Borylene Complexes

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Reversible σ-Borane-to-Borylene Transformation: A Little Something For Everyone**

Holger Braunschweig and Rian D. Dewhurst*

σ-borane ligands · B ligands · borylene complexes · hydrogen · ruthenium

The concept of the σ-borane ligand is essential to the study of catalyzed borylation protocols, including ubiquitous catalytic hydroboration reactions[1] and the remarkable discovery, several years ago, of borylation of unactivated arenes and alkanes.[2] Given the centrality of σ-borane ligands in these processes, it is somewhat confounding that examples of isolated transition-metal complexes with unsupported σ-borane ligands are still relatively rare.

Hartwig,[3] Sabo-Etienne,[4] and others[5] have gone a long way towards addressing this problem, by preparing a number of σ-borane/borate complexes from commonly used and synthetically relevant boranes (often borabicyclononane, pinacol- or catecholborane). In many cases, the metal–ligand interaction lies at some point on a continuum comprising many subtly different bonding descriptions (for instance, situations **A**–**C**, Figure 1). Thus the true nature of the bonding

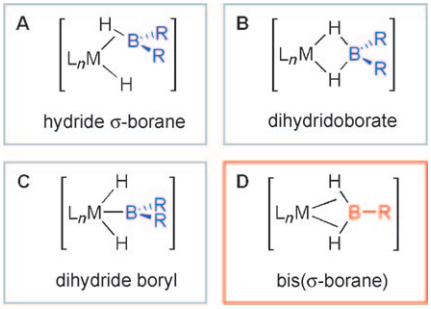
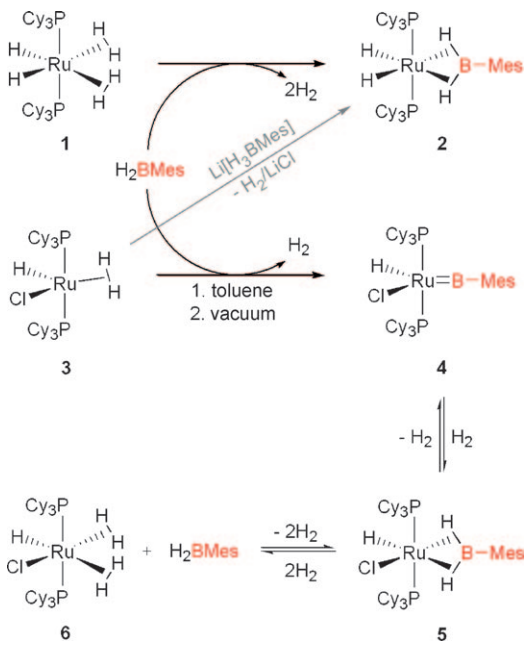


Figure 1. Interactions of hydroborane ligands with transition metals.

is often difficult to conclusively determine, and requires significant spectroscopic, crystallographic and computational input to solve.

An inventive and elegant sideline to this chemistry taken by Sabo-Etienne and co-workers was to explore the chemistry of dihydroboranes, which, given their two B–H bonds, are potentially better ligands for transition metals than monohydroboranes. By this rationale, they synthesized the first complex with an unusual bis(σ-borane) ligand (Figure 1, **D**).[6] The ruthenium(II) complex $[RuH_2(\eta:\eta^2\text{-}H_2BMes)(PCy_3)_2]$ (**2**, Scheme 1) was generated upon treatment of $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**1**) with H_2BMes, with concomitant hydrogen gas evolution. Similarly, **2** could be prepared from $[RuHCl(\eta^2\text{-}H_2)(PCy_3)_2]$ (**3**) and $Li[H_3BMes]$ with elimination of LiCl.



Scheme 1. Reactions of σ-dihydrogen complexes of ruthenium with mesitylborane. Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl.

Very recently, Sabo-Etienne and co-workers have published an extension of this chemistry, in the reaction of **3** with mesitylborane.[7] In the absence of salt elimination, as seen above in the synthesis of **2**, the chloride ligand is retained, and under vacuum two equivalents of dihydrogen are liberated, giving borylene complex $[RuHCl(=BMes)(PCy_3)_2]$ (**4**). Upon treatment of a solution of **4** with hydrogen gas, signals corresponding to **4** disappeared from the ^{31}P NMR spectrum,

[*] Prof. Dr. H. Braunschweig, Dr. R. D. Dewhurst
Institut für Anorganische Chemie
Bayerische Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/Braunschweig/index.html

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replaced by those for two new species, the unsymmetrical mesitylborane adduct **5** and the hydrogen-rich complex **6**. These results were rationalized as an equilibrium between complexes **4**, **5**, and **6**, which can be driven to the left (→**4**) or right (→**6**) by using vacuum or hydrogen pressurization, respectively.

The ^{11}B NMR signal of **4** was found at $\delta = 106$ ppm,[7] far downfield of those of bis(σ-borane) complexes **2** ($\delta =$ 58 ppm), **5** ($\delta = 73$ ppm) and precursor mesitylborane ($\delta =$ 22 ppm).[6] A triplet hydride signal at $\delta = -14.9$ ppm in the ^{1}H NMR spectrum was found to collapse to a singlet upon ^{31}P decoupling, yet no significant sharpening of the signal occurred given broadband ^{11}B decoupling. These data, along with the very short Ru–B distance (1.780(4) Å), provide convincing evidence for borylene-type bonding in the absence of location of the hydride ligand in the X-ray crystallographic study. Further support for the borylene linkage in **4** came from density functional theory and natural bond orbital analyses, both of which indicated long B–H distances.

This reaction is remarkable in that the dihydrogen activation and reformation are both room-temperature processes, making the borylene complex **4** evocative of a "frustrated Lewis pair", a class of compounds currently attracting attention for their hydrogen storage properties.[8,9] Although the expense and high molecular mass of **4** obviously precludes this system from any real application in hydrogen storage, it is a surprisingly facile and reversible dihydrogen activation from an unexpected and unique system.

From the standpoint of transition-metal boron chemistry, the dehydrogenation process of Sabo-Etienne and co-workers is potentially a powerful route to new transition-metal borylene complexes.[10] Current routes to terminal borylene complexes include salt elimination from haloboranes and anionic transition-metal complexes (Mn, Cr, Mo, W), halide abstraction (Fe, Pt) and borylene transfer from group six borylene complexes (V, Cr, Ir) (Figure 2). Furthermore, terminal arylborylene complexes were previously accessible only by halide abstraction and were heretofore limited to cationic examples of Fe[11] and Pt.[12]

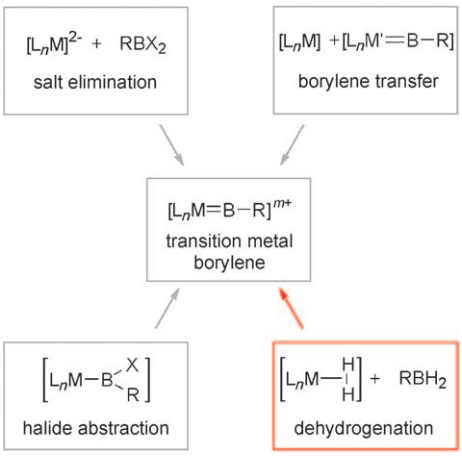

Figure 2. Routes to terminal transition-metal borylene complexes, including the new dehydrogenation process of Sabo-Etienne and co-workers (highlighted in red).

In terms of reactivity of the new ruthenium borylene complex, comparisons to the Grubbs system of metathesis catalysts[13] are obvious, and the significant precedent for metathesis chemistry of borylene complexes will only strengthen expectations. Borylene ligands have previously shown signs of mimicking the metathesis reactions of carbene ligands with the more reactive C=E (E = O, NR), P=E and As=E (E = O, S) bonds.[14] However, C=C bond metathesis with a borylene complex has not yet been reported. From **4** one would expect interesting additions to the already rich metathesis and transfer reactions of borylene complexes.

The discovery of Sabo-Etienne and co-workers has the potential to make a significant impact in many areas of chemical research. Herein, transition-metal chemists will see a boron analogue of the archetypal family of Grubbs metathesis catalysts. From the perspective of hydrogen storage, this system represents a mild, reversible dihydrogen activating system. Regarding boron chemistry, an interesting new route to elusive borylene complexes has been developed, demonstrated in this case by the first neutral, terminal group eight borylene complex. In short, the reaction is a fascinating discovery, which impacts upon many subdisciplines of chemistry. One can eagerly await further work on determining the scope of the reaction, in terms of variation of the borane substituent and/or metal centre, in addition to reactivity studies of the new borylene complex.

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