

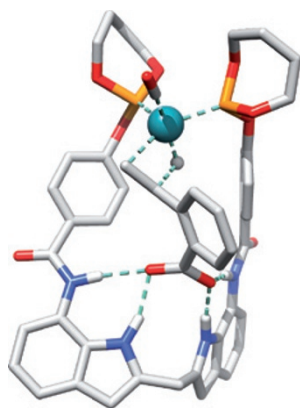
## CATALYST DESIGN

### Supra selectivity

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Hydroformylation is an industrially important reaction that converts alkenes into aldehydes by reacting them with a mixture of carbon monoxide and hydrogen. Millions of tonnes of a variety of very useful products are made from relatively cheap alkenes every year through hydroformylation. One particular class of alkene substrate, vinyl arenes, is of great interest. Theoretically, hydroformylation can lead to two possible products — an  $\alpha$ -aryl or  $\beta$ -aryl aldehyde — with formation of the branched ( $\alpha$ -aryl) product being favoured by interactions of the metal catalyst with the aryl ring. The branched product is chiral and several catalyst systems have been developed to produce this product with both high regio- and stereoselectivity.



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Despite being a synthetically useful product, few catalyst systems have been developed that can overcome the natural selectivity of the reaction to produce a linear ( $\beta$ -aryl) aldehyde. Now, Paweł Dydio and Joost Reek from the University of Amsterdam have done just that, by designing a ligand for a rhodium catalyst that dictates the

orientation in which a vinyl-2-carboxyarene substrate binds to the catalyst before reaction. The ligand contains two phosphite groups (which coordinate to the rhodium) connected by a diamidodiindolylmethane to form a 'pocket' which binds strongly to the carboxylate group in the substrate. In the key regiochemistry-defining step — migration of a hydride to the alkene (pictured) — it is this strong binding that makes the formation of an  $\alpha$ -phenylalkyl rhodium complex (that would ultimately lead to the usual branched product) significantly less favourable. In a control reaction in which the carboxylate group of the substrate is masked as an ester, the natural selectivity (producing 95% of the branched product) is restored.

Dydio and Reek show that the reaction tolerates many other substituents on the aryl ring in addition to the carboxylate directing group, and also demonstrate that the selectivity for the  $\beta$ -aryl aldehyde product is maintained even with additional substituents on the alkene.

## HYDROGEN BONDING

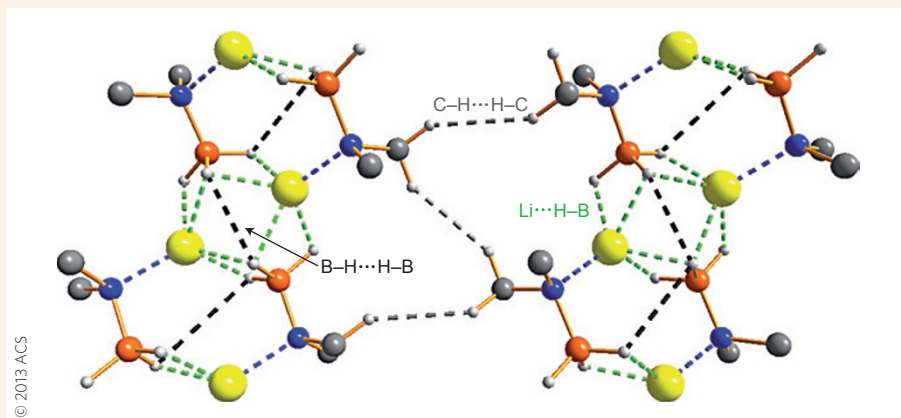
### Unconventional connections

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Hydrogen bonding can occur in a variety of situations and is not limited to interactions between polar hydrogens and electronegative atoms of adjacent molecules. Heteropolar dihydrogen interactions ( $X-H\cdots H-Y$ ) have been observed and, somewhat counter-intuitively, so have homopolar examples, such as between two CH groups. Rather than being governed by electrostatic interactions, these cases arise from attractive van der Waals forces.

By alkylating the NH group of  $LiNH_2BH_3$ , David J. Wolstenholme, G. Sean McGrady and colleagues from the University of New Brunswick have now suppressed the influence of the conventional proton-hydride  $N-H\cdots H-B$  interaction to study in detail the homopolar dihydrogen interactions occurring in solid-state  $LiNMe_2BH_3$ . The compound was extensively characterized through X-ray crystallography and an analysis of the calculated electron distribution. It was found that  $[Li]^+[NMe_2BH_3]^-$  adopts a one-dimensional chain structure (pictured; yellow, Li; orange, B; blue, N; grey, C; white, H) held together by inter-ion  $Li\cdots N$  and  $Li\cdots H-B$  interactions (shown as blue and green dashed lines, respectively).

Within a given chain, a zigzag arrangement (black dashed lines) of supporting weak  $B-H\cdots H-B$  interactions



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arising from mutual polarization of the BH groups was found between amidoborane moieties  $[NMe_2BH_3]^-$ . A significant accumulation of electron density between the two hydrogen atoms confirmed that the BH groups do interact with one another, rather than simply being in close proximity. This conclusion is also supported by the fact that similar  $B-H\cdots H-B$  distances were observed in the parent compound  $LiNH_2BH_3$ . The 1D chains are further connected to each other, albeit loosely, through weaker  $C-H\cdots H-C$  dispersion forces (grey dashed lines between the chains) and  $C-H\cdots H-B$  interactions (not shown; perpendicular to the plane pictured).

In contrast, the potassium analogue of the compound ( $KNMe_2BH_3$ ) was found to have a sheet-like structure with layers connected to each other through  $C-H\cdots H-C$  dispersion forces. This change in topology is caused by subtle differences in the main inter-ion interactions ( $K\cdots N$  and  $K\cdots H-B$ ), which in turn prevent the formation of the weaker  $B-H\cdots H-B$  and  $C-H\cdots H-B$  bonds. These structural studies underscore the fact that weak homopolar dihydrogen interactions play a substantial supporting role in supramolecular structures, and may contribute to the stability and reactivity of hydrogen-rich compounds. AP