Synthesis and structure of salts of a sterically shielded, lipophilic, C_2-symmetric, fluxional aluminate

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Abstract
Multi-gram amounts of halogen-free lipophilic aluminate salts have been prepared, featuring two sterically demanding chelating ligands derived from a methane-2,2´-bisphenolate. The ligand is prepared by condensation of two equivalents of 2,4-di-*tert*-butylphenol with acetone induced by boron fluoride etherate. The C_2-symmetry of this "almebate" anion implies helical chirality. Substantial steric shielding of the aluminate core results in high stability towards aqueous bases. Almebate salts hydrolyze in aqueous acetic acid at room temperature within days. Tetraphenylphosphonium and tetrabutylammonium salts have been prepared by salt metatheses. Sodium almebate can be activated thermally, generating electrophilic sodium(I) with a low coordination number. It eliminates chloride ligands from an N-heterocyclic carbene gold chloride complex, proven by a single-crystal X-ray diffraction study. The barrier of molecular racemization by a degenerate rearrangement of the intrinsically chiral almebate anion in acetone has been determined to be $\Delta G^{\ddagger}$ 53.6 ± 2 kJ mol^{-1} from four ^{1}H NMR coalescence phenomena (500 MHz; 258 K, 273 K, 283 K, 290 K).

Keywords: Aluminate, fluxional molecule, gold, helical chirality, racemization, salt metathesis, sodium, symmetry, weakly coordinating anion

Introduction

Weakly coordinating anions (WCAs)[1] have attracted wide interest due to their use in lithium batteries and as counterions for highly electrophilic cations. Examples for using WCAs in applied chemistry are the lithium(I)-catalyzed reactions[2-5] as well as transition metal-catalyzed reactions[6-9]. Applications comprise olefin polymerization[10] and electrochemistry.[11-13] There are numerous examples for the stabilization of reactive cationic electrophiles.[14-16]

Most weakly coordinating anions, however, contain either C-Cl bonds or persistent C-F-bonds. These substituents are beneficial for characteristics such as low nucleophilicity, chemical

inertness, and high solubility in polar organic solvents. The most prominent anions are tetrakis(pentafluorophenyl)borate $[B(C_6F_5)_4]^-$,[17] tetrakis[3,5-bis(trifluoromethyl)phenyl]borate $[B(Ar_F)_4]^-$,[18,19] a "chemically inert but explosive" carboranate with twelve CF_3 substituents,[20] tetrakis(trifluoromethyl)borate,[21] and the perfluorinated alkoxyaluminate $\{Al[OC(CF_3)_3]_4\}^-$,[22] as presented in Figure 1.

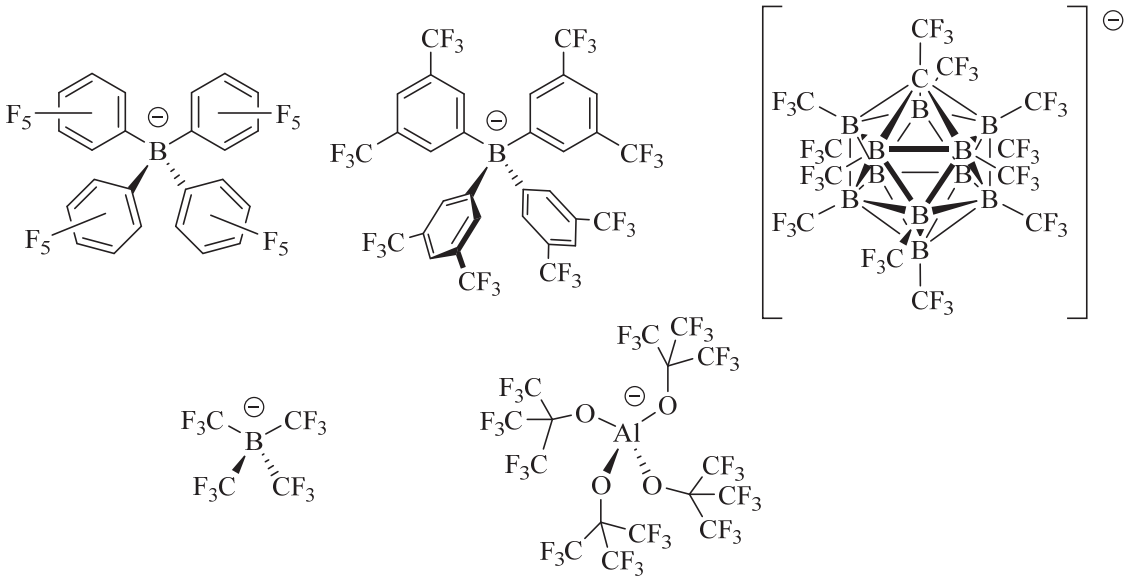


Figure 1. Well-known weakly-coordinating anions (WCA): $BArF_{20}$,[17] Kobayashi's and Brookhart's $BArF_{24}$,[18,19] the King-Michl carboranate,[20] Willner's $[B(CF_3)_4]^-$,[21] and Krossing's "Teflon ball" PFTB.[22]

There are only few examples of halogen-free lipophilic anions with low nucleophilicity. One class of these halogen-free anions are carboranates such as the $[CB_{11}H_{12}]^-$ anion (Figure 2).[23] These carboranates are unstable towards oxidation, and their expensive synthesis limits their use. Another halogen-free anion was recently reported by our group.[24] This "altebate" anion (Figure 2) is based on an AlO_4 core, which is sterically shielded by two tetra-*tert*-butyl substituted 2,2'-biphenolate ligands. The major benefits of this compound are the ease of its preparation and the low costs of the starting materials. However, its instability in protic environments limits the number of potential applications.

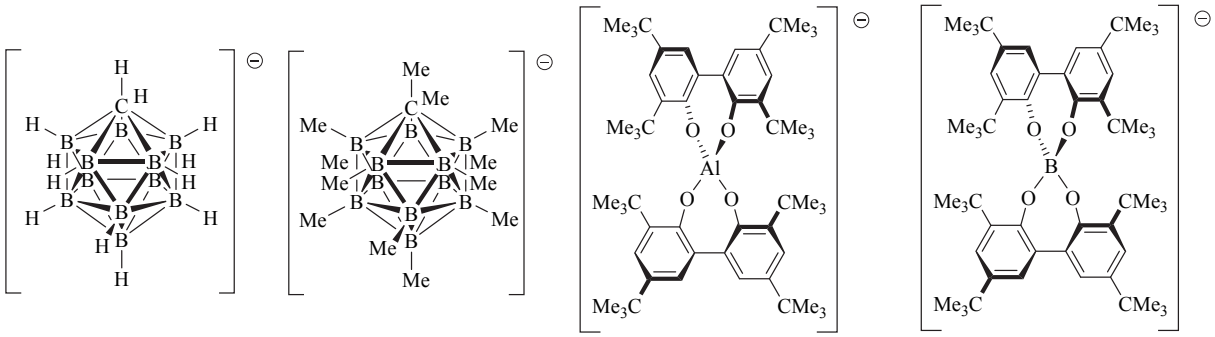


Figure 2. Lipophilic halogen-free anions: carboranates $[CB_{11}H_{12}]^-$,[23] $[CB_{11}Me_{12}]^-$,[25,26] "altebate",[24] and "bortebate".[27]

We aimed at preparing a cost-effective, lipophilic, halogen-free and therefore environmentally benign anion with weakly coordinating character and adequate hydrolytic stability. Herein we report the synthesis of a new aluminate based on two C1-linked phenols with alkali tetrahydrido alanates $MAlH_4$ (M = Li, Na). According to the naming of the altebate anion, we propose the name "almebate" for the new anion, derived from *al*umin*ate* with di*me*thyl*me*thylene linker and eight *tert*-*b*utyl groups (Figure 3).

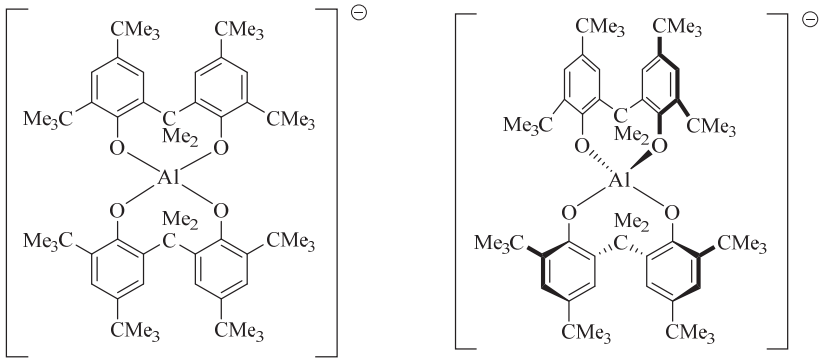
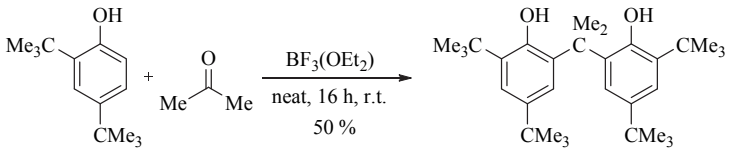


Figure 3. New aluminate anion ("almebate") in a flat and in a stereochemical representation.

Results and Discussion

Synthesis of the bisphenol

We synthesized 6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenol) (**1**)[28,29] following an optimized protocol of Meier et al. for less sterically crowded bisphenols.[30] Acetic acid as solvent was not mandatory to obtain a homogeneous reaction mixture. Thus, neat acetone and boron trifluoride etherate were used stoichiometrically as reactants (Scheme 1). After a reaction time of 16 hours, the crude product was recrystallized from diethyl ether / methanol. Single-crystals suitable for a X-ray diffraction study were obtained by recrystallization in acetic acid (Figure 4).



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Scheme 1. Synthesis of the ligand precursor **1**.

Other Lewis acids result in lower yields: By using concentrated sulfuric acid, the isolated yield decreased to 12 %. $AlCl_3$ or operating at higher temperature lead to dealkylation of *ortho*-*tert*-butyl substituents as described by Sartori et al.[31]

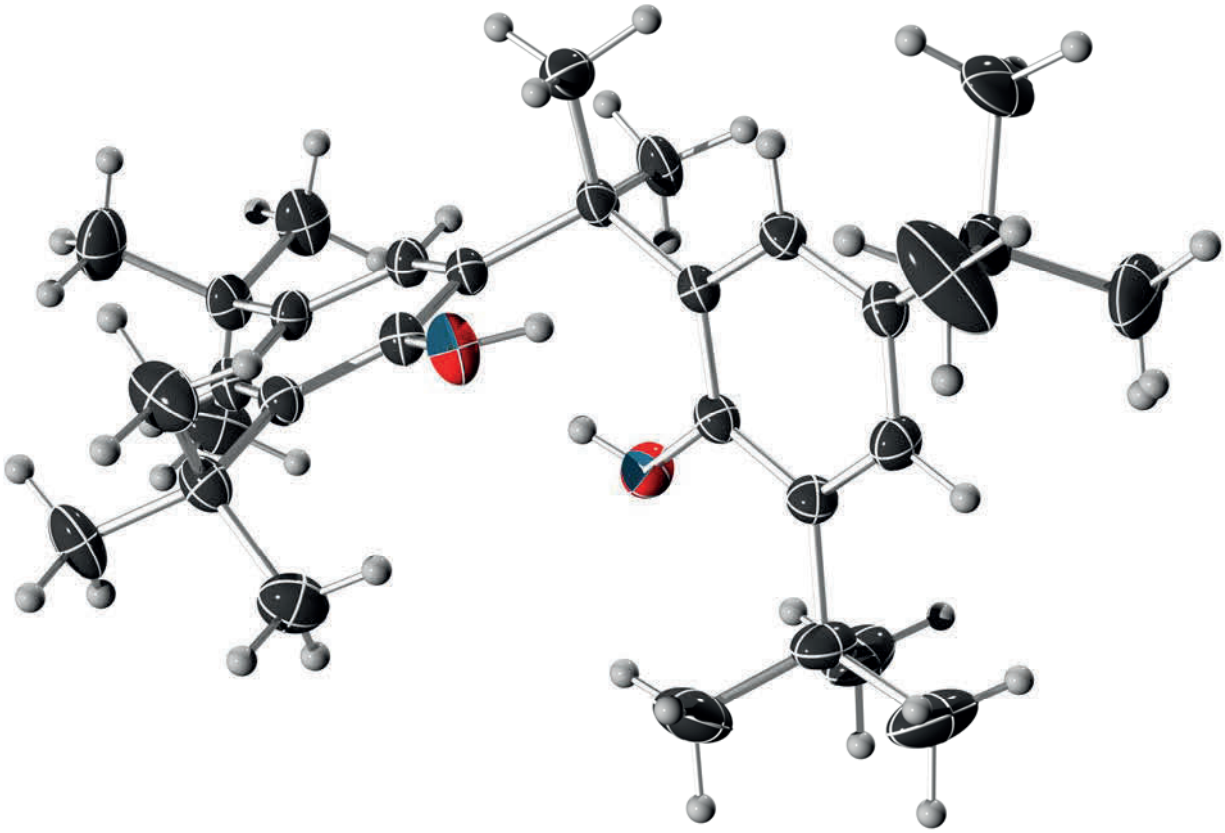
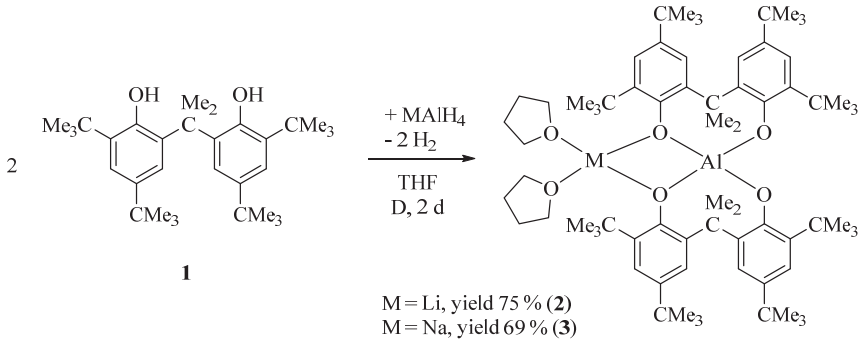


Figure 4. ORTEP ellipsoid-and-stick model of the single-crystal X-ray structure of 6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenol) (**1**). Color code: C black, H gray, O red.[32,33]

Synthesis of alkali metal almebate complexes

The synthesis of the new compounds $Li(thf)_2$ almebate and $Na(thf)_2$ almebate was inspired by the standard literature procedure of the Pan group.[34] Instead of $AlMe_3$, we used $LiAlH_4$ and $NaAlH_4$ for the synthesis of the aluminate complexes (Scheme 2). The reaction time was increased to

48 hours due to the higher steric demand of the substrate 6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenol) (**1**) as compared to Pan's ethylidenebis-2,2′-(4,6-di-*tert*-butylphenol). Our attempts to synthesize the analogous borate species (hypothetical "bormebates") from MBH_4 have not been successful so far. Apparently, the lower polarity of the B-H bond and the smaller radius of the boron center lead to significantly higher reaction barriers and increased steric repulsion.



Scheme 2. Synthesis of $Li(thf)_2$ almebate (**2**) and $Na(thf)_2$ almebate (**3**).

As a result of almebate's symmetry, we expected four CH signal sets in the aromatic region of the spectrum and six singlets in the aliphatic region. The almebate anion comprises two diastereotopic pairs of homotopic methyl groups and two constitutionally different diastereomeric pairs of two homotopic *tert*-butyl groups. The ^1H NMR spectrum of sodium almebate in acetone-d_6 at room temperature provides evidence for the aluminate's fluxionality: the proton signal of the propane-2,2-diyl bridge is a broad coalescing peak with at a chemical shift of 1.85 ppm. A signal at 1.26 ppm with the intensity of four *tert*-butyl groups features a low full width at half maximum. The other *tert*-butyl signal at 1.06 ppm is again very broad, indicating a signal coalescence due to an intramolecular exchange process (Figure 5 and *vide infra*).

The thf ligands at the sodium ion can be easily exchanged by acetone. Dissolving $Na(thf)_2$ almebate (**3**) in acetone and removal of the solvent in vacuo quantitatively yields $Na(acetone)_2$ almebate (**4**) (Scheme 4). Single-crystals were obtained by recrystallization from acetone/pentane (Figure 6). The complex crystallizes in the monoclinic space group C2/c, and the adduct features C_2 symmetry. The aluminium's coordination geometry is distorted tetrahedral. One pair of oxygen atoms bridges a sodium atom and an aluminium atom, the other pair of phenolates is coordinated only to the aluminium center.

The coordinated solvent molecules can be eliminated thermally. By heating $Na(thf)_2$ almebate (**3**) at 150 °C and ca. 1 mbar for 24 hours, the thf ligands are removed quantitatively. In analogy to acetone complex **4**, we expect that sodium in the resulting aluminium adduct **5** is coordinated by two oxygen atoms of the almebate's backbone and by two methyl groups via agostic interactions (Scheme 3). The sodium atom's low coordination number in structure **5** is

synthetically advantageous for the abstraction of halide ligands from uncharged transition metal precatalysts (*vide infra*).

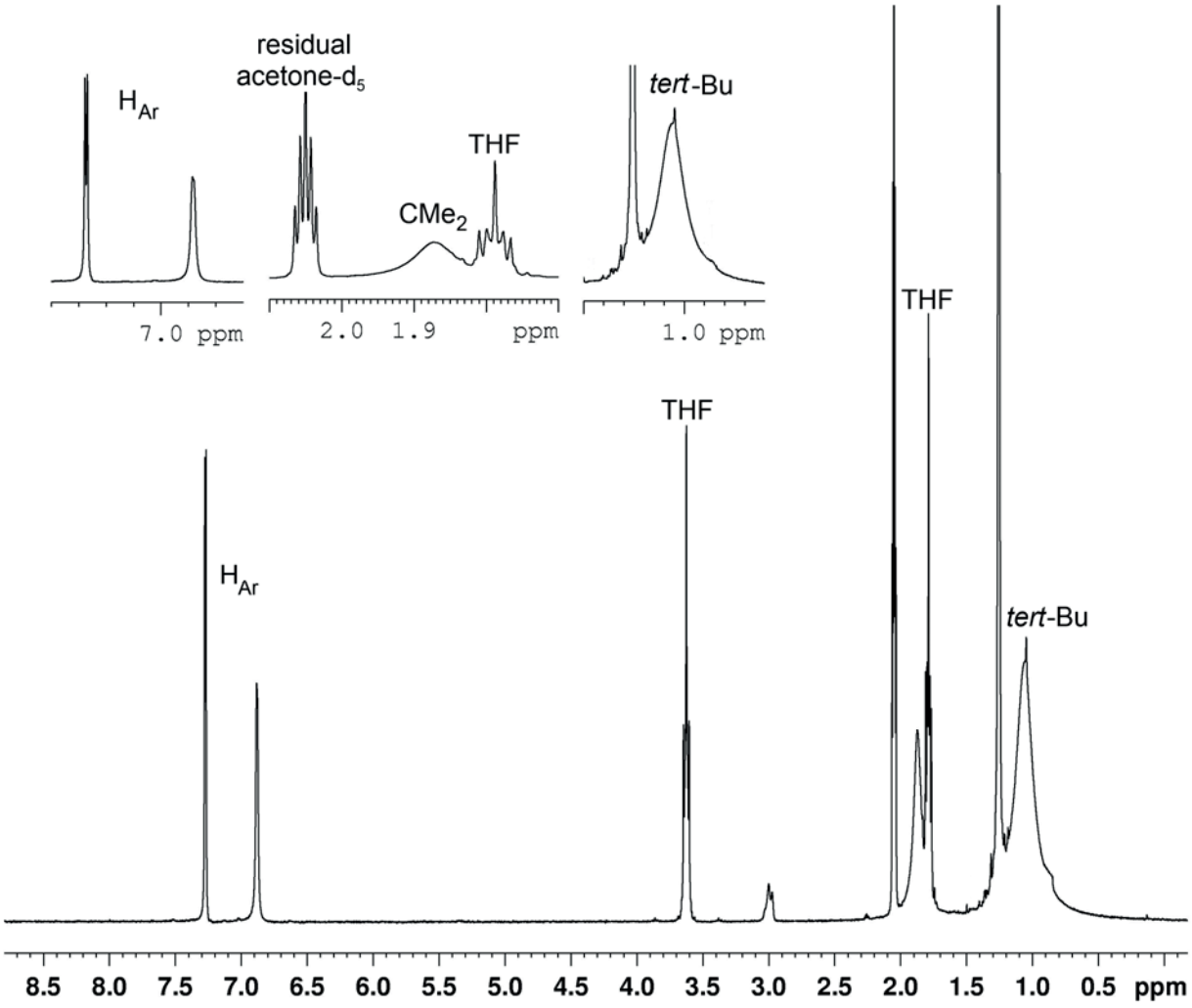
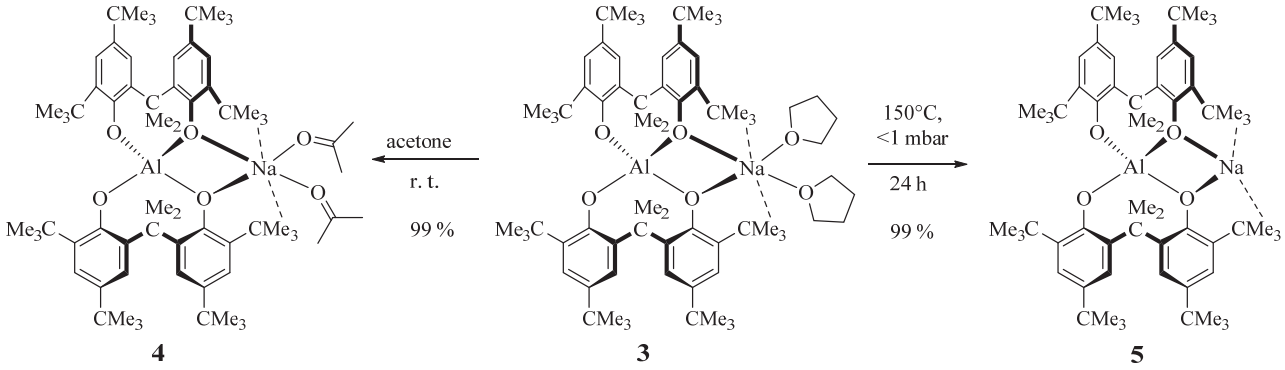


Figure 5. ^{1}H NMR spectrum of Na(thf)$_2$ almebate (**3**) in acetone-d$_6$ (300.5 MHz, 300 K).



Scheme 3. Substitution (left) and elimination (right) of ligated solvent molecules.

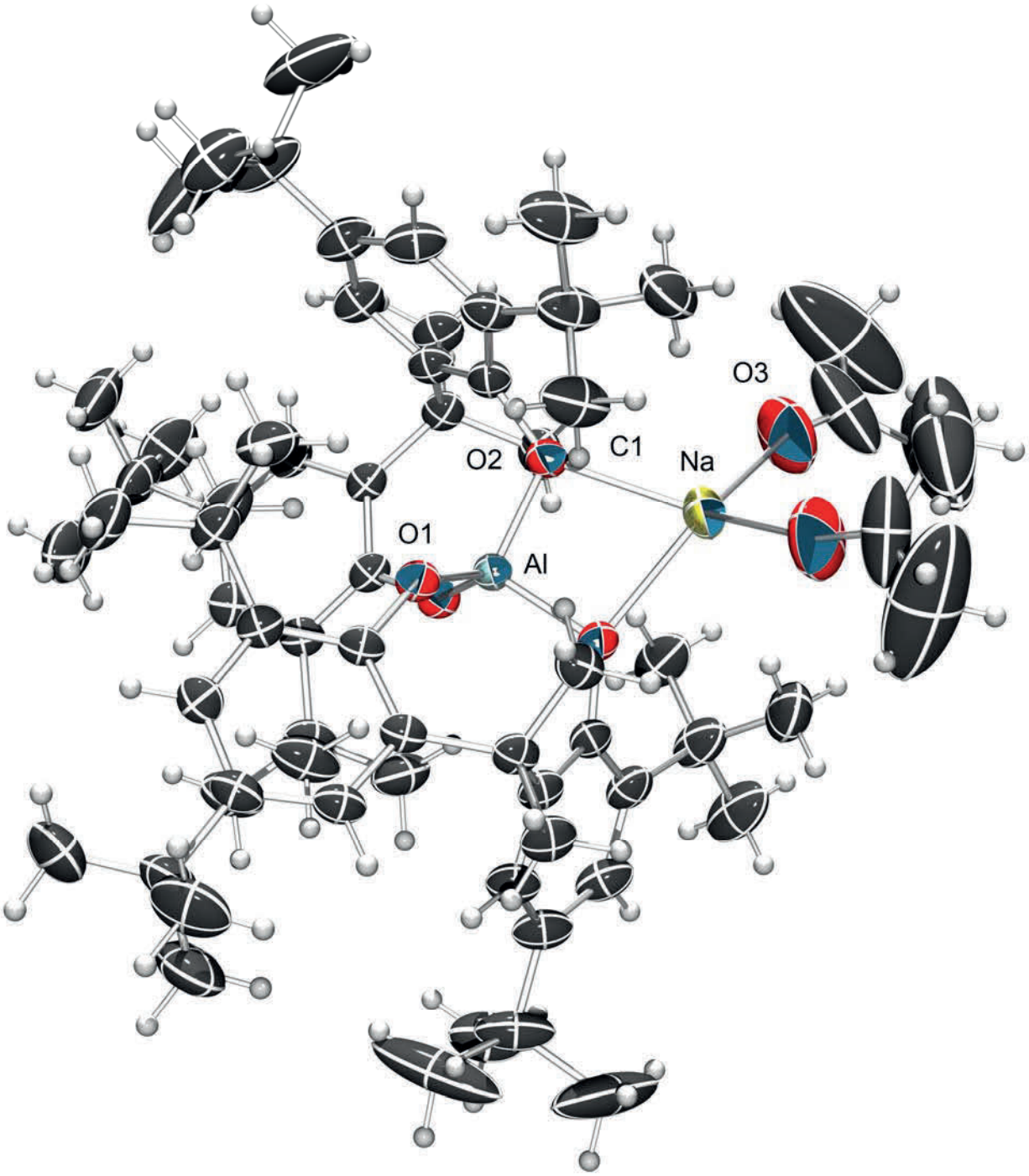
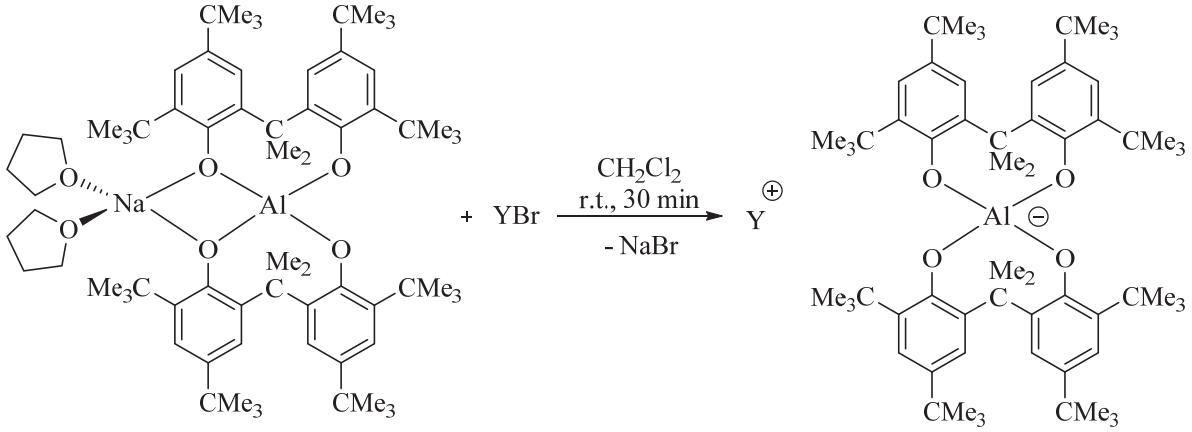


Figure 6. ORTEP ellipsoid-and-stick model of the single-crystal X-ray structure of the acetone adduct of sodium almebate (**4**). Color code: C black, H gray, O red, Al blue, Na yellow. Selected bond lengths (Å): Al-O2 1.7181(18), Al-O1 1.7742(18), Na-O2 2.344(2), Na-O1 2.244(3), Na-C1 2.830(17).[32,33]

Salt metathesis and slow hydrolysis

In salt metathesis reactions, the lithium or sodium cation can easily be exchanged by organic cations. We synthesized tetraphenylphosphonium almebate (**6**) with 95 % yield and tetrabutyl-ammonium almebate (**7**) with 99 % yield (Scheme 4). Single-crystals of tetraphenylphosphonium almebate were obtained by recrystallization from dichloromethane/pentane (Figure 7). Compound **7** is structurally characterized as a salt with separated ions. Tetraphenylphosphonium almebate is stable in a mixture of THF-d_8 and D_2O (4:1) at room temperature for several days. The rate of hydrolysis amounts to 2.5 % per week. The same result was observed with a tenfold excess of NaOH or NEt_3 in the same solvent system. In weakly acidic media, however, the hydrolysis proceeded faster than in the presence of base. Nevertheless, hydrolysis was much slower than with the analogous altebate salts that do not comprise the 2,2-propanediyl linker.[19] In a mixure of THF-d_8 and 1 M acetic acid in D_2O, 10 % of the almebate was decomposed after 21 hours and 45 % after a week. Upon addition of trifluoroacetic acid, the decomposition proceeded rapidly and the almebate anion was completely hydrolyzed within 30 minutes. This is consistent with increased steric hindrance towards nucleophilic attack at the aluminium center, while protonation-induced hydrolysis remains favorable.



Scheme 4. Salt metathesis of sodium almebate with phosphonium and ammonium bromides.

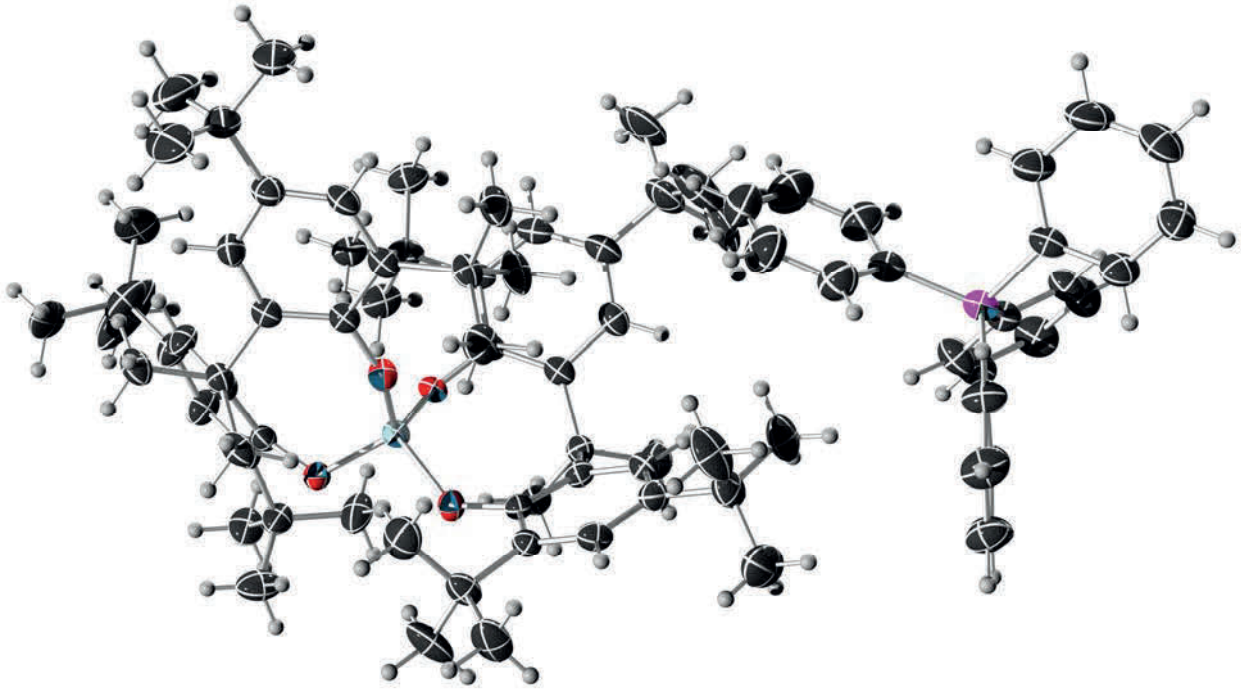
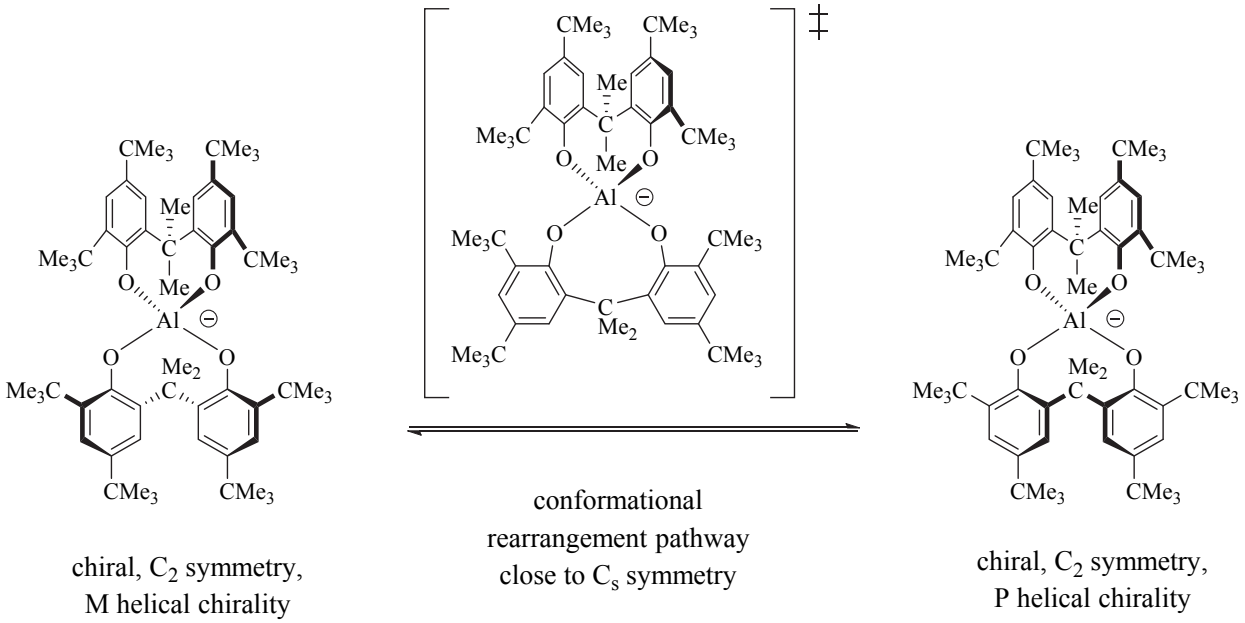


Figure 7. ORTEP ellipsoid-and-stick model of the single-crystal X-ray structure of tetraphenylphosphonium almebate (**6**). Color code: C black, H gray, O red, Al blue, P magenta.[32,33]

Degenerate rearrangement and five NMR coalescences

The inversion of the bowl-shaped bisphenolate aluminium fragment of the intrinsically chiral almebate anion leads to the formation of its enantiomer (Scheme 5). The almebate anion does not comprise stereogenic centers, but it features helical chirality.[35,36] The degenerate racemization reaction proceeds rapidly at room temperatures and below. We used the tetraphenylphosphonium salt **6** to rule out the influence of electrophilic alkali metal cations. We observed five coalescence phenomena by temperature-dependent ^{1}H NMR spectroscopy in acetone-d_6: two pairs of aromatic CH fragments, two CMe_2 groups and two pairs of *tert*-butyl substituents interconvert with an experimentally determined Gibbs free activation energy of $\Delta G^{\ddagger}$ 53.6 ± 2 kJ mol^{-1} (Table 1).

We were unable to use one particular coalescence of two pairs of aromatic CH fragment signals for the calculation of the racemization barrier due to the signals' apparently temperature-dependent chemical shifts even at low temperatures (Figure 8). Each of the five coalescence temperatures was determined at 500.13 MHz with an accuracy of 5 K, resulting in a computed barrier with low or no temperature-dependence (Figures 9, 10, and 11).



Scheme 5. Molecular origin of almebate's dynamic properties: racemization by a degenerate rearrangement.

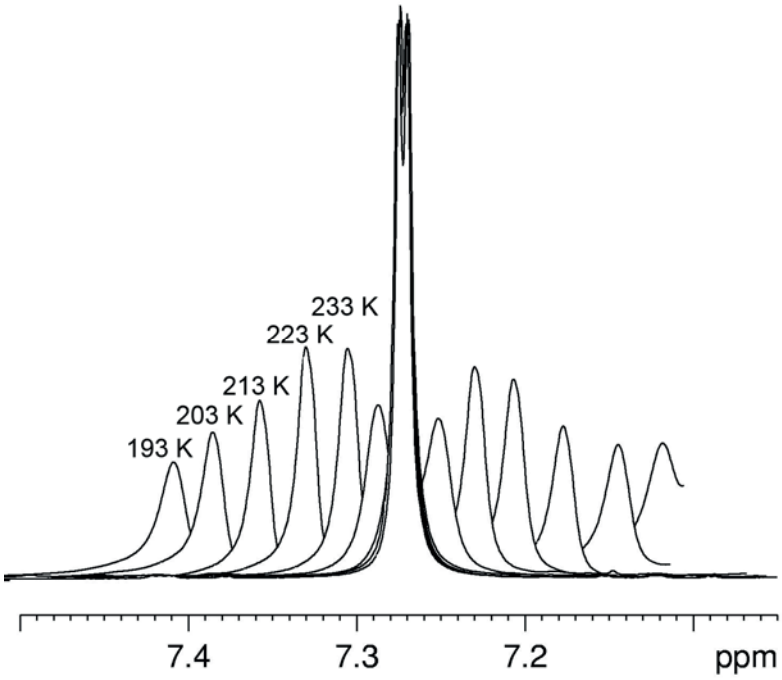


Figure 8. Front view on a temperature-dependent series of ^{1}H NMR spectra, aromatic signals of tetraphenylphosphonium almebate **6** in acetone-d_6, 500.13 MHz.

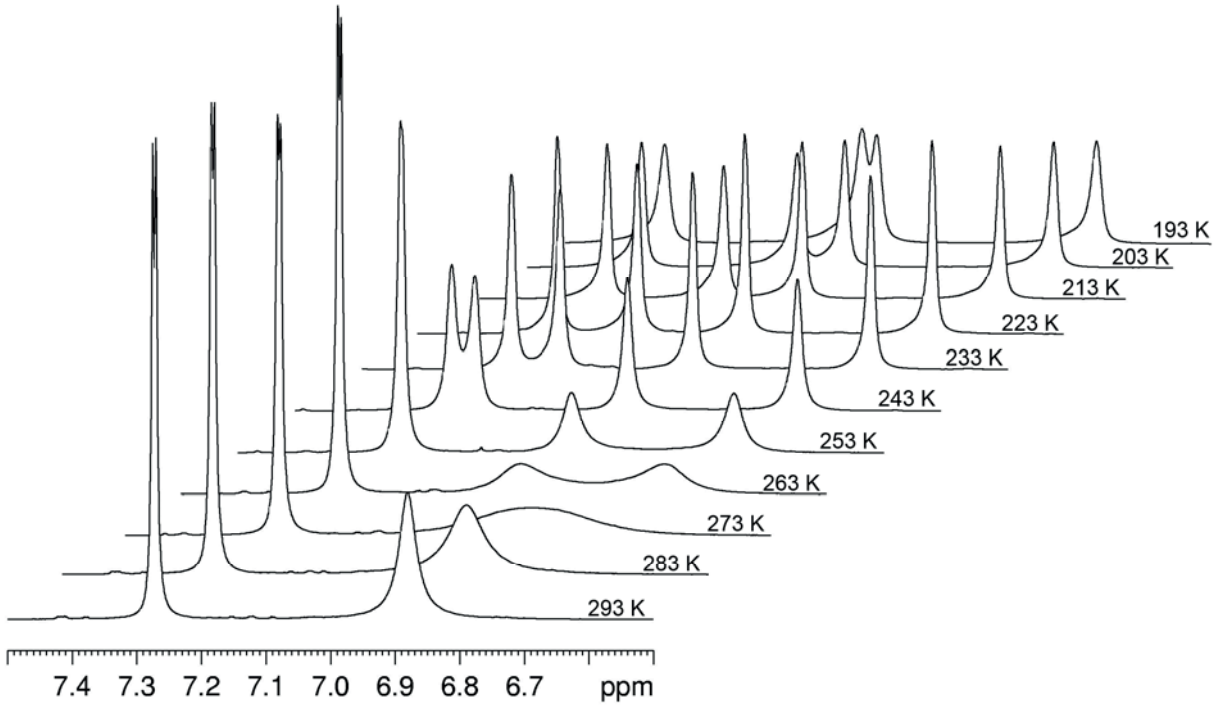


Figure 9. Side view on a temperature-dependent series of ^{1}H NMR spectra, aromatic signals of tetraphenylphosphonium almebate **6** in acetone-d_6, 500.13 MHz.

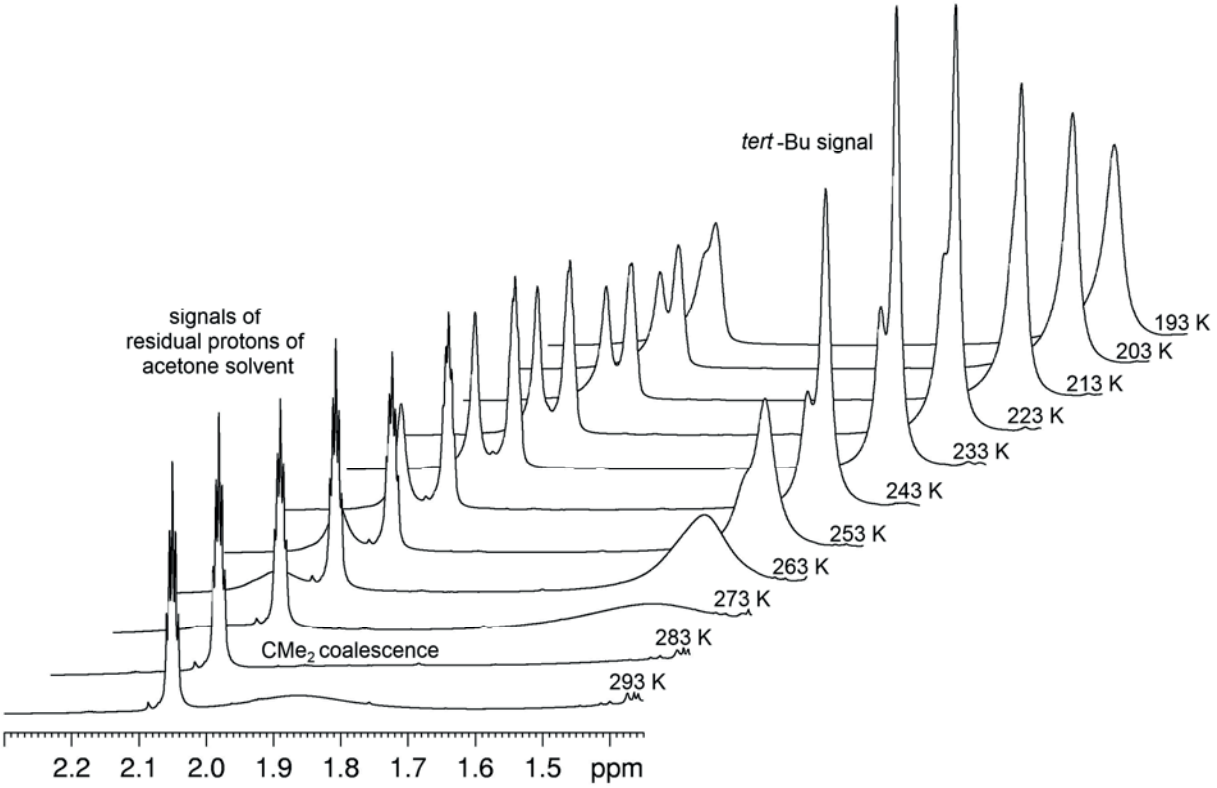


Figure 10. Side view on a temperature-dependent series of ^{1}H NMR spectra, CMe_2 signals of tetraphenylphosphonium almebate **6** in acetone-d_6, 500.13 MHz.

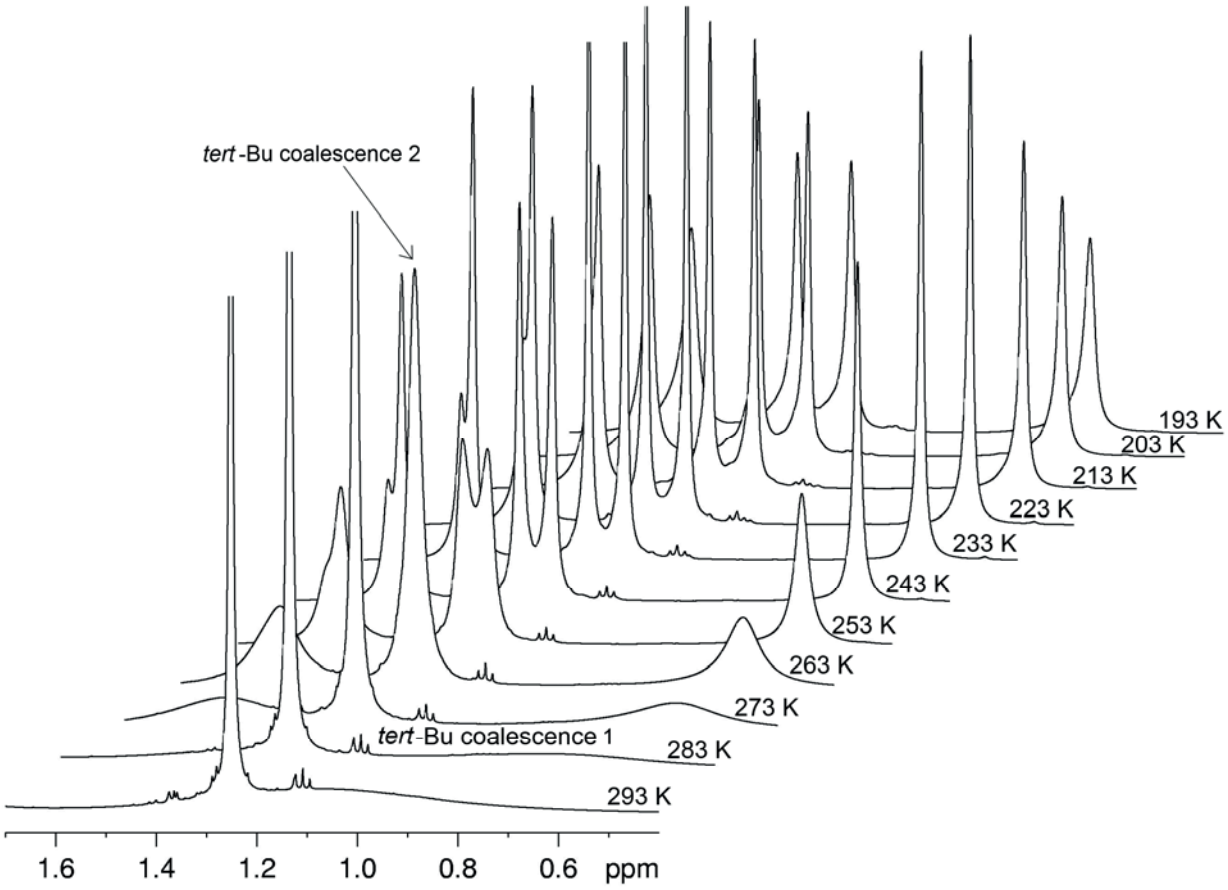


Figure 11. Side view on a temperature-dependent series of ^{1}H NMR spectra, *tert*-butyl signals of tetraphenylphosphonium almebate **6** in acetone-d_6, 500.13 MHz.

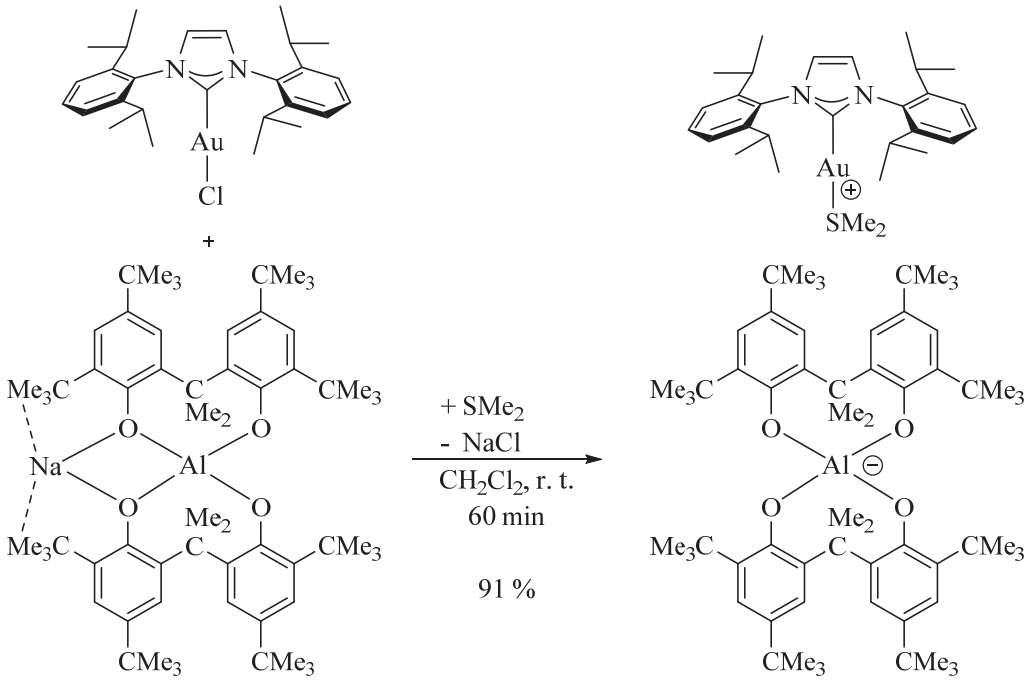
Table 1. Coalescence temperatures, interconverting molecular fragments, ^{1}H NMR chemical shift differences at 193 K, calculated exchange rates at the respective coalescence temperature, and Gibbs free activation barriers at the respective coalescence temperature for almebate salt **6** in acetone-d_6

T_c (± 5 K)	Fragment	Chemical shift difference [ppm]	k_c [s^{-1}]	$\Delta G_c^{\ddagger}$ [kJ mol^{-1}] (± 1 kJ mol^{-1})
250 K	$CH_{aromatic}$	T-dependent	-	-
258 K	*tert*-Bu	0.107	119	52.6
273 K	$CH_{aromatic}$	0.341	378	53.2
283 K	CMe_2	0.602	668	53.9
290 K	*tert*-Bu	0.794	881	54.6

Based on its facile rearrangement-racemization, the almebate ion or its derivatives might be suitable for applications in supramolecular chemistry and for chiroptic materials.[37]

Halide ligand elimination

In this section, we provide evidence for the weakly-coordinating nature of the almebate anion. Cationic gold complexes are potent electrophiles and excellent catalysts for alkyne transformation reactions.[38-43] The synthesis of IPrAu(SMe)$_2$ almebate (**8**) has been accomplished in high yield by the reaction of the "activated" sodium almebate (**5**) with IPrAuCl (Scheme 6). In a single-crystal X-ray structure, the almebate's almost tetrahedral AlO_4 core features Al-O bond lengths in the range of 1.734 - 1.741 Å (Figure 12).



Scheme 6. Chloride ligand elimination by thermally activated sodium almebate **5**.

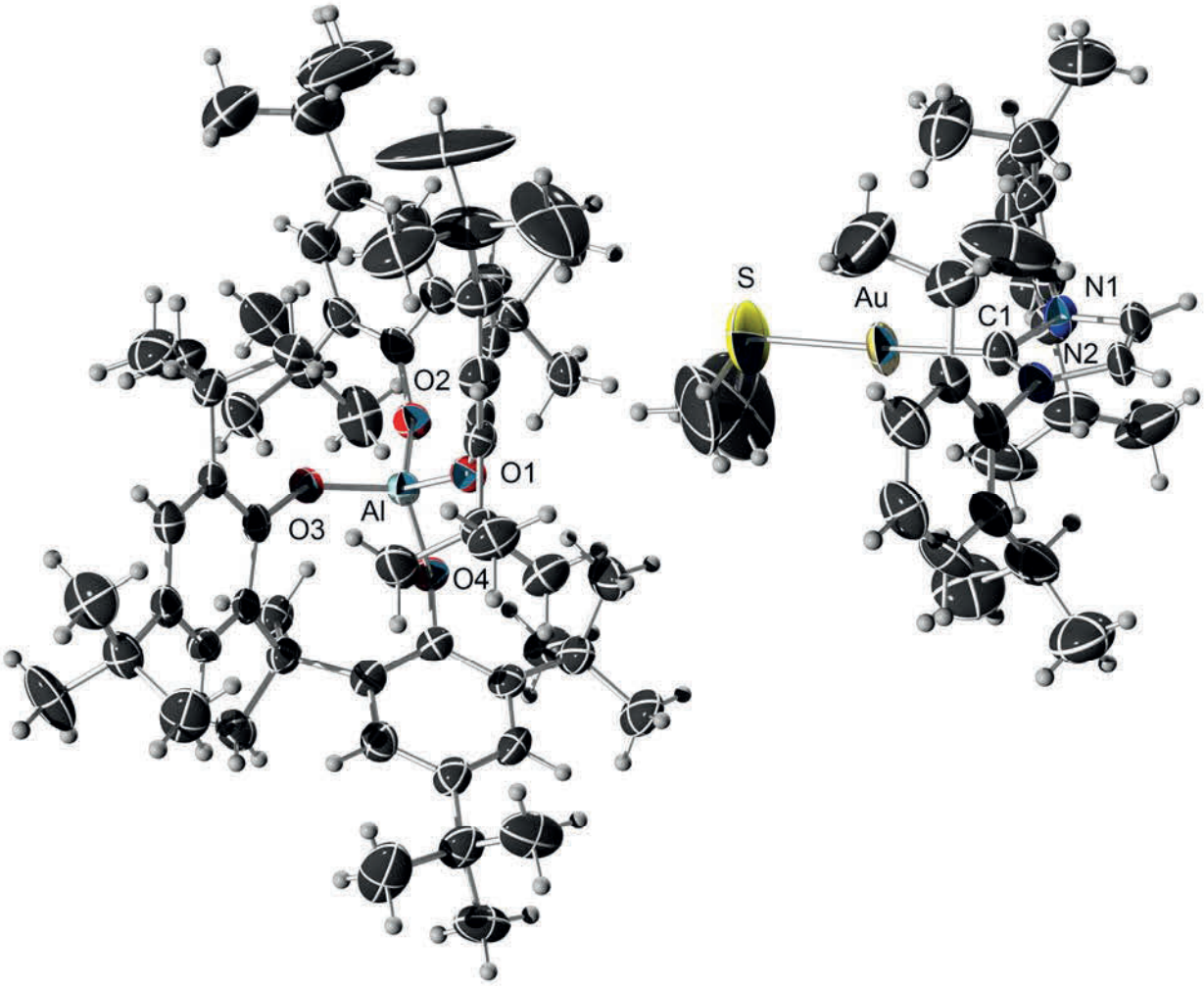
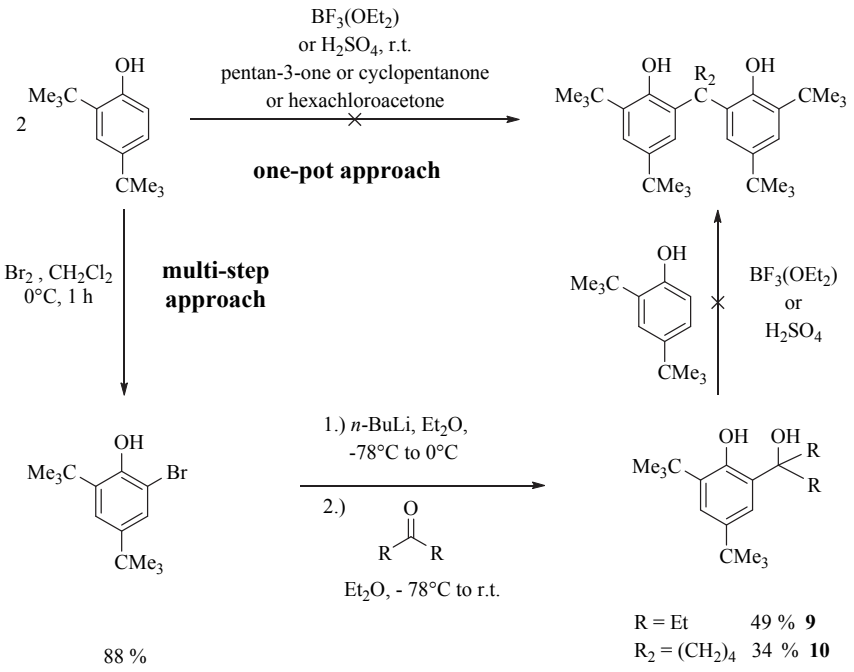


Figure 12. ORTEP ellipsoid-and-stick model of the single-crystal X-ray structure of IPrAu(SMe_2) almebate **8**. Color code: C black, H gray, N blue, O red, S yellow, Au gold, Al cadet blue. Selected bond lengths (Å): Au-S 2.293(5), Au-C1 1.997(6), N1-C1 1.343(8), N2-C1 1.348(7), Al-O1 1.733(4), Al-O2 1.733(4), Al-O3 1.737(4), Al-O4 1.741(4). Selected bond angles: S1-Au-C1 176.0°.[32,33]

Limitations of increasing the steric demand

We tried to formally exchange the CMe_2 linker by more bulky fragments, to further increase the steric shielding of the anionic AlO_4 core. The intention was to improve the hydrolytic stability, to weaken the aluminate's nucleophilicity and to limit its ability to coordinate to electrophilic metal cations. Other ketone substrates such as pentan-3-one or cyclopentanone, however, did not yield the desired bisphenols (Scheme 7), presumably due to inhibitive steric crowding in the intermediates.[44] Even a multi-step approach with isolated 1-hydroxyalkylphenol intermediates failed. Apparently, the accumulation of bulky substituents is not only a cause for higher activation energies in the final step of the synthesis of lipophilic aluminates, but already poses a challenge for the preparation of their respective ligand starting materials.



Scheme 7. Two failed strategies for the synthesis of even more sterically shielded bisphenols.

Summary

Salts of a new halogen-free, thermally stable aluminate anion have been synthesized from cost-efficient starting materials. The dimethylmethylene units that each link two phenolate ligand fragments enforce a C_2 symmetry of the aluminate anion. The dynamics of the racemization-rearrangement have been determined quantitatively by a temperature-dependent NMR study. The hydrolytic stability is significantly higher than that of other lipophilic aluminates described in literature. The thermally activated sodium salt readily eliminates chloride ligands from transition metal chloride complexes. The "almebate" anion coordinates to alkali metal cations, but has a low affinity for sterically demanding electrophiles such as a cationic NHC gold complex.

Experimental Section

General procedures. Chemicals were supplied by Acros, Aldrich, and TCI, and were used without further purification. Reactions involving air-sensitive reagents were carried out under N_2 or argon by using standard Schlenk techniques. Solvents were dried in an Mbraun MB SCS-800 solvent purification system. NMR spectra were recorded at 300 K by using Bruker ARX-250, Bruker Avance 300, Bruker Avance 500, or Bruker Avance 600 spectrometers. Chemical shifts

are reported in ppm relative to TMS, and were determined by reference to the ^{13}C or ^{1}H residual solvent peaks. Melting points were determined by using a Gallenkamp hot-stage microscope. THF was dried by an MBRAUN solvent purification system MB SPS-800.

6,6′-(Propane-2,2-diyl)bis(2,4-di-*tert*-butylphenol) (1).[28,29] Under inert gas conditions, boron trifluoride diethyl etherate (5.6 ml, 46 mmol, 1 eq) was slowly added to a solution of 2,4-di-*tert*-butylphenol (19.0 g, 92 mmol, 2 eq) in acetone (2.6 g, 46.0 mmol, 1 eq) at room temperature. The reaction mixture was stirred at room temperature for 16 h. Methanol at 0°C was added and stirred for 1 h. The resulting suspension was filtered, and the crude product was washed with methanol at 0°C. The crude product was purified by recrystallization from acetic acid.
Colorless crystals, yield 50 %, 10.5 g, mp: 191 °C (literature 174-175 °C)[28]; IR (KBr cm^{-1}): ῡ 3465, 2963, 2909, 2872, 1467, 1438, 1418, 1392, 1362, 1331, 1296, 1272, 1250, 1220, 1199, 1163, 876, 821, 796, 771. ^{1}H NMR (600.2 MHz, $CDCl_3$): δ_H 1.30 (18H, s, $C(CH_3)_3$) 1.37 (18H, s, $C(CH_3)_3$), 1.75 (6H, s, CH_3), 5.00 (2H, s, OH), 7.32 (2H, d, $^{4}J_{HH}$ 2.3 Hz, H_{Ph}), 7.43 (2H, d, $^{4}J_{HH}$ 2.3 Hz, H_{Ph}). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ_C 28.9 ($C(CH_3)_2$) 29.5 ($C(CH_3)_3$), , 31.7 ($C(CH_3)_3$), 34.7 (q- $C(CH_3)_3$), 35.3 (q- $C(CH_3)_3$), 40.4 (q- $C(CH_3)_2$), 119.7 (C_{Ph}), 124.0 (C_{Ph}), 130.7 (q-C_{Ph}) 137.4 (q-C_{Ph}), 143.0 (q-C_{Ph}) 151.8 (q-C_{Ph}) ppm. HR-MS (EI), m/z (%) for $C_{31}H_{48}O_2^{+}$: calcd. 452.3654, found 452.3662; Anal. Calcd. for $C_{31}H_{48}O_2$ C 82.24; H 10.69%; Found: C 82.05; H 10.72%. CCDC 958107.

Bis(tetrahydrofuran)lithium almebate (2). Under inert gas a solution of 6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenol) (**1**) (13.6 g, 30.0 mmol, 2 eq) in 90 ml dry THF was added slowly to a solution of $NaAlH_4$ (0.87 g, 15.0 mmol) in 10 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 2 d, and filtered through Celite. After removal of the solvent in vacuo, the resulting colorless foam was recrystallized from THF/pentane.
Colorless powder, yield: 75 %, 1.60 g, mp: 141°C. IR (KBr cm^{-1}): ῡ 3472, 2957, 2870, 1623, 1477, 1435, 1390, 1360, 1331, 1295, 1271, 1237, 1202, 1178, 1044, 880, 830, 783, 775, 660, 611. ^{1}H NMR (300.5 MHz, acetone-d_6): δ 0.72-1.32 (36 H, br s, $C(CH_3)_3$) 1.25 (36 H, s, $C(CH_3)_3$), 1.75-1.82 (8 H, m, thf), 1.67- 2.01 (12H, br s, $C(CH_3)_2$), 3.56-3.68 (m, 8 H, thf), 6.82-6.95 (4H, br s, H_{Ph}), 7.27 (4H, d, $^{4}J_{HH}$ 2.5 Hz, H_{Ph})) ppm. $^{13}C\{^{1}H\}$ NMR (75.4 MHz, acetone-d_6): δ 26.1 (thf), 28.9 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$) 32.3 ($C(CH_3)_2$), 34.5 (q-$C(CH_3)_3$) 35.6 (q-$C(CH_3)_3$), 42.8 (q-$C(CH_3)_2$), 68.0 (thf), 120.8 (C_{Ph}), 123.2 (C_{Ph}), 136.1 (q-C_{Ph}), 137.3 (qC_{Ph}), 138.6 (q-C_{Ph}), 157.2 (qC_{Ph}) ppm. HR-MS (ESI), m/z (%) for $C_{62}H_{92}AlO_4^{-}$ calcd. 927.6811, found 927.6791.

Bis(tetrahydrofuran)sodium almebate (3). Under inert gas a solution of 6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenol) (**1**) (13.6 g, 30.0 mmol, 2 eq) in 90 ml dry THF was added slowly to a solution of $NaAlH_4$ (0.87 g, 15.0 mmol, 1 eq) in 10 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 2 d, and filtered

through Celite. After removal of the solvent in vacuo, the resulting colorless foam was recrystallized from THF/pentane.
Colorless powder, yield: 70 %, 11.5 g, mp: 237°C decomp. with gas evolution. IR (KBr cm^{-1}): ϋ 3472, 2961, 2870, 1621, 1477, 1434, 1389, 1360, 1271, 1236, 1202, 1179, 1049, 885, 832, 783, 775, 751, 660, 610. ^{1}H NMR (300.5 MHz, acetone-d_6): δ 0.65-1.32 (36 H, br s, $C(CH_3)_3$) 1.26 (36 H, s, $C(CH_3)_3$), 1.75-1.82 (8 H, m, thf), 1.67- 2.01 (12H, br s, $C(CH_3)_2$), 3.56-3.68 (m, 8 H, thf), 6.78-6.92 (4H, br s, H_{Ph}), 7.27 (4H, d, $^4J_{HH}$ 2.5 Hz, H_{Ph})) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 26.1 (thf), 28.9 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$) 32.3 ($C(CH_3)_2$), 34.5 (q-$C(CH_3)_3$) 35.6 (q-$C(CH_3)_3$), 42.8 (q-$C(CH_3)_2$), 68.0 (thf), 120.8 (C_{Ph}), 123.3 (C_{Ph}), 136.1 (q-C_{Ph}), 137.3 (qC_{Ph}), 138.7 (q-C_{Ph}), 157.2 (q-C_{Ph}) ppm. HR-MS (ESI), m/z (%) for $C_{62}H_{92}AlO_4^-$ calcd. 927.6811, found 927.6793. Anal. Calcd. for $C_{70}H_{108}AlNaO_6$ C 76.74; H 9.94%; found C 76.52; H 9.54%.

Bis(acetone)sodium almebate (4). The ligand exchange at sodium was performed by dissolving bis(tetrahydrofuran)sodium bis[6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenolato)-]aluminate(III) (**3)** in acetone. Removal of the solvent in vacuo and recrystallization from acetone/pentane gave the product quantitatively.
Colorless powder, yield: 99 %, 1.51 g, mp: 253°C. IR (KBr cm^{-1}): ϋ 3413, 2961, 2868, 1710 (C=O), 1620, 1478, 1433, 1389, 1360, 1271, 1233, 1202, 1157, 928, 878, 832, 783, 776, 660. ^{1}H NMR (300.5 MHz, acetone-d_6): δ 0.65-1.31 (36 H, br s, $C(CH_3)_3$) 1.25 (36 H, s, $C(CH_3)_3$), 1.75-2.08 (12H, br s, $C(CH_3)_2$), 2.08 (s, 6 H,$CO(CH_3)_2$), 6.80-6.95 (4H, br s, H_{Ph}), 7.27 (4H, d, $^4J_{HH}$ 2.5 Hz, H_{Ph})) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, acetone-d_6): δ 30.2 (CH_3), 30.5 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$), 32.2 ($C(CH_3)_2$), 34.4 (q-$C(CH_3)_3$) 35.4 (q-$C(CH_3)_3$), 42.6 (q-$C(CH_3)_2$), 120.6 (C_{Ph}), 123.1 (C_{Ph}), 136.0 (q-C_{Ph}), 137.1 (qC_{Ph}), 138.5 (q-C_{Ph}), 157.1 (q-C_{Ph}), 209.9 (C=O) ppm. HR-MS (ESI), m/z (%) for $C_{62}H_{92}AlO_4^-$ calcd. 927.6811, found 927.6791. Anal. Calcd. for $C_{70}H_{108}AlNaO_6$:C 76.51; H 9.82%; found: C 76.44; H 10.02%. CCDC 958109.

Sodium almebate (5). This compound was obtained by elimination of the thf ligands at 120 °C and 0.1 mbar over 24 h in the solid state. The product was obtained as a colorless solid in quantitative yield.
Colorless powder, mp: 274°C. IR (KBr cm^{-1}): ϋ 3472, 2961, 2870, 1621, 1477, 1434, 1389, 1360, 1271, 1236, 1202, 1179, 1049, 885, 832, 783, 775, 751, 660, 610. ^{1}H NMR (600.2 MHz, acetone-d_6): δ 0.4-1.33 (72H, m, $C(CH_3)_3$), 1.62- 2.04 (12H, br s, $C(CH_3)_2$), 6.78-6.96 (4H, br s, H_{Ph}), 7.27 (4H, d, $^4J_{HH}$ 2.4 Hz, H_{Ph})) ppm. ^{1}H-NMR (400.1 MHz, CD_2Cl_2: δ 0.10-1.05 (18 H, br s, $C(CH_3)_3$), 1.28 (36 H, s, $C(CH_3)_3$), 1.06-1.72 (18 H, br s, $C(CH_3)_3$), 1.75- 2.45 (12H, br s, $C(CH_3)_2$), 6.82-7.18 (4H, br s, H_{Ph}), 6.82-7.18 (4H, br s, H_{Ph})) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, acetone-d_6): δ 30.3 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$) 32.3 ($C(CH_3)_2$), 34.5 (q-$C(CH_3)_3$) 35.5 (q-$C(CH_3)_3$), 42.7 (q-$C(CH_3)_2$), 120.7 (C_{Ph}), 123.2 (C_{Ph}), 136.0 (q-C_{Ph}), 137.2 (qC_{Ph}), 138.5 (q-C_{Ph}), 157.1 (q-C_{Ph}) ppm. $^{13}C\{^1H\}$-NMR (100.6 MHz, CD_2Cl_2): δ 29.5-30.5 ($C(CH_3)_3$ + $(C(CH_3)_2$), 31.9 ($C(CH_3)_3$) 34.5 (q-$C(CH_3)_3$) 35.3 (br s, q-$C(CH_3)_3$), 43.0 (q-$C(CH_3)_2$), 124.4 (2 C, br s, C_{Ph}), 136.9 (br s, q-C_{Ph}),, 138.5 (q-C_{Ph}), 139.5 (br, s, q-C_{Ph}), 153.7 (br s, q-C_{Ph}) ppm.

HR-MS (ESI), m/z (%) for $C_{62}H_{92}AlO_4^-$ calcd. 927.6811, found 927.6797.

Tetraphenylphosphonium almebate (6). Under inert gas, tetraphenylphosphonium bromide (100 mg, 0.25 mmol) in 4 mL dichloromethane was slowly added to a solution of bis(tetrahydrofuran)sodium bis[6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenolato)]aluminate(III) (**4**) (270 mg, 0.25 mmol) in 4 mL dichloromethane whilst stirring. A colorless solid (NaBr) precipitated. After stirring for 1 h at room temperature, the suspension was filtered through Celite and the solvent was removed in vacuo. Recrystallization from dichloromethane / diethyl ether gave the title product.

Colorless solid, yield: 95%, 300 mg, mp >300°C. IR (KBr): ῡ 2950, 2903, 2866, 1477, 1437, 1386, 1358, 1296, 1271, 1238, 1201, 1109, 876, 853, 786, 779, 724, 619, 528. ^{1}H NMR (300.5 MHz, acetone-d_6): δ 0.72-1.41 (36 H, br s, $C(CH_3)_3$), 1.26 (36 H, s, $C(CH_3)_3$) 1.65 – 2.05 (12H, br s, $C(CH_3)_2$), 6.78-6.96 (4H, br s, H_{Ph}), 7.27 (4H, d, $^4J_{HH}$= 2.2 Hz, H_{Ph}), 7.80-7.90 (16 H, m, H_{Ph}), 7.94-8.04 (4H, m, H_{Ph}) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, acetone-d_6): δ 31.8 ($C(CH_3)_3$), 32.4 ($C(CH_3)_2$), 34.7 (q-$C(CH_3)_3$), 35.8 (q-$C(CH_3)_3$), 42.9 (q-$C(CH_3)_2$), 118.5 (q-C_{Ph}), 119.7 (q-C_{Ph}), 121.0 (C_{Ph}), 123.4 (C_{Ph}), 131.5 (q-C_{Ph}), 131.6 (q-C_{Ph}), 135.7 (C_{Ph}), 136.3 (C_{Ph}), 136.5 (C_{Ph}), 136.6 (C_{Ph}), 137.5 (C_{Ph}), 138.8 (C_{Ph}), 157.4 (q-C_{Ph}) ppm. ^{31}P NMR (121 MHz, acetone-d_6): 23.0 ppm. HR-MS (ESI), m/z (%) for $C_{62}H_{92}AlO_4^-$ calcd. 927.6816, found 927.6809; for $C_{24}H_{20}P^+$ calcd. 339.1297, found 339.1293. Anal. Calcd. for $C_{86}H_{112}AlO_4P$: C 81.48, H 8.90; found: C 81.43, H 9.02. CCDC 958108.

Tetrabutylammonium almebate (7). Under inert gas tetrabutylammonium bromide (80 mg, 0.25 mmol) in 4 mL dichloromethane was slowly added to a solution of bis(tetrahydrofuran)sodium bis[6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenolato)]aluminate(III) (**4**) (270 mg, 0.25 mmol) in 4 mL dichloromethane whilst stirring. A colorless solid (NaBr) precipitated. After stirring for 1 h at room temperature, the suspension was filtered through Celite and the solvent was removed in vacuo. Recrystallization from diethyl ether / pentane gave the product.

Colorless solid, yield: 99%, 290 mg, mp 210 °C. IR (KBr): ῡ 3423, 2961, 1478, 1433, 1386, 1358, 1295, 1271, 1238, 1201, 1157, 925, 875, 806, 786, 778, 767, 661, 619. ^{1}H NMR (600.2 MHz, acetone-d_6): δ (0.72-1.41 (36 H, br s, $C(CH_3)_3$) 0.98 (12H, t, $^3J_{HH}$ 7.4 Hz, CH_3) 1.25 (36 H, s, $C(CH_3)_3$), 1.40-1.48 (8 H, m, CH_2), 1.69-2.02 (m, 20 H, CH_2, $C(CH_3)_2$), 3.44-3.49 (8 H, m, CH_2), 6.80-6.99 (4H, br s, H_{Ph}), 7.28 (4H, d, $^4J_{HH}$ 2.6 Hz, H_{Ph}) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 13.8 (CH_3), 20.3 (CH_2), 24.4, (CH_2), 31.6 ($C(CH_3)_3$), 32.4 ($C(CH_3)_2$), 34.6 (q-$C(CH_3)_3$)), 35.6 (q- $C(CH_3)_3$), 42.8 (q-$C(CH_3)_2$), 59.4 (N-CH_2), 120.8 (C_{Ph}), 123.2 (C_{Ph}), 136.1 (q-C_{Ph}), 137.4 (q-C_{Ph}), 138.7 (q-C_{Ph}), 157.3 (q-C_{Ph}) ppm. HR-MS (ESI), m/z (%) for $C_{62}H_{92}AlO_4^-$ calcd. 927.6816, found 927.6810; for $C_{16}H_{36}N^+$ calcd. 242.2842, found 282.2840. Anal. Calcd. for $C_{78}H_{112}AlNO_4$ C 80.01, H 11.02; N 1.20 found: C 79.56, H 11.05, N 1.22.

[Bis-1,3-(2,6-diisopropylphenyl)imidazole-2-ylidene](dimethylsulfide)gold almebate (8). Under inert gas a solution of mono(acetone)sodium bis[6,6′-(propane-2,2-diyl)bis(2,4-di-*tert*-butylphenolato]aluminate(III) (**5**) (88 mg 0.08 mmol) in 10 mL dry dichloromethane was added to a solution of (IPr)AuCl (50 mg, 0.09 mmol) and dimethylsulfide (0.1 ml, 0.14 mmol) at room temperature whilst stirring. A colorless solid (NaCl) precipitated. The resulting suspension was stirred for 1 h at room temperature. The suspension was filtered through Celite and the solvent was removed under vacuum. Recrystallization from dichloromethane / pentane gave the title product.

Colorless solid, yield: 91 %, 115 mg, mp 198°C. IR (KBr): ῡ 3445, 3158, 3112, 3075, 2961, 2869, 1595, 1550, 1458, 1433, 1386, 1358, 1295, 1271, 1238, 1201, 1180, 1157, 1129, 1059, 1033, 987, 948, 925, 875, 856, 804, 786, 778, 758, 704, 661, 619. ^{1}H NMR (600.2 MHz, acetone-d_6): δ 0.39-1.02 (36 H, br s, $C(CH_3)_3$) 1.17 - 1.21 (60 H, m, $C(CH_3)_3$, Me), 1.51-2.03 (12H, br s, $C(CH_3)_2$), 2.13 (6 H, s, $S(CH_3)_2$), 2.38 (4H, pseudo-sept, $^{3}J_{HH}$ 6.9 Hz, $CH(CH_3)_2$), 6.76-6.85 (4H, br s, H_{Ph}), 7.16 (4H, d, $^{4}J_{HH}$= 2.6 Hz, H_{Ph}), 7.20 (2H, s, NHC=CHN), 7.29 (4H, d, $^{3}J_{HH}$ 7.8 Hz, H_{Ph}), 7.50 (2H, t, $^{3}J_{HH}$= 7.8 Hz, H_{Ph}) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 24.2 ($CH(\mathbf{C}H_3)_2$), 25.1 ($\mathbf{C}H(CH_3)_2$), 29.8 ($\mathbf{C}H(CH_3)_2$), 30.5 ($S(CH_3)_2$), 31.8 ($C(CH_3)_3$), 32.6 (2 C, $C(CH_3)_2$, $(C(CH_3)_3$), 34.7 (q-$C(CH_3)_3$), 35.8 (q-$C(CH_3)_3$), 43.0 (q-$C(CH_3)_2$), 120.8 (C_{Ph}), 123.2 (C_{Ph}), 125.4 (C_{Ph}), 126.4 (C_{Ph}), 132.2 (C_{Ph}), 136.3 (C_{Ph}), 137.6 (C_{Ph}), 138.9 (C_{Ph}), 146.9, (q-C_{Ph}), 157.4 (q-C_{Ph}), 177.4 (N_2CAu) ppm. HR-MS (ESI), m/z (%) for $C_{62}H_{92}AlO_4^-$ calcd. 927.6816, found 927.6792; for $C_{29}H_{42}NAuS^+$ calcd. 647.2728, found 647.2720. Anal. Calcd. for $C_{91}H_{134}AlAuN_2O_4$ C 69.30, H 8.63; N 1.78 S 2.03 found: C 69.09, H 8.70, N 1.78 S 2.10. CCDC 958110.

Synthesis of 2-bromo-4,6-di-*tert*-butylphenol. The synthetic protocol of Akai et al. was used.[45] A solution of bromine (0.50 mL, 9.7 mmol) in dichloromethane (10 mL) was added dropwise to a solution of 2,4-di-*tert*-butylphenol in dichloromethane (2 mL) at 0°C. After stirring of the orange solution for an additional hour at this temperature, water was added and the phases were separated. The organic layer was washed six times with water and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation under reduced pressure and purified by silica gel column chromatography with pentane as eluent.

Colorless powder, yield 88 %, 2.4 g, mp 63 °C. IR (KBr cm^{-1}): ῡ 3509, 2997, 2965, 2870, 1786, 1567, 1476, 1447, 1403, 1394, 1364, 1334, 1280, 1253, 1202, 1178, 1137, 1090, 934, 896, 870, 840, 820, 745, 714, 645, 607, 545, 511. ^{1}H NMR (300.5 MHz, $CDCl_3$): δ_H 1.28 (9H, s, $C(CH_3)_3$), 1.40 (9H, s, $C(CH_3)_3$), 5.64 (1H, s, OH), 7.24 (2H, d, $^{4}J_{HH}$ 2.4 Hz, H_{Ph}), 7.32 (2H, d, $^{4}J_{HH}$ 2.4 Hz, H_{Ph}). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ_C 29.5 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 34.5 (q-$C(CH_3)_3$), 35.7 (q-$C(CH_3)_3$), 112.0 (q-C_{Ph}), 123.8 (C_{Ph}), 126.4 (C_{Ph}), 136.8 (q-C_{Ph}), 143.8 (q-C_{Ph}), 148.1 (q-C_{Ph}) ppm. HR-MS (ESI), m/z (%) for $C_{14}H_{20}BrO^+$: calcd. 283.0703, found 283.0702.

Synthesis of 2,4-di-*tert*-butyl-6-(3-hydroxypent-3-yl)phenol (9). In a flame dried flask 3.3 mL n-Buli (1.6 M in hexane, 5.4 mmol, 2 eq) was added at -78°C to a solution of 2-bromo-4,6-di-

tert-butylphenol (0.70 g, 2.7 mmol, 1 eq) in 50 mL of dry diethyl ether. The solution was warmed to 0°C and stirred for 30 min. After re-cooling to -78°C a solution of 0.25 g pentan-2-one (2.8 mmol, 1.1 eq.) in 6 mL diethyl ether was added dropwise. After warming to room temperature and stirring for two hours saturated aqueous ammonium chloride solution was added. Additional diethyl ether was added the organic layer was separated. The organic layer was washed three times with water and saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate and filtered. The solvent was removed by evaporation under reduced pressure and further purified by column chromatography on a silica gel column
Light yellow powder, yield 49 %, 0.39 g, m.p. 55 °C. IR (KBr cm^{-1}): ϑ 3424, 3115, 2961, 2880, 1768, 1614, 1440, 1391, 1373, 1361, 1278, 1234, 1202, 1159, 1135, 1122, 961, 879, 816, 764, 722. ^{1}H NMR (300.5 MHz, CD_2Cl_2): δ_H 0.89 (6H, t, $^{3}J_{HH}$ 7.4 Hz, CH_2CH_3), 1.28 (9H, s, $C(CH_3)_3$), 1.41 (9H, s, $C(CH_3)_3$), 1.83 -2.06 (4H, m, CH_2), 2.33 (1H, s, OH), 6.83 (2H, d, $^{4}J_{HH}$ 2.4 Hz, H_{Ph}), 7.20 (2H, d, $^{4}J_{HH}$ 2.4 Hz, H_{Ph}), 9.58 (1H, s, OH). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ_C 8.2 (CH_3), 29.9 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 33.7 (q-$C(CH_3)_3$), 34.4 (q-$C(CH_3)_3$), 35.4 (CH_2), 82.9 (1H, s, C-OH), 122.2 (C_{Ph}), 123.1 (C_{Ph}), 126.2 (q-C_{Ph}), 136.7 (q-C_{Ph}), 140.2 (q-C_{Ph}), 154.3 (q-C_{Ph}) ppm. HR-MS (ESI), m/z (%) for $C_{19}H_{31}O_2^+$: calcd. 291.2329, found 291.2327.

Synthesis of 2,4-di-*tert*-butyl-6-(1-hydroxycyclopentyl)phenol (10). In a flame dried flask 3.3 mL n-Buli (1.6 M in hexane, 5.4 mmol, 2 eq) was added at -78°C to a solution of 2-bromo-4,6-di-*tert*-butylphenol (0.70 g, 2.7 mmol, 1 eq) in 50 mL of dry diethyl ether. The solution was warmed to 0°C and stirred for 30 min. After re-cooling to -78°C a solution of 0.24 g cyclopentanone (2.8 mmol, 1.1 eq.) in 6 mL diethyl ether was added dropwise. After warming to room temperature and stirring for two hours saturated aqueous ammonium chloride solution was added. Additional diethyl ether was added the organic layer was separated. The organic layer was washed three times with water and saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate and filtered. The solvent was removed by evaporation under reduced pressure and further purified by column chromatography on a silica gel column and sublimation.
Light yellow powder, yield 34 %, 0.27 g, mp 125 °C. IR (KBr cm^{-1}): ϑ 3500, 3266, 3001, 2964, 2874, 1479, 1445, 1395, 1363, 1333, 1244, 1204, 1187, 1159, 1077, 991, 876, 834, 815, 719. ^{1}H NMR (300.5 MHz, CD_2Cl_2): δ_H 1.28 (9H, s, $C(CH_3)_3$), 1.41 (9H, s, $C(CH_3)_3$), 1.72-2.02 (4H, m, CH_2), 2.07 -2.15 (4H, m, CH_2), 2.24 (1H, s, OH), 7.03 (2H, d, $^{4}J_{HH}$ 2.4 Hz, H_{Ph}), 7.23 (2H, d, $^{4}J_{HH}$ 2.4 Hz, H_{Ph}), 8.89 (1H, s, OH). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ_C 23.3 (CH_2) 29.8 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 34.6 (q-$C(CH_3)_3$), 35.4 (q-$C(CH_3)_3$), 39.8 (CH_2), 86.7 (1H, s, q-C-OH), 120.0 (C_{Ph}), 123.6 (C_{Ph}), 129.1 (q-C_{Ph}), 136.8 (q-C_{Ph}), 140.8 (q-C_{Ph}), 153.7 (q-C_{Ph}) ppm. HR-MS (ESI), m/z (%) for $C_{19}H_{29}O_2^+$: calcd. 289.2173, found 289.2170.

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