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PAPER

Phosphidoboratabenzene-Rhodium(I) complexes as precatalysts for the hydrogenation of alkenes at room temperature and atmospheric pressure

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The di-*tert*-butylphosphido-boratabenzene ligand (DTBB) reacts with $[(C_2H_4)_2RhCl]_2$ yielding the dimeric species $[(C_2H_4)Rh(DTBB)]_2$ (**1**). This species was fully characterized by multinuclear NMR and X-ray crystallography. Complex **1** readily dissociates ethylene in solution and upon exposure to 1 atm of H_2 is capable of carrying out the hydrogenation of ethylene. The characterization of two Rh-H species by multinuclear NMR spectroscopy is provided. The reactivity of **1** towards the catalytic hydrogenation of alkenes and alkynes at room temperature and 1 atm of H_2 is reported and compared to the activity of Wilkinson's catalyst under the same reaction conditions.

Introduction

Since the first report of a boratabenzene complex by Herberich,[1] this heterocyclic moiety has been coordinated to most transition metals, either as a neutral borabenzene[2] or an anionic boratabenzene ligand (Fig. 1, **I** and **II**).[3] Borabenzene derivatives and their metal complexes have been shown to be active in the polymerization of alkenes,[4] the cyclotrimerization of alkynes and nitriles,[5] E-H bond activation,[6] acting as a chirality source[7] and generating interesting optoelectronic materials.[8]

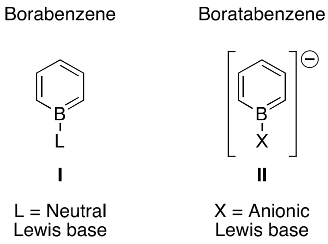

Fig. 1 Neutral and anionic boron heterocycles.[2,3]

The boratabenzene framework is an isoelectronic analogue of the cyclopentadienyl ligand and as such, interacts with transition metals by its π system and usually adopts a η^6-coordination mode.[9] Ring slippage to the η^5-coordination where the boron is away for the metal centre is however frequent, especially when facilitated by π-donating[10] or bulky substituents on boron.[11] Other types of hapticities are more scarce and include η^3-allylic-like coordination[12] and η^1-coordination where the substituent on boron interacts with the transition metal. Two different boratabenzene moieties have been shown to exhibit the latter coordination mode, including species **III** (Fig. 2) having a unique Pt-Cl-B interaction.[13a] Upon addition of a Lewis base, the Cl-boratabenzene anion can dissociate and undergo ligand exchange[13b] or coordinate to other transition metals.[13c] This atypical coordination mode is also observed for the diphenylphosphido-boratabenzene, first reported by Fu,[14] an anionic analogue of the ubiquitous PPh_3, where the lone pair on phosphorous remains available for σ-donation, as observed in Rh complex **IV** (Fig. 2).

Our group reported in 2012 the synthesis of di-*tert*-butylphosphido-boratabenzene (DTBB), a ligand designed to act as a bulky and anionic phosphine. It was shown that the DTBB fragment does not coordinate in a purely η^1-mode on electronically unsaturated metal centres. Instead, in addition to the phosphine binding one metal, it was possible to coordinate the DTBB ligand by the aromatic ring in a η^6-fashion on another nickel centre in species **VI**. DTBB also coordinated in a η^3 allylic-like mode, through a P-B-C interaction with Pt(II) (**V**).[12b] It is precisely the hemilability of the DTBB and its donor capability as a bulky phosphine that makes it an attractive framework for catalytic applications.[15] Herein we report the synthesis and characterization of a rhodium di-*tert*-butylphosphidoboratabenzene complex and its catalytic activity towards alkene hydrogenation at room temperature and atmospheric pressure.

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† Electronic Supplementary Information (ESI) available: [Multinuclear NMR characterization for complex **1** and hydride species **2** and **3**, 2D NMR and crystallographic data for **1**]. See DOI: 10.1039/x0xx00000x. The Crystallographic data for **1** have also been deposited with the CCDC (CCDC No. 1415613). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., by e-mail at deposit@ ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.

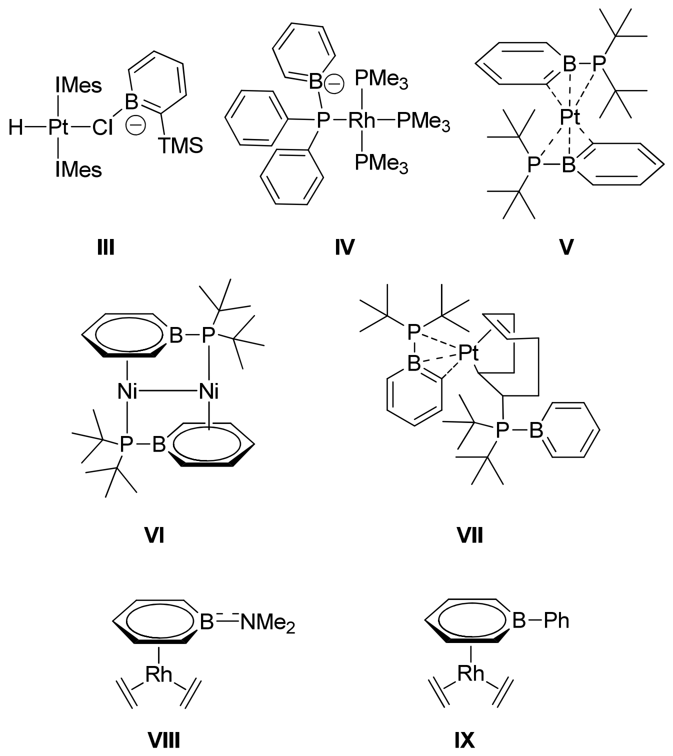
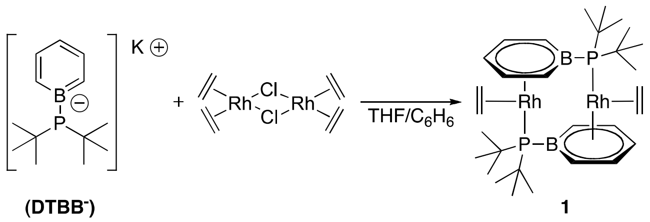


Fig. 2 Some borabenzene species related to this this study: [(IMes)$_2$Pt(H)(1-Cl-2-SiMe$_3$-BC$_5$H$_4$)] (**III**),[13a] Rh(PMe$_3$)$_3$(DPB) (**IV**),[14] Pt(DTBB)$_2$ (**V**),[12b] Ni$_2$(DTBB)]$_2$ (**VI**), and (η^3-(C,B,P)-C$_5$H$_5$BP(tBu)$_2$)(κ-η^2:η^1-C$_8$H$_{12}$(P(tBu)$_2$BC$_5$H$_5$)Pt (**VII**), [(C$_2$H$_4$)$_2$Rh(C$_5$H$_5$B-NMe$_2$)] [6a] (**VIII**) and [(C$_2$H$_4$)$_2$Rh(C$_5$H$_5$B-Ph)] (**IX**).[6a]

Results and discussion

The reaction of 2.2 equiv. of ligand DTBB with [RhCl(C$_2$H$_4$)$_2$]$_2$ in a benzene/THF mixture at room temperature, followed by removal of volatiles and extraction with diethyl ether, provided complex **1** as a red-brown crystalline powder in 40% yield (Scheme 1).



Scheme 1 Synthesis of [(C$_2$H$_4$)Rh(DTBB)]$_2$ (**1**).

Crystalline red needles, suitable for X-ray diffraction studies, were obtained from the slow evaporation of a benzene-d_6 solution of **1**. The bimetallic complex crystallized in a monoclinic P2$_1$/n space group (Table S2). Species **1** was confirmed to be a centrosymmetric dimer where each of the two DTBB ligands bridges two rhodium(I) centres, with the boratabenzene moiety binding in a η^6-fashion to one Rh(I) and the lone pair of the phosphine coordinating the other metal centre. A η^2-ethylene molecule is completing the 18-electron count of each rhodium (Fig. 3).

The homobimetallic species has a B-Rh distance of 2.510(4) Å, which is larger than in related π-boratabenzene complex [(C$_5$H$_5$BPh)Rh(CH$_2$CH$_2$)$_2$] (**IX**) which has a B-Rh distance of 2.398(4) Å.[12b] The B-Rh distance in **1** is somewhat comparable to species [(C$_5$H$_5$BNMe$_2$)Rh(CH$_2$CH$_2$)$_2$] (**VIII**), which has a B-Rh bond length of 2.521(2) Å,[6a] despite the fact that there is no π-bonding between P-B since the lone pair on phosphorous is engaged in a bond with one metal centre.[16] Interestingly, complex **1** displays some asymmetry in the coordination of the borabenzene moiety since one of the Rh-C$_{ortho}$ bond is significantly elongated (Rh-C(1) = 2.435(3) Å) compared to the other Rh-C$_{ortho}$ bond (Rh-C(5) = 2.237(3) Å), suggesting that the heterocyclic moiety might be closer to an η^4-coordination rather than a typical η^6-coordination (Fig. 3).[17] The C=C bond length for the ethylene molecule is 1.370(6) Å and the Rh-C$_{ethylene}$ distances are very similar (2.131(4) and 2.140(4) Å). These values compare well to those observed in species **IX** (Rh-C$_{ethylene}$ = 2.145(4), 2.143(4) Å and C=C = 1.385(6) Å)[6a] and **VIII** (Rh-C$_{ethylene}$ = 2.118(7), 2.133(7) Å and C=C = 1.376(9) Å)[6a]. Finally, the Rh-bound phosphine ligand retains its tetrahedral geometry, as expected. Whereas most of the angles around phosphorous are close to the expected value for a tetrahedral centre, the B-P-C(8) angle of 97.2(2)° is smaller than 109° and diverts significantly from the related angle in the metal-free ligand (108.6(2)°).[12b]

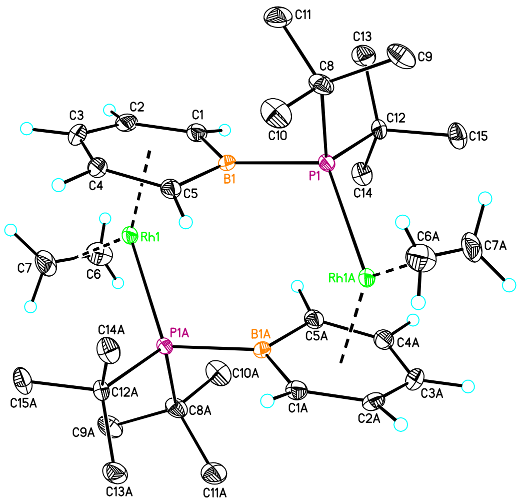


Fig. 3 ORTEP plot of **1** with thermal ellipsoids set at the 50% probability level. H atoms are shown as spheres with arbitrary radii. H atoms on all methyl groups are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A: -x+1,-y,-z+1. Selected bond distances [Å] and angles [deg]: P1-B1 1.962(4), B1-Rh1 2.510(4), Rh1-P1 2.3226(9), Rh1-C1 2.435(3), Rh1-C2 2.267(4), Rh1-C3 2.259(3), Rh1-C4 2.259(4), Rh1-C5 2.237(3), Rh1-C6 2.140(4), Rh1-C7 2.131(4); Rh1-P1-C12 110.8(1), Rh1-P1-C8 118.4(1), Rh-P1-B1 112.4(1), C8-P1-C12 108.6(2), B1-P1-C8 97.2(2), B1-P1-C12 108.6(2), C7-Rh1-P1 97.8(1), C6-Rh1-P1 100.3(1), Rh1-P1-B1 112.4(1), B1-Rh1-P1 100.63(9), C1-B1-C5 113.9(3), B1-Rh-1-C7 161.2(1), B1-Rh1-C6 133.6(1).

The multinuclear NMR characterization confirmed the presence of **1** in solution. The similarity between the boratabenzene proton resonances in the ^{1}H NMR spectrum for

1 at δ = 5.96, 5.55 and 4.48 for the *ortho*, *meta* and *para* positions, respectively, with the ones observed for rhodium complexes **VIII** (δ = 5.82 *ortho*, 4.87 *meta*, 4.27 *para*) and **IX** (δ = 6.0 *ortho* and *meta*, 4.34 *para*) suggest similar η^6 coordination modes.[6a] Both the *ortho* and *meta* protons appear as a single resonance in the ^{1}H NMR spectrum, as expected for a symmetric coordination of the heterocycle to the metal centre in **1**, suggesting that the asymmetry present at the solid-state is not observed in solution at room temperature. As expected, the *t*Bu$_2$P- fragment is present as a doublet at 1.34 ppm ($^3J_{HP}$ = 11.6 Hz). Two resonances observed at 3.00 (*J* = 11.7, 2.2 Hz) and 2.74 ppm (*J* = 12.0, 2.2 Hz) put in evidence the presence of an ethylene ligand in the coordination sphere. Regardless of the high donor capability of DTBB, which should allow the metal to be more electron rich and engaging more efficiently into back-donation with a π-coordinated alkene ligand, the ethylene protons on complex **1** are observed to be less shielded compared to those previously reported for Rh(I)-η^6-boratabenzene species (δ = 2.19 for **VIII** and 1.22, 2.82 for **IX**).

The broad doublet observed in the ^{31}P NMR spectrum at 23.7 ppm and the J_{PRh} value of 160 Hz support the coordination of the phosphorous atom on a rhodium(I) centre. Only one resonance is observed because of the presence of a centre of symmetry on the complex. The chemical shift is significantly different than the one observed for the nickel species **VIII** (-8.9 ppm). In contrast, the complexes where the (DTBB$^-$) ligand is η^3-coordinated to Pt exhibit similar resonances at 31.9 and 37.2 ppm for **V** and **VII**, respectively.

Boratabenzene species **VIII** and **IX**, having ethylene ligands, were shown to exhibit dynamic behaviour attributed to the rotation of ethylene, as confirmed by variable temperature NMR experiments.[6a] However, it was not possible to observe ethylene rotation with species **1** because of the dissociation of the ethylene molecule observed when dissolved in solution. When the solution reached 40 °C, the broadening of the aromatic and ethylene resonances was observed but the rate of ethylene dissociation was significant as suggested by the increase in intensity of the singlet at 5.2 ppm. Traces of unidentified products were observed spectroscopically along with some precipitate, suggesting that degradation was taking place. Therefore complex **1** was stored at -30 °C and protected from light, since Rh ethylene species such as CpRh(C_2H_4)$_2$ have been shown to undergo rearrangements under photochemical conditions.[18,19]

Reactivity with H$_2$

Whereas some preliminary studies have been done on the reactivity of species **IV** and [(cod)Rh(C_5H_5B-L)][OTs] (L = Py, PMe$_3$; OTs = $CH_3C_6H_4SO_3^-$) with hydrogen suggesting that rhodium hydride species have been generated, no details were given on the characterization and reactivity of these compounds.[14,20] We were able to show that complex **1** reacts with 1 atm of H_2 to generate free ethylene and ethane, observed as resonances at δ = 5.20 and 0.90, respectively, by ^{1}H NMR spectroscopy. As mentioned above, it should be noted that free ethylene is always observed when **1** is dissolved in solution, along with uncharacterized species. When H_2 is allowed to react with **1** over a period of 3 h in an airtight J-Young NMR tube, two hydride resonances, attributed to two different species, were observed at -13.94 (**2**) and -17.83 ppm (**3**), along with new aromatic resonances. It was unfortunately impossible in our hand to isolate these two compounds in the solid state. It should be noted that even when handled under strict anhydrous and air free conditions, the presence of precipitate was observed (evidenced by a modification in the integration for the *t*Bu moieties by ^{1}H NMR) along with small amounts of the phosphine oxide *t*Bu$_2$PH(O) (^{31}P{^{1}H} δ = 61.6; ^{1}H (C_6D_6) = 0.99 (d, 18H, *t*Bu$_2$), 5.82 (d, 1H, *t*Bu$_2$PH)),[21] which might be caused by traces of water or oxygen in the molecular hydrogen. It is however possible to obtain selectively each hydride as main species in solution depending on the reaction conditions. When left for a period of 3 days under a hydrogen atmosphere, species **2** was the main species observed in solution. However, when the solvent of a solution containing both **2** and **3** was removed under reduced pressure and the oily solid residue was dissolved back under a nitrogen atmosphere, only species **3** was observed. It proved impossible to revert from **3** to **2** under one atmosphere of hydrogen. All attempts to obtain a crystalline solid from solutions of **2** or **3** failed.

As mentioned above, a hydride resonance appearing as a doublet of doublets at δ -13.94 with two distinct coupling constants of 23.3 and 21.3 Hz is characteristic of species **2** by ^{1}H NMR spectroscopy (Fig. 4a). Aromatic resonances were also observed at δ = 6.00 (t, *meta*), 5.78 (dd, *ortho*), and 5.38 (t, *para*), along with a doublet at 1.35 ppm. The integration ratio of the hydride and of the aromatic resonances demonstrates that there are two hydrides per boratabenzene moiety. The similarity of the splitting pattern of **2** with species **1** suggests that similar coordination environments are present. The ^{31}P{^{1}H} NMR spectrum of species **2** shows a very broad multiplet at ≈52 ppm. The lack of intensity of the ^{31}P{^{1}H} resonance, even after an acquisition of 1 hour at -90 °C, suggests that in addition of the broadness caused by the ^{11}B quadrupolar moment and the coupling with the ^{103}Rh nuclei, some rapid fluxional process also takes place. The same problem was observed by ^{11}B{^{1}H} NMR spectroscopy where after 12 hours of acquisition (over 34 000 scans) no discernible resonance was observed. It should be noted that the difficulty in acquiring good ^{11}B NMR spectra has been previously observed for borabenzene complexes.[13a] Nevertheless, it was possible to confirm that the ^{31}P{^{1}H} resonance at 52 ppm was indeed for species **2** by the acquisition of a ^{1}H{^{31}P} spectrum with selective decoupling at the latter frequency. Indeed, the hydride resonance at -13.94 ppm was observed as a doublet of 23.4 Hz, attributed to a Rh-H interaction, therefore confirming that the 21.2 Hz coupling constant corresponds to a $J_{P\text{-}H}$. It was further confirmed that the *ortho* proton of the boratabenzene moiety, previously observed as a triplet, was now a doublet of 9.3 Hz and that the doublet at 1.37 ppm for the *t*Bu groups was now a singlet.

The ^{1}H NMR hydride resonance at -17.83 ppm for species **3** (Fig. 4b) also exhibits two distinct coupling constants of 21.5

and 14.6 Hz. However, five distinct resonances at δ = 6.25 (overlapped, 2H), 6.03, 4.95, and 4.80, can be observed for the boratabenzene moiety, suggesting a loss of symmetry of the complex in solution. It is noteworthy to mention that the integration ratio observed is now of 1:1 between the hydride and the boratabenzene resonances. Carrying a $^{1}H\{^{31}P\}$ NMR experiment by selectively decoupling the ill-defined ^{31}P resonance of **3** at 54 ppm did show that the doublet of doublets at -17.83 ppm in the ^{1}H NMR spectrum now appeared as a doublet of 15.9 Hz, which can be attributed to a $J_{Rh\text{-}H}$. Additionally, two resonances in the aliphatic region, attributed to the *t*Bu groups, were observed as singlets at 1.46 and 1.29 ppm rather than doublets.

It should also be noted that it was very difficult to obtain good NMR spectra for elements other than proton regardless of the concentration of the sample and the acquisition time. For example, when carrying $^{13}C\{^{1}H\}$ NMR experiments with 12-hour acquisition for **2** and **3**, no resonance other than the one for the *t*Bu group were observed. HSQCAD and gHMBCAD correlation experiments also proved unsuccessful for both hydride species.

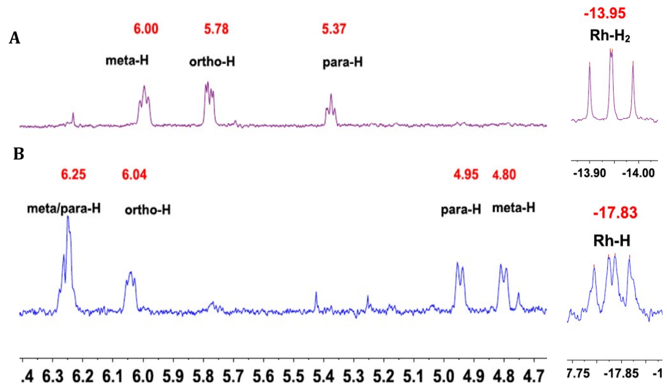


Fig. 4 Selected region of the ^{1}H NMR spectra (benzene-d$_{6}$, 500 MHz) for the boratabenzene and high field Rh-H resonances for hydride **2** (a) and **3** (b).

T1 measurements were nevertheless informative regarding the bonding mode of hydrogen to metal centres since they can help discriminating between bridging and terminal hydrides, or put in evidence non-classical sigma bonded H_2.[22] Species **2** shows a minimum T1 of 4.49 s at 183 K in toluene-d_8 on a 500 MHz spectrometer. At 283 K, the T1 value was 8.62 s. On the other hand, the minimum T1 value for **3** is 6.35 s at 183 K in toluene-d_8 and a maximum of 6.75 s at 295 K (See Table S1 for T1 measurements at different temperatures). Dipole-dipole relaxation for classical metal hydrides lies in the range of seconds, while dihydrogen complexes show a much shorter T1 in the range of 4-100 ms.[19,22,23] On this basis, because **2** and **3** display long T1 dipole relaxation times, the existence of a H-H bond can be ruled out.

Based on its spectral properties and on the structure of precursor **1**, one can propose **2** to be a classical Rh(III) dihydride species $[(DTBB)Rh(H)_2]_2$ (Fig. 5). Indeed, the spectral properties of the hydride at -13.94 ppm with a $J_{H\text{-}Rh}$ coupling constant of 23.2 Hz are very similar to those of $[Cp^{*}Rh(PMe_3)(H)_2]$ (-13.65 ppm, dd, $J_{Rh\text{-}H}$ = 29.8 Hz, $J_{P\text{-}H}$ = 41.8 Hz)[24a,b] and $[CpRh(PiPr_3)(H)_2]$ (-14.73 ppm, dd, $J_{Rh\text{-}H}$ = 27.5 Hz, $J_{P\text{-}H}$ = 33.5 Hz)[24c].

It should be noted that only species **3** remains when a mixture of **2** and **3** are put under reduced pressure. Interestingly, species **3** is shown to have two hydrogen atoms less than species **2** according to ^{1}H NMR spectroscopy. The ^{1}H NMR chemical shift of the hydride is more shielded and the $J_{Rh\text{-}H}$ coupling of **3** is significantly smaller compared to **2**. Several cyclopentadienyl rhodium hydride species have been shown to have similar spectroscopic features when the complexes were cationic[23c,25] or when the hydrides were bridging,[23a,24c] which is not expected to occur for **3** since no ionization source was added and a triplet would be observed in the case of a hydride bridging two active ^{103}Rh centres. The most likely speculation as for the structure of **3** (Fig. 5) would be a dimeric Rh(II) species having a Rh-Rh interaction and one hydride on each metal. Because of the Rh-Rh interaction and the limited flexibility one might imagine for such complex, the asymmetry observed in the coordination mode of the boratabenzene moiety in the crystal structure of **1** could be present in **3** and kept "locked" in solution, something that was not observed for the ethylene complex. Thereby, a centre of symmetry might be present for **3** but each proton of the boratabenzene would remain inequivalent. However, several other conformations are possible for this species, especially since DTBB was shown to have very rich coordination chemistry.

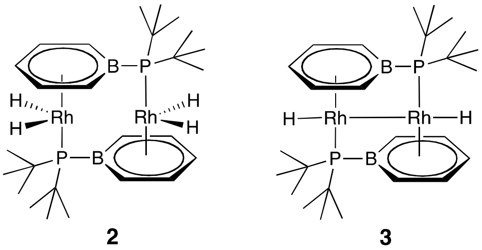
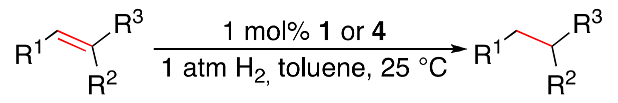


Fig. 5 Proposed molecular structures for hydride species $[(DTBB)Rh(H)_2]_2$ (**2**) and $[(DTBB)Rh(H)]_2$ (**3**).

Hydrogenation of alkenes

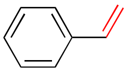
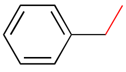
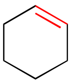
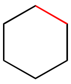
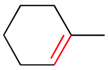
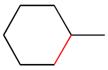
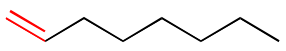
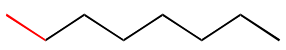
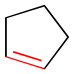
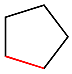
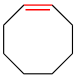
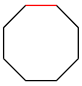
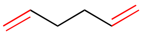
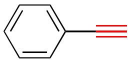
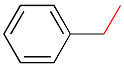
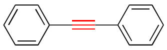
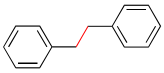
Boratabenzene complexes reported by Bazan[6a] were shown to effectively catalyse the C-H activation of octane. However the activity quickly decays overtime due to the low thermal stability of the complex. Because of the activity of species **1** at ambient temperature and pressure with hydrogen, we were interested in looking at the possibility for **1** to act as an alkene hydrogenation catalyst (Scheme 2). Although several rhodium complexes are known to be efficient catalysts for the hydrogenation of olefins, to our knowledge no boratabenzene complex has been studied for such transformation. Furthermore, very few studies have been done in the homogeneous hydrogenation of alkenes at ambient temperature and pressure.[26] For comparison purpose, the activity of Wilkinson's catalyst $ClRh(PPh_3)_3$ (**4**) was also investigated in the same mild conditions.



Scheme 2 Catalytic hydrogenation of alkenes.

Table 1 shows the activity of catalyst **1** and **4** for the hydrogenation of alkenes and alkynes, at room temperature and ≈ 1 atm of H_2. It can be observed that for most of the substrates the conversions obtained for the hydrogenation of alkenes are similar when comparing **1** to **4**. In the case of styrene and cyclohexene the conversion yields are of 29 and 20%, respectively, using **1** as a catalyst (entries 1 and 2). The conversion is significantly higher with 1-methyl-cyclohexene and 1-octene, with 84% and 73% yield, although the conversion is complete when using Wilkinson's catalyst in both entries (entries 3 and 4). A significant difference is observed for the hydrogenation of cyclopentene, where the hydrogenation using **1** is half of what is observed using **4** (43 vs 90%, respectively; entry 5). In the case of cyclooctene, both catalysts **1** and **4** give poor yields (entry 6). The hydrogenation of alkynes to the corresponding alkanes is also possible, although the conversion is relatively low (2 and 21% for phenyl- and diphenylacetylene, respectively). It should be noted that it is possible to observe by NMR spectroscopy that the alkenes are generated during the hydrogenation of alkynes, suggesting that the hydrogenation is occurring through sequential steps. Therefore, the reactivity of species **1** as a precatalyst for the hydrogenation of alkenes and alkynes follows the trend reported for Wilkinson's catalyst.[26b] It should be noted that according to ^1H NMR species **2** is no longer present when catalysis starts whereas species **3** remains throughout catalysis. However, since some degradation products are present throughout catalysis, it is difficult to confirm which species is acting as catalyst.

Table 1 Hydrogenation of alkenes and alkynes using **1** and Wilkinson catalyst (**4**).

entry	substrate	product	% conversion[a]
(1)			**1**: 29% **4**: 27%
(2)			**1**: 20% **4**: 30%
(3)			**1**: 84% **4**:100%
(4)			**1**: 73% **4**: 100%
(5)			**1**: 43% **4**: 90%
(6)			**1**: 12% **4**: 19%
(7)			**1**: 24% **4**: 26%
(8)			**1**: 2% **4**: 3%
(9)			**1**: 21% **4**: 13%

[a] Conversion determined by GC-FID after 24 h of reaction.

Experimental Section

General considerations

All manipulations were carried under inert atmosphere of nitrogen using either Schlenk line techniques or a MBraun glovebox. THF and Et_2O were distilled under N_2 atmosphere over sodium/benzophenone; toluene, benzene, benzene-d_6, toluene-d_8, alkenes, alkynes and alkanes were pre-treated with Na/K alloy and vacuum transferred or distilled. DTBB was prepared according to a literature precedent.[12a] Wilkinson catalyst, alkenes and alkanes were purchased from Sigma-Aldrich. $[RhCl(C_2H_4)_2]_2$ was purchased from Strem chemicals. H_2 gas UHP 5.0 was purchased from Praxair. NMR spectra were recorded in a sealed J-Young quartz NMR tube on an Agilent Technologies NMR spectrometer, ^1H NMR (500 MHz), ^{13}C NMR (125.721 MHz), ^{31}P NMR (202.404 MHz), ^{11}B NMR (160.419 MHz). The coupling constants (J) should be considered as an average with standard deviation of +/- 0.2 Hz. 2D NMR gHSQCAD, and gCOSY experiments were used to elucidate ^{13}C-^1H and ^1H-^1H correlations. FTIR spectra were obtained with a Nicolet Bomem Magna-850. The solid was suspended in Nujol previously degassed by bubbling N_2 and the sample was prepared inside an inert atmosphere glove box. GC-FID was carried out using a Thermo Scientific trace GC ultra coupled with an ITQ 900 mass spectrometer using electronic impact ionization (EI), standard curves of the corresponding alkanes were used to calculate the concentration in ppm, internal standards were used and yields were calculated against the theoretical yield for each substrate. All species exhibited decomposition and did not give satisfactory elemental analysis.

Synthesis of $[Rh(C_2H_4)(DTPBB)]_2$ (1)

DTBB (0.073 g, 0.28 mmol) was dissolved in 6 mL of THF. To the yellow solution was added 4 mL of $[ClRh(C_2H_4)]_2$ (0.050 g, 0.13 mmol) solution in benzene. The resulting red solution was stirred at room temperature for 2h. The reaction mixture was evaporated to dryness. The remaining red solid was washed with 2 x 8 mL of Et_2O and dried under vacuum. Yield = 0.066 g, 40%. ^{1}H NMR (500 MHz, benzene-*d*$_6$): δ 5.96 (m, 4H, *o*-C_5H_4B), 5.55 (t, *J* = 6.5 Hz, 4H, *m*-C_5H_4B), 4.48 (t, *J* = 5.8 Hz, 2H, *p*-C_5H_4B), 3.00 (dd, *J* = 11.7 and 2.2 Hz, 4H, C_2H_4), 2.74 (dt, ^1J = 12.0 and 2.2 Hz, 4H, C_2H_4), 1.34 (d, *J* = 11.6 Hz, 36H, *t*Bu_2). ^{13}C{^{1}H} (125.72 MHz, benzene-*d*$_6$): δ 101.4 (*m*-C_5H_4B), 99.6 (*o*-C_5H_4B), 91.8 (*p*-C_5H_4B), 36.4 (d, *J* = 12.8 Hz, C-*t*Bu_2), 33.2 (d, *J* = 3.2 Hz, CH_3 *t*Bu_2), 32.9 (dd, *J* = 13.7 and 1.6 Hz, C_2H_4). ^{31}P{^{1}H} (202.40 MHz, benzene-*d*$_6$): δ 23.7 (br d, *J* = 160 Hz, $[Rh(C_2H_4)(DTPBB)]_2$). ^{11}B{^{1}H} (160.41 MHz, benzene-*d*$_6$): δ 31.

Reaction of $[Rh(C_2H_4)(DTPBB)]_2$ (1) with H_2

In a sealed J-Young NMR tube (0.002 g, 2.8 μmol) were dissolved in 0.6 mL of benzene-*d*$_6$, the yellow solution was degassed by 3 cycles of freeze-pump-thaw in a liquid nitrogen bath and ≈ 1 atm of H_2 was added by removing the liquid nitrogen bath and opening the valve to H_2 flow for 30 seconds. The sample was then allowed to reach room temperature slowly. The NMR spectrum recorded after 3 h displayed the signals for two different hydrides along with some of the starting material. After 3 days only species **2** was observed in solution. Removal of the hydrogen atmosphere generates species **3**. Only **3** proved to be stable enough to undergo FT-IR analysis.

Hydride 2: ^{1}H NMR (500 MHz, benzene-*d*$_6$): δ 6.00 (t, *J* = 7.5 Hz, 2H, *m*-C_5H_4B), 5.78 (dd, *J* = 8.9 and 4.1 Hz, 2H, *o*-C_5H_4B), 5.38 (t, *J* = 6.0 Hz, 1H, *p*-C_5H_4B), 1.37 (d, *J* = 12.7 Hz, P*t*Bu_2), -13.94 (dd, *J* = 23.3 and 21.3 Hz, 2H, Rh-H). ^{1}H{^{31}P} (51.8 ppm) NMR (500 MHz, benzene-*d*$_6$): δ 6.00 (dd, *J* = 9.3 and 5.8 Hz, 2H, *m*-C_5H_4B), 5.78 (d, *J* = 8.6 Hz, 2H, *o*-C_5H_4B), 5.38 (t, *J* = 6.0 Hz, 1H, *p*-C_5H_4B), 1.37 (s, P*t*Bu_2), -13.94 (d, *J* = 23.4 Hz, 2H, Rh-H). ^{31}P{^{1}H} (202.40 MHz, benzene-*d*$_6$): δ 51 (br).

Hydride 3: ^{1}H NMR (500 MHz, benzene-*d*$_6$): δ 6.25 (m, 2H), 6.04 (m, 1H), 4.95 (d, *J* = 8.9 Hz, 2H), 4.80 (d, *J23* = 9.7 Hz, 2H), 1.46 (d, *J* = 12.8 Hz, 18H), 1.29 (d, *J* = 12.3 Hz, 20H), 0.99 (d, *J* = 14.5 Hz, 4H), -17.83 (dd, *J* = 21.32, 14.7 Hz, 1H, Rh-H). ^{1}H{^{31}P} (54.2 ppm) NMR (500 MHz, benzene-*d*$_6$): δ 6.25 (m, 4H), 6.04 (dd, *J* = 8.4, 6.1 Hz, 2H), 4.95 (d, *J* = 8.5 Hz, 2H), 4.80 (d, *J* = 9.2 Hz, 1H) 1.46 (s, 36H, P*t*Bu_2), 1.29 (s, 54H, P*t*Bu_2), -17.83 (d, *J* = 15.9 Hz, 1H, Rh-H). ^{31}P{^{1}H} (202.40 MHz, benzene-*d*$_6$): δ 54 (br). FT-IR (Nujol, cm^{-1}): 3663, 3308, 3196, 3107, 3063, 3035, 2919, 2849, 2662, 2351, 2291, 2161, 2084, 1979, 1753, 1679, 1591, 1567, 1453, 1375, 1240, 1116, 1084, 1027, 968, 895, 869, 810, 796, 774.

X-ray Crystallography

A red crystal of **1** (0.26 x 0.10 x 0.08 mm^3) was mounted on a glass fibre using Paratone N hydrocarbon oil. Measurements were made at 150(2) K on a Bruker APEX II area detector diffractometer equipped with graphite monochromated MoKα radiation. The program used for retrieving cell parameters and data collection was APEX 2.[27] Data were integrated using the program SAINT,[28] and corrected for Lorentz and polarization effects. The structure was solved and refined using SHELXS-97.[29] All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions. Crystallographic data have been deposited at CCDC (CCDC no. 1415613). The crystallographic details are presented in Table S1 (ESI). This data can be obtained upon request from the Cambridge Crystallographic Data Centre.

General procedure for hydrogenation reactions

Hydrogenation reactions were carried out in Schlenk flasks over 24 h of continuous flow of H_2, at room temperature. Aliquots of 0.1 mL were withdrawn after 1, 6, 12 and 24 h of reaction, filtered through a 1 cm silica plug and diluted with 0.3 mL of toluene. All liquids were measured with automated pipets. In a typical hydrogenation reaction substrate, internal standard, 1 mol % of catalyst and 10 mL of toluene were loaded into a 18 mL Schlenk flask, equipped with a magnetic stirring bar.

Conclusions

We have carried out the synthesis of species $[(C_2H_4)Rh(DTBB)]_2$ where the DTBB moiety bridges two rhodium centre by an η^6-coordination of the boratabenzene moiety and by the lone pair on phosphorous. In the latter complex, the ethylene ligand proves to be quite labile. Under a hydrogen atmosphere, complex **2** transforms into complexes **2** and **3** having respectively two and one hydride per metal centre, according to multinuclear NMR spectroscopy. Interestingly, complex **1** can serve as a precatalyst for the hydrogenation of alkenes and alkynes at ambient temperature and pressure. Interestingly, the activity observed is very similar to the one observed for Wilkinson's catalyst in similar conditions, even if formally the metal in **1** does not exhibit the same unsaturation observed for the ubiquitous $ClRh(PPh_3)_3$ catalyst. It can be therefore proposed that in order for catalysis to occur, the DTBB ligand needs to present some hemilability in order to open up coordination sites. Although the DTBB exhibits a rich and diverse coordination chemistry, its usefulness as a ligand for catalysis seems to be impeded by the sensitivity of the P-B bond to hydrolysis and or oxidation, which we are currently studying in more detail.

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