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Synthesis and optical activity analysis of chiral titanium(IV) *sec*-butoxide and its group IV analogues

Samantha N. MacMillan, Kaysia T. Ludford and Joseph M. Tanski*

Department of Chemistry, Vassar College, Poughkeepsie, NY 12604, USA

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Abstract—The complete series of chiral group IV *sec*-butoxides has been obtained by the treatment of $M(NMe_2)_4$ (M = Ti, Zr, Hf) with resolved (*R*)-(−)- or (*S*)-(+)-2-butanol. These complexes were analyzed by polarimetry, revealing a decreasing trend in molar rotation down the group, from titanium to hafnium. Catalysis screenings showed that the resolved titanium *sec*-butoxides, in conjunction with the resolved BINOL (BINOL = 1,1′-bi-2-naphthol) of the opposite configuration designation, catalyzed the addition of dimethyl zinc to benzaldehyde with higher enanteoselectivity than that observed for resolved BINOL with titanium(IV) isopropoxide or with the titanium(IV) *sec*-butoxide of the same configuration designation.

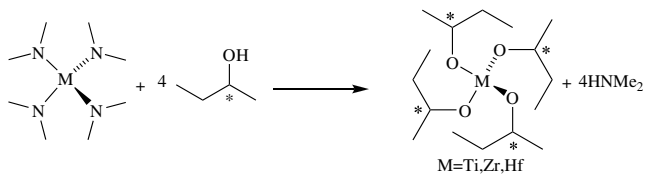
1. Introduction

Group IV alkoxides are a topic of continued interest with respect to their structure and varied chemistry.[1–5] These compounds act as important precursors in metal oxide materials; high dielectric constant hafnium materials will soon be used in sub-100 nm computer chip technology.[5] Group IV alkoxides, most notably $Ti(O^iPr)_4$, also serve as catalysts in numerous organic transformations. As growth in the pharmaceutical and chemical industries has increased the demand for the production of enantiomerically pure products, strategies employing chiral intermediates have been developed to carry out enantioselective syntheses with high stereoselectivity.[6–9] Increased enantiomeric excess has been observed when bulky or coordinating groups are added to chiral ligand frameworks, necessitating multi-step organic ligand synthesis prior to metal coordination and catalyst screening. In the stereoselective addition of alkyl groups to aromatic aldehydes, strategies include the use of chelating chiral auxiliary ligands, such as amino alcohols,[10,11] BINOL,[12–14] TADDOL,[15,16] Salan,[17] N-sulfonylated amino alcohols,[18,19] and bis(sulfonamide)[20,21] to afford high enantiomeric excess. Employing simple *terminal* chiral alkoxides is an alternative approach.[12,21–24] Herein, we report the synthesis and characterization of the previously unreported complete series of chiral group IV *sec*-butoxides, $M(O^2Bu)_4$ (M = Ti, Zr, Hf), and the results of the stereoselective addition of dimethyl zinc to benzaldehyde, mediated by the resolved $Ti(O^2Bu)_4$ species.

2. Results and discussion

2.1. Synthesis

Alcoholysis of tetrakis(dimethylamido)titanium with an excess (6 equiv) of (*R*)-(−)- or (*S*)-(+)-2-butanol in benzene, followed by vacuum distillation, provided the chiral titanium(IV) alkoxides, $Ti(O^{R\text{-}2}Bu)_4$ and $Ti(O^{S\text{-}2}Bu)_4$, as colorless liquids in high yield (Scheme 1). The procedure for the synthesis of the zirconium and hafnium complexes was similar; the treatment of tetrakis(dimethylamido)zirconium and hafnium with a stoichiometric amount of (*R*)-(−)- or (*S*)-(+)-2-butanol in benzene, followed by a high temperature vacuum distillation, gave the corresponding chiral



Scheme 1. Synthesis of resolved group IV *sec*-butoxides (M = Ti, Zr, Hf).

* Corresponding author. Tel.: +1 845 437 7503; fax: +1 845 437 5732; e-mail: jotanski@vassar.edu

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zirconium(IV) and hafnium(IV) alkoxides as colorless, viscous oils.

2.2. Optical activity analysis

Optical activity analyses were performed for each of the alkoxides synthesized. Both the specific rotation (α) and molar rotation (Φ) were determined (Table 1), and were found to decrease down the group, from titanium to hafnium. Although not a complete series, a similar trend was found for the group 10 complexes [(1*R*,1′*R*)-2,6-bis-[1-(diphenylphosphino)ethyl]phenyl]chloro-platinum and -palladium, with specific rotations of −297.8 and −323.6, respectively.[25] To date, no other complete series of homologues of a transition metal group with chiral ligands, homoleptic or heteroleptic, characterized by optical activity has been reported.

When comparing the specific rotation of homologues, this decreasing trend is not unexpected; if two substances have unequal molecular weights, but similar rotatory strength, or power to rotate polarized light, the substance with the smaller molecular weight will have a larger rotation simply because there are more molecules per unit weight.[26] For the group IV *sec*-butoxides, the decreasing trend in molar rotation may be due to differences in both rotatory strength and molecular size. The $Zr(O^2Bu)_4$ and $Hf(O^2Bu)_4$ alkoxides have similar molar rotations and may reflect that these complexes are similar in size due to the metals having essentially equivalent covalent radii. In order to evaluate the concentration dependence of the optical activity, polarimetry analyses were carried out for the (*R*)-isomers of the group IV *sec*-butoxides at concentrations of 1, 5, and 10 (Fig. 1). The slope of each line of best fit is equal to the specific rotation of the corresponding complex. Over the range of concentrations studied, the rotation for each compound decreases linearly with sample concentration, indicating that solution structure does not affect the magnitude of rotation.

Table 1. Specific and molar rotation values for $M(O^2Bu)_4$ (*c* 1, C_6H_6)

$M(O^2Bu)_4$	α (deg.)	$[\alpha]_D$ (10^{-1} deg cm^2 g^{-1})	$[\Phi]$ (10 deg cm^2 mol^{-1})
$Ti(O^{R\text{-}2}Bu)_4$	−0.906	−83.1	−282.9
$Ti(O^{S\text{-}2}Bu)_4$	+0.881	+83.1	+282.85
$Zr(O^{R\text{-}2}Bu)_4$	−0.230	−20.9	−80.2
$Zr(O^{S\text{-}2}Bu)_4$	+0.222	+22.65	+86.9
$Hf(O^{R\text{-}2}Bu)_4$	−0.121	−11.75	−55.3
$Hf(O^{S\text{-}2}Bu)_4$	+0.120	+12.4	+58.3

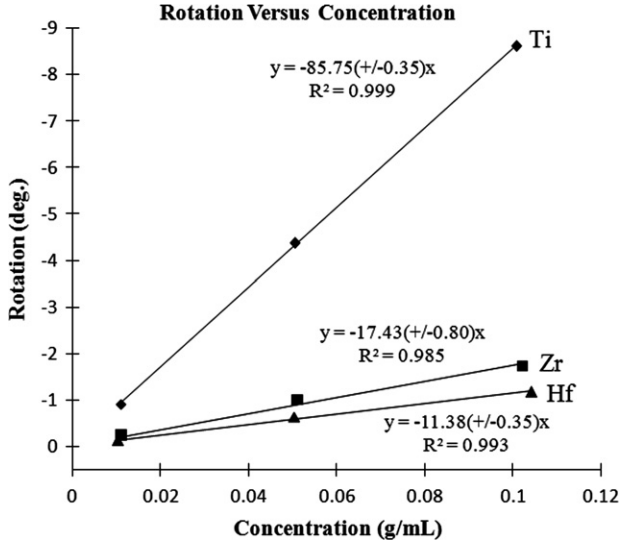
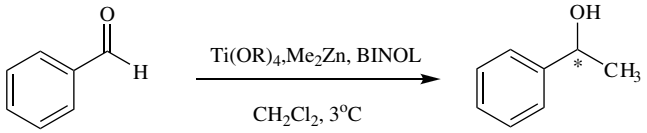


Figure 1. Concentration dependence of observed rotations for $M(O^{R\text{-}2}Bu)_4$ (M = Ti, Zr, Hf).

2.3. Asymmetric methylation of benzaldehyde

To assess the potential of chiral group IV *sec*-butoxides as asymmetric catalysts, the methylation of benzaldehyde to give 1-phenylethanol in the presence of dimethyl zinc and $Ti(OR)_4$ (R = ^{i}Pr, $^{R\text{-}2}$Bu, or $^{S\text{-}2}$Bu) was studied, employing a procedure similar to that previously developed for diethyl zinc (Scheme 2).[27] Analogous studies employing diethyl zinc and achrial $Ti(O^iPr)_4$ have already been reported.[14,27] The alkylation of aldehydes with dimethyl zinc gives much lower enantiomeric excesses than diethyl zinc,[13,16,19,28] although it is known that for both the cases, the dialkyl zinc reagent does not directly alkylate the aldehyde substrate.[13]

In the presence of $Ti(O^{R\text{-}2}Bu)_4$ and $Ti(O^{S\text{-}2}Bu)_4$, a 17% excess of *R*- and 12% excess of *S*-1-phenylethanol were observed, respectively (Table 2).[29]



Scheme 2. Dimethyl zinc addition to benzaldehyde.

Table 2. Data for the addition of dimethyl zinc to benzaldehyde[a]

Entry	$Ti(OR)_4$	BINOL	% Conv[b]	% ee[c]	Config.[d]
1	O^iPr	None	81	—	—
2	$O^{R\text{-}2}Bu$	None	54	17	(*R*)
3	$O^{S\text{-}2}Bu$	None	33	12	(*S*)
4	O^iPr	Racemic	98	—	—
5	$O^{R\text{-}2}Bu$	Racemic	99	8	(*S*)
6	$O^{S\text{-}2}Bu$	Racemic	99	11	(*R*)
7	O^iPr	(*R*)	99	46	(*R*)
8	O^iPr	(*S*)	99	40	(*S*)
9	$O^{R\text{-}2}Bu$	(*R*)	99	37	(*R*)
10	$O^{S\text{-}2}Bu$	(*S*)	99	40	(*S*)
11	$O^{R\text{-}2}Bu$	(*S*)	99	58	(*S*)
12	$O^{S\text{-}2}Bu$	(*R*)	99	56	(*R*)

[a] $Ti(OR)_4$ (1.4 mmol in 5 mL CH_2Cl_2), 0.21 mmol BINOL, 6.0 mmol Me_2Zn/toluene, 1.0 mmol benzaldehyde.
[b] After 24 h, as determined by ^{1}H NMR.
[c] Determined by chiral GC, Alltech Chiraldex B-DM.
[d] As determined by the analysis of an authentic sample of (*R*)-(+)-1-phenylethanol.

Owing to the low percentage conversion observed, the reactions were repeated, by adding a catalytic amount of racemic BINOL (BINOL = 1,1′-bi-2-naphthol); the percentage conversion for each titanium alkoxide increased to over 98%. Notably, for the reactions involving racemic BINOL and chiral alkoxides, the enantiomeric excesses decreased and were accompanied by a switch in the configuration of the alcohol in excess. The change in the enantiomeric excess of the alcohol in excess (Δee) was observed to be 25% and 23% for $Ti(O^{R\text{-}2}Bu)_4$ and $Ti(O^{S\text{-}2}Bu)_4$, respectively. In the addition of diethylzinc to benzaldehyde, the addition of chiral additives, including chiral alcohols, has been shown to influence the selectivity of the reaction when a chiral tridentate bis(sulfonamide) titanium catalyst was used.[20] An analogous observation has also been reported for the addition of diethyl zinc to benzaldehyde mediated by an achiral bis(phenol) and the chiral monodentate alkoxide $Ti[O^{S}CH(Et)(p\text{-Tol})]_4$.[23] These results prompted an investigation employing resolved (*R*)- or (*S*)-BINOL to potentially increase the enantiomeric excess of the product alcohol.

In the presence of achiral $Ti(O^{i}Pr)_4$ and (*R*)- or (*S*)-BINOL, the enantiomeric excesses of 46% for (*R*)- and 40% (*S*)-1-phenylethanol were observed, respectively, similar to values reported in the literature.[30] The addition of resolved BINOL to chiral titanium alkoxides of the same configuration resulted in product configurations and enantiomeric excesses similar to the addition of resolved BINOL to achiral $Ti(O^{i}Pr)_4$. However, the addition of resolved BINOL to chiral titanium alkoxides of the *opposite* configuration designation increased the enantiomeric excess by at least 16% over the combinations with the same configuration. In either case, the product alcohol obtained was of the same configuration as the resolved BINOL used. Both the (*S*)-BINOL/$Ti(O^{R\text{-}2}Bu)_4$ and the (*R*)-BINOL/$Ti(O^{S\text{-}2}Bu)_4$ pairs produce higher enantiomeric excesses, 58% and 56% respectively, than the 50% excess previously reported for the addition of dimethyl zinc to benzaldehyde under similar catalytic conditions.[30]

We propose that this observation is an example of a matched pair asymmetric activation phenomena[31] related to 'double diastereoselectivity', as described by Masamune,[32] and 'specific interactivity', as described by Danishefsky.[33] According to Masamune, double asymmetric synthesis resulting in higher enantiomeric excess, as well as enantiomeric control, can be achieved by the interaction of a matched pair of homochiral reactants. Danishefsky adds that the substantial diastereomeric preference may be achieved beyond that afforded by the chiral components, based on a 'specific interactivity' between them. In the matched pairs of (*S*)-BINOL/$Ti(O^{R\text{-}2}Bu)_4$ and (*R*)-BINOL/$Ti(O^{S\text{-}2}Bu)_4$, the choice of BINOL in the matched pair determines enantiomeric control; however, the chirality of the terminal alkoxide ligands and the BINOL influences the facial selectivity of the alkyl group as it is transferred to the aldehyde, resulting in higher enantiomeric excess than obtained either from chiral component by itself or from a mismatched pair. In BINOL/$Ti(OR)_4$ systems in particular, the proposed intermediate implicated in the mechanism of the alkylation of arylaldehydes is a dinuclear species.[13,30] The chirality of both the terminal alkoxide ligands and the BINOL presumably affects both the stability of the dinuclear species and the facial selectivity of subsequent aldehyde binding.[16]

Different from the 'chiral environment amplification' approach,[21] which uses an achiral chelating ligand to *transmit* and amplify enantioselectivity from a single chiral component, this dichiral approach uses complementary matched pairs composed of two different chiral ligands to form an activated complex that *reinforces* enantioselectivity.[34] Interestingly, in a similar study of the addition of diethyl zinc to 4-tolualdehyde using the chiral monodentate alkoxide $Ti[O^{S}CH(Et)(Ph)]_4$ and a chiral bis(sulfonamide), the magnitude of the product alcohol's enantiomeric excess was also observed to be different when chelating bis(sulfonamide) of the opposite configuration was used: (*R*,*R*)-bis(sulfonamide) 84%, (*S*,*S*)-bis(sulfonamide) 81%.[21] However, a similar enantiomeric excess was observed when the achiral terminal alkoxide $Ti(O^{i}Pr)_4$ was studied with the resolved (*R*,*R*)-bis(sulfonamide) 79%. In this system, the chiral alkoxide derived from $HO^{S}CH(Et)(Ph)$ had little influence on the enantioselectivity, contrasting the BINOL/$Ti(O^{2}Bu)_4$ system reported here, in which the enantiomeric excess observed from the matched pair is significantly larger than that observed from the mismatched pair or achiral alkoxide with resolved BINOL. Ongoing studies are currently focused on using resolved group IV *sec*-butoxides in the dichiral asymmetric activation approach to further increase enantioselectivity in reactions such as the alkylation of aromatic aldehydes with dialkyl zinc reagents.

3. Conclusions

In conclusion, a previously unreported complete series of chiral group IV *sec*-butoxides was synthesized from resolved (*R*)-(−)- and (*S*)-(+)-2-butanol and was analyzed by polarimetry. A decreasing trend in the specific rotation was observed down the group, from titanium to hafnium. An example of asymmetric activation, the simple resolved titanium *sec*-butoxide, combined with resolved BINOL of the opposite configuration designation, yields a dichiral matched pair that mediates the addition of dimethyl zinc to benzaldehyde with higher enantioselectivity than resolved BINOL with $Ti(O^{i}Pr)_4$ or the mismatched dichiral pair.

4. Experimental

4.1. General experimental

Unless otherwise stated, all manipulations were carried out at room temperature in an inert atmosphere glove box or under a nitrogen atmosphere using standard Schlenk techniques. Anhydrous solvents were purchased from Aldrich and stored under nitrogen. Resolved (*R*)-(−)- and (*S*)-(+)-*sec*-butanols were purchased from Aldrich and degassed by the freeze–pump–thaw–degas method prior to use. Tetrakis(dimethylamido)titanium was prepared by

the literature method.[35] Tetrakis(dimethylamido)zirconium and hafnium were purchased from Strem. All other reagents were purchased from commercial sources and used as received. All glasswares were oven dried at a temperature of 235 °C prior to use.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at room temperature using a Bruker Avance DPX 300 MHz spectrometer. ^{1}H and ^{13}C chemical shifts are reported and referenced to the residual solvent resonances of 7.15 ppm (^{1}H) and 128.62 (t) (^{13}C) for benzene-d_6. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer and are reported in cm^{-1}. Optical rotation analyses were recorded on a Rudolph Research Analytical Autopol III polarimeter in anhydrous benzene solution. Chiral GC (Alltech Chirladex B-DM column) analyses were carried out on a HP 6890 Series GC system. Elemental analyses were carried out by Desert Analytics, Inc., AZ, USA; samples were handled under an inert atmosphere.

4.2. General procedure for the asymmetric addition of Me_2Zn to benzaldehyde

To a stirring solution of BINOL (0.21 mmol) in CH_2Cl_2 (5 mL) was added $Ti(OR)_4$ (1.4 mmol). After 1 h, the reaction mixture was cooled to 3 °C and 3 mL of dimethylzinc solution (2 M in toluene, 6 mmol) was added. After stirring for 30 min, benzaldehyde was added (1 mmol) and the mixture was stirred at 3 °C for 24 h. The reaction was quenched with 1 M HCl (20 mL), filtered, and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The remaining oil was analyzed by ^{1}H NMR and chiral GC (Alltech Chiraldex B-DM) to determine the percent conversion of 1-phenylethanol and its enantiomeric excess, respectively.

4.3. Synthesis of resolved $Ti(O^{R\text{-}2}Bu)_4$

A solution of (*R*)-(−)-2-butanol (6 equiv, 4.920 g, 66.38 mmol) in benzene was treated with tetrakis(dimethylamido)titanium (2.470 g, 11.02 mmol) in benzene at 0 °C. The reaction mixture was allowed to come to room temperature and then heated to 40 °C over the course of 1 h, evacuating the headspace throughout. The solvent was removed in vacuo and the residue purified by vacuum distillation (90 °C, 10 mmHg) yielding a clear, colorless liquid (3.41 g, 91%). IR Data (KBr salt plate, cm^{-1}): 2967 (s), 2925 (s), 2876 (s), 2732 (w), 2713 (w), 2698 (w), 2658 (w), 2626 (w), 2581 (w), 1463 (s), 1369 (s), 1356 (m), 1336 (s), 1296 (m), 1267 (m), 1161 (s), 1128 (s), 1037 (s), 1000 (s), 977 (s), 942 (s), 830 (s), 806 (m), 793 (m), 781 (m), 652 (s), 613 (s), 544 (w), 525 (w), 544 (w), 497 (w), 454 (m). ^{1}H NMR (300 MHz, C_6D_6): δ 4.29 (m, 1H, –C*H*), 1.59 (m, 1H, –CH_2), 1.46 (m, 1H, –CH_2), 1.28 (d, 3H, $J = 6.2$, CH–CH_3), 1.01 (t, 3H, $J = 7.4$, CH_2–CH_3). ^{13}C NMR (MHz, C_6D_6): δ 82.50 (–*C*H), 34.20 (–*C*H_2), 25.26 (CH–*C*H_3), 11.21 (CH_2–*C*H_3). Anal. Calcd for $C_{16}H_{36}O_4Ti$: C, 56.47; H 10.66; N, 0.00. Found: C, 56.23; H, 10.45; N, <0.02. $[\alpha]_D^{24} = -83.1$ (*c* 1.0, C_6H_6).

4.4. Synthesis of resolved $Ti(O^{S\text{-}2}Bu)_4$

A solution of (*S*)-(+)-2-butanol (6 equiv, 4.67 g, 63.10 mmol) in benzene was treated with tetrakis(dimethylamido)titanium (2.349 g, 10.48 mmol) in benzene at 0 °C. The reaction mixture was allowed to return to room temperature and was then heated to 40 °C over the course of 1 h, evacuating the headspace throughout. The solvent was removed in vacuo and the residue purified by vacuum distillation (95 °C, 10 mmHg) yielding a clear, colorless liquid (2.721 g, 76%). IR Data (KBr salt plate, cm^{-1}): 2967 (s), 2925 (s), 2876 (s), 2730 (w), 2717 (w), 2698 (w), 2657 (w), 2625 (w), 2580 (w), 1463 (s), 1369 (s), 1356 (m), 1345 (m), 1336 (s), 1296 (m), 1266 (m), 1161 (s), 1128 (s), 1036 (s), 1001 (s), 977 (s), 942 (s), 830 (s), 793 (m), 806 (m), 779 (m), 652 (s), 613 (s), 544 (w), 528 (w), 497 (w), 454 (m). ^{1}H NMR (300 MHz, C_6D_6): δ 4.25 (m, 1H, –C*H*), 1.55 (m, 1H, –CH_2), 1.44 (m, 1H, –CH_2), 1.24 (d, 3H, $J = 6.0$ Hz, CH–CH_3), 0.98 (t, 3H, $J = 7.4$ Hz, CH_2–CH_3). ^{13}C NMR (MHz, C_6D_6): δ 82.50 (–*C*H), 34.20 (–*C*H_2), 25.26 (CH–*C*H_3), 11.21 (CH_2–*C*H_3). Anal. Calcd for $C_{16}H_{36}O_4Ti$: C, 56.47; H 10.66; N, 0.00. Found: C, 56.65; H, 10.67; N, 0.13. $[\alpha]_D^{24} = +83.1$ (*c* 1.0, C_6H_6).

4.5. Synthesis of resolved $Zr(O^{R\text{-}2}Bu)_4$

To a benzene solution of tetrakis(dimethylamido)zirconium (2.239 g, 8.37 mmol) at 17 °C was slowly added a slight excess of (*R*)-(−)-2-butanol (2.543 g, 34.31 mmol) in benzene. The reaction mixture was stirred under a positive nitrogen flow at 17 °C for 20 min. The solution was allowed to return to room temperature and the headspace evacuated several more times over a 2 h period. The reaction was stirred overnight, after which time the volume was reduced by half. The remaining mixture was transferred to a distillation apparatus and the solvent removed in vacuo. The residue was purified by high temperature distillation (185 °C, 10 mmHg) yielding a clear, colorless viscous oil (2.180 g, 66%). IR Data (KBr salt plate, cm^{-1}): 2965 (s), 2917 (s), 2875 (s), 2839 (s), 2644 (w), 2625 (w), 2573 (w), 1464 (s), 1367 (s), 1347 (s), 1316 (w), 1296 (w), 1263 (m), 1124 (s), 1048 (s), 1004 (s), 960 (m), 931 (s), 916 (s), 892 (s), 826 (s), 801 (m), 780 (m), 675 (w), 606 (s), 555 (s), 463 (s). ^{1}H NMR (300 MHz, C_6D_6): δ 4.38 (m, 1H, –C*H*), 1.95 (m, 1H, –CH_2), 1.78 (m, 1H, –CH_2), 1.47 (d, 3H, $J = 6.0$ Hz, CH–CH_3), 1.02 (t, 3H, $J = 7.4$ Hz, CH_2–CH_3). ^{13}C NMR (MHz, C_6D_6): δ 77.80 (–*C*H), 33.90 (–*C*H_2), 24.11 (CH–*C*H_3), 11.59 (CH_2–*C*H_3). Anal. Calcd for $C_{16}H_{36}O_4Zr$: C, 50.09; H 9.46; N, 0.00. Found: C, 49.25; H, 10.23; N, 2.01. $[\alpha]_D^{24} = -20.9$ (*c* 1.0, C_6H_6).

4.6. Synthesis of resolved $Zr(O^{S\text{-}2}Bu)_4$

To a benzene solution of tetrakis(dimethylamido)zirconium (2.500 g, 9.34 mmol) at 17 °C was slowly added a slight excess of *S*-(+)-2-butanol (2.850 g, 38.5 mmol) in benzene. The reaction mixture was stirred under a positive nitrogen flow at 17 °C for 20 min. The solution was allowed to return to room temperature and the headspace evacuated several more times over a 2 h period. The reaction was stirred overnight, after which time the volume

was reduced by half. The remaining mixture was transferred to a distillation apparatus and the solvent removed in vacuo. The residue was purified by high temperature distillation (150 °C, 10 mmHg) yielding a clear, colorless viscous oil (2.295 g, 62%). IR Data (KBr salt plate, cm^{-1}): 2963 (s), 2930 (s), 2875 (s), 2839 (s), 2657 (w), 2625 (w), 2580 (w), 1464 (s), 1367 (s), 1347 (m), 1317 (w), 1296 (w), 1267 (m), 1133 (s), 1046 (s), 1004 (s), 983 (s), 931 (s), 916 (s), 826 (m), 797 (w), 779 (m), 675 (m), 606 (s), 555 (s), 489 (s). ^{1}H NMR (300 MHz, C_6D_6): δ 4.37 (m, 1H, –C*H*), 1.95 (m, 1H, –CH_2), 1.76 (m, 1H, –CH_2), 1.46 (d, 3H, $J = 6.2$ Hz, CH–CH_3), 1.00 (t, 3H, $J = 7.5$ Hz, CH_2–CH_3). ^{13}C NMR (MHz, C_6D_6): δ 77.79 (–C*H*), 33.87 (–CH_2), 24.10 (CH–CH_3), 11.58 (CH_2–CH_3). Anal. Calcd for $C_{16}H_{36}O_4Zr$: C, 50.09; H 9.46; N, 0.00. Found: C, 49.39; H, 11.69; N, 1.75. $[\alpha]_D^{24} = +22.65$ (*c* 1.0, C_6H_6).

4.7. Synthesis of resolved Hf($O^{R\text{-}2}$Bu)$_4$

To a benzene solution of tetrakis(dimethylamido)hafnium (2.204 g, 6.21 mmol) at 17 °C was slowly added a slight excess of *R*-(−)-2-butanol (1.890 g, 25.50 mmol) in benzene. The reaction mixture was stirred under a positive nitrogen flow at 17 °C for about 30 min. The solution was allowed to return to room temperature and the headspace evacuated several more times over a 2 h period. The reaction was stirred overnight, after which time the volume was reduced by half. The remaining mixture was transferred to a distillation apparatus and the solvent removed in vacuo. The residue was purified by high temperature distillation (180 °C, 10 mmHg) yielding a clear, colorless viscous oil (2.313 g, 79%). IR Data (KBr salt plate, cm^{-1}): 2970 (s), 2932 (s), 2876 (s), 2844 (s), 2786 (m), 2733 (w), 2659 (w), 2629 (w), 2586 (w), 1463 (s), 1367 (s), 1349 (s), 1318 (w), 1297 (w), 1268 (m), 1229 (w), 1139 (s), 1097 (s), 1050 (s), 1006 (s), 982 (s), 962 (s), 933 (s), 904 (s), 827 (s), 802 (w), 779 (m), 603 (s), 582 (s), 559 (s), 493 (s), 433 (s). ^{1}H NMR (300 MHz, C_6D_6): δ 4.48 (m, 1H, –C*H*), 1.96 (m, 1H, –CH_2), 1.79 (m, 1H, –CH_2), 1.48 (d, 3H, $J = 5.1$ Hz, CH–CH_3), 1.01 (t, 3H, $J = 7.5$ Hz, CH_2–CH_3). ^{13}C NMR (MHz, C_6D_6): δ 77.59 (–C*H*), 34.07 (–CH_2), 24.19 (CH–CH_3), 11.55 (CH_2–CH_3). Anal. Calcd for $C_{16}H_{36}O_4Hf$: C, 40.81; H, 7.70; N, 0.00. Found: C, 41.01; H, 7.42; N, <0.05. $[\alpha]_D^{24} = -11.75$ (*c* 1.0, C_6H_6).

4.8. Synthesis of resolved Hf($O^{S\text{-}2}$Bu)$_4$

To a benzene solution of tetrakis(dimethylamido)hafnium (2.335 g, 6.58 mmol) at 17 °C was slowly added a slight excess of (*S*)-(+)-2-butanol (2.000 g, 27.00 mmol) in benzene. The reaction mixture was stirred under positive nitrogen flow at 17 °C for about 30 min. The solution was allowed to return to room temperature and the headspace evacuated several more times over a 2 h period. The reaction was stirred overnight, after which time the volume was reduced by half. The remaining mixture was transferred to a distillation apparatus and the solvent removed in vacuo. The residue was purified by high temperature distillation (180 °C, 10 mmHg) yielding a clear, colorless viscous oil (2.028 g, 65%). IR Data (KBr salt plate, cm^{-1}): 2965 (s), 2933 (s), 2876 (s), 2844 (s), 2733 (w), 2659 (w), 2630 (w), 2586 (w), 1463 (s), 1368 (s), 1350 (s), 1318 (w), 1297 (w), 1268 (m), 1134 (s), 1096 (s), 1049 (s), 1006 (s), 981 (s), 962 (m), 934 (s), 904 (s), 827 (s), 802 (w), 779 (m), 604 (s), 581 (s), 559 (s), 493 (s), 430 (m). ^{1}H NMR (300 MHz, C_6D_6): δ 4.49 (m, 1H, –C*H*), 1.97 (m, 1H, –CH_2), 1.80 (m, 1H, –CH_2), 1.48 (d, 3H, $J = 5.5$ Hz, CH–CH_3), 1.01 (t, 3H, $J = 7.5$ Hz, CH_2–CH_3). ^{13}C NMR (MHz, C_6D_6): δ 77.60 (–C*H*), 33.95 (–CH_2), 24.23 (CH–CH_3), 11.54 (CH_2–CH_3). Anal. Calcd for $C_{16}H_{36}O_4Hf$: C, 40.81; H 7.70; N, 0.00. Found: C, 40.75; H, 7.51; N, <0.05. $[\alpha]_D^{24} = +12.4$ (*c* 1.0, C_6H_6).

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