$[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)_4]^{3-}$

A new Al$_{15}$ aggregate which forms a supramolecular zeotype

Encapsulation of {Al$_7$(OH)$_{12}$}$^{9+}$ by dinuclear Al$_2$(hpdta) units

$[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)_4]^{3-}$

Supramolecular array of Al$_{15}$ aggregates

For more information see the following pages.

[Al$_{15}$(μ_3-O)$_4$(μ_3-OH)$_6$(μ-OH)$_{14}$(hpdta)$_4$]$^{3-}$— A New Al$_{15}$ Aggregate Which Forms a Supramolecular Zeotype**

Wolfgang Schmitt, Elham Baissa, Alexander Mandel, Christopher E. Anson, and Annie K. Powell*

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

The chemistry of aluminum(III) in aqueous solution is largely driven by the high charge density of the small Al^{3+} ion. This property leads to extensive hydrolytic processes and this has been utilized in the preparation of a number of aggregated oxyhydroxy species containing from thirteen to thirty aluminum centers.[1–4] Such cluster aggregates are of interest both in the investigation of Al^{III} hydrolysis, which is relevant to environmental and biological situations where the metal ion is present, and also as a means of producing small and reactive hydroxide-rich aggregates which might be useful for promoting or even catalyzing hydrolytic reaction chemistry. Amongst the examples of purely inorganic aggregates is the Al$_{13}$ cluster [AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$,[1] which has the Keggin ion structure, and the related and largest Al^{III} aggregate so far crystallographically characterized [AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$]$_2$-[Al$_4$(OH)$_8$(H$_2$O)$_6$]$^{18+}$.[2] There are two further, related Al$_{13}$ species, the purely inorganic [Al$_{13}$(OH)$_{24}$(H$_2$O)$_{24}$]$^{15+}$ and the cluster formed in the presence of the ligand heidi (H$_3$heidi = N(CH$_2$COOH)$_2$(CH$_2$CH$_2$OH)) [Al$_{13}$(OH)$_{18}$(heidi)$_6$-(H$_2$O)$_6$]$^{3+}$.[3, 4] In these two compounds the structure of the Al-oxyhydroxide core corresponds to the brucite-type structure. This type of structure has also been observed in the Fe$_{19}$ aggregates formed with heidi and the related Me-heidi and Et-heidi ligands which have methyl and ethyl groups, respectively, on the α-C atom of the hydroxyethyl moiety.[5, 6] The encapsulation of such core aggregates in organic shells offers the possibility of modifying packing arrangements through changes to the organic part and also allows for the preparation of hybrid materials where regions with different polarities can be incorporated into the same structure. For example, the purely inorganic Al$_{13}$ clusters crystallize with a dense packing that optimizes the hydrogen-bonding interactions and gives a substance with a density of 1.78 g cm^{-3}, whereas the hybrid Al$_{13}$-heidi clusters crystallize in a trigonal space group; the molecules are hexagonally packed in layers which stack into columns with parts of the heidi ligands forming spacers between the layers. This arrangement gives a relatively open structure with a density of only 1.35 g cm^{-3}. Another way of viewing such Al$_{13}$ aggregates is to take the basic close-packed brucite core structure of

{Al$_7$(OH)$_{12}$}$^{9+}$ and to regard the encapsulating portion as consisting of a ring of six Al-ligand units, each of which is connected to the core by double bridges containing oxygen atoms: in the case of the inorganic "naked" aggregate these are both hydroxides, whilst for the Al-heidi compound there is one hydroxide plus one alkoxide bridge from the hydroxyethyl side chain of the ligand.

We find that when we use the ligand hpdta (H$_5$hpdta = HOCH$_2$[CH$_2$N(CH$_2$COOH)$_2$]$_2$), which has two iminodiacetic acid moieties linked by a 2-hydroxypropane group, the dinucleating alkoxide side chain is now placed between two iminodiacetate units and leads to a different arrangement of the Al-ligand units on the periphery. In this case hydrolytic reactions lead to the isolation of Al$_{15}$ cluster aggregates. Single-crystal structure analyses on two examples, **1a** and **2**, reveal that the cluster anions, [Al$_{15}$(μ_3-O)$_4$(μ_3-OH)$_6$(μ-OH)$_{14}$(hpdta)$_4$]$^{3-}$ possess the same type of core as the Al$_{13}$ structures, but this is now captured by four dinuclear {Al$_2$(hpdta)} units in which the Al^{III} centers are bridged by the alkoxide function of the ligand. One aluminum ion of each unit is connected to the core by two hydroxide bridges, the other by one hydroxide and a μ_3-oxide ligand. The latter case corresponds to the deprotonated form of one of the peripheral hydroxides of the inner {Al$_7$(OH)$_{12}$}$^{9+}$ core (Figure 1).

This different ligand coordination at the periphery of the aggregates combined with a templating effect from the organic base used in the hydrolysis leads to a packing arrangement in which the aggregates are arranged in such a way as to create two types of channel running through the structure parallel to the c axis (Figure 2). We find that this overall structure can be reproduced using both piperazine (**1a**) and ethylenediamine (**2**) as the templating hydrolyzing base. The structure of **1a** is better defined in terms of the solvent content of the large channels and we confine our attention to this for further discussion. The smaller channels are mainly lined with noncoordinated oxygen atoms of the hpdta ligands and contain the countercations, which appear to act as templates for the observed structure. An oxonium cation lies at the center of a distorted square of such carboxylate oxygen atoms, each of which originates from a different cluster unit. At any one time, the oxonium cation can form hydrogen bonds to three of these four oxygen atoms, and dynamic disorder is presumably in operation here.

Alternating with the H$_3$O$^+$ ions in these smaller channels are piperazinium ions (pipzH$_2^{2+}$); the N-H protons of these piperazinium ions are also involved in hydrogen bonding to carboxylate oxygen atoms from different clusters. The cations thus play an important role in maintaining the supramolecular structure. The larger channels are principally lined with arrays of hydroxyl groups from the cluster cores but there are also carboxylate oxygen atoms and methylene groups from the peripheral ligands on the cluster present. These larger channels are filled with neutral water and base molecules. In this way we can see how the incorporation of an organic ligand into the outer shell of the aggregate allows for the separation of the structure into areas of different polarities.

Overall the Al$_{15}$ units pack to form a supramolecular array which reproduces aspects of the structural features of zeolites such as Linde A and other such molecular sieves. If we

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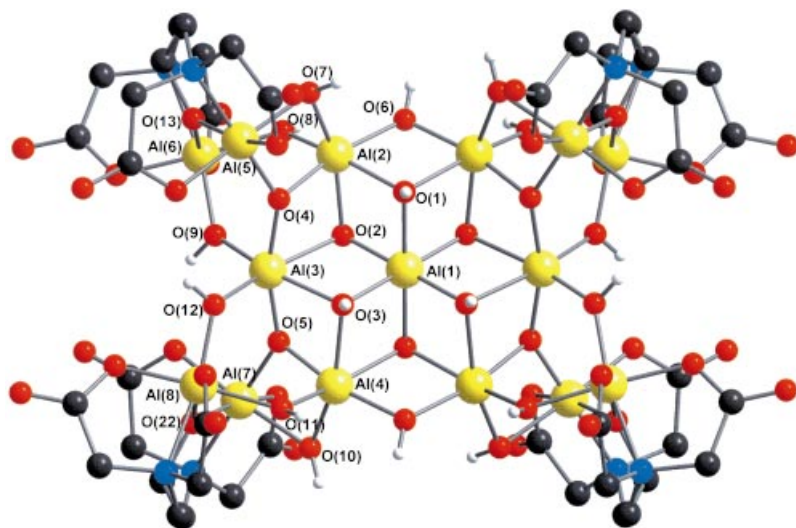Norwich NR4 7TJ (UK)

[**] H$_5$hpdta = HOCH$_2$[CH$_2$N(CH$_2$COOH)$_2$]$_2$.

Figure 1. The supramolecular structure of the cluster ion $[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}\text{-}(hpdta)_4]^{3-}$ in **1a**. The hydrogen atoms on the peripheral ligands are omitted for clarity. Al−O bond lengths (Al-O-Al angles) are in the ranges: 1.847(3)–2.083(3) Å (92.3(1)–101.7 (2)°) for Al−$(\mu_3\text{-}OH)$; 1.824(3)–1.969(4) Å (92.5(1)–130.0(2)°) for Al−$(\mu_2\text{-}OH)$; 1.753(3)–1.841(3) Å (101.8(2)–142.8(2)°) for Al−$(\mu_3\text{-}O)$. The Al−N bond lengths are in the range 2.036(4)–2.116(4) Å.
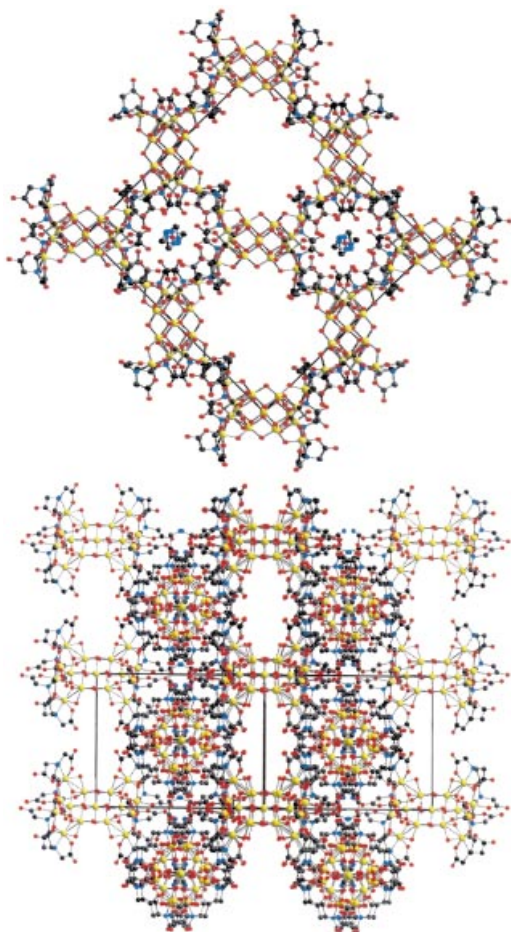

Figure 2. The supramolecular array of the Al_{15} cluster in **1a** (Al yellow, O red, N blue, C black). The protonated base and water molecules in the smaller channels act as a template and stabilize the structure. The solvent and base molecules have been omitted from the larger channels for clarity. The top view is looking down the *c* axis, the lower view is a projection on to [110] and shows the side entrances to the large channels.

examine the size and shape of the larger channels we find these are an average of about 11 Å in diameter and are connected together by cavities running perpendicular with diameters of about 5 Å (Figure 2). The available space within these interlinked larger channels can be calculated as 4494 Å^3, or 36.7 % of the total unit cell volume.[7] In the crystal structure analysis of compound **1a** the solvent and base molecules in the larger channels were relatively well-defined and we were able to assign the electron density to forty-one water molecules and one base molecule per aggregate to give an overall formula of $(pipzH_2)(H_3O)[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)_4] \cdot pipz \cdot 41\,H_2O$. This assignment takes into account the results of the CHN analysis and also seems reasonable when we look at the hydrogen-bonding interactions between the water molecules and the hydroxy groups of the cluster. Thus, we can readily identify three strongly hydrogen-bonded water molecules per cluster surface which are hydrogen-bonded to further water molecules with the very center of the channels containing twofold disordered base and water molecules (Figure 3a). Thermal analysis on this compound substantiates this further and shows that by 300 °C all the solvent molecules have been lost from the sample. Beyond this temperature the rest of the organic residues are driven off to give Al_2O_3.

In the light of the results of the differential thermal analysis (DTA) experiments we decided to investigate the crystal structures of single crystals which had been heated to 150 °C for 4 h and at 200 °C overnight in an oven. The sample which had been heated to 200 °C proved to be extremely hygroscopic and although it was possible initially to observe some very diffuse diffraction spots, the crystal deteriorated too rapidly to allow for the collection of a data set. This result indicates that the structure is capable of taking up solvent molecules extremely readily. The sample which was heated to 150 °C retained its integrity and we were able to collect and analyze a full data set on this (compound **1b**). The structure solution reveals that the overall supramolecular framework structure remains the same, but a significant amount of solvent from the larger channels has been lost (Figure 3). Not surprisingly, it is the less strongly bound molecules in the centers of the channels which have disappeared so that 1 piperazine molecule and about 18 water molecules are lost per cluster from the 1 piperazine and 41 water molecules originally present (Figure 3b).

These results show how it is possible to create supramolecular arrays of aluminum-oxyhydroxy aggregates that display zeotypic structures and properties. The structural similarities to zeotypic systems are even more striking when the structure is viewed in a polyhedral representation (Figure 4). Some of the giant polyoxomolybdate wheels synthesized in the research group of Müller can form supramolecular arrays containing nanoscale channels that are produced by the concentric stacking of the units with the phosphinic acid derived ligands captured within the channels.[8] In our case it is
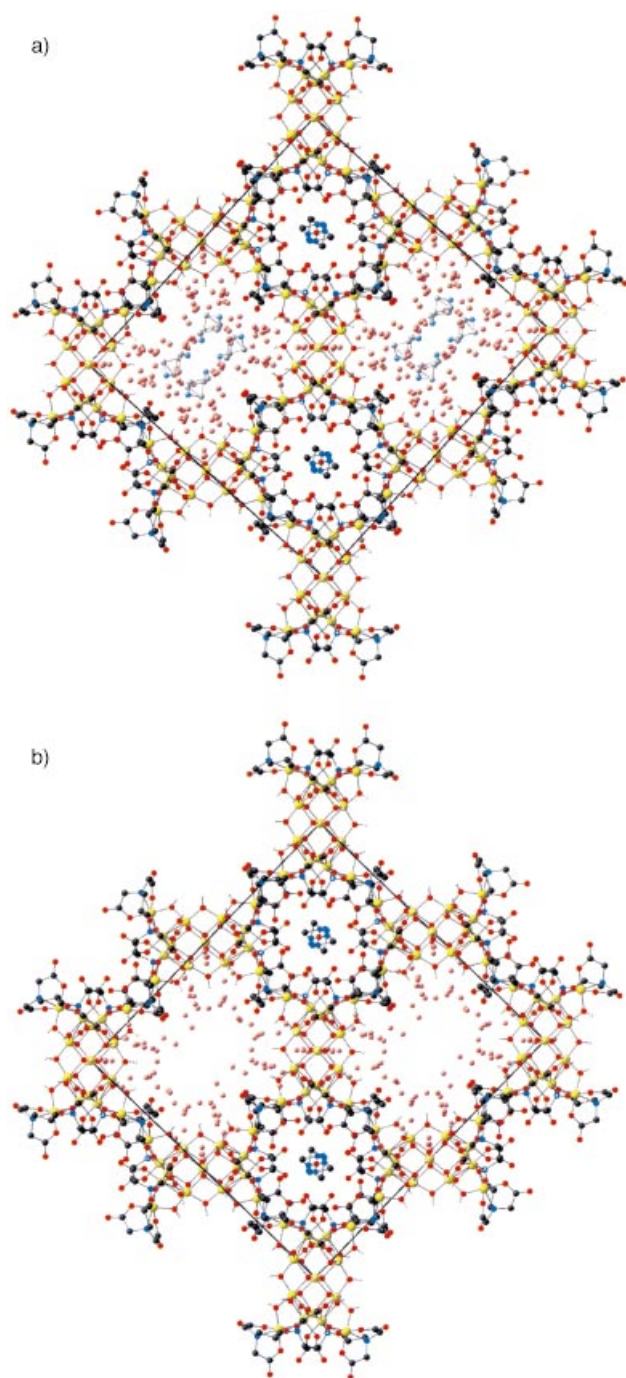
a)

b)

Figure 3. a) The structure of a freshly prepared crystal (colors as for Figure 2). The paler shaded atoms are the solvent and base molecules in the large channels. b) The structure of a crystal heated at 150 °C for 4 h showing the loss of the central molecules from the large channels.
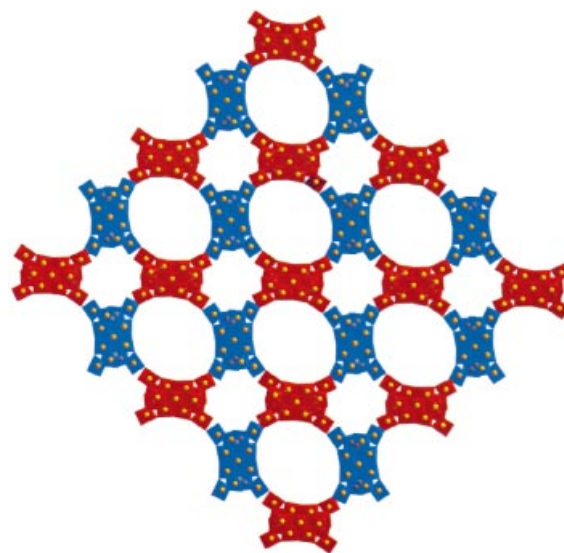

Figure 4. Polyhedral representation of the supramolecular cluster structure looking down the *c*-axis. The blue clusters are in a plane half a unit cell length below the plane containing the red clusters.

the direct interaction of the oxonium and base-derived cations with the hpdta ligands on the outside of the aggregates which stabilizes the "host" channel structure observed. These interactions are such that the supramolecular structure is maintained even when the guest molecules (water and base) are driven from the large host channels. Of particular relevance for possible future applications is the ability to construct such a hybrid material from well-defined nanoscale alumina-derived building blocks. We are not aware of any

similar structure based on hybrid molecular aggregates. Perhaps even more interesting could be the possible hydrolytic activation or catalytic reactions using suitably sized substrates within the hydroxide-rich cavities of this structure; this is an area we are now poised to explore.

Experimental Section

Synthesis: Compound **1** was prepared from 2-hydroxypropane-1,3-diamine-*N,N,N′,N′*-tetraacetic acid (H$_5$hpdta, 1.66g, 5 mmol) dissolved in a mixture of H$_2$O (30 mL) and an aqueous piperazine solution (1M, 20 mL). The resulting solution was added with stirring to a solution of aluminum nitrate nonahydrate (7.5 g, 20 mmol) dissolved in H$_2$O (50 mL). The pH was adjusted to 8.85 by the dropwise addition of an aqueous piperazine solution (1M). Addition of dimethylacetamide (100 mL) followed by slow evaporation of the solvent gave colorless crystals of **1** after approximately 8 days. Elemental analysis (%) calcd for C$_{52}$H$_{161}$Al$_{15}$N$_{12}$O$_{92}$ (which corresponds to the crystallographically determined formulation with the loss of 9 water molecules from the structure): C 21.92, H 5.77, N 5.9; found: C 21.99, H 6.19, N 6.01; IR (KBr): $\tilde{\nu} = 3455$ (vs,br), 2969 (sh), 1692 (vs), 1650 (vs), 1392 (s), 1085 (m), 1051 (m), 970 (m), 917 (ms), 754 (ms), 641 cm^{-1} (s).

Compound **2** was prepared in a similar manner to compound **1** but ethylenediamine was used as base.

Thermal analysis: The differential thermal analysis (DTA) and the differential thermogravimetry (DTG) experiments were carried out using a Netzsch STA 409C system. The measurement was performed in an oxygen atmosphere with a flow rate of 50 L h^{-1}. Sample **1a** (4.7 mg) was heated in a crucible to 1000 °C at a heating rate of 2 K min^{-1}. Between room temperature and 300 °C, two overlapping processes corresponding to the loss of solvent of crystallization were observed: 20 – 140 °C (15 % mass loss, DTG curve centered at ca. 55 °C) and 140 – 300 °C (11 % mass loss, DTG curve centered at ca. 190 °C). Between 300 and 370 °C, oxidation of the ligands (46 % mass loss, DTG curve centered at ca. 345 °C) in an exothermic process led to the formation of Al$_2$O$_3$.

X-ray crystallography for **1a** and **1b**:[11] Data were collected at 200 K on a Bruker SMART Apex diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation. Semi-empirical absorption correction with SADABS.[9] Structure solution by direct methods and refinement with SHELXTL.[10] **1a**: (C$_{52}$H$_{179}$Al$_{15}$N$_{12}$O$_{101}$ 2706.19 g mol^{-1}): colorless octahedron 0.30 × 0.25 × 0.20 mm, orthorhombic, space group *Pccn*, $a = 26.8226(14)$, $b = 28.2975(15)$, $c = 15.5604(8)$ Å, $V = 11810.5(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.68$ g cm^{-3}, $F(000) = 6312$, μ(Mo$_{K\alpha}$) = 0.260 mm^{-1}. 57679 reflections were

measured ($4.0 < 2\theta < 55.6°$), of which 13 778 were unique ($R_{int} = 0.0862$). Refinement against F^2 to $wR_2 = 0.2438$, $S = 1.068$ (all data), R_1 (9753 reflections with $I > 2\sigma(I)$) = 0.0916. 858 parameters, 18 restraints; all non-H atoms were anisotropic apart from some of the disordered solvent molecules; hydroxy hydrogen atoms were located and refined. The unit cell was close to tetragonal ($P4_2/ncm$) but no twinning was observed. **1b**: ($C_{48}H_{133}Al_{15}N_{10}O_{83}$ 2583.34 g mol^{-1}): colorless octahedron $0.35 \times 0.30 \times 0.30$ mm, orthorhombic, space group $Pccn$, $a = 26.871(3)$, $b = 28.001(3)$, $c = 15.5309(17)$ Å, $V = 11\,686(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.47$ g cm^{-3}, $F(000) = 5400$, $\mu(Mo_{K\alpha}) = 0.238$ mm^{-1}. 56 757 reflections were measured ($4.2 < 2\theta < 56.1°$), of which 13 542 were unique ($R_{int} = 0.0733$) The crystal quality was significantly poorer than for **1a**. Refinement against F^2 to $wR_2 = 0.3459$, $S = 1.101$ (all data), R_1 (9859 reflections with $I > 2\sigma(I)$) = 0.1237. 776 parameters, 10 restraints; all non-H atoms in the cluster and counterions were anisotropic. Some disordered solvent waters were assigned partial occupancies.
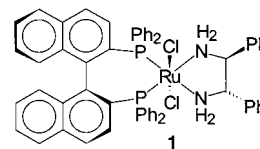
Crystal data for **2**: ($C_{58}H_{84}Al_{15}N_{24}O_{74}$; 2706.19 g mol^{-1}): colorless octahedron $0.14 \times 0.07 \times 0.06$ mm, tetragonal, space group $P4_2/ncm$, $a = 27.979(3)$, $c = 15.623(2)$ Å, $V = 12\,230.1(24)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.47$ g cm^{-3}, $F(000) = 5548$, $\mu(Mo_{K\alpha}) = 0.230$ mm^{-1}. Data were collected at 293 K on a Rigaku R-Axis IIc area detector diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation. 56 705 reflections were measured ($4.1 < 2\theta < 50.8°$), of which 5737 were unique ($R_{int} = 0.2335$). Structure solution by direct methods; refinement against F^2 (SHELXTL[10]) to $wR_2 = 0.1886$, $S = 1.125$ (all data), R_1 (2450 reflections with $I > 2\sigma(I)$) = 0.0604. 484 parameters; all non-H atoms in the cluster and counterions were anisotropic. The solvent molecules were heavily disordered, and only those directly H-bonded to the cluster could be modeled realistically; the solvent content is likely to be similar to that in **1a** and the parameters given here only refer to the atoms which were located during the refinement.

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[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-163561 – 163563. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam. ac.uk).

Noyori's Hydrogenation Catalyst Needs a Lewis Acid Cocatalyst for High Activity**

Rudolf Hartmann and Peter Chen*

The asymmetric hydrogenation of simple ketones[1] in isopropyl alcohol by using *trans*-RuCl$_2$[(*S*)-binap][(*S,S*)-dpen] **1** (binap = [1,1′-binaphthalene-2,2′-diylbis(diphenylphosphane)]; dpen = diphenyl-ethylenediamine), an excess of an inorganic base, and 10–50 bar H$_2$ at 30–60 °C is remarkable in several respects: quantitative chemical yield within hours, enantiomeric excesses (*ee*) up to 99 %, high chemoselectivity for carbonyl over olefin reduction, and a substrate-to-catalyst ratio (S/C) > 100 000. The combination of desirable features makes this catalytic reaction of great practical interest.[2] Moreover, the catalytic cycle is mechanistically novel, with most of the attention having been focussed on the step in which the ketone is reduced. Much less attention has been devoted to the cleavage of hydrogen to form the active ruthenium hydride. However, it is this step that differentiates the new class of hydrogen-cleaving Ru^{II} catalysts from the structurally similar transfer hydrogenation Ru^{II} complexes.[3, 4] We report herein an experimental study of the mechanism of catalytic hydrogenation with **1** which shows that the catalyst requires the presence of alkali metal cations, or more generally, a Lewis acid, as a cocatalyst for efficient turnover.

The preparation and purification of Noyori's catalyst **1** as well as the other reagents used in this study is described in the Supporting Information. Solution-phase reactivity studies were performed in thick-walled Pyrex pressure tubes fitted with a Bourdon-tube manometer on a stainless-steel head fitted with high-pressure valves (Whitey SS-43MA-S4, specified up to 200 bar). The solution (typically 2.9 mL) was degassed by three freeze-pump-thaw cycles, and then magnetically stirred in a temperature-controlled oil bath. The apparatus was found to be leak-proof over 48 h with up to 6 bar H$_2$. Test reactions with **1** (3 mg), *t*BuOK (10 equiva-

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