Homo- vs. heterometallic organoaluminum fencholates: Structures and selectivities

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ABSTRACT

Homo (Al)- and heterometallic (Al, Li)-fencholates and TADDOLates (**5–12**) yield in methylations of benzaldehyde 1-phenylethanol with up to 90% ee. Surprisingly, the new BISFOL-based (Al, Li)-heterometallic fencholate (**11**) shows an strong increase and a change of the sense of enantioselectivity from 19% ee (S) to 62% ee (R) in comparison to its (Al)-homometallic fencholate (**7**). Despite of the presence of nucleophilic methylide groups, the O-BIFOL-based (Al, Li)-heterometallic fencholate (**10**) yields a stable complex with benzaldehyde, a lithium ion binds the carbonyl group.

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1. Introduction

Enantioselective alkylations of carbonyl compounds with organometallic reagents are among the most useful methods for the preparation of chiral alcohols [1]. Additions of organolithiums to aldehydes (Scheme 1) are synthetically well established and afford enantiopure alcohols in the presence of stoichiometric amounts of chiral additives. Catalytic procedures, e.g. with less than 5 mol% of chiral additives, are hardly achievable, due to the high reactivity of non-modified organolithiums towards aldehydes [1a,1b,1l].

In contrast, dialkylzinc reagents react with aldehydes extremely slowly in the absence of a catalyst [2]. Chiral ligands, e.g. β-amino alcohols [3], enable the catalytic asymmetric addition of dialkylzinc to aldehydes with high enantioselectivities [4].

Unlike the dialkylzinc addition to aldehydes, organoaluminum reagents are known to add rapidly to aldehydes, e.g. benzaldehyde, at room temperature in the absence of any additives [5]. Benzaldehyde forms, e.g., with one equivalent trimethylaluminum in dichloromethane at −78 °C a monomeric 1:1 complex, which subsequently reacts to 1-phenylethanol at −20 °C [6]. Molecular structures of such complexes can provide explanations for the mode of coordination of organic carbonyls to aluminum, but only few examples of such Lewis acid–base complexes with aldehydes are known in the literature [7]. Barron et al. reported the X-ray structure of the Lewis acid MAD [8] (methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide)) with 2,2-dimethylpropanal as Lewis base (Scheme 2) [9]. Scott et al. reported the X-ray crystal structure of a Lewis acid–base complex between the bulky homobimetallic aluminum complex and benzaldehyde (Scheme 2) [10].

Recently, Maruoka et al. evaluated the reactivity of the aluminum Lewis acid **A** (Scheme 3) in comparison to the *bis*-aluminum Lewis acid **B** in the alkylation of benzaldehyde with trimethylaluminum [11]. They found that the bimetallic Lewis acid **B** alkylates benzaldehyde more rapidly and more efficiently than the monometallic Lewis acid **A**.

A series of aluminum reagents and catalysts based on chiral chelating C_2-symmetric diols such as BINOLs **C** [12], TADDOLs **D** [13] and its derivates (Scheme 3) have been synthesized and play as Lewis acids a fundamental role in the synthesis of optically pure compounds [14].

Shibasaki and co-workers also developed a series of heterobimetallic [15] complexes based on BINOL and demonstrated their potential as multifunctional catalysts, e.g. ALB: aluminum lithium bis (binaphthoxide) in several catalytic asymmetric reactions, e.g. aldol additions [16].

We have recently employed modular fencholates [17] in chiral organolithium [1a,1b,18] reagents as well as in organozinc [19], organocopper [20] and organopalladium [21] catalysts to study origins of enantioselectivities in C–C-couplings. Herein, we present new fenchone based chiral organoaluminum reagents, their application as methylide transfer reagent to alkylate benzaldehyde and study the influence of the metal ions, i.e. Li⁺ vs. Al³⁺ in homo- and heterometallic systems.

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[1] X-ray analyses.
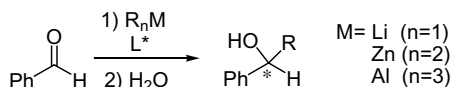
Scheme 1. Enantioselective addition of organometallic reagents to benzaldehyde with the chiral ligand L*. Organolithiums and organoaluminums add to benzaldehyde in the absence of any additives. Organozinc reagents react extremely slowly in the absence of a catalyst.
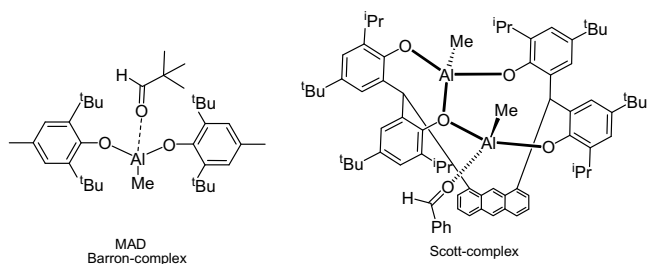
Scheme 2. Literature known molecular structures of the complexes of aluminum organyls with aldehydes from Barron and Scott.
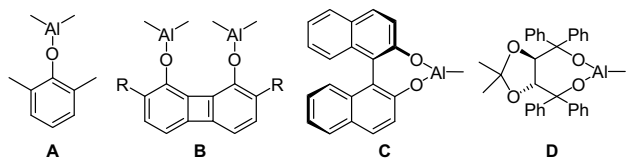
Scheme 3. Homometallic organoaluminum reagents as Lewis acids for the activation of the carbonyl moiety.

2. Results and discussion

The chiral, enantiopure organoaluminum compounds **5**–**8** are accessible from reactions of toluene solutions of trimethylalumi-
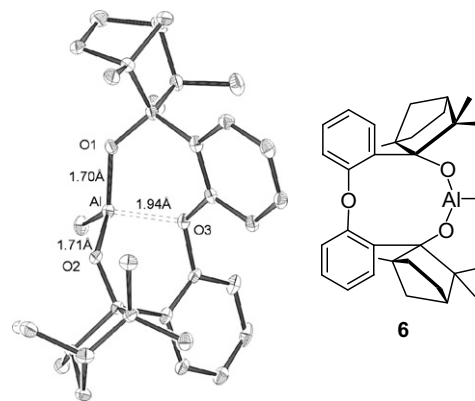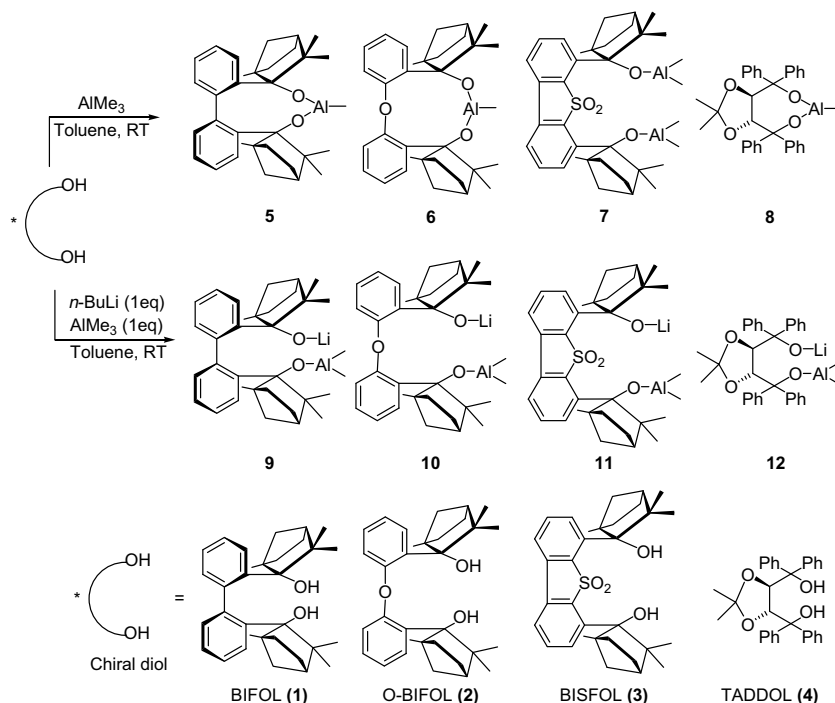

Fig. 1. X-ray crystal structure of **6**. The phenyl group of the diphenylether moiety is fixed between the methyl group and the methylene bridge at C1 of the bicyclo[2.2.1]-heptane scaffold. Hydrogen atoms are omitted for clarity and the probability of the thermal ellipsoids is 30%.

num with the suspensions of diols (*M*)-BIFOL [17d] (**1**), O-BIFOL [22] (**2**), BISFOL [17b] (**3**) and TADDOL [23] (**4**) (Scheme 4). In addition to three fencholate-based diols, TADDOL (**4**) was used as a prominent chiral diol with sterically crowded hydroxyl groups, similar to BIFOL.

The molecular structures of the organoaluminum reagents (**6**–**8**) were confirmed by single-crystal X-ray diffraction (Figs. 1–3). All three crystal structures show *tetra* coordinated aluminum ions and form well defined chelate rings. The molecular structure of **7** (Fig. 2) is, in contrast to the homometallic aluminum complexes **6** and **8**, a homobimetallic aluminum complex whereas each Al-ion is joined by the oxygen atom of the fenchyl moiety (Al–O1: 1.72 Å) and of the sulfone group (Al–O3: 1.94 Å) and two further methylide groups (Al–C: 1.95 Å). In all fencholate based structures (Figs. 1 and 2) aryl groups are conformationally fixed between the methyl group and the methylene bridge at C1 of the fenchane scaffolds [17–20].

Scheme 4. Chiral homo (Al)- and heterometallic (Al, Li) reagents, accessible from diols, trimethylaluminum and *n*-butyllithium.
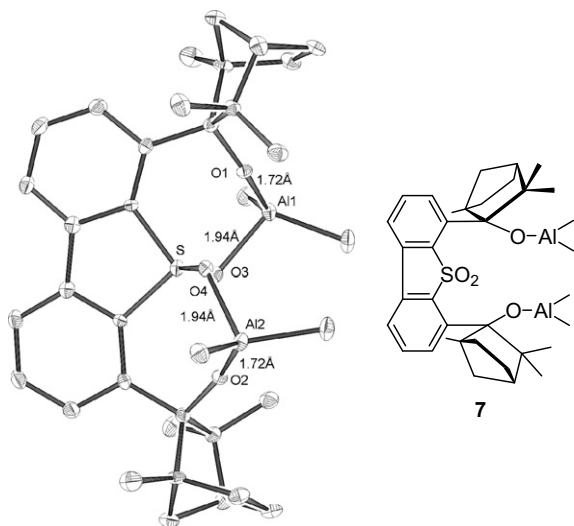
Fig. 2. X-ray crystal structure of **7**. The phenyl group of the cyclic sulfone is fixed between the methyl group and the methylene bridge at C1 of the bicyclo[2.2.1]-heptane scaffold. Hydrogen atoms are omitted for clarity and the probability of the thermal ellipsoids is 30%.
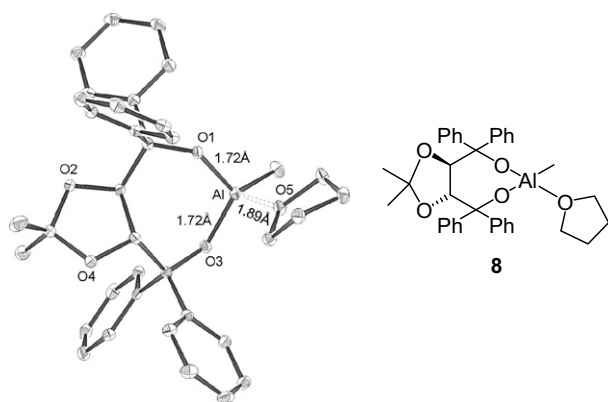

Fig. 3. X-ray crystal structure of **8**. Hydrogen atoms are omitted for clarity and the probability of the thermal ellipsoids is 30%.

Addition of one equivalent of a hexane solution of *n*-butyllithium and one equivalent of a toluene solution of trimethylaluminum to the suspensions of **1–4** in toluene at room temperature under argon atmosphere and subsequent stirring afforded the (Al, Li)-heterometallic complexes **9–12** (Scheme 4).

To gain information on the reactivity and selectivity of the (Al)-homo- and (Al, Li)-heterometallic organyls (**5–12**) in alkylations of carbonyl compounds, the methylation of benzaldehyde with these compounds was used as model reaction (Scheme 5).

Treatment of benzaldehyde with the *in situ* prepared reagents (**5–8**) in toluene at −20 °C for 6 h afforded after hydrolytic work-up 1-phenylethanol in 12–73% yield and in 5–90% ee (Scheme 5, Table 1). While (Al)-BIFOL (**5**) and (Al)-O-BIFOL (**6**) provide only 5% ee of the *R*-enantiomeric product, (Al)-BISFOL (**7**) yields 1-phenylethanol with 19% ee (*S*-enantiomer). In contrast to other (Al)-homometallic organoaluminum complexes (**5**, **6** and **8**), (Al)-BISFOL (**7**) provides the best reactivity (65%), pointing to a strong electrophilic activation of the carbonyl moiety by the two Lewis-acidic aluminum ions in **7**. The TADDOL based Al-organyl (**8**) provides the highest enantioselectivity (90% ee) but shows only a low yield (12%).

While no enhancement of the enantioselectivities and only a slight increase of the reactivities are observed with (Al, Li)-hetero-
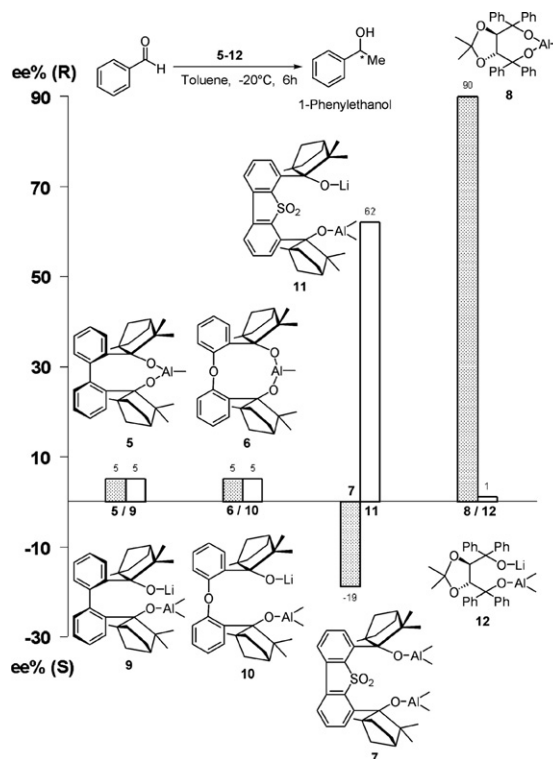
Scheme 5. Alkylation of benzaldehyde by homometallic (Al, grey)-and heterometallic (Al, Li, white) reagents (**5–12**).

Table 1
Alkylation of benzaldehyde by homo-and heterometallic reagents (**5–12**) according to Scheme 5

Reagents	% Yield[a]	% ee (Config.)[b]	v (CO) (cm^{-1})[c]
BIFOL-Al (**5**)	43	5 (*R*)	1662
O-BIFOL-Al (**6**)	45	5 (*R*)	1702
BISFOL-Al (**7**)	65	19 (*S*)	1698
TADDOL-Al (**8**)	12	90 (*R*)	1695
BIFOL-Al-Li (**9**)	57	5 (*R*)	1652
O-BIFOL-Al-Li (**10**)	55	5 (*R*)	1700
BISFOL-Al-Li (**11**)	73	62 (*R*)	1661
TADDOL-Al-Li (**12**)	35	1 (*R*)	1691

[a] Isolated yield of 1-phenylethanol by a reaction time of 6 h (−20 °C) in toluene.
[b] The enantiomeric excess was analyzed by GC (Chiraldex G-TA column).
[c] Carbonyl stretching frequencies of the toluene solutions of the homo- and heterometallic reagents (**5–12**) with benzaldehyde (0 °C, neat, benzaldehyde v (CO): 1699 cm^{-1}).

metallic compounds **9** (5% ee, 57% yield) and **10** (5% ee, 55% yield) in comparison to (Al)-homometallic (**5**) (5% ee, 43% yield) and (**6**) (5% ee, 45% yield), the introduction of lithium as second metal ion gives rise to a surprisingly strong and also change of the sense of the enantioselectivity for (Al, Li)-BISFOL (**11**) (62% ee *R*, 73% yield) vs. (Al)-BISFOL (**7**) (19% ee *S*, 65% yield; Scheme 5, Table 1). This dramatic increase of the enantioselectivity points to a modified coordination of the carbonyl group in the substrate by the Lewis-acidic reagent. Indeed, IR-spectroscopic investigation of a toluene solutions of the (Al, Li)-heterometallic fencholate (**11**) with benzaldehyde exhibits a strong decrease of the carbonyl stretching frequency (1661 cm^{-1}, Table 1), compared to the (Al)-homometallic fencholate (**7**) with benzaldehyde (1698 cm^{-1}). This points to a stronger coordination of the carbonyl oxygen atom to the lithium ion in (Al, Li)-heterometallic fencholate (**11**) relative to the aluminum ions of (Al)-homometallic (**7**). In contrast to **11** and **7**, the (Al, Li)-heterometallic TADDOLate (**12**) exhibits a

strongly decreased enantioselectivity for the methylation of benzaldehyde (35% yield, 1% ee) in comparison to the (Al)-homometallic TADDOLate (**8**) (12% yield, 90% ee). Attempts to crystallize the heterometallic reagents **11** and **12** both at room temperature and −20 °C yielded no suitable crystals for X-ray analyses. However, the reaction of *n*-butyllithium with a hexane solution of BISFOL (**3**) at 0 °C and recrystallization from hexane yields a macrocyclic, dimeric, C_2-symmetric alkyllithium complex (**13**) with four *tetra* coordinated lithium ions. Each lithium ion coordinates to two oxygen atoms of the alkoxide moieties and two oxygen atoms of the sulfone group (Fig. 4).

Another macrocyclic, dimeric, C_2-symmetric alkyllithium complex was obtained by the reaction of *n*-butyllithium with a tetrahydrofuran solution of TADDOL (**4**) at 0 °C and recrystallization from hexane. The molecular structure of the complex shows two tricoordinated lithium ions whereas each lithium ion coordinates to two oxygen atoms of the alkoxide moieties and one oxygen atom of the THF-molecule. The core of this complex consists of a lithium-bridged and hydrogen-bonded $Li_2O_4H_2$ eight-membered ring (Fig. 5) [24].

Attempts to isolate a (Al, Li)-heterometallic reagent based on TADDOL yields the unprecedented [17a,25,26] lithium aluminate (**15**), in which Al^{3+} is coordinated by two TADDOLate units and the Li^+ ion bridges two of the alkoxide ions. Free coordination sites at Li^+ are coordinated by THF (Fig. 6).

The (Al, Li)-heterometallic fencholate (**10**) provides both a low reactivity and selectivity (55% yield and 5% ee). The nucleophilic methylide groups of the O-BIFOL-based (Al, Li)-heterometallic fencholate (**10**) are both quite distant to and especially "in plane" of the formyl group of benzaldehyde (Fig. 7), this "symmetry-forbidden" arrangement of the Me-nucleophiles to the π^*-carbonyl acceptor explains moderate yields of methylation. The low enantioselectivity of **10** points to a non-complexed and not preorganized aldehyde substrate ion during the reaction. A rare example of a
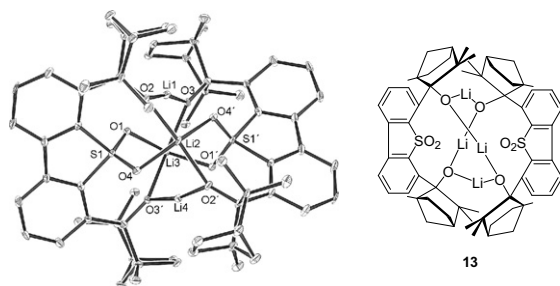

Fig. 6. X-ray crystal structure of TADDOL-lithiumaluminate (**15**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent a 30% probability. Selected atom distances (in Å): Al–O3 1.71, Al–O4 1.75, Al–O5 1.71, Al–O6 1.75, Li–O4 2.07, Li–O6 2.03, Li–O9 1.93, Li–O10 1.97.

Fig. 7. X-ray crystal structure of **10** with benzaldehyde. Hydrogen atoms are omitted for clarity except the hydrogen atoms of the endo methyl group of one fenchane unit and the hydrogen atom of benzaldehyde. The probability of the thermal ellipsoids is 30%. Selected atom distances (in Å): Li–O1 1.91, Li–O2 2.07, Li–O3 1.92, Li–O4 1.92, Li–H1 2.27, Li–H2 2.44, Al–O2 1.78, Al–O4 1.79, C_{Al}–C_{carb} 4.8; 7.2.

well defined aldehyde complex with a methyl aluminum Lewis acid is apparent from a X-ray crystal structure analysis of a complex of the (Al, Li)-heterometallic O-BIFOL reagent (**10**) with benzaldehyde (Fig. 7). This Lewis acid–base complex represents the first isolated and structurally characterized enantiopure complex of benzaldehyde with a lithium dimethylaluminate [27]. At the core of the structure is a AlO_2Li four-membered ring (Al–O2: 1.78 Å, Al–O4: 1.79 Å, Li–O2: 2.07 Å, Li–O4: 1.92 Å). The lithium ion is coordinated by three oxygen atoms of the O-BIFOL ligand and by one oxygen atom of the external Lewis base benzaldehyde.

The Li–H distances between the *endo* methyl group of the fenchane unit and the Li-ion are short (Li–H1: 2.27 Å, Li–H2: 2.44 Å) and point to the tendency of "agostic" Li–HC interactions; all other Li–H distances are >2.50 Å [28].

3. Conclusions

Besides the (Al)-homometallic organoaluminum reagents, (Al, Li)-heterometallic methylation reagents based on fenchols and TADDOL can be employed in methylation of benzaldehyde. Methylations with **5–12** afford 1-phenylethanol in up to 73% yield and 90% ee. The homometallic TADDOLate (**8**) reaches the highest enantioselectivity (90%) amongst the (Al)-homometallic reagents but provides only a low yield (12%). The introduction of lithium as second metal ion gives rise to a dramatic enhancement and also a change in the sense of the enantioselectivity for (Al, Li)-BISFOLate

Fig. 4. X-ray crystal structure of BISFOL-Li. Hydrogen atoms are omitted for clarity and the probability of the thermal ellipsoids is 30%. Selected atom distances (in Å): Li1–O1 2.10, Li1–O2 1.91, Li1–O3 1.90, Li1–O4′ 2.10, Li2–O2 2.02, Li2–O4 2.02, Li3–O1 2.03, Li3–O3 2.00; Li4–O1′ 2.10, Li4–O2′ 1.91, Li4–O3′ 1.90, Li4–O4 2.10.
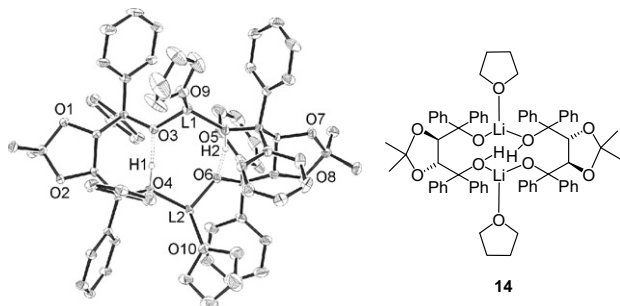

Fig. 5. X-ray crystal structure of Li-TADDOLate (**14**). Hydrogen atoms are omitted for clarity except H1 and H2. Thermal ellipsoids represent a 30% probability. Selected atom distances (in Å): O3–H1 1.47, O6–H2 1.43, O3–O4 2.44, O5–O6 2.42, Li1–O3 1.86, Li1–O5 1.82, Li1–O9 1.89, Li2–O4 1.85, Li2–O6 1.86, Li2–O10 1.90.
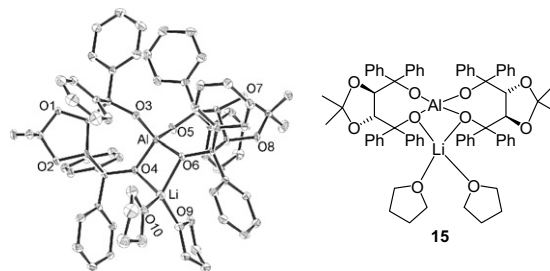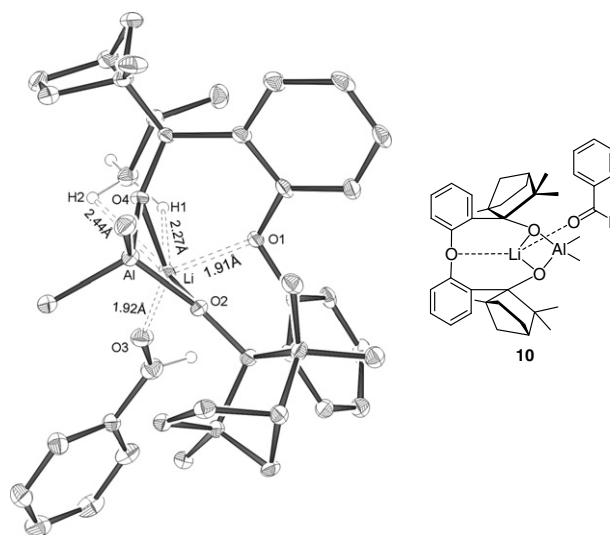
(**11**) (62% ee) vs. (Al)-BISFOLate (**7**) (19% ee). The (Al, Li)-heterometallic O-BIFOLate (**10**) forms a stabile and structurally characterized Lewis acid–base complex with benzaldehyde. This demonstrates the high Lewis-acidity of the (Al, Li)-heterometallic complexes and their tendency to coordinate Lewis bases, such as aldehydes, via the lithium ion.

4. Experimental

All reactions were carried out under argon atmosphere (by using Schlenk and needle/septum techniques) with dried and degassed solvents. X-ray crystal analyses were performed on a Bruker Nonius-Kappa-CCD diffractometer with use of Mo Kα radiation, NMR spectra were recorded on a Brucker DPX 300 instrument, IR spectra on a Perkin Elmer paragon 1000 FT-IR spectrometer, melting point on a Stuart Scientific SMP3 machine and optical rotations on an IBZ polar L_μ P-WR machine. GC analyses were carried out on a Hewlett Packard HP 6890 instrument.

4.1. Synthesis of methylaluminumbiphenyl-2,2′-bisfencholate (5)

A solution of trimethylaluminum (1.1 mL, 2.2 mmol, 2.0 M in toluene) was added at room temperature to a solution of biphenyl-2,2′-bisfenchol (BIFOL) (1.0 g, 2.2 mmol) in toluene (3 mL). The resulting mixture was stirred for 2 h. After cooling the solution to −78 °C and thawing three times, the precipitate formed was dissolved in hot toluene. Slow cooling to room temperature yielded **5** (0.88 g, 80 %) as white powder. m.p.: >245 °C (decomposition); $[\alpha]_D^{20} = -125$ ($c = 0.2$ in toluene); IR (KBr, cm^{-1}) 3548 (s), 3423 (b), 2924, 1472. ^{1}H NMR (toluene-d_8, 300 MHz): $\delta = -0.79$ (3H, s), 0.65 (3H, s), 0.70 (3H, s), 1.10 (3H, s), 1.30–2.35 (6H, m), 2.35 (3H, s), 6.91 (1H, d), 7.10 (1H, t), 7.23 (1H, t), 7.62 (1H, d). ^{13}C NMR (toluene-d_8, 75 MHz) $\delta = 144.45$, 141.52, 131.62, 130.23, 125.41, 125.20, 86.52, 54.99, 49.58, 46.80, 42.75, 34.48, 30.29, 24.06, 21.42, 17.87, −4.33.

4.2. Synthesis of methylaluminumbiphenylether-2,2′-bisfencholate (6)

A solution of trimethylaluminum (1.1 mL, 2.1 mmol, 2.0 M in toluene) was added at room temperature to a solution of biphenylether-2,2′-bisfenchol (O-BIFOL) (1.0 g, 2.1 mmol) in toluene (3 mL). The resulting mixture was stirred for 2 h. After cooling the solution to −78 °C and thawing three times, the precipitate formed was dissolved in hot THF. Slow cooling to room temperature yielded **6** (0.83 g, 77%) as colorless crystals. m.p.: >270 °C (decomposition); $[\alpha]_D^{20} = -112$ ($c = 0.3$ in toluene); IR (KBr, cm^{-1}) 3487 (s), 2924, 1477, 1436. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.29$ (3H, s), 0.54–0.70 (6H, s), 1.00–1.74 (18H, m), 2.43 (8H, s), 7.00–7.50 (6H, m), 7.84 (2H, d). ^{13}C NMR (CDCl$_3$, 75 MHz) $\delta = 137.85$, 131.66, 129.02, 128.21, 125.29, 113.55, 92.90, 86.33, 56.05, 49.63, 47.29, 41.99, 34.21, 29.91, 23.81, 21.47, 17.74. X-ray crystal data of **6**: C$_{33}$H$_{43}$AlO$_3$, $M = 514.65$; space group $P2_1$; $a = 10.1607(4)$ Å, $b = 18.2498(9)$ Å, $c = 15.3081(5)$ Å, $\beta = 101.817(2)$, $V = 2778.4(2)$ Å^3; $Z = 4$; $T = 100(2)$ K; $\mu = 0.106$ mm^{-1}; reflections total: 13511, unique: 10620, observed: 7713 ($I > 2\sigma(I)$); parameters refined: 745; $R1 = 0.0501$, $wR2 = 0.0957$; GOF = 0.996.

4.3. Synthesis of tetramethylaluminumbiphenyl-2,2′-sulfone-3,3′-bisfencholate (7)

A solution of trimethylaluminum (1.92 mL, 3.84 mmol, 2.0 M in toluene) was added at room temperature to a solution of biphenyl-2,2′-sulfone-3,3′-bisfenchol (BISFOL) (1.0 g, 1.92 mmol) in toluene (3 mL). The resulting mixture was stirred for 2 h. After cooling

the solution to −78 °C and thawing three times, the precipitate formed was dissolved in hot toluene. Slow cooling to room temperature yielded **7** (0.79 g, 65%) as colorless crystals. m.p.: >281 °C (decomposition); $[\alpha]_D^{20} = -130$ ($c = 0.1$ in toluene); IR (KBr, cm^{-1}) 3523 (b), 2924, 1572, 1456. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.15$ (6H, s), 0.58 (3H, s), 1.12–1.60 (3H, m), 1.23–1.34 (4H, m), 1.45–1.60 (2H, m), 1.81 (1H, d), 1.96 (1H, d), 2.43 (2H, s), 7.24-7.33 (1H, dd), 7.70–7.80 (1H, m), 7.89–8.05 (1H, m). ^{13}C NMR (CDCl$_3$, 75 MHz) $\delta = 145.50$, 137.37, 132.49, 131.99, 130.74, 119.09, 86.04, 54.49, 48.86, 47.74, 42.72, 33.64, 29.56, 23.95, 21.23, 17.64, 1.52. X-ray crystal data of **7**: C$_{43}$H$_{58}$Al$_2$O$_4$S, $M = 724.91$; space group $P4_122$; $a = 10.4517(7)$ Å, $b = 10.4517(7)$ Å, $c = 36.343(2)$ Å, $V = 3970.0(4)$ Å^3; $Z = 4$; $T = 100(2)$ K; $\mu = 0.166$ mm^{-1}; reflections total: 11769, unique: 3662, observed: 2070 ($I > 2\sigma(I)$); parameters refined: 284; $R1 = 0.0473$, $wR2 = 0.0701$; GOF = 0.863.

4.4. Synthesis of methylaluminum TADDOLate (8)

A solution of trimethylaluminum (1.07 mL, 2.14 mmol, 2.0 M in toluene) was added at room temperature to a solution of TADDOL (1.0 g, 2.14 mmol) in toluene (3 mL). The resulting mixture was stirred for 2 h. After cooling the solution to −78 °C and thawing three times, the precipitate formed was dissolved in hot toluene. Slow cooling to room temperature yielded **8** (0.92 g, 85%) as colorless crystals. m.p.: >193 °C (decomposition); $[\alpha]_D^{20} = -66$ ($c = 0.2$ in toluene), IR (KBr, cm^{-1}) 3284 (b), 2983, 1598, 1493, 1445. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.14$ (3H, s), 0.96 (6H, s), 4.09 (1H, s), 4.25 (1H, s), 7.18 (5H, s) 7.27–7.37 (16H, m) 7.57 (4H, d), ^{13}C NMR (CDCl$_3$, 75 MHz) $\delta = 145.98$, 142.74, 128.63, 128.11, 127.64, 127.55, 127.28, 109.51, 80.98, 77.46, 27.15. X-ray crystal data of **8**: C$_{36}$H$_{39}$AlO$_5$, $M = 578.65$; space group $P2_12_12_1$; $a = 9.3849(2)$ Å, $b = 15.8649(5)$ Å, $c = 20.3281(6)$ Å, $V = 3026.66(15)$ Å^3; $Z = 4$; $T = 100(2)$ K; $\mu = 0.110$ mm^{-1}; reflections total: 16841, unique: 6557, observed: 4922 ($I > 2\sigma(I)$); parameters refined: 382; $R1 = 0.0413$, $wR2 = 0.0733$; GOF = 0.952.

4.5. Synthesis of lithiumdimethylaluminumbiphenyl-2,2′-bisfencholate (9)

A solution of n-BuLi (1.4 mL, 2.2 mmol, 1.6 M in hexane) was added at room temperature to a solution of biphenyl-2,2′-bisfenchol (BIFOL) (1.0 g, 2.2 mmol) in toluene (3 mL). The resulting mixture was stirred for 2 h. To this mixture, a solution of trimethylaluminum (1.1 mL, 2.2 mmol, 2.0 M in toluene) was added at room temperature and the solution was stirred for further 2 h. Slow evaporation of the solvent yielded **9** (0.95 g, 83%) as white powder. m.p.: >299 °C (decomposition); $[\alpha]_D^{20} = -74$ ($c = 0.2$ in toluene), IR (KBr, cm^{-1}) 3548 (s), 3418 (b), 2922, 1662, 1471, 1381. ^{1}H NMR (toluene-d_8, 300 MHz): $\delta = -0.29$ (6H, s), 0.29 (3H, s), 0.33 (3H, s), 0.58 (3H, s), 0.96 (2H, d), 1.00 (3H, s), 1.32 (2H, s), 1.41 (2H, s), 1.44 (3H, s), 1.55 (2H, s), 1.68 (2H, s), 1.76 (2H, s), 2.27–2.34 (1H, m), 2.46 (1H, s), 6.63–6.67 (1H, m), 6.78–6.84 (2H, m), 7.12 (3H, s), 7.69–7.74 (2H, m). ^{13}C NMR (toluene-d_8, 75 MHz) $\delta = 144.18$, 141.23, 131.42, 130.07, 129.09, 124.69, 86.22, 54.81, 49.20, 46.49, 42.39, 34.25, 30.27, 23.93, 21.38, 17.85.

4.6. Synthesis of lithiumdimethylaluminumbiphenylether-2,2′-bisfencholate (10)

A solution of n-BuLi (1.4 mL, 2.2 mmol, 1.6 M in hexane) was added at room temperature to a solution of biphenylether-2,2′-bisfenchol (O-BIFOL) (1.04 g, 2.2 mmol) in toluene (3 mL). The resulting mixture was stirred for 2 h. To this mixture, a solution of trimethylaluminum (1.1 mL, 2.2 mmol, 2.0 M in toluene) was added at room temperature and the solution was stirred for further 2 h. Slow evaporation of the solvent yielded **10** (1.0 g, 86%) as

white powder. m.p.: >287 °C (decomposition); $[\alpha]_D^{20} = -121$ ($c = 0.1$ in toluene), IR (KBr, cm^{-1}) 3482 (b), 2924, 1593, 1477, 1437. ^{1}H NMR (toluene-d_8, 300 MHz): δ = −0.35 (6H, s), 0.29 (3H, s), 0.68 (3H, s), 0.81-0.887 (3H, m), 1.01 (3H, t), 1.02 (3H, d), 1.14–131 (3H, m), 165 (2H, s), 1.87 (2H, s), 2.30 (2H, d), 2.78 (2H, d), 3.14–3.23 (2H, m), 3.05 (1H, s), 6.81 (1H, s), 6.88 (2H, t), 7.12 (3H, s), 7.72 (2H, t). ^{13}C NMR (toluene-d_8, 75 MHz) δ = 157.34, 155.07, 135.27, 135.20, 129.90, 129.68, 128.98, 126.71, 123.24, 122.97, 121.12, 117.88, 85.45, 84.99, 53.62, 53.38, 50.16, 49.21, 45.55, 44.76, 41.13, 40.58, 33.94, 33.36, 30.36, 29.75, 24.59, 24.39, 22.45, 22.34, 18.31, 18.16.

4.7. Synthesis and characterization of the benzaldehyde complex with 10

Benzaldehyde (0.2 g, 1.89 mmol) and **10** (1.0 g, 1.89 mmol) were dissolved in toluene (3 mL) at room temperature. The mixture was stirred for 5 h at room temperature and the solution was cooled to −20 °C. Yellow oil formed, which crystallized after 2 days. Slow evaporation of the solvent yielded crystals suitable for X-ray analysis. m.p.: 198 °C (decomposition), X-ray crystal data of benzaldehyde 10 complex: $C_{41}H_{52}AlLiO_4$, $M = 642.75$; space group $P2_12_12_1$; $a = 9.7197(6)$ Å, $b = 16.866(2)$ Å, $c = 21.538(2)$ Å, $V = 3530.8(6)$ Å^3; $Z = 4$; $T = 100(2)$ K; $\mu = 0.098$ mm^{-1}; reflections total: 16 902, unique: 7487, observed: 3823 ($I > 2\sigma(I)$); parameters refined: 488; R1 = 0.0469, wR2 = 0.0618; GOF = 0.839.

4.8. Synthesis of lithiumdimethylaluminumbiphenyl-2,2′-sulfone-3,3′-bisfencholate (11)

A solution of n-BuLi (1.4 mL, 2.2 mmol, 1.6 M) in hexane was added at room temperature to a solution of biphenyl-2,2′-sulfone-3,3′-bisfenchol (BISFOL) (1.14 g, 2.2 mmol) in toluene (3 mL). The resulting mixture was stirred for 2 h. To this mixture, a solution of trimethylaluminum (1.1 mL, 2.2 mmol, 2.0 M) in toluene was added at room temperature and the solution was stirred for further 2 h. Slow evaporation of the solvent yielded **11** (1.1 g, 83%) as white powder. m.p.: >287 °C (decomposition); $[\alpha]_D^{20} = -145$ ($c = 0.3$ in toluene), IR (KBr, cm^{-1}) 3523 (b), 2924, 1572, 1456. ^{1}H NMR (toluene-d_8, 300 MHz): δ = −0.43 (6H, s), 0.58 (3H, s), 1.08 (3H, s), 1.26 (3H, s), 1.43–2.38 (6H, m), 3.05 (1H, s), 7.52 (1H, t), 7.70 (2H, d). ^{13}C NMR (toluene-d_8, 75 MHz) δ = 145.09, 132.19, 131.61, 130.07, 128.98, 118.98, 54.28, 50.06, 48.85, 47.64, 42.42, 33.67, 29.67, 24.16, 21.38, 17.19.

4.9. Synthesis of lithiumdimethylaluminum-TADDOLate (12)

A solution of n-BuLi (1.4 mL, 2.2 mmol, 1.6 M) in hexane was added at room temperature to a solution of (1.03 g, 2.2 mmol) TADDOL in toluene (3 mL). The resulting mixture was stirred for 2 h. To this mixture, a solution of trimethylaluminum (1.1 mL, 2.2 mmol, 2.0 M in toluene) was added at room temperature and the solution was stirred for further 2 h. Slow evaporation of the solvent yielded **12** (1.0 g, 85%) as white powder. m.p.: >296 °C (decomposition); $[\alpha]_D^{20} = -57$ ($c = 0.3$ in toluene), IR (KBr, cm^{-1}) 3373 (b), 1493, 1444. ^{1}H NMR (toluene-d_8, 300 MHz): δ = 0.95 (6H, s), 1.56 (6H, s), 4.88 (2H, s), 7.04–7.50 (16, m), 7.53 (2H, d), 7.70 (2H, d). ^{13}C NMR (toluene-d_8, 75 MHz) δ = 146.59, 143.29, 129.02, 127.91, 127.07, 81.47, 78.12, 29.63, 26.95.

4.10. Synthesis and characterization of Li-BISFOLate (13)

BISFOL (**3**) (1.0 g, 1.92 mmol) was added at room temperature to n-BuLi (2.4 mL, 3.84 mmol, 1.6 M solution in hexane), and the mixture was stirred at 25 °C for 3 h. After cooling the solution to −78 °C and thawing three times, the precipitate formed was dis-

solved in hot hexane. Slow cooling to room temperature yielded crystals suitable for X-ray analysis. m.p.: 171 °C (decomposition), X-ray crystal data of Li-BISFOLate: $C_{37}H_{38}Li_2O_4S$, $M = 592.61$; space group $C2$; $a = 24.295(2)$ Å, $b = 11.8729(5)$ Å, $c = 13.5915(10)$ Å, $\beta = 120.033(1)$, $V = 3394.2(4)$ Å^3; $Z = 4$; $T = 100(2)$ K; $\mu = 0.131$ mm^{-1}; reflections total: 7768, unique: 5625, observed: 3991 ($I > 2\sigma(I)$); parameters refined: 379; R1 = 0.0671, wR2 = 0.1581; GOF = 0.985.

4.11. Synthesis and characterization of Li-TADDOLate (14)

TADDOL (**4**) (1.0 g, 2.14 mmol) was added at room temperature to n-BuLi (2.7 mL, 4.30 mmol, 1.6 M solution in hexane), and the mixture was stirred at 25 °C for 3 h. After cooling the solution to −78 °C and thawing three times, the precipitate formed was dissolved in hot THF. Slow cooling to room temperature yielded crystals suitable for X-ray analysis. m.p.: 165 °C (decomposition), X-ray crystal data of Li-TADDOLate: $C_{152}H_{176}Li_4O_{20}$, $M = 2350.69$; space group $P2_1$; $a = 11.5093(4)$ Å, $b = 15.7585(3)$ Å, $c = 19.0123(5)$ Å, $\beta = 105.092(1)$, $V = 3329.31(16)$ Å^3; $Z = 1$; $T = 100(2)$ K; $\mu = 0.076$ mm^{-1}; reflections total: 11 993, unique: 11 993, observed: 7979 ($I > 2\sigma(I)$); parameters refined: 807; R1 = 0.0702, wR2 = 0.1500; GOF = 1.026.

4.12. Synthesis and characterization of TADDOL-lithiumaluminate (15)

TADDOL (**4**) (1.0 g, 2.14 mmol) was added at room temperature to LiAlH$_4$ (0.9 mL, 2.14 mmol, 2.4 M solution in THF), and the mixture was stirred at 25 °C for 3 h. After cooling the solution to −78 °C and thawing three times, the precipitate formed was dissolved in hot hexane. Slow cooling to room temperature yielded crystals suitable for X-ray analysis. m.p.: 182 °C (decomposition), X-ray crystal data of TADDOL-lithiumaluminate: $C_{76}H_{86}AlLiO_{10}$, $M = 1193.37$; space group $P2_1$; $a = 12.5099(6)$ Å, $b = 39.861(2)$ Å, $c = 13.5707(7)$ Å, $\beta = 104.5330(1)$, $V = 6550.6(6)$ Å^3; $Z = 4$; $T = 100(2)$ K; $\mu = 0.091$ mm^{-1}; reflections total: 27 944, unique: 24 342, observed: 13 317 ($I > 2\sigma(I)$); parameters refined: 1597; R1 = 0.0623, wR2 = 0.1233; GOF = 0.909.

4.13. General procedure for the alkylation of benzaldehyde with homometallic reagents

A suspension of diol (1 mmol) was treated with a solution of trimethylaluminum (1 or 2 mmol, 2.0 M in toluene) at room temperature for 2 h. After cooling the solution at −20 °C, benzaldehyde (1 mmol) was added and the resulting mixture was stirred for 6 h at the same temperature. After quenching with water, the water layer was extracted with 20 mL Et$_2$O. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. Filtration and distillation of the solvents left yellow oil. The enantiomeric excess was analyzed by GC (Chiraldex G-TA column).

4.14. General procedure for the alkylation of benzaldehyde with heterometallic reagents

A suspension of diol (1 mmol) was treated with a solution of n-BuLi (1 mmol, 1.6 M in hexane) at room temperature for 2 h. To this mixture, a solution of trimethylaluminum (1 mmol, 2.0 M in toluene) was added at room temperature and the solution was stirred for further 2 h. After cooling the solution at −20 °C, benzaldehyde (1 mmol) was added and the resulting mixture was stirred for 6 hours at the same temperature. After quenching with water, the water layer was extracted with 20 mL Et$_2$O. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. Filtration and distilla-

tion of the solvents left yellow oil. The enantiomeric excess was analyzed by GC (Chiraldex G-TA column).

5. Supplementary material

Acknowledgements

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