

A Lipophilic, Fluorine-Free, Thermostable, Inexpensive, S_4 -Symmetric, Highly Soluble, Weakly Coordinating, Protolabile Aluminate

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This communication presents the facile and cost-effective synthesis as well as properties of salts of a lipophilic aluminate anion. Its unprecedented solubility in pentane makes possible tetrabutylammonium salt extraction with pentane. Nevertheless, its symmetry leads to high melting points of its thermostable salts. Several single crystals for X-ray diffrac-

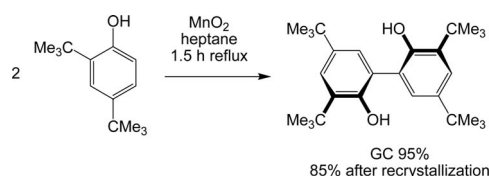
tion studies have been obtained. The anion is devoid of halogens, but is stable against sterically demanding electrophiles such as the trityl cation. However, it is unstable in protic media and hydrolyzes in the presence of water within days.

Introduction

The term “lipophilic anion” appears to be a paradox. The electric charge separation of salts in cations and anions is best stabilized by a polar, hydrophilic environment. However, lipophilic anions are characterized by a low negative charge, large molecular dimensions, and a lipophilic molecular surface. Related weakly coordinating anions (WCA) usually comprise fluorine substituents,^[1] resulting in more fluorophilic behavior. The most important structural features of WCAs are, on the one hand, multiple C–F fragments in order to electronically conceal and, on the other hand, bulky substituents to sterically conceal nucleophilic sites within the anion. In contrast, the main principles of designing lipophilic anions are the minimization of electrostatic contact with the positive counterion and maximization of van der Waals interactions with nonpolar solvents. The permethylated carboranes of the Michl group can be considered as lipophilic anions.^[2] Our strategy for a lipophilic aluminate anion avoids expensive and persistent C–F bonds and uses large and inexpensive *tert*-butylated 2,2'-biphenols for an extended hydrocarbon molecular surface.

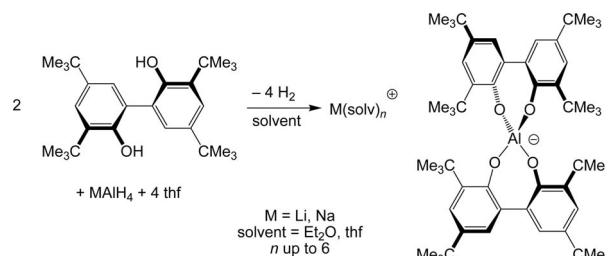
Results and Discussion

3,3',5,5'-Tetra-*tert*-butyl-2,2'-biphenol can be synthesized under ambient conditions by a modified literature protocol comprising oxidative C–C coupling of commercially available 2,4-di-*tert*-butylphenol with MnO_2 and recrystallization from acetic acid (Scheme 1).^[3]



Scheme 1. Oxidative C–C coupling for biphenol ligand synthesis.^[3a]

The reaction of this 2,2'-biphenol with $LiAlH_4$ or $NaAlH_4$ in diethyl ether or THF is fast and quantitative (Scheme 2). The resulting AlO_4 core of the *aluminate* anion is sterically shielded by eight *tert*-butyl groups. Accordingly, we named this anion *altebate*. At room temperature, the *altebate* anion hydrolyzes slowly within days in thf/H_2O solution. However, addition of aqueous NaOH or CF_3CO_2H leads to rapid hydrolysis. The solid lithium *altebate* thf adduct can be handled in air, but it has to be stored in the absence of water.



Scheme 2. Quantitative preparation of ether adducts of alkali metal *altebate* salts.

The S_4 symmetric *altebate* is an achiral *meso* structure due to an inner racemate of its two atropisomeric 2,2'-biphenolate ligands (Figure 1, left). The diastereomer with D_2 symmetry is higher in energy by 18.8 kJ/mol at the B3LYP/LACV3P**++ level of theory, because of the disadvantageous repulsion of *tert*-butyl groups (Figure 1, right).^[4]

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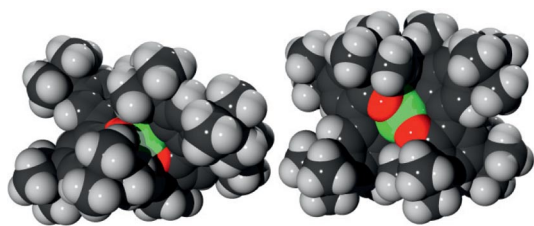


Figure 1. Computed space-filling albate model structure with S_4 symmetry (left) and its never-observed higher-energy diastereomer with D_2 symmetry (right); C black, H gray, O red, Al green.^[5]

The thf adduct of lithium albate is exceptionally soluble in pentane (7 g/L at room temperature). We are unaware of alkali metal salts with nonbonded anions and cations that are reasonably soluble in pentane or hexanes.^[6] However, the electric conductivity of the pentane solution remains unaffected, indicating the presence of contact ion pairs in solution. We attribute the unprecedented solubility to the aliphatic and therefore truly lipophilic molecular surface of the albate anion.^[7] The hydrogen atoms at the top layer of the molecular surface are positively polarized (Figure 2, top). In contrast to more fluorophilic WCAs such as the “Teflon ball” of the Krossing group (Figure 2, bottom),^[8] the albate can be considered as an anionic “wax ball”.^[9]

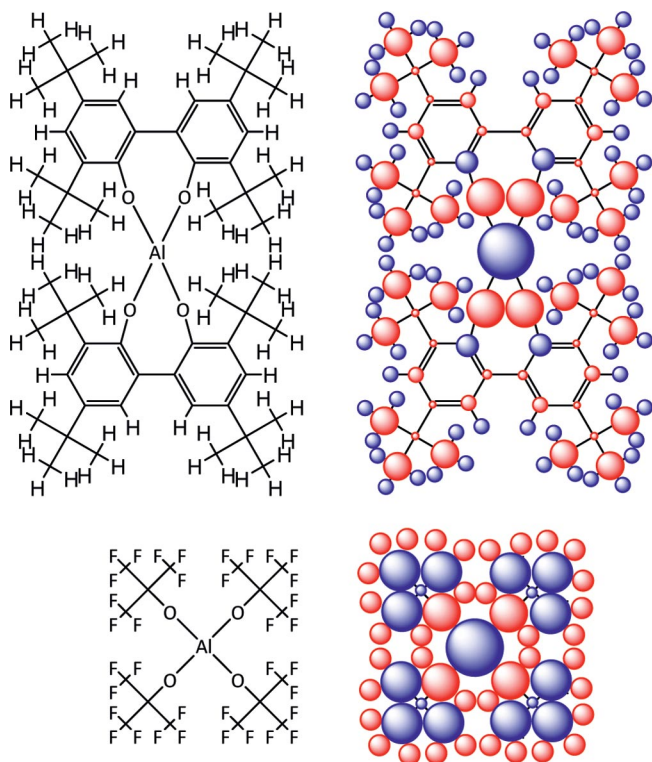


Figure 2. Computed atomic natural bond charge (NBC)^[10] distribution of the lipophilic albate “wax ball” (top) and of Krossing’s fluorophilic “Teflon ball” (bottom). Blue indicates positive atomic charge, red denotes negative charge. The area is proportional to the amount of partial charge.

As a result of their high symmetry, albate salts have a high tendency to crystallize (Figure 3). Furthermore, their NMR spectra display only few signals.

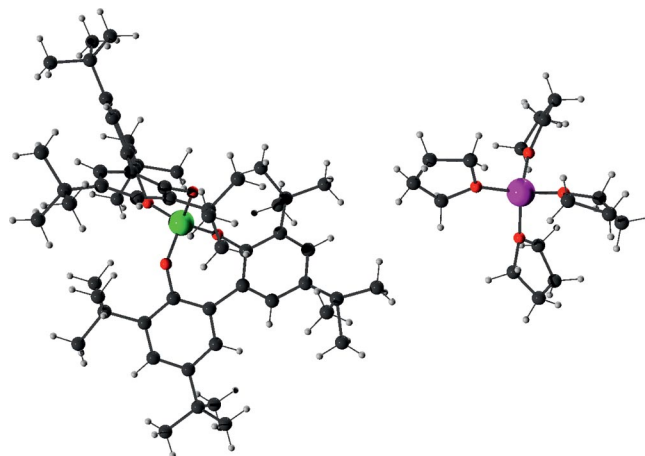


Figure 3. Single-crystal X-ray structure of the thf adduct of lithium albate; C black, H gray, O red, Li scarlet, Al green.^[5]

In salt metathesis reactions, alkali metal cations can easily be exchanged by more lipophilic cations. Addition of imidazolinium chlorides to lithium albate in CH_2Cl_2 gives a precipitate of LiCl . Hydrogen bonding of an imidazolinium cation to an ether molecule in the solid state clearly reflects the comparatively weak coordination ability of the albate anion (Figure 4). Albate salts of lipophilic (imidazolinium) cations do not require storage in inert gas even over prolonged periods of time.

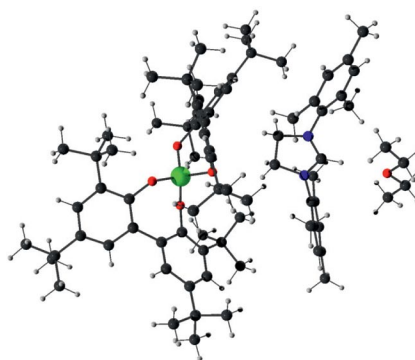
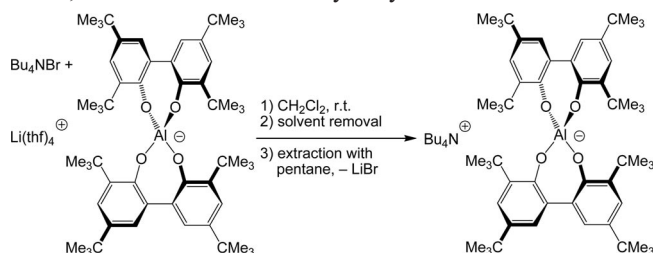


Figure 4. Single-crystal X-ray structure of diethyl ether with a hydrogen bond to the cation of 1,3-dimesitylimidazolinium albate; C black, H gray, O red, N blue, Al green.^[5]

The high lipophilicity of albate salts can advantageously be used for salt metathesis: Reaction of tetrabutylammonium bromide with lithium albate in CH_2Cl_2 , removal of the solvent in vacuo, extraction of the remaining solid with pentane, and eventual pentane removal in vacuo yields pure tetrabutylammonium albate (Scheme 3). Its solubility in pentane at room temperature is an unprecedented 33 g/L. We are unaware of any reports of salts featuring a comparable solubility in pentane. Tetrabutylammo-

nium albeate decomposes slowly at room temp. in a mixture of 0.4 mL $[D_8]thf$ and 0.1 mL D_2O . Within seven hours, 5% of the albeate is hydrolyzed.



Scheme 3. Unprecedented extraction of a salt with pentane.

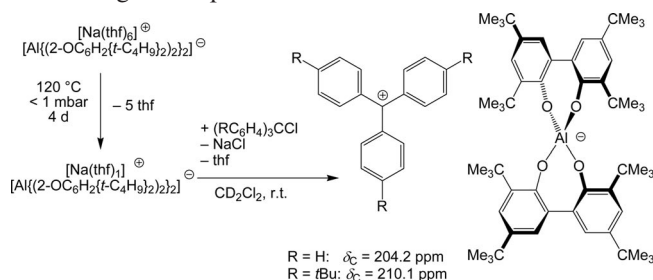
The costs of the starting materials 2,4-di-*tert*-butylphenol, MnO_2 , and $LiAlH_4$ lead to lithium albeate prices of less than 0.1 €/g (see Table 1).

Table 1. Prices of salts of lipophilic and weakly coordinating anions.

Salt	Catalogue price in €/g (€/mol) ^[a]	Price of starting materials in €/g (€/mol) ^[b]
$Na[B(C_6F_5)_4]^{[11]}$	305 (232 000)	5 (4 000)
$Na[B(C_6H_3(CF_3)_2)_4]^{[12]}$	270 (239 000)	17 (15 000)
$LiAl[OC(CF_3)_3]_4^{[8]}$	285 (278 000)	48 (47 000)
$Cs[CB_{11}H_{12}]^{[13]}$	630 (174 000)	63 (17 500)
$PPh_4[CB_{11}Me_{12}]^{[2a]}$	–	212 (135 000) ^[c]
$Li(thf)_4$ albeate	–	< 0.1 (< 100)
$Na[BPh_4]$	< 1 (300)	< 0.1 (< 50)

[a] Neither tax nor rebate included, based on largest and cheapest package. [b] Without solvents, based on literature yields and catalogue prices. [c] With 2,6-di-*tert*-butylpyridine recovery; for more details see Supporting Information.

The *thf* ligands of sodium albeate can be eliminated by heating at 120 °C under vacuum (< 1 mbar) for four days.^[14] The resulting sodium salt with a ratio *thf*/Na $\approx$ 1 reacts instantaneously with triarylchloromethanes in CD_2Cl_2 , leading to yellow to orange thermally stable solutions (Scheme 4). $^{13}C\{^1H\}$ NMR spectra display carbocation signals. The “frustrated” trityl Lewis acid/albeate Lewis base pair, however, is easily and rapidly decomposed by water. Thus, its use as WCA will be limited to sterically demanding electrophiles.



Scheme 4. Reaction of sodium albeate with trityl chlorides.

Conclusions

We have presented the synthesis and unique properties of sterically shielded aluminate salts and demonstrated the

unprecedented lipophilicity, thermal stability, solubility in pentane, and low tendency of the albeate anion towards coordination to trityl cations. NMR spectroscopic studies, single-crystal X-ray diffraction of salts with large cations, the preparation of salts with cationic transition metal catalysts, and application in polymers and materials are further targets of the albeate anion. Preparation and use of inexpensive and comparatively environmentally benign albeate salts appears feasible even on an industrial scale.

Experimental Section

3,3',5,5'-Tetra-*tert*-butyl-2,2'-biphenol:^[15] A round-bottomed flask was charged with 2,4-di-*tert*-butylphenol (50 g, 0.24 mol) and MnO_2 (31 g, 88% purity, 0.31 mol). The solids were suspended in heptane (400 mL). The reaction mixture was refluxed for 1.5 h. Ambient conditions are tolerated. After reaction control (GC: 95% conversion), the suspension was filtered through Celite and washed with CH_2Cl_2 . Removal of the solvent gave a brown crude product. After recrystallization from glacial acetic acid, colorless crystals were obtained. Yield: 42.1 g (103 mmol, 85%). 1H NMR (300.13 MHz $CDCl_3$, 25 °C): δ = 7.41 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Ar-H), 7.31 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Ar-H), 5.23 (br. s, 2 H, OH), 1.47 (s, 18 H, CMe_3), 1.34 (s, 18 H, CMe_3) ppm. 1H NMR (250.13 MHz, $[D_8]thf$, 25 °C): δ = 7.29 (m, 2 H, Ar-H), 7.06 (d, $^4J_{H,H}$ = 5.0 Hz, 2 H, Ar-H), 1.42 (s, 18 H, CMe_3), 1.27 (s, 18 H, CMe_3) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 149.8 (C_{Ar}), 143.0 (C_{Ar}), 136.2 (C_{Ar}), 125.3 (C_{Ar}), 124.8 (C_{Ar}), 122.3 (C_{Ar}), 35.2 (CMe_3), 34.5 (CMe_3), 31.6 (CH_3), 29.7 (CH_3) ppm. Mp: 204 °C. IR (KBr): $\tilde{\nu}$ = 3525, 3960, 2908, 2807, 1476, 1436, 1402, 1391, 1363, 1333, 1282, 1267, 1235, 1200, 1170, 1134, 1094, 883, 815, 770 cm^{-1} . $C_{28}H_{42}O_2$ (410.63): calcd. C 81.90, H 10.31; found C 82.13, H 10.50. MS (ESI+): m/z (%) = 410.5 (25) $[M]^+$, 409.5 (100) $[M - H]^+$.

Lithium Tetrakis(tetrahydrofuran)bis(3,3',5,5'-tetra-*tert*-butyl-2,2'-diphenolato)aluminate(III): Under inert gas, $LiAlH_4$ (110 mg, 2.90 mmol) of good quality was dissolved in *thf* (5 mL), obtained by distillation from Na/Ph_2CO . A solution of 3,3',5,5'-tetra-*tert*-butyl-2,2'-biphenol (2.38 g, 5.80 mmol) in *thf* (5 mL) was added slowly until H_2 formation ceased. Removal of the solvent in vacuo gave 3.28 g of a colorless powder in 99% yield. 1H NMR (300.13 MHz, $[D_8]thf$, 25 °C): δ = 7.06 (d, $^4J_{H,H}$ = 2.5 Hz, 4 H, Ar-H), 6.88 (d, $^4J_{H,H}$ = 2.5 Hz, 4 H, Ar-H), 1.25 (s, 36 H, CMe_3), 1.24 (s, 36 H, CMe_3) ppm. 1H NMR (250.13 MHz, $CDCl_3$, 25 °C): δ = 7.29 (d, $^4J_{H,H}$ = 2.5 Hz, 4 H, Ar-H), 7.06 (d, $^4J_{H,H}$ = 2.5 Hz, 4 H, Ar-H), 1.33 (s, 36 H, CMe_3), 1.28 (s, 36 H, CMe_3) ppm. $^{13}C\{^1H\}$ NMR (75.476 MHz, $[D_8]thf$, 25 °C): δ = 158.3 (C_{Ar}), 140.0 (C_{Ar}), 139.0 (C_{Ar}), 134.8 (C_{Ar}), 129.7 (C_{Ar}), 123.0 (C_{Ar}), 37.2 (CMe_3), 35.9 (CMe_3), 33.7 (Me), 32.6 (Me) ppm. Mp. 197 °C. IR (KBr): $\tilde{\nu}$ = 3419, 2960, 2906, 2863, 1640, 1464, 1431, 1405, 1387, 1360, 1284, 1242, 1200, 1100, 1049, 917, 874, 802, 783, 769, 683, 606 cm^{-1} . $C_{72}H_{112}AlLiO_8$ (1139.58): calcd. C 75.89, H 9.91; found C 75.53, H 9.82. MS (ESI): m/z (%) = 843.6 (100) $[M]^+$. X-ray: a single-crystal was obtained by crystallization from CH_2Cl_2 .

Sodium Pentakis(tetrahydrofuran) Albeate: Under inert gas, sodium aluminum hydride (270 mg, 5.11 mmol) was dissolved in *thf* (15 mL). A solution of 3,3',5,5'-tetra-*tert*-butyl-2,2'-biphenol (4.41 g, 10.73 mmol) in *thf* (5 mL) was added slowly until gas formation ceased. The reaction mixture was stirred for 1 h at room temp. Removal of the solvent gave a colorless powder in quantitative yield. 1H NMR (250.13 MHz, C_6D_6 , 25 °C): δ = 7.54 (d, $^4J_{H,H}$

= 2.4 Hz, 4 H, Ar-H), 7.33 (d, $^4J_{\text{H,H}} = 2.2$ Hz, 4 H, Ar-H), 1.56 (s, 36 H, CMe_3), 1.36 (s, 36 H, CMe_3) ppm. ^1H NMR (250.13 MHz, CDCl_3 , 25 °C): $\delta = 7.26$ (d, $^4J_{\text{H,H}} = 2.0$ Hz, 4 H, Ar-H), 7.05 (d, $^4J_{\text{H,H}} = 1.7$ Hz, 4 H, Ar-H), 1.31 (s, 36 H, CMe_3), 1.26 (s, 36 H, CMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 149.9$ (C_{Ar}), 143.3 (C_{Ar}), 138.4 (C_{Ar}), 132.6 (C_{Ar}), 126.2 (C_{Ar}), 124.4 (C_{Ar}), 35.5 (CMe_3), 34.7 (CMe_3), 34.4 (Me), 32.3 (Me) ppm. Mp > 305 °C. IR (KBr): $\tilde{\nu} = 3452$, 2960, 2906, 2870, 1465, 1433, 1405, 1389, 1361, 1282, 1243, 1201, 1100, 877, 849, 802, 783, 768, 682, 607 cm^{-1} . $\text{C}_{76}\text{H}_{120}\text{AlNaO}_9$ (1227.73): calcd. C 74.35, H 9.85; found C 74.18, H 9.52. MS (ESI $^-$): m/z (%) = 834.71 (100), 844.61 (60), 845.70 (19) $[\text{M} - \text{Na}]^-$.

Sodium Mono(tetrahydrofuran) Alatebate: This compound was obtained by thf elimination at 120 °C and 1 mbar over a period of four days, whereby the solubility of the sodium alatebate salt decreases. After thf elimination, a colorless product was obtained. Yield: 4.60 g (0.49 mmol, 96%). ^1H NMR (300.13 MHz, $[\text{D}_6]$ -acetone, 25 °C): $\delta = 7.18$ (d, $^4J_{\text{H,H}} = 3.7$ Hz, 4 H, Ar-H), 6.97 (d, $^4J_{\text{H,H}} = 3.7$ Hz, 4 H, Ar-H), 3.64 (m, < 4 H, thf), 1.80 (m, < 4 H, thf), 1.31 (s, 36 H, CMe_3), 1.31 (s, 36 H, CMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, $[\text{D}_6]$ -acetone, 25 °C): $\delta = 156.8$ (C_{Ar}), 138.7 (C_{Ar}), 138.4 (C_{Ar}), 133.5 (C_{Ar}), 128.4 (C_{Ar}), 122.0 (C_{Ar}), 68.1 (thf), 35.8 (CMe_3), 34.6 (CMe_3), 33.2 (Me), 31.2 (Me) ppm. Decomp. 261 °C. IR (KBr): $\tilde{\nu} = 3528$, 3414, 2961, 2907, 2870, 1644, 1464, 1431, 1405, 1389, 1361, 1282, 1242, 1201, 1099, 875, 802, 782, 769, 683, 606 cm^{-1} .

1,3-Bis(2,6-diisopropylphenyl)imidazolinium Alatebate: Under inert gas, 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (300 mg, 0.701 mmol) was dissolved in CH_2Cl_2 (20 mL). A solution of lithium bis(3,5,3',5'-tetra-*tert*-butyl-2,2'-diphenolato)aluminate(III)·4thf (825 mg, 0.724 mmol) in CH_2Cl_2 (20 mL) was added whilst stirring. A colorless precipitate of LiCl was formed. The suspension was filtered through Celite and washed with CH_2Cl_2 . Removal of the solvent gave a colorless product. Yield: 860 mg (0.695 mmol, 96%). ^1H NMR (300.13 MHz, CDCl_3 , 25 °C): $\delta = 7.53$ (t, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, Ar-H), 7.38 (s, 1 H, N=CH-N), 7.28 (s, 4 H, Ar-H), 7.13 (d, $^4J_{\text{H,H}} = 2.6$ Hz, 4 H, Ar-H), 7.00 (d, $^4J_{\text{H,H}} = 2.6$ Hz, 4 H, Ar-H), 3.77 (s, 4 H, CH_2), 3.49 (q, Et_2O), 3.73 (sept., $^3J_{\text{H,H}} = 6.8$ Hz, 4 H, MeCHMe), 1.10–1.50 (m, 96 H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3 , 25 °C): $\delta = 157.5$ (N=CH-N), 156.2 (C_{Ar}), 146.2 (C_{Ar}), 138.7 (C_{Ar}), 138.2 (C_{Ar}), 132.5 (C_{Ar}), 132.3 (C_{Ar}), 129.2 (C_{Ar}), 128.0 (C_{Ar}), 125.7 (C_{Ar}), 122.1 (C_{Ar}), 66.2, 54.1, 35.5, 34.4, 32.2 (Me), 30.8 (Me), 29.5, 25.9, 24.1, 15.7 ppm. Mp > 300 °C. IR (KBr): $\tilde{\nu} = 3435$, 2960, 2870, 1634, 1464, 1431, 1405, 1387, 1359, 1325, 1281, 1243, 1200, 1100, 874, 803, 783, 769, 683, 607 cm^{-1} . $\text{C}_{87}\text{H}_{129}\text{AlN}_2\text{O}_5$ (1309.95): calcd. C 79.77, H 9.93, N 2.14; found C 79.55, H 9.86, N 2.01. HRMS (ESI $^-$): m/z (%) = 843.58400 (100), 844.58738 (60), 845.59074 (19) $[\text{M}]^-$; (ESI $^+$): m/z (%) = 391.31072 (100). X-ray: a single crystal was obtained by crystallization from Et_2O .

1,3-Dimesitylimidazolinium Alatebate-Diethyl Ether: Under inert gas, 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (300 mg, 0.872 mmol) was dissolved in CH_2Cl_2 (20 mL). A solution of lithium bis(3,5,3',5'-tetra-*tert*-butyl-2,2'-diphenolato)aluminate(III)·4thf (1.03 g, 0.904 mmol) in CH_2Cl_2 (20 mL) was added whilst stirring. A colorless precipitate of LiCl was formed. The suspension was filtered through Celite and washed with CH_2Cl_2 . Removal of the solvent in vacuo afforded a colorless solid. Yield: 1.01 g (0.877 mmol, 97%). ^1H NMR (300.13 MHz, CDCl_3 , 25 °C): $\delta = 7.44$ (s, 1 H, N=CH-N), 7.13 (d, $^4J_{\text{H,H}} = 2.6$ Hz, 4 H, Ar-H), 6.99 (d, $^4J_{\text{H,H}} = 2.6$ Hz, 4 H, Ar-H), 6.96 (s, 4 H, Ar-H), 3.76 (s, 4 H, CH_2), 3.49 (q, Et_2O), 2.31 (s, 6 H, ArMe), 2.16 (s, 12 H, ArMe),

1.10–1.50 (m, 72 H, CMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3 , 25 °C): $\delta = 157.4$ (N=CH-N), 156.1 (C_{Ar}), 141.1 (C_{Ar}), 138.6 (C_{Ar}), 138.3 (C_{Ar}), 134.8 (C_{Ar}), 132.6 (C_{Ar}), 130.7 (C_{Ar}), 129.9 (C_{Ar}), 128.3 (C_{Ar}), 125.7 (C_{Ar}), 125.2 (C_{Ar}), 122.1 (C_{Ar}), 52.0, 35.5, 34.5, 32.3 (Me), 32.1 (Me), 30.8, 30.1, 21.4, 18.1, 15.7 ppm. HRMS (ESI $^-$): m/z (%) = 843.58778 (100), 844.59124 (60), 845.59550 (16) $[\text{M}]^-$; (ESI $^+$): m/z (%) = 307.21708 (100), 308.22045 (25); Mp > 300 °C. IR (KBr): $\tilde{\nu} = 3436$, 2952, 2905, 2868, 1632, 1463, 1431, 1404, 1387, 1359, 1281, 1242, 1200, 1100, 873, 803, 783, 769, 683, 607 cm^{-1} . $\text{C}_{81}\text{H}_{117}\text{AlN}_2\text{O}_5$ (1225.79): calcd. C 79.37, H 9.62, N 2.29; found C 79.20, H 9.67, N 2.18. X-ray: a single-crystal was obtained from Et_2O .

Tetrabutylammonium Alatebate: A round-bottomed flask was charged with lithium bis(3,5,3',5'-tetra-*tert*-butyl-2,2'-diphenolato)aluminate(III) (thf) $_4$ adduct (2.00 g, 1.80 mmol) dissolved in CH_2Cl_2 (10 mL). A solution of tetrabutylammonium bromide (1.00 g, 3.10 mmol) in CH_2Cl_2 (10 mL) was added. A colorless precipitate (LiBr) was formed. The suspension was filtered through Celite and washed with CH_2Cl_2 . After removal of the solvent in vacuo, the product was extracted with pentane. Evaporation of the solvent afforded a colorless powder. Yield: 1.05 g (0.97 mmol, 54%). ^1H NMR (300.13 MHz, $[\text{D}_6]$ -acetone, 25 °C): $\delta = 7.17$ (d, $^4J_{\text{H,H}} = 2.7$ Hz, 4 H, Ar-H), 6.96 (d, $^4J_{\text{H,H}} = 2.7$ Hz, 4 H, Ar-H), 3.46 (t, $^3J_{\text{H,H}} = 8.4$ Hz, 8 H, NCH_2), 1.84 (m, 8 H, CH_2), 1.45 (m, 8 H, CH_2), 1.30 (m, 72 H, CMe_3), 0.98 (t, $^3J_{\text{H,H}} = 8.4$ Hz, 12 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, $[\text{D}_6]$ -acetone, 25 °C): $\delta = 157.2$ (C_{Ar}), 139.2 (C_{Ar}), 138.8 (C_{Ar}), 133.9 (C_{Ar}), 128.8 (C_{Ar}), 122.5 (C_{Ar}), 59.8 (NCH_2), 36.2, 35.0, 32.7 (Me), 32.4 (Me), 31.6, 24.8, 20.8, 14.3 ppm. Mp 150 °C. IR (KBr): $\tilde{\nu} = 3424$, 2957, 2905, 2874, 1464, 1432, 1405, 1387, 1359, 1283, 1241, 1200, 875, 847, 783, 767, 702, 682, 620, 607 cm^{-1} . $\text{C}_{72}\text{H}_{116}\text{AlNO}_4$ (1086.68): calcd. C 79.58, H 10.76, N 1.29; found C 79.34, H 10.90, N 1.19. HRMS (ESI $^-$): m/z (%) = 843.58236 (100), 844.58700 (70), 845.59225 (20) $[\text{M}]^-$; (ESI $^+$): m/z (%) = 242.28395 (100).

CCDC-767474 [for lithium tetrakis(tetrahydrofuran)bis(3,3',5,5'-tetra-*tert*-butyl-2,2'-diphenolato)aluminate(III)], -767475 [for 1,3-dimesitylimidazolinium alatebate], and -767997 [for 1,3-bis(2,6-diisopropylphenyl)imidazolinium alatebate] 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.

Supporting Information (see footnote on the first page of this article): Additional synthetic protocols, data relevant for yields and costs of the WCA in Table 1, NMR spectra, additional color figures, and Cartesian coordinates for DFT calculations.

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