Bis σ-Bond Dihydrogen and Borane Ruthenium Complexes: Bonding Nature, Catalytic Applications, and Reversible Hydrogen Release

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CONSPECTUS

Hydrogen, the simplest element in the periodic table, plays a tremendous role in organic and inorganic chemistry. For years, it was inconceivable that dihydrogen could be bound to a metal center without breaking the H—H bond. Thus, oxidative addition of H_2 was universally recognized as a key elementary step in hydrogenation processes. In 1984, Kubas and co-workers reported the first example of a complex in which dihydrogen was coordinated to a metal center without breaking of the H—H bond. This opened a new area in coordination chemistry: σ-complexes were born, complementing the well-known Werner-type family of complexes. Since then, hundreds of stable dihydrogen complexes have been isolated, and their properties have been investigated in detail. By comparison, very little information is available for the analogous class of σ-borane complexes, in which σ-H—B bonds are complexed to a metal (in the manner of H—H bonds in σ-dihydrogen complexes). Since the first example published in 1996 by Hartwig and co-workers, very few σ-borane complexes have been isolated.

Scientists have maintained a continuous interest in catalytic hydrogenation reactions. Almost a century ago, in 1912, Paul Sabatier, the father of the hydrogenation process, received the Nobel prize, and the selection of Noyori and Knowles in 2001 for their studies on enantioselective catalyzed hydrogenations amply demonstrates the ongoing importance of the field. Moreover, during the past decade, dihydrogen has attracted considerable attention as a possible "fuel of the future". This endeavor has furthered interest in σ-borane complexes, as more and more evidence links their chemistry to that of amine—borane derivatives. Indeed, ammonia—borane (NH_3BH_3) is attracting significant interest for hydrogen storage applications. One of the main limitations is the lack of reversibility associated with the production of dehydrogenated $(BNH)_x$ materials. Of major importance will be a better understanding of the coordination of H_2 to a metal center, and more generally of the coordination of H—E bonds (E = B, C), which are likely to play a critical role in the reversible dehydrogenation process.

In this Account, we review our recent results in the field of dihydrogen and borane activation, with a specific focus on the problem of reversible dehydrogenation pathways. We concentrate on the chemistry of ruthenium complexes incorporating two σ-ligands: either two dihydrogen or two σ-B—H bonds. We describe our synthetic strategies to prepare such unusual structures. Their characterization is discussed in detail, highlighting the importance of an experimental and theoretical approach (NMR, structural, and theoretical studies). Some catalytic applications are discussed and put into context, and their reactivity toward reversible hydrogen release is detailed.
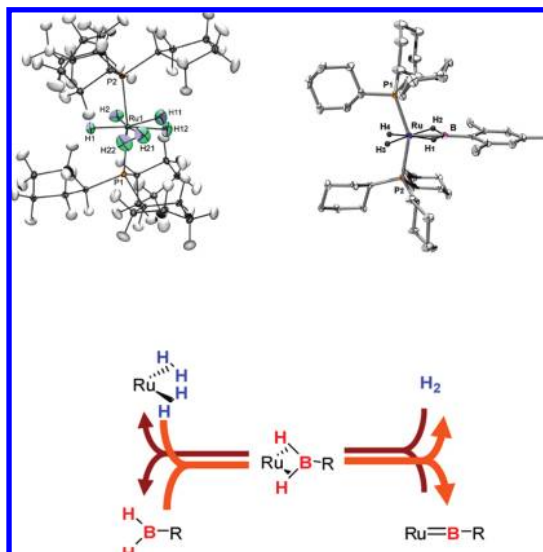
Introduction and Background

Dihydrogen coordination to a metal center was first established in 1984. Subsequently, hundreds of stable dihydrogen complexes have been isolated, and much knowledge has been gained regarding their properties.[1] G. Kubas has recently published a review article that clearly summarizes the area and highlights the dihydrogen coordination chemistry in the context of hydrogen storage.[2]

Hydrogen as a fuel can be stored in gas, liquid, or solid form, each of which offers its own advantages and disadvantages. Probably the most promising approach is the solid form. However, we are still far from a viable solution.[3] Key points will be to control the reversible hydrogen filling of the material and to find new metal hydrides, since there are no hydrogen storage materials that meet all the required criteria. There is thus a need to discover new systems and to understand the dehydrogenation/hydrogenation pathways, with the aim to progress on hydrogen storage capacity and reversibility, two important hurdles. It is noteworthy that ammonia—borane (NH_3BH_3) is attracting significant interest for hydrogen storage applications.[4] One of the main limitations in using such a compound is that it cannot be regenerated from the produced dehydrogenated BNH_x materials.[5] Transition metal catalyzed dehydrogenation has only been recently addressed, and Manners et al. have prepared the first soluble polyaminoborane materials, by using an iridium pincer complex known to be an effective catalyst for alkane dehydrogenation. The groups of Heinekey and Goldberg were the first to take profit from the established properties of these pincer complexes and used a dihydride to catalyze hydrogen release from H_3NBH_3 at unprecedented rates.[6] In 2007, Baker et al. reported the first example of a nickel system and postulated the intermediary of a σ-complex.[7] The most recent examples come from the group of Weller for rhodium[8] and from Fagnou for ruthenium.[9]

By comparison to σ-dihydrogen complexes, very little information is available for the analogous class of σ-borane complexes which are now connected to the chemistry of amine—borane derivatives. Since the first example published in 1996 by Hartwig et al.,[10] very few complexes have been isolated,[11−14] and most of the examples come from the group of Hartwig and our group.

In this Account, we summarize the progress that we have made in the design of a unique class of complexes incorporating two σ-H—H or two σ-H—B bonds (Chart 1), with a specific focus on the problem of reversible dehydrogenation pathways.

CHART 1
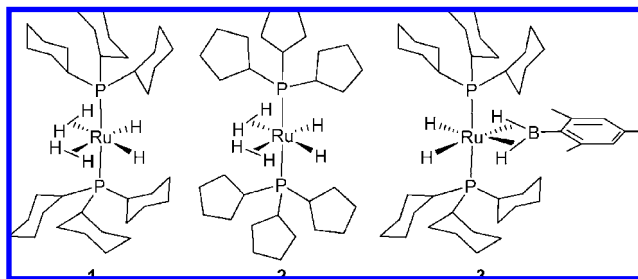
Bonding Nature and Characterization

The σ-coordination is reminiscent of the Chatt—Dewar—Duncanson model for olefin coordination. In the case of dihydrogen coordination, the bonding picture is rather simple as illustrated in Figure 1. Dihydrogen coordination is dependent on the nature of the ligands around the metal and on the metal itself. Indeed, a subtle balance has to be found between σ-donation from the σ-orbital of the H_2 ligand to an empty d orbital of the metal and back-donation from the metal to the antibonding σ* orbital of the H_2 ligand. There are now examples of dihydrogen complexes for almost all the transition metals of the periodic table and for all kind of ligands, but the preferred systems involve octahedral low-valent d^6 metals and carbonyl or basic phosphine ligands.[1] The bis(dihydrogen) ruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) occupies a special position in this area due to the presence of two dihydrogen ligands (Chart 1).[15,16] Complex **1** is a perfect illustration of an ideal balance between σ-donation and back-donation with two unstretched dihydrogen ligands that proved to be very labile. A versatile reactivity, dominated by substitution reactions and catalytic activity, has derived from the use of this complex,[15,17−20] but we will concentrate on the most recent developments.

In the case of borane coordination, the situation is much more complex than for dihydrogen coordination, which might explain the scarcity of isolated "true" σ-complexes. Prior to our most recent work, the σ-borane compounds were obtained from the reaction of metal precursors with conventional disubstituted borane reagents R_2BH (R_2 = pinacol, catechol, dialkyl).[11] By comparison to the dihydrogen ligand, the σ-borane ligand is dissymmetric and the boron bears substituents
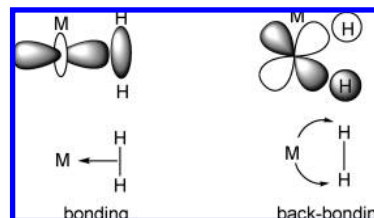

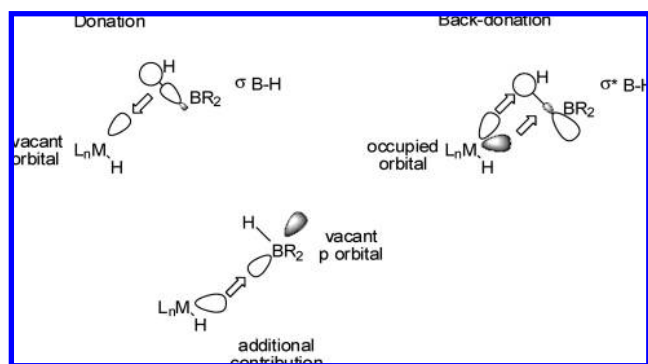**FIGURE 1.** Bonding scheme for dihydrogen coordination.

FIGURE 2. Bonding schemes for borane coordination.

that, depending on their steric and electronic properties, might play a role in tuning the coordination and the Lewis acidity of the borane. Even more importantly, the boron has a vacant p orbital that plays a dramatic role in this area and represents an additional contribution to the classical Chatt–Dewar–Duncanson model (Figure 2). It is important to emphasize that until our most recent work (see below), one would refer to a σ-ligand as a group displaying a three-center two-electron bond with no other intramolecular binding to the metal center. The three-center two-electron bond is formed without strongly altering the integrity of the ligand apart from a B–H elongation. For ligands involving intramolecular binding, the term of agostic bond should be used.[21]

When back-donation becomes too important, the σ-bond can be broken leading to the product of oxidative addition.

Again in borane chemistry, the situation can be more complex and the formation of dihydroborates (a well-known family of boron-containing compounds) can be competitive, in particular when working with polyhydrides (Scheme 1).[10,11,22] In 2002, we were able to isolate the first complex incorporating two borane ligands coordinated to the metal with two different modes: σ-coordination and dihydroborate ligation.[23] The intermediate situation exhibiting a σ-coordination with an additional lateral M−H···B interaction has also been evidenced, in the case of ruthenium with pinacol and catecholborane (Figure 3).[24]

Since the first paper by Kubas in 1984, much effort has been devoted to improving the methods of characterization to ascertain a σ-coordination mode.[1] Three main techniques can be used: structural characterization by X-ray or neutron, spectroscopic measurements mainly by NMR (IR can in some cases be very helpful), and theoretical studies, mainly through DFT calculations. Each one displays some disadvantages and a combination of all of them remains the best way to support a σ-coordination. As we have recently published a review on the interest of NMR as a tool for the characterization of σ-silane and σ-borane complexes,[11] we will only summarize a few key findings. Neutron diffraction remains the method of choice for the location of hydrogen atoms involved in a σ-coordination, but such a technique requires access to a limited number of instruments world-wide, as well as large crystals, despite the
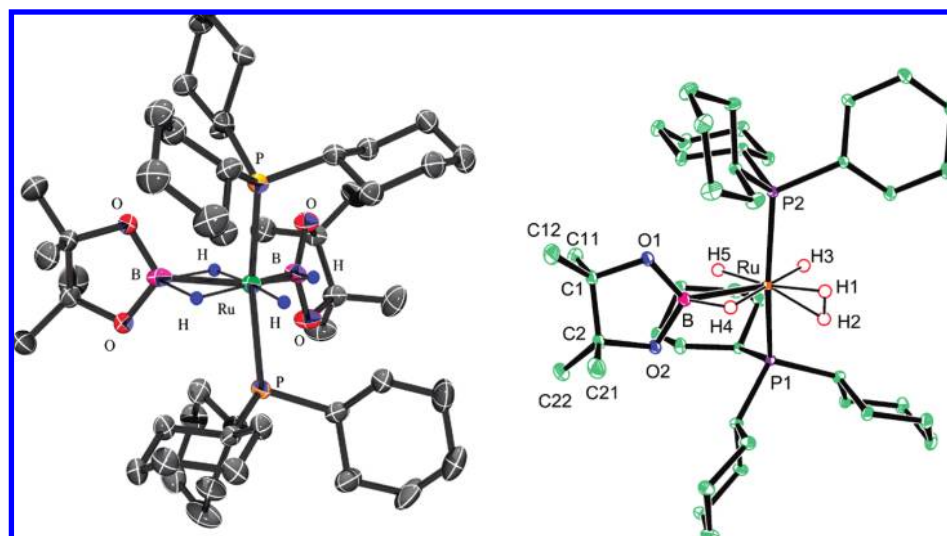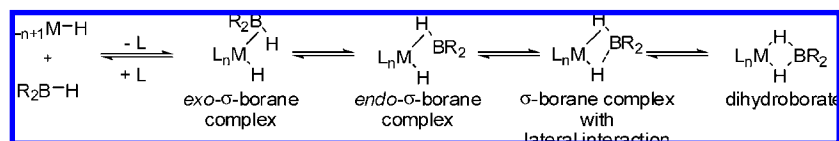

FIGURE 3. X-ray structures of a σ-borane(dihydroborate) and a σ-borane(σ-dihydrogen) complex.

SCHEME 1

recent progress. Location of hydrogen atoms by X-ray diffraction is still a subject of debate, despite once again the improvement observed in the recent years. It is indeed very helpful to support X-ray hydrogen location by DFT calculations. The development of the chemistry of dihydrogen complexes was greatly due to the extensive use of NMR and particularly of T_1 measurements and deuterium labeling. These two methods allow a good determination of the H−H distance. In borane chemistry, we can benefit from additional information gained by ^{11}B NMR measurements, despite a quadrupolar boron nucleus, which leads to broad signals and thus renders the measurements of J_{BH} coupling constant values quite challenging.

Synthetic Strategies

We have deliberately focused our Account on complexes incorporating two σ-ligands, with the general formulation RuHX(H−E)$_n$(PR$_3$)$_2$ (with X = H, Cl; E = H, n = 2; E = BHR, n =1). As a σ-ligand is known to be very labile and subject to substitution reactions, it is possible to have access to a very active 14-electron fragment "RuH$_2$(PR$_3$)$_2$". The origin of this interest goes back to the early 1980s when B. Chaudret et al. isolated the so-called RuH$_6$(PCy$_3$)$_2$ that was reformulated in 1988 as RuH$_2$(H$_2$)$_2$(PCy$_3$)$_2$ (**1**), the first stable bis(dihydrogen) complex.[25] Since that time, very few bis(dihydrogen) complexes have been isolated,[26−29] and the chemistry deriving from **1** has led to tremendous development both in coordination chemistry and in catalysis. Based on such a fascinating reactivity the search for other bis σ-complexes was undertaken, and in 1997, the first bis σ-silane complex RuH$_2${(η^2-HSiMe$_2$)$_2$X}(PCy$_3$)$_2$ was isolated.[30] In borane chemistry, by using rather classical borane reagents (pinacolborane or catecholborane), we were able to isolate in 2002 the first complex incorporating two borane ligands coordinated to the metal with two different modes.[23] With these results in mind, we wanted to address two issues: the search for new bis(dihydrogen) complexes and the use of unconventional borane reagents to favor unusual coordination modes.

Synthesis of New Bis(dihydrogen) Complexes. The first issue resulted from a side reaction we observed when using **1** as a catalyst precursor. Partial dehydrogenation of the cyclohexyl rings of the tricyclohexylphosphine (PCy$_3$) in **1** could be established upon exposure to an alkene.[31] In some cases, such a reaction could be seen as an advantage: the phosphine becomes bidentate and coordinates to the metal through the phosphorus and either a C=C bond or an allylic fragment.

Thus, stabilization was gained and decoordination of the phosphine was avoided as is often the case in many catalytic cycles.

The unique properties of **1** come from the presence of two bulky and basic phosphines that allow a subtle balance between σ-donation and back-donation: the dihydrogen ligands are moderately strongly bound to the ruthenium but are still very labile to ensure a versatile reactivity. We reasoned that the use of a smaller cycloalkyl ring could prevent the dehydrogenation pathway without destabilizing too much the overall structure. Our first attempt to prepare a new bis(dihydrogen) complex by using the tricyclopentylphosphine (PCyp$_3$) was very successful. As for the synthesis of **1**, we started from the zero-valent precursor Ru(COD)(COT) in the presence of 2 equiv of PCyp$_3$ under 3 bar of H$_2$, and we could isolate the corresponding complex RuH$_2$(H$_2$)$_2$(PCyp$_3$)$_2$ (**2**) in very good yield (Chart 1).[32] Complex **2** was fully characterized, including by neutron diffraction. All the hydrogen atoms around the ruthenium were well located, and the H−H distances of 0.825(8) and 0.835(8) Å confirm that the two dihydrogen ligands are unstretched. We will see in the next section that if our first goal to avoid dehydrogenation of the cycloalkyl rings was not fulfilled, the chemistry deriving from this compound is indeed blooming.

Use of Unconventional Borane Reagents. The group of Hartwig was a pioneer in using tricoordinated boron reagents to favor the stabilization of σ-borane complexes. He isolated a series of titanium, niobium, manganese, and rhenium complexes by using conventional HBR$_2$ reagents (pinacolborane, substituted catecholboranes, or dialkylboranes).[10] In our group, ruthenium is our favorite metal for the synthesis of σ-complexes. We successfully prepared a series of σ-borane ruthenium complexes with pinacolborane and catecholborane and showed them to be active catalyst precursors in hydroboration and dehydrogenative borylation of alkenes.[20,23,24] Interestingly, during the same period, G. Alcaraz et al. had demonstrated interest in dialkylaminoboranes R$_2$NBH$_2$ in pallado-catalyzed reactions.[33] By comparison, it is worth noting that in silane chemistry, the use of dihydrogenosilanes R$_2$SiH$_2$ in place of tertiary hydrogenosilanes HSiR$_3$ led us to the discovery of Ru$_2$H$_4$(μ-η^2:η^2:η^2:η^2-SiH$_4$)(PCy$_3$)$_4$, the first complex incorporating the simplest silane trapped between two metals.[34] The stabilization occurred through multiple σ-Si−H bond interactions. We thus decided to build a new area based on the rational design of dihydrogenoborane reagents and to investigate their coordination to polyhydride precursors.

The reaction of a stoichiometric amount of mesitylborane with RuH$_2$(η^2-H$_2$)$_2$(PCy$_3$)$_2$ or lithium mesitylborohydride with
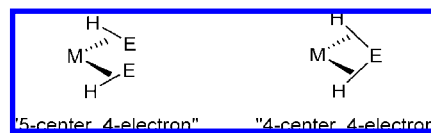
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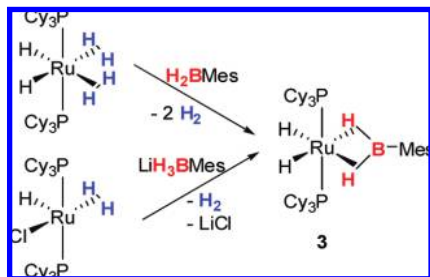
**TABLE 1.** NMR Data for the Bis(σ-borane) and the Borylene Complexes

Selected NMR data	^{31}P NMR (δ)	^{11}B NMR (δ)	^{1}H NMR (δ)
Cy₃P, H,,Ru≡B-Mes, Cl, Cy₃P	50.75 (C₆D₆)	106 (C₆D₆)	-14.88 (t, 1H, $^2J_{PH}$=18.1 Hz)
Cy₃P, H,, Hₐ, Cl-Ru-B-Mes, Hb, Cy₃P	59.1 (C₆D₆)	72.6 (C₆D₆)	-15.96 (m, 1H, RuHₐB)
			-7.27 (m, 1H, RuH)
			0.83 (m, 1H, RuHbB)
Cy₃P, H,, H, H-Ru-B-Mes, H, Cy₃P	83.78 (C₇D₈)	58 (C₇D₈)	-11.05 (t, 2H, $^2J_{PH}$=25.2 Hz RuH)
			-5.90 (br, 2H, RuHB)
Cy₃P, H,, H, H-Ru-B-tBu, H, Cy₃P	84.03 (C₆D₆)	69 (C₆D₆)	-10.99 (t, 2H, $^2J_{PH}$=27.0 Hz RuH)
			-6.48 (br, 2H, RuHB)

RuHCl(η^2-H$_2$)(PCy$_3$)$_2$ proceeds with dihydrogen evolution and leads to the isolation in high yield of RuH$_2$(η^2:η^2-H$_2$BMes)(PCy$_3$)$_2$ (**3**), the first metal−borane complex, with one borane bound to the metal center through two geminal σ-B−H bonds (Scheme 2).[35]

Complex **3** was fully characterized by NMR and X-ray diffraction crystallography. The ^{1}H NMR pattern in the hydride zone can serve as a signature of such a formulation. A broad singlet and a triplet in a 1:1 integration ratio at δ −5.90 and δ −11.05 are assigned to the B−H and the Ru−H hydrogen atoms, respectively (Table 1). The broad singlet sharpened upon boron decoupling, whereas the triplet collapsed into a sharp singlet upon phosphorus decoupling. The X-ray structure determined at 110 K displays a ruthenium atom in a pseudo-octahedral environment with the phosphines in axial positions and four coplanar *mer*-hydrogen atoms. The Ru−B distance of 1.938(4) Å is extremely short (2.09 Å for the sum of the covalent radii) suggesting an interaction between the metal and the boron atom. The DFT/B3PW91 optimized geometry of this complex supports the location of the hydrogen atoms around the ruthenium, indicative of a borane adduct to a Ru^{II} dihydrido fragment. By comparison to the

FIGURE 4. Coordination modes of two σ-ligands on a metal center.

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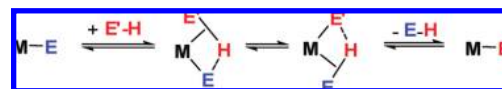
computed free mesitylborane, the increase of both B−H and B−C bond distances was interpreted as the result of a synergetic transfer of electron density from σ-B−H to Ru and from Ru into the p orbital on B. The metal−borane interaction was also rationalized by NBO analysis. Upon coordination, a significant increase of population in the p orbital at boron (0.51e) was computed (0.15e in free mesitylborane).

A similar coordination mode of mesitylborane to ruthenium has been recently reported by Stradiotto et al.[13] The cationic complex [Cp*Ru(^{i}Pr$_3$P)(η^2:η^2-H$_2$BMes)][B(C$_6$F$_5$)$_4$] was synthesized by chloride abstraction from Cp*Ru[(μ-H$_2$)BMesCl](P^{i}Pr$_3$) with LiB(C$_6$F$_5$)$_4$.

As a result of two geminal σ-B−H bonds on the same boron atom, RuH$_2$(η^2:η^2H$_2$BMes)(PCy$_3$)$_2$ is the first complex displaying an interaction that could be qualified as a "four-center, four-electron bond" instead of a "five-center, four-electron bond", normally found for a metal bonded to two σ-ligands (Figure 4). The reaction is not limited to mesityl borane since we have now shown that the analogous complex RuH$_2$(η^2:η^2-H$_2$B^{t}Bu)(PCy$_3$)$_2$, incorporating a B-alkyl substituent can be isolated.[36] As we will see in the final section, a recent extension of this chemistry, utilizing the chloro complex RuHCl(η^2-H$_2$)(PCy$_3$)$_2$, allowed us to find a facile entry to the formation of the first borylene ruthenium complex.[37]

Catalytic Applications

One of the main applications of dihydrogen complexes is obviously their use as catalyst precursors in hydrogenation of unsaturated compounds. Alternatively, they can just play a role as intermediates in two key steps of the catalysis, oxidative addition and the microscopic reverse reductive elimination. In 2007, Perutz and Sabo-Etienne rationalized the role of σ-complexes of late transition metals in catalysis by the establishment of the σ-CAM concept (σ-complex assisted metathesis).[38] σ-H−E complexes are highly dynamic structures that favor the formation of secondary interactions between the H−E bond and a neighboring atom E′ (Scheme 3). The main difference with the two other well-known mechanisms, oxidative addition/reductive elimination and σ-bond metathesis, is

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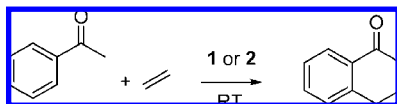
the existence of at least two isomeric observable σ-complexes. Functionalization of a substrate can thus be performed by keeping, throughout the catalytic cycle, all the intermediates at constant oxidation state. Evidence is found for hydrogen, borane, silane, and alkane activation proceeding catalytically through the σ-CAM route.

When dealing with bis σ-complexes, we expect to have access to very reactive species. Indeed, three patents from DuPont were published in 1996 on the use of **1** and related ruthenium compounds as hydrogenation catalysts, especially for the hydrogenation of nitriles and dinitriles (most preferred pressures and temperatures, 50−70 bar and 80−100 °C). We are currently revisiting this reaction and found a dramatic effect when using **1** or **2** as catalyst precursors. For example, only 5% of benzonitrile is reduced to benzylamine with **1** versus 95% with **2** after 2 h at room temperature and under 3 bar of H_2. Work is currently in progress to extend the scope of this reaction and characterize the intermediates.

The difference in activity between **1** and **2** is also highlighted by their behavior toward H/D exchange. For example, monitoring a C_6D_6 solution of **2** by NMR shows deuterium incorporation into the hydride signal within 5 min, whereas 24 h are needed in the case of **1**. Such an activity supports a more facile C−H bond activation process in **2**. This is also illustrated in the Murai reaction for which C−C coupling of alkenes with functionalized arenes is achieved via C−H activation. In 1998, we disclosed that **1** was remarkably active for this reaction *at room temperature*. We were able to identify not only the active product, an orthometalated complex, but also the product of deactivation, a bis(cyclometalated) species.[39] The difference between **1** and **2** is spectacular: **1** converts 20% of acetophenone within 35 min whereas 90% conversion is achieved with **2** under the same catalytic conditions (Scheme 4).[32]

Reversible Hydrogen Release

From the Bis(dihydrogen) Complexes. Polyhydrides are interesting species to study reversible dihydrogen release processes, a key point in the general problem of hydrogen storage. In this context, complexes **1** and **2** deserve specific attention. If in solution, the hydrides and the dihydrogen ligands are in fast exchange, extensive knowledge has been gained regarding the coordination modes of the hydrogen

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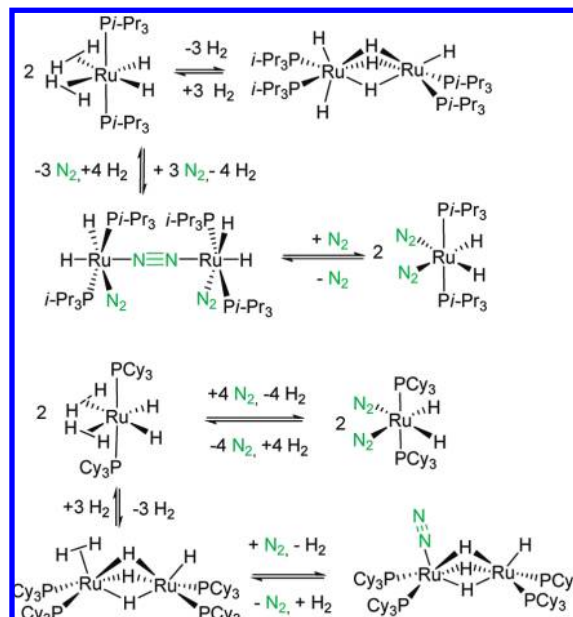
atoms around the coordination sphere of the metal in the solid state. The most recent achievements are the solid-state NMR data for **1**[40] and the neutron structure for **2**.[32] With six hydrogen atoms around the ruthenium, one can expect evolution of 3 equiv of dihydrogen, but we have shown that the phosphine ligands are also a potential source of dihydrogen evolution through C−H activation.

The bis(dihydrogen) $RuH_2(\eta^2-H_2)_2(PR_3)_2$ (R = ^{i}Pr, Cy) can easily lose dihydrogen to give the corresponding dimers of general formulation $Ru_2H_6(PR_3)_4$ and formal loss of three hydrogen atoms per ruthenium (Scheme 5). The dehydrogenation process can occur in the solid state under vacuum or in solution under irradiation or upon heating. In the case of PCy_3, the compound was formulated by Chaudret et al. as a dihydrogen complex $Ru_2H_4(H_2)(PCy_3)_4$ on the basis of T_1 NMR data and reactivity with N_2.[25] A dihydrogen formulation was also proposed for the PPh_3 compound. In contrast, when using P^iPr_3, Morris ruled out the presence of any dihydrogen ligand on the basis of NMR, X-ray diffraction, and the absence of reaction with N_2.[27] A dimer was also obtained by direct hydrogenation of $Ru(COD)(bis$ methylallyl$)_2$ in the presence of chelating phosphines. In the case of $Cy_2P(CH_2)_3PCy_2$, the X-ray structure of the corresponding dimeric complex and T_1 measurements favor a dihydrogen formulation, which is supported by the reaction with N_2.[29] We are currently studying the dehydrogenation process of **2** in the solid state and found that in contrast to **1**, the resulting dinuclear complex displays a classical formulation on the basis of NMR, DFT, and X-ray data. More importantly, the formulation is supported by a neutron

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SCHEME 7
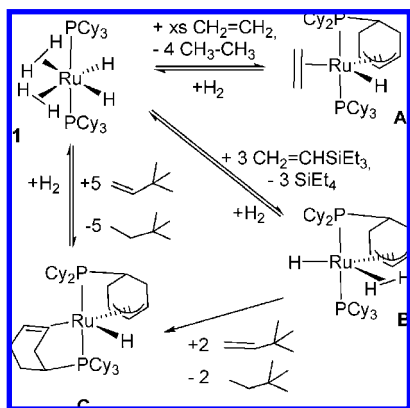
structure. Full details will be published in due course. All these reactions show the importance of the phosphine substituents in controlling the formation of a dihydrogen ligand. Not only are electronic properties important, but also conformational factors play a crucial role in this chemistry. Remarkably, irrespective of the nature of the monophosphine substituents, all the dinuclear compounds react with dihydrogen to regenerate the monomeric $RuH_2(\eta^2\text{-}H_2)_2(PR_3)_2$ complexes.

All the isolated bis(dihydrogen) $RuH_2(\eta^2\text{-}H_2)_2(PR_3)_2$ complexes incorporate basic alkyl phosphines. The saturated alkyl groups are a potential source of hydrogen via C−H bond breaking induced by the metal center.[41] This hydrogen release requires the presence of a hydrogen abstractor such as an alkene. The C−H bond activation and thus the number of hydrogen released can be controlled by the alkene/complex stoichiometric ratio. Indeed, step by step dehydrogenation of **1** leads to the synthesis of three new complexes, **A**, **B**, or **C**, after partial dehydrogenation of one or two cyclohexyl rings (Scheme 6). Complexes **A**−**C** correspond to the formal loss of 3−5 equiv of dihydrogen. Complex **C**, which can be obtained from **1** or **B** depending on the stoichiometric ratio, presents two types of partially dehydrogenated phosphines: an η^3-allyl and a cyclohexenyl fragment, both coordinated to ruthenium. This hydrogen release is fully reversible when **A**−**C** are exposed under H_2, **1** being quantitatively restored. Complex **C** is particularly more stable than **1**, which gives an opportunity to use it as a convenient stable reservoir compound to generate **1** in solution under H_2.

With respect to catalytic applications, the presence of these bifunctional phosphines could be an advantage to avoid any phosphine decoordination, but one drawback is to face two competitive catalytic pathways: one running with a $Ru(PCy_3)_2$ fragment and another one involving a $Ru(PCy_3)P'$ fragment, P' being a partially dehydrogenated phosphine. In order to prevent such a dehydrogenation process, we reasoned that the
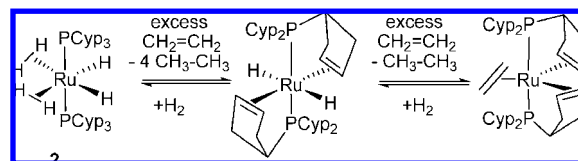
use of a shorter cycloalkyl ring could be a good compromise. This turned out not to be the case because the cyclopentyl fragments can also give rise to C−H bond activation. Exposure of $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ (**2**) to an ethylene atmosphere leads in a first step to the formation of an unusual *trans* dihydride complex with two cyclopentenyl fragments coordinated to the ruthenium (Scheme 7).[42] It is worth noting that C−H activation of such a phosphine was also reported by Weller et al. for rhodium complexes.[43]

The *trans* dihydride complex results from the loss of two H_2 coordinated ligands of **2** and the release of 2 equiv more of H_2 through the activation of four C−H bonds of the cyclopentyl fragments. Upon a longer exposure under ethylene, a ruthenium(0) ethylene complex could be isolated. Available ruthenium(0) precursors are rather rare, and one can expect a versatile chemistry.[44] This contrasts with the results obtained from **1**, which, upon ethylene pressure, led to the formation of the ruthenium(II) complex **A**. Overall, the dehydrogenation process corresponds to a formal loss of 10 hydrogen atoms. Here again, the process is fully reversible: **2** is restored upon exposure to H_2.

Access to a Ruthenium Borylene Complex. Compared with the reaction of mesitylborane with **1**, which led straightforwardly to the symmetrical bis(σ-borane) **3**, its reaction with $RuHCl(\eta^2\text{-}H_2)(PCy_3)_2$ turned out to be much more complex. Loss of dihydrogen was also observed, but monitoring the solution by ^{31}P NMR spectroscopy showed the formation of two new compounds (ca. 1:1 ratio), which were later identified as the unsymmetrical bis(σ-borane) complex $RuHCl(\eta^2:\eta^2\text{-}H_2BMes)(PCy_3)_2$ (**5**) and the mesityl borylene complex $RuHCl(BMes)(PCy_3)_2$ (**6**). The borylene complex **6** could be simply isolated in high yield by pumping under vacuum the initial mixture (Scheme 8).

Complexes **5** and **6** have been fully characterized by multinuclear NMR spectroscopy (Table 1) and by X-ray crystallography at 110 K in the case of the borylene complex. The ^{11}B data illustrate the modification of the metal−boron ligation. The ^{11}B NMR spectrum of **6** exhibits a strongly deshielded broad signal at δ 106, compared with the resonances of the symmetrical (δ 58) and unsymmetrical (δ 72.6) bis(σ-borane) complexes **3** and **5**, respectively.

SCHEME 8
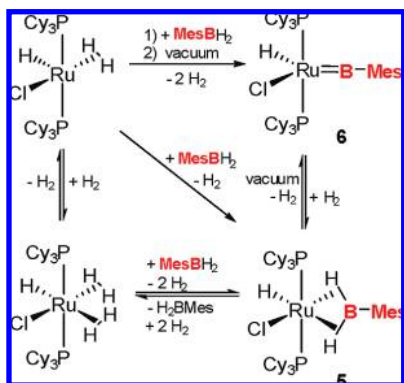
The X-ray structure shows an extremely short Ru—B distance of 1.780(4) Å, in agreement with a borylene formulation. In the absence of hydride location, support was gained by optimization of the structure by DFT/B3PW91 calculations (Ru—B = 1.793 Å), which showed no direct contact between the hydride and the boron. NBO analysis confirms the description of **6** as a true borylene complex. The borylene acts as a neutral ligand similarly to CO.

Remarkably, at room temperature and upon pressurization with dihydrogen (3 bar), a C_6D_6 solution of **6** was fully converted into a mixture of **5** and the bis(dihydrogen) complex $RuHCl(\eta^2\text{-}H_2)_2(PCy_3)_2$ (Scheme 8). Several cycles (H_2 pressurization in solution/vacuum pumping) could be repeated leading back to the starting borylene complex **6**. We have here a reversible borane/dihydrogen exchange process, simply driven by using vacuum or dihydrogen pressurization, which can be repeated several times from **6** without altering the course of the reaction. In this room-temperature reaction, reversible dihydrogen activation is assisted by boron-containing ligands (borane or borylene) but is strongly dependent on electronic effects at ruthenium. Indeed, the chloride ligand plays a key role since no reaction took place for the symmetrical bis σ-borane complex $RuH_2(\eta^2:\eta^2\text{-}H_2BMes)(PCy_3)_2$ in similar conditions: **3** is stable under vacuum and under 3 bar of H_2. Our system represents an original pathway to synthesize borylene species with respect to the routes extensively developed by Braunschweig.[45,46] The facile reversible dihydrogen activation makes this system unique.

Summary and Prospects

This Account summarizes ongoing efforts in exploring the properties of complexes incorporating two η^2-H-E ligands (E = H, B). Three main lines have been developed: the search for new bis σ-complexes, their use in catalytic reactions, and their properties toward reversible hydrogen release. The new bis-(dihydrogen) complex $RuH_2(H_2)_2(PCyp_3)_2$ incorporating two tri-

cyclopentylphosphines can reversibly remove under mild conditions up to ten hydrogen atoms. This represents 1.71% weight of the complex, which is of course far from the 9 wt % DOE target for 2015 for the development of a competitive hydrogen storage process. It is now important to study the properties displayed by this new class of tricyclopentylphosphine complexes and of related species and benefit from systems based on the storage of hydrogen atoms not only as hydrides or dihydrogen ligands but also within phosphines, which cannot be considered as "innocent or spectator" ligands. The rather weak interaction of dihydrogen with a metal center represents a key step to achieve a fast and controlled dihydrogen uptake. Polyhydride species could serve as a catalyst both to store and to release H_2, and ideally, their association with a high wt % hydrogen system, such as light metal hydrides, could allow the design of a multimaterial based tank and lead to significant improvements.

It is remarkable that by simply removing one CH_2 group within the cycloalkyl ring of the phosphine, thus using **2** instead of **1** as catalyst precursor, a tremendous improvement is obtained in the hydrogenation of nitriles or in C—C coupling. We have now launched a program to better understand the role of any modification within the trialkylphosphine ligand by synthesizing a whole series of new bis(dihydrogen) complexes and studying the correlation of structure and catalytic activity.

The bis(dihydrogen) complex **1** has shown over the years a versatile chemistry dominated by substitution reactions. By reacting it with a dihydrogenoborane, we have been able to disclose a new borane coordination mode with geminal σ-BH bonds. We are now dealing with a system in which only four atoms are involved in order to create two σ bonds instead of a "classical model" of five centers for two independent σ-bonds. Remarkably, this led us to find a new entry to prepare a borylene complex and even more importantly to show that reversible dihydrogen release can be performed from the borylene complex through the intermediate formation of a bis(σ-borane) species. Complex **6**, obtained via an original synthetic pathway, displays a reactivity toward dihydrogen that has no precedent in borylene chemistry. We can expect a large variety of applications by analogy to the chemistry deriving from the analogous Grubbs carbene complex.

Further work is in progress in our group dealing with the chemistry of complexes incorporating two σ-ligands, particularly η^2-dihydrogen and η^2-borane ligands because they appear to be interesting targets for the design of innovative materials. We anticipate that the chemistry of σ-complexes

should continue to surprise and challenge us both at the fundamental level and for a wide variety of applications.

BIOGRAPHICAL INFORMATION

Gilles Alcaraz obtained his Ph.D. from the University of Toulouse with Guy Bertrand, and after a postdoctoral fellowship at ETH in Zürich with Hansjörg Grützmacher, he joined the CNRS in Rennes in 1997 to work in the Vaultier group until 2005. He then moved to the LCC in Toulouse, and his research in Sylviane Sabo-Etienne's group is focused on organometallic borane chemistry.

Mary Grellier received his Ph.D. in 1996 from the University of Strasbourg with Michel Pfeffer. He obtained a "Professeur Agrégé" position in Strasbourg in 1995. In 2000, he was promoted to "Maître de Conférences" at the University of Toulouse. His research at the LCC mainly concerns coordination and catalysis in organometallic chemistry.

Sylviane Sabo-Etienne received her "Doctorat d'Etat" from the University of Toulouse. In 1985, she moved to the University of Brest, to work as "Chargée de Recherche CNRS" in Hervé des Abbayes group. After a year as a NSF-CNRS research associate with Maurice Brookhart (USA), she returned to Toulouse to work in collaboration with Bruno Chaudret on polyhydride chemistry. She was promoted to "Directrice de Recherche" in 1997. She is currently Group Leader at the LCC, and her research interests include organometallic chemistry and catalysis.

FOOTNOTES

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