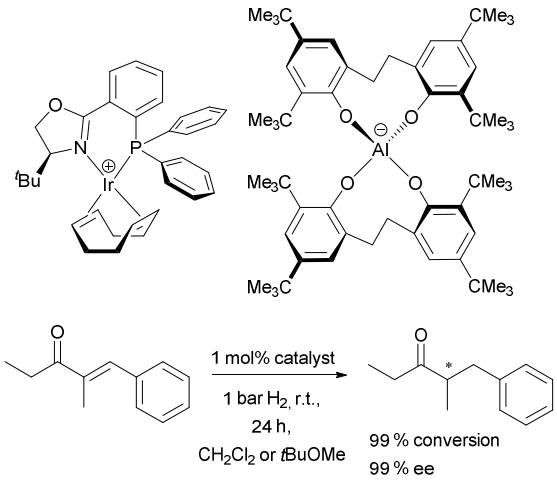
Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem



Cost-efficient aluminates successfully replace expensive and persistent counterions in transition-metal catalyses such as Bolm's stereoselective enone hydrogenation.

Green Chemistry

RSCPublishing

ARTICLE

Halogen-free water-stable aluminates as replacement for persistent fluorinated weakly-coordinating anions

Cite this: DOI: 10.1039/xoxxoooooox

T. Söhner, F. Braun, L. C. Over, S. Mehlhose, F. Rominger, and B. F. Straub*

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Multigram amounts of halogen-free aluminate salts were prepared from cost-efficient ethylene-bridged bisphenols and alkali aluminium hydrides. The lipophilic, weakly-coordinating "aletbate" anion with eight *tert*-butyl substituents, the "aletpate" anion with eight *tert*-pentyl substituents and a formidable solubility reaching from aromatic hydrocarbon solvents to ethanol, and the "alphetbate" anion with four *tert*-butyl and four 1,1-diphenylethyl substituents, are structurally characterised by highly sterically shielded aluminium(III) centres. The aluminates feature excellent stability towards alcohols, water and aqueous base, and good stability in acidic medium. The sodium aluminates undergo facile salt metathesis reactions in various solvents. Its extraordinary tendency for crystallisation makes aletbate an ideal counterion for salt isolation and purification. Aletpate salts can be highly soluble even in cyclohexene, diethyl ether and toluene. Coordinated tetrahydrofuran can be thermally eliminated from sodium aletbate to yield a reactive sodium(I) adduct that abstracts chloride ligands from transition metal complexes. Iridium(I) aletbate complexes are highly active in the atom-efficient hydrogenation of a,β-unsaturated ketones and aromatic imines at room temperature at an H_2 pressure of 1 bar. Thus, the aletbate and aletpate anions can replace halogenated and persistent counterions such as BArF.

Introduction

Weakly coordinating anions (WCA)[1] play a crucial role in the chemistry of highly electrophilic cations[2] as well as in transition metal catalysis.[3] The anions' low nucleophilicity is mandatory for the availability of free coordination sites at the cationic catalyst's metal center. The most prominent and most stable WCAs are presented in Figure 1, namely the borates $BArF_{20}$ and $BArF_{24}$,[4] Waldvogel's fluorinated bis(2,2'-biphenoxy)borates with increased redox-stability,[5] Krossing's perfluoroalkylated $Al(OR_F)_4^-$,[6] Willner's $B(CF_3)_4^-$,[7] Lacour's tris(tetrachlorobenzenediolato)-phosphate(V),[8] and halogenated or trifluoromethylated carboranates $[CB_{11}X_nH_{12-n}]^-$ (n = 1 to 12; X = F, Cl, Br, I, CF_3).[9] Halogen substituents promote a high solubility in organic solvents and chemical inertness towards electrophiles and oxidants. From an environmental perspective, however, the major problem of these WCAs is the persistency of the kinetically inert C-Cl and C-F bonds. Thermal decomposition of perfluorocarbons such as PTFE (Teflon©) yields highly toxic perfluoroisobutene (PFIB), which is a Schedule 2 substance of the Chemical Weapons Convention[10] and is one of the substances causing polymer fume fever.[11] The combustion of fluorohydrocarbons liberates toxic and corrosive hydrogen fluoride.[12] A typical oxidation product of fluorinated compounds is trifluoroacetic acid, whose salts slowly release the greenhouse gas trifluoromethane "HFC-23" with a global warming potential of 14,800 relative to CO_2 and an atmospheric life-time of 270 years.[13] The very potent pesticide fluoroacetic acid inhibits the metabolic citric acid cycle.[14] Perfluoroalkanesulfonates such as PFOS (Figure 1) are persistent fluorosurfactants in hydrocarbon fuel fire extinguishers that have been associated to chronic kidney disease and were added to the Annex B of the Stockholm Convention on Persistent Organic Pollutants.[15]

Halogen-free weakly-coordinating anions are very rare. The carboranates $CB_{11}H_{12}^-$[16] and $CB_{11}Me_{12}^-$[17] are such anions, but their sensitivity to oxidation and the high cost of synthesis have so far prevented widespread applications.

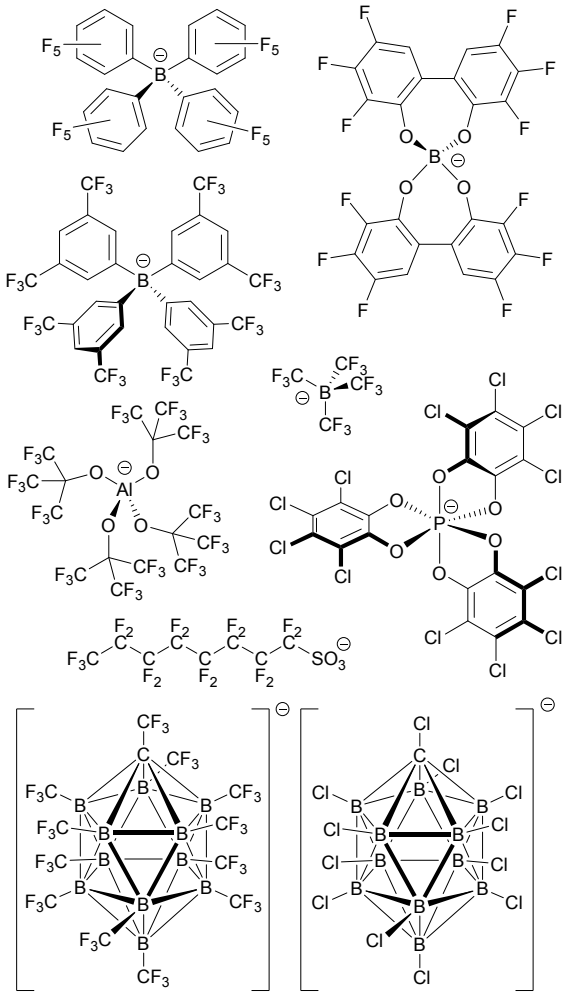


Figure 1: Prominent halogen-containing, weakly-coordinating or redox-stable anions

Our aim was to develop cost-effective and more environmentally benign, halogen-free, lipophilic anions with sufficiently low nucleophilicity and high stability towards water. Our group recently reported the syntheses of two halogen-free aluminates (Figure 2).[18] The required bisphenols can be synthesised from low-cost 2,4-di-*tert*-butylphenol in good yields, and have properties such as high solubility in organic solvents and a low tendency of coordination towards electrophiles. The Achilles heel of aluminates is their rapid hydrolysis in protic solvents. The "altebate" anion (Figure 2, left side) with eight *tert*-butyl substituents hydrolyses even in neutral aqueous solution within days, which limits its usability. The dimethylmethylene-linked "almebate" anion (Figure 2, right side) comprises better stability in protic solvents and is nearly stable in basic solution, but it decomposes in weak acids within hours.

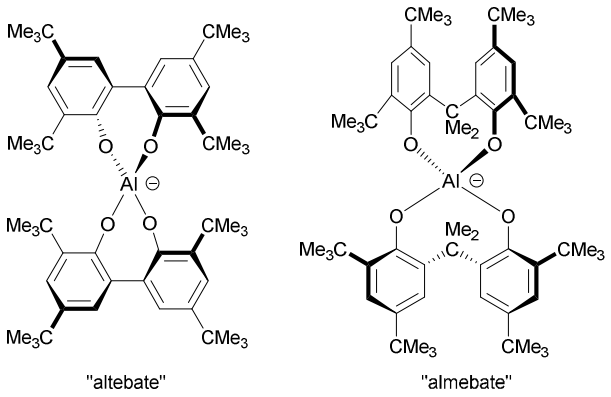


Figure 2: Halogen-free aluminates: S_4-symmetric altebate (left)[18a] and fluxional C_2-symmetric almebate (right)[18b]

Here, we report the syntheses and the properties of salts of three closely related water-stable bisphenolate-based weakly-coordinating aluminate anions (Figure 3), and exemplary applications in transition metal catalysis.

The IUPAC names of the lipophilic aluminates are prohibitively long and complicated. Thus, we would like to provide more convenient short names (Table 1), thereby hoping to facilitate the popularisation of this class of lipophilic anions.

Table 1. Structural characteristics of lipophilic aluminate anions

aluminate name	bisphenolate linker	*ortho*-substituents	*para*-substituents
al**teb**ate[18a]	-	*tert*-butyl	*tert*-butyl
al**meb**ate[18b]	CMe_2	*tert*-butyl	*tert*-butyl
al**etb**ate	CH_2CH_2	*tert*-butyl	*tert*-butyl
al**etp**ate	CH_2CH_2	*tert*-pentyl	*tert*-pentyl
al**phetb**ate	CH_2CH_2	$CMePh_2$	*tert*-butyl

We named the first new anion "aletbate": an aluminate with ethylene-linked bisphenolates and eight *tert*-butyl groups. Analogously, the "aletpate" anion comprises eight *tert*-pentyl substituents. The even more sterically demanding "alphetbate" anion comprises four *tert*-butyl groups in *para*-position and four 1,1-diphenylethyl groups in *ortho*-position to the respective oxygen atom.

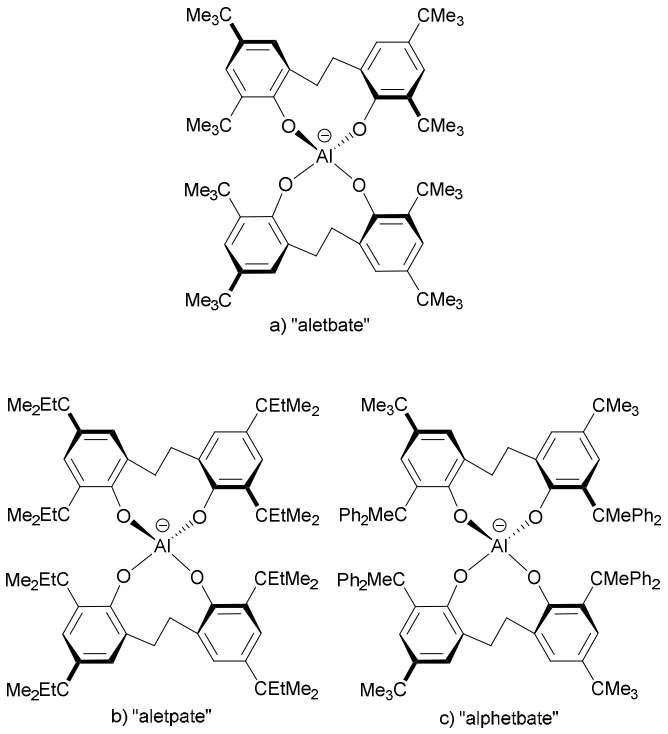
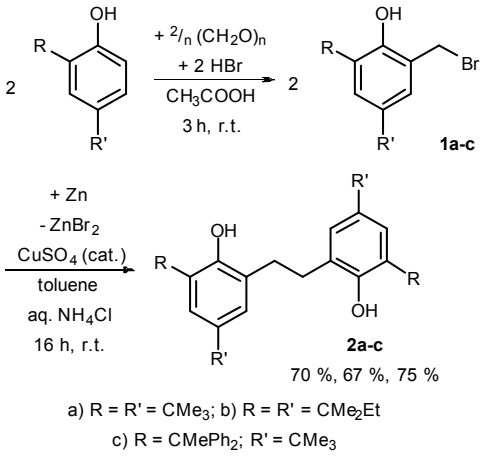


Figure 3: New aluminates based on ethylene-linked bisphenolates

Results and discussion

Synthesis of the bisphenols

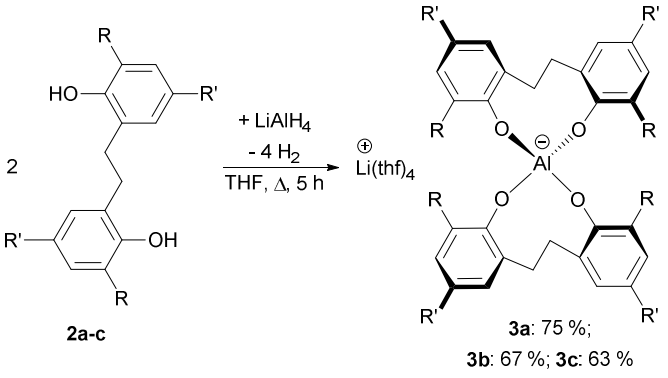
The first step of the bisphenol synthesis followed a modified protocol of Miyatake.[19] Instead of using three equivalents of hydrobromic acid, only two equivalents were mandatory for a complete *ortho*-bromomethylation of the starting material 2,4-di-*tert*-alkyl phenol. The use of a highly pure HBr solution in acetic acid proved to be essential. Exposure to the humidity of air leads to a significant decrease of the yield of the bromomethylated product **1**. Filtration over a pad of silica gel of a solution of the raw product in pentane provides a nearly pure product. The reductive coupling in the second step was inspired by a protocol of Malvestiti (Scheme 1).[20] The Wurtz-type reductive coupling with zinc metal can be used for the coupling of both benzylic bromides and unprotected bromomethylated phenols. The reductive dimerisation of a structurally similar *ortho*-bromomethylated, but acetyl-protected phenol with magnesium metal has been reported to yield only 15% of an ethylene-linked bisphenol.[20b] Toluene and benzene co-solvent lead to similar yields. Without co-solvent or in saturated ammonium chloride solutions in methanol or ethanol, no conversion was observed. Because of the carcinogenity of benzene, toluene is evidently the solvent of choice. Reaction times of 16 h resulted in a yield of 70 % for 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-butylphenol) **(2a)**, 67 % for 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-pentylphenol) **(2b)** and 75 % for 6,6'-(ethane-1,2-diyl)bis[4-*tert*-butyl-2-(1,1-diphenylethyl)phenol] **(2c)** over two steps, respectively. Single-crystals of the bisphenols suitable for an X-ray diffraction study were obtained by recrystallisation from acetonitrile or tetrahydrofuran (for Figures of ball-and-stick models, see Supporting Information).



Scheme 1: Synthesis of ethylene-linked bisphenols by bromomethylation and subsequent reductive coupling

Synthesis of alkali metal aluminates

$Li(thf)_4$ and $Na(thf)_2$ aluminates were synthesised by heating the respective bisphenolates with $LiAlH_4$ or $NaAlH_4$ in THF for five hours under reflux conditions in analogy to a literature protocol.[18] The reaction towards $Li(thf)_4$ alphetbate was more sluggish, so that heating for four days was necessary. The increased steric demand and the more pronounced steric repulsion of the phenyl groups apparently lower the reaction rate. $Li(thf)_4$ aletbate (**3a**) was isolated in 75 % yield, $Li(thf)_4$ aletpate (**3b**) in 67 % yield and $Li(thf)_4$ alphetbate (**3c**) in a yield of 63 % (Scheme 2). Single-crystals suitable for an X-ray diffraction study of $Li(thf)_4$ aletbate (**3a**) precipitated from CH_2Cl_2 / pentane. This salt comprises separated alkali cation and S_4-symmetrical anion (Figure 4). The aletbate's anionic AlO_4 core is almost completely shielded by the four aromatic rings, the *tert*-butyl groups and the two ethylene linkers (Figure 5).



Scheme 2: Synthesis of $Li(thf)_4$ aletbate **3a**, $Li(thf)_4$ aletpate **3b**, and $Li(thf)_4$ alphebate **3c**

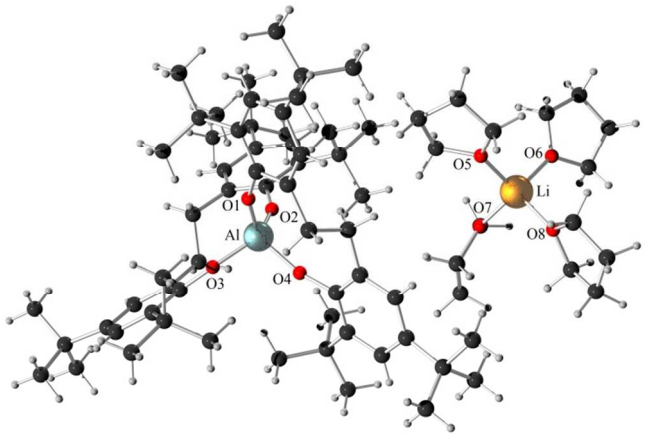


Figure 4: Ball-and-stick model of the single-crystal X-ray structure of tetrakis(tetrahydrofuran)lithium aletbate **3a**. Colour code: C black, H grey, O red, Al light blue, Li orange.[21]

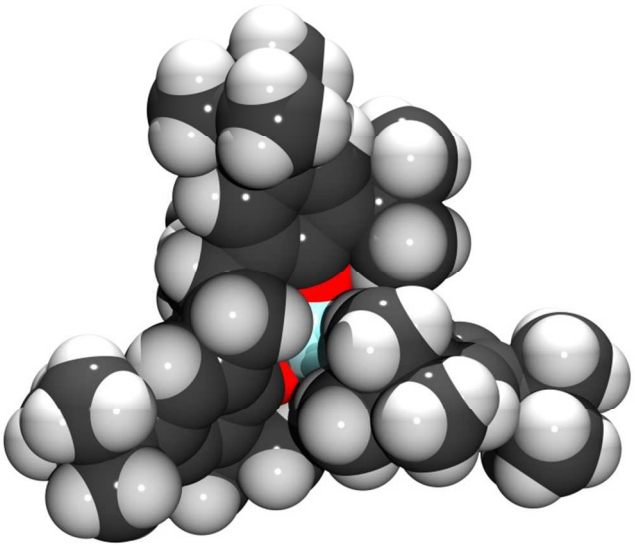
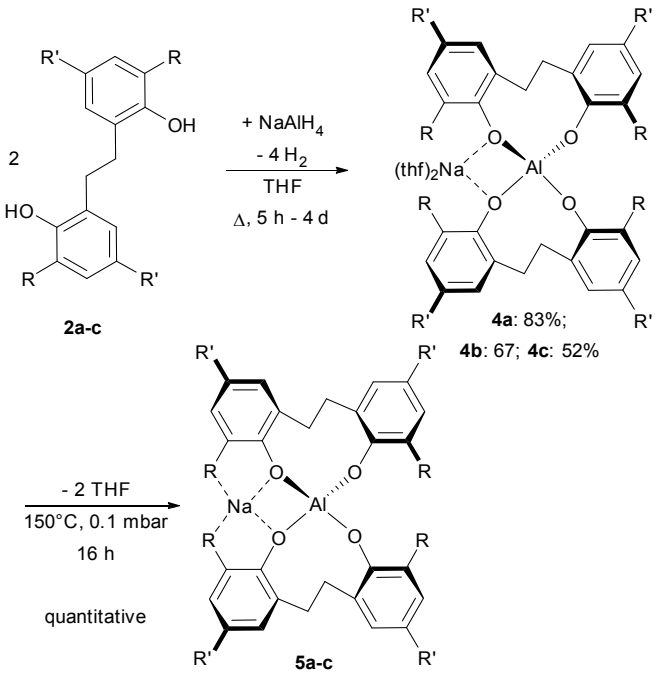


Figure 5: Space-filling model of a single-crystal X-ray structure of the aletbate anion. Colour code: C black, H grey, O red, Al light blue.[21]

$Na(thf)_2$ aletbate (**4a**) was obtained in a yield of 83 % in a multigram scale. The isolated relative yields of $Na(thf)_2$ aletpate (**4b**) and of $Na(thf)_2$ alphetbate (**4c**) were lower (Scheme 3). Surprisingly, only two tetrahydrofuran molecules coordinated at the sodium atom. The crystal structure of $Na(thf)_2$ aletbate provides valuable information to the nature of the coordination of the sodium cation (Figure 6). One pair of oxygen ligand atoms bridges the sodium and the aluminium atom, the other pair of oxygen ligand atoms is coordinated only to aluminium. The thf adduct of the sodium aletbate features C_2 symmetry. This is in contrast to the anion's S_4 symmetry as observed in solid-state $Li(thf)_4$ aletbate. An ionic derivative of sodium aletbate was obtained by crystallisation from THF / pentane (Figure 7). There, the sodium atom is coordinated by four thf ligands, and the cation and anion are separated. The anion essentially features C_2 symmetry, with a distinct distortion from an ideal D_2 symmetry. This complex has only been characterised by X-ray diffraction: upon removing excess solvent *in vacuo*, $Na(thf)_2$ aletbate (**4a**) was obtained, providing evidence for the competitive coordinative strength of a chelating aletbate anion compared to two thf ligands.



Scheme 3: Syntheses of sodium aluminates with thf ligands, and their thermal elimination

Heating of the thf adducts **4a-c** at 150 °C for 16 hours at 0.1 mbar releases two equivalents of tetrahydrofuran, and produces quantitatively sodium aluminates **5a-c** with unsaturated, reactive sodium(I) (Scheme 3). The aluminates presumably act as tetradentate ligands with two oxygen ligand atoms and two agostic interactions in a pseudo-tetrahedral coordination mode at the sodium cation.

The ease of crystallisation facilitates the identification of cationic structures by single-crystal X-ray diffraction. The widespread disorder of the *tert*-butyl and even more so of the *tert*-pentyl groups in the aluminate anions, however, limits the accuracy of the bond length and bond angle measurements.

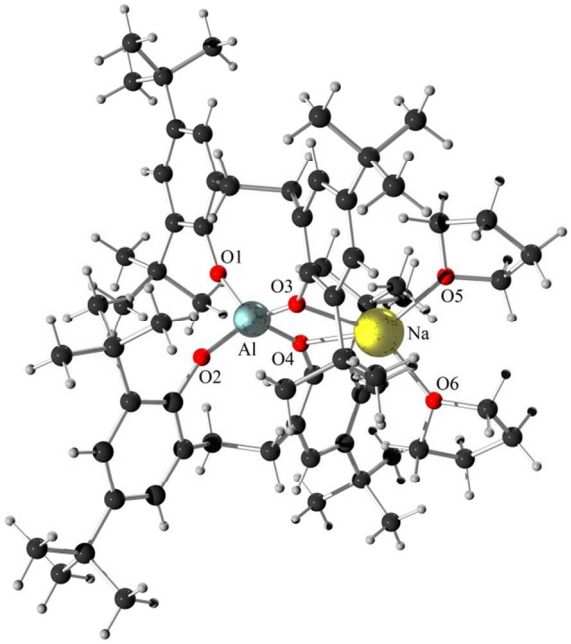


Figure 6: Ball-and-stick model of the single-crystal X-ray structure of bis(tetrahydrofuran) aletbate **4a**. Colour code: C black, H grey, O red, Al light blue, Na yellow.[21]

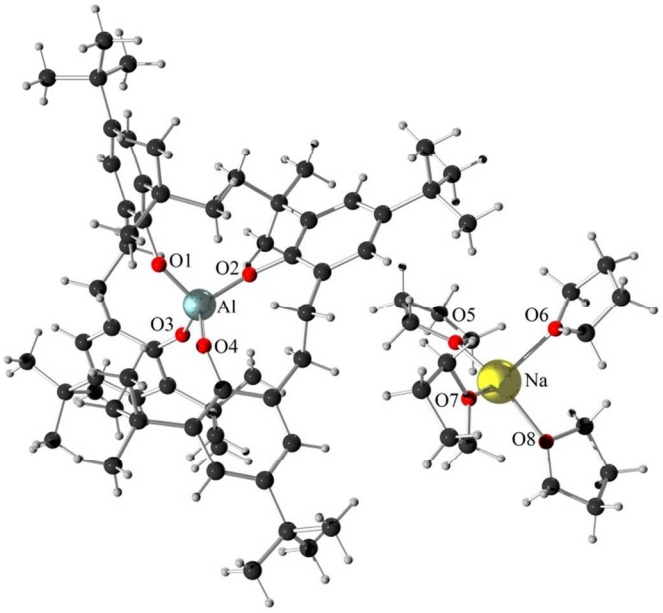
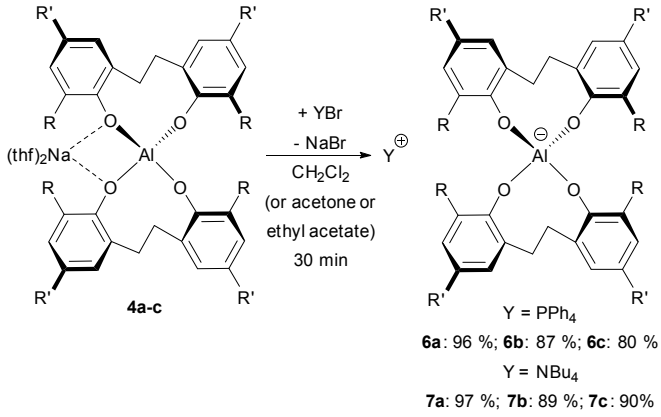


Figure 7: Ball-and-stick model of the single-crystal X-ray structure of tetrakis(tetrahydrofuran)sodium aletbate. Colour code: C black, H grey, O red, Al light blue, Na yellow.[21]

Salt metathesis and hydrolysis

Via salt metathesis reactions, the sodium or lithium cations of the aletbate/aletpate anion can easily be exchanged in high yield by larger, more lipophilic cations (Scheme 4). With PPh_4Br, yields of 96 % for the aletbate salt **6a,** 87 % for the aletpate salt **6b**, and 80 % for the alphetbate salt **6c** were isolated. High yields were also obtained in the synthesis of tetrabutylammonium aletbate (97 %, **7a**), tetrabutylammonium aletpate (89 %, **7b**) and tetrabutylammonium alphetbate (90 %, **7c**). Salt metathesis reactions also proceeded successfully in "greener", non-chlorinated solvents such as acetone, ethyl acetate and toluene. Addition of an alkane such as pentane to these solvents was mandatory for precipitation and crystallisation of aluminate salts **6a-c** and **7a-c**.



Scheme 4: Salt metathesis reactions of sodium aluminates with PPh_4Br or NBu_4Br.

Single-crystals suitable for X-ray diffraction studies of tetraphenylphosphonium and tetrabutylammonium aletbate, of tetraphenylphosphonium aletpate, and of tetraphenylphosphonium alphetbate were obtained from dichloromethane / pentane. Interestingly, the solid-state unit cell of tetraphenylphosphonium aletbate contains two aletbate conformations of different symmetry. An aletbate anion with S_4 symmetry is displayed in Figure 8. An aletbate anion with C_2 symmetry, derived by distortion from D_2 symmetry, is shown in Figure 9.

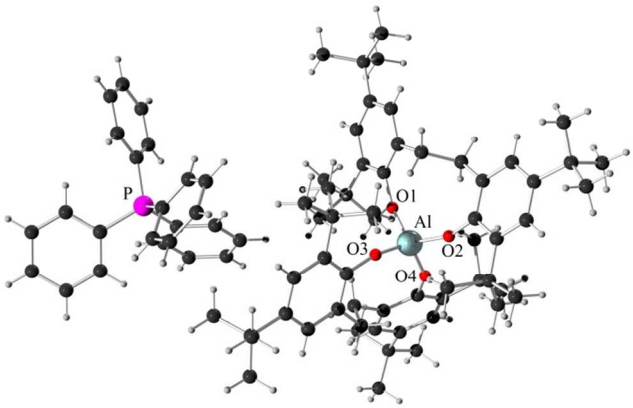


Figure 8: Ball-and-stick model of the single-crystal X-ray structure of PPh_4 aletbate **6a** with S_4 symmetry of the anion. Colour code: C black, H grey, O red, Al light blue, P magenta.[21]

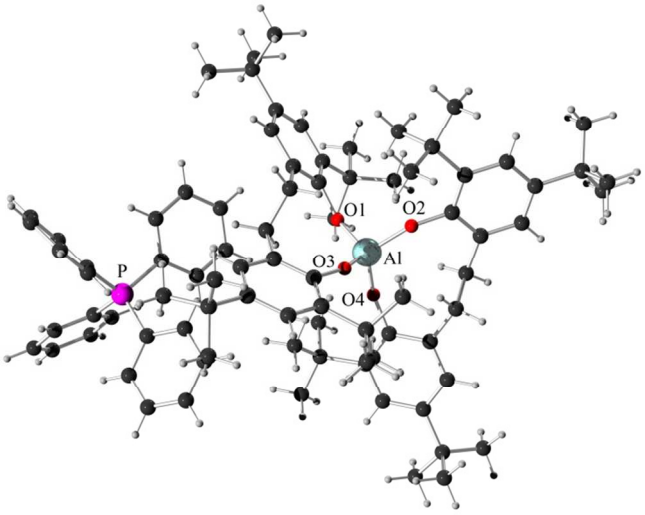


Figure 9: Ball-and-stick model of the single-crystal X-ray structure of PPh_4 aletbate **6a** with C_2 symmetry of the anion. Colour code: C black, H grey, O red, Al light blue, P magenta.[21]

The crystal structures of aletpate and alphetbate salts comprise only the conformer derived from the C_2 symmetrical aluminate core (Figures 10 and 11). This might be explained by the higher steric demand of the *tert*-pentyl groups and the 1,1-diphenylethyl groups. Tetrabutylammonium aletbate comprises only the aluminate's S_4 conformer in the solid state (Figure 12).

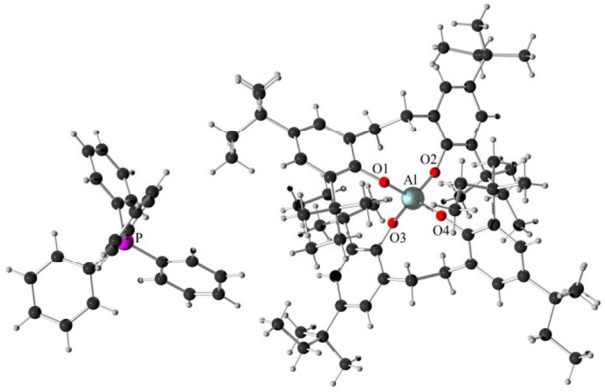


Figure 10: Ball-and-stick model of the single-crystal X-ray structure of PPh_4 aletpate **6b**. Colour code: C black, H grey, O red, Al light blue, P magenta.[21]

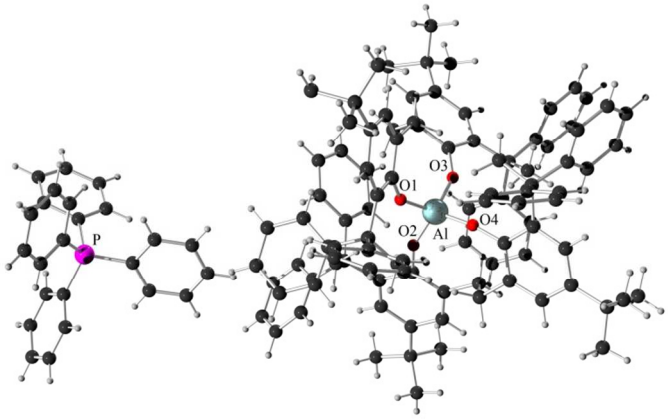


Figure 11: Ball-and-stick model of the single-crystal X-ray structure of PPh_4 alphetpate **6c**. Color code: C black, H grey, O red, Al light blue, P magenta.[21]

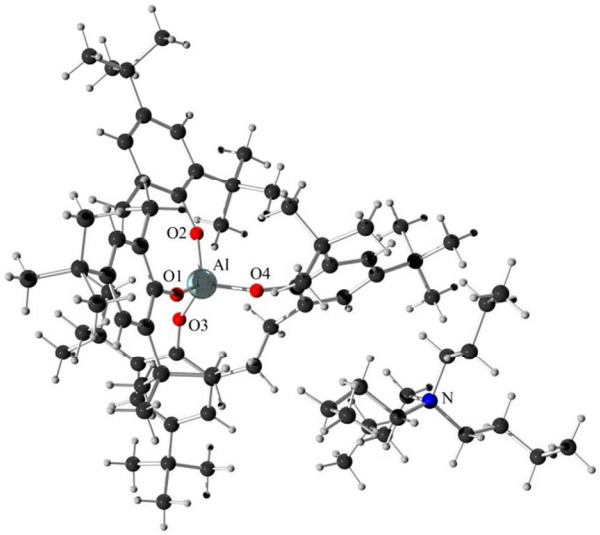


Figure 12: Ball-and-stick model of the single-crystal X-ray structure of NBu_4 aletbate **7a**. Colour code: C black, H grey, O red, Al light blue, N blue.[21]

The hydrolytic stability of the two aluminate anions was quantified. The tetraphenylphosphonium salts were dissolved in a mixture of d_8-THF and D_2O (4:1). Their stability was determined by ^1H NMR spectroscopy. All three aluminates proved to be stable over weeks at room temperature. The same result was observed in basic media: with a tenfold excess of NEt_3 or 1 M NaOH, no hydrolysis has been detected at all. With a tenfold excess of acetic acid, however, the aletbate anion decomposes with a rate of 1.6 % per week. The aletpate anion is less stable towards hydrolysis and decomposes with an initial rate of 3 % per week. By increasing the steric demand in *ortho* position in case of the alphetbate, the hydrolysis is even faster and amounts to 30 % after six days. With a tenfold excess of trifluoroacetic acid, the hydrolysis of the aletbate anion amounts to 6 % after one hour, 44 % after 19 hours and 90 % after 67 hours. In case of the aletpate anion, the hydrolysis proceeds with 38 % conversion after seven hours, and 84 % after 24 h. The alphetbate anion is completely hydrolysed after 16 h. This discrepancy can be rationalised by the predominant C_2 symmetrical conformation with a less shielded AlO_4 core of the aletpate and alphetbate anion, and by the higher thermodynamic driving force of the hydrolysis in the case of larger *ortho*-substituents. Nevertheless, altebate salts with their 2,2`-biphenyl backbone (Figure 2, left structure) hydrolyse in a mixture of THF and water within days, and are rapidly hydrolysed both in basic or acidic media.[18] Almebate salts (Figure 2, right structure) are reasonably stable in aqueous and basic media, but are rapidly hydrolysed in acidic media. Thus, the achievement of a higher hydrolytic stability of aletbate and aletpate salts compared to previously reported aluminates is apparent.

NMR spectra and aluminate conformations

Two aletbate conformers were established by single-crystal X-ray analyses. This conformational equilibrium is also detected by ^{1}H NMR spectroscopy. One aletbate conformer leads to two doublet signals in the aromatic region, and two signals for the protons of the ethylene linker, and two singlets for the *tert*-butyl groups in the aliphatic region. As shown in Figure 13, two pairs of pairs of doublet in the aromatic region with a ratio of 4:1 point to the existence of two conformers: a major S_4 symmetrical conformer and a minor C_2 or D_2 symmetrical conformer. The identical conformer ratio is also observed for a set of protons from the ethylene linker in the region of 3.55 to 3.85 ppm. These signals correspond to the protons close to the aluminium core and are hence more shielded. The distance of ethylene protons to the aluminium core is a little smaller (~ 2.85 Å, Figure 14) compared to the protons of the S_4 symmetrical conformer (~ 2.98 Å, Figure 15). In the aliphatic region from 1.20 – 1.30 ppm, the multiplet is presumably based on two pairs of overlapping singlets.

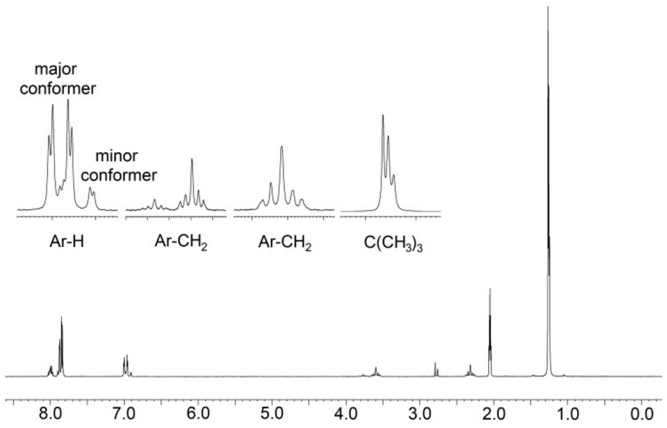


Figure 13: ^{1}H NMR spectrum of PPh_4 aletbate **7a** in d_6-acetone (300.51 Hz, 300 K)

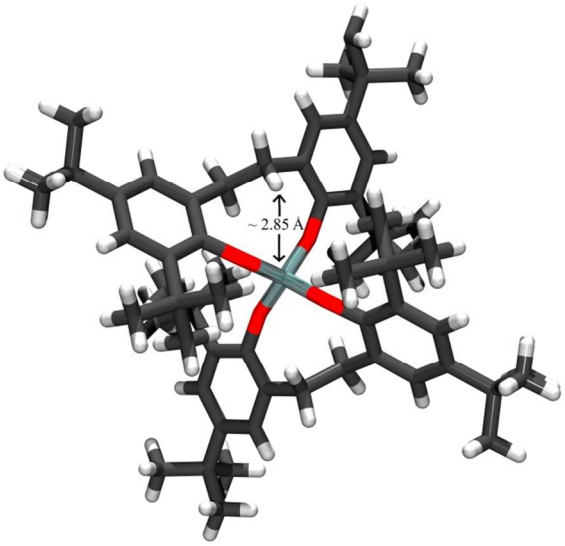


Figure 14: Rod model of a single-crystal X-ray structure of the aletbate anion close to C_2 (distorted D_2) symmetry. Colour code: C black, H grey, O red, Al light blue.[21]

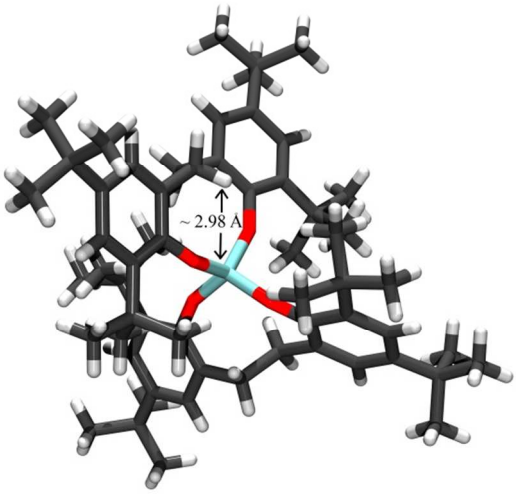


Figure 15: Rod model of a single-crystal X-ray structure of the aletbate anion close to S_4 symmetry. Colour code: C black, H grey, O red, Al light blue.[21]

In the ^{1}H NMR spectra of the aletpate salts, the chemical shifts of the proton signals are similar (Figure 16). In the aromatic region, two pairs of doublets are characterised by a major signal to minor signal ratio of 63:37. The identical signal ratio is present in the aliphatic region of 3.50 – 3.85 ppm for the bridging ethylene signals, and in the region of 0.25 – 0.45 ppm for the CH_3 signals of the ethyl groups. In contrast to the aletbate anion, the major conformer of the aletpate anion features C_2 or D_2 symmetry.

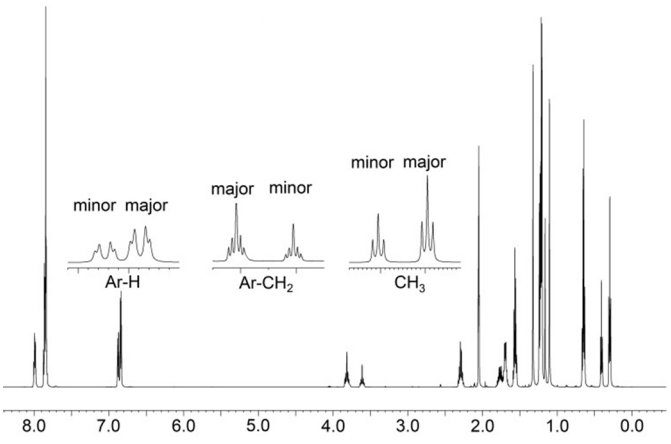


Figure 16: ^{1}H NMR spectrum of PPh_4 aletpate **7b** in d_6-acetone (600.24 Hz, 300 K)

Solubilities of tetrabutylammonium aluminates

The high solubility of aletbate and aletpate salts in organic solvents is a key advantage for potential applications of these aluminates. Generally, tetrabutylammonium aletpate has higher solubilities than the analogous aletbate salt, the only exception being dichloro-methane (Table 2). The higher tendency of aletpates for the dissolved state can be explained by the unlocking of up to eight

degrees of freedom: *tert*-pentyl rotation is usually locked in the solid state, while *tert*-butyl groups are well known for their free rotation in the solid state and the accompanying high degree of disorder in X-ray structure analyses. Solvent systems with Reichardt's E_T^N values[22] of 0.2 to 0.5 are best suited for achieving high salt concentrations. An extraordinary large aletbate/aletpate solubility difference is observed for solvents with E_T^N values of ca. 0.04 – 0.13 (cyclohexene, toluene, diethyl ether, and *t*BuOMe). In this range of solvent polarities, NBu_4 aletpate is highly soluble (250 – 800 mg/mL), while concentrations of 5 – 120 mg/mL prevail for the analogous aletbate salt. In isopropanol and ethanol, aletpate solubilities are also significantly higher. Aletbate and aletpate salt concentrations in alkanes are low, but not negligible. In water, possible minute traces of dissolved aluminate salts are undetectable by our weighing procedure.

Table 2: Maximum concentrations of tetrabutylammonium aletbate and tetrabutylammonium aletpate in solvents at 296 K ± 2 K.

Solvent	E_T^N	c_{max} (mg/mL)[a] of NBu_4 aletbate	c_{max} (mg/mL)[a] of NBu_4 aletpate
pentane	0.009	0.5[b,c]	0.5[b,c]
hexane	0.009	1[b,c]	1[b,c]
cyclohexene	0.046	7[d]	279[d]
toluene	0.099	40[b]	620
diethyl ether	0.117	43[b]	664
tert-butyl methyl ether	0.124	111	768
tetrahydrofuran	0.207	570	820
ethyl acetate	0.228	378	658
chloroform	0.257	543	590
dichloromethane	0.309	596	532
acetone	0.355	400	530
acetonitrile	0.460	318	660
isopropanol	0.546	7[b]	293
ethanol	0.654	30[b]	150
methanol	0.762	24[b]	30[b]
water	1.000	< 0.01[b]	< 0.01[b]

[a] Maximum concentrations averaged from two experiments with removal of solvent from a 0.5 mL sample of a saturated solution and weighing, respectively. Solvent traces in the solid residue were quantified by ^{1}H NMR and corrected. Reproducibilities are within 2 %. [b] Solvent samples with 10 mL [c] Reproducibilities are within 10 %. [d] Solvent samples with 2 mL

Hydrolysis and alcoholysis are major limitations for aluminate applications.[18a] Aletbate and aletpate salts are completely stable in methanolic solution at room temperature, according to ^{1}H NMR spectroscopic measurements over seven days.

Organic solvents in research laboratories and in the chemical industry have a huge impact on environmental and health aspects.[23] The wide solvent suitability of the aluminates has the beneficial effect that an optimal solvent can be chosen.

Synthesis of a gold aletbate salt

NHC gold complexes can be used in many different organic catalysis reactions[24] but are also in the focus of biomedicine applications[25] or material science.[26] We present a silver free protocol to synthesis a $IPrAu(SMe)_2$ aluminate. $IPrAu(SMe)_2$ aluminates (**8a, 8b**) have been synthesised by elimination of their gold precursor's chloride ligand by the thermally activated sodium aluminates in good yields (Scheme 5). Single-crystals suitable for X-Ray diffraction of $IPrAu(SMe)_2$ aletbate (**8a**) were obtained by recrystallisation from dichloromethane and pentane. There, the aletbate anion features a S_4 symmetrical structure (Figure 17).

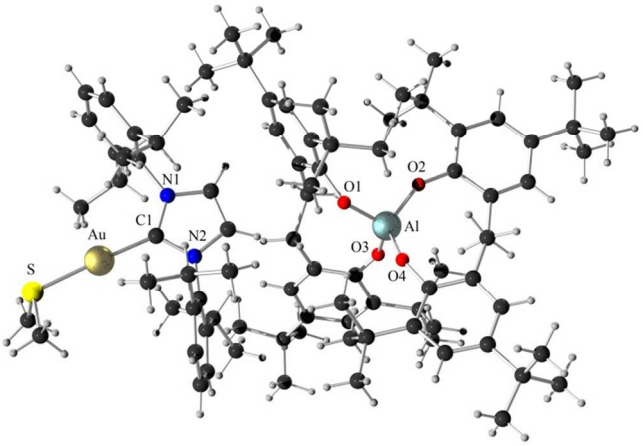
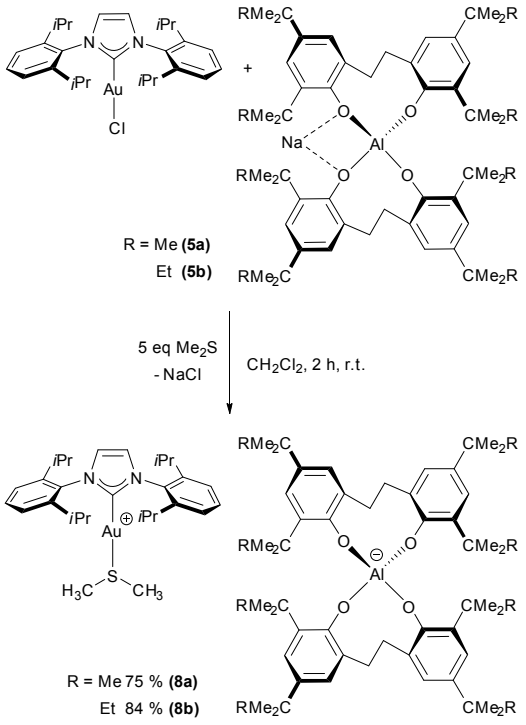


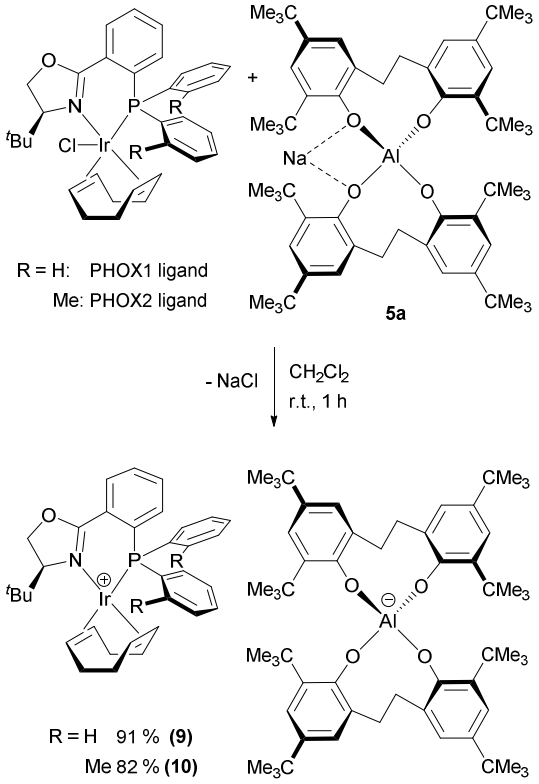
Figure 17: Ball-and-stick model of the single-crystal X-ray structure $IPrAu(SMe_2)$ aletbate **8**. Colour code: C black, H grey, O red, Al light blue, N blue, S yellow, Au gold.[21]



Scheme 5: Syntheses of $IPrAu(SMe_2)$ aluminates

Synthesis of iridium aletbates and catalytic hydrogenation

The field of iridium-catalyzed asymmetric hydrogenation reactions underwent a dramatic development with the optimisation of Crabtree's catalyst[27] by using the chelating PHOX ligand developed by Pfaltz and Helmchen[28]. The most prominent examples for hydrogenations reactions are the hydrogenation of alkenes,[29] imines,[30] and enones.[30, 31] Several iridium-catalyzed hydrogenation reactions with P,N ligands were published in the past fifteen years. Theoretical studies[32] and investigations on counterion effects[3, 33] provided a deeper insight into the reaction mechanisms. The catalytic activity and productivity strongly depends on the low nucleophilicity of the counterion. Fluorinated borate anions such as $BArF_{24}$ have been employed in almost all catalytic studies. The group of Feringa presented an alternative by using methylaluminoxane MAO.[34] However, the high loading with at least fifty equivalents of MAO limits its scope of application. Inspired by these results, we tested our aletbate anion in the asymmetric hydrogenation reaction of imines and enones. Two iridium catalysts were synthesised by standard procedures.[30] The first iridium catalyst with the (S)-4-(*tert*-butyl)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-1,3-oxazol (PHOX1) **9** gave a yield of 91 %, the other catalyst with (S)-4-(*tert*-butyl)-2-[2-(di-*ortho*-tolylphosphino)phenyl]-4,5-dihydro-1,3-oxazol (PHOX2) **10** gave a yield of 82 % (Scheme 6).



Scheme 6: Syntheses of [Ir(PHOX)(COD)] aletbate salts

The asymmetric hydrogenation reactions of (E)-*N*-(1-phenylethylidene)aniline catalyzed by Ir(PHOX1)(cod) aletbate were carried out at room temperature for 24 h in five different organic solvents (Table 3).

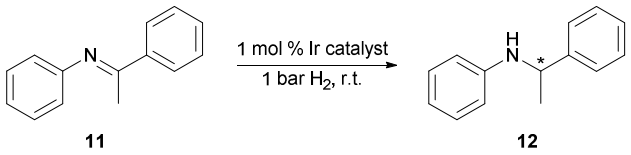


Table 3: Asymmetric hydrogenation of (E)-*N*-(1-phenylethylidene)-aniline (**11**)

Solvent	Catalyst (loading)	t [h]	conversion [%]	*ee* [%]
CH_2Cl_2	**9** (1 mol%)	24	63	77
CH_2Cl_2	**9** (2 mol%)	24	91	68
toluene	**9** (1 mol%)	24	66	71
heptane	**9** (1 mol%)	24	17	n.d.
acetonitrile	**9** (1 mol%)	24	27	n.d.
methanol	**9** (1 mol%)	24	0	-
CH_2Cl_2	[Ir(PHOX1)(COD)]Cl	24	0	-

[a] reaction conditions **13** (1.0 mol), catalyst (1 mol %) solvent (1.0 mL). All reactions were carried out at r.t. with a hydrogen pressure of 1 bar for 24 h. [b] conversion was determined by 1H NMR of the crude product. [c] ee values were determined by HPLC on a Chiralcel OJ column.

A high substrate conversion was obtained in dichloromethane and toluene (Table 3). In polar or protic solvents such as acetonitrile and methanol, the conversion was very low. With the nonpolar solvent heptane, only a low conversion was achieved due to the catalyst's poor solubility in this solvent. By increasing the catalyst loading in dichloromethane, the conversion increased to 91 %, but the enantioselectivity slightly decreased. This effect had also been reported by the Pfaltz group.[30] Expectedly, no imine conversion was observed upon addition of Ir(PHOX1)(cod)Cl as catalyst candidate.

In analogy the hydrogenation protocol of Bolm et. al. with $BArF_{24}$–derived iridium catalysts,[31] the asymmetric hydrogenation reaction of (E)-2-methyl-1-phenylpent-1-en-3-one (**13**) yielded full conversion with both iridium aletbate catalysts **9** and **10** after 24 hours in dichloromethane with a hydrogen pressure of 1 bar and 1 mol% catalyst loading (Table 4). These results are comparable to those in the literature.[31] Catalyst **9** hydrogenates enone **13** completely, cleanly and enantioselectively also in *tert*-butyl methyl ether, thereby providing the option to replace dichloromethane solvent. Catalyst **10**, however, yields only 48 % of product **14** after 24 hours in *t*BuOMe. Toluene solvent leads to an even much more sluggish reaction with 82 % hydrogenation yield in the case of catalyst **9** and only 13 % yield with catalyst **10** after 24 hours.

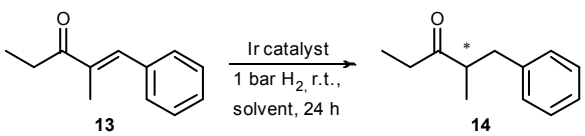


Table 4: Enantioselective hydrogenation of (E)-2-methyl-1-phenyl-pent-1-en-3-one (**13**)

Solvent	Catalyst	t [h]	conversion [%]	*ee* [%]
CH_2Cl_2	**9** (1 mol%)	24	99	99
CH_2Cl_2	**10** (1 mol%)	24	99	99
*t*BuOMe	**9** (1 mol%)	24	99	99

[a] reaction conditions: **13** (1.0 mol), catalyst (1 mol %), solvent (1.0 mL). All reactions were carried out at r.t. under a hydrogen pressure of 1 bar for 24 h. [b] Conversion was determined by ^{1}H NMR of the crude product. [c] Enantioselectivities were determined by HPLC on a Chiralcel OJ column.

Conclusions

Salts of three halogen-free, water-stable, lipophilic, thermally stable, weakly-coordinating aluminate anions have been prepared in multigram amounts in high yield from low-cost chemicals without the use of halogenated solvents or toxic metal reagents. The solubility of the aluminate salts in a wide range of organic solvents is excellent, particularly for the *tert*-pentyl derivative "aletpate". The tendency for crystallisation is outstanding, particularly for the *tert*-butyl derivative "aletbate". The ethylene linker of the bisphenolate ligands promotes the almost complete steric shielding of the tetraoxo aluminium core, and therefore leads to a high kinetic stability in neutral and basic solvent mixtures. The aluminates are hydrolysed only in highly acidic aqueous media. The thermally activated sodium aluminate adducts eliminate chloride ligands from transition metal complexes such as *N*-heterocyclic carbene gold chloride or [Ir(PHOX)(cod)Cl]. The conversion and the enantioselectivities in iridium aletbate-catalyzed hydrogenations are comparable to reactions with conventional weakly coordinating anions. This is a proof of concept that the lipophilic aletbate and aletpate anions can replace expensive fluorinated anions in applications that have so far depended on environmentally persistent counterions.

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 ^{13}C or residual ^{1}H solvent peaks. Mass spectra were recorded by the Mass Spectrometry Service Facility of the Chemical Department at the Ruprecht-Karls-Universität Heidelberg. The following machines were employed: Bruker ICR Apex-Qe, Finnigan MAT LCQ and JEOL JMS-700. Elemental analyses were carried out by the Laboratory of Microanalysis in the Department of Chemistry at the Ruprecht-Karls-Universität Heidelberg. Melting points were determined by using a Gallenkamp hot-stage microscope.

Synthesis of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (1a)

A flask was equipped with 51.5 g (0.25 mol) 2,4-di-*tert*-butylphenol in 150 mL acetic acid at room temperature. Paraformaldehyde (8.3 g, 0.27 mol) was added. The suspension was stirred at room temperature for 2 h. 95 mL (0.50 mol) of 33 w% HBr in acetic acid was added within 15 min and the resulting orange solution was stirred for additional 30 min. After removal of the solvent *in vacuo*, pentane (200 mL) was added, and the solution was filtered through a pad of silica gel. The solvent was removed *in vacuo*, resulting in 70.8 g of a clear yellow oil of crude product **1a**. This oil was used for the synthesis of bisphenol **2a** without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δH (ppm): 1.29 {9H, s, C($\underline{CH_3}$)$_3$}, 1.43 {9H, s, C($\underline{CH_3}$)$_3$}, 4.58 (2H, s, $\underline{CH_2}$), 5.27 (1H, s, OH), 7.10 (1H, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 7.36 (1H, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$).

Synthesis of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-butylphenol) (2a)

2-(Bromomethyl)-4,6-di-*tert*-butylphenol **1a** (70.8 g, 0.24 mol) was dissolved in 125 mL of toluene. A solution of 2.36 g $CuCl_2$ in 375 mL saturated aqueous ammonium chloride solution was added whilst stirring. After addition of 23.6 g (0.36 mol) of zinc powder, the suspension was stirred vigorously for 16 h at room temperature. The excess of zinc metal was dissolved by addition of 2 M hydrochloric acid. Diethyl ether was added, and the phases were separated. The aqueous phase was extracted twice with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed *in vacuo.* After recrystallisation from aceto-nitrile, the product was isolated as a colourless powder (yield: 38.5 g, 70 %). ^{1}H NMR (600.24 MHz, $CDCl_3$) δH (ppm): 1.32 {18H, s, C($\underline{CH_3}$)$_3$}, 1.47 {18H, s, C($\underline{CH_3}$)$_3$}, 2.86 (4H, s, $\underline{CH_2}$), 5.69 (2H, s, $\underline{OH}$), 7.10 (2H, d, $^4J_{HH}$ = 2.3 Hz, Ar-$\underline{H}$), 7.22 (2H, d, $^4J_{HH}$ = 2.3 Hz, Ar-$\underline{H}$). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$) δC (ppm): 30.3, 31.8, 32.7, 34.4, 34.6, 122.3, 124.9, 127.7, 134.8, 142.6, 150.3. ESI-HRMS (m/z)$^-$ [M-H]$^-$ calc. mass: 437.34250 found: 437.34196. FTIR (ATR) ν_{max} (cm^{-1}): 3352 (br. s), 2957 (m), 2868 (w), 1593 (w), 1477 (m), 1444 (w), 1413 (w), 1391 (w), 1360 (m), 1308 (w), 1277 (w), 1245 (w), 1182 (s), 1146 (w), 1121 (w), 1104 (w), 1024 (w), 942 (w), 904 (w), 876 (m), 822 (w), 807 (w), 762 (w), 721 (w), 651 (w). $C_{30}H_{46}O_2$: calculated C 82.14%, H 10.57%; found C 82.08%, H 10.79%. Melting point: 175 °C

Synthesis of bis(tetrahydrofuran)sodium aletbate (4a)

Under inert-gas conditions, a solution of 6,6'-(ethane-1,2-diyl)bis(2,4-di-*tert*-butylphenol) **2a (**17.4 g, 40.0 mmol) in 110 mL dry THF was slowly added to a solution of $NaAlH_4$ (1.20 g, 20.0 mmol) in 10 mL dry THF at room temperature. The reaction mixture was heated under reflux conditions for 5 h, cooled to room temperature, and filtered through Celite. After removal of the solvent *in vacuo*, pentane was added and the suspension was stirred for 30 min. After filtration, the colourless powder was dried *in vacuo*, yielding 19.5 g of compound **4** (83%). ^{1}H NMR (600.24 MHz, d_6-acetone, 300 K) aletbate major : minor conformer ratio (80:20) δH (ppm): 1.23 – 1.30 {72H, m, C($\underline{CH_3}$)$_3$}, 1.75 – 1.83 (8H, m, thf), 2.27 – 2.37 (4H, m, Ar-$\underline{CH_2}$), 3.55 – 3.65 (20H, major, m, Ar-$\underline{CH_2}$/thf), 3.73 – 3.81 (4H, major, m, Ar-$\underline{CH_2}$), 6.91 (4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.96 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-$\underline{H}$), 6.98

(4H, minor, d, $^4J_{HH}$ = 2.6 Hz, Ar-H), 7.00 (4H, major, d, $^4J_{HH}$ = 2.6 Hz, Ar-H). $^{13}C\{^1H\}$ NMR (150.93 MHz, $CDCl_3$, 300 K) δC (ppm): 26.1, 31.0, 31.1, 32.3, 32.4, 34.3, 34.4, 35.3, 35.4, 35.7, 68.0, 121.0, 121.2, 124.2, 124.4, 131.5, 131.6, 136.8, 137.0, 137.2, 156.0, 156.3. ESI-HRMS (m/z)$^-$ $[M]^-$ calc. mass: 899.65035 found: 899.64839. FTIR (ATR) ν_{max} (cm^{-1}): 2950 (s), 2902 (m), 2866 (m), 1760 (w), 1605 (m), 1472 (s), 1442 (s), 1414 (m), 1389 (w), 1359 (m), 1316 (m), 1303 (m), 1282 (s), 1254 (m), 1236 (m), 1201 (m), 1168 (m), 1133 (w), 1114 (w), 995 (w), 912 (w), 876 (s), 855 (w), 810 (w), 772 (w), 647 (w), 611 (m). $C_{68}H_{104}NaAlO_6$: calculated C 76.51%, H 9.82%; found C 76.29%, H 10.07%. Melting point: 278 °C (decomposition).

Synthesis of sodium aletbate (5a)

The thf ligands from sodium complex **4a** were thermally eliminated at 150 °C and 0.1 mbar within 24 h in the solid state. The product was obtained as a colourless solid in quantitative yield. ^1H NMR (600.24 MHz, CD_2Cl_2, 300 K) δH (ppm): 1.22 – 1.26 {36H, br. s, $C(CH_3)_3$}, 1.28 {36H, s, $C(CH_3)_3$}, 2.32 – 2.82 (4H, br. s, Ar-CH_2), 3.06 – 3.73 (4H, br. s, Ar-CH_2), 7.04 (4H, d, $^4J_{HH}$ = 2.6 Hz, Ar-H), 7.10 (4H, d, $^4J_{HH}$ = 2.6 Hz, Ar-H). $^{13}C\{^1H\}$ NMR (150.33 MHz, CD_2Cl_2, 300 K) δC (ppm): 30.5, 31.8, 34.3, 35.0, 35.1, 122.5, 125.1, 131.3, 136.8, 140.1 153.7. ESI-HRMS (m/z)$^-$ $[M]^-$ calc. mass: 899.6035 found: 899.64834. FTIR (ATR) ν_{max} (cm^{-1}): 3613 (w), 2952 (m), 2867 (w), 1617 (w), 1470 (s), 1440 (s), 1413 (m), 1390 (w), 1360 (m), 1316 (m), 1271 (s), 1235 (s), 1202 (w), 1167 (w), 1134 (w), 1025 (w), 996 (w), 912 (m), 865 (s), 810 (w), 763 (m), 648 (w), 615 (s). Melting point: 275 °C.

Acknowledgements

Financial support by the Universität Heidelberg is gratefully acknowledged. We thank Dr. Jürgen Graf for NMR spectra and Ms Petra Krämer for IR spectra.

Notes and references

[a] Prof. Dr. Bernd F. Straub, Dipl.-Chem. Timo Söhner, B.Sc. Felix Braun, M.Sc. L. Charlotte Over, B.Sc. Sven Mehlhose, Dr. Frank Rominger, Universität Heidelberg, Organisch-Chemisches Institut, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany. Email: straub@oci.uni-heidelberg.de

Electronic Supplementary Information (ESI) available: The ESI contains the general procedures, spectroscopic and crystallographic data, hydrolysis experiments, and representative ^1H NMR spectra. See DOI: 10.1039/b000000x/

1 I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* 2004, **43**, 2066.

2 a) C. A. Reed, K.-C. Kim, R. D. Bolskar, L. J. Mueller, *Science* 2000, **289**, 101; b) T. Küppers, E. Bernhardt, R. Eujen, H. Willner, C. W. Lehmann, *Angew. Chem. Int. Ed.* 2007, **46**, 6346; c) M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* 1992, **11**, 3920; d) M. R. Lichtenthaler, A. Higelin, A. Kraft, S. Hughes, A. Steffani, D. A. Plattner, J. M. Slattery, I. Krossing, *Organometallics* 2013, **32**, 6725; e) A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler, T. Müller, *Organometallics* 2013, **32**, 4713.

3 a) E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* 2000, **100**, 1391; b) Y. Li, M. Cokoja, F. E. Kühn, *Coord. Chem. Rev.* 2011, **255**, 1541; c) S. F. Rach, F. E. Kühn, *Chem. Rev.* 2009, **109**, 2061; d) S. P. Smidt, N. Zimmermann, M. Studer, A. Pfaltz, *Chem. Eur. J.* 2004, **10**, 4685; e) C. Böing, G. Franciò, W. Leitner, *Adv. Synth. Catal.* 2005, **347**, 1537; f) Y. Li, J. He, V. Khankhoje, E. Herdtweck, K. Kohler, O. Storcheva, M. Cokoja, F. E. Kuhn, *Dalton Trans.* 2011, **40**, 5746.

4 a) A. J. P. A. G. Massey, F. G. A. Stone, *Proceedings of the Chemical Society* 1963, 212; b) A. G. Massey, A. J. Park, J. *Organomet. Chem.* 1964, **2**, 245; c) H. Kobayashi, T. Sonoda, H. Iwamoto, M. Yoshimura, *Chem. Lett.* 1981, **10**, 579.

5 R. Francke, D. Cericola, R. Kötz, G. Schnakenburg, S. R. Waldvogel, *Chem. Eur. J.* 2011, **17**, 3082.

6 I. Krossing, *Chem. Eur. J.* 2001, **7**, 490.

7 a) E. Bernhardt, G. Henkel, H. Willner, G. Pawelke, H. Bürger, *Chem. Eur. J.* 2001, **7**, 4696; b) M. Finze, E. Bernhardt, M. Berkei, H. Willner, J. Hung, R. M. Waymouth, *Organometallics* 2005, **24**, 5103.

8 a) J. Lacour, C. Ginglinger, C. Grivet, G. Bernardinelli, *Angew. Chem. Int. Ed.* 1997, **36**, 608; b) F. Favarger, C. Goujon-Ginglinger, D. Monchaud, J. Lacour, *J. Org. Chem.* 2004, **69**, 8521.

9 a) S. V. Ivanov, A. J. Lupinetti, S. M. Miller, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *Inorg. Chem.* 1995, **34**, 6419; b) B. T. King, J. Michl, *J. Am. Chem. Soc.* 2000, **122**, 10255; c) Z. Xie, B.-M. Wu, T. C. W. Mak, J. Manning, C. A. Reed, *J. Chem. Soc., Dalton Trans.* 1997, 1213.

10 www.opcw.org/chemical-weapons-convention/annex-on-chemicals/b-schedules-of-chemicals/schedule-2/

11 C. Lee, Y. Guo, P. Tsai, H. Chang, C. Chen, C. Chen, T. Hsiue, *Eur. Resp. J.* 1997, **10**, 1408.

12 I. Roblin, M. Urban, D. Flicoteau, C. Martin, D. Pradeau, *J. Burn Care & Res.* 2006, **27**, 889.

13 P. Forster, V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. Van Dorland, 2007: Changes in Atmospheric Constituents and in Radiative Forcing. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

14 A. Proudfoot, S. Bradberry, J. A. Vale, *Toxicol Rev.* 2006, **25**, 213.

15 a) M. K. Moe, S. Huber, J. Svenson, A. Hagenaars, M. Pabon, M. Trümper, U. Berger, D. Knapen, D. Herzke, *Chemosphere* 2012, **89**, 869; b) A. Shankar, J. Xiao, A. Ducatman, *Am. J. Epidem.* 2011, **174**, 893.

16 C. A. Reed, *Acc. Chem. Res.* 1998, **31**, 133.

17 B. T. King, Z. Janoušek, B. Grüner, M. Trammell, B. C. Noll, J. Michl, *J. Am. Chem. Soc.* 1996, **118**, 3313.

18 a) B. F. Straub, M. Wrede, K. Schmid, F. Rominger, *Eur. J. Inorg. Chem.* 2010, 1907; b) T. Söhner, W. Wackerow, F. Rominger, B. F. Straub, *ARKIVOC* 2014, *4*, 296-318.

19 M. Konkol, M. Nabika, T. Kohno, T. Hino, T. Miyatake, J. *Organomet. Chem.* 2011, **696**, 1792.
20 a) A. C. P. F. d. Sá, G. M. A. Pontes, J. A. L. d. Anjos, S. R. Santana, L. W. Bieber, I. Malvestiti, *J. Braz. Chem. Soc.* 2003, **14**, 429; b) S. Fokken, T. P. Spaniol, J. Okuda, F. G. Sernetz, R. Mülhaupt, *Organometallics* 1997, **16**, 4240.
21 a) L. Farrugia, *J. Appl. Cryst.* 1997, **30**, 565; b) Persistence of Vision Ray Tracer (POV-Ray), www.povray.org.
22 C. Reichardt, *Chem. Rev.* 1994, **94**, 2319.
23 C. Capello, U. Fischer, K. Hungerbühler, *Green Chem.* 2007, **9**, 927.
24 a) A. Correa, S. Nolan, L. Cavallo, *Computational Mechanisms of Au and Pt Catalyzed Reactions*, Vol. 302 (Eds.: E. Soriano, J. Marco-Contelles), Springer Berlin Heidelberg, 2011, pp. 131-155; b) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* 2008, **37**, 1776; c) M. C. B. Jaimes, A. S. K. Hashmi, *Modern Gold Catalyzed Synthesis,* Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 273-296; d) W. E. Brenzovich, *Angew. Chem. Int. Ed.* 2012, **51**, 8933; e) P. J. Pérez, M. M. Díaz-Requejo, I. Rivilla, *Beilstein J. Org. Chem.* 2011, **7**, 653; f) B. Alcaide, P. Almendros, J. M. Alonso, *Molecules* 2011, **16**, 7815.
25 L. Messori, L. Marchetti, L. Massai, F. Scaletti, A. Guerri, I. Landini, S. Nobili, G. Perrone, E. Mini, P. Leoni, M. Pasquali, C. Gabbiani, *Inorg. Chem.* 2014, **53**, 2396.
26 a) W. Wang, A. Zheng, P. Zhao, C. Xia, F. Li, *ACS Catalysis* 2013, **4**, 321; b) R. Visbal, I. Ospino, J. M. López-de-Luzuriaga, A. Laguna, M. C. Gimeno, *J. Am. Chem. Soc.* 2013, **135**, 4712; c) R. Visbal, J. M. Lopez-de-Luzuriaga, A. Laguna, M. C. Gimeno, *Dalton Trans.* 2014, **43**, 328.
27 R. Crabtree, *Acc. Chem. Res.* 1979, **12**, 331.
28 G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* 2000, **33**, 336.
29 S. J. Roseblade, A. Pfaltz, *Acc. Chem. Res.* 2007, **40**, 1402.
30 a) P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger, A. Pfaltz, *Chem. Eur. J.* 1997, **3**, 887; b) S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz, *J. Am. Chem. Soc.* 1999, **121**, 6421; c) N. a. Mršić, A. J. Minnaard, B. L. Feringa, J. G. d. Vries, *J. Am. Chem. Soc.* 2009, **131**, 8358; d) A. Bartoszewicz, N. Ahlsten, B. Martín-Matute, *Chem. Eur. J.* 2013, **19**, 7274.
31 a) S.-M. Lu, C. Bolm, *Angew. Chem. Int. Ed.* 2008, **47**, 8920; b) F. Maurer, V. Huch, A. Ullrich, U. Kazmaier, *J. Org. Chem.* 2012, **77**, 5139.
32 K. H. Hopmann, A. Bayer, *Organometallics* 2011, **30**, 2483.
33 a) B. Wüstenberg, A. Pfaltz, *Adv. Synth. Catal.* 2008, **350**, 174; b) E. Martínez-Viviente, P. S. Pregosin, *Inorg. Chem.* 2003, **42**, 2209.
34 N. Mršić, L. Panella, E. G. Ijpeij, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *ChemCatChem* 2011, **3**, 1139.

