

# A study of Noyori's reagent

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Dedicated to Professor Dr Henri Brunner on the occasion of his 65th birthday

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## Abstract

The reaction of  $\text{LiAlH}_4$  with ROH ( $R = {}^i\text{Pr}$ ,  ${}^t\text{Bu}$ ) and binaphthol ( $\text{binapH}_2$ ) in a 1:1:1 ratio in ether–THF yields a dominant  ${}^{27}\text{Al}$ -NMR signal which is attributed to  $\text{LiAlH}(\text{OR})(\text{binap})$  (**1**). However, within a short time more signals emerge, and, depending on concentration, temperature and time the following compounds were isolated and characterized by X-ray structure analysis:  $\text{LiAlH}_2(\text{binap})\cdot 2\text{THF}$  (**2**·2THF),  $\text{Li}_3\text{Al}(\text{binap})_3\cdot 6\text{THF}$  (**3**·6THF),  $\text{Li}_2\text{Al}_2(\text{binap})_4\cdot 4\text{THF}$  (**4**·4THF),  $\text{LiAl}(\text{OR})_2\text{binap}\cdot 2\text{THF}$  (**5**·2THF),  $\text{LiAl}(\text{OR})_2\text{binap}\cdot \text{PMDTA}$  (**5**·PMDTA) and  $\text{Li}_2\text{AlH}(\text{binap})_2\cdot 4\text{THF}$  (**6**·4THF). Moreover, the alane derivative  $\text{AlH}(\text{binap})\cdot \text{THF}$  (**6**), which is dimeric in the solid state, has been prepared and its structure determined. Thus, ligand redistribution is a typical feature for the Noyori reagent in consonance with other lithium alkoxyaluminates. The active species of Noyori's reagent still needs to be discovered. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydridoaluminates; Binaphtholato aluminates; NMR; X-ray structures

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## 1. Introduction

The development of hydridic reducing reagents for functional organic groups which allow the synthesis of optically pure products is still a challenge. One of the best approaches by using modified lithium aluminum hydride is Noyori's reagent which is obtained by treating  $\text{LiAlH}_4$  in THF with one equivalent of an alcohol or phenol followed by addition of 1 mol of binaphthol ( $\text{binapH}_2$ ) (see Eq. (1)). Up to 100% ee in high chemical yield can be realized in the reduction of ketones [1,2]. Lack of aging of the reagent and the temperature dependent ratio of enantiomers formed was taken as evidence that there is a single active species in solution responsible for the enantioselective reduction. However, the nature of the reducing species is still unknown. This species is definitely not an alane derivative because binaphthol modified  $\text{AlH}_3$  shows only marginal chiral induction. Noyori et al. [2] were aware that there may be several AlH species in the solution although they postulate that the active species might be  $\text{LiAl}$ -

$\text{H}(\text{OR})(\text{binap})$  (**1**), or a species of type  $\text{LiAlH}(\text{OR}')_3$ , a binaphthol modified lithium aluminum hydride reagent.

It is well known that the reaction of alcohols and phenols with  $\text{LiAlH}_4$  produces the stoichiometric amount of  $\text{H}_2$ , but depending on the steric requirements of the added alcohol ROH a mixture of species of the series  $\text{LiAlH}_{4-n}(\text{OR})_n$  is present in solution as shown by  ${}^{27}\text{Al}$ -NMR spectroscopy [3–8]. Well-defined compounds have been isolated and structurally characterized by X-ray crystallography only recently [7,8]. Most of these species carry a rather bulky group R, and, depending on the solvent and size of the RO group, various types of  $\text{Li}\cdots\text{H}$  or  $\text{Li}-\text{O}$  interactions were observed. In continuing these studies we became interested in the  $\text{LiAlH}_4/\text{ROH}/\text{binapH}_2$  system for three main reasons: (i) to find the active species of Noyori's reagent, (ii) to isolate other well-defined species that may be present in solutions of Noyori's reagent, and (iii) to test these compounds with respect to their enantioselectivity provided that they redissolve in THF as single compounds. In this paper we report on the first two aspects and concentrate on reaction with *tert*-butanol as the alcohol although some results with *iso*-propanol will also be described.

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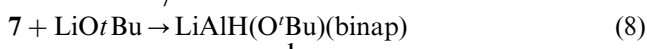
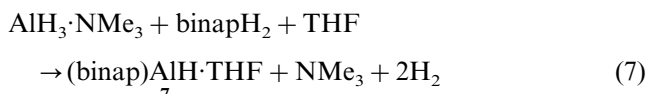
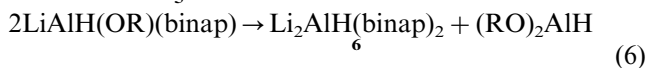
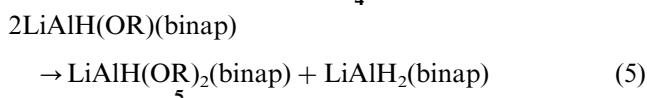
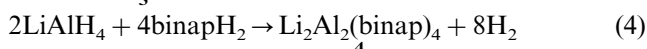
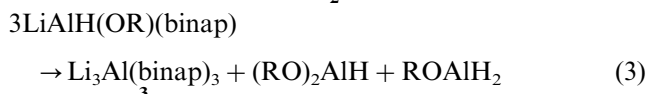
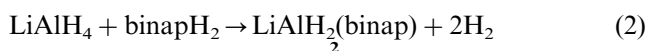
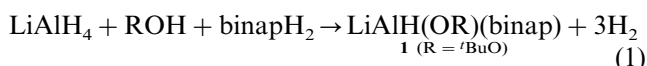
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## 2. Reactions

Binaphthol reacts readily with  $\text{LiAlH}_4$  in an ether–THF mixture to produce  $\text{LiAlH}_2(\text{binap})$ , as shown in Eq. (2). The product was isolated in high yield (81%) at  $-20^\circ\text{C}$  as  $\text{LiAlH}_2(\text{binap})\cdot 0.4\text{Et}_2\text{O}\cdot 0.5\text{THF}$ ,  $2\cdot 0.4\text{OEt}_2\cdot 0.5\text{THF}$ . IR spectroscopy showed two bands in the AlH stretching region ( $1831, 1804\text{ cm}^{-1}$ ) indicative of the presence of a terminal AlH<sub>2</sub> group. In addition, from the solution a few other crystals separated which proved to be  $\text{Li}_3\text{Al}(\text{binap})_3\cdot 6\text{THF}$  (**3**·6THF). This compound separates in high yield from a solution made up from  $\text{LiAlH}_4/\text{tert-BuOH}/\text{binapH}_2$  — either in an ether–THF mixture or in pure THF — on reducing its volume or by simply letting the solution age over a month [9].

A  $^{27}\text{Al}$ -NMR study of a freshly prepared solution made from  $\text{LiAlH}_4$ , *tert*-BuOH, and  $\text{binapH}_2$  (1:1:1) showed a *dominant* signal at  $\delta = 101$  ( $h(1/2) = 380\text{ Hz}$ ) which became sharper on proton decoupling ( $h(1/2) = 80\text{ Hz}$ ) revealing that hydrogen is bonded to Al. We assume that this signal is indicative for compound **1**. An IR spectrum revealed a broad band in the region from  $1792$  to  $1698\text{ cm}^{-1}$  with a maximum at  $1756\text{ cm}^{-1}$  for an AlH species. This solution on aging (several days) produced new Al containing species as shown by new  $^{27}\text{Al}$ -NMR signals at 110, 85, and 24 ppm. These signals can be assigned to  $\text{LiAlH}_2(\text{O}^t\text{Bu})_2$  [**3**] and  $(^t\text{BuO})_2\text{AlH}$  in THF [10]. Characteristic for this latter compound is an AlH stretching frequency at  $1845\text{ cm}^{-1}$ . The signal for  $^t\text{BuOAlH}_2$  in THF is known to be rather broad with a  $^{27}\text{Al}$ -NMR signal at  $105 \pm 6\text{ ppm}$  coinciding with the signal for **1**. Crystals of this compound separated from the solution within 8 weeks.



A different kind of behavior was observed for the system  $\text{LiAlH}_4/\text{PrOH}/\text{binapH}_2$  in ether–THF (ratio 1:15). After  $\text{LiAlH}_4$  was allowed to react with binaph-

thol (1:1) and after addition of isopropanol to complete the 1:1:1 reaction the turbid solution was kept under reflux for 0.5 h. The filtrate was then layered with hexane. This resulted in the formation of needles which showed a  $^{27}\text{Al}$ -NMR signal at 42 ppm. This signal results from the complex  $\text{Li}_2\text{Al}_2(\text{binap})_4\cdot 4\text{THF}$  (**4**·4THF), a compound that can be prepared also by reacting  $\text{LiAlH}_4$  with binaphthol in a 1:2 ratio (Eq. (4)).

However, changing conditions for crystallization also changes the composition of the products to be isolated. Thus, when the 1:1:1 reaction performed with *tert*-butanol in the presence of a large amount of THF the product that separated at  $-20^\circ\text{C}$  was neither **1**, nor **3** or **4** but  $\text{LiAl}(\text{O}^t\text{Bu})_2(\text{binap})$  (**5**). It crystallizes as **5**·2 THF. Its  $^{27}\text{Al}$ -NMR signal at  $\delta = 70$  indicates that the Al center is tetracoordinated ( $^{27}\text{Al}$  signals for tetraalkoxo aluminates are found in the region 75–60 ppm) [11], and this has been proven for **5**·4THF by its molecular structure (v.i.). The formation of **5** is formally described by a redistribution according to Eq. (5). The coordinated THF is readily replaced by pentamethyldiethylenetriamine (PMDTA) to form the complex **5**·PMDTA.

On the other hand, when the THF solution of the 1:1:1 reaction was kept under reflux for 1 h, a suspension forms. Clear needles separated in a short time after layering the filtrate with methyl-cyclohexane. These crystals proved to be  $\text{Li}_2\text{AlH}(\text{binap})\cdot 4\text{THF}$  (**6**·4THF). They dissolved in a mixture of benzene and pyridine, and this solution gave a  $^{27}\text{Al}$ -NMR signal at 25 ppm which is comparatively sharp [ $h(1/2) = 690\text{ Hz}$ ] and points to the presence of a pentacoordinated Al center.

Another possibility to prepare compound **1** is by reacting  $(\text{binap})\text{AlH}$  (**7**), with  $\text{LiO}^t\text{Bu}$  as shown in Eq. (7) and (8). This synthesis would have the advantage that less hydride would be lost as  $\text{H}_2$  in comparison to the classical route. While the synthesis of the binaphtholato alane (**7**) posed no problem, the result of reaction according to Eq. (7) is nevertheless surprising because trimethylamine is replaced by THF, and moreover, compound **7** is actually a dimer. This was already indicated by a  $^{27}\text{Al}$ -NMR signal at 51 ppm and finally proven by an X-ray structure determination. When a THF solution of **7** was allowed to react with  $\text{LiO}^t\text{Bu}$  signals at 110, 91, 79 and 67 ppm appeared in the  $^{27}\text{Al}$ -NMR spectrum. Thus, once again no single species is being formed as expected in a reaction delineated in Eq. (8). It is evident from these data that the assumption of Noyori that his reagent would probably not consist of a single species is definitely justified.

## 3. Molecular structures in crystals

Six well defined crystalline compounds could be isolated from the THF solutions in form of single crystals.

Their structures were determined by X-ray diffraction analysis. Fig. 1 depicts the contents of the asymmetric unit of compound  $[\text{LiAlH}_2(\text{binap})\cdot 2\text{THF}]_4\cdot 0.5\text{Et}_2\text{O}\cdot 0.5\text{THF}$ . The 'surplus'  $\text{Et}_2\text{O}$  and THF are not coordi-

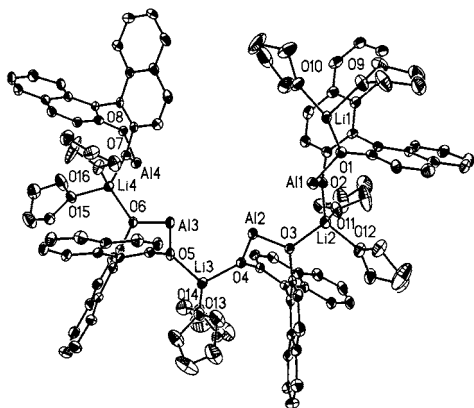


Fig. 1. Molecular structure of  $(2\cdot 2\text{THF})_4\cdot 0.5\text{Et}_2\text{O}\cdot 0.5\text{THF}$  in the crystal. Only the contents of the asymmetric unit *without* the crystal solvents is depicted. Thermal ellipsoids are represented with 25% probability. Selected atom distances (in Å): Al1–O1 1.796(9), Al1–O2 1.803(4), Al2–O3 1.807(5), Al2–O4 1.812(4), Al4–O8 1.817(5), Li2–O11 1.93(1), Li2–O12 1.95(1), Al2–O2 1.94(1), Al2–O3 1.94(1); bond angles (in °): O12–Li2–O11 101.0(6), O1–Al1–O2 100.1(2), Al1–O1–Li1 117.6(4), Al1–O2–Li2 121.3(4), Al1–O2–C20 117.5(4), Al1–O1–C1 118.0(3), Li1–O1–C1 124.4(5), O2–Li2–O3 114.6(6), O4–Li3–O5 114.7(6), O2–Li2–O11 108.1(6), O2–Li2–O12 112.8(5).

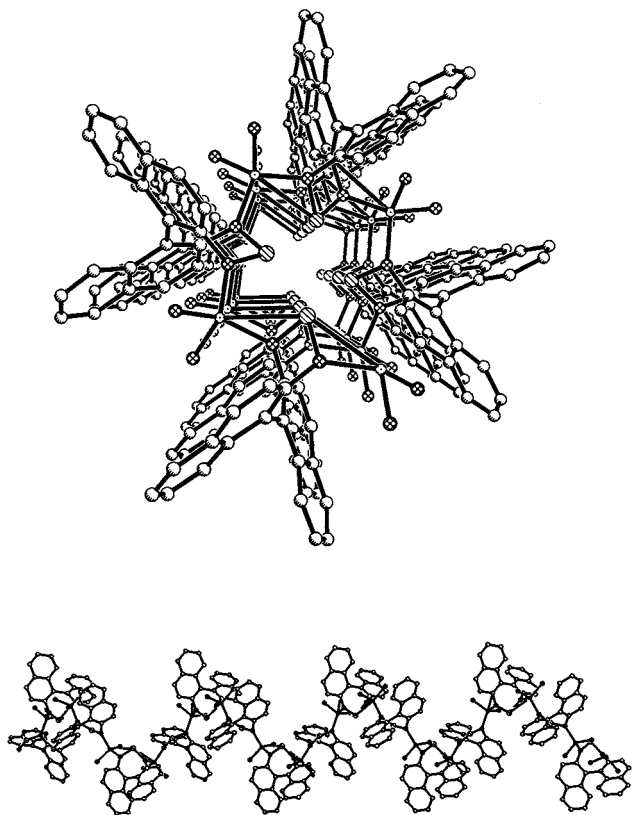


Fig. 2. The helical structure of complex  $2\cdot 2\text{THF}$

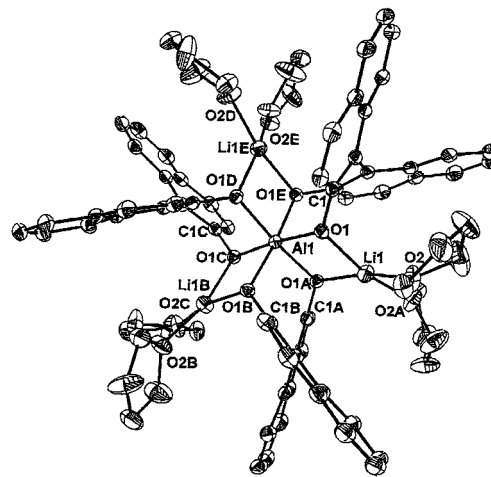


Fig. 3. Molecular structure of  $6\cdot 6\text{THF}$  in ORTEP description. Thermal ellipsoids represent a 25% probability level. Selected bond lengths (in Å): Li1–O1 1.937(6), Li1–O2 2.037(5), Al1–O1 1.897(2); selected bond angles (in °): O1–Al1–O1A 81.6(1), O1–Al1–O1E 94.68(1), O1–Al1–O1D 89.2(1), O1–Al1–O1C 174.9(1), Li1–O1–Al1 99.4(2), O2–Li1–O2A 87.2(3), O1–Li1–O1A 79.6(3), O1–Li1–O 98.68(8), C1–O1–Al1 124.0(2).

nated to Li or Al centers but fill voids in the lattice. Unfortunately Al bonded hydrogen atoms of this compound could not be located with certainty, but it is evident from the structure that they have to be found at the Al centers (see Fig. 1). Every binap unit joins to one Al center with formation of a seven membered AlOC4 ring. The Li centers are coordinated by two oxygen atoms of two different binap's and by the O atoms of two THF molecules. Al–O distances range from 1.786(5) to 1.817(5) Å, and the Li–O distances from 1.93(1) to 1.95(1) Å. Therefore, each class of M–O atom distances can be considered to be of equal lengths in contrast to bond angles which span the range from 117.5 to 121.3° for Al–O–Al, and 101.0(6) to 114.7(6)° for Li–O–Li. Astonishingly, the Li–O distances to the THF oxygen atoms and the binap oxygens are practically the same. This points to the conclusion that these interactions are highly polar.

Fig. 2 demonstrates the action of the screw axis on the asymmetric unit. A helix is formed, and this leads to a chiral arrangement in the crystal. Voids in the lattice are filled with the ether–THF molecules.

In contrast to the helical polymeric structure of **2**, compound **3** which crystallizes as  $3\cdot 6\text{THF}$  in the hexagonal system, space group  $P6_322$ , shows a highly symmetric structure with the Al atom positioned on a  $6_3$  crystallographic axis. Fig. 3 demonstrates that the three  $\text{Li}(\text{THF})_2$  units are positioned between two oxygen atoms of neighboring binap ligands. This results in a

'starlike' arrangement of a  $\text{Li}_3\text{AlO}_6$  skeleton. The Al–O distances are all of equal lengths while there are two different Li–O atom distances of 2.037(5) and 1.937(6) Å. The Al atom is hexacoordinated: there are six O–Al–O bonds close to  $90^\circ$  (81.6(1) and  $94.7(1)^\circ$ ), and three O–Al–O angles with  $174.9(1)^\circ$ . Bond angles at the oxygen atoms of the binap unit are  $124.0(2)^\circ$  while the geometry around the tetracoordinated Li centers is quite distorted compared to a tetrahedron. (see data in the legend to Fig. 3). Nevertheless, the  $\text{LiO}_2\text{Al}$  four membered rings are planar in contrast to the seven-membered  $\text{AlO}_2\text{C}_4$  rings involving the binap groups.

A dinuclear Al species is present in compound  $[(\text{THF})_2\text{Li}]_2\text{Al}_2(\text{binap})_4$  (**4·4THF**). Its structure is shown in Fig. 4. In contrast to the previous example this molecule features pentacoordinated Al centers. The binap ligand bridges two Al atoms resulting in a central  $\text{Al}_2\text{O}_2$  ring. The geometry about the Al atoms is best described as being trigonal bipyramidal. There are six

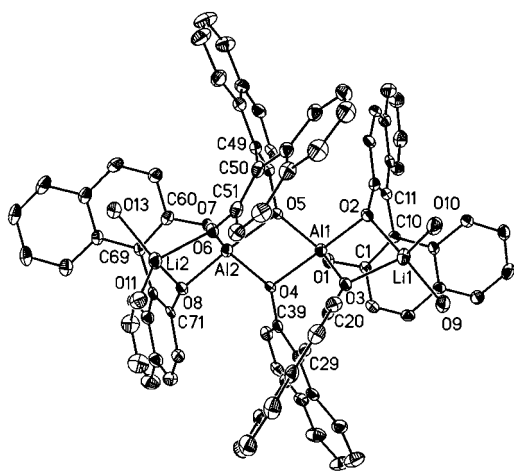


Fig. 4. Molecular structure of **4·4THF** in ORTEP description. The two crystal solvent THFs are not shown. The Li bonded THF molecules characterized by O9 and O10 are disordered, one with two C atoms (O10) the other with one C atom (O9). Thermal ellipsoids represent a 25% probability level. Selected atom distances (in Å): Al1–O1 1.759(3), Al1–O2 1.826(3), Al1–O3 1.795(3), Al1–O4 1.966(3), Al1–O5 1.815(3), Al2–O4 1.805(3), Al2–O6 1.794(3), Al2–O7 1.750(3), Al2–O8 1.836(3), Al1–Al2 2.796(7), Li1–O2 1.934(8), Li1–O3 1.958(9), Li1–O9 1.956(8), Li1–O10 1.914(9), Li2–O6 1.941(8), Li2–O8 1.924(7), Li2–O11 1.913(8), Li2–O13 1.928(8), O2–C12 1.356(5), O3–C20 1.353(5), O4–C39 1.379(5), O5–C20 1.380(5), O8–C71 1.369(5); selected bond angles (in  $^\circ$ ): O1–Al1–O2 97.2(1), O1–Al1–O3 121.3(1), O1–Al1–O4 91.6(1), O1–Al1–O5 114.9(1), O2–Al1–O3 84.9(1), O2–Al1–O4 171.2(1), O2–Al1–O5 101.8(1), O3–Al1–O4 89.9(1), O3–Al1–O5 122.0(1), O4–Al1–O5 73.9(1), O4–Al2–O5 75.4(1), O4–Al2–O6 123.2(1), O4–Al2–O7 114.2(1), O4–Al2–O8 101.7(1), O5–Al2–O6 89.5(1), O5–Al2–O7 91.8(1), O5–Al2–O8 171.4(1), O6–Al2–O7 120.9(1), O6–Al2–O8 85.3(1), O7–Al2–O8 96.7(1), O2–Li1–O3 77.8(3), O2–Li1–O9 135.4(4), O2–Li1–O10 106.3(4), O3–Li1–O9 105.1(4), O3–Li1–O10 124.4(4), O9–Li1–O10 105.8(4), O6–Li2–O8 79.1(3), O6–Li2–O11 120.9(4), O6–Li2–O13 101.8(4), O8–Li2–O11 115.6(4), O8–Li2–O13 129.4(4), O11–Li2–O13 107.1(3).

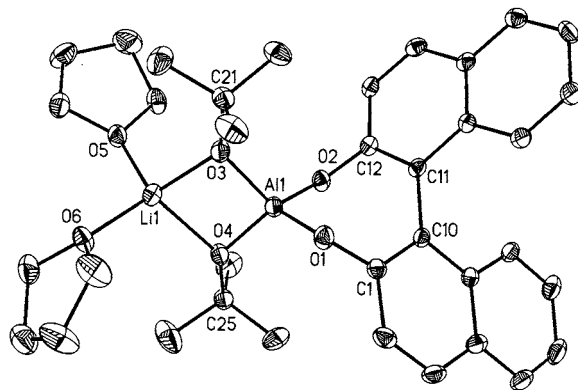


Fig. 5. Molecular structure of **5·2THF** in ORTEP description. Thermal ellipsoids are depicted on a 25% probability level. Selected bond lengths (in Å): Al1–O1 1.749(4), Al1–O2 1.753(4), Al1–O3 1.739(4), Al1–O4 1.730(4), O1–C1 1.331(6), O2–C12 1.345(6), O3–C21 1.432(6), O4–C25 1.429(7), Li1–O3 1.956(1), Li1–O4 1.99(1), Li1–O5 1.932(9), Li1–O6 1.90(1); selected bond angles (in  $^\circ$ ): O1–Al1–O2 104.4(2), O3–Al1O4 93.3(2), O1–Al1–O3 110.2(2), O1–Al1–O4 121.8(2), O2–Al1–O3 119.1(2), O2–Al1–O4 108.9(2), Al1–O3–Li1 93.9(3), Al1–O4–Li1 93.2(5), O3–Li1–O4 79.4(4), O5–Li1–O6 106.3(5), O3–Li1–O5 109.2(4), O3–Li1–O6 123.3(5), O4–Li1–O5 126.1(5), O4–Li1–O6 196.3(6), Al1–O3–C21 132.4(3), Al1–O4–C25 132.2(3), Li1–O3–C21 132.5(4), Li1–O4–C25 131.0(4).

O–Al–O angles in the range of  $87.9$ – $97.2(1)^\circ$ , three in the range of  $114.9$ – $122.0(1)^\circ$  and one (O2–Al1–O4) equals  $171.2(1)^\circ$ . Similar angles are found for atom Al2. The axial Al–O bonds (Al1–O2 and Al1–O4) are 1.826(3) and 1.966(3) Å. As expected, these are significantly longer than the equatorial Al–O bonds (1.759–1.815(3) Å). Compared to the Li–O distances to the binap ligands (1.934–1.958(8) Å, average 1.939 Å) one finds Li–O distances to the THF ligands to be slightly shorter (average 1.927(8), range 1.913–1.956(8) Å). The O–Li–O bond angle to the two different binaps is rather sharp ( $79.1(7)^\circ$ ) while the O–Li–O bond angle between the two THF molecules is close to tetrahedral ( $107.1(3)^\circ$ ). The largest O–Li–O angle is found for O3–Li2–O6 with  $129.4(4)^\circ$ . All in all, the symmetry in this noncentric molecule is fairly low.

The molecular structure of compound **5·2THF** (see Fig. 5) shows both a tetracoordinated Li and Al atom. The Li center coordinates to two oxygen atoms of two THF ligands with Li–O distances of 1.96(1) and 1.99(1) Å, respectively, while the two Li–O distances to the binap ligand appear to be shorter (1.93, 1.90(1) Å). On the other hand, the Al–O distances to the *tert*-butoxy group is on average 1.735(4) Å, while the Li–O<sub>binap</sub> bond lengths are 1.743(9) and 1.753(4) Å and, therefore longer than the Li–O distances. This, once again, is a good indication that these bonds are highly polar. Bond angles at the binap oxygen atoms are close to  $120^\circ$  while the Al–O–C bond angles to the 'BuO groups are 131.0 and  $131.2(4)^\circ$ . This is, of course, the consequence of the O3–Al1–O4 bond angle of  $93.3(2)^\circ$  and the

rather acute O3–Li1–O4 bond angle of only 79.4(4)°. Bond angles O(THF)–Li–O('Bu) vary from 109.2 to 126.1(4)°. All in all, the geometry of the O2AlO2LiO2 skeleton is comparatively symmetric.

Replacement of the THF molecules by PMDTA in 5·2THF leads to a molecule with pentacoordinated Li centers. This was not unexpected, because generally the PMDTA ligand acts as a tridentate chelating ligand

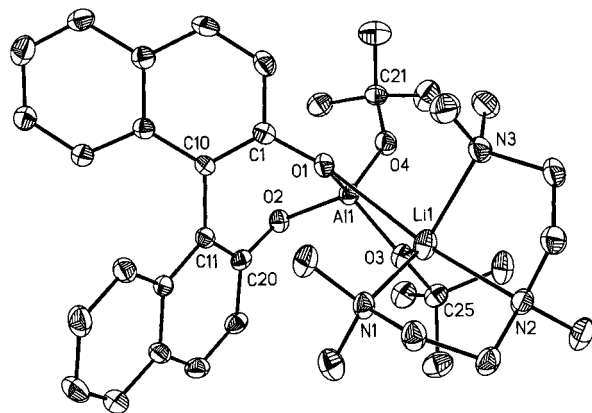


Fig. 6. ORTEP plot of compound 5-PMDTA. Thermal ellipsoids represent 25% probability. Selected bond lengths (in Å): Al1–O4 1.700(3), Al1–O3 1.754(3), Li1–O1 2.651(7), Li1–O3 1.983(7), Li1–N1 2.137(8), Li1–N2 2.310(7), Li1–N3 2.162(8); selected bond angles (in °): O1–Al1–O2 102.8(1), O1–Al1–O4 117.1(2), O1–Al1–O3 98.7(1), O2–Al1–O3 113.9(1), O2–Al1–O4 113.0(1), N2–Li1–N2 82.6(3), N1–Li1–N3 120.1(3), N2–Li1–N3 83.1(3), N2–Li1–O1 166.3(3).

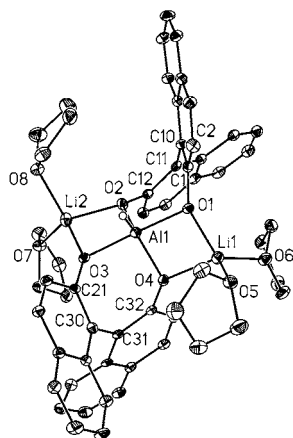


Fig. 7. Molecular structure of compound 6·4THF in the crystal. Thermal ellipsoids are shown on a 25% probability level. Selected atom distances (in Å): Al1–H1 1.65(4), Al1–O1 1.903(3), Al1–O2 1.834(3), Al1–O3 1.917(3), Al1–O4 1.834(3), Li1–O1 1.873(8), Li1–O4 1.985(7), Li2–O2 1.973(6), Li2–O3 1.886(9), Li1–O5 1.991(8), Li1–O6 1.938(7), Li2–O7 1.940(7), Li2–O8 1.999(8), Li1–Al1 2.823(7), Li2–Al1 2.827(7); selected bond angles (in °): H1–Al1–O2 122(2), H1–Al1–O1 93(1), H1–Al1–O3 93(1), H1–Al1–O4 121(1), O1–Al1–O2 92.8(1), O1–Al1–O3 174.0(1), O2–Al1–O3 83.8(1), O2–Al1–O4 117.3(1), O3–Al1–O4 93.0(1), O1–Li1–O4 80.9(3), O1–Li1–O5 118.5(3), O1–Li1–O6 113.7(4), O4–Li1–O5 103.3(4), O4–Li1–O6 126.5(3), O5–Li1–O6 111.4(4), O2–Li2–O3 81.0(3), O2–Li2–O7 127.8(3), O2–Li2–O8 102.7(3), O3–Li2–O7 110.3(4), O3–Li2–O8 120.2(3), O7–Li2–O8 112.4(4).

toward Li<sup>+</sup> [13] However, it was unexpected that the Li center does no longer coordinate to the oxygen atoms of the two 'BuO groups but now rather to only one, and, in addition, to an oxygen atom of the binap ligand which bridges between Li and Al. The molecular structure of 5·PMDTA is depicted in Fig. 6.

Its LiO<sub>2</sub>Al ring is not planar, the sum of bond angles being 370.2°. The geometry around the Li center is neither trigonal bipyramidal nor square pyramidal. The 'axial' bonds exhibit an N2–Li1–O1 bond angle of 166.3(3)°. In consonance with structures having a Li(PMDTA) unit the Li–N bond to the NMe group is longer (2.310(7) Å) than to the Me<sub>2</sub>N units (2.137 and 2.310(7) Å). Bond lengths Li–O are significantly different, 2.651(7) Å to O1 of the binap unit, and 1.983(7) Å to the bridging 'BuO group. This corresponds with a weak coordination. The terminal Al–O bond to the *tert*-butoxo group is shorter than the Al–O bond to the bridging 'BuO group, but the difference in bond length is only 0.05 Å. Bond angles at the Al center vary from 98.7 to 117.1(2)°, no great deviation from the tetrahedral geometry taking into account that the binap unit forms a seven membered ring with the Al atom. The large variation of the C–O–Al bond angles support again the assumption of highly polar O–Al bonds.

A molecule which is closer related to 1 than any of the others so far described is 6·4THF whose molecular structure can be found in Fig. 7. It possesses an Al center carrying an Al–H bond in a slightly distorted trigonal bipyramidal environment. The axial Al–O bond to the binap ligands are 1.917(3) and 1.903(3) Å while those to the equatorially bound oxygen atoms are of equal lengths (1.834(3) Å) and shorter than the axial bonds. The O1–Al1–O3 bond angle is 174.0(1)°, and the O2–Al1–O4 bond angle 117.3(1)°. Bond angles involving the O<sub>axial</sub>–Al–O<sub>equatorial</sub> bonds range from 83.8(1) to 92.8(1)°. The Li centers are tetracoordinated. The Li–O distances span the small range from 1.873 to 1.991(7) Å, and there is no noticeable difference whether the O atom stems from THF or binap. The O–Li–O bond angles between the THF molecules are close to tetrahedral (111.4(4) 112.4(4)°) while the O–Li–O bond angles involving the oxygen atoms of the binap ligands are acute (80.9(3), 81.0(3)°).

The *R*(+)-binaphtholatoalane crystallizes from THF as 7·THF. Recrystallized from toluene it is present in the solid state as a dimeric binuclear alane derivative with pentacoordinated Al centers in a distorted trigonal bipyramidal environment (see Fig. 8). The monoclinic unit cell, space group *P*<sub>2</sub><sub>1</sub>, contains also two molecules of toluene. Dimerization occurs via oxygen atoms of the binap ligands, one each adopts a bridging position, the other binds terminally. This arrangement leads to a planar four membered Al<sub>2</sub>O<sub>2</sub> ring with acute O–Al–O bond angles (close to 75°). The sum of the bond angles around the bridging O atoms is 360°; it is tempting to consider them as sp<sup>2</sup> hybridized. Al–O bond lengths to

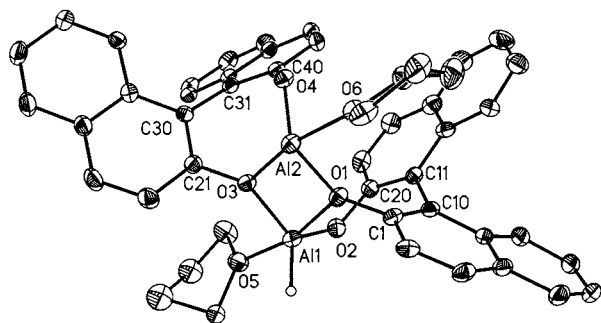


Fig. 8. Molecular structure of dimeric **7** in ORTEP representation. The toluene solvent is not shown. One THF molecule is disordered involving the two  $\beta$ -C atoms. Thermal ellipsoids are drawn on a 25% probability level. Atom distances (in Å): Al1–H1 1.39(4), Al1–O1 1.943(3), Al1–O2 1.755(3), Al1–O3 1.833(3), Al1–O5 1.963(4), Al2–O1 1.824(3), Al2–O3 1.962(3), Al2–O4 1.747(3), Al2–O6 1.963(3); Al1–Al2 2.991(2); bond angles (in °): H1–Al1–O2 120(2), H1–Al1–O3 118(2), H1–Al1–O1 99(2), O2–Al1–O3 122.5(1), O1–Al1–O5 166.0(1), O1–Al1–O2 75.4(1), Al1–O1–Al2 105.0(1), Al1–O3–Al2 103.9(1), O1–Al2–O4 112.8(1), O3–Al2–O6 165.6(1), O3–Al2–O1 75.1(1), O3–Al2–O4 93.1(1).

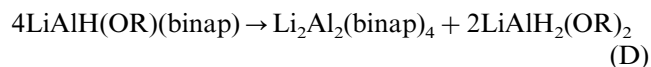
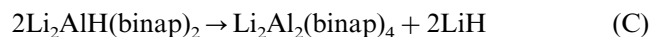
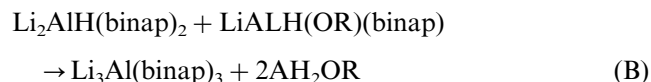
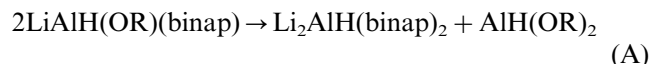
the bridging O atoms are longer than to the terminal O atoms of the binap groups. Only one H atom of the expected two AlH groups was found and refined well. The found position of an H atom on Al2 did not refine well.

Each Al atom carries also a THF ligand. While one THF refined properly, the second (at Al) is disordered.

#### 4. Discussion

The investigation of Noyori's reagent by  $^{27}\text{Al}$ -NMR shows that the 1:1:1 reaction of  $\text{LiAlH}_4$ ,  $t\text{-BuOH}$  and binaphthol in ether–THF (ca. 1:10) solution leads in the first to place to a dominating species which is most likely due to  $\text{LiAlH}(\text{O}^t\text{Bu})\text{binap}$  (**1**). In addition two much less intense signals can be observed. However, **1** could not be isolated because on concentration of its solution or on heating or on standing at ambient temperature the composition of the solution changes as indicated by the emerging of new  $^{27}\text{Al}$ -NMR signals. The precipitate that forms most readily is due to the formation of compound **3**. While ligand redistribution is a general phenomenon of alkoxy and aryloxyalanes  $\text{AlH}_{3-n}(\text{OR})_n$  [3,4,11] and lithium or tetrabutylammonium hydridoaluminates [4–6,8,11] the new feature in case of Noyori's reagent is the formation of penta- and hexacoordinated aluminate anions. Most likely, the first step in the redistribution involving **1** is a reaction according to Eq. (A) leading to compound **6**. This in turn may react according to Eq. (B) to yield the tris(binaphtholato)-aluminate (**3**). While only small quantities of **3** separate from solution of the *tert*-butoxy reagent its formation can lead to yields exceeding 80% when the

reaction mixture is allowed to stand for a prolonged period, or is heated to reflux, and particularly high yields are observed when the reaction is carried out in THF as the sole solvent.



The pentacoordinated hydridoaluminate **6**, the first of its kind, possesses a disymmetric anion and may therefore be responsible for the high enantioselectivity observed in the reduction of ketones [2]. This, however has to be proven by further experiments.

Finally, a third kind of ligand exchange product leading to the dilithium tetrakis(binaphtholato)-dialuminate **4** was observed. At the present time it can only be speculated how this compound is generated. Eqs. (C) and (D) may be considered, and it is quite clear that these summarize multistep processes. We consider route (C) as less likely than route (D) because a  $^{27}\text{Al}$ -NMR signal at about 110 ppm is in consonance with a  $\text{LiAlH}_2(\text{OR})_2$  species [8].

The tendency of **1** to form finally **3** and alkoxyalanes is a consequence of the fairly low solubility of **3** in THF and particularly ether–THF or hexane–THF mixtures. Higher concentration and higher temperature favor its formation.

However, in contrast to these processes we observed that lithium binaphtholato aluminate (**5**), exhibited practically no ligand exchange. Therefore, it was easily isolated in high yield from THF. Its Al center is tetra-coordinated, and its Li center co-ordinates only with the oxygen atoms of the  $t\text{-BuO}$  groups. As already described a different kind of coordination occurs when the THF ligands are replaced by the tridentate amine base PMDTA. The  $\text{Li}(\text{PMDTA})$  unit observed in **5**·PMDTA is very similar in its structure as found in other  $\text{LiX} \cdot \text{PMDTA}$  complexes ( $\text{X} = \text{Cl}, \text{Br}$ ) [12,13]. In these complexes the Li atom is also pentacoordinated.

An important feature found for the compounds described here is the observation of only very small differences in the Li–O distances involving the binap ligand and the THF ligands. Normally one would consider the Li–O(THF) bond as being 'coordinative' while the Li–O(bin) bond might have more covalent character. When such situations exist than one finds much longer atom distances to the coordinatively associated ligand (here THF) [14]. Since there are only small differences in Li–O atom distances we conclude that these bonds are all highly polar.

The structures determined for the binap aluminates all exhibit seven-membered  $\text{AlO}_2\text{C}_4$  rings. However the coordination at the Al center is either 4, 5 or 6. Therefore, this might be reflected in the interplanar angle of the neighboring OCC/CCO planes within the ring. An inspection of Table 1 shows that there is almost no significant difference. The interplanar angle spans only a range from 51.6 to 58.6°, and this can be considered not to be of too great an influence. Differences in Al–O–C bond angles are more pronounced as well as the Al–O–C–C torsion angles.

In case of the hexacoordinated aluminate **3** the Al–O–C bond angles are equal, but the Al–O–C–C are quite different as shown by the values of  $-75.6$  and  $59.6^\circ$ .

Among the three pentacoordinated binaphtholato aluminates only small differences are to be noted both for the Al–O–C bond angle and the the Al–O–C–C torsion angles. However, a closer inspection of the data show that there are structurally relevant differences. Thus, the Al–O bond angles in **5**·PMDTA are 117.4 and 120.1°, and the two torsion angles are 65.0 and 69.2°, respectively. However, in **6**·4THF the Al–O–C bond angles lie between 113.3 and 125.5°, the larger angles are those with the O atoms in axial position. For the torsion angles we find a much smaller range:  $-67.4$  to  $80.7^\circ$ . In the case of compound **7** a different situation exists because the binap ligand bridges the two Al atoms of the dimeric unit. Therefore, one finds two sets of torsion angles (61.3, 65.4° and 73.0, 741.°) and three sets of Al–O–C bond angles, two with 116.4°, two with 130.2° and two with 138.7° (average values).

While the tetraordinated compound **5**·2THF shows similar Al–O–C bond angles as its PMDTA adduct, its torsion angles are smaller (on average by 5.6°). A fairly large variation for both types of angles is found for **4**·4THF. In this compound two binap ligands bridge the two Al centers while the other two bridge between Li and Al. Therefore, one finds a rather wide range for Al–O–C bond angles (113–139°), while the torsion angles spread from 60 to 76°. In contrast the helical compound (**4**·2THF)<sub>4</sub>, where the binaps bridge monotonously between Li and Al, Al–O–C bond angles (113–118°) and torsion angles (68–75°) cover a comparatively small range.

Finally, no redistribution of the ligands was observed for the dimeric alane derivative (binap)-AlH·THF (**7**).

According to Noyori the reagent that yields the best ee values for the alcohols formed in the reduction of ketones was prepared from LiAlH<sub>4</sub>, EtOH and binaphthol (1:1:1 ratio). We are presently including this reagent in our ongoing studies on the nature of Noyori's reagent.

## 5. Experimental

The hydrolytic sensitivity of LiAlH<sub>4</sub> and its derivatives require the exclusion of moisture. Therefore, the Schlenck Technique was used throughout under vacuum or dinitrogen as a protecting gas. All solvents were carefully dried, and dry flamed glassware was used. LiAlH<sub>4</sub> was supplied by Chemetall GmbH in form of pellets. These were dissolved with stirring either in ether or THF. Insoluble material was removed by separating the solution via a cannula. NMR spectra were recorded with a JEOL GSX 270 or an EX 400 instrument (standards: TMF (<sup>1</sup>H, <sup>13</sup>C), 1 M aqueous LiCl solution (<sup>7</sup>Li), 1 M aqueous AlCl<sub>3</sub> solution (<sup>27</sup>Al), the latter two as external standards. IR spectra were recorded with a Perkin–Elmer spectrometer (Nujol mulls) and the Raman spectrum with a Perkin–Elmer 2800 NL. Assignment of <sup>1</sup>H- and <sup>13</sup>C-NMR signals was performed via <sup>1</sup>H<sup>13</sup>C HETCOR experiments.

### 5.1. *R*(+)-binaphtholatoalane tetrahydrofuran (**8**·THF)

AlH<sub>3</sub>·NMe<sub>3</sub> (0.57 g, 6.39 mmol) was dissolved in toluene (5 ml) and *R*(+)-1,1'-binaphthol (1.83 g, 6.39 mmol) in toluene (5 ml) and THF (5 ml) was added with stirring. Gas evolution started. The mixture was stirred for 1 h at ambient temperature then some insoluble material was removed by filtration (G4 frit). The solution was reduced to approximately 7 ml in vacuo. Crystals separated from the solution in several days. Yield: 4.14 g of **8**·THF (68%). Dec. temp. > 360°C.

NMR: <sup>27</sup>Al (*d*<sub>8</sub>-THF)  $\delta = 51$  ( $h(1/2) = 7380$  Hz);  $\delta^1\text{H}$  (*d*<sub>8</sub>-THF): 1.71 (m, 8H,  $\beta\text{CH}_2$  THF), 2.30 (s, 6H, Me of toluene), 3.58 (m, 8H,  $\alpha\text{-H}$ , THF), 6.9–7.4/7.8–7.9 (m, 34H, arom. H);  $\delta^{13}\text{C}$ : 21.3 (CH<sub>3</sub>), 26.2, ( $\beta\text{-C}$  THF), 68.0 ( $\alpha\text{-c}$  THF), 125.6, 128.5, 129.2, 138.7, 117.3, 122.5, 124.0, 124.3, 14.8, 126.3, 126.6, 129.0, 129.2, 129.5, 129.7, 131.2, 131.7, 134.9, 135.3, 150.0, 158.4; IR (cm<sup>-1</sup>): 3052 m, 2979 m, 2931m, 2905 m, 2883, 1836 (S, AlH), 1627 vs, 1594 vs, a561 m, 1504 vs, 1466 vs<sub>a,s</sub> 1426, s, 1369 vs, 1338 vs, 1276 vs, 1264 vs, 1249 vs, 1233 vs, 1211 m, 1073 s, 1019 m, 1000 vs, 959 vs, 940 m, 869 m, 861 m, 796 vs, 750 vs, 730 s, 672 s, 643 vs, 618 vs, 586 m. C<sub>62</sub>H<sub>58</sub>Al<sub>2</sub>O<sub>6</sub> (953.04) Calc.: C, 76.72; H, 6.15; Al, 5.33; Anal. Found: C, 78.14; H, 6.13; Al, 5.66%.

### 5.2. Lithium

#### *R*(+)-binaphtholato(*tert*-butoxo)hydrido-aluminate (**1**)

*tert*-Butanol (1.05 mmol, 0.080 g) dissolved in *d*<sub>8</sub>-THF (1 ml) was added to a solution of LiAlH<sub>4</sub> in diethylether (1.8 M, 0.58 ml) at ambient temperature. After hydrogen evolution had ceased a freshly pre-

Table 1  
Interplanar angles, torsion angles and angles at the binap oxygen atoms of the binaphtholato aluminate

Compound	Interplanar angles (°)	Torsion angles (°)	Torsion angles (°)	Torsion angles (°)	Bond angles (°)	Bond angles (°)				
<b>2</b>	O1-C1-C10/O2-C20-C11	56.0	All-O1-C1-C10	71.5	A13-O5-C41-C50	All-O1-C1	118.0	A13-O5-C41	115.4	
	O3-C21-C30/O4-C40-C31	58.6	All-O2-C20-C11	70.7	A13-O6-C60-C51	All-O2-C20	All-O2-C20	117.5	A13-O6-C60	117.5
	O5-C41-C50/O6-C60-C51	57.9	A12-O3-C21-C30	73.0	A14-O7-C61-C70	A12-O3-C21	A12-O3-C21	115.9	A14-O7-C61	113.3
	O7-C61-C70/O8-C80-C71	58.2	A12-O4-C40-C31	73.8	A14-O8-C80-C71	A12-O4-C40	A12-O4-C40	114.2	A14-O8-C80	117.5
	O1-C1-C10/O1E-C1E-C10E	54.2	All-O1-C1-C10	107.1	All-O2-C20-C11	All-O1-C1	All-O1-C1	124.0		
<b>4</b>	O1-C1-C10/O2-C12-C11	51.8	All-O1-C1-C10	-67.9	A12-O5-C40-C49	All-O1-C1	All-O1-C1	123.8	A12-O5-C40	114.8
	O3-C20-C29/O4-C39-C30	54.8	All-O2-C12-C11	-70.2	A12-O6-C51-C50	All-O2-C12	All-O2-C12	120.6	A12-O6-C51	132.4
	O5-C40-C49/O6-C51-C50	52.9	All-O3-C20-C29	62.3	A12-O7-C70-C69	All-O3-C20	All-O3-C20	131.0	A12-O7-C60	124.8
	O7-C60-C69/O8-C71-C70	52.6	All-O4-C39-C30	76.4	A12-O8-C71-C70	All-O4-C39	All-O4-C39	140.4	A12-O8-C71	119.7
	O1-C1-C10/O2-C12-C11	52.1	All-O1-C1-C10	61.1	All-O2-C12-C11	All-O1-C1	All-O1-C1	121.4	All-O2-C12	120.3
<b>5</b> PMDTA	O1-C1-C10/O2-C12-C11	54.0	All-O1-C1-C10	65.0	All-O2-C20-C11	All-O1-C1	All-O1-C1	120.1	All-O2-C20	117.4
	O1-C1-C10/O2-C12-C11	55.5	All-O1-C1-C10	-80.7	All-O3-C21-C30	All-O1-C1	All-O1-C1	113.7	All-O3-C21	125.5
<b>6</b>	O3-C21-C30/O4-C32-C31	55.8	All-O2-C12-C11	-68.9	All-O4-C32-C31	All-O2-C12	All-O2-C12	124.7	All-O4-C32	113.3
	O1-C1-C10/O2-C20-C11	51.6	All-O1-C1-C10	74.1	A12-O3-C21-C30	All-O1-C1	All-O1-C1	117.1	A12-O1-C1	137.1
<b>7</b>	O3-C21-C30/O4-C40-C31	54.0	All-O2-C20-C11	61.3	A12-O4-C40-C31	All-O2-C20	All-O2-C20	130.9	A12-O3-C21	115.4
						All-O3-C21	All-O3-C21	137.1	A12-O4-C40	129.5



pared solution of *R*(+)-1,1'-binaphthol (Aldrich) (1.05 mmol, 0.30 g) dissolved in 2 ml of *d*<sub>8</sub>-THF was added with stirring. A <sup>27</sup>Al-NMR spectrum was recorded as soon as possible after the reaction was complete. The following data were obtained: δ <sup>27</sup>Al = 101 (*h*(1/2) = 285 Hz, proton decoupled 85 Hz), dominating signal > 90%; 113 (*h*(1/2) = 1800 Hz, and 80 (*h*(1/2) = 2500 Hz). δ <sup>7</sup>Li = 2.4; δ <sup>1</sup>H = 1.25, 1.30, 1.35 (s, 9H, CH<sub>3</sub>C<sub>q</sub>), 6.98–7.29/7.70–7.80 (m, 12H, H<sub>aryl</sub>); δ <sup>13</sup>C = 32.6, 33.0, 33.5 (Me<sub>3</sub>C), 67.4, 67.6, 68.3 (Me<sub>3</sub>C), 119.7, 121.3, 121.5, 121.7, 122.1, 122.2, 123.6, 124.2, 124.4, 124.6, 124.7, 124.8, 126.2, 126.7, 126.8, 127.5, 127.6, 127.7, 127.8, 127.9, 128.3, 128.5, 128.6, 129.2, 129.4, 134.4, 134.7, 135.0 (C<sub>arom</sub>), 155.0, 156.7, 157.4 (C<sub>arom</sub>O). IR (THF, cm<sup>-1</sup>): 1792(sh), 1698 s, 1653,sh, 1747 sh, 1616 s, 1592 s, 1563, m, 1540 2, 858 2, 844 2, 820 s, 764, s, 749 sh, 712 m, 696 m, 678 w, sh, 622 m.

### 5.3. Dilithium di(binaphtholato) hydrido aluminate-4 tetrahydrofuran (6·4THF)

Prepared in analogy to **1** from LiAlH<sub>4</sub>, in diethylether (1.8 M, 1.65 ml, 2.97 mmol), *tert*-butanol ((3.0 mmol, 0.28 g) and racemic binaphthol (3.0 mmol, 0.86 g) dissolved in 10 ml of tetrahydrofuran. After heating to reflux for one hour the suspension was freed from some solid by filtration and the solution layered with methylcyclohexane. Needles separated on standing at ambient temperature. Yield: 0.73 g of 6·4THF (27%).

δ <sup>27</sup>Al (pyridine, C<sub>6</sub>D<sub>6</sub>): 25 (*h*(1/2) = 690 Hz; IR (Nujol, cm<sup>-1</sup>): 3694 m, 1768 w, 1708 m, AlH, 1614 s, 1591 s, 1564 m, 1503 s, 1485 s, 1445 w, 1426 s, 1396 m, 1367 s, 1342 s, 1299 s, 1251 s, 1238 s, 1212 s, 1192 w, 1154 w, 1140 w, 1127 w, 1089 2, 1072 m, 1041 s, 999 m, 955 s, 937 m, 906 sh, 883 m, 822 s, 791 m, 778 m, 750 s, 712 m, 695 m. C<sub>56</sub>H<sub>57</sub>O<sub>8</sub>Li<sub>2</sub>Al (898.88) Calc.: C, 74.82; H, 6.39; Al, 3.00; Anal. Found: C, 70.96; H, 6.42; Al, 2.95%.

### 5.4. Trilithium *R*(+)-tris(binaphtholato)aluminate-6 tetrahydrofuran (3·6THF)

To LiAlH<sub>4</sub> in ether solution (1.8 M, 1.1 ml) was added *tert*-butanol (0.16 g, 2.2 mmol in 3 ml of THF) followed by (+)-1,1'-binaphthol (0.57 g, 2.0 mmol) in 5 ml of THF. Some solid material was removed by filtration. From the solution the solvent was slowly removed (stepwise within 2 weeks): In the course of this procedure crystal of 3·6THF separated. Yield: 0.77 g of 3·6THF, 80%. The filtrate showed signals at δ <sup>27</sup>Al = 83 (*h*(1/2) = 1100 Hz) and 63 (*h*(1/2) = 1280 Hz); δ <sup>7</sup>Li = -0.7.

NMR data of the crystals: δ <sup>27</sup>Al (THF, C<sub>6</sub>D<sub>6</sub>) = 23 (*h*(1/2) = 380 Hz); δ <sup>7</sup>Li: 2.1; δ <sup>1</sup>H = 6.85 (td, <sup>3</sup>*J*(H,H) = 7.7 Hz, <sup>4</sup>*J*(H,H) = 1.4 Hz, 1 H), 7.02 (dt, <sup>3</sup>*J*(H,H) = 7.4 Hz, <sup>4</sup>*J*(H,H) = 1.1 Hz, 1H), 7.36 (d,

<sup>3</sup>*J*(H,H) = 8.4 Hz, 1H), 7.75 (d, <sup>3</sup>*J*(H,H) = 8.1 Hz, 1 H), 8.01 (d, <sup>3</sup>*J*(H,H) = 8.6 Hz, 1H), 8.22 (d, <sup>3</sup>*J*(H,H) = 8.8 Hz, 1H); δ <sup>13</sup>C = 120.3, 121.4, 124.7, 126.3, 127.4, 127.7, 18.2, 128.4, 134.4, 160.9; Raman (THF, cm<sup>-1</sup>): 3050 m, 2961 br, 2975 m, 1613 m, 1600 m, 1552 m, 1462 m, 1427 m, 1387 m, 1357 s, 1288 w, 1179 w, 1139 w, 1070 w, 848 m, 790 w, 759 w, 703 w, 667 m, 605 w, 534 m.

A similar reaction carried out only in THF as a solvent led to the precipitation of 3·6THF within 1 day. Yield: > 90%.

### 5.5. Dilithium tetra(binaphtholato) dialuminate-4 tetrahydrofuran (4·4THF)

A suspension of racemic 1,1'-binaphthol (1.50 g, 5.24 mmol) in THF (15 ml) was added dropwise within 20 min to a stirred solution of LiAlH<sub>4</sub> in diethylether (1.8 M, 1.6 ml, 2.90 mmol). After stirring for 1 h at ambient temperature a solution of isopropanol (5.2 mmol) in THF (10 ml) was added, the mixture heated to reflux for 1 h, the insoluble material removed by filtration (G4 frit) and the filtrate layered with hexane. Well shaped needles of 4·4THF, separated. Yield: 0.88 g 19%.

δ <sup>27</sup>Al (pyridine/THF) 42 (*h*(1/2) = 8600 Hz); δ <sup>7</sup>Li (THF, C<sub>6</sub>D<sub>6</sub>) = 2.7.

### 5.6. Lithium *R*(+)-binaphtholato di(*tert*-butoxo) aluminate-2 tetrahydrofuran (5·2THF)

Prepared in analogy to **1** from LiAlH<sub>4</sub> (1.8 M, 0.65 ml), *tert*-butanol (0.16 g 2.2 mmol) and *R*(+)-binaphthol (0.57 g, 2.0 mmol) dissolved in 10 ml of THF. Insoluble material was removed from the turbid solution and the filtrate cooled to -20°C. Clear prisms formed in the solution. These crystals proved to be 5·2THF.

δ <sup>27</sup>Al (THF, C<sub>6</sub>D<sub>6</sub>) = 70 (*h*(1/2) = 2140 Hz); δ <sup>7</sup>Li: 2.8.

### 5.7. Lithium *R*(+)-binaphtholato di(*tert*-butoxo) aluminate-pentamethyldiethylenetriamine (5·PMDTA)

To a solution of 5·2THF in THF containing ca. 1 mmol of 5·2THF was added a solution of PMDTA (1 mmol) in 5 ml of THF. After reducing the volume of the solution to about 4 ml, crystals separated at -20°C within a few days.

δ <sup>27</sup>Al (THF): 68 (*h*(1/2) = 3840 Hz). The compound was otherwise only analysed by X-ray structure determination.

### 5.8. Lithium μ-(+)-binaphtholato dihydrido aluminate-2 tetrahydrofuran (2·THF)

To a solution of LiAlH<sub>4</sub> in diethylether (3.59 mmol in 7.0 ml) was added with stirring a THF solution of

Table 2  
Crystallographic data and data related to data collection and structure refinement<sup>a</sup>

Compound	2-8THF	3-6THF	4-4THF	5-4THF	5-PMDTA	6-4THF	7-THF
Chemical formula	$C_{123}H_{135}Al_4Li_4O_{18.5}$	$C_{84}AlLi_3O_{12}$	$C_{112}H_{96}Al_2Li_2O_{16}$	$C_{36}H_{46}AlLiO_6$	$C_{37}H_{53}AlLiN_3O_4$	$C_{56}H_{57}AlLi_5O_8$	$C_{63}H_{57}Al_2O_6$
Formula weight	2044.99	1333.32	1765.73	608.65	637.74	898.88	952.04
Crystal size (mm)	$0.2 \times 0.2 \times 0.2$	$0.10 \times 0.30 \times 0.40$	$0.05 \times 0.10 \times 0.20$	$0.20 \times 0.20 \times 0.30$	$0.10 \times 0.10 \times 0.20$	$0.10 \times 0.10 \times 0.20$	$0.15 \times 0.30 \times 0.35$
Crystal system	Monoclinic	Hexagonal	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	$P6_322$	$P\bar{1}$	$P2_1$	$P2(1)$	$P\bar{1}$	$P2(1)$
Unit cell dimensions							
$a$ (Å)	15.806(2)	14.5489(1)	15.048(2)	9.7128(1)	9.990(1)	12.394(1)	12.2487(2)
$b$ (Å)	25.717(3)	14.5489(1)	16.940(2)	16.198(2)	18.118(1)	13.117(1)	17.4504(3)
$c$ (Å)	16.058(2)	19.739	18.492(2)	10.7709(2)	10.579(1)	17.474(2)	14.3506(1)
$\alpha$ (°)	90	90	92.290(2)	90	90	73.437(2)	90
$\beta$ (°)	97.162(2)	90	92.138(2)	90.344(2)	102.015(2)	89.478(2)	113.190(1)
$\gamma$ (°)	90	120	93.661(2)	90	90	61.844(2)	90
$V$ (Å <sup>3</sup> )	6476(1)	3618.4	4696.5(9)	1694.6(4)	1873.0(3)	2374.1(4)	2819.53(7)
$Z$	2	2	2	2	2	2	2
$\rho_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.049	1.224	1.249	1.193	1.131	1.257	1.121
$\mu$ (mm <sup>-1</sup> )	0.093	0.091	0.099	0.103	0.094	0.099	0.099
$F(000)$	2170	1412	1856	652	688	952	1006
Index range	$-20 \leq h \leq 20$ , $-33 \leq k \leq 33$ , $-22 \leq l \leq 18$	$-18 \leq h \leq 18$ , $-18 \leq k \leq 18$ , $-17 \leq l \leq 26$	$-18 \leq h \leq 18$ , $-22 \leq k \leq 15$ , $-23 \leq l \leq 23$	$-7 \leq h \leq 12$ , $-20 \leq k \leq 20$ , $-13 \leq l \leq 13$	$-12 \leq h \leq 12$ , $-17 \leq k \leq 24$ , $-13 \leq l \leq 13$	$-15 \leq h \leq 15$ , $-16 \leq k \leq 15$ , $-21 \leq l \leq 22$	$-15 \leq h \leq 15$ , $-22 \leq k \leq 22$ , $-16 \leq l \leq 17$
$2\theta$ (°)	58.46	57.88	58.24	57.70	58.10	57.84	58.44
Temperature (K)	193(2)	183	193(2)	193(2)	193(2)	193(2)	183(2)
Reflections collected	388371	21150	26975	9765	11041	13161	16040
Reflections unique	24436	2681	14161	5775	6814	6979	10629
Reflections observed ( $4\sigma$ )	15883	1770	8317	3746	3711	4987	8092
$R_{\text{int}}$	0.0325	0.0691	0.0492	0.0483	0.0538	0.0317	0.0226
No. variables	1407	183	1198	403	426	607	707
Weighting scheme $w_1/w_2$	0.2000/0.0000	0.1133/0.7132	0.0818/6.1531	0.0865/1.0689	0.0575/0.0000	0.1388	
3.1354	0.112900						
0.724400							
GoF	1.154	1.090	1.010	1.015	0.960	1.469	1.086
Final $R$ ( $4\sigma$ )	0.1077	0.0638	0.0807	0.0734	0.0607	0.0856	0.0677
Final $wR_2$	0.2900	0.1192	0.1749	0.1582	0.1121	0.2071	0.1739
Largest residual peak ( $e \text{ \AA}^{-3}$ )	1.730	0.201	0.468	0.211	0.198	1.156	0.559

<sup>a</sup>  $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$ ;  $P = (F_o^2 + 2F_c^2)/3$ .

R-(+)-binaphthol (1.03 g, 3.6 mmol in 5 ml of THF) at ambient temperature. After gas evolution had ceased a clear solution was obtained from which crystals separated on cooling to  $-20^{\circ}\text{C}$ ., m.p.  $>165^{\circ}\text{C}$ . Yield: 1.46 g (81.2%).

$\delta$   $^{27}\text{Al}$  (THF) = 100 ( $h(1/2) = 410$  Hz);  $\delta$   $^7\text{Li}$  ( $\text{C}_6\text{D}_6$ ) =  $-0.03$  ( $h(1/2) = 5.6$  Hz); (in THF):  $-0.60$ ;  $\delta$   $^1\text{H}$  ( $\text{C}_6\text{D}_6$ ) = 1.13 (m, 8H,  $\text{OCH}_2$ ), 3.27 (m,  $\text{CH}_2\text{-C}$ ), 3.98 (br, 2H,  $\text{AlH}_2$ ), 7.04–7.43/7.60–7.84 (m.);  $\delta$   $^{13}\text{C}$  ( $d_8$ -THF) = 15.5 ( $\text{MeCH}_2$ ), 26.1 ( $\beta\text{-CH}_2$  THF), 66.0 ( $\text{CH}_2\text{O}$ ), 68.0 ( $\alpha\text{-CH}_2$  THF), 122.1, 122.3, 124.9, 125.1, 126.9, 128.7, 129.6, 135.2, 157.8 (arom. C); IR (Nujol, Hostafon;  $\text{cm}^{-1}$ ): 3064 m, 3055 m, 2035 m, 2978 vs, 2956 sh, 2937 sh, 2873 vs, 1831 vs, 2804 vs, 1616 s, 1591 s, 1567 s, 1503 vs, 1466 vs, 1459 vs, 1427 vs, 1365 vs, 1355 s, 1336 vs, 1271 vs, 1260 vs, 1247 vs, 1230 vs, 1211 s, 1156 2, 11452 2, 1133 w, 1071 vs, 1065 vs, 1260 vs, 1247 s, 1230 vs, 1211 s, 1156 w, 1142 w, 1133 w, 1076 vs, 1065 vs, 1051 vs, 952 vs, 938 s, 607 s, 586 vs.

$\text{C}_{120}\text{H}_{138}\text{O}_{18}\text{Al}_4\text{Li}_4$  (2004.10) Calc.: C, 71.11; H, 6.51; Al, 5.25; Anal. Found: C, 71.91; H, 6.94; Al 5.39%.

### 5.9. X-ray structure determinations

Single crystals were formed on slow evaporation of the solutions or by layering the THF solutions with a hydrocarbon (hexane, methylcyclohexane) at  $-20^{\circ}\text{C}$ . The crystals were removed from the solutions and transferred directly into precooled fluoropolyether oil at  $-40^{\circ}\text{C}$ . The selected specimen was then mounted on the tip of a glass fiber and transferred to the goniometer head which was flushed with cold dinitrogen ( $-80^{\circ}\text{C}$ ). A Siemens P4 diffractometer equipped with an area detector and a cold stream LT2 device was employed for data collection using the program SMART [15]. Graphite-monochromated  $\text{Mo-K}\alpha$  radiation was used for data collection. The data were reduced with the program SAINT [16]. For structure solution the direct methods implemented in the SHELXTL PLUS software or SHELX-97 programs were successful [17]. Non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms bound to Al centers were found in the difference Fourier syntheses but not for compound **2** as well as for one Al bonded H atom in compound **7**. H atoms bound to C atoms were placed in calculated positions and refined isotropically as riding on the respective C atom. Relevant crystallographic data are compiled in Table 2.

## 6. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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## References

- [1] R. Noyori, *Pure Appl. Chem.* 53 (1981) 2315.
- [2] R. Noyori, I. Tomino, M. Yamada, M. Nishizawa, *J. Am. Chem. Soc.* 106 (1984) 6701.
- [3] S. Hermanek, O. Kriz, Z. Cerny, B. Casensky, *J. Chem. Soc. Perkin Trans. II* (1989) 987.
- [4] S. Hermanek, J. Fusek, O. Kriz, C. Casensky, Z. Cerny, *Z. Naturforsch. Part B* 42 (1987) 539.
- [5] D.A. Horne, *J. Am. Chem. Soc.* 102 (1980) 6011.
- [6] Z. Cerny, J. Fusek, J. Machacek, O. Kriz, B. Casensky, *J. Organomet. Chem.* 516 (1996) 115.
- [7] J.C. Huffman, R.L. Geerh, K.G. Caulton, *J. Crystallogr. Spectrosc. Res.* 14 (1984) 541.
- [8] H. Nöth, A. Schlegel, J. Knizek, I. Krossing, W. Ponikvar, T. Seifert, *Chem. Eur. J.* 4 (1998) 2191.
- [9] The insoluble material formed in preparing Noyori's reagent [2] is compound **3**.
- [10] (a) H. Nöth, A. Schlegel, J. Knizek, H. Schwenk, *Angew. Chem.* 109 (1997) 2754; *Angew. Chem. Intern. Ed. Engl.* 36 (1998) 2640. (b) M. Veith, S. Faber, A. Wolfanger, V. Huch, *Chem. Ber.* 129 (1996) 381.
- [11] (a) V.V. Gavrilenko, M.I. Vinnikova, V.A. Antonovich, L.I. Zaharkin, *Isv. Akad. Nauk SSSR Ser. Khim.* 6 (1979) 1273; *Bull. Acad. Sci. USSR. Chem. Ser. (Engl. Transl.)* (1984) 1188; *Isv. Akad. Nauk. SSSR Ser. Khim.* 14 (1984) 865.
- [12] S.R. Hall, C.L. Raston, B.W. Skelton, A.H. White, *Inorg. Chem.* 22 (1983) 4070.
- [13] C.L. Raston, B.W. Skelton, C.R. Whitaker, A.H. White, *J. Chem. Soc. Dalton Trans.* (1988) 987.
- [14] A. Haaland, *Angew. Chem.* 101 (1989) 1017; *Angew. Chem. Int. Ed. Engl.* 28 (1989) 992.
- [15] SMART, Siemens Analytical, Version 4.1, 1991.
- [16] SAINT, Siemens Analytical Div. Version 4.1, 1991.
- [17] (a) SHELXTL PLUS, Siemens Analytical Division, Version 4.1, 1994. (b) G.W. Sheldrick, SHELX-97, University of Göttingen, Germany.