_{calcd} = -40 \text{ kcal/mol of } \text{(acetylene)} \qquad (63)$$

88 kcal/mol (that in ethane), and $D(C=C) \approx 146$ kcal/mol (that in ethylene). While classical structures E and F are most amenable to thermodynamic analysis, nonclassical structures such as G[12b,54]

and H[13b] have been identified[12b,53] or proposed.[13b] Such structures are not readily analyzed by the present approach; however, eq 62 and 63 afford a qualitative estimate of how exothermic such dinuclear additions may be.[55] It is likely that these types of species or vinyl compounds (cf. eq 53) are intermediates in the Cp'$_2$Sm-(THF)$_2$/Cp'$_2$Sm-initiated polymerization of ethylene.[13b,56] Formally related are alkene/alkyne reductive coupling processes (e.g., eq 64) which should also be highly exothermic. Although
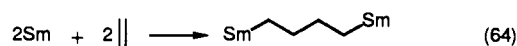
$$\Delta H_{calcd} = -23 \text{ kcal/mol of Sm} \qquad (64)$$

we have not carried out a thermodynamic analysis of Cp'$_2$Sm-induced reductive CO coupling reactions,[13b,c] the present results and the pervasive exothermicity of Sm–O bond formation seen here leave little doubt that such processes will be highly exothermic.

Conclusions

The results of the present study afford the first detailed view of absolute metal–ligand bond disruption enthalpies in an archetypical organolanthanide series. Strong parallels are seen to $D(M-X)$ orderings previously observed for Th, U, and group 4 organometallics. Particularly striking are the small observed value of $D(Sm-H) - D(Sm-alkyl)$, the large value of $D(Sm-I) - D(Sm-alkyl)$, and the large $D(Sm-X)$ values involving group 16 (OR, SR) and, to a lesser extent, group 15 (NR$_2$, PR$_2$) ligands. As noted previously for U/Cp''/I but now expanded to encompass the sequence Sm/Cp'/Cl/Br/I, cyclopentadienyl versus halogen ancillary ligand effects are surprisingly similar. This observation argues that metal–halogen bond enthalpies should be reasonably reliable thermodynamic anchors for referencing determinations of relative metal–ligand bond disruption enthalpies in this part of the periodic table. The present data afford insight not only into a variety of Cp'$_2$Sm-R $\rightarrow$ Cp'$_2$Sm-R' transposition processes, but also into a number of oxidative addition/reductive elimination sequences. In both cases, the formation of strong Sm–heteroatom

(52) (a) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56. (b) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 435–437.

(53) See also: Ulibarri, T. A.; Ziller, J. W.; Evans, W. J. *Abstracts of Papers*, 194th National Meeting of the American Chemical Society, New Orleans, LA; American Chemical Society: Washington, DC, 1987; INOR 262.

(54) Cotton, F. A.; Kibala, P. *Polyhedron* **1987**, *6*, 645–646.

(55) Evidence that these estimates provide an upper limit to the bond enthalpies is provided by the observation[13e] that (Cp'$_2$Sm)$_2$PhC$_2$Ph reverts to some degree to Cp'$_2$Sm(THF)$_2$ and PhC$_2$Ph in excess THF.

(56) (a) Nolan, S. P.; Marks, T. J., unpublished observations. (b) See also: Ulibarri, T. A.; Evans, W. J. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO; American Chemical Society: Washington, DC, 1987; INOR 315.

or strong C–C/C–H bonds makes an important contribution to the driving force. Although Cp′₂Sm–H and Cp′₂Sm–alkyl bonds are relatively strong, they are insufficiently strong to effectively drive hydrocarbon functionalization by dinuclear oxidative addition processes. The exceptions are hydrocarbons having weak C–H bonds and forming strong metal–ligand bonds (e.g., propylene → η^3-allyl), or cases where a highly exothermic follow-up process can be coupled to C–H scission. Further exploitation of these bond enthalpy trends and extensions to other lanthanides will be the subjects of future contributions.

Ferromagnetically Coupled Linear Electron-Transfer Complexes. Structural and Magnetic Characterization of [Cr(η^6-C₆MeₓH₆₋ₓ)₂][TCNE] (x = 0, 3, 6) and S = 0 [TCNE]₂²⁻

Joel S. Miller,[*,1a] **Dermot M. O'Hare,**[1a,b] **Animesh Chakraborty,**[1c] and **Arthur J. Epstein**[*,1c]

Contribution No. 5045 from Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station E328, Wilmington, Delaware 19880-0328, and Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received March 3, 1989

Abstract: The reaction of Cr⁰(C₆MeₓH₆₋ₓ)₂ (x = 0, 3, 6), D, with TCNE, A, results in formation of 1:1 electron-transfer salts of [Cr¹(C₆MeₓH₆₋ₓ)₂][TCNE] (x = 0, 3, 6) composition. The x = 0 and 3 complexes have been structurally characterized. The [Cr¹(C₆H₆)₂]•⁺ salt belongs to the centrosymmetric $P2_1/m$ space group [a = 10.347 (4) Å, b = 12.423 (10) Å, c = 12.763 (4) Å, β = 111.33 (3)°, Z = 4, T = 23 °C, V = 1528 (3) Å³, R_u = 0.042, and R_w = 0.044]. The [TCNE]•⁻ anion has average C–C, C–CN, and C≡N bonds of 1.436, 1.414, and 1.140 Å, respectively, and the NC–C–CN, NC–C–C, and N≡C–C angles average 118.6, 120.2, and 178.4°, respectively. The solid-state structure consists of linear chains of ···D•⁺A₂²⁻D•⁺D•⁺A₂²⁻D•⁺··· with the anion existing as dimeric dianions, [TCNE]₂²⁻. The [TCNE]₂²⁻ is centrosymmetric, and the intradimer C···C bond distance is 2.904 Å. The S = 0 [TCNE]₂²⁻ dimer is nonplanar and bent 10° via a b₃ᵤ out-of-plane distortion. One habit of the [Cr(C₆Me₃H₃)₂]•⁺ salt crystallizes in the *P*1̄ space group [a = 10.475 (5) Å, b = 11.427 (4) Å, c = 8.419 (6) Å, α = 64.20 (3)°, β = 78.59 (4)°, γ = 81.56 (3)°, Z = 2, T = 23 °C, V = 1266 (9) Å³, R_u = 0.075, and R_w = 0.081]. This is a poorer quality structure with average C–C, C–CN, and C≡N bonds of 1.45, 1.40, and 1.10 Å, respectively, while the NC–C–CN, NC–C–C, and N≡C–C angles average 133, 114, and 162°, respectively. The solid-state structure also consists of linear chains of ···D•⁺A₂²⁻D•⁺D•⁺A₂²⁻D•⁺··· with the intradimer separation of 3.09 Å for the [TCNE]₂²⁻. The [TCNE]₂²⁻ dimer exhibits three characteristic C≡N vibrations in the infrared region at 2160 s, 2169 s, and 2190 m cm⁻¹. The [Cr¹(C₆H₆)₂]•⁺ and this [Cr¹(C₆Me₃H₃)₂]•⁺ structure have eclipsed and staggered conformations, respectively. The average Cr–C and C–C separations are 2.143 and 1.395 Å, respectively, for [Cr¹(C₆H₆)₂]•⁺, and the average Cr–C, C–C, and C–Me separations for [Cr¹(C₆Me₃H₃)₂]•⁺ are 2.16, 1.40, and 1.51 Å, respectively. The Cr–C₆(ring) centroids are equivalent at 1.625 (5) Å. The magnetic susceptibility between 2 and 320 K for these [TCNE]₂²⁻ complexes can be fit by the Curie–Weiss law, χ = C/(T − θ), for one independent per spin repeat unit. In solution two signals with g = 2.001 and 1.896 characteristic of [TCNE]•⁻ and [Cr(η-arene)₂]•⁺ are observed; thus, [TCNE]•⁻ and not [TCNE]₂²⁻ is present in solution. For the solid phase the spin is assigned to the cation; with the dimer being diamagnetic. A second structure type is suggested for the [Cr¹(C₆MeₓH₆₋ₓ)₂]•⁺ (x = 3, 6) salts as they exhibit the characteristic ν(C≡N) vibrations for an isolated [TCNE]•⁻. Their high-temperature susceptibility can be fit by the Curie–Weiss law with θ = ~+11.4 K and μₑff = ~2.4 μB consistent with ferromagnetic coupling; thus, we propose that these complexes possess a ···D•⁺A•⁻D•⁺A•⁻··· chain structure. The magnetization saturated faster than accountable by the Brillouin function for independent spins; however, bulk 3-D ordering is not evident. The configurational mixing of a charge-transfer excited state with the ground-state model predicts antiferromagnetic coupling should be stabilized for this compound as both the donor and acceptor possess an ²A₁g ground state. Charge-transfer excitation from the next highest occupied molecular orbital, however, is consistent with the stabilization of ferromagnetic coupling for this system. Thus, other molecular/organic systems with ²A ground states might be suitable components for a bulk ferromagnet.

One-dimensional, 1-D, electron-transfer complexes have been frequently characterized to exhibit unusual optical and electrical[2–4]

and recently unusual cooperative magnetic properties.[5] For example, the reaction of decamethylferrocene, Fe(C₅Me₅)₂, and

---

(1) (a) du Pont. (b) Current address: Oxford University. (c) Ohio State University.
(2) See for example: *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York; 1982, Vol. 1, 2; 1983, Vol. 3. Simon, J.; Andre, J. J. *Molecular Semiconductors*, Springer-Verlag: New York, 1985.

(3) For detailed overview, see the proceedings of the recent series of international conferences: *Synth. Met.* **1987**, 17–19. *Mol. Cryst. Liq. Cryst.* **1985**, 117–121. *J. Phys. (Paris) Coll.* **1983**, 44–C3. *Mol. Cryst. Liq. Cryst.* **1981**, 77, 79, 82, 83, 85, 86, **1982**. *Chem. Scr.* **1981**, 17. *Lect. Notes Phys.* **1979**, 95, 96. *Ann. N.Y. Acad. Sci.* **1978**, 313.