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Synthesis, Structure, and α-Elimination Chemistry of Hafnocene Triarylstannyl Complexes

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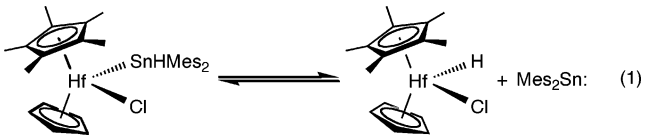
Abstract: New hafnocene triarylstannyl complexes were prepared and were shown to undergo clean thermal decompositions via α-aryl-elimination to produce the corresponding stannylene and a hafnocene aryl complex. The rate of the decomposition is highly dependent on the nature of the ancillary ligand, with the stabilities of the CpCp*Hf($SnPh_3$)X compounds following the order X = NMe_2 > Np (α-agostic) > OMe > Cl > Me. Mechanistic information suggests that α-aryl-elimination may be viewed as a concerted process involving nucleophilic attack of the migrating aryl group onto the electrophilic metal center.

Introduction

Investigations of d^0 metal silyl compounds have revealed a number of new reactivity modes,[1] including insertions of unsaturated substrates into M−Si bonds[2] and σ-bond metathesis processes that can result in metal-mediated polymerizations of silanes[3] and the productive functionalization of hydrocarbons.[4] The reactive (and presumably weak) nature of d^0 M−Si bonds, and established trends in bond energies for the group 14 elements,[5] suggested that complexes containing d^0 M−E (E = Ge, Sn, Pb) bonds should also display a rich reaction chemistry. In fact, we have found that zirconocene derivatives catalyze the dehydropolymerization of stannanes to the first high molecular-weight polystannanes.[5] These polymerizations presumably involve intermediate zirconium stannyl derivatives, but attempts to observe these intermediates in the dehydropolymerization reactions have thus far been unsuccessful.[5b] Although complexes with d^0 M−Sn bonds have been known for a long time, surprisingly few examples have been reported over the years.[6] In addition, few reactivity studies on such complexes have been carried out.

A recent report from our laboratories described the isolation of a stable hydrostannyl d^0 complex, CpCp*Hf($SnHMes_2$)Cl (Cp* = η^5-C_5Me_5; Mes = 2,4,6-trimethylphenyl).[7] This complex was found to react via a process that has not been observed for analogous silyl complexes: facile α-H-elimination to give CpCp*Hf(H)Cl and the free stannylene Mes_2Sn (eq 1). This



(1)

α-elimination process appears to be involved in the hafnium-catalyzed dehydrocoupling of Mes_2SnH_2 to $Mes_2HSnSnHMes_2$, which occurs via insertion of the stannylene into the Sn−H bond of Mes_2SnH_2. Related observations were made in an earlier attempt to prepare CpCp*Zr($SnPh_3$)Cl, via the reaction of CpCp*$ZrCl_2$ with $LiSnPh_3$, which instead produced the phenyl

(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24. (b) Tilley, T. D. In *The Silicon−Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 10. (c) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol 2, Part 3, Chapter 35. (d) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175−292.

(2) (a) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049−2056. (b) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 3318−3322. (c) Elsner, F. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Organomet. Chem.* **1988**, *358*, 169−183. (d) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149−164. (e) Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284−2286. (f) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 324−330. (g) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 2011−2013. (h) Woo, H.-G.; Tilley, T. D. *J. Organomet. Chem.* **1990**, *393*, C6−C9. (i) Campion, B. K.; Heyn, R. H., Tilley, T. D. *Inorg. Chem.* **1990**, *29*, 4355−4356 and references in the above.

(3) (a) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37−51. (b) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239−1245. (c) Corey, J. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, p 327−387. (d) Laine, R. M. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Academic Publishers: Amsterdam, 1990; p 37−63.

(4) (a) Sadow, T. D.; Tilley, T. D. *Organometallics* **2001**, *20*, 4457−4459. (b) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 6814−6815. (c) Sadow, A. D.; Tilley, T. D. *Angew. Chem. Int. Ed.* **2003**, *42*, 803−805. (d) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 7971−7977. (e) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 9462−9475. (f) Sadow, A. D.; Tilley, T. D. *Organometallics* **2003**, *22*, 3577−3585.

(5) (a) Imori, T.; Tilley, T. D. *Chem. Commun.* **1993**, *21*, 1607−1609. (b) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931−9940. (c) Lu, V.; Tilley, T. D. *Macromolecules* **1996**, *29*, 5763−5764.

(6) (a) Coutts, R. S. P.; Wailes, P. C. *J. Chem. Soc., Chem. Commun.* **1968**, 260−261. (b) Creemers, H. M. J. C.; Verbeek, F.; Noltes, J. G. *J. Organomet. Chem.* **1968**, *15*, 125−130. (c) Kingston, B. M.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 69. (d) Schumann, H.; Cygon, M. *J. Organomet. Chem.* **1978**, *144*, C43−C45. (e) Razuvaev, F. A.; Kalinina, G. S.; Fedorova, E. A. *J. Organomet. Chem.* **1980**, *190*, 157−165. (f) Lappert, M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1985**, 51−57. (g) Porchia, M.; Casellato, U.; Ossala, F.; Rossetto, G.; Zanella, P.; Graziani, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1034−1035. (h) Zheng, W.; Stephan, D. W. *Inorg. Chem.* **1988**, *27*, 2386−2388. (i) Woo, H.-G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198−2205. (j) Lutz, M.; Findeis, B.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. *Organometallics* **2001**, *20*, 2505−2509.

(7) Neale, N. R.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 3802−3803.

complex CpCp*Zr(Ph)Cl. In addition, isolated CpCp*Zr($SnPh_3$)-Cl (prepared by the σ-bond metathesis reaction of Ph_3SnH and CpCp*Zr[$Si(SiMe_3)_3$]Cl) was found to decompose slowly over days at 80 °C to a number of products, including CpCp*Zr-(Ph)Cl.[6i]

The α-elimination process described above is quite unusual, as degradation of a d^0 M−ER_nR' complex (E = main group element) to M−R′ and ER_n has been reported in only a few cases. For example, Erker has described the decomposition of $Cp_2Zr[C(OMe)Ph_2]Cl$ at room temperature to give $Cp_2Zr(OMe)$-Cl and tetraphenylethylene (presumably formed by dimerization of the initial product, diphenylcarbene).[8] Related reactions involve decarbonylations of group 4 metallocene acyl complexes, for which there are many examples.[9] Given the possibility that α-eliminations in d^0 stannyl complexes might be of more general utility in early transition metal chemistry, we have investigated this reaction type in more detail. Here we describe the syntheses of a number of new hafnium triarylstannyl derivatives and mechanistic aspects of α-aryl-elimination processes in these complexes.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a nitrogen-filled glovebox. Dry, oxygen-free solvents were employed throughout. Pentane, diethyl ether, and tetrahydrofuran were distilled from sodium/benzophenone, benzene was distilled from potassium, toluene was distilled from sodium, and benzene-d_6 and toluene-d_8 were dried over NaK alloy and Na, respectively, and then vacuum transferred and stored over 4-Å molecular sieves. Chloroform was purified by shaking with several small portions of concentrated H_2SO_4, washing with several portions of water, and then drying over $CaCl_2$ before distillation. Trimethylsilyl chloride (Gelest or Aldrich) was distilled prior to use. The compounds $Hf(NMe_2)_4$,[10] $Me_2C(C_5H_5)_2$,[11] Ph_3SnH,[12] PhLi,[13] $LiNMe_2$ (from Li^0 and excess $HNMe_2$; isolated by evaporating excess $HNMe_2$),[14] CpCp*Hf-(Me)OTf (**6**),[4a] NaOMe,[15] $(THF)_{3.5}LiSnPh_3$,[16,17] CpCp*Hf(H)Cl,[18] and $ClSn(p\text{-}FC_6H_4)_3$[19] were prepared according to literature procedures. The compounds CpCp*Hf(H)OMe and CpCp*Hf(H)NMe_2 were prepared by the reaction of 1 equiv of NaOMe or $LiNMe_2$, respectively, with CpCp*Hf(H)Cl in THF at room temperature for 12 h. These species could not be isolated in pure form and were used as prepared. Triaryltin chlorides $ClSn(p\text{-}(CF_3)C_6H_4)_3$ and $ClSn(p\text{-}(OMe)C_6H_4)_3$ were prepared using the Kocheshkov disproportionation reaction.[20] Heating times, temperatures, and purities were as follows: for $ClSn(p\text{-}(CF_3)C_6H_4)_3$, 24 h, 215 °C, 72%; for $ClSn(p\text{-}(OMe)C_6H_4)_3$, 4 h, 275 °C, 70%. These impure compounds were used without further purification in the procedures below. For the NMR tube kinetic measurements and all reactions involving a hafnium hydride, glassware was silylated with Me_3SiCl/chloroform solution (1:9, v/v), washed three times with acetone, and then rinsed with distilled water and ethanol before oven-drying.

NMR spectra were recorded in benzene-d_6 solutions (unless otherwise noted) at 300 or 500 MHz (^1H) with Bruker AMX-300 and DRX-500 spectrometers, at 125.77 MHz ($^{13}C\{^1H\}$) or at 186.50 MHz ($^{119}Sn\{^1H\}$) with a DRX-500 spectrometer, or at 376.45 MHz ($^{19}F\{^1H\}$) with an AMX-400 spectrometer at ambient temperature and were referenced to the residual solvent peak. Many of the ^1H NMR resonances for the aryl groups of the triarylstannyl species appear as complex multiplets due to coupling to both ^{117}Sn and ^{119}Sn nuclei. Before NMR characterization of compounds **8**, **9**, and **10**, the solvent of crystallization was removed by crushing the crystals in a mortar and pestle and placing the resulting powder under vacuum for 4 h. Elemental and mass spectral analyses were carried out by the Microanalytics Laboratory at the University of California, Berkeley. IR samples of solid materials were prepared as Nujol mulls between two KBr plates. All IR absorptions are reported in cm^{-1} and were recorded with a Mattson Infinity 60 MI FTIR spectrometer.

$[Me_2C(C_5H_4)_2]Hf(NMe_2)_2$ (1). Toluene (80 mL) was added to a 500-mL round-bottom Schlenk flask containing $Hf(NMe_2)_4$ (4.00 g, 11.3 mmol). A solution of $Me_2C(C_5H_5)_2$ (0.49 g, 2.8 mmol, deoxygenated by sparging with N_2) in toluene (20 mL) was added, and a condenser fitted with a flow-control adapter was attached. The solution was heated at 110 °C for 18 h, cooled to room temperature, and filtered via cannula. The resulting yellow solution was concentrated to ca. 30 mL, pentane (20 mL) was added, and the biphasic mixture was cooled to −80 °C. A yellow solid was isolated by cannula filtration, and this impure product was recrystallized from toluene (15 mL) at −80 °C to give the product as a bright yellow crystalline solid in 52% yield (2.57 g, 5.88 mmol). Note: upon warming of the yellow solid to room temperature after cannula filtration at −80 °C, it dissolved in the residual toluene. However, after removing the toluene under vacuum, a yellow crystalline solid was obtained. ^1H NMR: δ 1.45 (s, 6 H, [$Me_2C(C_5H_4)_2$]), 2.87 (s, 12 H, NMe_2), 5.35 (t, 4 H, [$Me_2C(C_5H_4)_2$]), 6.16 (t, 4 H, [$Me_2C(C_5H_4)_2$]). $^{13}C\{^1H\}$ NMR: δ 25.0, 36.9, 48.6, 102.1, 111.7, 128.0. Anal. Calcd for $C_{17}H_{26}N_2Hf$: C, 46.74; H, 6.00; N, 6.41. Found: C, 46.75; H, 6.06; N, 6.11.

$[Me_2C(C_5H_4)_2]Hf(SnPh_3)NMe_2$ (2). A solution of $HSnPh_3$ (0.804 g, 2.29 mmol) in benzene (20 mL) was added to a yellow solution of $[Me_2C(C_5H_4)_2]Hf(NMe_2)_2$ (1.00 g, 2.29 mmol) in benzene (30 mL). The mixture was stirred in the dark at room temperature for 5 min, at which point benzene was removed in vacuo. The resulting red-orange foam was extracted with Et_2O (2 × 40 mL), and the red-orange ether solution was filtered via cannula, concentrated to ca. 30 mL, and cooled to −30 °C. The product was isolated as yellow crystals in 68% yield (1.15 g, 1.55 mmol). ^1H NMR: δ 0.86 (s, 3 H, [$Me_2C(C_5H_4)_2$]), 1.15 (s, 3 H, [$Me_2C(C_5H_4)_2$]), 2.79 (s, 6 H, NMe_2), 5.06 (m, 2 H, [$Me_2C(C_5H_4)_2$]), 5.38 (m, 2 H, [$Me_2C(C_5H_4)_2$]), 5.50 (m, 2 H, [$Me_2C(C_5H_4)_2$]), 5.68 (m, 2 H, [$Me_2C(C_5H_4)_2$]), 7.20−7.26 (m, 3 H, p-C_6H_5), 7.32−7.37 (m, 6 H, m-C_6H_5), 7.82−7.94 (m, 6 H, o-C_6H_5). $^{13}C\{^1H\}$ NMR: δ 23.0, 24.4, 36.6, 50.7, 99.9, 102.3, 109.3, 111.4, 118.5, 127.7, 128.8, 138.5, 151.7. $^{119}Sn\{^1H\}$ NMR: δ 67.05. Anal. Calcd for $C_{33}H_{35}$-NSnHf: C, 53.36; H, 4.75; N, 1.89. Found: C, 53.59; H, 4.70; N, 1.67.

$[Me_2C(C_5H_4)_2]Hf(SnPh_3)Cl$. Trimethylsilyl chloride (0.080 g, 0.74 mmol, 26 equiv) was added to a solution of **2** (0.021 g, 0.028 mmol) in benzene-d_6. Immediately a color change was observed from yellow to yellow-orange, and after 20 min the product was observed in 74% yield by ^1H NMR spectroscopy. ^1H NMR: δ 0.63 (s, 3 H, [$Me_2C(C_5H_4)_2$]), 0.98 (s, 3 H, [$Me_2C(C_5H_4)_2$]), 4.60 (m, 2 H, [$Me_2C(C_5H_4)_2$]), 5.54 (m, 2 H, [$Me_2C(C_5H_4)_2$]), 5.69 (m, 2 H, [$Me_2C(C_5H_4)_2$]), 7.23 (m,

(8) Erker, G.; Rosenfeldt, F. *Tetrahedron Lett.* **1981**, *22*, 1379−1382.
(9) (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc. Dalton Trans.* **1977**, 1946−1950. (b) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440−4451. (c) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56−67. (d) *Advanced Inorganic Chemistry*, 5th ed.; Cotton, F. A., Wilkinson, G.; Wiley: New York, 1988; Chapters 27 and 28. (e) Cavell, K. J. *Coord. Chem. Rev.* **1996**, *155*, 209−243.
(10) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030−4037.
(11) Nifant'ev, I. E.; Yarnykh, V. L.; Borzov, M. V.; Mazurchik, B. A.; Mstyslavsky, V. I.; Roznyatovsky, V. A.; Ustynyuk, Y. A. *Organometallics* **1991**, *10*, 3739−3745.
(12) van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366.
(13) Screttas, C. G.; Micha-Screttas, M. *Organometallics* **1984**, *3*, 904−907.
(14) Sard, H.; Duffley, R. P.; Razadan, R. K. *Synth. Comm.* **1983**, *13*, 813.
(15) *Organic Syntheses*; Tishler, M., Ed.; John Wiley and Sons: New York: 1959; Vol. 39, p 51.
(16) Lu, V. Ph.D. Thesis, University of California, Berkeley, 1999.
(17) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1−3.
(18) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047−7055.
(19) Schenk, W. A.; Khadra, A.; Burschka, C. *J. Organomet. Chem.* **1994**, *468*, 75−86.
(20) Kosheshkov, K. A. *Chem. Ber.* **1926**, 996.

2 H, [$Me_2C(C_5H_4)_2$]), 7.17−7.20 (m, 3 H, *p*-C_6H_5), 7.29−7.33 (m, 6 H, *m*-C_6H_5), 7.86−7.95 (m, 6 H, *o*-C_6H_5). $^{119}Sn\{^1H\}$ NMR: δ 97.0.

Alternative Synthesis of [$Me_2C(C_5H_4)_2$]$HfCl_2$ (3).[22] Neat $ClSiMe_3$ (2.05 mL, 16.2 mmol, 7 equiv) was added dropwise to a yellow solution of **1** (1.00 g, 2.29 mmol) in benzene (20 mL). After stirring for 12 h, an opaque light yellow mixture was obtained. Solvent was removed in vacuo, leaving a beige residue. Chloroform (100 mL) was added, and the mixture was filtered via cannula. The resulting pale yellow solution was concentrated to ca. 10 mL, causing precipitation of a beige powder. The remaining solution was filtered off, leaving the product as a beige powder in 69% yield (0.667 mg, 1.59 mmol). ^1H NMR: δ 1.10 (s, 6 H, [$Me_2C(C_5H_4)_2$]), 5.10 (t, $^3J_{HH}$ = 2.6 Hz, 4 H, [$Me_2C(C_5H_4)_2$]), 6.30 (t, $^3J_{HH}$ = 2.6 Hz, 4 H, [$Me_2C(C_5H_4)_2$]).

Observation of [$Me_2C(C_5H_4)_2$]$HfPh_2$. A solution of **3** (0.0026 g, 0.0062 mmol) in benzene-d_6 (0.5 mL) was added to solid $(THF)_{3.5}LiSnPh_3$ (0.0064 g, 0.012 mmol), causing an immediate color change to bright yellow. A ^1H NMR experiment after 15 min suggested that the diphenyl complex had formed. ^1H NMR: δ 1.23 (s, 6 H, [$Me_2C(C_5H_4)_2$]), 5.26 (t, $^3J_{HH}$ = 2.4 Hz, 4 H, [$Me_2C(C_5H_4)_2$]), 6.20 (t, $^3J_{HH}$ = 2.4 Hz, 4 H, [$Me_2C(C_5H_4)_2$]), phenyl resonances obscured by $(Ph_2Sn)_n$.

CpCp*Hf(SnPh$_3$)Cl (4).[6i] A solution of $(THF)_{3.5}LiSnPh_3$ (0.743 g, 1.22 mmol) in THF (20 mL) was added dropwise to a solution of $CpCp^*HfCl_2$ (0.515 g, 1.15 mmol) in THF (20 mL) at −78 °C. The solution was allowed to warm slowly to room temperature with stirring for 12 h in the dark. Solvent was removed from the deep yellow solution, leaving a yellow foam. The foam was extracted with Et_2O (2 × 20 mL), filtered via cannula, concentrated to ca. 15 mL, and cooled to −80 °C. The product was isolated as yellow crystals in 75% yield (0.655 g, 0.857 mmol). $^{119}Sn\{^1H\}$ NMR: δ 112.8.

CpCp*Hf(NMe$_2$)Cl (5). A solution of $LiNMe_2$ (0.115 g, 2.25 mmol) in THF (15 mL) was added dropwise to a solution of $CpCp^*HfCl_2$ (1.01 g, 2.25 mmol) in THF (25 mL) at −78 °C. The resulting yellow solution was warmed slowly to room temperature with stirring for 12 h. This reaction was not clean, and a mixture of $CpCp^*HfCl_2$, $CpCp^*Hf(NMe_2)Cl$, and $CpCp^*Hf(NMe_2)_2$ in a ratio of 0.34:1:0.28 was obtained. More lithium dimethylamide (0.027 g, 0.53 mmol, 0.24 equiv) in THF (20 mL) at 0 °C was added to this solution, and the mixture was stirred for an additional 1 h. Solvent was removed from the yellow solution, and the resulting yellow residue was extracted with Et_2O (2 × 25 mL), filtered via cannula, concentrated to ca. 30 mL, and cooled to −80 °C. After 3 days at this temperature the product was isolated by filtration as yellow crystals in 53% yield (0.546 g, 1.19 mmol). ^1H NMR: δ 1.84 (s, 15 H, C_5Me_5), 2.86 (s, 6 H, NMe_2), 5.84 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR: δ 12.10 (s, C_5Me_5), 49.33 (s, NMe_2), 112.4 (s, C_5H_5), 119.7 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 12.10, 49.33, 112.4, 119.7. Anal. Calcd for $C_{17}H_{26}NClHf$: C, 44.54; H, 5.72; N, 3.06. Found: C, 44.37; H, 5.79; N, 2.72.

CpCp*Hf(OMe)Cl (7). A Schlenk tube was charged with $CpCp^*HfCl_2$ (0.609 g, 1.35 mmol) and NaOMe (0.073 g, 1.35 mmol). THF (25 mL) was added, and the suspension was stirred at room temperature for 12 h. Solvent was removed from the cloudy mixture, and the beige residue was extracted with pentane (2 × 15 mL). The combined extracts were concentrated to ca. 25 mL and then cooled to −30 °C. The product was isolated as a light beige crystalline solid in 77% yield (0.460 g, 0.103 mmol). ^1H NMR: δ 1.84 (s, 15 H, C_5Me_5), 3.86 (s, 3 H, O*Me*), 5.90 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR: δ 11.88, 61.78, 112.5, 119.8. Anal. Calcd for $C_{16}H_{23}OClHf$: C, 43.16; H, 5.21. Found: C, 43.05; H, 5.39.

CpCp*Hf(SnPh$_3$)NMe$_2$·0.75($C_4H_{10}O$) (8). A solution of $(THF)_{3.5}LiSnPh_3$ (0.291 g, 0.477 mmol) in THF (20 mL) was added to a solution of **5** (0.202 g, 0.477 mmol) in THF (15 mL). The solution was stirred in the dark at room temperature for 12 h. Solvent was removed from the yellow-green solution, leaving a yellow foam. The foam was extracted with Et_2O (2 × 15 mL), the combined extracts were filtered via cannula, and the resulting deep yellow filtrate was concentrated to ca. 15 mL and then cooled to −30 °C. The product was isolated by filtration as yellow crystals in 58% yield (0.224 g, 0.303 mmol). ^1H NMR: δ 1.76 (s, 15 H, C_5Me_5), 2.84 (s, 6 H, NMe_2), 5.72 (s, $^3J_{SnH}$ = 6.7 Hz, 5 H, C_5H_5), 7.23 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.5 Hz, 3 H, *p*-C_6H_5), 7.32 (m, 6 H, *o*-C_6H_5), 7.82 (m, 6 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR: δ 13.01, 49.09, 109.5, 118.3, 127.5, 139.0, 152.5. $^{119}Sn\{^1H\}$ NMR: δ 74.3. Anal. Calcd for $C_{38}H_{48.5}NO_{0.75}SnHf$: C, 55.09; H, 5.90; N, 1.69. Found: C, 54.70; H, 5.58; N, 1.66.

CpCp*Hf(SnPh$_3$)Me·0.5(C_5H_{12}) (9). A solution of $(THF)_{3.5}LiSnPh_3$ (0.197 g, 0.324 mmol) in THF (10 mL) was added to a solution of **6** (0.173 g, 0.319 mmol) in THF (10 mL) at −78 °C. The solution was allowed to come to room temperature with stirring, and stirring was continued in the dark for 12 h. Solvent was removed in vacuo, leaving a yellow residue. The residue was extracted with pentane (2 × 25 mL), the combined extracts were filtered via cannula, and the resulting yellow solution was concentrated to ca. 25 mL and then cooled to −30 °C. The product was isolated as yellow crystals in 67% yield (0.168 g, 0.215 mmol). ^1H NMR: δ −0.46 (s, Hf-*Me*, 3 H), 1.73 (s, 15 H, C_5Me_5), 5.78 (s, $^3J_{SnH}$ = 6.6 Hz, 5 H, C_5H_5), 7.19 (tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 3 H, *p*-C_6H_5), 7.29 (m, 6 H, *m*-C_6H_5), 7.76 (m, 6 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR: δ 12.77, 58.67, 111.4, 119.1, 127.6, 128.8, 138.7, 153.0. $^{119}Sn\{^1H\}$ NMR: δ 111.5. Anal. Calcd for $C_{36.5}H_{44}SnHf$: C, 56.21; H, 5.69. Found: C, 56.00; H, 5.92.

CpCp*Hf(SnPh$_3$)OMe·0.5(C_7H_8) (10). A solution of $(THF)_{3.5}LiSnPh_3$ (0.420 g, 0.689 mmol) in THF (10 mL) was added to a solution of **7** (0.299 g, 0.671 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred in the dark at room temperature for 12 h. Solvent was removed from the yellow solution in vacuo, and the resulting light yellow foam was extracted with toluene (20 mL). The extract was filtered via cannula, and the resulting solution was concentrated to ca. 5 mL and cooled to −30 °C. The product was isolated as a near colorless (very pale-yellow) crystalline solid in 72% yield (0.367 g, 0.467 mmol). ^1H NMR: δ 1.65 (s, 15 H, C_5Me_5), 5.93 (s, $^3J_{SnH}$ = 5 Hz, 5 H, C_5H_5), 7.23 (tt, $^3J_{HH}$ = 9 Hz, $^4J_{HH}$ = 2.1 Hz, 3 H, *p*-C_6H_5), 7.34 (m, 6 H, *m*-C_6H_5), 7.90 (m, 6 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR: δ 12.49, 62.16, 109.6, 118.1, 127.6, 128.7, 138.8, 152.3. $^{119}Sn\{^1H\}$ NMR: δ 64.3. Anal. Calcd for $C_{37.5}H_{42}OSnHf$: C, 55.89; H, 5.25. Found: C, 56.08; H, 5.42.

CpCp*Hf(SnPh$_3$)Ph (11). A solution of **4** (0.012 g, 0.016 mmol) and PhLi (0.0014 g, 0.017 mmol) was prepared in benzene-d_6 (ca. 0.5 mL) and THF (2 drops). The cloudy red-orange mixture was immediately placed in an NMR tube wrapped with Al foil for protection from light. The reaction had gone to 81% completion after ca. 10 min, and after 2 d the product was observed in 91% yield. ^1H NMR: δ 1.65 (s, 15 H, C_5Me_5), 5.94 (s, $^3J_{SnH}$ = 6.2 Hz, 5 H, C_5H_5), 6.93 (m, 2 H, *o*-C_6H_5), 7.06 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, 3 H, *p*-C_6H_5), 7.17 (tt, $^3J_{HH}$ = 11 Hz, $^4J_{HH}$ = 2 Hz, 3 H, Sn(*p*-$C_6H_5)_3$), 7.24 (t, $^3J_{HH}$ = 13 Hz, 6 H, Sn(*m*-$C_6H_5)_3$), 7.30 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, *m*-C_6H_5), 7.74 (m, 6 H, Sn(*o*-$C_6H_5)_3$). The *o*-C_6H_5 resonance could not be definitively identified. $^{119}Sn\{^1H\}$ NMR: δ 106.6.

CpCp*Hf(Ph)Cl (12). A thick-walled Teflon-sealable flask was charged with **4** (0.253 g, 0.331 mmol), and benzene (10 mL) was added. The flask was wrapped in aluminum foil for protection from light, and the reaction mixture was then heated to 100 °C for 3 days. Solvent was removed in vacuo, and the yellow residue was extracted with pentane (2 × 25 mL). The combined extracts were concentrated to ca. 35 mL and cooled to −80 °C. The product was isolated as light-yellow crystals in 69% yield (0.112 g, 0.228 mmol). ^1H NMR: δ 1.66 (s, 15 H, C_5Me_5), 5.82 (s, 5 H, C_5H_5), 7.08 (m, 1 H, *p*-C_6H_5), 7.26 (m, 2 H, *m*-C_6H_5), 7.25−7.45 (br s, 2 H, *o*-C_6H_5). Upon cooling to −70 °C, the *o*-C_6H_5 resonances sharpened in both the ^1H and ^{13}C NMR spectra. ^1H NMR (C_7D_8, −70 °C): δ 1.63 (s, 15 H, C_5Me_5), 5.74 (s, 5 H, C_5H_5), 6.88 (d, $^3J_{HH}$ = 6.5 Hz, 1 H, *o*-C_6H_5), *p*-C_6H_5 coincident with the aryl C_7D_7H resonances, 7.30 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *m*-C_6H_5), 7.35 (t, $^3J_{HH}$ = 7.0 Hz, 1 H, *m*-C_6H_5), 7.85 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (C_7D_8, −70 °C): δ 12.28, 113.7, 120.4, 125.2, 127.8, 139.7,

(21) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11−49.
(22) Shaltout, R. M.; Corey, J. C. *Tetrahedron* **1995**, *51*, 4309−4320.

139.9, 196.1. Anal. Calcd for $C_{21}H_{25}HfCl$: C, 51.33; H, 5.13. Found: C, 51.27; H, 5.37.

CpCp*Hf(H)Ph (13). CpCp*Hf(H)Cl (0.200 g, 0.482 mmol) and PhLi (0.041 g, 0.49 mmol) were combined in a Teflon-sealable flask. THF (10 mL) was vacuum transferred onto the solids, and the mixture was slowly warmed to room temperature. After ca. 10 min at ambient temperature, solvent was removed in vacuo, leaving a beige oil. The oil was extracted with toluene (10 mL) and filtered through a bed of Celite (1 cm). The resulting solution was concentrated to ca. 2 mL and cooled to −30 °C. The product was isolated as a beige solid in 75% yield (0.164 g, 0.359 mmol). ^{1}H NMR: δ 1.78 (s, 15 H, C_5Me_5), 5.79 (s, 5 H, C_5H_5), 6.89 (br d, $^3J_{HH}$ = 6.5 Hz, 2 H, *m*-C_6H_5), 7.29 (tt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, *p*-C_6H_5), 7.32 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, *o*-C_6H_5), 13.02 (s, 1 H, Hf-*H*). ^{13}C{^{1}H} NMR: δ 12.48, 110.1, 118.1, 125.8, 127.5, 201.2. Anal. Calcd for $C_{21}H_{46}Hf$: C, 55.20; H, 5.74. Found: C, 54.94; H, 5.82.

CpCp*Hf(SnPh$_3$)Np (14). A solution of NpLi (0.027 g, 0.35 mmol) in toluene (15 mL) was added dropwise to a solution of **4** (0.266 g, 0.348 mmol) in THF (10 mL) at −78 °C. This solution was allowed to gradually warm to room temperature over 2 h, at which point solvent was removed in vacuo. The resulting yellow-brown oil was extracted with Et_2O (1 × 10 mL, 1 × 5 mL), and the combined extracts were concentrated to ca. 5 mL. Pentane (2 mL) was added, and the resulting solution was cooled to −30 °C. A deep orange solution was filtered away from the sticky yellow residue that had precipitated. After filtration, the orange filtrate precipitated yellow crystals at room temperature, which contained the product in ca. 70% purity. These yellow crystals were redissolved in Et_2O (10 mL), and the resulting yellow solution was concentrated to ca. 2 mL and cooled to −30 °C. The product (80% purity) was isolated by cannula filtration as yellow crystals in 14% yield, including the impurities (0.038 g, 0.048 mmol). Additional crystallizations did not further purify the product. ^{1}H NMR: δ −3.81 (d, 1 H, $^2J_{HH}$ = 9.9 Hz, $^2J_{117/119SnH}$ = 39.8, 48.3 Hz, α-agostic, C*H*$_2$CMe$_3$), 1.08 (s, CH$_2$C*Me*$_3$), 1.76 (s, 15 H, C_5Me_5), 2.60 (d, 1 H, $^2J_{HH}$ = 9.9 Hz, $^2J_{SnH}$ = 39.8 Hz, C*H*$_2$CMe$_3$), 5.84 (s, $^3J_{SnH}$ = 6.5 Hz, 5 H, C_5H_5), 7.17−7.21 (m, 3 H, *p*-C_6H_5), 7.28−7.31 (m, 6 H, *m*-C_6H_5), 7.81−7.88 (m, 6 H, *o*-C_6H_5). ^{13}C{^{1}H} NMR: δ 12.24, 35.80, 40.95, 108.5, 118.1, 124.8, 127.7, 128.7, 138.7, 152.5. ^{119}Sn{^{1}H} NMR: δ 91.3.

CpCp*Hf{Sn[*p*-(OMe)C$_6$H$_4$]$_3$}Cl (18). HSn[*p*-(OMe)C$_6$H$_4$]$_3$ (0.266 g, 0.603 mmol) and CpCp*Hf(H)Cl (0.250 g, 0.602 mmol) were added to a Teflon-sealable Schlenk flask, and THF (10 mL) was vacuum transferred onto the solids. The mixture was stirred and warmed to room temperature over 10 min in the dark. Solvent was removed from the resulting orange solution in vacuo, leaving an orange-yellow foam. This foam was extracted with toluene (40 mL), and the extract was filtered via cannula. The resulting solution was concentrated to ca. 15 mL, layered with Et_2O (10 mL), and cooled to −30 °C. The product was isolated via cannula filtration as a yellow powder in 46% yield (0.237 g, 0.277 mmol). ^{1}H NMR: δ 1.83 (s, 15 H, C_5Me_5), 3.38 (s, 9 H, (O*Me*)C$_6$H$_4$), 5.87 (s, $^3J_{SnH}$ = 7.0 Hz, 5 H, C_5H_5), 7.01 (m, 6 H, *m*-(OMe)C$_6$*H*$_4$), 7.81−7.88 (m, 6 H, *o*-(OMe)C$_6$*H*$_4$). ^{13}C{^{1}H} NMR: δ 13.1, 54.9, 112.1, 115.0, 120.9, 139.7, 142.3, 160.2. ^{119}Sn{^{1}H} NMR: δ 120.9. Anal. Calcd for $C_{36}H_{41}O_3ClSnHf$: C, 50.61; H, 4.84. Found: C, 50.94; H, 4.81.

CpCp*Hf[Sn(*p*-FC$_6$H$_4$)$_3$]Cl (19). HSn(*p*-FC$_6$H$_4$)$_3$ (0.175 g, 0.432 mmol) and CpCp*Hf(H)Cl (0.179 g, 0.431 mmol) were added to a Teflon-sealable Schlenk flask, and THF (10 mL) was vacuum transferred onto the solids. The mixture was stirred and allowed to come to room temperature in the dark for 12 h. Solvent was removed from the resulting yellow solution in vacuo, leaving a yellow foam. This foam was extracted with pentane (40 mL), and the extract was filtered via cannula. The resulting yellow solution was concentrated to ca. 10 mL and cooled to −30 °C. The product was isolated via cannula filtration as a yellow, crystalline solid in 59% yield (0.208 g, 0.254 mmol). ^{1}H NMR: δ 1.72 (s, 15 H, C_5Me_5), 5.72 (s, $^3J_{SnH}$ = 7.6 Hz, 5 H, C_5H_5), 7.01 (m, 6 H, *m*-FC$_6$*H*$_4$), 7.53−7.67 (m, 6 H, *o*-FC$_6$*H*$_4$). ^{13}C{^{1}H} NMR: δ 13.0, 112.1, 116.0, 121.2, 139.9, 146.2, 163.9. ^{19}F{^{1}H} NMR: δ −114.3. ^{119}Sn{^{1}H} NMR: δ 116.5. Anal. Calcd for $C_{32}H_{32}F_3ClSnHf$: C, 48.44; H, 3.94. Found: C, 48.53; H, 3.80.

CpCp*Hf{Sn[*p*-(CF$_3$)C$_6$H$_4$]$_3$}Cl (20). HSn[(CF$_3$)C$_6$H$_4$]$_3$ (0.263 g, 0.474 mmol) and CpCp*Hf(H)Cl (0.200 g, 0.482 mmol) were added to a Teflon-sealable Schlenk flask, and THF (10 mL) was vacuum transferred onto the solids. The mixture was stirred and allowed to come to room temperature over 1 h in the dark. Solvent was removed from the resulting orange solution in vacuo, leaving an orange foam. This foam was extracted with pentane (15 mL) and filtered via cannula. The resulting orange pentane solution was concentrated to ca. 12 mL and cooled to −30 °C. Impure material was isolated via cannula filtration as an orange, crystalline solid. Recrystallization from an Et_2O solution (3 mL) layered with pentane (3 mL) at −80 °C gave analytically pure product as a yellow powder in 26% yield (0.120 g, 0.124 mmol). ^{1}H NMR: δ 1.67 (s, 15 H, C_5Me_5), 5.63 (s, $^3J_{SnH}$ = 7.9 Hz, 5 H, C_5H_5), 7.49 (m, 6 H, *m*-CF$_3$C$_6$*H*$_4$), 7.62−7.69 (m, 6 H, *o*-(CF$_3$)C$_6$*H*$_4$). ^{13}C{^{1}H} NMR: δ 13.0, 112.1, 121.2, 125.3, 125.7, 130.4, 138.5, 156.2. ^{19}F{^{1}H} NMR: δ −62.20. ^{119}Sn{^{1}H} NMR: δ 106.4. Anal. Calcd for $C_{36}H_{32}F_9ClSnHf$: C, 44.66; H, 3.33. Found: C, 44.60; H, 3.29.

Kinetic Study of the α-Elimination of Metal Stannyl Complexes. Samples for kinetic studies with **4** were prepared as follows: **4** (ca. 0.015 μmol) and ferrocene (ca. 0.010 μmol) were weighed into a 2.00 ± 0.01 mL volumetric flask, and toluene-d_8 was added to give a total volume of 2.00 mL. Two portions (ca. 0.6 mL each) of this solution were transferred to separate J. Young NMR tubes, which were wrapped in aluminum foil to protect the solution from light. The tubes were lowered into a temperature-controlled oil bath (temperature variation ≤1.0 °C). Data points were collected by removing the tubes from the oil and immediately cooling to room temperature. The tubes were typically at room temperature for about 15 min before being returned to the oil bath. The interim time at ambient temperature was not included in the data analysis. Samples for other kinetic studies of **2**, **4**, **8**, **9**, **10**, **18**, **19**, and **20** were prepared by combining the Hf−SnAr$_3$ compound (ca. 0.015 μmol) and ferrocene (ca. 0.010 μmol) in a 1.00 ± 0.01 mL volumetric flask, and toluene-d_8 was added to give a total volume of 1.00 mL.

Data points were gathered by ^{1}H NMR spectroscopy, and the rate of disappearance of hafnium stannyl species was monitored by integrating the C_5Me_5 or C_5H_5 peak relative to that of Cp_2Fe. Rate constants were calculated from first-order plots using data from the first three to five half-lives. Finally, during some reactions other decomposition species besides the α-elimination product were observed as impurities. In the case where impurities were observed, the rate of decomposition of **4** slowed slightly (by a factor of 0.8) relative to the case where clean decomposition products were generated. However, by silylating all glassware, 99% conversion of **4** to the α-elimination product was observed.

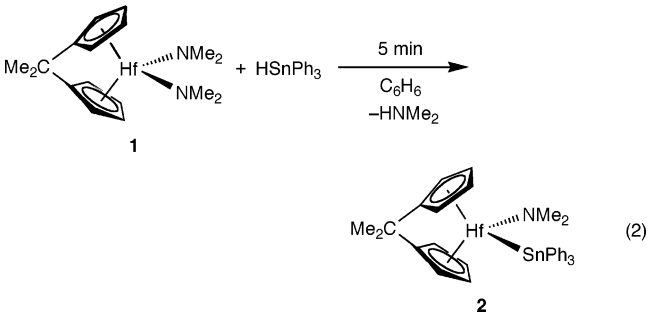
Results

As described above, earlier investigations established the operation of a facile α-H-elimination process for a hafnium hydrostannyl complex, and additional observations suggested that aryl groups in zirconium stannyl complexes might also undergo α-elimination. To investigate this possibility in detail, we targeted the synthesis of pure triarylstannyl complexes of hafnium. It was thought that such hafnium complexes might be more stable than the analogous zirconium derivatives and therefore be more readily isolated in pure form. Stable triarylstannyl complexes of this type could serve as a starting point in the search for well-behaved α-aryl-elimination reactions. It seemed that such systems should also allow mechanistic studies on this novel transformation. For the latter purpose, we desired

a series of hafnium stannyl complexes for which the steric and electronic properties at both Hf and Sn were varied. This was accomplished by the synthesis of hafnocene stannyl derivatives with various cyclopentadienyl-based ancillary ligands (for varying steric factors) and with different aryl groups in the stannyl ligand (for varying electronic factors).

Synthesis of Hafnium Stannyl Complexes by Amine Elimination. An established synthetic method for the preparation of metal stannyl derivatives involves the elimination of an amine upon reaction of a metal amido complex with a hydrostannane.[21] For example, tetrakis(triphenylstannyl)titanium was synthesized from Ph_3SnH and $Ti(NMe_2)_4$.[6b] For application of this method to the preparation of a hafnocene stannyl complex, the bis(amido) complex $[Me_2C(C_5H_4)_2]Hf(NMe_2)_2$ (**1**) was prepared in 52% yield by refluxing a toluene solution of $Me_2C(C_5H_5)_2$[22] and $Hf(NMe_2)_4$ for 18 h. This methylene-bridged dicyclopentadienyl ligand, which provides a very open metallocene framework,[16] was expected to present minimal steric resistance to rearrangements involving the metal center.

The reaction of **1** with Ph_3SnH in benzene at room temperature produced a red-orange solution from which $[Me_2C(C_5H_4)_2]Hf(SnPh_3)NMe_2$ (**2**) was isolated as air-sensitive, yellow crystals in 68% yield (eq 2). The ^{1}H NMR spectrum of **2** contains four

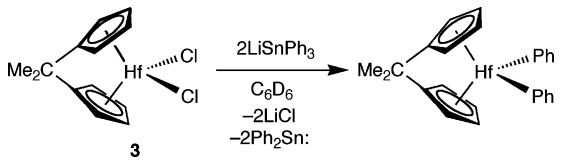


(2)

resonances (δ 5.06, 5.38, 5.50, and 5.68), corresponding to the cyclopentadienyl ligand protons, and two peaks for the diastereotopic methyl groups of the ligand backbone (δ 0.86 and 1.15). This complex is further characterized by a ^{119}Sn NMR shift of δ 67.1, which is in a downfield region similar to that observed for another d^0 hafnium triarylstannyl derivative ($Cp^*_2Hf(SnPh_3)Cl$; δ 114.7).[16,22] As was previously noted for Zr and Hf stannyl compounds,[6i] **2** is light-sensitive and decomposes completely under ambient room lighting after 4 days (room temperature, benzene-d_6 solution), to $HNMe_2$ (1 equiv), Ph_6Sn_2 (0.3 equiv), and a complex mixture of metal species. Due to the light sensitivity of such hafnium stannyls, the complexes described here were manipulated under minimal ambient lighting conditions.

For access to a series of related stannyl derivatives for which the adjacent ancillary ligand is varied, it was of interest to substitute the dimethylamide group in **2**. Attempts to replace the amide with halide substituents using $HNMe_2$·HCl, MeI, or acetyl chloride in benzene-d_6 gave complex mixtures of products. However, when trimethylsilyl chloride (26 equiv) was added to **2** at room temperature, a 74% conversion to $[Me_2C(C_5H_4)_2]Hf(SnPh_3)Cl$ was observed after 20 min (benzene-d_6 solution, by ^{1}H NMR spectroscopy). After 8 h, this new stannyl complex had decomposed to a number of species, including $[Me_2C(C_5H_4)_2]HfCl_2$ (**3**). The addition of 1 equiv of Me_3SiCl to **2** provided $[Me_2C(C_5H_4)_2]Hf(SnPh_3)Cl$ in a low yield (13%) after 10 min, and the amount of this compound increased marginally over time (20% after 20 min, and 23% after 7 h). These results suggest that the reaction of **2** with Me_3SiCl does not go to completion, and perhaps for this reason $[Me_2C(C_5H_4)_2]Hf(SnPh_3)Cl$ could not be isolated from preparatory-scale reactions. This difficulty may result from the volatility of Me_3SiCl, which is removed by evaporation during workup, resulting in a shift of the equilibrium back to **2**. Given the problems in converting the stannyl amide **2** to additional stannyl derivatives, we explored other synthetic routes to hafnocene stannyl complexes.

Synthesis of Hafnium Stannyl Complexes by Salt Elimination. Another method previously reported for the synthesis of hafnium stannyl compounds is based on salt elimination between a metal halide and a stannyllithium reagent.[6a,c−d,i] For application of this method, a hafnocene dichloride was desired. The addition of an excess (7 equiv) of Me_3SiCl to **1** provided the hafnium dichloride starting material **3** in good yield (69%). The reaction of this complex with $LiSnPh_3$ (1 equiv) in benzene-d_6 did not produce the expected compound $[Me_2C(C_5H_4)_2]Hf(SnPh_3)Cl$, but instead gave a mixture of $[Me_2C(C_5H_4)_2]Hf(Ph)Cl$ (47%), $[Me_2C(C_5H_4)_2]HfPh_2$ (22%), and unreacted **3** (25%). The monophenyl species is characterized by ligand resonances in the ^{1}H NMR spectrum that reflect the unsymmetrical nature of this compound [δ 1.15 and 1.17 (Me); 4.97, 5.41, 6.16, and 6.21 (C_5H_4)], while those for the diphenyl derivative are consistent with C_2 symmetry [δ 1.23 (Me); 5.26 and 6.20 (C_5H_4)]. Both of these compounds were independently generated in reactions of **3** and PhLi (benzene-d_6/THF solution) and identified by ^{1}H NMR spectroscopy. The 1:2 reaction of **3** with $LiSnPh_3$ (benzene-d_6, room temperature, 15 min) also resulted only in phenylation of the hafnium center, to give the diphenyl complex $[Me_2C(C_5H_4)_2]HfPh_2$ in 95% yield by ^{1}H NMR spectroscopy (eq 3). These results suggested that, like CpCp*Zr-



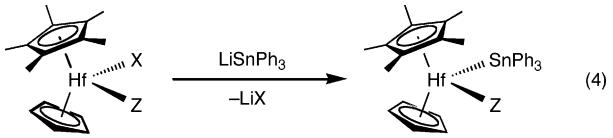
(3)

$(SnPh_3)Cl$,[6i] the desired triphenylstannyl complexes are unstable under the reaction conditions and decompose via an α-elimination process.[23]

Since this methylene-bridged ligand system appeared to give hafnium stannyl compounds that were unstable toward α-elimination, we turned to the $CpCp^*ML_n$ mixed-ring system, which had previously been useful in the synthesis of metal stannyl complexes.[6i,7] Fortunately, this ligand set has allowed the synthesis and isolation of a series of stannyl complexes for use in studies on α-aryl-elimination. Bright yellow crystals of $CpCp^*Hf(SnPh_3)Cl$ (**4**) were obtained as previously reported from $LiSnPh_3$ and $CpCp^*HfCl_2$,[6i] and this compound was isolated in an improved yield of 75% (see Experimental Section). Other hafnocene starting materials, $CpCp^*Hf(NMe_2)Cl$ (**5**),

(23) Note that redistribution processes, which may be catalyzed by the LiCl byproduct, may also occur, and in general, this could give more than one product. See: Alcock, N. W.; Clase, H. J.; Duncalf, D. J.; Hart, S. L.; McCamley, A.; McCormack, P. J.; Taylor, P. C. *J. Organomet. Chem.* **2000**, *605*, 45−54. However, the α-elimination process observed in eq 3 should be unaffected by any such Ph/Cl scrambling, as both chloride ligands are substituted.

CpCp*Hf(Me)OTf (**6**), and CpCp*Hf(OMe)Cl (**7**), were prepared from salt metathesis reactions between CpCp*$HfCl_2$ and $LiNMe_2$ (**5**) or NaOMe (**7**) or by a published procedure (**6**).[4a] Reactions of compounds **5**−**7** with $LiSnPh_3$ resulted in isolation of the stannyl complexes CpCp*Hf($SnPh_3$)NMe_2 (**8**), CpCp*Hf($SnPh_3$)Me (**9**), and CpCp*Hf($SnPh_3$)OMe (**10**) in good yields (58−72%) (eq 4). All three of these stannyl derivatives



(4)

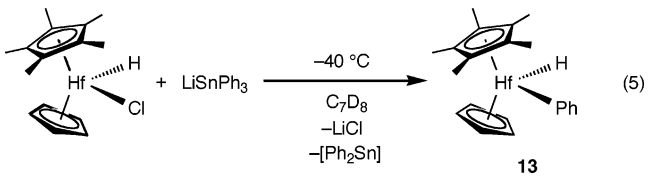
X = Cl, Z = NMe_2 (**5**)
X = OTf, Z = Me (**6**)
X = Cl, Z = OMe (**7**)

Z = NMe_2 (**8**)
Z = Me (**9**)
Z = OMe (**10**)

crystallize with solvent [**8**·0.75($C_4H_{10}O$), **9**·0.5(C_5H_{12}), **10**·0.5(C_7H_8)], and the solvent-free complexes may be obtained by crushing the crystals to a fine powder and then applying a vacuum. These compounds are air-sensitive and (like **2**) light-sensitive in solution. Finally, similar to other hafnocene stannyl compounds,[6i,7] **4**, **8**, **9**, and **10** exhibit a yellow color that results from weak, broad LMCT transitions centered at ca. 350 nm. For example, the UV−visible spectra for the two dimethylamide derivatives contain absorptions at 358 nm (**2**, $\epsilon = 4700$ dm^3 mol^{-1} cm^{-1}) and 340 nm (**8**, $\epsilon = 5000$ dm^3 mol^{-1} cm^{-1}).

Another hafnium stannyl complex was generated by the reaction of 1 equiv of PhLi with **4** in benzene-d_6/THF. This reaction mixture produced a deep red solution containing one major species in 91% yield, which appears to be CpCp*Hf($SnPh_3$)Ph (**11**) based on ^1H and ^{119}Sn NMR spectroscopy. The downfield ^{119}Sn NMR shift observed for **11** (δ 106.6) is diagnostic for hafnocene triarylstannyl compounds, which are characterized by resonances near δ 100 (cf. δ 112.7 for **4**, δ 74.3 for **8**, δ 111.5 for **9**, and δ 64.3 for **10**). Unfortunately, attempts to isolate the pure compound from preparative scale reactions were not successful. The same species was formed from the reaction of CpCp*Hf(Ph)Cl (**12**) and $LiSnPh_3$ (1 equiv), but again the product could not be isolated cleanly via crystallization from a variety of solvents (toluene, toluene/pentane, toluene/Et_2O, in varying ratios). Interestingly, **11** was also produced by the addition of 2 equiv of $LiSnPh_3$ to CpCp*$HfCl_2$ (benzene-d_6 solution), presumably via the intermediate CpCp*Hf($SnPh_3$)$_2$, which may undergo rapid α-elimination of Ph_2Sn. These results clearly indicate that the CpCp* ligand set provides greater stability to hafnium triphenylstannyl derivatives than does the less sterically demanding $Me_2C(C_5H_4)_2$ ligand.

An attempt to obtain a stannyl hydride complex was based on reaction of the hydride CpCp*Hf(H)Cl[18] with $LiSnPh_3$. As shown in eq 5, this reaction exclusively produced the phenyl



(5)

13

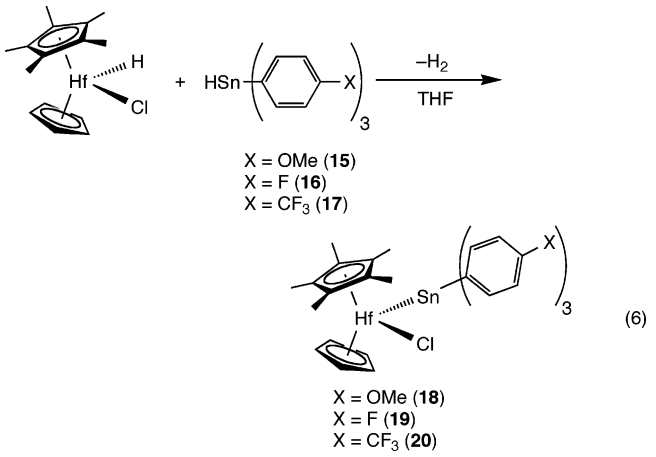
hydride complex CpCp*Hf(H)Ph (**13**), even at −40 °C (by ^1H NMR spectroscopy, in toluene-d_8 solution). This result suggests that the α-elimination of a phenyl group in CpCp*Hf($SnPh_3$)H is quite rapid. Compound **13** was independently isolated from the reaction of CpCp*Hf(H)Cl with PhLi in THF, and the terminal hydride ligand is characterized by a ^1H NMR shift at δ 13.02 and an infrared stretch at 1600 cm^{-1}.

To investigate the effect of a sterically demanding ligand on α-elimination chemistry, an attempt was made to prepare the neopentyl derivative CpCp*Hf($SnPh_3$)Np (Np = neopentyl). Unexpectedly, the reaction of **4** with NpLi (Np = neopentyl) gave a mixture consistent with both LiCl and $LiSnPh_3$ elimination. After slowly warming a toluene solution from −78 °C to room temperature over 2 h, CpCp*Hf($SnPh_3$)Np (**14**, 54%), the triphenylstannyl phenyl derivative **11** (16%), an unidentified product (16%), and unreacted **4** (14%) were present. Repeated crystallizations from Et_2O allowed the isolation of a small amount of **14** [80% pure; impurities were **4** (13%) and **11** (6%)] as yellow crystals in 14% yield. Compound **14** appears to exhibit an unusual ^1H NMR spectrum due to an α-agostic interaction between one of the neopentyl methylene C−H bonds and Hf. The two diastereotopic methylene protons are observed at δ −3.80 and 2.59 ($^2J_{HH}$ = 9.9 Hz), and the C−H coupling constants obtained from a proton-coupled heteronuclear multiple quantum coherence (HMQC) experiment are 87.2 Hz (δ −3.80) and 109 Hz (δ 2.59). The C−H coupling constant of 114 Hz for the methyl group of CpCp*Hf($SnPh_3$)Me (**9**) lends further support to the characterization of **14** as possessing an α-agostic neopentyl group.[24] Finally, the ^{13}C NMR resonance for the methylene group in **14** is observed at δ 124.8, far downfield from the resonance observed for the hafnium methyl group in **9** (δ 58.67). It is of note that the infrared spectrum of this compound revealed no peaks in a region of lower frequency, as might be expected for compounds with an α-agostic interaction,[23] but the C−H coupling constants strongly suggest the presence of a secondary interaction between the CH_2 group and Hf.

Synthesis of Hafnium Stannyl Complexes by *σ*-Bond Metathesis. It has previously been observed that σ-bond metathesis can be used to prepare metal stannyl complexes, such as CpCp*Zr($SnPh_3$)Cl, that could not be obtained through salt metathesis.[6i] In such procedures, a hydrostannane (R_3SnH or R_2SnH_2) reacts with a metal hydride or silyl complex (M−H or M−SiR_3) to eliminate H_2 or $HSiR_3$ with formation of a M−Sn bond. This method can be synthetically more convenient than that involving salt metathesis, since hydrostannanes are in general more readily available than stannyllithium reagents. In the following syntheses, purification of the stannyl complexes was simplified by using hydrogen rather than silane elimination, as hydrogen is more readily removed from the product.

To probe electronic factors in the migration of an aryl group from Sn to Hf, a series of para-substitued triarylstannyl species was synthesized. By ^1H NMR spectroscopy, it was observed that reactions of CpCp*Hf(H)Cl with various stannanes Ar_3SnH [Ar = *p*-(OMe)C_6H_4 (**15**), *p*-FC_6H_4 (**16**), and *p*-(CF_3)C_6H_4 (**17**)] produced good yields (68−84%) of the stannyl complexes CpCp*Hf[Sn(*p*-(OMe)C_6H_4)$_3$]Cl (**18**), CpCp*Hf[Sn(*p*-FC_6H_4)$_3$]Cl (**19**), and CpCp*Hf[Sn(*p*-(CF_3)C_6H_4)$_3$]Cl (**20**) (eq 6). The lower isolated yields (26−59%) for **18**−**20** appear to result from competing decomposition of the hafnium hydride starting

(24) (a) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc. Chem. Commun.* **1983**, 691−693. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395−408.



(6)

material during synthetic manipulations. The new stannyl complexes are yellow in the solid state and in solution and give rise to ^{119}Sn NMR resonances of δ 120.9 (**18**), 116.5 (**19**), and 106.4 (**20**). The pattern of increasingly upfield ^{119}Sn NMR shifts is consistent with a decrease in electron density at Sn in going from **18** to **19** to **20**.[25]

Crystallographic Studies. Given the paucity of structural data for d^0 metal stannyl complexes,[6g,h,j,7] it was of interest to investigate several of the complexes described above by X-ray crystallography. The compounds $[Me_2C(C_5H_4)_2]Hf(SnPh_3)NMe_2$ (**2**) and CpCp*Hf($SnPh_3$)X [X = Cl (**4**), X = NMe_2 (**8**), X = Me (**9**), and X = OMe (**10**)] all form single crystals that provided suitable diffraction patterns for crystallographic characterization (the ORTEP diagram for CpCp*Hf($SnPh_3$)NMe_2·0.75(C_4H_{10}) is shown in Figure 1). Surprisingly, the Hf−Sn bond distances in these complexes do not vary considerably (2.94−2.97 Å, Table 1). The dimethylamide derivatives **2** and **8** were found to possess planar nitrogen atoms (sum of angles about nitrogen 180°), and the dihedral C(Me)−N−Hf−Sn angle for both species is approximately 60°. Dihedral angles of ca. 60° are typical for amide ligands in metallocene complexes exhibiting steric strain.[26] The corresponding C(Me)−O−Hf−Sn angle in the methoxy-substituted species **10** is slightly greater (81.9°), presumably due to reduced steric repulsion between the Cp* and OMe ligands.

Mechanistic Studies on α-Aryl-Elimination Reactions. In an initial examination of α-aryl-elimination in these hafnium stannyl compounds, a toluene-d_8 solution of the triphenylstannyl chloride derivative **4** was heated to 100 °C. After 4 days, complete conversion of **4** to the phenyl chloride **12** (99% yield) was observed by ^{1}H NMR spectroscopy (eq 7). By ^{119}Sn NMR spectroscopy, the cyclic polystannanes $(Ph_2Sn)_5$ and $(Ph_2Sn)_6$ were observed as the only tin-containing products (δ −205.9 and −217.2, respectively).[5b,c,27,28] Presumably, these products result from elimination of the stannylene Ph_2Sn, which then condenses to form the cyclic species. Similar stannylene

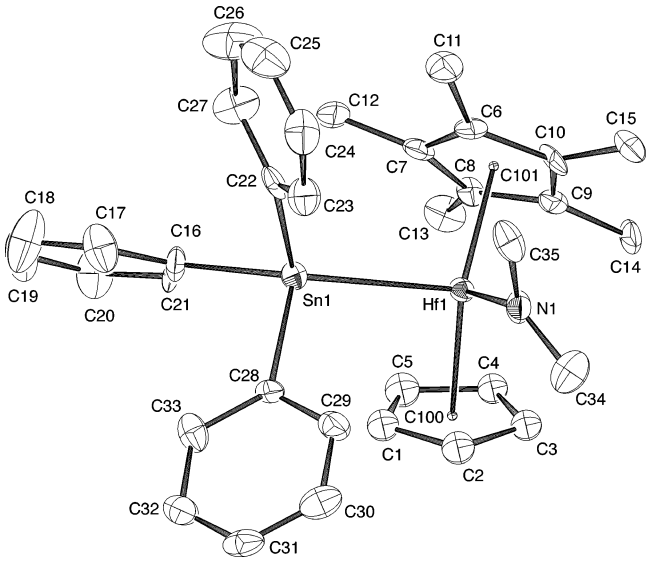
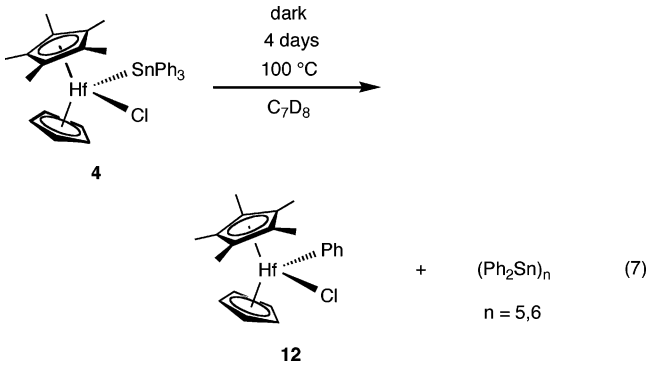


Figure 1. ORTEP diagram of CpCp*Hf($SnPh_3$)NMe_2·0.75($C_4H_{10}O$) [**8**·0.75($C_4H_{10}O$)]. Only one of the two molecules in the unit cell is shown. The hydrogen atoms and the $C_4H_{10}O$ molecules were removed for clarity. Atoms are shown as 50% probablility ellipsoids.

Table 1. Selected Crystallographic Data

compound	**2**	**4**	**8**	**9**	**10**
Hf−Sn bond distance (Å)	2.9428(7)	2.9650(4)	(a) 2.9694(8) (b) 2.9658(8)	2.9740(5)	2.9556(5)
Sn−Hf−X angle (deg)	93.3(2) X = NMe_2	87.65(4) X = Cl	(a) 90.6(2) (b) 89.7(2) X = NMe2	92.7(2) X = Me	90.6(2) X = OMe
average Hf−Sn−C(Ph) angle (deg)	116.8	116.8	(a) 117.3 (b) 117.7	115.8	114.3

condensation was observed upon the elimination of Mes_2Sn from CpCp*Hf($SnHMes_2$)Cl, and this stannylene was trapped by 2,3-dimethylbutadiene[29] to give 1,1′-dimesityl-3,4-dimethylstannacyclopent-3-ene.[7] However, in the presence of 9 equiv of 2,3-



(7)

dimethylbutadiene (9 equiv), the reaction of eq 7 did not produce the anticipated stannacyclopentene. The lack of efficient trapping in this case may be due to the very rapid oligomerization of Ph_2Sn ($k = 10^8$ M^{-1} s^{-1}) to $(Ph_2Sn)_n$.[21] A small amount of yellow precipitate was also observed during the course of the reaction, which was insoluble in benzene or toluene and was only sparingly soluble in THF (despite coloring THF solutions pale yellow, no peaks were observed from a GPC trace of this

(25) (a) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979−4987. (b) Swain, C. G.; Lupton, Jr., E. C. *J. Am. Chem. Soc.* **1968**, *80*, 4328−4337. (c) Johnson, C. D. *The Hammett Equation*; Cambridge University Press: London, 1973.

(26) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309−1312.

(27) Jousseaume, B.; Noiret, N.; Pereyre, M.; Saux, A.; Francès, J.-M. *Organometallics* **1994**, *13*, 1034−1038.

(28) The ^{119}Sn NMR shift of δ −208 previously reported for $(Ph_2Sn)_6$ was observed in chloroform-d_1. Dräger, B.; Mathiasch, B.; Ross, L.; Ross, M. *Z. Anorg. Allg. Chem.* **1983**, *506*, 99−109.

(29) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311−334.

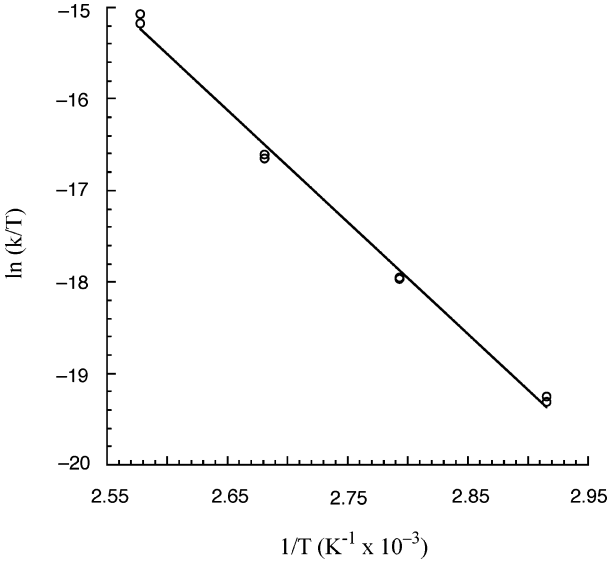


Figure 2. Eyring plot for the rate of disappearance of [**4**] at different temperatures.

solution). This insoluble precipitate could therefore be due to higher molecular weight $(Ph_2Sn)_n$, as it has previously been noted that Ph_2Sn oligomers (M_w/M_n = 2200/900) are only slightly soluble in THF.[5b] Further support for this conclusion comes from an elemental analysis of this precipitate, which gave a carbon/hydrogen ratio consistent with $(Ph_2Sn)_n$. The reaction of eq 7 appears to be irreversible, as the product mixture did not contain observable quantities of **4** (by ^{1}H NMR spectroscopy) after 1 week at room temperature.

The disappearance of **4**, monitored by NMR spectroscopy, obeys first-order kinetics. An Eyring plot (Figure 2) of rate data for the temperature range 70−115 °C provided the activation parameters $\Delta H^{\ddagger} = 24$ (1) kcal/mol and $\Delta S^{\ddagger} = -15$ (1) eu. These numbers are consistent with an ordered transition state, as might be expected for a unimolecular α-elimination in which a phenyl group migrates from Sn to Hf. In the polar solvent *o*-dichlorobenzene ($\epsilon = 10.12$; versus $\epsilon = 2.379$ for toluene), the rate of α-elimination at 100 °C was not significantly affected ($k = 2.5 \times 10^{-5}$ s^{-1}; versus $k = 2.3 \times 10^{-5}$ s^{-1} in toluene). Thus, the reaction appears to involve a relatively nonpolar transition state.

Despite the fact that the final product mixtures for some of the decompositions discussed herein suggest a nonselective process (observed yields of hafnium aryl products 66−99%), their clean, first-order kinetics (with respect to decay of the initial stannyl complex) are consistent with a single, initial step in the decomposition process. We propose that this step corresponds to an α-aryl-elimination. The unidentified side products likely result from secondary reactions involving the Hf−Ar product at these high temperatures (e.g. redistribution at hafnium, reactions with the solvent, etc.).

The influence of ancillary ligands on the rate of α-elimination was investigated with the compounds $[Me_2C(C_5H_4)_2]Hf(SnPh_3)$-$NMe_2$ (**2**) and CpCp*Hf($SnPh_3$)X [X = NMe_2 (**8**), Me (**9**), and OMe (**10**)]. The methyl derivative **9** was found to be the least stable, decomposing very rapidly at 70 °C ($k = 9.6 \times 10^{-5}$ s^{-1}; 5.6×10^{-6} s^{-1} at 45 °C), to CpCp*Hf(Ph)Me in 82% yield. In contrast to the relatively rapid decomposition of the methyl derivative **9**, the dimethylamide-substituted compounds **2** and **8** did not decompose at an appreciable rate until 115 °C. Complex **9** decomposes 64 times faster than **4** (at 70 °C), which undergoes α-elimination 230 times faster than **8** (at 115 °C). On the basis of these differences, it can be determined that the dimethylamide species **8** is more stable than the methyl derivative **9** by at least a factor of 280. Thus, the π-donating NMe_2 ligand greatly stabilizes hafnocene stannyl complexes toward α-phenyl-elimination, relative to a σ-only ligand such as methyl.

Interestingly, there is a significant difference in the stabilities of the two amide derivatives, as evidenced by the rate constants of $k = 9.4 \times 10^{-5}$ s^{-1} (**2**) and $k = 4.3 \times 10^{-7}$ s^{-1} (**8**) for disappearance of the starting compound at 115 °C. After heating **2** for 1 week at this temperature, the species identified by ^{1}H NMR spectroscopy were unreacted **2** (4%), $[Me_2C(C_5H_4)_2]$Hf-(Ph)NMe_2 (71%), and the bis(amido) complex **1** (13%). The decomposition of **8** at 115 °C was monitored for 58 days, and after this time the α-elimination product CpCp*Hf(Ph)NMe_2 (66%), unreacted **8** (11%), and the bis(amido) product CpCp*Hf-$(NMe_2)_2$ (2%) were present. These rate data provide additional evidence that the methylene-bridged ligand system affords stannyl complexes that are more susceptible to α-elimination than analogous complexes of the CpCp* ligand set.

The methoxy derivative **10** exhibited only a 2-fold increase in stability (k (100 °C) = 8.8×10^{-6} s^{-1}) relative to that for the chloride **4** and decomposed to give CpCp*Hf(Ph)OMe in 96% yield after 3.5 days. Further, comparisons of rates lead to the conclusion that **10** is 23 times less stable than **8**. This relatively rapid rate of decomposition is somewhat surprising, since the σ+π-donating abilities of OMe and NMe_2 are expected to be comparable and should lead to similarly stable compounds.[30] However, in this case, the lower steric bulk of OMe may be an important factor in determining the higher rate of α-elimination for **10**.

Finally, decomposition of the neopentyl complex CpCp*Hf-($SnPh_3$)Np (**14**) at 100 °C occurred with a rate constant of $k = 4 \times 10^{-6}$ s^{-1} (over three half-lives), providing evidence that this stannyl complex is 160 times more stable than the methyl derivative **9** (determined from similar relationships as above). Although there is an added electronic effect due to the α-agostic interaction observed between this ligand and Hf, it is likely that the enhanced steric bulk of the neopentyl ligand is the primary factor in slowing the rate of decomposition relative to the methyl derivative **9** (vide infra). In summary, the order of stability toward α-phenyl-elimination provided by the ancillary ligands is NMe_2 > Np > OMe > Cl > Me.

To investigate the influence of electronic inductive effects on the rate of α-elimination, kinetic studies of the decompositions of CpCp*Hf($SnPh_3$)Cl (**4**), CpCp*Hf[Sn(*p*-$(OMe)C_6H_4)_3$]-Cl (**18**), CpCp*Hf[Sn(*p*-$FC_6H_4)_3$]Cl (**19**), and CpCp*Hf[Sn(*p*-$(CF_3)C_6H_4)_3$]Cl (**20**) were undertaken. The fastest rate of α-elimination was observed for the *p*-methoxy-substituted derivative **18** [k (100 °C) = 1.8×10^{-4} s^{-1}; 95% yield of CpCp*Hf(*p*-$(OMe)C_6H_4$)Cl], while the *p*-trifluoromethyl species **20** was the most stable complex in this series [k (100 °C) = 3.1×10^{-6} s^{-1}; 85% yield of CpCp*Hf(*p*-$(CF_3)C_6H_4$)Cl]. The *p*-fluorophenyl compound **19** [k (100 °C) = 2.9×10^{-5} s^{-1}; 98% yield of CpCp*Hf(*p*- FC_6H_4)Cl] was found to undergo α-elimination at the same rate as **4**. The Hammett plot

(30) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.

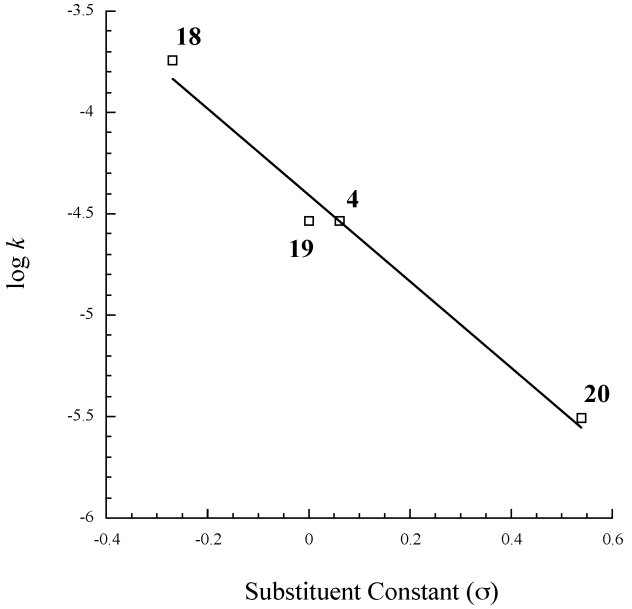


Figure 3. Hammett correlation for α-aryl-elimination.

constructed from these data (Figure 3) represents a linear correlation with a negative slope ($\rho = -2.13$). The magnitude of this ρ value indicates that there is a significant electronic effect on the rate of decomposition, and the negative sign implies that electron donor groups promote the α-elimination process.

Discussion

A variety of methods have been reported for the synthesis of d^0 stannyl complexes.[21,31] In the investigations described here, methods based on amine elimination, salt elimination, and σ-bond metathesis were used to prepare a number of new hafnium stannyl compounds. The salt elimination route, employing a stannyllithium derivative, is somewhat limited in its utility. For example, the syntheses of $CpCp^*Zr(SnPh_3)Cl$[6i] and $CpCp^*Hf(SnMe_3)Cl$[32] were not successful using salt elimination but could be achieved via σ-bond metathesis routes. As previously noted (vide supra), hydrostannanes are more practical stannylating reagents, as they are more convenient than stannyllithium reagents to prepare and store. In general, the most useful synthetic route to hafnocene stannyl species appears to involve the σ-bond metathesis reaction of a metal hydride with a hydrostannane.

The Hf−Sn bond distances for $[Me_2C(C_5H_4)_2]Hf(SnPh_3)NMe_2$ (**2**), $CpCp^*Hf(SnPh_3)Cl$ (**4**), $CpCp^*Hf(SnPh_3)NMe_2$ (**8**), $CpCp^*Hf(SnPh_3)Me$ (**9**), and $CpCp^*Hf(SnPh_3)OMe$ (**10**) do not vary significantly. Further, these Hf−Sn bond distances are slightly shorter than the analogous values reported for the sterically encumbered stannyl complexes $CpCp^*Hf(SnHMes_2)Cl$ [3.0073(6) Å][7] and $\{MeSi[SiMe_2N(4\text{-}CH_3C_6H_4)]_3\}SnHfCp_2Cl$ [3.0231(2) Å].[6j] Thus, these results suggest that the Hf−Sn bond in compounds **2**, **4**, **8**, **9**, and **10** is not under significant steric pressure. Finally, a greater Hf−Sn bond length does not necessarily lead to an increased rate of α-elimination, as might have been expected if this factor was significant in destabilizing the complex.

Given the planar geometry for the nitrogen atoms in both dimethylamide derivatives **2** and **8**, we can assume the existence of a π-bond between the hafnium and nitrogen atoms. As was previously noted, π-donation of this type is typical for early metal amide complexes.[26] Despite the interaction between the nitrogen lone pair and hafnium, rotation about the Hf−N bond is quite facile (by ^{1}H NMR spectroscopy; the amide methyl groups are equivalent in toluene-d_8 solution down to −80 °C). Also, π-bonding may be assumed for the Hf−O interaction in **10**, and the larger C(Me)−O−Hf−Sn dihedral angle of 81.9° (cf. ca. 60° for the C(Me)−N−Hf−Sn dihedral angles in **2** and **8**) is presumably made possible by the less bulky methoxy ancillary ligand (vide supra). Since **10** undergoes α-phenyl-elimination significantly faster than **2** and **8**, this result suggests that steric properties of the ancillary ligands are quite important in determining the rate of decomposition.

The results presented here provide further evidence that hafnocene stannyl complexes have a marked tendency to decompose via α-elimination. Interestingly, this type of decomposition reaction appears to be quite rare for d^0 complexes, although few analogous d^0 metal-main group systems have been investigated. More generally, migratory α-eliminations are well-known in transition metal chemistry, but such reactions are typically associated with higher d^n configurations. Such rearrangements usually result in conversion of a complex of the type L_nM-ER_nR' to $L_nM(=ER_n)R'$. Thus, in this case the "eliminated" fragment remains bonded to the metal center. For this type of α-elimination reaction, at least two electrons are required for the reacting metal center (d^n configurations with $n \geq 2$). For example, Green's complex $[Cp_2W(C_2H_4)(CH_3)]^+[PF_6]^-$ loses ethylene and undergoes α-H-elimination to produce the methylidene hydride $[Cp_2W(=CH_2)(H)]^+[PF_6]^-$.[33] Also, Schrock found that the reduction of $Cp^*Ta(CH_2CMe_3)Cl_3$ with 2 equiv of Na/Hg amalgam in the presence of PMe_3 gives the α-migration product $Cp^*Ta(=CHCMe_3)(H)(PMe_3)Cl$.[34] Decarbonylation[9b−e] and desulfination[35] reactions from transition metal acyl and sulfinato complexes, respectively, represent related processes.

Reactions that are more relevant to those described here involve elimination of an ER_n species from a L_nM-ER_nR' complex, to form L_nM-R'. In cases where L_nM-R' is the first observed product, the d^n electron configuration is typically d^0, which often leads to a weak $L_n(R')M-ER_n$ interaction and rapid loss of ER_n. This is seen, for example, in decarbonylations of d^0 acyl derivatives.[8,9a] Other examples of this type of reactivity involve higher d^n configurations and elimination of a relatively stable ER_n species. For example, $CpM(CO)_3PbMe_3$ (M = Cr, Mo, W; d^4) and $CpFe(CO)_2PbMe_3$ (d^6) decompose thermally or photolytically to the corresponding methyl species, with elimination of Me_2Pb.[36]

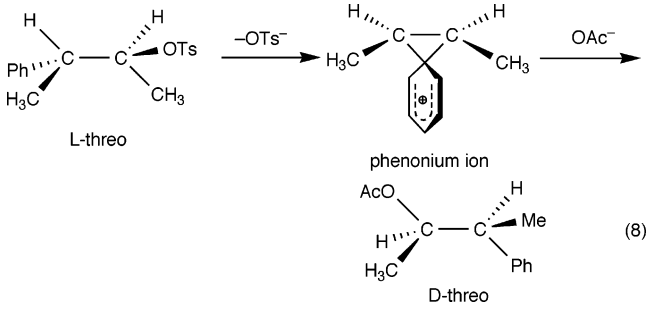
α-Elimination processes related to those described here have also been described for main group compounds in which the reacting main group center is closed shell. Such α-elimination

(31) Petz, W. *Chem. Rev.* **1986**, *86*, 1019−1047.
(32) Neale, N. R.; Tilley, T. D. *Tetrahedron* **2004**, *60*, 7247−7260.
(33) (a) Cooper, J. N.; Green, M. L. H. *J. Chem. Soc. Chem. Comm.* **1974**, 208−209 and 761−762 (b) Cooper, J. N.; Green, M. L. H. *J. Chem. Soc. Dalton Trans.* **1979**, 1121−1127.
(34) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98−104.
(35) (a) Kubota, M.; Blake, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 1368−1373. (b) Downs, R. L.; Wojcicki, A. *Inorg. Chim. Acta* **1978**, *27*, 91−103.
(36) (a) Pannell, K. H. *J. Organomet. Chem.* **1980**, *198*, 37−40. (b) Pannell, K. H.; Kapoor, R. N. *J. Organomet. Chem.* **1981**, *214*, 47−52 and **1984**, *269*, 59−63.

decomposition pathways have been extensively studied for oligo- and polysilanes.[37] These studies suggest that polysilanes $R_3Si(SiR_2)_nR$ undergo α-elimination as a major decomposition pathway, to give $R_3Si(SiR_2)_{n-1}R$ and R_2Si. Such reactions have been observed in other group 14 compounds, such as $PhMe_2GeSiMe_3$, which thermally decomposes via competitive Me_2Si and Me_2Ge elimination.[38]

We have previously shown that $CpCp^*Hf(SnHMes_2)Cl$ undergoes decomposition via stannylene elimination,[7] and this now appears to be a general decomposition mode for d^0 hafnium stannyl complexes. For the triarylstannyl compounds described here, solution-phase thermal decompositions are well-behaved and amenable to kinetic studies, which have provided insight into the mechanism of this reaction. The α-elimination decomposition process was studied in most detail for the parent compound $CpCp^*Hf(SnPh_3)Cl$ (**4**). Kinetic studies of this transformation revealed a first-order decomposition process, which is consistent with an α-elimination pathway in which intramolecular phenyl migration occurs. The activation parameters suggest an ordered transition state ($\Delta S^{\ddagger} < 0$), which might be expected for migration of the phenyl group from Sn to Hf. Also, since a polar solvent has almost no effect on the rate of reaction, we conclude that significant charge separation is not involved in the rate-determining step.

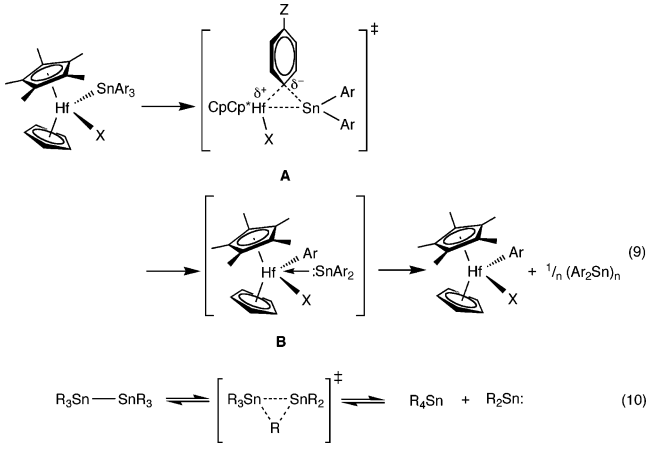
A Hammett correlation based on data derived from the para-substituted triaryl derivatives gave a negative slope ($\rho = -2.13$), which indicates transition state stabilization (and rate enhancement) by electron donor groups. Related Hammett correlations have previously been determined for reactions involving the migration of para-substituted phenyl groups to an electrophilic center. A classic example of a migration of an aryl group to an electrophilic carbon center is found in the pinacol rearrangement (eq 8).[39] Cram suggested that the stereospecificity of this process



(8)

may be explained by a mechanism involving an intermediate phenonium ion having an sp^3-hybridized carbon atom on the phenyl ring.[40] In subsequent mechanistic studies that supported the existence of this phenonium ion, Brown et al. determined that for the migration of para-substituted phenyl groups, the Hammett correlation has a regression constant of $\rho = -1.46$.[41]

The negative ρ value observed for the Hammett correlation described here suggests that these reactions may be described as nucleophilic migrations of the aryl group. We therefore propose the concerted transition state **A** (eq 9), which involves



(9)

(10)

an interaction of the electrophilic hafnium center with the nucleophilic migrating group. Related transition states, possessing this three-center, four-electron bonding, have previously been proposed for α-eliminations in disilanes[37d,e,j] and distannanes[42] (e.g., eq 10). A second, perhaps less significant, factor that may contribute to this Hammett correlation relates to stabilization of the stannylene elimination product, as electron-donating groups are known to stabilize such species.[29]

Further evidence in support of this mechanism was obtained from kinetic studies of the thermal decompositions of $CpCp^*Hf(SnAr_3)X$ (X = Cl, NMe_2, Me, OMe, and Np). The observed influence of the X ligand on the stability of the complex (NMe_2 > Np (α-agostic) > OMe > Cl > Me ≫ H, SnR_3) appears to reflect the π-donating ability of this ancillary ligand. A greater degree of π-donation should result in a less electrophilic hafnium center, and therefore a slower α-elimination rate. This π-donation should populate the otherwise vacant metallocene a_1 orbital,[43] which appears to be required to accommodate the migrating aryl group. The effect of π-bonding is therefore to decrease the interaction of this orbital with the Sn−C(Ph) bond. Presumably, this orbital is also required for formation of the initial product of elimination, the 18-electron stannylene complex $CpCp^*Hf(Ar)(X)(SnAr_2)$. This unobserved intermediate (**B**) would possess a very weakly bound stannylene ligand (eq 9). Although formation of such an intermediate is not required for the mechanism proposed here, similar species have been observed as products of analogous transformations (e.g., de-

(37) (a) Pitt, C. G. In *Homoaromatic Rings, Chains and Macromolecules of Main-Group Elements*; Rheingold, A. L., Ed.; Elsevier Scientific: New York, 1977; Chapter 8. (b) Braunstein, P.; Morise, X. *Chem. Rev.* **2000**, *100*, 3541−3552 and references therein. Specific reviews on polysilanes: (c) Ziegler, J. M. *Mol. Cryst. Liq. Cryst.* **1990**, *190*, 265−282. (d) Vanderwielen, A. J.; Ring, M. A.; O'Neal, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 993−998. (e) Dzarnoski, J.; Rickborn, S. F.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1982**, *1*, 1217−1220. (f) Nares, K. E.; Harris, M. E.; Ring, M. A.; O'Neal, H. E. *Organometallics* **1989**, *8*, 1964−1967. (g) Walker, K. L.; Jardine, R. E.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1998**, *30*, 69−88. (h) Ring, M. A.; O'Neal, H. E.; Walker, K. L. *Int. J. Chem. Kinet.* **1998**, *30*, 89−97. (i) Trefonas, P., III; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737−2742. (j) Karatsu, T.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 1140−1141. (k) Walsh, R. *Organometallics* **1988**, *7*, 75−77. (l) Bell, T. N.; Perkins, K. A.; Perkins, P. G. *J. Phys. Chem.* **1984**, *88*, 116−118.

(38) Bobbitt, K.; Maloney, V. M.; Gaspar, P. P. *Organometallics* **1991**, *10*, 2772−2777.

(39) Bachmann, W. E.; Ferguson, J. W. *J. Am. Chem. Soc.* **1934**, *56*, 2081−2084.

(40) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3863−3870.

(41) (a) Brown, H. C.; Kim, C. J.; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5244−5245. (b) Brown, H. C.; Kim, C. J. *J. Am. Chem. Soc.* **1971**, *93*, 5765−5773.

(42) (a) Schröer, U.; Neumann, W. P. *Angew. Chem. Int. Ed. Eng.* **1975**, *14*, 246−247. (b) Scherping, K.-H.; Neumann, W. P. *Organometallics* **1982**, *1*, 1017−1020. (c) Fobbe, H.; Neumann, W. P. *J. Organomet. Chem.* **1986**, *303*, 87−98.

(43) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; Section 20.4.

carbonylation reactions of transition metal acyl complexes, for which the rates are slowed by π-donating ancillary ligands).[44]

The nature of the bis(cyclopentadienyl) ligand set also appears to play a significant role in determining the stability of the stannyl complex. Decompositions of the dimethylamide compounds **2** and **8** demonstrate that, relative to the methylene-bridged [$Me_2C(C_5H_4)_2$] ligand, the mixed-ring CpCp* ligand set stabilizes a hafnium stannyl complex toward α-elimination by over 2 orders of magnitude. The difference between these two ligand systems may stem from both electronic and steric factors. First, the permethylated Cp* ligand is significantly more electron-donating than a cyclopentadienyl ring in [$Me_2C(C_5H_4)_2$], and the ansa structure of the latter ligand leads to less efficient donation to the metal center.[45] In addition, it is likely that the more bulky ligand system stabilizes the hafnium stannyl complexes by inhibiting the migration process. This steric effect appears to be operative in the much slower decomposition of CpCp*Hf($SnPh_3$)NMe_2 (**8**) compared to CpCp*Hf($SnPh_3$)OMe (**10**), since NMe_2 and OMe are expected to have similar π-donor abilities,[30] and in the drastically reduced decomposition rate for CpCp*Hf($SnPh_3$)Np (**14**) relative to CpCp*Hf($SnPh_3$)Me (**9**).

(44) (a) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389−398. (b) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360−6368.

(45) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.

Conclusions

The results reported here describe a previously little known reaction type for d^0 metal complexes. More research with early transition metal−main group compounds may well show that this elimination process represents a common transformation for such systems. Since α-elimination appears to be rather facile for d^0 group 4 stannyl compounds, this is likely an important process in the dehydropolymerization of secondary hydrostannanes to polystannanes by d^0 transition-metal catalysts.[32] Finally, this chemistry may have significant implications for the development of new catalytic reactions, and these issues will be addressed in future investigations.

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Supporting Information Available: Detailed ^{13}C NMR characterization and IR and melting point data for new compounds; synthesis for stannanes **15**, **16**, and **17**; crystal data (for **2**, **4**, **8**, **9**, **10**) and ORTEP diagrams (for **2**, **4**, **9**, **10**); and tables of kinetic data, rate constants for the disappearance of CpCp*Hf[Sn(p-$XC_6H_4)_3$]Cl, and rate constants for the disappearance of **2**, **4**, **8**, **9**, and **10** at different temperatures are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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