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Thermodynamic, Kinetic, Structural, and Computational Studies of the Ph₃Sn–H, Ph₃Sn–SnPh₃, and Ph₃Sn–Cr(CO)₃C₅Me₅ Bond **Dissociation Enthalpies**

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S Supporting Information

ABSTRACT: The kinetics of the reaction of Ph₃SnH with excess \bullet Cr(CO)₃C₅Me₅ = •Cr, producing HCr and Ph₃Sn-Cr, was studied in toluene solution under 2-3atm CO pressure in the temperature range of 17-43.5 °C. It was found to obey the rate equation $d[Ph_3Sn-Cr]/dt = k[Ph_3SnH][\bullet Cr]$ and exhibit a normal kinetic isotope effect ($k_{\rm H}/k_{\rm D}$ = 1.12 ± 0.04). Variable-temperature studies yielded ΔH^{\ddagger} = 15.7 ± 1.5 kcal/mol and $\Delta S^{\ddagger} = -11 \pm 5$ cal/(mol·K) for the reaction. These data are interpreted in terms of a two-step mechanism involving a thermodynamically uphill hydrogen atom transfer (HAT) producing Ph₃Sn• and HCr, followed by rapid trapping of Ph₃Sn• by excess •Cr to produce Ph₃Sn-Cr. Assuming an overbarrier of 2 ± 1 kcal/mol in the HAT step leads to a derived value of 76.0 \pm 3.0 kcal/mol for the Ph_3Sn-H bond dissociation enthalpy (BDE) in toluene solution. The reaction enthalpy of Ph_3SnH with excess •Cr was measured by reaction calorimetry in toluene solution, and a value of the Sn-Cr BDE in Ph₃Sn-Cr of 50.4 \pm 3.5 kcal/mol was derived. Qualitative studies of the reactions of other R_3 SnH compounds with •Cr are



described for R = ⁿBu, ^tBu, and Cy. The dehydrogenation reaction of $2Ph_3SnH \rightarrow H_2 + Ph_3SnSnPh_3$ was found to be rapid and quantitative in the presence of catalytic amounts of the complex $Pd(IPr)(P(p-toly)_3)$. The thermochemistry of this process was also studied in toluene solution using varying amounts of the Pd(0) catalyst. The value of $\Delta H = -15.8 \pm 2.2$ kcal/mol yields a value of the Sn–Sn BDE in Ph₃SnSnPh₃ of 63.8 ± 3.7 kcal/mol. Computational studies of the Sn–H, Sn–Sn, and Sn–Cr BDEs are in good agreement with experimental data and provide additional insight into factors controlling reactivity in these systems. The structures of Ph₃Sn-Cr and Cy₃Sn-Cr were determined by X-ray crystallography and are reported. Mechanistic aspects of oxidative addition reactions in this system are discussed.

INTRODUCTION

Recently in individual¹⁻⁴ and collaborative⁵ work, we reported investigations of use of the sterically demanding triorganotin hydride ^tBu₃SnH with transition metal complexes capable of small molecule activation. There is a rich history of synthesis of bulky tin ligands in the pioneering work of Neumann, Lappert,⁷ Davies,⁸ and others. In comparison, there is a dearth of thermochemical data on organotin complexes due to the experimental challenges innate in their study. Experimental enthalpies of formation of organotin compounds are scarce, and the existing values in the literature were mainly determined before 1970. There are several compilations and revisions of these data, since newer and more reliable data used to derive the reported values are now available.⁹ However, some of the articles do not give enough experimental information to allow recalculating the values, and some data were never published in the primary literature. The enthalpies of formation of tin compounds have been determined mainly by static-bomb calorimetry. While no rotating-bomb calorimetric studies

appear to have been reported for tin, it was shown for lead compounds¹⁰ that the rotating-bomb method was critical to obtaining reliable results. However, Davies, Pope, and Skinner¹¹ found that combustions performed at higher than usual pressures gave satisfactory results in static-bomb calorimetry for organic tin compounds.¹² There are a limited number of tin compounds for which independent measurements of enthalpies of formation have been reported to check the consistency of the values. In most of the cases, reasonable agreement between the different values obtained by independent means is observed. However, in several cases such as the enthalpy of formation of Ph₃SnSnPh₃, a marked lack of agreement in the results of almost 25 kcal/mol was found.^{13,14} In addition to the combustion experiments, photoacoustic calorimetric,^{15,16} threshold photoelectron-photoion coincidence,¹⁷ appearance potential,^{11,16,18-20} gas-phase acidity,²¹ kinetics,²² and variable-

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temperature electron spin resonance $(ESR)^{23}$ studies were performed to derive Sn–H, Sn–Sn, and Sn–M (M = transition metal) bond dissociation enthalpies (BDE).

In spite of the wide use of stannanes as reducing agents in organic reactions, there are only sparse reports of experimental determination²⁴ of the Sn–H BDE in R₃SnH compounds. Comprehensive theoretical studies of organostannane thermochemistry were recently reported by Boyd and co-workers²⁵ who tested 14 different levels of theory including high-level CCSD(T) calculations²⁶ in computation of the Sn–H BDE in Me₃SnH. Eight of the 14 results agreed to within 1 kcal/mol or better with the experimental value of 76 kcal/mol reported by Drozdova and Denisov.²²

In this paper, we report our initial efforts at mapping the solution thermochemistry of organotin compounds. This stems from our interest in oxidative addition reactions of bulky stannane ligands and the strength of the Pt–Sn bond in L_nPt –SnR₃ complexes. Prior to initiating those investigations, it was deemed necessary to generate data in toluene solution to allow comparison of these BDE values to existing gas-phase and computational data.

Two experimental approaches are taken in this work. The first is based on studies of hydrogen atom transfer (HAT) from R_3SnH to the 17 e⁻ radical complex $\bullet Cr(CO)_3C_5Me_5$. Baird and co-workers²⁷ had reported earlier that the dimeric complex $[Cr(CO)_3C_5H_5]_2$ reacts relatively rapidly with ⁿBu₃SnH to yield 1 mol of HCr(CO)₃C₅H₅ and 1 mol of ⁿBu₃Sn-Cr(CO)₃C₅H₅, but that HCr(CO)₃C₅H₅ may also undergo further reaction with excess stannane. This reaction was believed to occur by attack of the $\bullet Cr(CO)_3C_5H_5$ radical formed by dissociation of $[Cr(CO)_3C_5H_5]_2$. Subsequent synthetic and reactivity studies of a host of reagents with the $\bullet Cr(CO)_3C_5Me_5$ radical also included spectroscopic data in keeping with oxidative addition of R_3SnH (R = ⁿBu) by 2 mol of $\bullet Cr(CO)_3C_5Me_5$ as shown in reaction 1.

$$2 \bullet Cr(CO)_3 C_5 Me_5 + {}^{n}Bu_3 SnH$$

$$\rightarrow {}^{n}Bu_3 Sn - Cr(CO)_3 C_5 Me_5 + HCr(CO)_3 C_5 Me_5 \qquad (1)$$

The formed complex ⁿBu₃Sn–Cr(CO)₃C₅Me₅ was reportedly too labile to isolate, but spectroscopic and other relevant synthetic studies performed by Baird and co-workers confirmed the product assignments. Provided appropriate conditions could be found, study of reaction 1 in principle provides a convenient entry into thermochemical study of stannanes, since the value of the Cr–H BDE in HCr(CO)₃C₅Me₅ is known²⁸ (62.3 ± 1.0 kcal/mol). In addition, if conditions could be found where the rate-determining step in reaction 1 corresponded to the thermodynamically uphill HAT reaction shown in eq 2, then information regarding the Sn–H BDE could be derived from kinetic data.

$$\bullet Cr(CO)_3 C_5 Me_5 + R_3 SnH \rightarrow HCr(CO)_3 C_5 Me_5 + R_3 Sn \bullet$$
(2)

The overbarrier for related radical reactions is very low and on the order of 2 \pm 1 kcal/mol as shown by Franz and co-workers.²⁹

The earlier observation of Baird and co-workers regarding the presence of side reactions and the lability of the products formed indicated that a search for suitable reaction conditions to allow kinetic study would have to be made, since the critical part of any kinetic study is establishment of the mechanism. Investigation of reactions of several stannanes with \bullet Cr $(CO)_3C_5Me_5$ indicated that the best conditions for kinetic study would involve reaction under CO pressures of 2–3 atm of Ph₃SnH in the presence of a large pseudo-first-order excess of \bullet Cr(CO)₃C₅Me₅.

The second method utilized for entry into the organotin solution thermochemistry is based on attempts to develop a direct method to measure the enthalpy of the well-known spontaneous dehydrogenation of tin hydrides as shown in eq 3.

 $2R_3SnH \rightarrow H_2 + R_3Sn - SnR_3 \tag{3}$

Dehydrogenation of tin hydrides such as shown in reaction 3 is normally something to be avoided. It is well-known that solutions of tin hydrides lose their activity due to slow formation of distannanes. As cited in the classic book of Neumann,⁶ reaction 3 can be catalyzed by several agents including $PtCl_2$. In this work, we deliberately sought active catalysts capable of accelerating reaction 3 for the purpose of calorimetric measurement of it under different loads of catalyst to give an accurate and reliable direct value for its reaction metal catalyst is used to obtain valid thermochemical data for a main-group organometallic reaction.

A complementary approach is utilization of high-level computational techniques. The value of calculations to thermochemistry in the hitherto primarily experimental NIPER group was realized as early as in the 1990s.³⁰ The blending of experiment and theory is now standard in physical organometallic chemistry. In the current work, agreement between computed and experimental data gives needed confidence to both approaches.

EXPERIMENTAL SECTION

Unless stated otherwise, all operations were performed in a Vacuum Atmospheres or MBraun drybox under an atmosphere of purified nitrogen or argon. Toluene was dried and deoxygenated by distillation from sodium benzophenone ketyl under argon atmosphere. Spectroscopic-grade anhydrous heptane was degassed prior to use. Anhydrous benzene- d_6 and toluene- d_8 were purchased from Aldrich and degassed by evacuation and refilling with argon and stored over 4 Å molecular sieves in the glovebox prior to use. Triphenyl tin hydride was obtained from Aldrich and stored in the glovebox at an ambient temperature of ~20 °C. A small amount of supernatant liquid, presumably an impure eutectic mixture, was found above the pure solid (as determined by NMR), and this was decanted. Triphenyl tin deuteride was prepared from Ph₃SnCl by use of LiAlD₄ in place of LiAlH₄³¹ and recrystallized from a concentrated heptane solution at -20 °C. Preparation of ^tBu₃SnH was done as described earlier.³ ⁿBu₃SnH and Cy₃SnH were obtained from Aldrich and Strem, respectively, and used without further purification. FTIR spectra were obtained using a PerkinElmer Spectrum 400 FTIR Spectrometer. Calorimetric measurements were made using a Setaram C-80 Calvet microcalorimeter.

Qualitative Study of Reactions of $\circ Cr(CO)_3C_5Me_5$ and Stannanes. Qualitative studies were performed using techniques similar to those described in a later section. The presence of $\circ Cr(CO)_3C_5Me_5$ with known FTIR bands at 1994 and 1890 cm⁻¹ in toluene solution as well as the formation of $HCr(CO)_3C_5Me_5$ with bands at 1995 and 1912 cm⁻¹ were readily identified, and iterative computer subtraction was used to identify bands due to the R₃Sn- $Cr(CO)_3C_5Me_5$ products formed. Doubt regarding product identify based on the in situ FTIR data is small due to structural determination by single-crystal X-ray diffraction analysis of two of the Cr–Sn products. In toluene solution, the complexes R₃Sn- $Cr(CO)_3C_5Me_5$ had bands in the FTIR spectrum at 1959 and 1872 cm⁻¹ (R = ⁿBu); 1955 and 1872 cm⁻¹ (R = Cy); 1957 and 1887 cm⁻¹ (R = ^tBu); 1970 and 1889 cm⁻¹ (R = Ph). The presence of the triply bonded Cr=Cr complex $[Cr(CO)_2C_5Me_5]_2$ was detected by its characteristic bands at 1850 and 1870 cm⁻¹. This complex was at times present in stock solutions of \bullet Cr(CO)₃C₅Me₅ that had been stored overnight and did not interfere with kinetics studies. In some cases, as discussed in the results section, small amounts of $[Cr(CO)_2C_5Me_5]_2$ were formed in reactions performed under Ar atmosphere but not under CO. All qualitative studies of stannanes and distannanes were performed using standard Schlenk tube techniques and are discussed specifically in the results section.

Qualitative Study of Catalytic Dehydrogenation of Ph₃SnH and Cy₃SnH. Elimination of H₂ from R₃SnH was investigated by reaction of a mixture of ~0.2 g of R₃SnH in 5 mL of C₆D₆ to which ~0.006 g of catalyst was added. The complex Pd(IPr)(P(*p*-tolyl)₃)³² was found to be an efficient catalyst for dehydrogenation of both Ph₃SnH and Cy₃SnH. The complex $[(\mu$ -H)Pt(I^tBu)(Sn^tBu₃)]₂⁵ was found to show only limited activity.

Quantitative Kinetic Study of Reaction of \circ Cr(CO)₃C₅Me₅ and R₃SnH. Preliminary qualitative studies had shown that reactions run under argon were faster than those under CO. Reactions run at an overpressure of 10, 20, and 30 psi of CO showed that at temperatures lower than 45 °C there was a decrease in rate between 10 and 20 psi but no significant decrease in rate between 20 and 30 psi overpressure of CO. Therefore, data were typically collected at 20–25 psi CO pressure in a thermostated glass reactor fitted with thick-walled Teflon tubing lines used to transfer 1–3 mL of solution to a high-pressure Fourier transform infrared (FTIR) cell allowing a fresh sample to be studied for each data point. The procedure described below for studying the rate of reaction of Ph₃SnH and Ph₃SnD is representative of all studies.

In the glovebox, a stock solution of $\bullet Cr(CO)_3C_5Me_5$ was prepared by dissolving 4.6773 g of $[Cr(CO)_3C_5Me_5]_2$ in 560 mL of toluene and was filtered in the glovebox into a separate Schlenk flask. In separate vials, stock solutions of Ph₃SnH (0.0425 g) and Ph₃SnD (0.0474 g) were each prepared in 2 mL of toluene. A 33 mL sample of the \bullet Cr(CO)₃C₅Me₅ solution was loaded into a syringe, taken from the glovebox, and loaded under an atmosphere of 22 psi CO into the glass reactor thermostated at 38.5 °C. Approximately 20 min were allowed for temperature equilibration. A 3 mL aliquot of the stock solution of the Cr radical was taken to run an FTIR spectrum prior to initiation of the reaction. A 0.500 mL sample of the Ph₃SnH solution was loaded into a Hamilton gas-tight syringe fitted with a valve. Reaction was initiated by injection of the Ph₃SnH solution followed by periodic sampling of the reaction progress by removing a 2-3 mL aliquot to the FTIR cell and recording the spectrum. A total of six runs were studied using three samples of Ph₃SnH and three samples of Ph₃SnD and alternating the order in which the samples were run. The reactions were run under pseudo-first-order conditions of excess •Cr- $(CO)_{3}C_{5}Me_{5}$ and were found to be first order in Ph₃SnH(D) through at least three half-lives. Reactions run at differing absolute •Cr- $(CO)_3C_5Me_5$ concentration showed that the reaction was first order in this reagent as well. Reported experimental data are typically the average of at least three separate runs at each temperature. Representative spectroscopic data and kinetic plots and an Eyring plot are found in the results section.

Calorimetric Measurement of Reaction of •Cr(CO)₃C₅Me₅ and Ph_3SnH . In the glovebox, a solution of crystalline Ph_3SnH (0.0866 g) was prepared in 2 mL of C_6D_6 , and and aliquot of 0.250 mL of this solution was loaded into one chamber of a slightly modified Setaram Calvet calorimeter mixing cell. A second solution containing 0.0449 g of $[Cr(CO)_3C_5Me_5]_2$ was dissolved in 6 mL of C_6D_6 . Approximately 5.0 mL of this solution was filtered through a syringe filter into a second mixing chamber. The calorimeter cell was sealed, taken from the glovebox, and loaded into the Setaram C-80 calorimeter. Following temperature equilibration, the reaction was initiated, and the calorimeter was rotated to achieve mixing. Following return to baseline the calorimeter cell was taken into the glovebox. Aliquots were taken of the calorimetric solution and analyzed by FTIR and NMR spectroscopy. The measured value of -34.3 ± 1.1 kcal/mol is adjusted to be more exothermic by -2.3 ± 0.7 kcal/mol to compensate for endothermic dissociation of small amounts of $[Cr(CO)_3C_5Me_5]_2$ present in solutions of $\bullet Cr(CO)_3C_5Me_5$ and which occurs due to dilution effects during the reaction as $\bullet Cr(CO)_3C_5Me_5$ is consumed and some $[Cr(CO)_3C_5Me_5]_2$ dissociates in keeping with previously reported equilibrium data.³³ The final accepted value is -36.7 ± 1.8 kcal/mol and corresponds to the reaction enthalpy if $[Cr(CO)_3C_5Me_5]_2$ was completely dissociated to $\bullet Cr(CO)_3C_5Me_5$ under calorimetric condition measurements.

Calorimetric Measurement of Catalytic Dehydrogenation of Ph₃SnH by Pd(IPr)(P(p-tolyl)₃). In the glovebox, a solution of crystalline Ph₃SnH (0.1975 g) was prepared in 2 mL of C₆D₆, and this solution was loaded into one chamber of a slightly modified Setaram Calvet calorimeter mixing cell. A second solution containing between 1 and 5 mol % of $Pd(IPr)(P(p-tolyl)_3)$ was dissolved in 1 mL of C_6D_6 and added to the second mixing chamber. The calorimeter cell was sealed, taken from the glovebox, and loaded into the calorimeter. Following temperature equilibration, the reaction was initiated, and the calorimeter was rotated to achieve mixing. Following return to baseline the calorimeter cell was taken into the glovebox. An aliquot was taken of the calorimetric solution and analyzed by NMR spectroscopy. Conversion of Ph₃SnH to Ph₃SnSnPh₃ was found to be quantitative within 1%. Use of one-half or twice the amount of catalytic $Pd(IPr)(P(p-tolyl)_3)$ showed no apparent change in enthalpy of reaction leading to the conclusion that the dominant heat effect measured corresponded to dehydrogenation of Ph₃SnH with negligible contributions from changes in $Pd(IPr)(P(p-tolyl)_3)$. The accepted value of -15.8 ± 2.2 kcal/mol is the average of six separate measurements.

Growth of Crystals of Ph₃Sn–Cr(CO)₃C₅Me₅. In the glovebox, a solution was made in ~15 mL of heptane of 0.0284 g of $[Cr(CO)_3C_5Me_5]_2$ and 0.0368 g of Ph₃SnH. The solution was kept in a sealed vial for over a week in the glovebox and in the dark. During that time yellow crystals grew, and these were separated, covered with mineral oil, and taken for crystallographic study.

Growth of Crystals of Cy_3Sn-Cr(CO)_3C_5Me_5. In the glovebox, a solution was made in 5 mL of toluene of 0.0453 g of [Cr-(CO)_3C_5Me_5]_2 and 0.0587 g of Cy_3SnH. The solution was kept in a sealed vial for over a week in the glovebox and in the dark. During that time yellow crystals grew, and these were separated, covered with mineral oil, and taken for crystallographic study.

Crystallographic Analyses. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å).³⁴ The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.³⁴ Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses and were refined by full-matrix least-squares on F^2 by using the SHELXTL software package.³⁵ All non-hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Yellow single crystals of Ph₃Sn–Cr(CO)₃C₅Me₅ suitable for X-ray diffraction analyses were obtained by reaction in heptane solvent as described previously and crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with either of the space groups *Cc* or *C2/c*, the latter of which was confirmed by the successful solution and refinement of the structure. With *Z* = 16, there are two formula equivalents of the molecule present in the asymmetric crystal unit. Yellow single crystals of Cy₃Sn–Cr(CO)₃C₅Me₅ suitable for X-ray diffraction analyses were obtained by reaction in heptane solvent as described previously and crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/c$.

Computational Details. Electronic structure calculations were performed using the B3LYP density functional³⁶ with the D3(BJ)

Table 1. Crystallographic Data for $R_3Sn-Cr(CO)_3C_5Me_5$ (R = $R_3Sn-Cr(CO)_3C_5Me_5$)

=	Ph, C	y) Co	mpounds	

	Ph_3Sn- $Cr(CO)_3C_5Me_5$	Cy ₃ Sn– Cr(CO) ₃ C ₅ Me ₅
empirical formula	CrSnO ₃ C ₃₁ H ₃₀	$CrSnO_{3}C_{31}H_{48}$
formula weight	621.24	639.38
crystal system	monoclinic	monoclinic
lattice parameters		
a (Å)	36.9426(19)	18.1471(8)
b (Å)	8.7211(5)	17.7577(8)
c (Å)	37.1627(19)	9.7232(4)
α (deg)	90	90
β (deg)	109.098(1)	95.814(1)
γ (deg)	90	90
V (Å ³)	11 314.1(10)	3117.2(2)
space group	C2/c (No. 15)	$P2_1/c$ (No. 14)
Z value	16	4
$ ho_{\rm calc}~({ m g/cm^3})$	1.459	1.362
μ (Mo K α) (mm ⁻¹)	1.296	1.177
temperature (K)	296(2)	296(2)
$2\Theta_{\rm max}$ (deg)	59.00	59.00
No. obs. $(I > 2\sigma(I))$	12268	6250
No. parameters	659	330
goodness of fit	1.035	1.062
max. shift in cycle	0.004	0.003
residuals ^a : R1; wR2	0.0332; 0.0693	0.0454; 0.1177
absorption correction, max/min	multiscan 0.8813/0.5635	multiscan 0.9768/0.6377
largest peak in final diff. map (e^-/\tilde{A}^3)	0.516	1.621

 ${}^{a}R1 = \sum_{hkl} (||F_{obs}| - |F_{calc}||) / \sum_{hkl} |F_{obs}|; wR2 = [\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^{2} / \sum_{hkl} wF_{obs}^{-2}]^{1/2}, w = 1/\sigma^{2}(F_{obs}); \text{GOF} = [\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^{2} / (n_{data} - n_{vari})]^{1/2}.$

empirical dispersion correction³⁷ along with the Def2-SV(P)³⁸ basis set. Geometry optimizations were performed without any symmetry restrictions, and all stationary points were optimized by computing analytical energy gradients. The obtained minima were characterized by performing energy second derivatives, confirming them as minima by the absence of negative eigenvalues of the Hessian matrix of the energy. To further refine the energies obtained from the B3LYP-D3(BJ)/Def2-SV(P) calculations, single-point calculations were performed using the larger $Def2\text{-}TZVP^{38}$ basis set. In addition, analogous single-point calculations were also performed with the PBE0 density functional.³⁹ To test the influence of the solvation effects in the BDEs calculated, single-point calculations in toluene solution using the IEF-PCM model⁴⁰ on the previously optimized gas-phase structures were finally performed for selected species. Computed electronic energies were corrected for zero-point energy and thermal energy to determine $\Delta H^0(298 \text{ K})$ values. The X-H BDE were calculated computing the enthalpy of reaction with molecular H₂ for the corresponding radicals using the H–H BDE in H_2 of 104.2 kcal/mol⁴¹ analogously to the procedure described by Lee and Holm⁴² to derive X-O BDE values. All calculations were performed with the Gaussian 09 suite of programs.43

RESULTS

X-ray Structures of $R_3Sn-Cr(CO)_3C_5Me_5$ (R = Ph, Cy). Pure $R_3Sn-Cr(CO)_3C_5Me_5$ complexes were prepared by slow reaction of $\bullet Cr(CO)_3C_5Me_5$ in the presence of excess R_3SnH . X-ray quality crystals were produced in this way for Ph₃Sn-Cr(CO)₃C₅Me₅ and Cy₃Sn-Cr(CO)₃C₅Me₅, and their structures are shown in Figures 1 and 2.

The Sn–Cr bond distance is longer for the Cy₃Sn (2.816 Å) derivative compared to the Ph₃Sn complex (2.734 Å), which



Figure 1. An ORTEP of the molecular structure of $Ph_3Sn-Cr(CO)_3C_3Me_5$ showing 40% probability thermal ellipsoids. Cr1-Sn1 = 2.7393(4) Å; Cr2-Sn2 = 2.7294(4) Å (molecule 2).



Figure 2. An ORTEP of the molecular structure of $Cy_3Sn-Cr(CO)_3C_5Me_5$ showing 40% probability thermal ellipsoids. Cr1-Sn1 = 2.8158(6) Å.

would appear to imply a stronger bond for the aryl stannane derivative. The most closely related literature structure the authors could find was that of Cl₂Sn[Cr(CO)₃C₅H₅]₂, which has two Sn–Cr bond lengths (2.695 and 2.701 Å)⁴⁴ that are similar to the value measured here for Ph₃Sn–Cr(CO)₃C₅Me₅. The ν_{CO} bands at 1955 and 1872 cm⁻¹ for Cy₃Sn–Cr(CO)₃C₅Me₅ and at 1970 and 1889 cm⁻¹ for Ph₃Sn–Cr(CO)₃C₅Me₅ are in keeping with the more electron-donating power of the Cy group compared to Ph.

Reaction of R₃SnH and •Cr(CO)₃C₅Me₅. Production of the Sn-Cr products can occur from the reaction of the stannane with either •Cr(CO)₃C₅Me₅ as shown in reaction 4 or with HCr(CO)₃C₅Me₅ as shown in reaction 5. It can also exist as an admixture of reaction 4 + reaction 5 as shown in eqs 6 ($\alpha = 1$) and 7 ($0 \le \alpha \ge 1$).

$$2 \bullet Cr(CO)_3 C_5 Me_5 + R_3 SnH$$

$$\rightarrow R_3 Sn - Cr(CO)_3 C_5 Me_5 + HCr(CO)_3 C_5 Me_5 \qquad (4)$$

 $HCr(CO)_{3}C_{5}Me_{5} + R_{3}SnH$

$$\rightarrow R_3 \text{Sn} - \text{Cr}(\text{CO})_3 \text{C}_5 \text{Me}_5 + \text{H}_2 \tag{5}$$

 $2 \bullet Cr(CO)_3 C_5 Me_5 + 2R_3 SnH$

$$\rightarrow H_2 + 2R_3 Sn - Cr(CO)_3 C_5 Me_5 \tag{6}$$

 $2 \bullet Cr + (1 + \alpha) R_3 SnH$

$$\rightarrow (1+\alpha)R_3Sn-Cr + (\alpha)H_2 + (1-\alpha)HCr$$
(7)

Reactions 4 and 5 refer only to the source of the Sn-Cr product being either the chromium radical (eq 4) or the corresponding hydride (eq 5) and not the mechanism, which may be more complex and can also vary as a function of reaction conditions (see below). In the absence of added additional chromium hydride, at the start of the reaction, the initial $[HCr(CO)_3C_5Me_5] = 0$, and reaction 5 depends upon its generation by reaction 4. At the start of the reaction, reaction 4 predominates, and the concentration of $HCr(CO)_3C_5Me_5$ will increase in parallel to that of the Sn-Cr product. Under some reaction conditions, once sufficient chromium hydride has been generated from reaction 4, reaction 5 may gain in significance. A mixture of the two reactions will result in little change in $HCr(CO)_3C_5Me_5$ concentration even as the Sn-Cr complex increases. Because of the highly air-sensitive nature of the reactants and the unusual pseudo-first-order reaction conditions studied, such overall views are useful in delineating the mechanism.

Kinetic Studies of the Reaction of $\bullet Cr(CO)_3C_5Me_5$ with Pseudo-First-Order Conditions of Excess Cy₃SnH. The initial reaction studied was between Cy₃SnH present in pseudofirst-order excess and $\bullet Cr(CO)_3C_5Me_5$ in toluene under either Ar or CO atmosphere. This reaction proved unsuitable for kinetic study, because reactions 4 and 5 could not be separated, which made accurate kinetic analysis difficult. Typical spectroscopic data under Ar atmosphere are shown in Figure 3.

The major FTIR band of the radical at 1994 cm⁻¹ decreases to about half its intensity and converts to the 1995 cm⁻¹ (HCr(CO)₃C₅Me₅) as the bands at 1955 and 1872 cm⁻¹ due to Cy₃Sn-Cr(CO)₃C₅Me₅ grow. This process is relatively rapid and occurs during the first 20 min. Over the next 2 h, the bands



Figure 3. FTIR spectra of the reaction of \bullet Cr(CO)₃C₅Me₅ (~0.015 M) with Cy₃SnH (~0.075 M, a 10-fold molar excess according to the stoichiometry of reaction 4) in toluene at 25 °C under argon atmosphere.

due to Cy₃Sn–Cr(CO)₃C₅Me₅ continue to grow, and the bands due to HCr(CO)₃C₅Me₅ (1995 and 1912 cm⁻¹) shrink, as does the band near 1784 cm⁻¹ due to Cy₃SnH. Note that the extinction coefficient of ν_{Sn-H} is much lower than the carbonyl bands, and the stannane was present in 10-fold molar excess. Note also that the inset to Figure 3 shows that near 1906 cm⁻¹ there is an unstable isosbestic point, which is held through ~30% reaction. Following that it shifts away. This is because at first it is predominantly reaction 4, and then it is a changing mixture of reactions 4 and 5 that occurs (eq 7).

The data in Figure 3 are plotted as a function of time in Figure 4 for the absorption at 1955 (Sn-Cr complex) and 1915



Figure 4. Plot of decrease in A_{1896} (•Cr) and increase in A_{1955} (Sn–Cr) (magenta) and A_{1915} (HCr) (green) vs time for the data in Figure 3. From ~1000 s the concentration of the chromium hydride stays nearly constant and then begins to decrease after 3500 s.

cm⁻¹ (Cr hydride). It can be seen that for the first six or seven points the two curves show similar rates of increases. Following that, the rate of increase of the Sn–Cr product continues, but between 1000 and 3000 s the concentration of the hydride is roughly constant and then begins to decrease. This is attributed to the predominant channel being reaction 4 for the first 1000 s, followed by a mixture of eqs 4 and 5 between 1000 and 3000 s, and a dominance of reaction 5 following that. The reaction was not followed to completion, but in synthetic studies a nearly quantitative yield of $Cy_3Sn-Cr(CO)_3C_5Me_5$ is obtained with essentially no $HCr(CO)_3C_5Me_5$ production indicating that the slower reaction 5 does continue on. Note that almost all the Cr radical is consumed in the first step, and we believe that it serves as a catalyst in the second step as discussed later.

Finally, it is informative in terms of interpretation of other data to look at the spectroscopic differences at the beginning and end of the reaction. Shown in Figures 5 and 6 are the spectroscopic changes that occur at the beginning and end of the reaction.

No attempt to resolve these two steps quantitatively into their separate rate laws was made, since extracting one reaction from the other was deemed as being too difficult. Instead, better reaction conditions were sought. The data from these studies, however, are in qualitative agreement with the kinetic behavior studied under different conditions, when allowances are made for the differing concentrations. A probable mechanism for both reactions 4 and 5 is discussed in a later section.

Kinetic Studies of the Reaction of Cy_3SnH with Pseudo-First-Order Conditions of Excess $\bullet Cr(CO)_3C_5Me_5$



Figure 5. Spectroscopic changes at the beginning of the reaction showing 2-1, 3-1, 4-1, 5-1 in which the first spectrum is subtracted from each of the following four spectra. These data show a clear increase in the chromium hydride and the Sn–Cr product as well as a decrease in Cr radical. Because of overlap of the peaks some reaction changes nearly cancel. For example, the Cr radical has an absorption at 1994 cm⁻¹ and the hydride at 1995 cm⁻¹, and so only a small growth of the band at 1995 cm⁻¹ is observed. The growth of the hydride at 1912 cm⁻¹ however is clear in spite of the fact that there is some overlap with the strongly decreasing band of the Cr radical at 1896 cm⁻¹.



Figure 6. Spectroscopic changes at the end of the reaction showing 13-12, 14-12, 15-12, 16-12 in which the first spectrum is subtracted from each of the following four spectra. These data show that, whereas there is an increase in the Sn–Cr product, the concentration of the chromium hydride remains constant and then decreases as the path changes from reaction 4, to reaction 7 (4 + α 5), and then to reaction 5.

under Ar and CO Atmosphere. The difficulty in kinetically resolving these two processes led us to seek other reaction conditions for study. Reaction of a limited amount of Cy_3SnH in the presence of a large excess of $\bullet Cr(CO)_3C_5Me_5$ was studied under Ar atmospheres. In spite of changing the reagent present in excess from Cy_3SnH to $\bullet Cr(CO)_3C_5Me_5$, toward the end of the reaction, reaction 5 became significant. The only situation where reliable monophasic kinetic data could be obtained was under CO pressure and excess $\bullet Cr(CO)_3C_5Me_5$. Representative spectroscopic data are shown in Figure 7. Analysis of the band shapes for the large radical peaks indicated that reaction 4 was followed and that the chromium hydride



Figure 7. FTIR spectra of the reaction of \bullet Cr(CO)₃C₅Me₅ with Cy₃SnH in toluene at 36 °C under CO atmosphere. The chromium radical is present in ~15-fold molar excess as shown by the dominant peaks near 1994 and 1890 cm⁻¹.

was generated as the reaction proceeded throughout the reaction period.

The small band near 1955 cm⁻¹ assigned to the Sn–Cr product and shown in the inset allows accurate quantitative analysis. Note that in the region between 1920 and 1900 cm⁻¹, due to a higher initial Cr radical concentration, the isosbestic point near 1905 does not result in line crossing, but the behavior is clean and in keeping with only reaction 4 occurring over this time period under CO atmosphere. The limited Cy₃SnH reacts preferentially with the Cr radical, which is present in ~20-fold excess relative to the chromium hydride. The presence of CO rather than Ar serves to reduce to negligible reaction 5, and the kinetics studied correspond predominantly to reaction 4. A first-order plot of $\ln(A_{\infty} - A)$ versus time is linear through four half-lives as shown in Figure 8.



Figure 8. Plot of $\ln(A_{\infty} - A)$ vs time for the data in Figure 7.

Reaction of ⁿBu₃SnH and ^tBu₃SnH with •Cr-(CO)₃C₅Me₅. The reaction pattern for ⁿBu₃SnH was found to be similar to that of Cy₃SnH in all respects. Because of the greater tendency of solutions of ⁿBu₃SnH to lose H₂ and form ⁿBu₃SnSnⁿBu₃, only one series of kinetic data was generated for ⁿBu₃SnH as listed later in Table 2. In contrast, the reactivity observed for ^tBu₃SnH was different in behavior to the other

Table 2. Derived Rate Constants for Reactions of R_3 SnH in Toluene under Pseudo-First-Order Conditions of Excess \bullet Cr(CO)₃C₅Me₅

$T(^{\circ}C)$	stannane	atmosphere	$k (M^{-1} s^{-1})$
17	Ph ₃ SnH	1.7 CO	0.028
17	Ph ₃ SnH	2.7 CO	0.029
17	Ph ₃ SnH	3.2 CO	0.031
27	Ph ₃ SnH	1.7 Ar	0.165
27	Ph ₃ SnH	1.7 CO	0.097
27	Ph ₃ SnH	2.7 CO	0.097
35.5	Ph ₃ SnH	2-3 CO	0.188
36	Cy ₃ SnH	1.7 CO	0.07
36	Cy ₃ SnH	1.7 Ar	0.17
36	ⁿ Bu ₃ SnH	2-3 CO	0.05
38.5	Ph ₃ SnH	2-3 CO	0.236
38.5	Ph ₃ SnD	2-3 CO	0.210
43.5	Ph_3SnH	2-3 CO	0.395

stannanes studied. Oxidative addition producing HCr-(CO)₃C₅Me₅ and ^tBu₃Sn-Cr(CO)₃C₅Me₅ was observed spectroscopically; however, further reaction with excess free stannane occurred before the reaction was completed. In contrast to the other stannanes studied, where the further reaction increased the yield of the R₃Sn-Cr(CO)₃C₅Me₅ product, the Sn-Cr complex was found to convert quantitatively to the chromium hydride as shown in reaction 8.

$$^{t}Bu_{3}Sn-Cr(CO)_{3}C_{5}Me_{5} + ^{t}Bu_{3}SnH$$

→ HCr(CO)_{3}C_{5}Me_{5} + unknown Sn^tBu_{3} product (8)

The presumed product of reaction is $Sn_2^{t}Bu_6$, but no effort was made to study further this reaction, which did not yield a stable $R_3Sn-Cr(CO)_3C_5Me_5$ complex.

Kinetic Studies of the Reaction of Ph_3SnH Under CO with Pseudo-First-Order Excess of $\bullet Cr(CO)_3C_5Me_5$. As determined from studies of Cy₃SnH, the best conditions to obtain kinetic data proved to be under a CO atmosphere using a pseudo-first-order of the Cr radical. Kinetic data under pseudo-first-order conditions are linear through four half-lives. As was the case with Cy₃SnH, CO pressure was found to slow the reaction, and this effect leveled off at 1–2 atm at lower temperatures and 2–3 atm at higher temperatures. Spectroscopic data correspond closely to those shown above for Cy₃SnH. A plot of rate data at different conditions is shown in Figure 9.

As described later, a qualitative investigation at 36 atm CO showed that reaction 1 occurred at a rate in keeping with data at 2–3 atm pressure. In all cases, the reaction was found to be first order in Ph₃SnH. Doubling or cutting in half the concentration of excess chromium radical resulted in doubling or halving the observed rate of reaction indicating the reaction was also first order and not second order in metal radical. A normal kinetic isotope ratio of 1.12 was measured at 38.5 °C. The reactions of both Ph₃SnH and Cy₃SnH are faster under Ar by a factor of 2–3, and the reactions of Ph₃SnH under CO are 2–3 times faster than Cy₃SnH and 3–4 times faster than ⁿBu₃SnH. Collected data are shown in Table 2.

Variable-temperature studies for reaction of Ph_3SnH from data in Table 2 were used to contruct an Eyring plot as shown in Figure 10.

Using the experimental value of $\Delta H^{\ddagger} = 15.7 \pm 1.5$ kcal/mol and assuming an overbarrier of $\sim 2 \pm 1$ kcal/mol and the



Figure 9. Plot of $\ln(A_{\infty} - A)$ vs time through the first three to four half-lives showing that the rate of reaction under Ar is faster than under CO but that studies at 10 psi (1.7 atm CO absolute pressure) and 27 psi (2.7 atm CO absolute pressure) are equivalent within experimental error. At this temperature, 27 °C, reaction 5 did not become significant until after the third half-life for Ph₃SnH.



Figure 10. Eyring plot for reaction of Ph₃SnH and •Cr(CO)₃C₅Me₅ in the temperature range of 15–43.5 °C from which derived activation parameters are $\Delta H^{\ddagger} = 15.7 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -11 \pm 5$ cal/ (mol·K).

computational data in this work (see below) yields an estimate of the thermochemical difference between the Cr–H and Sn–H bonds of 13.7 \pm 1.8 kcal/mol. Adopting a value of 62.3 \pm 1.0 kcal/mol for the Cr–H BDE²⁸ gives an estimate of 76.0 \pm 3.0 kcal/mol for the Ph₃Sn–H BDE in toluene solution.

Reaction of Ph₃SnH under CO at 36 atm with Pseudo-First-Order Excess of \bulletCr(CO)₃C₅Me₅. The greater rate of reaction under Ar versus CO atmosphere led us to test the reaction of 2 equiv of \bullet Cr(CO)₃C₅Me₅ and 1 equiv of Ph₃SnH in toluene at 36 atm of CO. The stannane solution was isolated from the Cr radical solution in a small glass tube in a Hoke bomb. After the system was pressurized with 36 atm of CO at room temperature in toluene solution, the reaction was initiated by inverting the bomb and mixing the two solutions. After ~1 h the CO was vented, and a sample was loaded into an IR cell. As shown in the spectra in Figure 11, the reaction had gone to completion, and the HCr and Sn–Cr products were present in the correct stoichiometric ratio of reaction 4.

Solution Calorimetric Studies of Reaction of •Cr-(CO)₃C₅Me₅ and Ph₃SnH. The reaction enthalpy of Ph₃SnH



Figure 11. FTIR spectra of the stock solution of Cr radical (black) and product of reaction with Ph_3SnH (red) in toluene solution at 22 °C under 36 atm of CO pressure. Quantitative production of an equimolar mixture of the HCr and SnCr products occurs in ~1 h in keeping with kinetic studies and indicating that the radical reaction is not inhibited by higher pressures of CO. The intensity of the product bands relative to starting material bands is somewhat higher than occurs during kinetic studies where filtered solutions of the Cr radical are used. In this study the reaction was not filtered into the bomb, and some microcrystalline Cr–Cr dimer may have dissolved and reacted during the reaction.

with 2 mol of \bullet Cr(CO)₃C₅Me₅ (reaction 4) was measured in toluene solution at 30 °C using a Setaram Calvet calorimeter in C₆D₆ solution, and the reaction stoichiometry was confirmed by both NMR and FTIR analysis. The value obtained of $\Delta H =$ -36.7 ± 1.8 kcal/mol can be used to estimate a value of the Sn-Cr BDE in Ph₃Sn-Cr(CO)₃C₅Me₅. Adopting a value of 62.3 ± 1.0 kcal/mol for the Cr-H BDE,²⁸ as well as a value of 76.0 ± 3.0 kcal/mol for the Ph₃Sn-H BDE (see above), yields a derived value of 50.4 ± 3.5 kcal/mol for the Ph₃Sn-Cr(CO)₃C₅Me₅ BDE in toluene solution.

Catalytic Dehydrogenation of Ph₃SnH by Late Transition Metal Complexes. The recently reported⁵ complex $[(\mu-H)Pt(I^tBu)(Sn^tBu_3)]_2$ was tested as a catalyst for dehydrogenation of Ph₃SnH as shown in eq 9 but was found to be of low activity.

$$2Ph_3SnH \to H_2 + Ph_3SnSnPh_3 \tag{9}$$

Nolan and co-workers have reported⁴⁵ synthesis and structure of $Pd(IPr)(PPh_3)$, and we prepared in strict analogy to the published procedure the closely related but more toluene-soluble complex $Pd(IPr)(P(p-tolyl)_3)$. This Pd(0)complex proved to be highly effective in catalysis of reaction 9. In typical reaction conditions samples of \sim 0.200 g of Ph₃SnH were quantitatively converted to Ph₃SnSnPh₃ in ~5 mL of C_6D_6 using 0.002 to 0.010 g of $Pd(IPr)(P(p-tolyl)_3)$. The enthalpy of reaction was found to be independent of the amount of catalyst used provided it was present in less than 5 mol percent. The enthalpy of reaction 9, $\Delta H = -15.8 \pm 2.2$ kcal/mol, is the average of six separate measurements. Adopting the values of 76.0 \pm 3.0 and 104.2 kcal/mol for the Ph₃Sn-H (see above) and H₂⁴¹ BDEs, respectively, a value of 63.8 \pm 3.7 kcal/mol can be derived for the Ph₃Sn-SnPh₃ BDE in toluene solution. There is good agreement between theory and experiment, as discussed later, and this gives some degree of confidence to the assigned values in spite of rather large assigned error limits.

Computational Results. Density functional theory (DFT) calculations were performed to further support the experimentally determined BDE values in this work. Moreover, other Sn–H, Sn–Sn, and Sn–Cr BDE values were computed for several R_3 SnH, R_3 SnSn R_3 , and R_3 Sn–Cr(CO)₃C₅Me₅ species, for which it was not possible to determine these data experimentally. Table 3 collects a summary of some selected structural parameters computed for the compounds studied.

Table 3. Selected Bond Lengths (Å) Computed for the Species Studied at the B3LYP-D3(BJ)/Def2-SV(P) Level

R	Sn-H in R_3 Sn-H	Sn-Sn in R ₃ Sn-SnR ₃	Sn-Cr in R_3 Sn-Cr ^a
Me	1.741	2.805 [2.764] ^b	2.771
Су	1.747	2.795 [2.805] ^c	$2.810 [2.816]^d$
^t Bu	1.751	2.907 [2.894] ^e	2.934
Ph	1.735	2.766 [2.763] ^f	$2.739 [2.739; 2.729]^d$

 a Cr = Cr(CO)₃C₅Me₅. Available experimental values determined by X-ray crystallography between brackets. b Taken from ref 46. c Taken from ref 47. d This work. e Taken from ref 48. f Taken from ref 49.

There is a perfect agreement between the gas-phase computed structures and those obtained by X-ray crystallography. Dispersion effects were found to be important especially for the description of the structures in crowded $R_3Sn-SnR_3$ and $R_3Sn-Cr(CO)_3C_5Me_5$ species. For instance, when the corresponding $R = {}^{t}Bu_3$ species were optimized without the inclusion of dispersion effects, Sn-Sn and Sn-Cr bond lengths of 3.005 and 3.061 Å, respectively, were obtained, ~0.1 Å longer than the experimentally determined distances.

As it can be seen in Table 3, the Sn-H bond length in the optimized structure of the stannanes is almost constant at 1.745 \pm 0.010 Å being not greatly influenced by the R substituents bound to the Sn atom. However, the Sn-Sn and Sn-Cr bond lengths are more dramatically affected by the steric hindrance imposed by the R substituents. The Sn-Sn bond length calculated is similar in Me₃SnSnMe₃ and Cy₃SnSnCy₃ compounds, but it increases by ~0.1 Å when bulkier 'Bu substituents are bound to the tin. Likewise, the Cr-Sn bond distance is more than 0.1 Å longer in the ^tBu₃Sn- $Cr(CO)_{3}C_{5}Me_{5}$ complex as compared to the analogous Cy complex. The sum of the three R-Sn-R angles in the optimized structure of all R₃Sn• radicals is in the range of 318-330° indicating the pyramidal geometry of the Sn atom in these species as it has been previously reported.⁵⁰ However, the Σ R-Sn-R value increases for bulkier substituents in alkyl radicals (318.6° (R = Cy) vs 329.5° (R = ^{t}Bu)). The computed Mulliken spin density located on the Sn atom in alkyl radicals is nearly constant (0.79 (R = Me), 0.76 (R = Cy, ^{t}Bu)). In the case of $Ph_3Sn \bullet$, the spin density slightly decreases (0.74) indicating little delocalization of the unpaired electron in the phenyl rings as previously reported.⁵¹

BDEs calculated at the PBE0-D3(BJ)/Def2-TZVP//B3LYP-D3(BJ)/Def2-SV(P) level are collected in Table 4. The BDEs computed in gas phase and in toluene solution are nearly identical with the larger differences lower than 1 kcal/mol. As previously reported by Boyd and co-workers,²⁵ the serious lack of well-established accurate experimental BDE values for organotin compounds make it difficult to assess the performance of the DFT methods employed. In this regard, they used high-level CCSD(T) calculations to test the reliability of their Table 4. Experimental (in bold) and Computational (in italics) Sn-H, Sn-Sn, and Sn-Cr Bond Dissociation Enthalpy Values in R_3SnH , R_3SnSnR_3 , and R_3Sn - $Cr(CO)_3C_5Me_5$ Species Obtained in This Work along with Previously Reported Experimental Data (in kcal/mol)

	Sn-H	Sn-Sn	Sn-Cr
R = Ph	76.0 ± 3.0	63.8 ± 3.7	50.4 ± 3.5
	74.5, 74.5 ^b	65.4, 64.7 ^b	52.4, 52.1 ^b
	71.0 ^c	51.4 ^d	
R = Me	76.3, 76.4 ^b	59.5, 59.4 ^b	50.2, 50.2 ^b
	76.1 ^c	60.4 ± 3.5^{e}	
	74.0 ± 2.6^{e}	68.5 ± 6.0^{f}	
	77.1 ± 4.1^{f}	61.6 ^h	
	75.0 ± 3.5^{g}		
R = Cy	75.9	66.9	49.6
$R = {}^{t}Bu$	75.8	58.7	37.0

^{*a*}Computed at the PBE0-D3(BJ)/Def2-TZVP//B3LYP-D3(BJ)/Def2-SV(P) level. ^{*b*}Computed values in toluene solution. ^{*c*}Taken from ref 22. ^{*d*}On the basis of the enthalpy of formation of Ph₃SnSnPh₃ reported in ref 13 in combination with appearance potential studies reported in ref 19. ^{*f*}Taken from ref 9a with the uncertainty as recalculated in ref 17. ^{*e*}Taken from ref 17. ^{*g*}Taken from ref 21. ^{*h*}Taken from ref 18.

DFT results. In this work, a good agreement between computed and available experimental BDEs (see Table 4) was generally obtained. As it can be seen in Table 4, for Me₃SnH, there are several experimental determinations of the Sn-H BDE by different methods, and all of the values are \sim 75.5 ± 1.5 kcal/mol. Moreover, Boyd and co-workers calculated a Sn-H BDE value of 76.1 kcal/mol at the CCSD(T)/SDB(Sn)-aug-cc-pVTZ(other atoms) level.²⁵ Furthermore, Allendorf and Mellius⁵² derived a value of 76.7 kcal/ mol applying the BAC-MP4 method that combines ab initio electronic calculations with empirical corrections to obtain accurate heats of formation. In spite of that we used a much lower level of theory in this paper and thus applicable to bigger molecules, the determined value of 76.3 kcal/mol (Table 4) is in perfect agreement to those obtained experimentally or using high-level calculations. In addition, the computed Sn-H BDE in Ph₃Sn-H of 74.5 kcal/mol is also in good agreement to the value of 76.0 \pm 3.0 kcal/mol derived experimentally by kinetic measurements in toluene solution in the current study (see above), but it is slightly higher than the previously reported experimental value of 71.0 kcal/mol (see Table 4). No experimental BDE data were found to compare with the calculated values for the rest of the compounds studied. Nonetheless, there are enough data to assess the accuracy of the computed Sn-H BDE values giving some measure of confidence to the data that were not previously measured experimentally.

The paucity of accurate experimental Sn–Sn and Sn–Cr BDE data to compare to the values predicted by DFT is even more problematic. Three independent experimental determinations of the Sn–Sn BDE in Me₃SnSnMe₃ are shown in Table 4, and they span a range of 8 kcal/mol. The value of 59.5 kcal/mol computed in this work is in good agreement with the most recent measurement of 60.4 ± 3.5 kcal/mol reported by Baer and co-workers.¹⁷ In the current work, a value of 63.8 ± 3.7 kcal/mol was derived for the Sn–Sn BDE in Ph₃SnSnPh₃ in toluene solution also in good agreement with the calculated value of 64.7 kcal/mol. However, a much lower value of 51.4

kcal/mol has been previously proposed by Steele and coworkers¹³ based on their enthalpy of formation measurements of Ph₃SnSnPh₃ by combustion calorimetry in combination with appearance potential studies reported by Chambers and Glocking.¹⁹

The only Sn–Cr BDE data the authors could find in the literature is that corresponding to the Me₃Sn–Cr(CO)₃C₅H₅ complex determined by a combination of appearance and ionization potential measurements.¹⁸ The experimental value reported of 53.4 kcal/mol is somewhat higher than our computed value of 50.1 kcal/mol. In this work, a Sn–Cr BDE value in toluene solution of 50.4 ± 3.5 kcal/mol for Ph₃Sn–Cr(CO)₃C₅Me₅ was determined in good agreement to the computed value of 52.4 kcal/mol in toluene solution. Moreover, a Cr–H BDE in HCr(CO)₃C₅Me₅ of 62.2 kcal/mol was calculated in the current work in perfect agreement to the experimental determination of 62.3 ± 1.0 kcal/mol.²⁸

The kinetics of the reaction of Ph_3SnH with excess $\bullet Cr(CO)_3C_5Me_5$ was studied as stated in a previous section. In this regard, a relaxed potential energy surface scan along the Cr…H distance for the thermodynamically uphill HAT from Ph_3SnH to $\bullet Cr(CO)_3C_5Me_5$ (reaction 2) was performed also by DFT calculations and is shown in Figure 12.



Figure 12. Computed change in energy with the Cr…H distance at the PBE0-D3(BJ)/Def2-TZVP//B3LYP-D3(BJ)/Def2-SVP level. At each fixed Cr…H distance, the minimum energy structure was computed and the deviations from the energy of the optimized structure at a Cr… H fixed distance of 3.0 Å are shown.

The starting point places the two separate fragments •Cr(CO)₃C₅Me₅ and Ph₃SnH at a H···Cr distance of 3.0 Å, and there is little change in energy as •Cr(CO)₃C₅Me₅ approaches the Sn–H bond at an angle. Starting at an H···Cr distance of 2.4 Å a more linear geometry is adopted, and the energy is computed to rise to a value of 10 kcal/mol at a Cr–H distance of 1.599 Å, which corresponds to the H–Cr bond length observed in the optimized structure of HCr(CO)₃C₅Me₅ while retaining some interaction with the incipient Ph₃Sn• (Sn···H = 2.173 Å). The optimized structure of the last point of the scan in Figure 12 is shown in Figure 13. The reverse reaction in which an Ph₃Sn• approaches the H–Cr-(CO)₃C₅Me₅ bond is computed in the gas phase to be essentially barrierless.

To support mechanistic studies relevant to reaction under Ar rather than CO atmosphere, the structure and energetics of the interaction in which triphenyl stannane undergoes the CO



Figure 13. Optimized structure of the last point of the scan shown in Figure 12.

displacement reaction shown in reaction 10 were also investigated.

$$\bullet Cr(CO)_3 C_5 Me_5 + Ph_3 SnH$$

$$\to CO + \bullet Cr(Ph_3 SnH)(CO)_2 C_5 Me_5$$
(10)

Computed thermochemical data for reaction 10 are $\Delta H = 6.7$ kcal/mol and $\Delta S = -21.1$ cal/(mol·K). The computed structure of the chromium species obtained after CO displacement by Ph₃SnH is shown in Figure 14, which displays three-center bonding between Cr, Sn, and H.



Figure 14. Computed structure of $\bullet Cr(\mu-Ph_3SnH)(CO)_2C_5Me_5$.

The computed structure of this 17 e⁻ complex closely resembles that of 18 e⁻ analogues prepared by Klabunde⁵³ and Schubert.⁵⁴ A comparison of the Cr–H–Sn triangles is shown in Table 5.

In spite of difficulties in assigning the crystallographic position of the bridging H atom, there is a surprising agreement between the data for the computed structure of the proposed bridging hydride $17 e^-$ cyclopentadienyl dicarbonyl radical

Table 5. Comparison of Metrical Parameters (in Å) for η^2 -H–SnPh₃ Complexes

	Cr–			
complex	Sn	Cr-H	Sn-H	Sn-Cr-H
$Cr-Sn^{a}, Cr-H^{a}, Sn-H^{a}$	2.73	1.60	1.73	
$(\bullet)(\mu$ -H-SnPh ₃) (Cr(CO) ₂ C ₅ Me ₅)	2.69	1.62	2.16	54
$(\mu$ -H–SnPh ₃) $(Cr(CO)_2(C_6H_3Me_3)^b$	2.69	1.50	2.23	56
$(\mu$ -H-SnPh ₃)	2.70	1.59	2.02	48
$(Cr(CO)_2(p-C_6H_4(OMe)_2)^c)$				

^{*a*}This line refers to the uncomplexed species: $Cr-Sn = Ph_3Sn-Cr(CO)_3C_5Me_5$, where d_{Sn-Cr} was determined by X-ray crystallography, this work; $Cr-H = HCr(CO)_3C_5Me_5$, where d_{H-Cr} was determined computationaly, this work; Sn-H refers to Ph_3SnH , whose distance was determined by X-ray crystallography; see Table 2. ^{*b*}See ref 54. ^{*c*}See ref 53.

complex and the crystallographically determined structures of the 18 e⁻ arene dicarbonyl complexes. The similarity in geometry suggests that the singly occupied molecular orbital (SOMO) electron does not reside in the three-center Sn-H-Cr bonding orbital set, and this is confirmed as shown in Figure 15.



Figure 15. View of the computed SOMO for structure in Figure 14 showing two avenues of attack. The diffuse SOMO in red and green is primarily located on the Cr atom with very little electron density located near the Cr– μ -H–Sn three-center bond depicted by the triangle, which is in the plane of the paper in the figure. The two unblocked avenues of approach shown as Path A and Path B appear to show the best angle for approach for HAT from Cr (Path A) or HAT donation to Cr (Path B). Computed spin densities show the SOMO electron to be primarily on Cr (+1.19), with several small negative spin densities located of C atoms bonded to Cr. The reported spin densities include spin densities of the attached H atoms. In the case of the Cr–H bonds the spin density (–0.044), which is an order of magnitude greater than all other individual H atoms.

This is in keeping with metrical parameters shown in Table 5, since if the unpaired electron in this system was in an orbital assigned to the μ -H–Sn–Cr triangle, it would be expected to differ more greatly in structure from the stable 18 e⁻ structures reported by others. The greatest difference in Table 5 when compared to model complexes shown in the first line occurs in the Sn–H distance, which is compared to Ph₃SnH. The Cr–Sn distance and the H–Cr distances are close to those assigned to Ph₃Sn–Cr(CO)₃C₅Me₅ and HCr(CO)₃C₅Me₅, respectively. A

simple estimate of the enthalpy of reaction 10 based on Cr–CO (37),⁵⁵ Ph₃Sn–H (76), H–Cr (62), and Sn–Cr BDEs (50) would be 1 kcal/mol. The computed enthalpy of the reaction is +6.7 kcal/mol, which is in reasonable agreement with this estimate.

DISCUSSION

The major goal of this work was to measure Sn–H, Sn–Sn, and Sn–Cr BDE to allow comparison to existing literature data and to results obtained by computational methods. To achieve that goal, the mechanism of oxidative addition of stannanes to a 17 e^- organometallic radical was also studied. It can be difficult to prove organometallic mechanisms, and a primary focus was to find a set of conditions where the rate determining in HAT corresponded to the radical transfer step shown in reaction 2. This result, coupled with solution calorimetric and computational studies, allowed us to generate Sn–H, Sn–Cr, and Sn–Sn BDEs as discussed in the thermochemical section. Considerable kinetics and mechanistic studies were done, and these are discussed in a second section.

Thermochemical Studies. The derived value of 76.0 ± 3.0 kcal/mol based on kinetics studies for the Ph₃Sn-H BDE in toluene solution is in good agreement with the computed value of 74.5 kcal/mol. Computational studies showed that the Sn-H BDE for alkyl stannanes was relatively constant at nearly 76 kcal/mol. As shown in Table 4, solution photoacoustic data place the ⁿBu₃Sn-H BDE as 74 or 78 kcal/mol, and gas-phase radical studies lead to derived values of $Me_3Sn-H = 76$ and $Ph_3Sn-H = 71$ kcal/mol, a gap of 5 kcal/mol between the trialkyl and triphenyl stannane Sn-H BDE. However, computational studies reported here show a much smaller gap (Me₃Sn-H (76.3), Cy₃Sn-H (75.9), ^tBu₃Sn-H (75.8), and Ph₃Sn-H (74.5 kcal/mol); see Table 4). Though full kinetics studies were not performed for Cy₃SnH, it was found to obey an overall second-order reaction, and under comparable conditions to be no more than 5 times slower than Ph_3SnH (Table 2). That is in keeping with an activation energy lower than 1 kcal/mol less favorable for the Cy derivative and would not appear to be in keeping with a difference of 5 kcal/mol in BDE.

At first consideration, it may seem that the Sn-H BDE difference between alkyl and phenyl stannanes obtained in this work of ~1 kcal/mol is too low due to the possibility of electron delocalization of the unpaired electron in the phenyl rings of the Ph₃Sn• radical. The greater stability⁶⁶ of arenesubstituted radicals in sulfur chemistry⁵⁶ is well-established, and the PhS-H and MeS-H BDE differ by ${\sim}10$ kcal/mol for that reason. The lower BDE of PhS-H is attributed to delocalization of the unpaired electron of the PhS• radical into the π^* orbitals on the phenyl ring. We had noted earlier⁵⁷ that delocalization decreases in descending the chalcogenides and that there is less electron density donated to the arene ring in the SOMO of the PhTe• radical. Similar arguments apply to Ph₃Sn•, which is pyramidal in nature and as discussed in the computational results section shows that Mulliken spin density on the Sn atom of the R₃Sn• radicals is similar for alkyl and aryl derivatives indicating little stabilization in the Ph₃Sn• species by delocalization of the unpaired electron into the phenyl rings. Furthermore, photoacoustic calorimetric studies have also shown a similar behavior in the Ge-H BDE of organogermanes, where the Ge-H BDE derived for Me₃Ge-H (81.6 \pm 0.5 kcal/mol) is only slightly higher than that observed for $Ph_3Ge-H (80.2 \pm 0.8 \text{ kcal/mol})$.

Direct measurement of the catalytic dehydrogenation of Ph₃SnH allowed us to derive a value of 63.8 ± 3.7 kcal/mol for the Ph₃Sn-SnPh₃ BDE. These data are in good agreement with the computational value of 64.7 kcal/mol. The utilization of $Pd(IPr)(P(p-tolyl)_3)$ as a catalyst for reaction 9 for calorimetric studies is novel, and we plan to extend this to other stannanes to determine their enthalpies of dehydrogenation. The mechanism of the catalyzed dehydrogenation was not investigated at this time, since it was not germane to the goal of the present work. It is reasonable to assume that the key intermediate might involve oxidative addition of 2 equiv of Ph₃SnH to form a Pd(IV) intermediate with possible dissociation of either an IPr or $P(p-tolyl)_3$ ligand to generate the active catalyst for dehydrogenation. Precedence for such a ditin dihydride complex exists in our recent report¹ of the structure of $Pt(H)_2(Sn^tBu_3)_2(CN^tBu)_2$.

In contrast to R₃SnH, the distannane compounds R₃SnSnR₃ are computed to be more influenced by substitution. As it can be seen in Table 3, the Sn-Sn distance is similar for the hexamethyl and hexacyclohexyl distannanes. However, in spite of Cy₃SnSnCy₃ being sterically more crowded than Me₃SnSnMe₃, the Sn-Sn BDE calculated is ~7 kcal/mol higher for the Cy derivative (Table 4) presumably for the existence of stabilizing dispersion forces.⁶⁵ Likewise, the Sn–Sn BDE is similar for the Me and 'Bu distannanes although the Sn-Sn bond length is 0.16 Å shorter in the former. Thus, the weaker nature of the Sn–Sn bond in the ^tBu derivative appears counterbalanced with the attractive London dispersion interactions established among the ^tBu bulky pendant groups bound to the different Sn atoms. Analogously, the gas phase Sn-Sn BDE in R₃SnSnR₃ is computed to be 5.9 kcal/mol higher for R = Ph than for R = Me, while the corresponding Sn-H BDE in the stannanes is reduced by 1.8 kcal/mol in going from R = Me to Ph.

Pioneering work of Neumann⁶ derived Sn–Sn BDE values for a series of R_3SnSnR_3 compounds. For R = phenyl, cyclohexyl, or 1-adamantyl dissociation did not occur even at 230 °C. However, for a series of 1,3,5-trisubsituted arene substituents dissociation did occur, and variable-temperature ESR data yielded values of Sn–Sn BDE of 49 kcal/mol for R = methyl, 26.6 kcal/mol for R = Et, and 8.5 kcal/mol for R = isopropyl. The isopropyl derivative is fully dissociated at room temperature in benzene solution, and ESR data indicate that it is pyramidal rather than planar in nature. It is clear from this that rather extreme crowding is necessary to significantly weaken the Sn–Sn bond.

Reaction calorimetric measurement of the enthalpy of reaction 1 of $\Delta H = -36.7 \pm 1.8$ kcal/mol, combined with the value of 76.0 ± 3.0 kcal/mol for the Sn-H BDE in Ph₃SnH, leads to a derived value of the Sn-Cr BDE in Ph₃Sn-Cr(CO)₃C₅Me₅ of 50.4 ± 3.5 kcal/mol in good agreement with the value of 52.1 kcal/mol computed in this work (Table 4). This is within experimental error of the earlier estimate based on appearance potential measurements derived by Lappert of 53.4 kcal/mol for Me₃Sn-Cr(CO)₃C₅Me₅ single bonds as shown in Table 6.

The computed value for the Sn–Cr BDE in the Cy₃Sn–Cr(CO)₃C₅Me₅ complex is ~3 kcal/mol lower than for the phenyl derivative in agreement with the longer Sn–Cr distance observed in both the X-ray and DFT-optimized structure of the former (see Figures 1 and 2 and Table 3). This trend is more marked in the case of the bulkier ^tBu derivative, where the Sn–

Table 6. Bond Dissociation Enthalpies (kcal/mol) for X– Cr(CO)₃C₅Me₅ (Cr = Cr(CO)₃C₅Me₅)

Cr-Cr ^a	15	Cr-S"Bu ^b	43	Cr-SnPh ₃ ^c	50
Cr-Hg ^d	21	Cr-SPh ^b	38	Cr-H ^e	62
Cr-Mo ^f	24	Cr-SePh ^g	36	Cr-NO ^h	70
Cr-SMe ⁱ	43	Cr-TePh ^g	31	Cr≡Cr ^j	75

^{*a*}See ref 33. ^{*b*}See ref 56. ^{*c*}This work. ^{*d*}Refers to the average Cr–Hg BDE in $C_5Me_5(CO)_3Cr-Hg-Cr(CO)_3C_5Me_5$; see ref 59. ^{*c*}See ref 55. ^{*f*}Refers to the BDE in $C_5H_5(CO)_3Mo-Cr(CO)_3C_5Me_5$; see ref 59. ^{*g*}See ref 60. ^{*h*}Refers to the BDE in $Cr(NO)(CO)_2C_5Me_5$; see ref 61. ^{*i*}See ref 57. ^{*j*}Refers to the BDE in $C_5Me_5(CO)_2Cr\equiv Cr(CO)_2C_5Me_5$; see ref 62.

Cr bond length in the optimized structure is ~0.1 Å longer than in the $Cy_3Sn-Cr(CO)_3C_5Me_5$ complex (see Table 3), and consequently the computed Sn-Cr BDE in ^tBu₃Sn-Cr-(CO)₃C₅Me₅ is almost 13 kcal/mol lower. The calculated Sn-Cr BDE value of 37.0 kcal/mol for the ^tBu derivative is very low due to steric factors. This is reflected in the labile nature of this Sn-Cr product that, unlike other R₃Sn-Cr(CO)₃C₅Me₅ adducts studied in this work, reacts further in the presence of excess ^tBu₃SnH as shown in eq 8.

Data for the Sn–Cr BDE of 50 kcal/mol in $Ph_3Sn-Cr(CO)_3C_5Me_5$ with a value of 64 kcal/mol for the Sn–Sn BDE in $Ph_3SnSnPh_3$ led to the calculation that oxidative addition of hexaphenyl ditin as shown in eq 11 should be exothermic by 36 kcal/mol.

$$2 \bullet Cr(CO)_3 C_5 Me_5 + Ph_3 SnSnPh_3 \rightarrow 2Ph_3 Sn - Cr(CO)_3 C_5 Me_5$$
(11)

In spite of thermodynamic favorability, reaction 11 was not observed to occur over several hours at room temperature. Two related reactions⁶³ shown in eqs 12 and 13 occur rapidly under comparable conditions.

$$2 \bullet Cr(CO)_3 C_5 Me_5 + PhS - SPh \rightarrow 2PhS - Cr(CO)_3 C_5 Me_5$$
(12)
$$2 \bullet Cr(CO) C Me_5 + Cp(CO) Mo - Mo(CO) Cp$$

$$\rightarrow 2Cp(CO)_3Mo-Cr(CO)_3C_5Me_5$$
(13)

A plausible explanation for these observations is that binding and electron transfer to hexaphenyl ditin is inhibited for \circ Cr(CO)₃C₅Me₅ by steric factors.

Mechanistic Studies. Oxidative addition reactions of the \bullet Cr(CO)₃C₅Me₅ radical have been shown to occur by different mechanisms depending upon the strength of the bond being broken and the reaction conditions and atmosphere. Reaction mechanisms shown in Scheme 1 do not involve CO dissociation and so would be expected to be largely independent of gas atmosphere.

The derived rate laws for both reaction manifolds are shown in Scheme 1. For path A, it is based on a steady-state assumption in the initial adduct formed with the ratedetermining step occurring when this is attacked by a second Cr radical. Path A in Scheme 1 results in most situations in an overall third-order rate law. Activation parameters in related systems have shown low enthalpies of activation and large unfavorable entropies of activation.⁶³ No sign of reactivity via Path A has been found so far in reactivity of R₃SnH with the chromium radical. Computational and additional experimental work to ascertain why the reaction of PhSH with an S–H BDE of 79 kcal/mol proceeds by a mechanism analogous to that shown in Path A and Ph₃SnH with an Sn–H BDE of 76 kcal/ mol does not is in progress.

Path B in Scheme 1 corresponds to single radical attack on the Sn-H bond, and this is the dominant mechanism observed for R₃SnH under CO pressure in the presence of a large excess of \bullet Cr(CO)₃C₅Me₅. The derived rate law using a steady-state assumption in \bullet SnR₃ is also shown at the bottom of Scheme 1. Note that the rate constants associated with Path A are negligible with respect to Path B and drop out of the equation under the conditions studied. Under conditions where $k_{-1B}[HCr(CO)_3C_5Me_5] \ll k_{2B}[\bullet Cr(CO)_3C_5Me_5]$ the observed rate constant corresponds to k_{1B} and is largely uninfluenced by CO pressure.

Two mechanisms that involve CO dissociation are shown in Scheme 2 together with the derived rate law based on a steadystate assumption in the concentration of the reactive intermediate $Cr-\mu$ -H-Sn radical.

The common first step in Paths C and D in Scheme 2 involves displacement of CO by R_3 SnH. Such reactions can be

Scheme 1. Mechanism of Reactions between Ph₃SnH and the Chromium Radical Not Involving CO Dissociation







relatively rapid for such 17 e⁻ radical species.⁶³ There is literature precedent for this playing a role in oxidative addition reactions of the chromium radical. The rate of displacement of CO in \bullet Cr(CO)₃C₅Me₅ by PMe₂Ph as shown in eq 14 was found to occur with $\Delta H^{\ddagger} = 8.7$ kcal/mol and to have a rate constant of $k_1 \approx 0.33$ M⁻¹ s⁻¹ at 10 °C.⁶³

$$\bullet \operatorname{Cr}(\operatorname{CO})_3 \operatorname{C}_5 \operatorname{Me}_5 + \operatorname{PMe}_2 \operatorname{Ph} \underset{k=1}{\overset{k_1}{\longleftrightarrow}} \operatorname{CO} + \bullet \operatorname{Cr}(\operatorname{PMe}_2 \operatorname{Ph})(\operatorname{CO})_2 \operatorname{C}_5 \operatorname{Me}_5$$
(14)

The rate of incorporation of ¹³CO into \bullet Cr(CO)₃C₅Me₅ was found to be extremely rapid even at low temperatures.⁶⁴ Thus, the rate of establishment of the equilibrium in ligand substitution reactions such as that shown in the first step 1C of Scheme 2 leading to formation of \bullet Cr(μ -HSnPh₃) (CO)₂C₅Me₅ is expected to be significantly less than the 15.7 kcal/mol for the single radical HAT step in Scheme 1 Path B. This implies that the equilibrium shown in the first common step in Scheme 2 to form the intermediate I = \bullet Cr(μ -HSnPh₃)(CO)₂C₅Me₅ is rapidly established and that it is only the degree of CO pressure present that directly influences this equilibrium, which regulates how competitive this pathway is compared to those offered in Scheme 1.

There are two different steps leading to the Sn–Cr product in Scheme 2. In the upper pathway 2C, the proposed intermediate complex I is attacked by a second •Cr- $(CO)_3C_5Me_5$ radical, and the H atom is transferred from I to •Cr $(CO)_3C_5Me_5$ producing HCr $(CO)_3C_5Me_5$ and "R₃Sn– Cr $(CO)_2C_5Me_5$ ", which picks up dissociated CO rapidly to form the observed product. This corresponds to reaction 4 and gives the normal product distribution when excess radical is present. The only observed difference with respect to reaction under CO is a faster rate, but the product distribution is the same.

An alternative closing step is reaction of I with HCr-(CO)₃C₅Me₅ rather than with \bullet Cr(CO)₃C₅Me₅ as shown in the lower path—step 2D of Scheme 2. In this case, an H atom from $HCr(CO)_3C_5Me_5$ is transferred to I to form $\bullet Cr(CO)_3C_5Me_5$ and $(H)(\mu$ -H-SnR₃)Cr(CO)₂C₅Me₅. Coupling of H atoms in *cis* dihydrides can be a rapid reaction by which R₃Sn-Cr(H₂)(CO)₂C₅Me₅ could be formed, which, following displacement of H₂ by CO, would lead to the final product according to the stoichiometry of reaction 5.

The authors made no attempt at this time to determine the rate constants for the reactions shown in Scheme 2, since it is not germane to the primary focus of this work. However, a large number of qualitative and semiquantitative work done on this system are all in accord with the mechanism in Scheme 2 operating under Ar or low CO pressure. The correspondence of the computed structure of the 17 e⁻ radical stannane complex • $(\mu$ -H-SnR₃)Cr(CO)₂C₅Me₅ with those reported for analogous 18 e⁻ diamagnetic complexes (μ -H-SnR₃)Cr(CO)₂C₆R₆ also supports this as does the computed enthalpy of formation which is endothermic by only \sim 7 kcal/mol but with an unfavorable entropic term of ca. -21 cal/(mol·K) indicating a moderately unfavorable equilibrium constant, which would support the feasibility of $\bullet(\mu$ -H-SnR₃)Cr(CO)₂C₅Me₅ as a reactive intermediate. The orbital diagram of the SOMO shown in Figure 15 indicates two reactive sites, which can be approached from different angles. The first is the μ -H atom, which can be abstracted by $\bullet Cr(CO)_3C_5Me_5$ as shown in path 2C in Scheme 2. The other site is the SOMO electron in an orbital located essentially on Cr and which should be capable of abstracting an H atom from $HCr(CO)_{3}C_{5}Me_{5}$ as shown in path 2D in Scheme 2.

The rather similar-looking rate laws for the mechanisms shown above add to the difficulty in kinetics resolution. Failure to observe the expected third-order behavior typified in path B in Scheme 1 in the reaction of stannanes with \bullet Cr(CO)₃C₅Me₅ was somewhat surprising to the authors, and additional experimental and computational work is planned. Nevertheless, there is reasonably strong support for the mechanisms proposed here, and the authors believe there are at least three reaction channels leading to products depending upon the specific conditions. There is little doubt regarding establishment that direct single radical attack as shown in Scheme 1 Path B is the dominant mechanism in the presence of a large excess of Cr radical under an atmosphere of 2–3 atm CO near room temperature. That conclusion is supported not only by the observed rate law being $k_1[\bullet Cr][Ph_3SnH]$ provided $k_2[\bullet Cr] \gg k_{-1}[HCr]$ but also by the normal kinetic isotope effect of $k_H/k_D = 1.12$, the modest negative entropy of activation, and the good agreement of the enthalpy of activation with computational results.

Whereas attainment of a trimolecular transition state in which two Cr atoms are involved in attack on the Sn-H bond does not appear to occur under CO pressure in which each Cr center retains three pendant carbonyls, under Ar atmosphere or suitably low CO pressure, loss of a CO may serve to free an avenue of approach while also activating the Sn-H bond. The branched mechanism shown in Scheme 2 explains two important observations made in this system. The first is the faster rate of reaction in the presence of a large excess of \bullet Cr(CO)₃C₅Me₅ when the reaction is performed under an Ar rather than CO atmosphere. The second is the observation that when the reaction is performed in the presence of excess R_3 SnH, the product distribution changes as HCr(CO)₃C₅Me₅ is produced during the reaction and in the later stages of the reaction surpasses the concentration of $\bullet Cr(CO)_3C_5Me_5$. In that case the stoichiometry of reaction is altered beyond the midpoint to utilize both $\bullet Cr(CO)_3C_5Me_5$ and HCr- $(CO)_{3}C_{5}Me_{5}$ to produce product as outlined in reactions 4–7.

CONCLUSIONS

Experimental measurements have yielded solution-phase BDE estimates for the Ph_3Sn-H (76 kcal/mol), $Ph_3Sn-SnPh_3$ (64 kcal/mol), and $Ph_3Sn-Cr(CO)_3C_5Me_5$ (50 kcal/mol) bonds. These estimates are considered reliable with an uncertainty on the order of ± 3 kcal/mol, typical of BDE data in solution and incorporate the experimental uncertainty of the data used to derive them. Moreover, good agreement between experimental and DFT-computed values was obtained. In addition to this, several additional conclusions are

- 1. Steric crowding does not significantly reduce the Sn–H BDE for alkylstannanes. Similar Sn–H BDE values in R_3 SnH species are computed for R = Me, Cy, and ^tBu on the order of 76.0 \pm 0.3 kcal/mol.
- 2. In contrast to PhSH and MeSH where the aryl substituent serves to significantly decrease the S–H BDE, little or no decrease is believed to occur for the corresponding stannanes, and the Ph₃Sn–H BDE is only 1.8 kcal/mol lower than that in Me₃Sn–H. This is attributed to little delocalization of the unpaired electron into the antibonding orbitals of the arenes.
- 3. The Sn–Sn BDE in the distannanes is more affected by the groups bound to the Sn atoms than are the hydrides. This is attributed to dispersion effects that serve to stabilize R₃SnSnR₃ species with bulky pendant R groups, which are capable of interacting with each other.
- 4. In spite of similar BDE values for PhS–H and Ph₃Sn–H, different oxidative addition mechanisms are followed for the reaction with the 17 e⁻ radical complex •Cr- $(CO)_3C_5Me_5$. Under normal concentration conditions oxidative addition of PhSH is faster even though it follows a third-order mechanism. Oxidative addition of

 Ph_3SnH would presumably be faster if it could follow such a pathway, but steric factors appear to limit the ability for concerted two-radical attack forcing adoption of a second-order HAT mechanism. This question is under further experimental and computational study.

- 5. Although it is thermodynamically quite favorable, $Ph_3SnSnPh_3$ was found to not undergo radical scission with 2 equiv of $\bullet Cr(CO)_3C_5Me_5$, and this is assigned to steric inaccessibility of the Sn–Sn bond to the relatively large Cr radical.
- 6. Catalytic dehydrogenation of Ph₃SnH by Pd(IPr)(P(*p*-tolyl)₃) to form Ph₃SnSnPh₃ is a valuable method for obtaining direct thermochemical data pertinent to the difference between the Sn–Sn and Sn–H BDE, and further utilization of this technique is planned.
- 7. Formation of an activated radical stannane complex $(\eta^2 H SnPh_3)(\bullet)Cr(CO)_2(C_5Me_5)$ provides a working explanation of observed kinetics behavior under Ar or low CO concentration conditions. Reaction of this species with additional $\bullet Cr(CO)_3C_5Me_5$ leads to acceleration of reaction 4. Reaction of this species with additional $HCr(CO)_3C_5Me_5$ leads to acceleration of reaction 5.

The dinuclear oxidative addition reactions described here provide a basis for future investigation of the energetics of oxidative addition to mononuclear Pt and Pd complexes related to those recently shown to oxidatively activate dihydrogen and other small molecules.^{1–5} The chemistry of stannyl radicals cannot be simply interpreted as being that of heavier analogues of carbon-based radicals. As illustrated in the review by Power,⁶⁵ main group radicals, including stannyl radicals, have a rich and unique chemistry. Additional work aimed at mapping the energetics of interactions between tin hydrides and complexes of Pd and Pt, as well as additional fundamental thermochemistry of organostannanes, are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01978.

Ph₃Sn-Cr(CO)₃C₅Me₅ and Cy₃Sn-Cr(CO)₃C₅Me₅ (CIF) DFT-optimized coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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