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# Reactivity of 3,3,3-Trifluoropropyne at Rhodium Complexes: Development of Hydroboration Reactions

Cortney N. von Hahmann,<sup>†,[a]</sup> Maria Talavera,<sup>†,[a]</sup> Conghui Xu,<sup>[a]</sup> and Thomas Braun<sup>\*[a]</sup>

**Abstract:** The rhodium complexes  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$  (**2**), *fac*- $[\text{RhH}(\text{C}\equiv\text{CCF}_3)_2(\text{PEt}_3)_3]$  (**3**), and *fac*- $[\text{Rh}\{\text{(E)-CH}=\text{CHCF}_3\}(\text{C}\equiv\text{CCF}_3)_2(\text{PEt}_3)_3]$  (**4**) were synthesised by reactions of rhodium(I) complexes  $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$  (**1**) and  $[\text{Rh}(\text{Bpin})(\text{PEt}_3)_3]$  (**5**) with the alkyne 3,3,3-trifluoropropyne. Reactivity studies of  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$  (**2**) were performed with CO and  $^{13}\text{C}$ O to form  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{CO})(\text{PEt}_3)_3]$  (**7**) and subsequently *trans*- $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{CO})(\text{PEt}_3)_2]$  (**8**) as well as the labelled derivatives. Using 1-4 as catalysts, hydroboration reactions selectively afforded borylated building blocks.

## Introduction

In the last decades, a versatile reactivity of alkynes with transition metals has been reported and various reaction pathways involve coordination, oxidative addition or insertion reactions to generate in some cases alkynyl, vinylidene or vinyl ligands among others.<sup>[1]</sup> Alkynes are also proven to undergo C–C coupling reactions releasing enynes.<sup>[2]</sup> The nature of the alkyne (terminal or internal) and the substituents are influencing their reactivity. Thus, an alkyne bearing a  $\text{CF}_3$  group could provide interesting reactivity as well as new fluorinated building blocks. Note that fluorinated building blocks behave differently in the coordination sphere of transition metals when compared to the non-fluorinated counterparts.<sup>[3]</sup> Additionally, fluorinated alkynes play a role in the functionalization of silicon nanowires.<sup>[4]</sup> The reactivity of the terminal alkyne 3,3,3-trifluoropropyne includes insertion reactions into metal-hydrogen bonds, as well as transition-metal mediated addition reactions of silanes and germanes.<sup>[5]</sup> Certain Pt complexes react with 3,3,3-trifluoropropyne to provide coordination of the alkyne<sup>[6]</sup> and in some cases ultimately forming polymers, vinyl or alkynyl complexes.<sup>[7]</sup> At rhodium,  $[\text{RhTp}'(\text{PR}_3)(\text{CH}_3)(\text{H})]$  ( $\text{R} = \text{OMe}, \text{Me}$ ) ( $\text{Tp}' = \text{tris-(3,5-dimethylpyrazolyl)borate}$ ) requires 140 °C of heat to fully induce a C–H bond cleavage of the fluorinated alkyne as well as the release of methane.<sup>[8]</sup> Low temperatures and base are needed for the C–H bond cleavage using  $[\text{Rh}(\text{cyclam})(\text{OTf})_2]\text{OTf}$  as a starting material (cyclam = 1,4,8,11-tetraazacyclotetradecane).<sup>[9]</sup> Furthermore, the oxidative addition of two equivalents of 3,3,3-trifluoropropyne by  $[\text{RhCl}(\text{CO})(\text{AsMe}_3)_2]$  and the concomitant release of  $\text{H}_2$  to provide a bistrifluoroalkynyl rhodium(III) complex has been also observed.<sup>[10]</sup> Although catalytic hydroboration, hydrosilation and

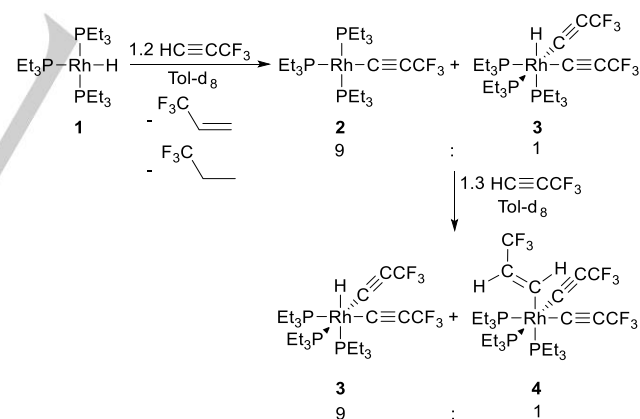
also hydrometallation reactions of alkynes have been widely studied,<sup>[11]</sup> none have been reported with 3,3,3-trifluoropropyne, to the best of our knowledge. However, palladium-catalysed hydrogermylation reactions of internal alkynes containing a  $\text{CF}_3$  group have been reported.<sup>[12]</sup>

Our approach features studies of 3,3,3-trifluoropropyne towards the highly reactive Rh(I) complexes  $[\text{RhH}(\text{PEt}_3)_3]$  (**1**) and  $[\text{Rh}(\text{Bpin})(\text{PEt}_3)_3]$  (**5**) to yield alkynyl and vinyl complexes. Reactivity studies involve catalytic hydroboration reactions to obtain fluorinated building blocks.

## Results and Discussion

### Reactivity of Rhodium(I) Complexes towards 3,3,3-Trifluoropropyne

Treatment of  $[\text{RhH}(\text{PEt}_3)_3]$  (**1**)<sup>[13]</sup> with 1.2 equivalents of 3,3,3-trifluoropropyne afforded a mixture of the rhodium(I) alkynyl complex  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$  (**2**) and the rhodium(III) hydrido complex *fac*- $[\text{RhH}(\text{C}\equiv\text{CCF}_3)_2(\text{PEt}_3)_3]$  (**3**) in a 9:1 ratio, as well as 1,1,1-trifluoropropane and minor amounts of 3,3,3-trifluoropropene (Scheme 1).



**Scheme 1** Reactivity of the hydrido complex **1** towards 3,3,3-trifluoropropyne.

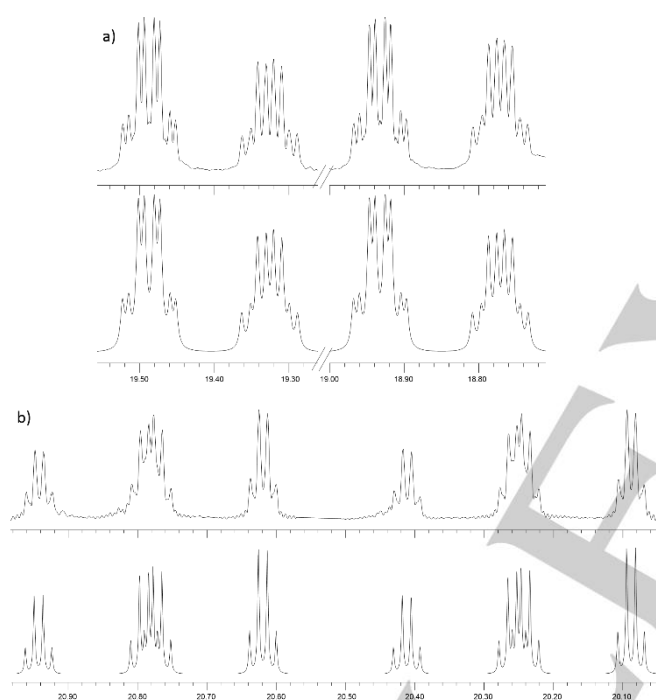
Attempts to increase the selectivity of the reaction by decreasing the amount of alkyne used did not provide full conversion of **1** into **2**, however **3** is already observed. Noteworthy is that complex **2** is one of the few examples of  $\sigma$ -bound trifluoropropynyl ligands at complexes of transition metals.<sup>[7-8, 9-10]</sup> In addition, literature-known compounds are usually, in contrast to complex **2**, not prepared using 3,3,3-trifluoropropyne itself as a starting material, but alkynyl metallates.<sup>[14a-f]</sup> Complex **2** shows a molecular peak at  $m/z$  550 in the liquid injection field desorption/ionization mass spectrum (LIFDI-MS).

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The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 121.5 MHz discloses a system of higher order which simplifies at 242.8 MHz (see ESI), although it still represents a spectrum of higher order. In order to obtain the coupling constants, the spectrum of **2** was simulated<sup>[15]</sup> (Figure 1) to be an  $A_2\text{BMX}_3$  spin system. Two resonances in a 1:2 ratio at  $\delta$  20.5 and 19.1 ppm are observed which have rhodium-phosphorus coupling constants typical for rhodium(I) complexes (128.9 and 134.8 Hz, respectively),<sup>[16]</sup> and the coupling constant between the phosphorus nuclei is 39.4 Hz. In addition, both resonances display a coupling with the fluorine atoms of the alkynyl ligand of 3.1 and -5.2 Hz for the phosphorus nuclei in the *trans* and *cis* positions, respectively. Note that other alkynyl complexes at rhodium such as  $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{PET}_3)_3]$  and  $[\text{Rh}(\text{C}\equiv\text{CSiMe}_3)(\text{PET}_3)_3]$  exhibit the expected coupling pattern of doublet of triplets and doublet of doublets.<sup>[17]</sup>

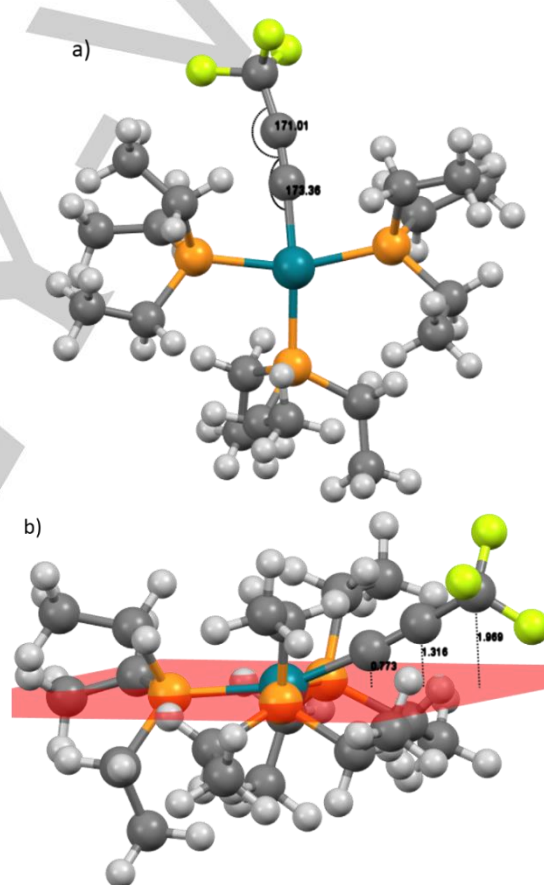


**Figure 1.** Signal of the  $\text{PET}_3$  ligands in the *cis* (a) and *trans* (b) positions to the alkynyl ligand in the  $^{31}\text{P}\{^1\text{H}\}$  spectrum (242.8 MHz) of complex **2**. Observed (above), simulated (below) using the following coupling constants (Hz):  $^1J(\text{P}_i, \text{Rh}) = 128.91$ ,  $^2J(\text{P}_i, \text{P}_j) = 39.38$ ,  $^5J(\text{P}_i, \text{F}) = 3.06$ ,  $^1J(\text{P}_c, \text{Rh}) = 134.81$ ,  $^5J(\text{P}_c, \text{F}) = -5.18$ .

The presence of the alkynyl ligand is supported by the  $^{19}\text{F}$  NMR spectrum with one  $\text{CF}_3$  signal at  $\delta$  -43.5 ppm as a pseudo triplet of doublet of doublets due to the coupling with the phosphorus and rhodium atoms. The spectrum was simulated<sup>[15]</sup> (see ESI) and it is consistent with the P,F coupling constants observed in the  $^{31}\text{P}$  NMR spectrum (2.76 Hz for the *trans* phosphine ligand; 4.98 Hz for the *cis* phosphine ligands). The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum also supports the structure proposed with three multiplets observed at  $\delta$  137.7, 114.9 and 95.4 ppm with C-F coupling constants determined by a  $^{19}\text{F}$ - $^{13}\text{C}$  HMBC NMR spectrum of 7, 253 and 45 Hz for  $\text{C}_\alpha$ ,  $\text{C}_\gamma$  and  $\text{C}_\beta$ , respectively.

Finally, the IR spectrum further confirms the presence of the  $\text{C}\equiv\text{C}$  triple bond with a stretching band at  $2111\text{ cm}^{-1}$ , similar to other rhodium alkynyl complexes.<sup>[2]</sup>

As it has been previously observed, fluorinated compounds can be electronically very different when compared to their non-fluorinated counterparts.<sup>[3,18]</sup> Therefore, with the aim to further study the nature of complex **2**, DFT calculations were performed. The optimized structure of  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PET}_3)_3]$  (**2**) (Figure 2) reveals a bending of the trifluoromethylalkynyl ligand towards one of the *cis* phosphines (Figure 3a;  $\text{RhC}\equiv\text{C}$   $173.4^\circ$ ,  $\text{C}\equiv\text{CC}$   $171.0^\circ$ ). Such a bending is not found for  $[\text{Rh}(\text{C}\equiv\text{CCH}_3)(\text{PET}_3)_3]$  ( $\text{RhC}\equiv\text{C}$   $175.6^\circ$ ,  $\text{C}\equiv\text{CC}$   $179.7^\circ$ ), the structure of which was also determined by DFT calculations. Furthermore, **2** exhibits an alignment out of a plane defined by Rh and the three phosphorous atoms. The  $\text{C}_\alpha$ ,  $\text{C}_\beta$  and  $\text{C}_\gamma$  atoms are 0.8 Å, 1.3 Å and 1.97 Å located above this plane (Figure 3b).



**Figure 2.** DFT optimized structure of complex **2** showing the bending of the alkynyl ligand (a) and its deviation from the square planarity (b); for computational details see ESI.

A hydrogen bond between the fluorine atoms and the protons of the phosphine ligands could in principle explain the bending observed. However, the corresponding carbon-fluorine distance of 3.6 Å suggests that such interaction is not present.<sup>[19]</sup> The alkynyl ligand is bent in structures of other rhodium complexes

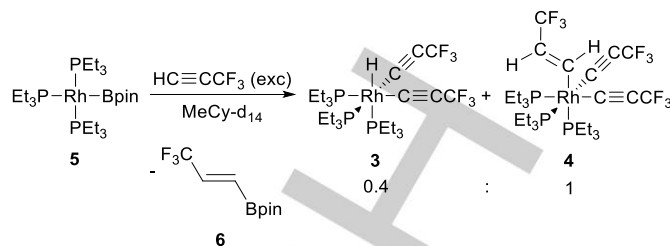
such as  $[\text{RhTp}'\{\text{PMe}_3\}(\text{C}\equiv\text{CCF}_3)(\text{H})]$  or  $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2]$  determined by X-ray crystallography, whereas  $[\text{Rh}(\text{C}\equiv\text{CSiMe}_3)(\text{PMe}_3)_3]$  reveals no bending.

In order to obtain full conversion into complex **3**, another 1.3 equivalents of 3,3,3-trifluoropropyne were added to the mixture of rhodium alkynyl complex **2** and complex **3** leading to the formation of the oxidative addition product *fac*- $[\text{RhH}(\text{C}\equiv\text{CCF}_3)_2(\text{PEt}_3)_3]$  (**3**), but also the rhodium(III) complex *fac*- $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{C}\equiv\text{CCF}_3)_2(\text{PEt}_3)_3]$  (**4**) in a 9:1 ratio after 5 minutes (Scheme 1).

The presence of the alkynyl groups in complex **3** is supported by the IR spectrum with a stretching band at  $2113\text{ cm}^{-1}$ . The hydrido ligand is undoubtedly confirmed by the  $^1\text{H}$  NMR spectrum with a signal at  $\delta$  -10.25 ppm as a doublet of pseudo-quartets. In the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum it appears as a doublet with a rhodium-proton coupling constant of 13.5 Hz, which is a similar value to the coupling with the phosphine ligands in the *cis* position, leading to the pseudo-quartet observed. Finally, the doublet coupling constant of 165.6 Hz is due to the *trans* arrangement of the phosphine and the hydrido ligand in complex **3**. This is consistent with data of other rhodium hydrido complexes in which the hydrido ligand is in the *trans* position to the phosphorus atom.<sup>[13, 20]</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum is also consistent with the structure proposed showing two signals in a 2:1 ratio at  $\delta$  18.9 and -3.2 ppm as a doublet of doublet of multiplets and a doublet of triplet of multiplets, respectively. The rhodium-phosphorus coupling constants of 89.6 and 78.5 Hz, correspondingly, further confirm the oxidation state (III) of the rhodium center.<sup>[13, 16a, 21]</sup> In the  $^{19}\text{F}$  NMR spectrum, a peak at  $\delta$  -44.8 ppm as a pseudo-quartet due to the coupling to the phosphorus atoms of around 4 Hz confirms the presence of the  $\text{CF}_3$  groups. Finally, two of the typical signals for the alkyne moieties in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum are observed at  $\delta$  95.1 and 113.5 ppm for  $\text{C}_\beta$  and  $\text{C}_\gamma$  with typical C–F coupling constants of 47.6 and 251.6 Hz, respectively. The alpha carbon atoms were only observed as resonances at  $\delta$  118.1 ppm with a coupling constant to fluorine of 7 Hz by a  $^{19}\text{F}$ - $^{13}\text{C}$  HMBC NMR experiment.

With the aim to obtain complex **4** in good yield, excess of 3,3,3-trifluoropropyne was added to **3/4** or **1** in two independent reactions. The ratio between complexes **3** and **4** were in both cases 0.8:1.

Alternatively, a reaction of an excess of 3,3,3-trifluoropropyne with  $[\text{Rh}(\text{Bpin})(\text{PEt}_3)_3]$  (**5**)<sup>[16e, 22]</sup> as a starting material, led to the formation of *fac*- $[\text{RhH}(\text{C}\equiv\text{CCF}_3)_2(\text{PEt}_3)_3]$  (**3**) and *fac*- $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{C}\equiv\text{CCF}_3)_2(\text{PEt}_3)_3]$  (**4**) in a 0.4:1 ratio as well as to the generation of (*E*)- $\text{CF}_3\text{CH=CHBpin}$  (**6**)<sup>[23]</sup> after 24 h (Scheme 2). Note that the synthesis of rhodium(I) complex **2** from the rhodium boryl complex **5** is also possible by controlling the amount of 3,3,3-trifluoropropyne added (see ESI).



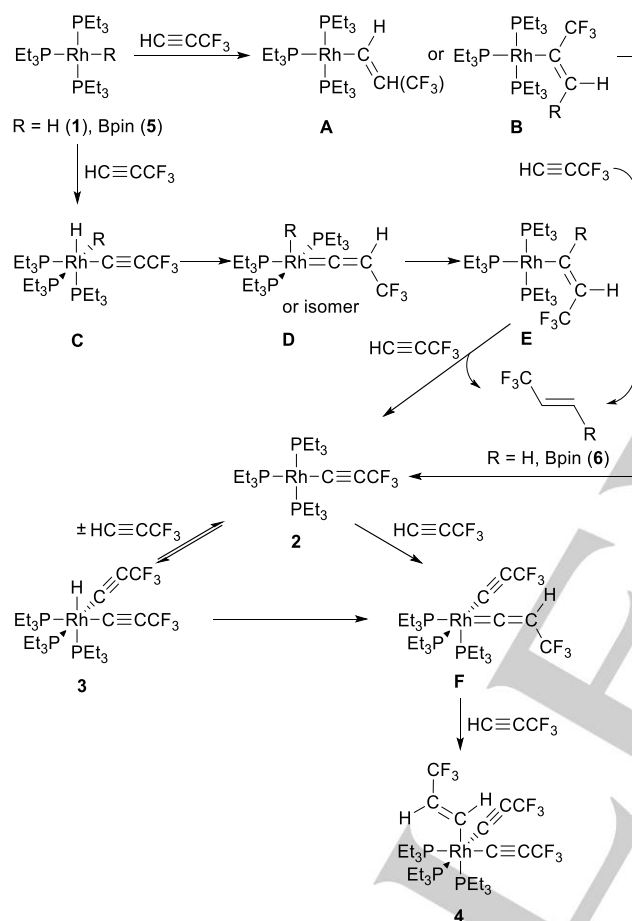
**Scheme 2** Reactivity of the rhodium boryl complex **5** towards 3,3,3-trifluoropropyne.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** exhibits two signals in a 2:1 ratio at  $\delta$  5.3 and -6.6 ppm as a doublet of doublet of multiplets and a doublet of triplet of multiplets, respectively, with comparable coupling constants to complex **3**, confirming its nature as a rhodium(III) complex. In the  $^1\text{H}$  NMR spectrum, the two resonances for the alkenyl ligand appear at  $\delta$  7.04 and 8.12 ppm, both as signals with couplings to phosphorus, fluorine, rhodium and a proton-proton coupling constant of 17.2 Hz, which suggests a *trans* arrangement.<sup>[2a, 24]</sup> In addition, the signal of the proton at higher field appears in the  $^1\text{H}\{^{31}\text{P}\}$  NMR as a doublet of quartet of doublets with a  $^3J(\text{H},\text{F}) = 6.1$  Hz and can be assigned to the proton in geminal position to the  $\text{CF}_3$  group.<sup>[5a, 25]</sup> In the  $^{19}\text{F}$  NMR spectrum two signals arise in a 2:1 ratio, one at  $\delta$  -45.7 ppm as a broad singlet and the other at  $\delta$  -63.1 ppm as a multiplet corresponding to the  $\text{CF}_3$  groups of the alkynyl and the vinyl ligands, respectively. Finally, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum together with the  $^{19}\text{F}$ - $^{13}\text{C}$  HMBC NMR experiments provide the signals of the carbon atoms of the alkenyl ligand at  $\delta$  154.2, 126.8 and 123.6 ppm with C–F coupling constants of 12, 31.2 and 269 Hz corresponding to  $\text{C}_\alpha$ ,  $\text{C}_\beta$  and  $\text{C}_\gamma$ , respectively. Additionally, the resonance for the  $\alpha$ -carbon atom shows a doublet of 98.1 Hz due to its coupling to the rhodium centre. Unfortunately, the mixture of products and overlapping of signals just allow the observation of the carbon signal of the  $\text{CF}_3$  group of the alkynyl ligands at  $\delta$  113.8 ppm with a C–F coupling constant of 253.0 Hz. However, the stretching band of the triple bond at  $2121\text{ cm}^{-1}$  in the IR spectrum indicates their presence.

Mechanistically, the generation of **2** and 3,3,3-trifluoropropene from **1** might occur via oxidative addition of the alkyne at **1** to form  $[\text{Rh}(\text{H})_2(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$  (**C**), which then might rearrange to a vinylidene complex  $[\text{RhH}(\text{C}=\text{CHCF}_3)(\text{PEt}_3)_3]$  (**D**) (Scheme 3). The latter could also be formed from **1** and alkyne by a metal-mediated 1,2-hydrogen migration.<sup>[26]</sup> Subsequent migration of the hydride to the vinylidene ligand yields a vinyl complex  $[\text{Rh}(\text{CH}=\text{CHCF}_3)(\text{PEt}_3)_3]$  (**E**) (Scheme 3). Note that vinylidene complexes can often be products in the reactivity of terminal alkynes towards late transition metal complexes and ligand migration to the  $\alpha$ -carbon to furnish vinyl species is well-known.<sup>[1b, 1h, 2, 5c, 11i, 14e, 27]</sup> Alternatively, the vinyl complex **A** or **B** could be formed from **1** by an insertion mechanism. **A** or **B** gives finally with further alkyne the alkynyl complex **2** and 3,3,3-trifluoropropene.  $[\text{Rh}(\text{H})_2(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$  (**C**) is in equilibrium with dihydrogen and **2**. The presence of dihydrogen can,



therefore, result in further hydrogenation of 3,3,3-trifluoropropene to afford the corresponding alkane. The generation of **2** and the borylated olefin **6** from **5** resembles the reaction pathways for the reactivity of **1** towards the alkyne. Finally, complex **3** could be obtained by an oxidative addition of another equivalent of alkyne at **2**. In addition, complex **2** might convert with two equivalents of alkyne into **4** via an alkynyl vinylidene intermediate **F**. Note that the latter complex could also be generated by 1,3-hydrogen migration from complex **3** (Scheme 3).<sup>[26]</sup>

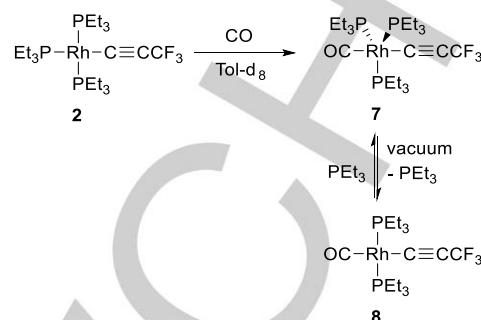


**Scheme 3** Possible mechanism for the generation of the complexes **2**, **3**, **4** and 3,3,3-trifluoropropene or **6** from **1** or **5**.

### Reactivity of $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$ (**2**) towards CO

To test the reactivity of the rhodium(I) alkynyl complex **2**,<sup>[28]</sup> carbon monoxide was added. This resulted in the bonding of a terminal carbonyl ligand producing a pentacoordinated rhodium(I) complex  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{CO})(\text{PEt}_3)_3]$  (**7**)<sup>[29]</sup> (Scheme 4). The isotopologue  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(^{13}\text{CO})(\text{PEt}_3)_3]$  (**7'**) was formed upon treatment of **2** with <sup>13</sup>CO. Complex **7** is only stable in solution, and *trans*- $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{CO})(\text{PEt}_3)_2]$  (**8**) is generated after evaporation of the solvent by the loss of a phosphine ligand.

The isotopologue *trans*- $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(^{13}\text{CO})(\text{PEt}_3)_2]$  (**8'**) was synthesised in a similar process as complex **7'**.



**Scheme 4** Reaction of rhodium(I) alkynyl complex **2** with CO.

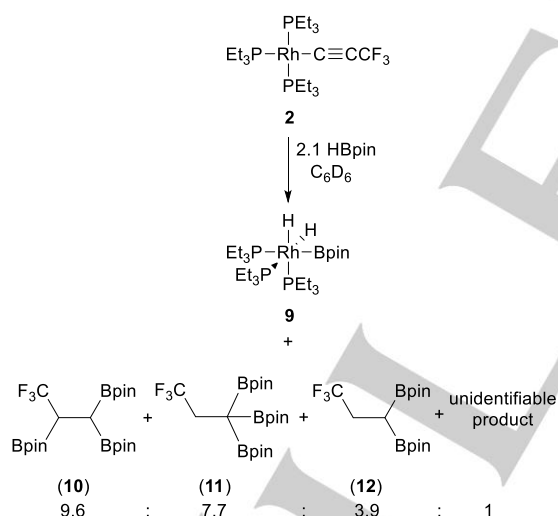
The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **7** shows a broad multiplet at room temperature. However, at 233 K a doublet of quartets is revealed at  $\delta$  11.4 ppm. The doublet results from a phosphorus coupling of 127.2 Hz to rhodium, which also provides evidence for the oxidation state of Rh(I) in carbonyl complexes.<sup>[19, 30]</sup> The quartet is associated with coupling to the trifluoromethyl group of 10.9 Hz. The presence of only one signal indicates that the PEt<sub>3</sub> ligands are equivalent on the NMR time-scale. Complex **7'** shows apart from the coupling of the phosphorus atoms to rhodium and fluorine also the carbon coupling to the labelled CO, distinguished as a doublet of quintets. This phosphorus-carbon coupling constant of 10.9 Hz agrees with the *cis*-configuration of the carbonyl and the PEt<sub>3</sub> ligands.<sup>[19, 30a, 31]</sup> In the <sup>19</sup>F NMR spectrum of **7** the CF<sub>3</sub> group appears at  $\delta$  -43.4 ppm as a quartet at 233K with a coupling to phosphorus of 8.2 Hz. The signal for the CF<sub>3</sub> group is also revealed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at  $\delta$  114.4 ppm as well as the resonance for C<sub>β</sub> at  $\delta$  100.4 ppm with coupling to fluorine of 252.6 and 45.9 Hz, respectively. The signal for C<sub>α</sub> can be distinguished at  $\delta$  124.9 ppm in the <sup>19</sup>F-<sup>13</sup>C HMBC NMR experiment as a multiplet of quartets with a coupling of 11 Hz to fluorine. The carbonyl moiety emerges at  $\delta$  201.6 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum as a broad multiplet. The <sup>13</sup>CO ligand for complex **7'** is identified at 203 K as a clear doublet of quartets accounting for the carbon-rhodium coupling of 48.7 Hz and the carbon-phosphorus coupling of 10.9 Hz further confirming the proposed structure. In the IR spectrum the absorption band for the CO ligand was measured at 1952 cm<sup>-1</sup> for the non-labelled complex **7**, which shifted to 1913 cm<sup>-1</sup> for the <sup>13</sup>C labelled complex **7'** which is consistent with CO and <sup>13</sup>CO IR spectroscopic shifts at rhodium.<sup>[30a]</sup> Finally, the alkynyl ligand exhibits a stretching band at 2110 cm<sup>-1</sup>.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 233 K of **8** revealed a doublet of quartets with a phosphorus-rhodium coupling of 118.8 Hz at  $\delta$  24.0 ppm, indicating equivalent PEt<sub>3</sub> ligands in a mutually *trans* position. In addition, there is a phosphorus-fluorine coupling of 5.1 Hz. The CF<sub>3</sub> group appears in the <sup>19</sup>F NMR spectrum at  $\delta$  -44.4 ppm as a triplet at 213K with a coupling to phosphorus of 4.6 Hz. Furthermore, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum verifies the

presence of the alkynyl ligand as well as of the carbonyl ligand with similar chemical shifts and coupling constants as for complex **7**. In contrast to **7**, the resonance for  $C_\alpha$  in the alkynyl ligand of complex **8** is detectable at  $\delta$  125.8 ppm with a carbon-fluorine coupling constant of 6.5 Hz. The  $^{13}\text{C}$  ligand in **8'** appears at  $\delta$  194.8 ppm at 203 K as a doublet of triplets with a carbon-rhodium coupling of 59.4 Hz and carbon-phosphorus coupling of 13.8 Hz confirming the equivalence of  $\text{PEt}_3$  ligands. The absorption band in the IR spectrum shifted from  $1966\text{ cm}^{-1}$  for the non-labelled complex **8** to  $1919\text{ cm}^{-1}$  for the  $^{13}\text{C}$  labelled complex **8'**. In addition, LIFDI-MS provided the mass peak at  $m/z$  460 for complex **8**.

### Reactivity of $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$ (**2**) towards HBpin

With the intention to develop hydroboration reactions,<sup>[11b-f, 11h, 11i, 27a]</sup> the rhodium(I) complex **2**<sup>[28]</sup> was treated with an excess of HBpin. In  $\text{C}_6\text{D}_6$ , the rhodium complex *fac*- $[\text{Rh}(\text{H})_2(\text{Bpin})(\text{PEt}_3)_3]$  (**9**)<sup>[32]</sup> and the products of borylation and hydroboration reactions  $\text{CF}_3\text{CH}(\text{Bpin})\text{CH}(\text{Bpin})_2$  (**10**) and  $\text{CF}_3\text{CH}_2\text{C}(\text{Bpin})_3$  (**11**) were generated as the main organic products. In addition,  $\text{CF}_3\text{CH}_2\text{CH}(\text{Bpin})_2$  (**12**)<sup>[32]</sup> and an unidentifiable product were observed in a 9.6:7.7:3.9:1 ratio of organic products after 3 h (Scheme 5). The NMR spectroscopic data and mass data for **10** and **11** are shown in Table 1 while the unidentifiable product could bear a  $\text{CF}_3\text{CH}(\text{Bpin})$  fragment due to the doublet at  $-64.9$  ( $J(\text{F},\text{H})=11.9\text{ Hz}$ ) ppm in the  $^{19}\text{F}$  NMR spectrum.



**Scheme 5** Hydroboration of 3,3,3-trifluoropropyne at complex **2**.

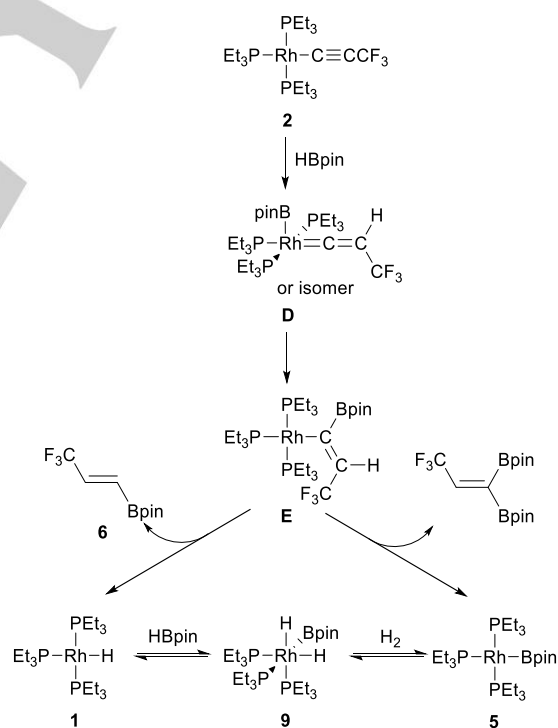
For the formation of compounds **10**, **11** and **12**, it can be presumed that borylated olefins such as compound **6** are intermediates. Therefore, the initial generation of the vinylidene complex  $[\text{Rh}(\text{Bpin})(=\text{C}=\text{CHCF}_3)(\text{PEt}_3)_3]$  (**D**) is conceivable and consistent by the stoichiometric reaction of **5** with the alkyne (Scheme 3). As outlined before, the proposed vinylidene **D** can then rearrange to the vinyl complex **E** by boryl migration. Then, a subsequent reaction with HBpin can release compound **6** or a diborylated fluorinated alkene, as well as **5** and **1** can be formed. Overall, rhodium-catalysed hydroboration and dehydrogenative

borylation steps might consecutively occur, leading to the mixture of borylated alkenes obtained.<sup>[32-33]</sup> *fac*- $[\text{Rh}(\text{H})_2(\text{Bpin})(\text{PEt}_3)_3]$  (**9**) was obtained as the main rhodium complex, the generation of which can be explained by the oxidative addition of  $\text{H}_2$  or HBpin to **5** or **1**, respectively (Scheme 6).<sup>[16e, 32, 34]</sup> Note that the  $\text{H}_2$  could originate from dehydrogenative borylation steps which have been previously proposed in hydroboration reactions of fluorinated olefinic compounds.<sup>[32]</sup>

**Table 1.** NMR spectroscopic and mass spectrometric data for **10** and **11**

Compound	$^{19}\text{F}$ NMR (ppm)	$^1\text{H}$ NMR <sup>a</sup> (ppm)	GC-MS ( $m/z$ )
<b>10</b>	-63.4 (d, $\text{CF}_3$ , $^3J(\text{F},\text{H}) = 12\text{ Hz}$ )	2.54 (qd, $^3J(\text{H},\text{F}) = 12.9\text{ Hz}$ , $^3J(\text{H},\text{H}) = 8.9\text{ Hz}$ , $\text{CF}_3\text{CH}$ ); 1.43 (m, $\text{CH}(\text{Bpin})_2$ ) <sup>b</sup>	476 [M] <sup>+</sup>
<b>11</b>	-63.5 (t, $\text{CF}_3$ , $^3J(\text{F},\text{H}) = 12\text{ Hz}$ )	2.94 (q, $^3J(\text{H},\text{F}) = 11.5\text{ Hz}$ , $\text{CH}_2$ )	461 [M-CH <sub>3</sub> ] <sup>+</sup>

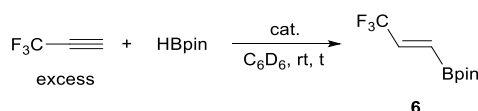
[a] Proton signals of Bpin group cannot be assigned due to the mixture of products. [b] Observed by  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum due to overlap with signals of the  $\text{PEt}_3$  ligand.



**Scheme 6** Possible mechanism for the reaction of **2** with HBpin; **10**, **11** and **12** are then subsequent products of hydroboration, hydrogenation and dehydrogenative borylation reactions.

### Catalytic Hydroboration of 3,3,3-Trifluoropropyne

In previous works, our group has shown the high activity of complex **1** towards catalytic C–F bond activation and hydroboration reactions of different fluorinated compounds,<sup>[32, 34]</sup> however fluorinated alkynes have yet to be tested. Therefore, in a catalytic reaction HBpin and an excess amount of 3,3,3-trifluoropropyne afforded the anti-Markovnikov hydroborated product (*E*)-CF<sub>3</sub>CH=CHBpin (**6**) in the presence of complex **1**. The reaction takes place with a high selectivity at room temperature in C<sub>6</sub>D<sub>6</sub> in a high yield and full conversion after 10 min (Scheme 7).



**Scheme 7** Catalytic hydroboration of 3,3,3-trifluoropropyne.

These reaction conditions are in contrast to an alternative copper-catalyzed defluoroborylation at 2,3,3,3-tetrafluoropropene to access **6** which requires higher temperature and longer reaction time.<sup>[23]</sup> Noteworthy is that C–C coupling products<sup>[1e, 2, 35]</sup> are not observed due to the faster reactivity of HBpin in comparison to the alkyne. For comparison, the new rhodium alkynyl complexes were used as catalysts obtaining similar results (Table 2). The alkene **6**, which is also obtained in stoichiometric amounts in the reaction of **5** and the fluorinated alkyne (Scheme 2), could be an important building block for further coupling reactions.<sup>[36]</sup>

**Table 2.** Catalysts comparison of the catalytic hydroboration of 3,3,3-trifluoropropyne to form **6**.

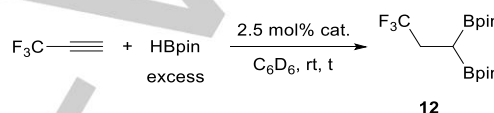
Catalyst	mol%	t	Conversion (%) <sup>a</sup>	Yield (%) <sup>b</sup>
<b>1</b>	8.5	10 min	> 99	94
<b>1</b>	5.0	4 h	> 99	96
<b>2</b>	5.0	3 h	> 99	96
<b>3</b> and <b>4</b> (ratio 5:1)	5.6	5h	> 99	94

[a] Based on HBpin consumption. [b] Based on NMR measurements.

For the catalytic conversions, several different mechanisms are conceivable. On the one hand, the rhodium hydrido complex **1** can form the borylated olefin **6** by an initial insertion of the alkyne to form the β-CF<sub>3</sub>-vinyl complex **A** which reacts further with HBpin to recover the catalyst and release the olefin by an oxidative addition-reductive elimination reaction (Scheme 8c). Complex **5** would present a similar behaviour when acting as a catalyst, although the insertion step would lead to the α-CF<sub>3</sub> vinyl complex **B** in order to finally release the *trans* olefin **6** (Scheme 8b). On the other hand, when complex **2** is used as a catalyst, the vinyl complex **E** could be generated by an initial oxidative addition of HBpin to form **C** followed by further rearrangement to

the vinylidene complex **D** and final migration of the Bpin ligand (Scheme 8a) as suggested for the stoichiometric reaction of **2** with HBpin (see above). As it was already mentioned, complex **3** might be a source of the alkynyl complex **2** leading to the same catalytic mechanism.

As it is known, alkenes can easily undergo hydroboration reactions.<sup>[32-33, 33c, 33d, 37]</sup> Therefore, the hydroboration reaction of compound **6** would lead to a diborylated trifluoropropane derivative. Compound **6** did not react with HBpin without an active catalyst, however, after isolation of the monoborylated olefin **6**, it can be completely converted into the dihydroborated product CF<sub>3</sub>CH<sub>2</sub>CH(Bpin)<sub>2</sub> (**12**) using rhodium(I) hydrido complex **1** in catalytic amounts in the presence of an excess of HBpin. In addition, the same product **12** is regioselectively obtained when HBpin is added in excess using different rhodium complexes as catalysts in the presence of 3,3,3-trifluoropropyne (Scheme 9).



**Scheme 9** Catalytic hydroboration of 3,3,3-trifluoropropyne with an excess amount of HBpin.

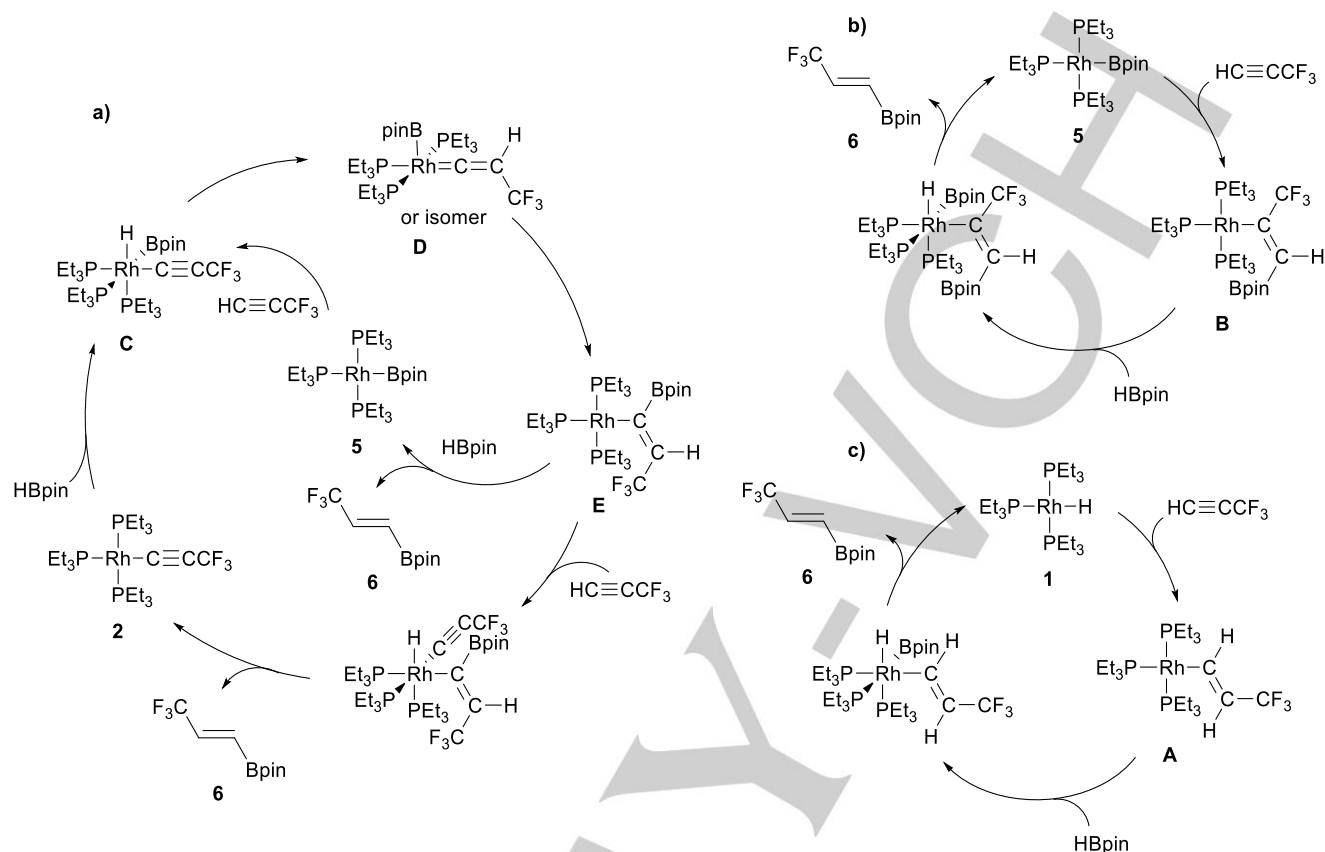
Similar to the monoborylation reaction, the three catalysts under study are equally efficient although the reaction time increases when using the mixture of **3** and **4**. The NMR monitoring of the latter reaction showed, with a 94% conversion of alkyne, the initial formation of 91% of compound **6** after 25 min. After that, the signals of compound **12** started to appear reaching the full conversion of the olefin to the diborylated alkane after 3h (Table 3). Note that rhodium(I) carbonyl complex **8** cannot catalyze the mono or dihydroboration reactions.

**Table 3.** Catalyst comparison of the catalytic hydroboration of 3,3,3-trifluoropropyne with an excess amount of HBpin to form **12**.

Catalyst	t	Conversion (%) <sup>a</sup>	Yield (%) <sup>b</sup>
<b>1</b>	20 min	> 99	96
<b>2</b>	10 min	> 99	95
<b>3</b> and <b>4</b> (ratio 5:1)	3 h	> 99	97

[a] Based on gas consumption. [b] Based on NMR measurements.

This synthesis differs to the previous work of our group where compound **12** could be obtained by the defluorohydroboration of hexafluoropropene or dehydrogenative hydroboration of trifluoropropene in a less selective way.<sup>[32]</sup> To the best of our knowledge, this is the first time that compound **12** can be generated in an efficient and highly selective hydroboration reaction. Note also that the triborylated derivatives **10** and **11** are observed in traces, in contrast to the stoichiometric reaction of **2** with HBpin where the main products were the triborylated species.



**Scheme 8.** Proposed mechanisms for the catalytic hydroboration of 3,3,3-trifluoropropyne.

## Conclusions

In conclusion, we have synthesised a series of trifluoroalkynyl rhodium complexes, which could undergo further coupling reactions to generate C–H, C–C or C–B bonds. Reactions of the rhodium(I) alkynyl complex **2** with CO provided new complexes. Catalytically, in a highly selective manner the trifluoropropene boryl derivative **6** or its hydroboration product **12** were obtained using different rhodium complexes as catalysts. The presence of HBpin suppresses the formation of other organic derivatives through C–C coupling reactions such as enynes. The catalytic studies performed with 3,3,3-trifluoropropyne might pave routes for the functionalization of fluorinated alkynes via the borylated olefins.

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**Keywords:** fluorine • rhodium • fluorinated alkynes • hydroboration • fluorinated ligands

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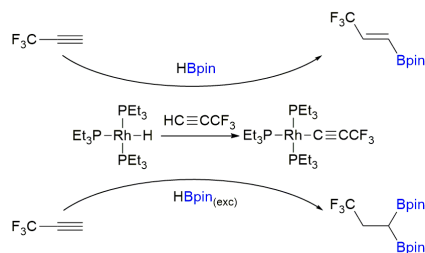


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## Entry for the Table of Contents

## FULL PAPER

Rhodium(I) complexes react to yield new alkynyl and vinyl complexes. These complexes selectively catalyse hydroboration reactions of 3,3,3-trifluoropropyne.



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Conghui Xu,<sup>[a]</sup> and Thomas Braun<sup>\*[a]</sup>

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**Reactivity of 3,3,3-Trifluoropropyne at Rhodium Complexes: Development of Hydroboration Reactions**