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Syntheses and Structures of Cationic and Neutral, Homo- and Heteroleptic *tert*-Butoxides of the Group 4 Metals

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The utility of tri-*tert*-butoxystannate as a chelating tridentate ligand for group 4 metals was investigated. The highly Lewis acidic metals degraded the stannate ion in a series of *tert*-butoxide abstraction steps to produce a variety of group 4 *tert*-butoxides. A total of 1 equiv of $NaSn(O^tBu)_3$ reacted with *cis*-$MCl_4(THF)_2$ [M = Zr (**1**), Hf (**2**)] in THF solutions to furnish the salts *fac*-$\{[M(O^tBu)_3(THF)_3](SnCl_3)\}$, which are separated ion pairs featuring weakly coordinating trichlorostannate ions. Neutral complexes, namely, $[M(O^tBu)_2Cl_2(THF)_2]$ [M = Zr (**3**), Hf (**4**)], were isolated when $^2/_3$ equiv of sodium stannate was used in these reactions. Titanium tetrachloride formed analogues neither of **1** and **2** nor of **3** and **4**, but $Ti(O^tBu)_3Cl$ reacted with silver triflate to give $[Ti(O^tBu)_2(OTf)_2(THF)_2]$ (**5**). Anion exchange of triflate for trichlorostannate transformed **1** to the contact ion pair *fac*-$[Zr(O^tBu)_3OTf(THF)_2]$ (**6**). A total of 2 equiv of $NaSn(O^tBu)_3$ reacted with *cis*-$MCl_4(THF)_2$ to give the complexes *fac*-$[Sn(\mu\text{-}O^tBu)_3M(O^tBu)_3]$ [M = Zr (**7**), Hf (**8**)]. Tri-*tert*-butoxystannate may be used as a selective alkoxylating agent for group 4 metals, and it can be transferred to these metals intact if their Lewis acidity is appropriately attenuated as in *fac*-$\{[M(O^tBu)_3(THF)_3](SnCl_3)\}$. Single-crystal X-ray studies revealed distorted octahedral coordination geometries for all compounds (**1**−**8**), with **1**, **2**, **7**, and **8** being crystallographically C_3 symmetric.

Introduction

Their ready availability, steric tunability, and hard-donor properties have made alkoxides some of the most versatile σ-bonding ligands in chemistry.[1] Alkoxides are outstanding ligands for early transition metals because the electron-rich oxygen atoms complement these chemically hard, electron-poor metals exceedingly well. Consequently, alkoxides have played a prominent role in the chemistry of the group 4−6 metals, particularly as ligands for multiply metal−metal-bonded species.[2] More recently, the utility of metal alkoxides as precursors for binary or ternary metal oxides has also stimulated commercial interest in these compounds.[3]

Despite their extensive synthetic and structural chemistry, early-transition-metal alkoxides were rarely used in stoichiometric or catalytic transformations prior to 1980. This absence was largely because of the propensity of alkoxide complexes to aggregate and undergo ligand-exchange reactions in solution,[4] which render controlled catalytic transformations with simple, early-transition-metal alkoxides difficult.

Among the first to exploit the catalytic properties of early-transition-metal alkoxides were Katsuki and Sharpless, who discovered that $Ti(O^iPr)_4$ catalyzed the asymmetric epoxidation of allylic alcohols by *tert*-butyl hydroperoxide.[5] Almost simultaneously, Schrock and co-workers reported their seminal research on alkyne metathesis reactions with $W(C^tBu)(O^tBu)_3$ and related catalysts.[6] Shortly thereafter, Wolczanski and co-workers[7−10] and Rothwell and co-workers[11−13] initiated systematic reactivity studies of group 4 and 5 metal

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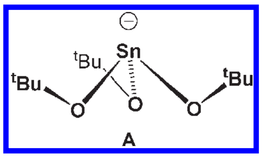
alkoxides with exceedingly bulky, monodentate alkoxides and aryloxides, respectively. The resulting sterically saturated, but electronically unsaturated, complexes provided insight into a fascinating array of catalytic transformations and, for the first time, revealed the full potential of early-transition-metal alkoxides in catalysis.[14]

Alternative routes to well-defined, early-transition-metal alkoxides relied on more elaborate chelating systems, based on phenolic residues, like catechols,[15] calixarenes,[16] mono- and bis(salicylaldimines),[17] and bis(phenols).[18] Although such multidentate ligands impart considerable stability to their complexes, the structural rigidity of these large scaffolds masks the innate electronic and coordination geometry preferences of the metals they chelate. Reactivity studies are thus rarely unambiguous, and in order to interpret the experimental findings, the ligands usually have to be structurally simplified anyway.

Notwithstanding the tremendous success of such ligands, we were interested in alkoxides with minimal steric bulk that retained the simplicity of classical ancillary ligands, like cyclopentadienide. We envisioned a synthetically easy, monoanionic, chelating alkoxide, similar to the spectacularly successful tris(pyrazolyl)borates,[19−23] and modifications thereof.[24] A review of the literature suggested that the potentially tridentate $[\mathrm{Sn(O^tBu)_3}]^-$, **A**, might be a suitable candidate.[25] Together with its germanium and lead analogues, this anion had demonstrated a remarkable ability to chelate main-group and transition-metal ions from across the periodic table.[26,27] Absent from the long list of derivatives of these anions were transition metals from groups 4 and 5.



A

This omission seemed all the more surprising because Caulton et al. had previously isolated *fac*-$[\mathrm{Sn}(\mu\text{-}\mathrm{O^tBu})_3\mathrm{Zr(O^tBu)_3}]$ by combining equimolar amounts of $\mathrm{Zr(O^tBu)_4}$ and $\mathrm{Sn(O^tBu)_2}$ in diethyl ether.[28] This heterometallic alkoxide can be considered formally derived from the $[\mathrm{Zr(^tBuO)_3}]^+$ cation and the $[\mathrm{Sn(O^tBu)_3}]^-$ anion, and this suggested that heterobimetallic group 4/14 *tert*-butoxides might be accessible via treatment of the group 4 tetrachlorides with the dimeric sodium salt of **A**, $[\mathrm{NaSn(O^tBu)_3}]_2$. Below we report on the interaction of sodium tri-*tert*-butoxystannate and other anions with various tetravalent group 4 species, with an emphasis on the solid-state structures of the products.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of argon, using standard Schlenk techniques. Solvents were dried and freed of molecular oxygen by distillation under an atmosphere of nitrogen from sodium or potassium benzophenone ketyl immediately before use. NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained at frequencies of 500.1 and 125.8 MHz, respectively, and are referenced relative to $\mathrm{C_6D_5}H$ (7.16 ppm), C_6D_6 (128.39 ppm), or $\mathrm{O(CD}H\mathrm{CD_2)_2}$ (3.58 ppm) and $\mathrm{O(CD_2CD}H\mathrm{)_2}$ (1.73 ppm), $\mathrm{O(}C\mathrm{D_2CD_2)_2}$ (67.57 ppm), or $\mathrm{O(CD_2}C\mathrm{D_2)_2}$ (25.37 ppm), respectively. The uncorrected melting points were obtained on a Mel-Temp apparatus. Midwest Microanalytical Services, Indianapolis, IN, performed elemental analyses. The reagents $\mathrm{ZrCl_4}$, $\mathrm{HfCl_4}$, $\mathrm{SnCl_2}$, $\mathrm{Ti(O^tBu)_4}$, and AgOTf were purchased from Aldrich or Alfa Aesar, while *cis*-$\mathrm{MCl_4(THF)_2}$[29] (M = Ti, Zr, Hf; THF = tetrahydrofuran), $[\mathrm{NaSn(O^tBu)_3}]_2$,[25] and $\mathrm{Ti(O^tBu)_3Cl}$[30] were prepared according to published procedures.

Syntheses. ***fac*-$\{[\mathrm{Zr(O^tBu)_3(THF)_3}](\mathrm{SnCl_3})\}$ (1).** To a cooled (−78 °C) solution of *cis*-$\mathrm{ZrCl_4(THF)_2}$ (2.00 g, 5.30 mmol) in THF (20 mL) was added dropwise $[\mathrm{NaSn(O^tBu)_3}]_2$ (1.91 g, 2.65 mmol) in THF (25 mL). The reaction mixture was stirred overnight and concentrated to 10 mL. It was then stored at −10 °C for several days, upon which time colorless hexagonal crystals, suitable for X-ray diffraction studies, were obtained. Yield: 3.70 g, 93%. Mp: 69−72 °C. ^{1}H NMR (THF-d_8, 25 °C): δ 3.62 (t, 12H, $\mathrm{OC}H_2\mathrm{CH_2}$), 1.77 (t, 12H, $\mathrm{OCH_2C}H_2$), 1.27 (s, 27H, $\mathrm{C(C}H_3)_3$), ^{13}C NMR (THF-d_8, 25 °C): δ 75.4 (s, $\mathrm{O}C\mathrm{(CH_3)_3}$), 68.3 (s, $\mathrm{O}C\mathrm{H_2}$), 33.0 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 26.4 (s, $\mathrm{OCH_2}C\mathrm{H_2}$). Anal. Calcd for $\mathrm{C_{24}H_{51}Cl_3O_6SnZr}$: C, 38.33; H, 6.84. Found: C, 37.98; H, 6.74.

***fac*-$\{[\mathrm{Hf(O^tBu)_3(THF)_3}](\mathrm{SnCl_3})\}$ (2).** Compound **2** was prepared analogously to **1** by treating *cis*-$\mathrm{HfCl_4(THF)_2}$ (1.58 g, 3.40 mmol) with $^1/_2$ equiv of $[\mathrm{NaSn(O^tBu)_3}]_2$ (1.23 g, 1.70 mmol) in THF at −78 °C. Colorless hexagonal crystals were grown from THF. Yield: 2.50 g, 87%. Mp: 58−60 °C. ^{1}H NMR (THF-d_8, 25 °C): δ 3.62 (t, 12H, $\mathrm{OC}H_2$), 1.77 (t, 12H, $\mathrm{OCH_2C}H_2$), 1.27 (s, 27H, $\mathrm{C(C}H_3)_3$). ^{13}C NMR (THF-d_8, 25 °C): δ 75.2 (s, $\mathrm{O}C\mathrm{(CH_3)_3}$), 68.4 (s, $\mathrm{O}C\mathrm{H_2CH_2}$), 33.4 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 26.5 (s, $\mathrm{OCH_2}C\mathrm{H_2}$). Anal. Calcd for $\mathrm{C_{24}H_{51}Cl_3HfO_6Sn}$: C, 34.35; H, 6.13. Found: C, 34.28; H, 5.92.

$[\mathrm{ZrCl_2(O^tBu)_2(THF)_2}]$ (3). To a cold (−78 °C) solution of *cis*-$\mathrm{ZrCl_4(THF)_2}$ (0.500 g, 1.33 mmol) in THF (20 mL) was added dropwise a solution of $[\mathrm{NaSn(O^tBu)_3}]_2$ (0.32 g, 0.44 mmol) in THF (20 mL). The mixture was stirred at room temperature for 16 h and concentrated to 10 mL. It was then stored at −10 °C for several days, upon which time colorless, hexagonal crystals, suitable for X-ray diffraction studies, were obtained. Yield: 0.46 g, 77%. Mp: 120 °C. ^{1}H NMR (THF-d_8, 25 °C): δ 3.62 (t, 8H, $\mathrm{OC}H_2\mathrm{CH_2}$), 1.77 (t, 8H, $\mathrm{OCH_2C}H_2$), 1.31 (s, 18H, $\mathrm{(OC(C}H_3)_3)$). ^{13}C NMR (THF-d_8, 25 °C): δ 78.9 (s, $\mathrm{O}C\mathrm{(CH_3)_3}$), 68.4

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(s, OCH$_2$CH$_2$), 32.3 (s, OC(CH$_3$)$_3$), 26.6 (s, OCH$_2$$CH_2$). Anal. Calcd for $C_{16}H_{34}Cl_2O_4Zr$: C, 42.46; H, 7.57. Found: C, 41.96; H, 7.26.

[HfCl$_2$(O^{t}Bu)$_2$(THF)$_2$] (4). In a manner identical with that used for the synthesis of **3**, *cis*-HfCl$_4$(THF)$_2$ (0.643 g, 2.00 mmol) was combined with [NaSn(O^{t}Bu)$_3$]$_2$ (0.722 g, 1.00 mmol) to afford colorless, hexagonal crystals. Yield: 0.981 g, 91%. Mp: 132−135 °C. ^{1}H NMR (THF-d_8, 25 °C): δ 3.62 (t, 8H, OCH_2CH$_2$), 1.77 (t, 8H, OCH$_2$CH_2), 1.30 (s, 18H). ^{13}C NMR (THF-d_8, 25 °C): δ 77.8 (s, OC(CH$_3$)$_3$), 68.4 (s, OCH$_2$CH$_2$), 32.6 (s, OC(CH$_3$)$_3$), 26.6 (s, OCH$_2$$CH_2$). Anal. Calcd for $C_{16}H_{34}Cl_2O_4Hf$: C, 35.60; H, 6.35. Found: C, 35.52; H, 5.98.

[Ti(O^{t}Bu)$_2$(OTf)$_2$(THF)$_2$] (5). To a solution of AgOTf (0.85 g, 3.3 mmol) in THF (10 mL) was added all at once a THF (20 mL) solution of Ti(O^{t}Bu)$_3$Cl (1.00 g, 3.30 mmol). The milky-white reaction mixture was stirred for 30 min before silver chloride was filtered off. The clear filtrate was then concentrated and stored at −4 °C to afford, after 3 days, colorless, hexagonal crystals. Yield: 1.5 g, 71%. Mp: 82−84 °C ^{1}H NMR (THF-d_8, 25 °C): δ 3.62 (t, 8H, OCH_2), 1.77 (t, 8H, OCH$_2$CH_2), 1.52 (s, 18H, OC(CH_3)$_3$). ^{13}C NMR (THF-d_8, 25 °C): δ 120.8 (q, J_{C-F} = 319 Hz, CF$_3$), 96.1 (s, OC(CH$_3$)$_3$), 68.3 (s, OCH$_2$CH$_2$), 31.4 (s, OC(CH$_3$)$_3$), 26.4 (s, OCH$_2$$CH_2$). Anal. Calcd for $C_{18}H_{34}F_6O_{10}S_2Ti$: C, 33.97; H, 5.38. Found: C, 34.45; H, 5.62.

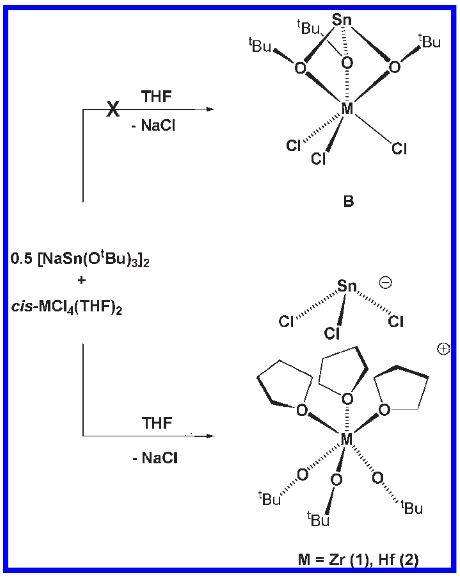
***fac*-[Zr(O^{t}Bu)$_3$(OTf)(THF)$_2$] (6).** A THF (20 mL) solution of silver triflate (0.47 g, 1.8 mmol) was treated dropwise with a THF solution (20 mL) of *fac*-{[Zr(O^{t}Bu)$_3$(THF)$_3$](SnCl$_3$)} (1.36 g, 1.82 mmol). The reaction mixture was then stirred for 15 min, freed from precipitated AgSnCl$_3$ by filtration, and concentrated in vacuo to 10 mL. After the clear solution had been stored at −4 °C for 3 days, colorless crystals formed. Yield: 0.92 g, 84%. Mp: 114 °C. ^{1}H NMR (THF-d_8, 25 °C): δ 3.62 (m, 8H, OCH_2), 1.77 (m, 8H, OCH$_2$CH_2), 1.30 (s, 18H, OC(CH_3)$_3$). ^{13}C NMR (THF-d_8, 25 °C): δ 121.1 (q, J_{C-F} = 318 Hz, CF$_3$), 76.8 (s, OC(CH$_3$)$_3$), 68.5 (s, OCH$_2$CH$_2$), 33.2 (s, C(CH$_3$)$_3$), 26.6 (s, OCH$_2$$CH_2$). Anal. Calcd for $C_{21}H_{43}F_3O_8SZr$: C, 41.77; H, 7.18. Found: C, 41.49; H, 6.77.

***fac*-[Sn(μ-O^{t}Bu)$_3$Zr(O^{t}Bu)$_3$] (7).** A sample of [NaSn(O^{t}Bu)$_3$]$_2$ (0.36 g, 0.50 mmol) was dissolved in 20 mL of THF and added dropwise to a precooled (−78 °C) solution of *cis*-ZrCl$_4$(THF)$_2$ (0.19 g, 0.50 mmol) in THF (20 mL). The reaction mixture was allowed to slowly warm to room temperature and then stirred overnight. The solvent was removed in vacuo, and the solid residue was extracted into hexanes. Colorless, rectangular crystals, suitable for X-ray diffraction, were obtained after the solution had been stored for several days at −10 °C. Yield: 0.28 g, 88%. Mp: sublimes (220 °C, 1 atm). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 1.53 (s, 27H, μ-OC(CH_3)$_3$), 1.47 (s, 27H, OC(CH_3)$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 76.0 (s, μ-OC(CH$_3$)$_3$), 73.9 (s, OC(CH$_3$)$_3$), 34.9 (s, μ-OC(CH$_3$)$_3$, J_{Sn-C} = 28.1 Hz), 34.0 (s, OC(CH$_3$)$_3$). Anal. Calcd for $C_{24}H_{54}O_6SnZr$: C, 44.44; H, 8.39. Found: C, 44.10; H, 8.20.

***fac*-[Sn(μ-O^{t}Bu)$_3$Hf(O^{t}Bu)$_3$] (8).** Compound **8** was prepared in a manner identical with that used for the synthesis of **7**, by treating *cis*-HfCl$_4$(THF)$_2$ (0.50 g, 1.1 mmol) with [NaSn(O^{t}Bu)$_3$]$_2$ (1.55 g, 2.15 mmol). Colorless, rectangular crystals were obtained from a cooled (−10 °C) hexane solution after a period of 1−2 weeks. Yield: 1.37 g, 87%. Mp: sublimes (226 °C, 1 atm). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 1.56 (s, 27H, μ-OC(CH_3)$_3$), 1.47 (s, 27H, C(CH_3)$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 75.9 (s, μ-OC(CH$_3$)$_3$), 74.2 (s, OC(CH$_3$)$_3$), 34.5 (s, μ-OC(CH$_3$)$_3$, J_{Sn-C} = 27.8 Hz), 34.3 (s, OC(CH$_3$)$_3$). Anal. Calcd for $C_{24}H_{54}HfO_6Sn$: C, 39.17; H, 7.40. Found: C, 38.71; H, 7.23.

X-ray Crystallography. Suitable single crystals were coated with Paratone N oil, affixed to Mitegen or Litholoop crystal holders, and centered on the diffractometer in a stream of cold nitrogen. Reflection intensities were collected with a Bruker Apex diffractometer, equipped with an Oxford Cryosystems 700 Series Cryostream cooler, operating at 173 K. Data were measured with ω scans of 0.3° per frame for 20 s until a complete hemisphere of data had been collected. Cell parameters were retrieved using *SMART*[31] software and reduced with *SAINTplus*,[32] which corrects for Lorentz and polarization effects and crystal decay. Empirical absorption corrections were applied with *SADABS*.[33] The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with *SHELXL-97*[34] incorporated in *SHELXTL*, version 6.14.[35]

Scheme 1



Results

Transition-metal alkoxides are most commonly synthesized by the alcoholysis of reactive metal halides and metal amides or by the interaction of metal halides with the appropriate alkali-metal alkoxides.[1] The latter method is suitable only for certain transition metals because undesirable double salts of alkali metals may be formed. Heterometallic alkoxides can also be obtained by mixing the appropriate homometallic alkoxides, although here the driving force for the reaction and the selectivity for a particular product are substantially reduced. By treating group 4 metal chlorides with sodium tri-*tert*-butoxystannate in THF (Scheme 1), we had hoped to synthesize the heteronuclear trichlorotri-*tert*-butoxystannates of the general formula Sn(μ-O^{t}Bu)$_3$MCl$_3$ (**B**; M = Zr, Hf) in metathesis reactions.

Salt elimination reactions were indeed observed, but the very clean ^{1}H NMR spectra of aliquots taken from the reaction mixtures revealed, in addition to one sharp singlet for the *tert*-butoxy groups, two sets of signals for free and coordinated THF. On the basis of integrations of the signals, it was apparent that the *tert*-butoxy and THF ligands were present in a 1:1 ratio. The crystalline, colorless products were very soluble in THF but insoluble in hydrocarbons, suggestive of an ionic nature. NMR spectra obtained on well-developed crystals of **1** and **2** were identical with those obtained on the reaction mixtures. Suitable single crystals

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[31] *SMART*; Siemens Analytical X-ray Systems: Madison, WI, **1995**.
[32] *SAINTplus*, version 6.45; Bruker AXS: Madison, WI, **2003**.
[33] *SADABS* program for absorption corrections using the Bruker CCD Detector System. Based on: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
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[35] *SHELXTL*, version 6.14; Bruker AXS, Inc.: Madison, WI, **2006**.

Table 1. Crystallographic Data for **1**−**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
chemical formula	$C_{24}H_{51}Cl_3O_6$-$SnZr$	$C_{24}H_{51}Cl_3O_6$-$HfSn$	$C_{16}H_{34}Cl_2O_4Zr$	$C_{16}H_{34}Cl_2$-HfO_4	$C_{18}H_{34}F_6O_{10}$-S_2Ti	$C_{21}H_{43}F_3O_8$-SZr	$C_{24}H_{54}O_6$-$SnZr$	$C_{24}H_{54}$-HfO_6Sn
fw	751.91	839.18	452.55	539.82	636.47	603.83	648.58	735.85
space group	$R3$ (No. 146)	$R3$ (No. 146)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{3}c1$ (No. 163)	$P2_12_12_1$ (No. 19)	$P3m1$ (No. 156)	$P3m1$ (No. 156)
T, °C	−100	−100	−100	−100	−100	−100	−100	−100
a, Å	14.7142(9)	14.6870(16)	12.2718(14)	12.2463(13)	16.6042(8)	9.2782(9)	17.1304(12)	14.6870(16)
b, Å	14.7142(9)	14.6870(16)	10.6016(12)	10.5873(11)	16.6042(8)	17.4312(17)	17.1304(12)	14.6870(16)
c, Å	13.8699(16)	13.854(3)	17.252(2)	17.2373(18)	17.7297(17)	18.1017(18)	9.4890(14)	13.854(3)
α, deg	90	90	90	90	90	90	90	90
β, deg	90	90	91.977(2)	92.164(2)	90	90	90	90
γ, deg	120	120	90	90	120	90	120	120
V, Å^3	2600.6(4)	2588.0(7)	2243.2(4)	2233.3(4)	4233.2(5)	2927.6(5)	2411.5(4)	2397.3(3)
Z	3	3	4	4	6	4	3	3
ρ_{calcd}, g cm^{-3}	1.440	1.615	1.340	1.606	1.498	1.370	1.340	1.529
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ, mm^{-1}	1.282	3.993	0.742	4.924	0.537	0.503	1.130	4.056
data collected	5383	5783	18687	9940	19737	25064	20647	15175
unique data (R_{int})	2368 (0.0278)	2448 (0.0664)	5180 (0.0211)	3249 (0.0392)	2340 (0.0231)	6792 (0.0170)	4162 (0.0182)	3061 (0.0372)
$R(F)^a$ $[I > 2\sigma(I)]$	0.0227	0.0333	0.0336	0.0291	0.0510	0.0306	0.0519	0.0694
$R_w(F^2)^b$ (all data)	0.0589	0.0815	0.0975	0.0737	0.1484	0.0867	0.1400	0.1902

^{a} $R = \sum|F_o - F_c|/\sum|F_o|$. ^{b} $R_w = \{[\sum w(F_o^2 - F_c)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$.

were subjected to X-ray studies, which showed both compounds to be separated ion pairs, consisting of *fac*-[M-$(O^tBu)_3(THF)_3]^+$ (M = Zr, Hf) cations and $(SnCl_3)^-$ anions. Detailed crystal data and refinement parameters for **1** and **2** are listed in Table 1.

The trigonal unit cells of the isomorphous **1** and **2** each contain six ion pairs that are located on the 3-fold axes of space group $R3$. The perspective view of **1** in Figure 1 emphasizes the distorted octahedral geometry of the cation, with one trigonal face being composed of three *tert*-butoxide ligands, while the opposite face is occupied by three molecules of THF, which are thus trans to the former. This arrangement can be rationalized in terms of the strongly π-donating alkoxide ligands preferring the weakly π-donating THF molecules trans to themselves. The three THF ligands adopt a propeller-like, and thus chiral, conformation. It should be noted that the crystals are both chiral, because of the homochirality of the cationic complexes, and polar, because of the global orientation of the ions, which face the same direction along the 3-fold axis.

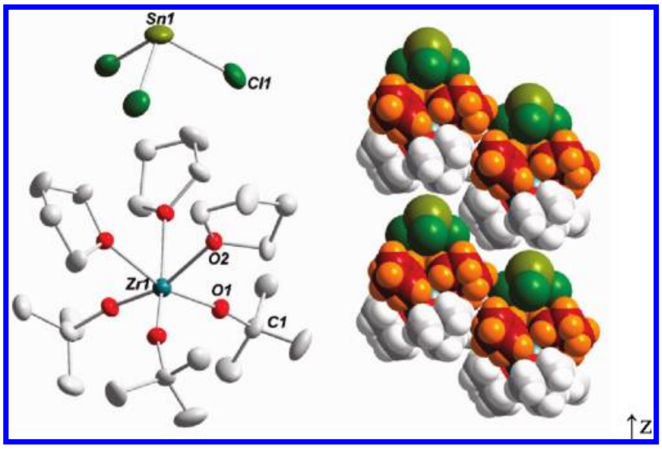

Figure 1. (left) Solid-state structure and partial labeling scheme of **1**. With the exception of carbon (35%), all atoms are drawn at the 50% probability level. Selected bond parameters: Sn1−Cl1 = 2.4651(11) Å, Zr1−O1 = 1.9232(16) Å, Zr1−O2 = 2.3296(16) Å; Cl1−Sn1−Cl1′ = 93.94(3)°, O1−Zr−O1′ = 102.33(7)°, O1−Zr1−O2 = 89.06(7)°, O2−Zr−O2″ = 79.07(6)°, Zr−O1−C1 = 164.00(16)°. (right) Portion of the crystal packing of **1** (THF ligands are drawn in red (carbon atoms) and orange (hydrogen atoms) to emphasize the interionic contacts with the chlorine atoms).

The zirconium−alkoxide bonds appear short [1.9232(16) Å] relative to the sum of the covalent radii,[36] but they are similar in length to those of related zirconium *tert*-butoxides. For example, in tetrahedral $Zr(O^tBu)_3Si(SiMe_3)_3$, the $Zr-O^tBu$ bonds are 1.889(7) Å long,[37] on average, with the slightly shorter distances likely being due to the lower coordination number in the tris(trimethylsilyl)silyl derivative. As in related alkoxides, the extensive double-bond character in this interaction is reflected by the short $Zr-O^tBu$ bond and the large bond angle [164.00(15)°] at oxygen. The O−Zr−O angles enclosed by these bonds are much larger [102.35(6)°] than those in ideal octahedral geometry, resulting in a rather flat $Zr(O^tBu)_3$ pyramid. The Zr−THF bonds [2.3272 (15) Å] are substantially longer than that in the tetraphenylborate salt $\{[Cp_2Zr(O^tBu)(THF)](BPh_4)\}$ [2.200(4) Å],[38] and they make angles of only 79.02(6)° with each other, thereby forming a much steeper $Zr(THF)_3$ pyramid than the one created by the alkoxides.

The closest distance between the rigorously C_3-symmetric *fac*-$[Zr(O^tBu)_3(THF)_3]^+$ cations and $(SnCl_3)^-$ anions, whose structures are shown in Figure 1, measures 2.80 Å and is observed between the chlorine atoms of the anions and the α-methylene protons of the THF ligands. These contacts, which compare fairly well with similar intermolecular or interionic contacts between the THF ligands and the metal-bound chlorine atoms,[39] can be attributed to interionic coulomb forces.

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[36] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[37] Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1989**, *28*, 1768–1769.

[38] Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092–2094.

[39] (a) A search in the Cambridge Structural Database revealed that there are 175 structures that contain intermolecular THF···Cl contacts that are shorter than the sum of the van der Waals radii (2.95 Å; search criteria included no disorder, no errors, R < 5%, etc.). For a general text on CH···anion bonds, see also: (b) Desiraju, R. D.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: New York, 1999.

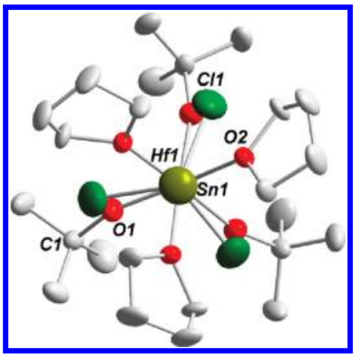


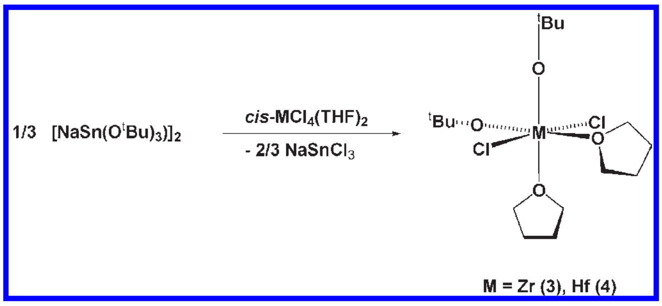
Figure 2. Solid-state structure and partial labeling scheme of **2**. With the exception of carbon (35%), all atoms are drawn as 50% probability ellipsoids. Selected bond parameters: Sn1−Cl1 = 2.4651(11) Å, Hf1−O1 = 1.920(4) Å, Hf1−O2 = 2.301(4) Å; Cl1−Sn1−Cl1′ = 93.88(7)°, O1−Hf−O1′ = 101.96(18)°, O1−Hf1−O2 = 163.49(15)°, O2−Hf−O2′ = 79.16(16)°, Hf−O1−C1 = 163.7(4)°.

Showing only weak CH···Cl interactions with the cation, trichlorostannate is truly a weakly coordinating anion in this salt.[40−42] It is located on the 3-fold axis of the space group and thus has crystallographic symmetry C_3 with bond lengths and angles of 2.4656(16) Å and 93.91(3)°, respectively. The Sn−Cl bond lengths are identical with that in $[(Pz^*_3Sn_2)(SnCl_3)]$, where Pz* = 2,3-dimethylpyrazole [2.467(2) Å],[43] but they are somewhat shorter than those in $[(H_3N^tBu)(SnCl_3)]$ [2.542(3) Å][44] and $[Sn(15\text{-crown-}5)_2(SnCl_3)_2]$ [2.499(2) Å],[45] both of which contain weakly coordinating trichlorostannate ions. The ion pairs are stacked along the crystallographic *z* axis in an overall polar arrangement (Figure 1, right). In contrast to the chlorine atoms, the tin atoms are not involved in short-range interionic interactions. The shortest such contacts are between the tin atom of one unit and the protons of the *tert*-butoxy ligands (3.80 Å) above it, but they are still about 0.4 Å larger than the sum of the van der Waals radii of hydrogen and tin.

Figure 2 shows the hafnium salt **2** in a view along the C_3 axis that emphasizes the interpenetration of cation and anion. To minimize steric repulsion, the propeller-like arrangement of the THF ligands interlocks with the three chlorides of the trichlorostannate moiety. As is usually the case for isomorphous zirconium and hafnium compounds, the metal-to-ligand bonds in **2** are slightly, but consistently, shorter than those in **1**, and this is reflected in the Hf−O^{t}Bu and Hf−THF bonds, which are 1.920(4) and 2.301(4) Å long, respectively. All bond parameters of the trichlorostannate ion are, within experimental uncertainties, identical with those in **1**. The interionic distances of **2** closely resemble those of **1**.

When *cis*-$MCl_4(THF)_2$ (M = Zr, Hf) were treated with less than $^1/_2$ equiv of $[NaSn(OtBu)_3]_2$ in a THF solvent, ^{1}H NMR spectra obtained on aliquot portions of the reaction mixtures revealed one additional product that also contained only *tert*-butoxy and THF ligands. These compounds, **3** and **4**, were subsequently synthesized as the sole products of the reactions with the stoichiometries shown in Scheme 2. The NMR spectra obtained on isolated crystals were identical with those obtained in situ and consisted of peak patterns similar to those of **1** and **2**, showing two sets of signals for bulk and coordinated THF, respectively, and one sharp singlet for the *tert*-butoxy groups.

Scheme 2



Single-crystal X-ray analyses on **3** and **4**, whose crystal data and refinement parameters are listed in Table 1, revealed that in contrast to **1** and **2** these were molecular compounds of distorted octahedral geometry. Figure 3 shows a thermal-ellipsoid plot of **4** with its three sets of paired ligands. The relative orientation of the ligands to each other reflects their π-donor strengths, namely, *tert*-butoxide > chloride > THF. Thus, the strongest π donors—the alkoxides—are trans to the weakest π donors (THF), while the chloride ligands are mutually trans.

It is worth noting that all chemically equivalent bonds in **4** are equidistant within experimental uncertainties. The hafnium−*tert*-butoxide bonds [1.894(4) and 1.904(4) Å] and the hafnium−THF bonds [2.285(4) and 2.293(4) Å] are shorter than those in **2**, but the hafnium−chloride bonds [2.4699(11) and 2.4704(12) Å] are substantially longer than those in the much less sterically encumbered *cis*-$HfCl_4(THF)_2$, whose average length is only 2.383(7) Å.[46]

The overall structure of **4** is closer to octahedral than that of **2**, but even here large deviations from the octahedral geometry are evident. For example, the angles enclosed by the *tert*-butoxide and THF ligands are 104.23(17)° and 76.65(14)°, respectively, with the difference reflecting the bulk of the alkoxides. This steric crowding is also demonstrated by the *tert*-butyl substituents being staggered with respect to each other and the marked deviation of the trans-configured chlorides [163.55(4)°] from linearity. The THF molecules are bisecting two of the opposing quadrants to minimize nonbonding contacts with the remaining ligands.

In Figure 4, the zirconium derivative **3** is depicted in a perspective approximately along the Cl−Zr−Cl vector to emphasize the large bond-length difference between the Zr−O bonds of the *tert*-butoxide and THF ligands, as well as the difference in the angles they enclose. The X-ray structure determination, which yielded somewhat more precise data than those of the hafnium complex, confirms that, as for **1** and **2**, the bonds between the metal and ligands are slightly longer in the zirconium complex. For comparison, in the sterically less encumbered $\{[ZrCl_3(THF)_2]_2C_6H_{10}O_2\}$,[47] in which a 1, 2-cyclohexanedioate bridges two meridionally coordinated zirconium centers, the Zr−Cl bonds have an average length of 2.433(2) Å, while the Zr−alkoxide and

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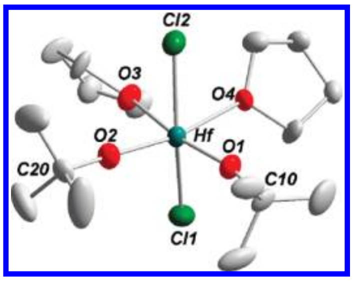


Figure 3. Solid-state structure and partial labeling scheme of **4**. With the exception of carbon (35%), all atoms are drawn as 50% probability ellipsoids. Selected bond parameters: Hf1−Cl1 = 2.4704(12) Å, Hf1−Cl2 = 2.4699(11) Å, Hf1−O1 = 1.904(4) Å, Hf1−O2 = 1.894(4) Å, Hf1−O3 = 2.293(4) Å. Hf1−O4 = 2.285(4) Å; Cl1−Hf1−Cl2 = 163.55(4)°, O1−Hf−O2 = 104.23(17)°, O3−Hf1−O4 = 76.65(14)°, O1−Hf−Cl1 = 92.976(12)°, Hf−O1−C10 = 166.6(4)°, Hf−O2−C20 = 170.2(4)°.

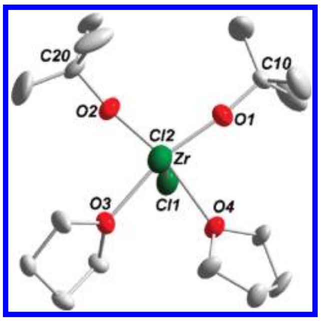
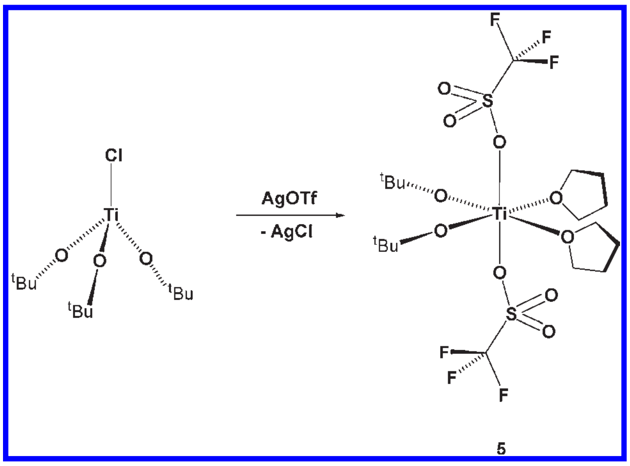


Figure 4. Solid-state structure and partial labeling scheme of **3**. With the exception of carbon (35%), all atoms are drawn as 50% probability ellipsoids. Selected bond parameters: Zr−Cl1 = 2.4936(6) Å, Zr−Cl2 = 2.4969(6) Å, Zr−O1 = 1.8960(16) Å, Zr−O2 = 1.9044(14) Å, Zr−O3 = 2.3184(15) Å. Zr−O4 = 2.3125(15) Å; Cl1−Zr−Cl2 = 163.15(2)°, O1−Zr−O4 = 89.60(6)°, O1−Zr−O3 = 166.16(6)°, O1−Zr−Cl1 = 92.88(5)°, Zr−O1−C10 = 171.34(16)°, Zr−O2−C20 = 167.51(17)°.

Scheme 3



5

Zr−THF bonds are 1.868(4) and 2.259(5) Å long, respectively.

Under the conditions described in Schemes 1 and 2, the interaction between *cis*- $TiCl_4(THF)_2$ and $[NaSn(O^tBu)_3]_2$ yielded analogues neither of **1** and **2** nor of **3** and **4**. Instead, various metal *tert*-butoxides and metal chlorides/*tert*-butoxides were formed—as evidenced by NMR spectroscopic studies—of which only *trans*-$[Sn(O^tBu)Cl]_2$ was isolated in a pure form. Attempts to generate a titanium analogue of **1** and **2** by abstracting the chloride ion from $Ti(O^tBu)_3Cl$ with $SnCl_2$ also failed to give a clean product. Treatment of $Ti(O^tBu)_3Cl$ with silver triflate (Scheme 3), however, did produce the colorless, crystalline **5** in high yields. On the basis of NMR data, we initially believed this THF-soluble, but hydrocarbon-insoluble, titanium compound to be a monotriflate analogue of **1** and **2**. A single-crystal X-ray analysis, however, showed it to be the ditriflate derivative depicted in Figure 5, whose crystal data and refinement parameters are listed in Table 1.

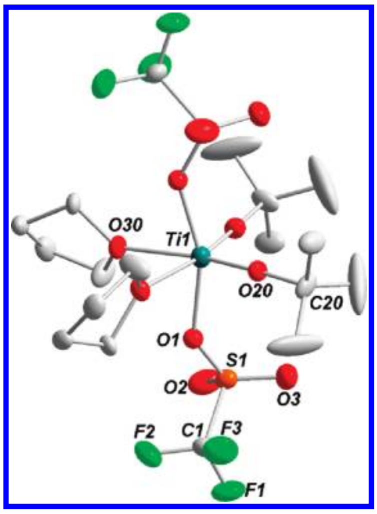


Figure 5. Solid-state structure and partial labeling scheme of **5**. With the exception of titanium (50%), all atoms are drawn as 35% probability ellipsoids. Selected bond parameters: Ti1−O1 = 2.0325(17) Å, Ti1−O20 = 1.7421(17) Å, Ti1−O30 = 2.1905(17) Å, S1−O1 = 1.4832(18) Å, S1−O2 = 1.426(2) Å, S1−O3 = 1.421(2) Å; O1−Ti1−O1′ = 159.28(10)°, O1−Ti1−O20 = 96.63(8)°, O20−Ti1−O20′ = 103.08(12)°, O20−Ti1−O30 = 166.99(7)°, O30−Ti1−O30′ = 77.07(9)°, Ti1−O20−C20 = 174.37(17)°.

Crystals of **5** are trigonal, space group $P\overline{3}c1$, isolated molecules residing on 2-fold axes, which render them rigorously C_2 symmetric. As can be seen in the ellipsoid plot, the complex has a structure analogous to those of **3** and **4** but with triflate ions in place of the chloride ions. Even the relative orientation of the six ligands to each other parallels that in the heavier congeners, in that the two *tert*-butoxide groups are trans to the weakly π-donating THF molecules, while the two triflate ligands are trans to each other.

The titanium−*tert*-butoxide bonds [1.7421(11) Å] are slightly shorter than that in $Cp^*TiO^tBuCl_2$ [1.760(3) Å][49] and comparable in length to the terminal Ti−O bonds in dimeric, six-coordinate $[TiCl_2(OCH_2CH_2Cl)_2 \cdot HOCH_2CH_2Cl]_2$[48] [1.746(5) Å] and in trinuclear $Ti_3(O^iPr)_9$ [1.753(9) Å].[50] On the basis of a survey of monodentate Ti−OTf bonds, which range from 1.957 to 2.098 Å,[51] the titanium−triflate bonds [2.0325(17) Å] have average lengths, as do the titanium−THF bonds, which are 2.1905(17) Å long, on average.

A simple metathesis reaction between $Ti(O^tBu)_3Cl$ and silver triflate can obviously be ruled out as a source of the ditriflate. It is possible that an initially generated $Ti(O^tBu)_3(OTf)$

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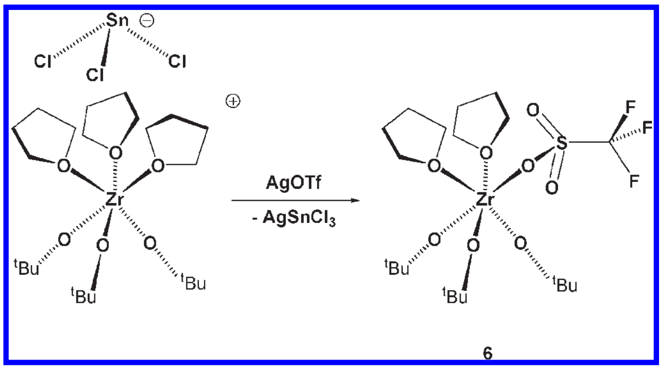
(50) Veith, M.; Mathur, S.; Huch, V. *Chem. Commun.* **1997**, 2197–2198.

(51) CCDC search of 51 titanium−triflate complexes with monodentate triflate ligands. Accessed June 30, 2009.

Scheme 4



6

disproportionated into **5** and Ti(O^{t}Bu)$_4$ because redistributions like these are common among group 4 alkoxide/chloride compounds.[47] For the more weakly coordinating triflate ions, such disproportionations are likely even more facile.

Our hope that the salts **1** and **2** would be good source materials for derivatives of the M(O^{t}Bu)$_3$ moiety (M = Zr, Hf) was thwarted. Thus, the attempted synthesis of the half-sandwich compound CpZr(O^{t}Bu)$_3$, by the treatment of **1** with NaCp, yielded, among other products, CpSnCl,[52,53] while all efforts to substitute the THF ligands with the cyclic polyether 15-crown-5 led to the isolation of the known sandwich {[(15-crown-5)$_2$Sn](SnCl$_3$)$_2$}.[45a,44b] Clearly, trichlorostannate is not an innocent counterion in this salt, but with some nucleophiles, it reacts even more readily than the cationic zirconium moiety.

To avoid such counterion interference, we treated **1** with silver triflate in THF in a straightforward metathesis reaction (Scheme 4) and obtained the hydrocarbon-insoluble **6**. The ^{1}H NMR spectra obtained on aliquot portions of the reaction mixture and on isolated crystals were virtually identical, showing only one sharp singlet for the *tert*-butoxy groups and, in contrast to **1**, broader signals for the THF ligands and bulk solvent. The ^{13}C NMR spectra were consistent with the ^{1}H NMR spectra and notably revealed only one sharp quartet for the $CF_3SO_3^-$ ion at 121.1 ppm. To ascertain whether a fast triflate exchange was operational, we added excess AgOTf to an NMR sample of **6**, but the results were inconclusive.

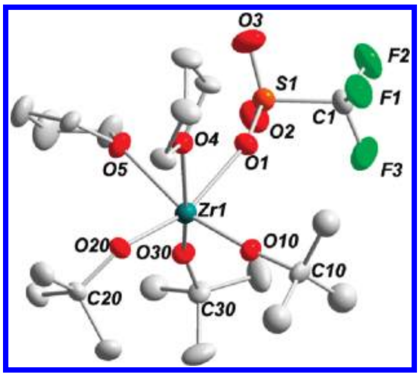
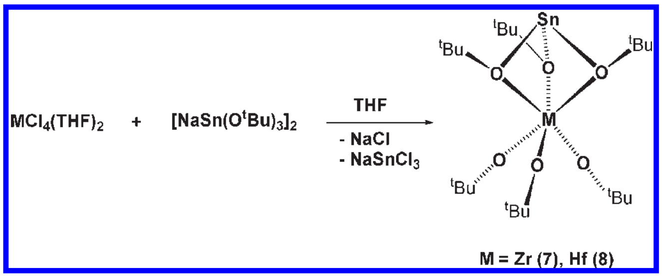


Figure 6. Solid-state structure and partial labeling scheme of **6**. With the exception of zirconium (50%), all atoms are drawn as 35% probability ellipsoids. Selected bond parameters: Zr1−O1 = 2.2371(17) Å, Zr1−O4 = 2.3241(16) Å, Zr1−O5 = 2.3180(16) Å, Zr1−O10 = 1.9150(17) Å, Zr1−O20 = 1.9326(16) Å, Zr1−O30 = 1.9170(16) Å, S1−O1 = 1.4671(18) Å, S1−O2 = 1.420(2) Å, S1−O3 = 1.425(2) Å; O1−Zr1−O4 = 78.96(6)°, O1−Zr1−O5 = 78.34(7)°, O4−Zr1−O5 = 77.55(7)°, O10−Zr1−O20 = 101.27(7)°, O10−Zr1−O30 = 102.29(8)°, O20−Zr1−O30 = 101.53(7)°, Zr1−O10−C10 = 175.05(18)°, Zr1−O20−C20 = 155.34(14)°, Zr1−O30−C30 = 159.97(17)°.

Scheme 5



M = Zr (**7**), Hf (**8**)

A single-crystal X-ray analysis on **6** showed that it was the targeted zirconium monotriflate analogue of **1**, but like the titanium ditriflate **5** and unlike **1**, it exists as a contact ion pair in the solid state. Crystal and refinement data of **6** are listed in Table 1, while Figure 6 shows the solid-state structure of this complex. Despite the dissimilar overall structures of **1** and **6**, the bond parameters about zirconium are almost identical in both compounds, and the Zr(O^{t}Bu)$_3$ moieties are, in fact, close to being isometric. Thus, the zirconium−*tert*-butoxide bonds [1.922(3) Å], which are equidistant with those in **1** [1.926(3) Å], enclose an only marginally smaller angle [101.70(7)°] than that in **1** [102.35(6)°]. There is, however, a slight asymmetry in the Zr−O^{t}Bu bonds, with those opposite the THF ligands being shorter [1.9160(16) Å] than the one trans to triflate, which is 1.9326(16) Å long. The zirconium−triflate bond length [2.2371(17) Å] is unremarkable, as are the slightly longer Zr−THF bonds [2.3180(16) and 2.3241(16) Å], which are quite comparable to those in **1**.

Upon the addition of 1 equiv of dimeric [NaSn(O^{t}Bu)$_3$]$_2$ to *cis*-MCl$_4$(THF)$_2$ (M = Zr, Hf) in THF (Scheme 5), the heterobimetallic alkoxides *fac*-[Sn(μ-O^{t}Bu)$_3$M(O^{t}Bu)$_3$] [M = Zr (**7**), Hf (**8**)] were obtained in high yields as sublimable, crystalline solids that were soluble in hexanes. Products identical with **7** and **8** were obtained when **1** or **2** was treated with $^1/_2$ equiv of [NaSn(O^{t}Bu)$_3$]$_2$, respectively. On the basis of the NMR spectra, we were able to confirm that **7** was the same compound that had previously been synthesized by Caulton et al. via the mixing of equimolar amounts of Zr(O^{t}Bu)$_4$ and Sn(O^{t}Bu)$_2$ in diethyl ether.[28] The hafnium derivative, **8**, whose NMR and analytical data identified it as an analogue of **7**, is a new compound. The ^{1}H NMR spectrum had only two closely spaced, sharp singlets at 1.47 and 1.53 ppm, respectively, with the signal to lower field being assigned to the bridging *tert*-butoxide groups, because its methyl carbons showed coupling to tin. The crystalline products obtained from THF solutions were unsuitable for single-crystal X-ray studies. Much better developed crystals were obtained from hexanes, and these were subjected to single-crystal X-ray studies.

The heterometallic compounds **7** and **8** crystallize in the polar trigonal space group *P*3*m*1. The structures contain three independent molecules of C_{3v} symmetry, which are positioned along the three special positions of site symmetry

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[52] (a) Bos, K. F.; Bulten, E. J.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1975**, *99*, 71–77. (b) Bos, K. F.; Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1972**, *39*, C52–C55.

[53] CpSnCl is conventionally synthesized via the comproportionation of Cp$_2$Sn and SnCl$_2$.[52b] We synthesized it cleanly, and in one step, from (SnCl$_3$)$^-$ and NaCp in THF.

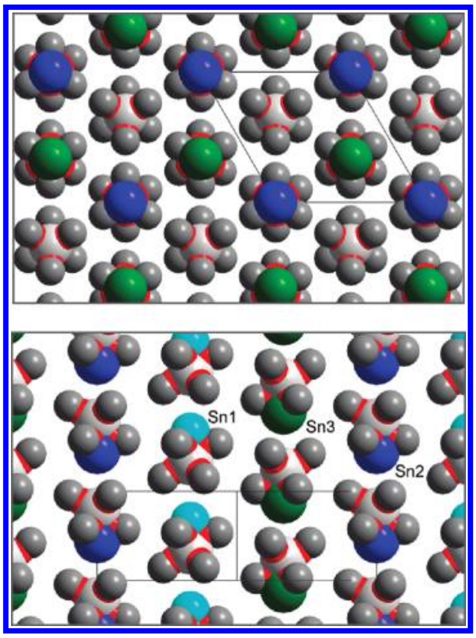


Figure 7. Crystal packing diagrams of **7** and **8**. Top: view along [001]. Bottom: view along [110]. The tin atoms of the three independent molecules are distinguished by different colors; Zr, light gray; O, red; C, dark gray (methyl groups are omitted for clarity).

3m (Wyckoff notations a, b, and c, respectively). Both the tin and the group 4 metal centers are located on the 3-fold axes, while the *tert*-butoxide ligands are situated on the crystallographic mirror planes. The polar molecules are stacked upon each other along the *z* axis. A close inspection of the crystal packing, shown in Figure 7, reveals that two crystallographically unique stacks (containing Sn2 and Sn3) face the same direction along the *z* axis, while the third stack (containing Sn1) faces the opposite way. The two stacks that face the same direction are shifted with respect to each other along the *z* axis by about half a unit cell length (e.g., 0.55 in **8**). This arrangement seems to provide the most effective packing for the polar dimetallic complex of C_{3v} symmetry because it facilitates optimal interlocking of the *tert*-butyl groups. It appears that this packing arrangement is prone to disorder (reversal of the molecular direction along *z*) and merohedral twinning (reversal of the polarity of the crystal domain). X-ray data of several crystals were collected and showed varying degrees of disorder and twinning. The best results were obtained when **7** was treated as a disordered structure (two unique molecules were split on two positions facing in opposite *z* directions) while **8** was refined as an inverse twin.

Like **1** and **2**, the heterometallic alkoxide **7**, shown in Figure 8, is a distorted octahedron, but here the distortions are even more pronounced than in those trichlorostannate salts. The greater deviations from O_h symmetry versus those in **1** and **2** are due to the presence of the tri-*tert*-butoxystannate moiety, which chelates one of the triangular faces and constrains the O^{t}Bu−Zr−O^{t}Bu angles to a very narrow 68.5(3)°, while keeping the O^{t}Bu−Sn−O^{t}Bu angles at a somewhat larger 77.2(6)°, corresponding to an angle sum of 231.6(6)° at tin. The opposite triangular face consists of a much flatter [296.4(6)°] Zr(O^{t}Bu)$_3$ pyramid that is almost isometric with those in **1** and **6**. The molecular structure of **7** may also be described as a Sn(O^{t}Bu)$_3$Zr trigonal bipyramid balanced on top of a trigonal Zr(O^{t}Bu)$_3$ pyramid. The nearly linear [173.2(6)°] zirconium−*tert*-butoxide bonds [1.930(5) Å] are similarly short as those in **1** and **6**, but the Zr−O bonds [2.309(8) Å] to the chelating tri-*tert*-butoxystannate moiety are surprisingly long. This elongation, which renders these bonds longer than even the zirconium−THF bonds in **1** and **6**, may reflect both the sp^3 hybridization of the oxygen atoms and their low charge.

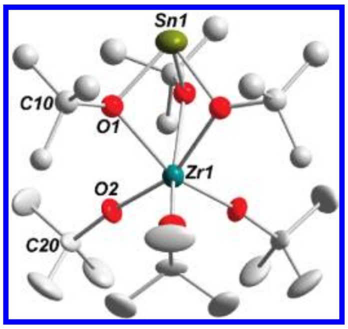


Figure 8. Solid-state structure and partial labeling scheme of one of the three independent molecules of **7**. With the exception of the metal atoms (50%), all atoms are drawn at the 35% probability density level. Selected bond parameters: Sn1−O1 = 2.082(8) Å, Zr1−O1 = 2.309(8) Å, Zr1−O2 = 1.948(6) Å; O1−Sn1−O1′ = 77.2(3)°, O1−Zr−O1′ = 68.5(3)°, Sn1−O1−Zr1 = 93.4(3)°, O2−Zr−O2′ = 98.8(3)°, Zr−O2−C20 = 173.2(6)°.

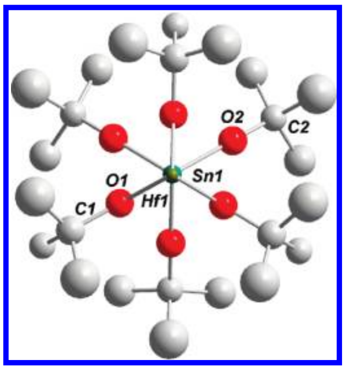
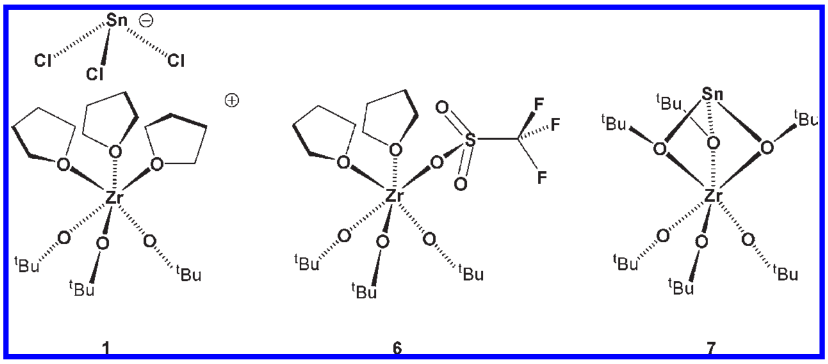


Figure 9. Perspective view and partial labeling scheme of one of the three crystallographically independent molecules of **8**. This projection along the tin−hafnium vector emphasizes the C_{3v} symmetry of the molecule in the solid state. Selected bond lengths and angles: Sn1−O1 = 2.107(14) Å, Hf1−O1 = 2.242(13) Å, Hf1−O2 = 1.941(13) Å; O1−Sn1−O1′ = 75.1(6)°, O1−Hf1−O1′ = 69.9(6)°, Sn1−O1−Hf1 = 93.4(3)°, O2−Hf1−O2′ = 99.3(8)°, Hf1−O2−C2 = 172.8(16)°.

Figure 9 shows a ball-and-stick drawing of the hafnium/tin hexa-*tert*-butoxide derivative **8** in a perspective that emphasizes the high site-symmetry imposed on the molecule. As for **7**, the bond parameters listed pertain only to the independent molecule shown, but those for the remaining two molecules are similar. Crystal and refinement data for **8** are collected in Table 1. Complex **8** is isomorphous with **7**, although the slightly lower crystal quality limited anisotropic refinement to the metal atoms. As can be seen in the figure caption, the estimated standard deviations on the bond parameters of **8** are approximately twice as large as those of **7**.

Compounds **7** and **8** may be viewed as having been formed from **1** and **2** and $^1/_2$ equiv of [NaSn(O^{t}Bu)$_3$]$_2$ in metathesis reactions. We cannot rule out, however, that the reaction proceeds through the initial formation of the neutral molecules M(O^{t}Bu)$_4$ and Sn(O^{t}Bu)$_2$, which then combined to yield the final products, as they did in Caulton's synthesis.

Chart 1



Discussion

Syntheses. Chelation is a valuable synthetic method for the kinetic and thermodynamic stabilization of metal complexes and is therefore eminently useful for the synthesis of group 4 metal alkoxides, which have a tendency to undergo ligand-exchange reactions. By employing the potentially tridentate $[Sn(O^tBu)_3]^-$, we had hoped to synthesize group 4 alkoxides that were structurally similar to the very robust tris(pyrazolyl)borate complexes of these metals.[19−21] Instead of replacing one or two of the chlorides with the tri-*tert*-butoxystannate ligand, however, sodium tri-*tert*-butoxystannate served as a selective alkoxide transfer reagent, yielding exclusively the salt tri-*tert*-butoxytris(tetrahydrofuran)zirconium trichlorostannate (**1**) and its hafnium analogue, **2**.

The degradation of **A** by *tert*-butoxide transfer from tin to the group 4 metals should come as no surprise because it merely confirms that the Zr−O^{t}Bu and Hf−O^{t}Bu bonds, with bond dissociation energies exceeding 102 kcal mol^{-1},[54] are considerably stronger than the corresponding Sn−O bond (82 kcal mol^{-1}).[55] While the action of the tri-*tert*-butoxystannate **A** on group 4 metal chlorides did not furnish the desired $Sn(\mu\text{-}O^tBu)_3MCl_3$ complex (**B**), it demonstrated that **A** is an excellent reagent for the selective synthesis of monomeric group 4 *tert*-butoxides. The action of sodium tri-*tert*-butoxystannate on group 4 tetrachlorides thus led to the isolation of seven new monomeric *tert*-butoxides of these metals, thereby significantly increasing our knowledge of monomeric group 4 complexes of these ligands and their structures.

What is surprising about the outcomes of these reactions, however, is that the ionic products **1** and **2** were formed, in favor of conceivable molecular species, such as $M(O^tBu)_3Cl$ (M = Zr, Hf). Apparently, once the monochloride stage is reached, the $SnCl_2(THF)$ byproduct abstracts a chloride ion in a Lewis acid−base reaction to generate $[M(O^tBu)_3]^+$ and $(SnCl_3)^-$. The cation is then solvated by three molecules of THF to yield the six-coordinate complexes **1** and **2**, which are arguably the most interesting new compounds presented herein. Monomeric, cationic alkoxides are exceedingly rare because the tendencies for aggregation and ligand exchange in these charged species are even more pronounced than those in the equivalent neutral molecules.[4]

When only $^2/_3$ equiv of sodium tri-*tert*-butoxystannate was used, the neutral group 4 di-*tert*-butoxides **3** and **4** were produced. Chloride substitutions can thus be effectively terminated at the $[M(O^tBu)_2Cl_2(THF)_2]$ [M = Zr (**3**), Hf (**4**)] stage—a feat that is difficult to accomplish with alkali-metal *tert*-butoxides. The formation of **3** and **4** also shows that $SnCl_2(THF)$ in the reaction mixture does not abstract chloride from di-*tert*-butoxide species but that three *tert*-butoxide groups are required for the chloride ion to become sufficiently weakened for abstraction.

The failure of *cis*-$TiCl_4(THF)_2$ to react in a manner analogous to its heavier congeners appears to be mainly due to the substantially smaller size of titanium, which prevents the formation of a salt of the type *fac*-$\{[Ti(O^tBu)_3(THF)_3](SnCl_3)\}$. Likely also for steric reasons, the action of AgOTf on $(^tBuO)_3TiCl$ did not produce *fac*-$[Ti(O^tBu)_3OTf(THF)_2]$ but gave instead the sterically less encumbered **5**.

Product Selection. Chart 1 contrasts the solid-state structures of the zirconium derivatives **1**, **6**, and **7**, all of which share the same pyramidal $Zr(O^tBu)_3$ unit. As we showed above, the metric parameters of this moiety are surprisingly invariant in all three species. It is therefore noteworthy that all three compounds adopted different solid-state structures, with **1** being a separated ion pair, **6** a contact ion pair, and **7** a molecular compound. NMR evidence suggests that at least for **7** (and likely also for **1**) the isolated (solid-state) structure is identical with the solution structure and that for these compounds the product selection is not a crystal-packing effect. The product formation may therefore be viewed as the result of a competition of the ubiquitous THF with the counterions $(SnCl_3)^-$, OTf^-, and $[Sn(O^tBu)_3]^-$ for a coordination site on the formal $[Zr(O^tBu)_3]^+$ cation. On the basis of NMR data and the isolated products, tri-*tert*-butoxystannate is the best ligand because it cleanly displaced all three THF moieties from the zirconium center. Even when **7** and **8** were dissolved in THF solutions, no evidence of coordinated THF or partially coordinated (arm off) $[Sn(O^tBu)_3]^-$ was observed. Triflate, which does not benefit from the chelate effect and must compete with the ever-present THF on bond enthalpy alone, does yield the contact ion pair **6** in the solid state. Our data, however, are inconclusive as to the solution-phase structure of this compound.

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(54) (a) The Ti−O^{t}Bu bond dissociation energy is reported to be 102 kcal mol^{-1}.[54b] The corresponding bond dissociation energies for zirconium and hafnium are expected to be somewhat larger.(b) Bradley, D. C.; Hillyer, M. J. *Trans. Faraday Soc.* **1966**, *62*, 2374–2380.

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Trichlorostannate is a good ligand for late transition metals and binds particularly strongly to members of the platinum metals, where π-acceptor properties are important. Even early transition metals form complexes with $(SnCl_3)^-$, as the isolation of $[Cp_2Mo(SnCl_3)_2]$ has shown. Trichlorostannate, however, does not compete well with the hard-donor THF for coordination sites on Zr^{IV} and Hf^{IV} because there are no d electrons available for back-bonding. The complex anion thus remains in the solid state, and likely also in solution, a weakly coordinating anion. That the "donor atom", tin, faces away from the cation in the solid state may simply be a packing effect, but it is possible that this structure persists in solution because coordinated and bulk THF can be clearly distinguished in the NMR spectra.

Coordination Geometries. The two principal coordination geometries for six-coordinate metal complexes are octahedral, O_h, and trigonal prismatic, D_{3h}, with the former being overwhelmingly favorable on steric grounds and thus much more common. Computational studies have shown that for d^0 complexes octahedral geometry is also favored electronically, unless the metal bears exclusively σ-donor ligands, like R and H, in which case the trigonal-prismatic structure is lower in energy.[56−62]

Because all complexes presented herein contain two or more strongly π-donating *tert*-butoxide ligands, octahedral geometry is thus both expected and observed. In some cases, the distortions from octahedral are so severe, however, that further comments are warranted. Geometric distortions from ideal octahedral are most noticeable for complexes **1**, **2**, **6**, **7**, and **8**, all of which contain the facial $M(O^tBu)_3$ moiety. Sterically, a meridional arrangement would clearly be preferable (and possible for **1**, **2**, and **6**), but this geometry is not realized. An arrangement with two mutually trans configured *tert*-butoxides is apparently electronically too destabilizing, despite the obvious steric strain caused by the facial arrangement of these bulky ligands. The steric pressure exerted by the $M(O^tBu)_3$ pyramid is thus mainly responsible for the distortions in these complexes, which in **7** and **8** is further accentuated by the presence of the steep $Sn(O^tBu)_3$ pyramid trans to the $M(O^tBu)_3$ moiety.

The remaining three compounds, namely, **3**−**5**, are di-*tert*-butoxides, whose diminished steric bulk caused lesser deviations from ideal geometry, yielding more regularly shaped octahedra. Here the overall structure is influenced by steric repulsions between the cis-configured *tert*-butoxides, whose enclosed bond angles invariably exceed 100°. This large angle and the bulkiness of the *tert*-butoxide ligands cause the remaining angles of the octahedron to be less than 90°. Thus, in **3** and **4**, the THF−M−THF and Cl−M−Cl angles (M = Zr, Hf) are compressed to 76.65(14) and 163.55(4)°, respectively.

Conclusion

A is not a good oxygen-donor analogue of tris(pyrazolyl)borate in its reactions with group 4 tetrachlorides. Instead, the highly Lewis acidic metals degrade the stannate ion via *tert*-butoxide abstractions. The various outcomes of these reactions showed, however, that **A** is a useful and selective alkoxylating agent for the heavier group 4 metals that furnishes monomeric group 4 metal *tert*-butoxide/chloride species. While the di-*tert*-butoxides/dichlorides, i.e., $M(O^tBu)_2Cl_2(THF)_2$, were isolated as neutral complexes, $M(O^tBu)_3Cl$ underwent chloride abstraction by $SnCl_2$-(THF), forming salts of the type *fac*-$\{[M(O^tBu)_3(THF)_3]$-$(SnCl_3)\}$ in which trichlorostannate is a weakly coordinating anion. This is in contrast to *fac*-$[Zr(O^tBu)_3OTf(THF)_2]$, formed by anion exchange of trichlorostannate with triflate, although the triflate ion may not be bound to the metal in solution.

Only when the Lewis acidity of the group 4 metal is sufficiently attenuated, as in *fac*-$\{[M(O^tBu)_3(THF)_3](SnCl_3)\}$ (M = Zr, Hf), can $[Sn(O^tBu)_3]^-$ be introduced cleanly to yield the sublimable, hexane-soluble *fac*-$[Sn(O^tBu)_3M(O^tBu)_3]$, which contains the intact tri-*tert*-butoxystannate. Less Lewis acidic metals, such as trivalent lanthanides or the larger, tetravalent actinides, may allow the direct transfer of 2 equiv of $[Sn(O^tBu)_3]^-$ to the corresponding metal tri- and tetrachlorides, respectively, and thus be better candidates for complexes of this ligand.

Acknowledgment. We thank the Chevron Phillips Chemical Company for financial support.

Supporting Information Available: Crystallographic data in CIF format for **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 749608−749615 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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