Insertion of Diphenylacetylene into Rh-hydride and Rh-boryl Bonds: Influence of the Boryl on the Behavior of the *β*-borylalkenyl Ligand

Sheila G. Curto, Miguel A. Esteruelas,* Montserrat Oliván, and Enrique Oñate

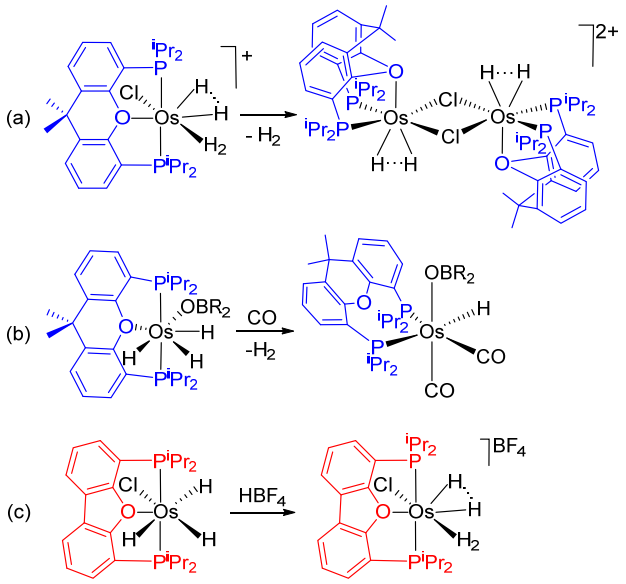
Departamento de Química Inorgánica – Instituto de Síntesis Química y Catálisis Homogénea (ISQCH) – Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Zaragoza – CSIC, 50009 Zaragoza, Spain

ABSTRACT: Reactions of complexes RhH{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**1**) and Rh(Bpin){κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**2**; Bpin = pinacolboryl, xant(P^iPr_2)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) with diphenylacetylene have been studied. Complex **1** reacts with the alkyne to give the *E*-alkenyl derivative Rh{(*E*)-C(Ph)=CHPh}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**3**) as a result of the *syn*-addition of the Rh-H bond to the C-C triple bond. In benzene, at room temperature, complex **3** is unstable and slowly evolves into its *Z*-alkenyl isomer Rh{(*Z*)-C(Ph)=CHPh}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**4**), which is also unstable and undergoes an alkenyl-to-*ortho*-alkenylaryl transformation to afford Rh{C_6H_4-2-(*E*-CH=CHPh)}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**5**). The latter adds HBpin. The resulting rhodium(III) species, RhH(Bpin){C_6H_4-2-(*E*-CH=CHPh)}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**6**), eliminates *trans*-4,4,5,5-tetramethyl-2-(2-styrylphenyl)-1,3,2-dioxaborolane and regenerates **1**, closing a cycle for the hydroboration of the alkyne to the *ortho*-alkenyl-aryl compound. However, this cycle is not catalytic. The direct reaction of the alkyne with the borane in presence of **1** leads to *Z*,*E*-mixtures of PhCH=C(Ph)Bpin. Diphenylacetylene also undergoes *syn*-addition of the Rh-B bond of **2**. The Bpin group accelerates the isomerization of the alkenyl ligand. Thus, the resulting *E*-*β*-borylalkenyl derivative Rh{(*E*)-C(Ph)=C(Bpin)Ph}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**7**) rapidly evolves into its *Z*-isomer Rh{(*Z*)-C(Ph)=C(Bpin)Ph}}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**8**), which also undergoes alkenyl-to-*ortho*-alkenylaryl transformation to give Rh{C_6H_4-2-[*E*-CH=C(Bpin)Ph]}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**9**). However, in contrast to **5**, complex **9** is less stable than its precursor **8**.

INTRODUCTION

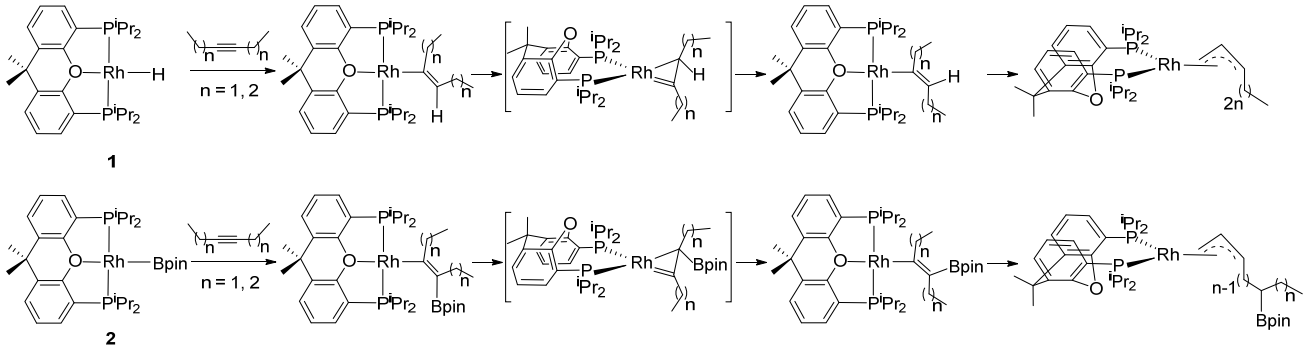
9,9-Dimethyl-4,5-bis(diisopropylphosphino)xanthene (xant(P^iPr_2)$_2$) is an ether-diphosphine,[1] which has demonstrated a higher capacity than other related diphosphines, such as its diphenyl-counterpart[2] xant(PPh_2)$_2$ or bis[(2-diphenylphosphino)phenyl]ether (DPEphos),[3] to coordinate κ^3-P,O,P-*mer*. Because of this notable ability, it can stabilize uncommon species as the *mer*-tris(boryl) derivative Ir(Bcat)$_3${κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (Bcat = catecholboryl), which challenges the concept of *trans*-influence.[4] In spite of this marked trend to act as pincer, it is a very valuable ligand because of its functional flexibility, which allows it to adapt its coordination to the steric and electronic requirements of the complexes to be stabilized (Scheme 1). It changes the coordination from *mer* to *fac* to minimize the steric hindrance between the P^iPr_2 groups, when the complex is a dimer (a),[5] or releases the oxygen atom to act as κ^2-P,P-bidentate when replacing hydride by carbonyl (b).[6] The change *mer* to *fac* is a consequence of the structural flexibility of the xanthene linker. In contrast to the latter, the more rigid dibenzofuran prevents the change and the formation of the dimer (c).[5,7]

Scheme 1. Structural Flexibility of xant(P^iPr_2)$_2$



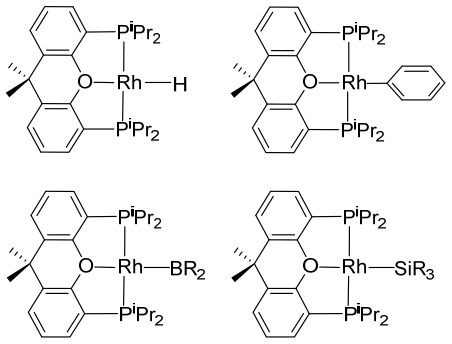
The π-donor ability of the xanthene oxygen atom increases the ligand value. Platinum group metal complexes containing 1-e$^-$ donor ligands are almost invariably saturated and resist

Scheme 2. Reactions of 1 and 2 with Bis(alkyl)alkynes

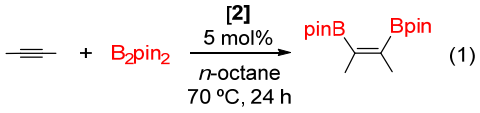


becoming unsaturated without the presence of a π-donor co-ligand or the steric protection of the metal center, as for example that provided by three phosphines in square planar rhodium(I) derivatives.[8] The π-donor co-ligand partially cancels the unsaturated character of the metal center. Thus, the formation of the pincer by coordination of the oxygen atom allows xant(P^iPr_2)$_2$ to stabilize square-planar hydride,[9] aryl,[10] boryl,[10a] and silyl[11] complexes of rhodium(I) without the above mentioned protection (Chart 1). This, along with the oxygen lability of the ligand, was revealed as key for developing catalysis with these compounds,[12] including borylation reactions[10a,13] that have particular interest because of the relevance of C-B bonds in organic synthesis.[14]

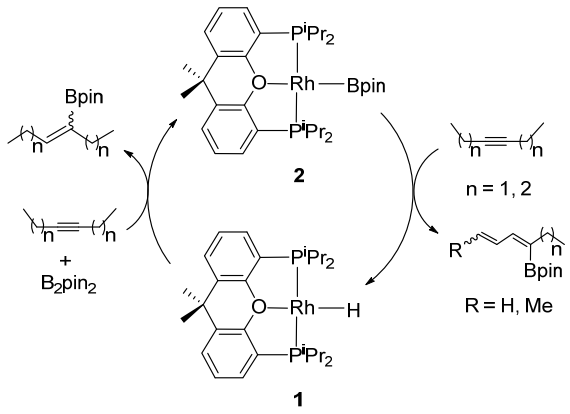
Chart 1. Square-planar Rhodium Complexes Stabilized by the xant(P^iPr_2)$_2$ Ligand



Hydride RhH{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**1**) and pinacolboryl Rh(Bpin){κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**2**) complexes add the Rh-H and Rh-B bonds to the C-C triple bond of bis(alkyl)alkynes, in a *syn*-manner.[13] The formed *E*-bis(alkyl)-alkenyl derivatives evolve into *Z*-bis(alkyl)-alkenyl counterparts, via four-coordinate rhodacyclopropene intermediates, resulting from the release of the xanthene oxygen and the coordination of the alkenyl-C$_\beta$ atom.[13a] The stability of these alkenyl species depends upon the length of the chain attached to the C$_\alpha$ atom. Chains longer than methyl undergo C$_\gamma$-H bond activation to form four-coordinate allyl compounds, bearing a κ^2-P,P-bidentate phosphine (Scheme 2).[13b] In the presence of bis(pinacolato)diboron, the alkenyl-isomerization, the C$_\gamma$-H bond activation, and the reaction with the diborane are competitive processes. As a consequence, complexes **1** and **2** catalyze borylation reactions to yield products that depend upon the alkyl substituent. 2-Butyne selectively affords (Z)-pinBC(Me)=C(Me)Bpin (eq 1),[13a] whereas 3-hexyne and 4-octyne give equimolecular mixtures of conjugated boryldienes and borylolefins (Scheme 3). The mixture is generated through a catalytic cycle formed by two stoichiometric reactions on the alkyne, a dehydrogenative borylation and a hydroborylation, in which **1** and **2** collaborate. Complex **2** promotes the dehydrogenative borylation to afford **1**. The latter is responsible of the hydroborylation, which regenerates **2**. The end result is the addition of the B-B bond of the diborane to different molecules of alkyne and a hydride transfer from one to the other.[13b]



Scheme 3. Borylation of 3-Hexyne and 4-Octyne



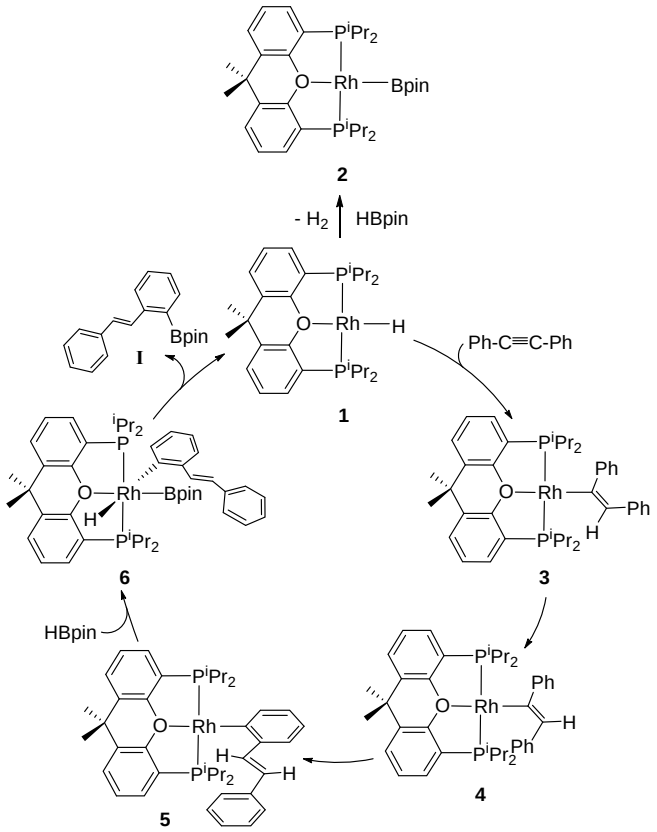
The relevance of the borylation processes to develop compounds bearing B-C bonds and the fascinating behavior of **1** and **2** with bis(alkyl)alkynes prompted us to study the reactions of both complexes with diphenylacetylene and the behavior of the resulting species with HBpin and B_2pin_2, respectively. This paper shows the influence of a Bpin substituent at the C$_\beta$ atom of the alkenyl group on the alkenyl-isomerization, the stability of the *ortho*-alkenylaryl compounds resulting of alkenyl-to-alkenylaryl transformations, and the reactions of the alkenyl and *ortho*-arylalkenyl complexes with B_2pin_2 and HBpin, respectively.

RESULTS AND DISCUSSION

Reactions of 1. The addition of diphenylacetylene to pentane solutions of **1** instantaneously gives the *E*-alkenyl derivative Rh{(*E*)-C(Ph)=CHPh}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**3**), as a result of the *syn*-addition of the C-C triple bond of the alkyne

into the Rh-H bond (Scheme 4). The reaction was performed at room temperature and the product was isolated as a red solid in 89% yield. Assignment of the product is strongly supported by the $^{13}C\{^1H\}$ NMR spectrum of the red solid in toluene-d_8, at 253 K, which shows at 168.4 ppm a doublet of triplets with C-Rh and C-P coupling constants of 40.1 and 12.1 Hz, respectively, corresponding to the alkenyl C_α-atom. The $^{31}P\{^1H\}$ NMR spectrum displays a doublet ($^1J_{P\text{-}Rh}$ = 182.4 Hz) at 32.8 ppm, as expected for a *mer*-coordination of the pincer with equivalent P^iPr_2 groups.

Scheme 4. Stoichiometric Reactions of 1, 3, 4, 5, and 6



Complex **3** is unstable in benzene solution and evolves into its *Z*-isomer Rh{(*Z*)-C(Ph)=CHPh}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**4**), in agreement with that observed for bis(alkyl)alkynes.[13] Noticeable spectroscopic features of the new species are a doublet of triplets ($^1J_{C\text{-}Rh}$ = 42.5 Hz and $^2J_{C\text{-}P}$ = 11.8 Hz) at 168.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum, due to the alkenyl C_α atom, and a doublet ($^1J_{P\text{-}Rh}$ = 177.6 Hz) at 33.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum, corresponding to the pincer. This compound is also unstable and undergoes the transformation into the functionalized aryl derivative Rh{C_6H_4-2-(*E*-CH=CHPh)}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**5**) before the alkenyl isomerization is finished. After 30 min, at 50 ºC, the **3**:**4**:**5** molar ratio is 31:45:24. As expected for a M-aryl bond stronger than a M-alkenyl bond,[15] the aryl derivative **5** is the only species in solution after 4 h.

The *ortho*-alkenylaryl complex **5** was isolated as a red solid in 78% yield and characterized by X-ray diffraction analysis. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 1 shows one of them. The most noticeable molecular feature is the *E*-stereochemistry (*trans*-diphenyl) at the C-C double bond of the aryl substituent, which is consistent with the isomerization followed by CH bond activation. In accordance with the *mer*-coordination of the etherdiphosphine, the Rh{xant(P^iPr_2)$_2$} skeleton is T-shaped with the rhodium atom in the common vertex. The geometry around the metal center can be rationalized as square-planar with the aryl ligand disposed *trans* to the phosphine oxygen atom. The Rh(1)-C(1) distances of 1.993(8) and 2.007(8) Å lie within the range reported for the scarcely characterized square-planar arylrhodium(I) compounds (1.84-2.10 Å).[10,16] In agreement with the *E*-stereochemistry at the C-C double bond of the aryl ligand, the ^1H NMR spectrum of the obtained red solid, in benzene-d_6, at room temperature contains two doublets, at 9.17 (C(7)H) and 7.52 (C(8)H) ppm, with a characteristic *trans* H-H coupling constant of 16.5 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the metalated aryl carbon atom C(1) is observed as a doublet of triplets ($^1J_{C\text{-}Rh}$ = 42.3 Hz and $^2J_{C\text{-}P}$ = 11.8 Hz) at 168.7 ppm, whereas the signals corresponding to the olefinic C(7) and C(8) atoms appear at 141.4 ($^3J_{C\text{-}Rh}$ = 3.3 Hz) and 122.3 ppm, respectively.[17] The $^{31}P\{^1H\}$ NMR spectrum shows a doublet ($^1J_{P\text{-}Rh}$ = 174.7 Hz) at 36.7 ppm, as expected for equivalent P^iPr_2 groups.

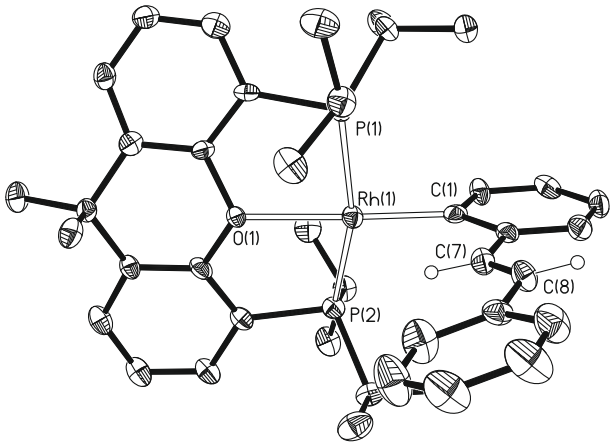
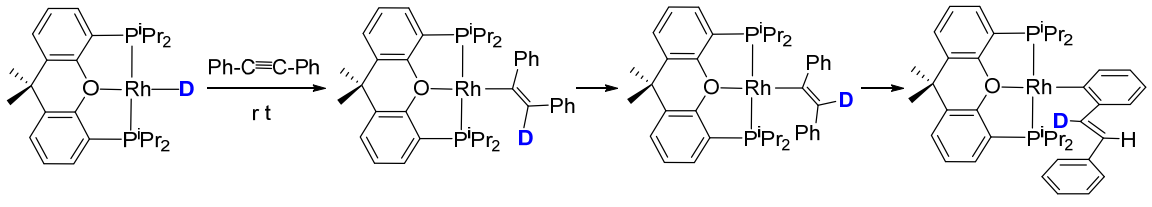


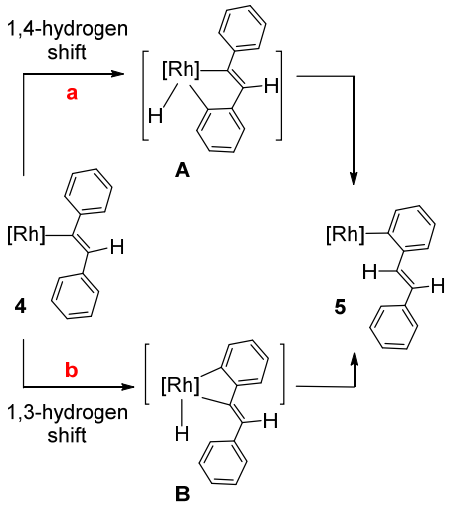
Figure 1. Molecular diagram of complex **5** (ellipsoids shown at 50% probability). All hydrogen atoms (except those of the alkenyl group) are omitted for clarity. Selected bond distances (Å) and angles (deg) for the two independent molecules in the asymmetric unit: Rh(1)-P(1) = 2.244(2), 2.251(2); Rh(1)-P(2) = 2.228(2), 2.246(2); Rh(1)-O(1) = 2.226(5), 2.218(5); Rh(1)-C(1) = 1.993(8), 2.007(8); C(7)-C(8) = 1.334(12), 1.339(11); P(1)-Rh(1)-P(2) = 162.27(6), 161.49(8); P(1)-Rh(1)-O(1) = 82.16(15), 82.29(15); P(2)-Rh(1)-O(1) = 83.04(15), 82.05(15); O(1)-Rh(1)-C(1) = 177.3(3), 177.9(3); P(1)-Rh(1)-C(1) = 97.1(2), 99.0(2); P(2)-Rh(1)-C(1) = 97.2(2), 96.4(2).

The transformation of **4** into **5** can be rationalized according to Scheme 5; i. e., the process could imply a rhodium-mediated 1,4-hydrogen shift from the phenyl substituent attached at the alkenyl C_β atom to the alkenyl C_α atom (a) or alternatively a rhodium-mediated 1,3-hydrogen shift from the phenyl substituent attached at C_α to C_α (b). The former should take place via the five-membered rhodacycle intermediate **A**, whereas the second pathway should proceed through the four-membered rhodacycle **B**.

Scheme 6. Reaction of 1-d_1 with Diphenylacetylene



Scheme 5. Plausible Pathways for the Transformation from 4 into 5



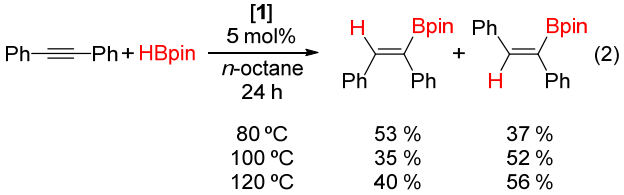
[Rh] = Rh{xant(P^iPr_2)$_2$}

The reaction of the deuteride complex RhD{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**1-d_1**) with diphenylacetylene was performed in order to know the pathway for the formation of **5**. The addition of 1.0 equiv of the alkyne to both benzene-d_6 and benzene solutions of **1-d_1** selectively led to Rh{C_6H_4-2-(*E*-CD=CHPh)}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**5-d_1**. δ_D, 9.14; $\delta_{C(8)H}$, 7.53 (s)), containing the deuterium atom at the olefinic C(7) position, after 4 h at 50 ºC. In agreement with Scheme 4 the transformation took place through the respective isomers **3-d_1** and **4-d_1** (Scheme 6). The position of the deuterium atom suggests that the formation of **5** from **4** takes place via pathway a of Scheme 5 by 1,4-hydrogen shift involving oxidative addition followed by reductive elimination.

Ortho-alkenylaryl complexes are rare. Chirik and co-workers have described the preparation of four-coordinate cobalt(I) derivatives by a similar procedure to that summarized by Schemes 4 and 5, which involves insertion of diphenylacetylene into Co-R bonds (R = H, CH_3) and subsequent 1,3- or 1,4-hydrogen shift.[18] Vicente and co-workers have reported the formation of *ortho*-alkenylaryl-palladium complexes by Wittig reaction of *ortho*-formylaryl-palladium precursors with ylides RCH=PPh_3 [19] and by oxidative addition of alkenyl substituted arylbromides to Pd(dba)$_2$ (dba = dibenzylideneacetone).[20] Palladium(II) and nickel(II) compounds have been prepared by reactions of *trans*-dihalo-bis(phosphine)-metal precursors with 2-vinylphenylmagnesium halides.[21] We have shown that the treatment of OsCl{(*E*)-CH=CHPh}(CO)(P^iPr_3)$_2$ with phenyllithium produces a phenyl-styryl coupling, which leads to an osmium(0)-(*trans*-stilbene) intermediate. The latter experiences aromatic *ortho*-CH bond activation to finally give OsH{C_6H_4-2-(*E*-CH=CHPh)}(CO)(P^iPr_3)$_2$.[22]

Complex **5** reacts with pinacolborane, in benzene, at 60 ºC to quantitatively give *trans*-4,4,5,5-tetramethyl-2-(2-styrylphenyl)-1,3,2-dioxaborolane (**I**) and to regenerate the monohydride **1**.[23] The reaction takes place via the hydride-boryl-rhodium(III) intermediate RhH(Bpin){C_6H_4-2-(*E*-CH=CHPh)}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**6**), which undergoes reductive elimination of the boronic ester. Noticeable spectroscopic features of **6** are a broad resonance at -5.99 ppm in the ^{1}H NMR spectrum, corresponding to the hydride ligand, and a doublet at 69.5 ppm in the ^{31}P{^{1}H} NMR spectrum, due to the diphosphine, which displays a typical P-Rh(III) coupling constant of 128.7 Hz.

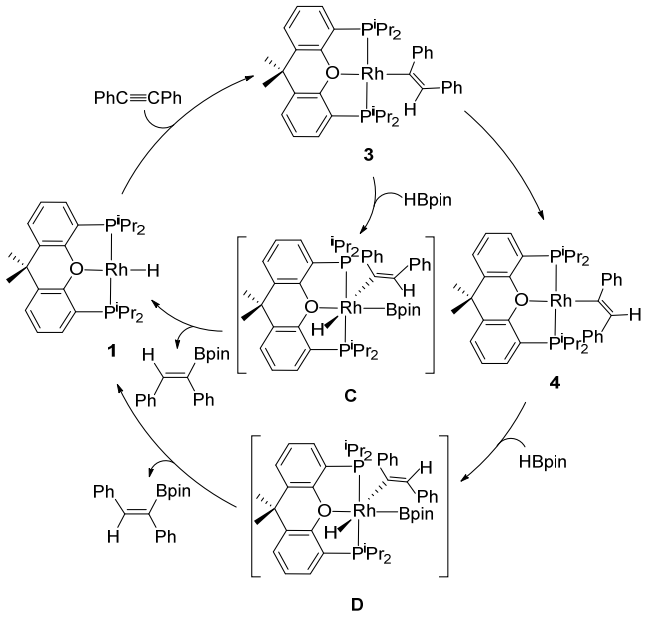
Scheme 4 shows a cycle for the addition of pinacolborane to diphenylacetylene, which affords *trans*-4,4,5,5-tetramethyl-2-(2-styrylphenyl)-1,3,2-dioxaborolane. In order to know the catalytic feasibility of the process, we performed the direct reaction of HBpin with diphenylacetylene, in octane, under argon, using 5 mol% of complex **1** as catalyst, and 0.18 M of borane and alkyne, in the temperature range 80-120 ºC. Under these conditions, the formation of the borylated *ortho*-alkenyl-aryl compound was not detected. In contrast, the almost quantitative transformation of the reagents (about 90%) into *Z*:*E* mixtures of PhCH=C(Ph)Bpin was observed, after 24 h. The *Z*:*E* molar ratio depends upon the reaction temperature, decreasing as the temperature increases (eq 2).



These results indicate that the cycle shown in Scheme 4 is not catalytic. The catalysis would imply the oxidative addition of the H-B bond of the borane to **3** and **4** and the subsequent reductive elimination of the borylated olefin from the corresponding hydride-boryl-alkenyl-rhodium(III) intermediates related to **6** (**C** and **D** in Scheme 7). According to the absence of borylated *ortho*-alkenyl-aryl compound in the catalytic mixture, both processes are faster than the formation of **5**.

However, they are competitive with the isomerization from **3** into **4**; i. e., the oxidative addition to **3** and **4** and the subsequent reductive eliminations have activation energies similar to the alkenyl isomerization and lower than the alkenyl-to-*ortho*-alkenylaryl transformation.

Scheme 7. Catalytic Cycle for the Hydroboration of Diphenylacetylene



Reactions of 2. Diphenylacetylene also undergoes *syn*-insertion into the Rh-B bond of **2**. The reaction leads to the *E*-*β*-borylalkenyl derivative Rh{(*E*)-C(Ph)=C(Bpin)Ph}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**7**), the boryl counterpart of **3** (Scheme 8). Nevertheless, complex **7** is much less stable than **3**. It was only observed and characterized at -20 ºC, in toluene solution. At room temperature, the rapid isomerization of the alkenyl group takes place, which gives rise to Rh{(*Z*)-C(Ph)=C(Bpin)Ph}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**8**), the boryl counterpart of **4**. Like the latter, complex **8** undergoes a alkenyl-to-*ortho*-alkenylaryl transformation, which affords Rh{C$_6$H$_4$-2-[*E*-CH=C(Bpin)Ph]}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**9**). However, in this case the *β*-borylalkenyl complex **8** is more stable than the *ortho*-alkenylaryl **9**. Both compounds form an equilibrium mixture, which displays an **8**:**9** molar ratio of 7:3, at room temperature.

The *β*-borylalkenyl complex **8** was separated from the mixture as red crystals suitable for X-ray diffraction analysis characterization. The structure (Figure 2) proves the disposition mutually *trans* of the phenyl groups at the alkenyl C-C double bond. The *β*-borylalkenyl ligand lies *trans* to the oxygen atom of the diphosphine (C(1)-Rh-O(2) = 169.3(3)º), which coordinates *mer* (P-Rh-P = 163.11(6)º and P-Rh-O(2) = 81.56(3)º) in a square-planar environment. The Rh-C(1) and C(1)-C(8) distances of 2.028(11) and 1.347(13) Å, respectively, compare well with those reported for other rhodium-alkenyl derivatives.[8a,13,24]

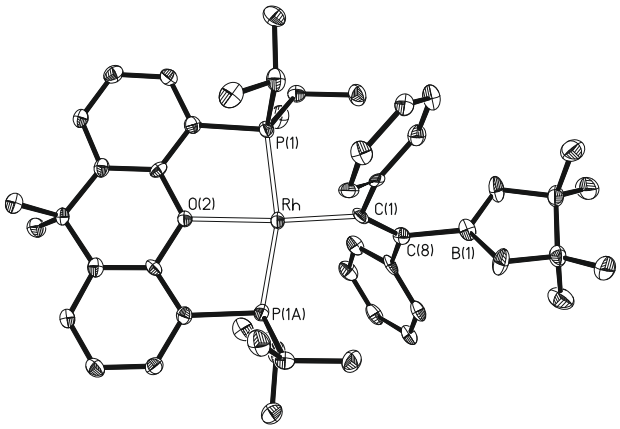
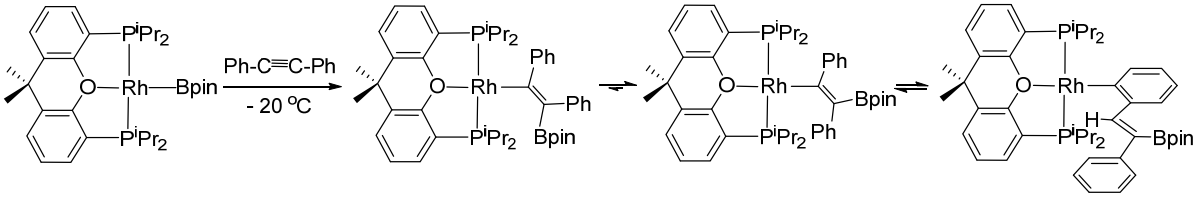


Figure 2. Molecular diagram of complex **8** (ellipsoids shown at 50% probability). All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh-P(1) = 2.2560(12), Rh-O(2) = 2.243(5), Rh-C(1) = 2.028(11), C(1)-C(8) = 1.347(13), P(1)-Rh-P(1A) = 163.11(6); P(1)-Rh-O(2) = 81.56(3), O(2)-Rh-C(1) = 169.3(3), P(1)-Rh-C(1) = 95.3(4).

The increase of the rate of the alkenyl isomerization, as a consequence of the replacement of the C$_\beta$H-hydrogen atom by a Bpin group, appears to be due to an increase of the contribution of the resonance form Rh$^+$=C(Ph)-C$^-$(Bpin)Ph to the Rh-alkenyl bond. The increment of both the nucleophilic power of the alkenyl C$_\beta$ atom and the double bond character of Rh-C$_\alpha$ favor the formation of the rhodacyclopropene intermediate, which is the key for the isomerization. The increase of the strength of the Rh-C$_\alpha$ bond in **7** and **8**, with regard to **3** and **4**, is strongly supported by the ^{13}C{^{1}H} NMR spectra, which show the resonance corresponding to the alkenyl C$_\alpha$ atom at 191.3 ($^1J_{C\text{-}Rh}$ = 42.0 Hz and $^2J_{C\text{-}P}$ = 8.3 Hz) ppm for **7** and at 184.8 ($^1J_{C\text{-}Rh}$ = 41.7 Hz and $^2J_{C\text{-}P}$ = 11.2 Hz) ppm for **8**, shifted by about 23 and by about 16 ppm towards lower field than that observed for the respective counterparts. The increase of strength of the Rh-C$_\alpha$ bond[25] in **8** could be also responsible of the inversion of stabilities, in the equilibrium between the alkenyl and *ortho*-alkenylaryl species, which results from the H/Bpin replacement. In this context, it should be mentioned that is the M-C bond strengths that dominate in the determination of the position of the hydrocarbon activation equilibria.[15] Interestingly the ^{1}H NMR spectrum of **9** shows the olefinic CH resonance at 10.86 ppm. This chemical shift agrees well with that of the C(7)H hydrogen atom of **5** and suggests that the formation of **9** takes place via 1,3-hydrogen shift (pathway b in Scheme 5), in contrast to **5**. In agreement with the latter, the ^{13}C{^{1}H} NMR spectra displays the resonance due to the

Scheme 8. Reaction of 2 with Diphenylacetylene



metalated carbon atom at 161.4 ppm, as a doublet of triplets with C-Rh and C-P coupling constants of 42.0 and 12.7 Hz, respectively. As expected for equivalent P^iPr_2 groups, the three boryl derivatives display a doublet between 30 and 35 ppm in the respective $^{31}P\{^1H\}$ NMR spectrum. A broad resonance at about 31 ppm in the ^{11}B NMR spectra is also a characteristic feature of these compounds.

The equilibrium mixture of **8** and **9** does not react with B_2pin_2, in contrast to that previously observed for Rh{C(alkyl)=C(Bpin)alkyl}{κ³-P,O,P-[xant(P^iPr_2)$_2$]} complexes.[13] As a consequence, complex **2** is not an active catalyst for the diboration of diphenylacetylene.

CONCLUDING REMARKS

This study shows that diphenylacetylene undergoes *syn*-insertion into the Rh-H and Rh-B bonds of RhH{κ³-P,O,P-[xant(P^iPr_2)$_2$]} and Rh(Bpin){κ³-P,O,P-[xant(P^iPr_2)$_2$]} to give the respective *E*-alkenyl derivatives. These species are not stable and evolve into their *Z*-alkenyl isomers, which experience rhodium-mediated 1,4- or 1,3-hydrogen shift, from a phenyl substituent to the alkenyl C_α atom, to reach an equilibrium mixture with *ortho*-alkenylaryl complexes. The comparison of these reactions, starting independently of each precursor, and their products reveals that the Bpin group attached at the C_β atom of the alkenyl moiety has a dramatic influence on the rate of the alkenyl isomerization and on the alkenyl-to-*ortho*-alkenylaryl transformation. Because it increases the contribution of the resonance form Rh^+=C(Ph)-$\bar{C}$(Bpin)Ph to the Rh-alkenyl bond, it increases the isomerization rate since favors the formation of the rhodacyclopropane intermediate, which is the key for the process. The increment of the zwitterionic resonance form to the metal-alkenyl bond translates into an increase of the Rh-C_α bond strengths, which results in a higher stability of the *β*-borylalkenyl species with regard to its *ortho*-(*β*-borylalkenyl)aryl counterpart.

In summary, there are significant differences between *β*-borylalkenyl and alkenyl ligands. Therefore, the extrapolation of the behavior of one of these classes of transition metal complexes into the other one should be made very carefully.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with exclusion of air using Schlenk-tube techniques or in a drybox. Instrumental methods and X-ray details are given in the Supporting Information. In the NMR spectra the chemical shifts (in ppm) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$), external 85% H_3PO_4 ($^{31}P\{^1H\}$), or $BF_3{\cdot}OEt_2$ (^{11}B). Coupling constants *J* and *N* are given in hertz. RhH{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (**1**)[9] and Rh(Bpin){κ³-P,O,P-[xant(P^iPr_2)$_2$]} (**2**)[10a] were prepared by the published methods.

Reaction of RhH{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (1) with Diphenylacetylene: Preparation of Rh{(*E*)-C(Ph)=CHPh}{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (3). Diphenylacetylene (33 mg, 0.18 mmol) was added to a solution of **1** (100 mg, 0.18 mmol) in pentane (5 mL). An instantaneous change of color from black to red was observed, and immediately, it was concentrated to dryness to afford a red residue. This residue was washed with the minimum amount of pentane (3 x 0.5 mL) to afford a red solid that was dried in vacuo. Yield: 118 mg (89%). Anal. calcd. for $C_{41}H_{51}OP_2Rh$: C, 67.95; H, 7.09. Found: C, 67.58; H, 7.43. HRMS (electrospray, *m/z*) calcd. for $C_{41}H_{51}OP_2Rh$ $[M]^+$: 724.2465; found: 723.2455. IR (cm^{-1}): ν(C=C) 1577 (w), 1556 (w), ν(C-O-C) 1026 (m). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.89 (d, $^3J_{H-H}$ = 7.6, 2H, CH Ph), 7.35 (d, $^3J_{H-H}$ = 7.7, 2H, CH Ph), 7.27 (m, 2H, CH POP), 7.23 (dd, $^3J_{H-H}$ = 7.6, $^3J_{H-H}$ = 7.6, 2H, CH Ph), 7.13 (dd, $^3J_{H-H}$ = 7.6, $^3J_{H-H}$ = 7.5, 2H, CH Ph), 7.06-7.02 (m, 4H, 1H CH Ph + 2H CH POP + 1H =CH), 6.90 (t, $^3J_{H-H}$ = 6.9, 1H, CH Ph), 6.85 (t, $^3J_{H-H}$ = 7.7, 2H, CH POP), 2.36 (br, 4H, PC*H*$(CH_3)_2$), 1.46-1.06 (br, 30H, 6H CH_3 + 24H PCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$-apt NMR (100.62 MHz, C_7D_8, 253 K plus HSQC and HMBC): δ 168.4 (dt, $^1J_{C-Rh}$ = 40.1, $^2J_{C-P}$ = 12.1, Rh-C=), 157.4 (vt, *N* = 15.7, C-arom POP), 152.2 (s, C Ph), 141.2 (d, J_{C-Rh} = 3.9, C Ph), 131.9 (vt, *N* = 5.3, C-arom POP), 131.5 (s, CH-arom POP), 129.5, 128.8, 128.6 (both s, CH Ph), (s, =CH), 128.5, 127.7 (both s, CH Ph), 127.2 (s, CH-arom POP), 125.1 (vt, *N* = 16.0, C-arom POP), 124.4 (s, CH-arom POP), 124.0, 123.0 (both s, CH Ph), 35.3 (br, C(*C*H$_3$)$_2$), 34.9 (s, *C*(CH$_3$)$_2$), 32.9 (br, C(*C*H$_3$)$_2$), 26.1, 24.6 (both br, P*C*H(CH$_3$)$_2$), 20.0, 19.5, 18.9, 18.1 (all br, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 32.8 (d, $^1J_{P-Rh}$ = 182.4).

Spectroscopic Detection of Rh{(*Z*)-C(Ph)=CHPh}{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (4). In an NMR tube, a solution of Rh{(*E*)-C(Ph)=CHPh}{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (**3**) (20 mg, 0.0027 mmol) in C_6D_6 (0.5 mL) was heated during 30 min at 50 ºC. The $^{31}P\{^1H\}$ NMR spectrum registered after this time shows a mixture of complexes **3:4:5** in a ratio 31:45:24.

Selected NMR data of Rh{(Z)-C(Ph)=CHPh}{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (4). ^1H NMR (500.13 MHz, C_6D_6, 298 K): δ 9.29 (br, 2H, CH Ph*)*, 8.35 (dd, J_{H-H} = 8.2, J_{H-H} = 1.5, 2H, CH Ph), 7.46 (m, 1H, =CH), 7.31-6.82 (m, overlapping with the resonances of **4** and **5**, 12H, Ph and CH-arom POP), 2.23, 2.10 (both m, 2H, PC*H*$(CH_3)_2$), 1.22 (s, 3H, CH_3), 1.18 (m, overlapping, 6H, PCH(C*H*$_3$)$_2$), 1.17 (s, 3H, CH_3), 1.13 (m, overlapping, 6H, PCH(C*H*$_3$)$_2$), 1.03 (dvt, $^3J_{H-H}$ = 7.1, *N* = 14.8, 6H, PCH(C*H*$_3$)$_2$), 0.99 (dvt, $^3J_{H-H}$ = 6.2, *N* = 12.5, 6H, PCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$-apt NMR (100.62 MHz, C_7D_8, 253 K plus HSQC and HMBC): δ 168.6 (dt, $^1J_{C-Rh}$ = 42.5, $^2J_{C-P}$ = 11.8, Rh-C=), 156.0 (s, C Ph), 155.6 (vt, *N* = 14.4, C-arom POP), 144.5 (s, C Ph), 131.4 (s, CH-arom POP), 130.8 (vt, *N* = 5.1, C-arom POP), 130.5 (s, CH Ph), 130.2 (s, CH Ph), 129.7 (t, $^3J_{C-P}$ = 3.6, =CH), 128.3 (s, CH Ph), 127.7 (s, CH Ph), 127.1 (s, CH-arom POP), 125.6 (m, C-arom POP), 124.3 (s, CH-arom POP), 123.9, 122.5 (both s, CH Ph), 34.5 (s, C(*C*H$_3$)$_2$), 34.4 (s, *C*(CH$_3$)$_2$), 32.7 (s, C(*C*H$_3$)$_2$), 26.0, 25.9 (both m, P*C*H(CH$_3$)$_2$), 18.6, 18.5 (br, PCH(*C*H$_3$)$_2$), 18.2, 17.6 (s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, 298 K): δ 33.4 (d, $^1J_{P-Rh}$ = 177.6).

Preparation of Rh{C_6H_4-2-(*E*-CH=CHPh)}{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (5). A solution of Rh{(*E*)-C(Ph)=CHPh}{κ³-P,O,P-[xant(P^iPr_2)$_2$]} (**3**, 100 mg, 0.14 mmol) in pentane (5 mL) was heated

during 4 h at 50 ºC. After this time, it was concentrated to dryness to afford a red solid. It was washed with the minimum amount of pentane (3 x 0.5 mL) and finally it was dried in vacuo. Yield: 78.4 mg (78%). Anal. calcd. for $C_{41}H_{51}OP_2Rh$: C, 67.95; H, 7.09. Found: C, 67.89; H, 6.73. HRMS (electrospray, *m/z*) calcd. for $C_{41}H_{51}OP_2Rh$ $[M]^+$: 724.2465; found 724.2358. IR (cm^{-1}): ν(C=C) 1594 (w), 1565 (w), ν(C-O-C) 1019 (m). ^1H NMR (500.13 MHz, C_6D_6, 298 K): δ 9.17 (d, $^3J_{H-H}$ = 16.5, 1H, =C(7)H), 8.20 (dt, $^3J_{H-H}$ = 7.5, $^4J_{H-P}$ = 1.9, 1H, Rh-Ph), 7.72 (t, $^3J_{H-H}$ = 8.0, 2H, Ph), 7.71 (d, $^3J_{H-H}$ = 7.1, 1H, Rh-Ph), 7.52 (d, $^3J_{H-H}$ = 16.5, 1H, =C(8)H), 7.20 (m, 2H, CH POP), 7.10 (m, 3H, Ph), 7.04 (m, 1H, Ph), 7.03 (dd, $^3J_{H-H}$ = 7.7, J_{H-P} = 1.1, 2H, CH POP), 6.97 (t, $^3J_{H-H}$ = 7.4, 1H, Ph), 6.83 (t, $^3J_{H-H}$ = 7.6, 2H, CH POP), 2.43 (m, 2H, PC*H*$(CH_3)_2$), 2.31 (m, 2H, PC*H*$(CH_3)_2$), 1.29 (s, 3H, CH_3), 1.24 (dvt, $^3J_{H-H}$ = 7.7, *N* = 15.5, 6H, PCH(C*H*$_3)_2$), 1.15 (dvt, $^3J_{H-H}$ = 6.8, *N* = 13.4, 6H, PCH(C*H*$_3)_2$), 1.12 (s, 3H, CH_3), 1.12 (dvt, $^3J_{H-H}$ = 7.6, *N* = 14.8, 6H, PCH(C*H*$_3)_2$), 1.08 (dvt, $^3J_{H-H}$ = 7.5, *N* = 15.8, 6H, PCH(C*H*$_3)_2$). $^{13}C\{^1H\}$-apt NMR (75.48 MHz, C_6D_6, 298 K plus HSQC and HMBC): δ 168.7 (dt, $^1J_{C-Rh}$ = 42.3, $^2J_{C-P}$ = 11.8, Rh-C), 156.1 (vt, *N* = 15.7, *C*-arom POP), 143.2 (t, J_{C-P} = 2.2, C Ph), 141.4 (d, $^3J_{C-Rh}$ = 3.3, =C(7)H), 140.4 (s, C Ph), 139.6 (t, $^3J_{C-P}$ = 2.6, CH Ph), 131.1 (s, CH-arom POP), 130.9 (vt, *N* = 5.3, C-arom POP), 128.8 (s, CH-arom POP), 128.7, 126.5, 125.9 (all s, CH Ph), 125.5 (vt, *N* = 15.4, C-arom POP), 124.5 (d, $^3J_{C-Rh}$ = 2.8, CH Ph), 124.1 (s, CH-arom POP), 123.4 (d, J_{C-Rh} = 1.3, CH Ph), 122.3 (s, =C(8)H), 119.4 (s, CH Ph), 34.3 (s, C(*C*$H_3)_2$), 34.1 (s, *C*$(CH_3)_2$), 31.4 (s, C(*C*$H_3)_2$), 25.7 (dvt, J_{C-Rh} = 2.6, *N* = 17.9, P*C*$H(CH_3)_2$), 24.7 (dvt, J_{C-Rh} = 3.3, *N* = 18.2, P*C*$H(CH_3)_2$), 19.3 (vt, *N* = 6.9, PCH(*C*$H_3)_2$), 18.8 (vt, *N* = 8.7, PCH(*C*$H_3)_2$), 18.4 (vt, *N* = 4.3, PCH(*C*$H_3)_2$), 17.9 (s, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6, 298 K): δ 36.7 (d, $^1J_{P-Rh}$ = 174.7).

Preparation of RhD{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (1-*d*$_1$). A solution of **1**(50 mg, 0.018 mmol) in a mixture of toluene-d_8 (1mL) and 2-propanol-d_7 (1 mL) was stirred during 24 h at room temperature. The resulting solution was concentrated to dryness to afford a dark solid that was dried in vacuo. The ^1H NMR spectrum shows that the deuterium incorporation at the hydride position is 85%. Yield: 47 mg (94%).

Reaction of RhD{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (1-*d*$_1$) with diphenylacetylene. Two NMR tubes were charged with **1-*d*$_1$** (15 mg, 0.03 mmol). To the first NMR tube was added 0.5 mL of bencene and to the second was added 0.5 mL of bencene-d_6. Diphenylacetylene (5 mg, 0.03 mmol) was added to both samples and they were heated during 4 h at 50 ºC. After that time, the ^1H and ^2H NMR spectra showed the presence of **5-d$_1$**. The ^1H NMR (400 MHz, C_6D_6, 298 K) data were identical to those reported for **5** with the exception of the intensity of the signals at 9.17 (0.15H, =CH) and a singlet at 7.53 ppm. ^2H NMR (76.77 MHz, C_6H_6, 298 K): δ 9.14 (s, =CD).

Reaction of Rh{C$_6$H$_4$-2-(*E*-CH=CHPh)}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (5) with HBpin. (a) *With 1 equiv of HBpin*: An NMR tube containing a solution of **5** (30 mg, 0.04 mmol) and HBpin (6 µL, 0.04 mmol) in C_6D_6 (0.4 mL) was heated at 60 ºC and it was checked periodically by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. After 3 h the $^{31}P\{^1H\}$ NMR spectrum shows signals corresponding to **5** (58%), Rh(Bpin){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**2**, 3%) and RhH{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**1**, 40%). (b) *With 2 equiv of HBpin:* An NMR tube containing a solution of **5** (30 mg, 0.04 mmol) and HBpin (12 µL, 0.08 mmol) in C_6D_6 (0.4 mL) was heated at 60 ºC and it was checked periodically by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. After 9 h the $^{31}P\{^1H\}$ NMR spectrum shows signals corresponding to **5** (4%), Rh(Bpin){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**2**, 75%), together with a doublet (21%) at 69.5 ppm ($^1J_{P-Rh}$ = 128.7) assigned to RhH(Bpin){C$_6$H$_4$-2-(*E*-CH=CHPh)}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**6**). The ^1H NMR spectrum shows a hydride resonance at -5.99 ppm. After 11 h the $^{31}P\{^1H\}$ NMR spectrum shows the quantitative conversion of **5** into **2**. Additionally, the formation of a precipitate at the bottom of the NMR tube was observed. After removing the solution via cannula, the solid was dried in vacuum and dissolved in $CDCl_3$. The $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra show peaks that agree with those previously reported for *trans*-4,4,5,5-tetramethyl-2-(2-styrylphenyl)-1,3,2-dioxaborolane.[26]

$^{13}C\{^1H\}$-apt NMR (75.48 MHz, $CDCl_3$, 298 K): δ 143.5, 138.1, 136.2, 131.2, 130.1, 129.4, 128.8, 127.2, 126.7, 124.6, 83.4, 24.7. $^{11}B\{^1H\}$ NMR (96.29 MHz, $CDCl_3$, 298 K): δ 31.2 (s).

Hydroboration of Diphenylacetylene Catalyzed by RhH{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (1). In an argon-filled glovebox, Ace pressure tubes were charged with **1** (5 mg, 0.009 mmol), HBpin (26.6 µL, 0.18 mmol), diphenylacetylene (33 mg, 0.18 mmol) and *n*-octane (1 mL). The resulting mixtures were stirred during 24 h at different temperatures to afford mixtures of (*Z*)- and (*E*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (at 80 ºC: *Z*:*E* 53%:37%. At 100 ºC: *Z*:*E* 35%:52%. At 120 ºC: *Z*:*E* 40%:56%). The yield of the reactions was determined by ^1H NMR by adding 1,2-dichloroethane as an internal standard, while the ratio *Z*:*E* was determined by gas chromatography.

Spectroscopic data of (Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:[27] ^1H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 7.36 (s, 1H, =CH), 7.29-7.27 (m, 1H, CH_{arom}), 7.25-7.20 (m, 2H, CH_{arom}), 7.17-7.15 (m, 2H, CH_{arom}), 7.11-7.09 (m, 3H, CH_{arom}), 7.06-7.03 (m, 2H, CH_{arom}), 1.30 (s, 12H, CH_3). $^{13}C\{^1H\}$-apt NMR (100.63 MHz, $CDCl_3$, 298 K): δ 143.3 (=CH), 140.5, 137.1 (both C_{ipso}), 130.1, 128.9, 128.3, 127.9, 127.7, 126.4 (all CH_{arom}), 83.9 (*C*$(CH_3)_2$), 24.9 (CH_3). ^{11}B NMR (96.29 MHz, $CDCl_3$, 298 K): δ 30.9 (br). MS: 306 $[M^+]$.

Spectroscopic data of (E)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: ^1H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 7.51-7.44 (m, 4H, CH_{arom}), 7.36-7.24 (m, 7H, =CH and CH_{arom}), 1.29 (s, 12H, CH_3). $^{13}C\{^1H\}$-apt NMR (100.63 MHz, $CDCl_3$, 298 K): δ 142.7 (C_{ipso}), 140.9 (=CH), 138.9 (C_{ipso}), 128.6, 128.4, 128.2, 127.1, 127.0, 126.6 (all CH_{arom}), 84.2 (*C*$(CH_3)_2$), 25.0 (CH_3). ^{11}B NMR (96.29 MHz, $CDCl_3$, 298 K): δ 30.9 (br). MS: 306 $[M^+]$.

Reaction of Rh(Bpin){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (2) with Diphenylacetylene a Low Temperature: Spectroscopic Detection of Rh{(*E*)-C(Ph)=C(Bpin)Ph}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (7). A screw-top NMR tube containing a solution of **2** (15 mg, 0.02 mmol) in toluene-d_8 (0.3 mL) and cooled at -78 ºC was treated with a solution of diphenylacetylene (4 mg, 0.02 mmol) in toluene-d_8 (0.2 mL). The NMR tube was immediately introduced into an NMR probe cooled at -20 ºC. The immediate and quantitative conversion of **2** to Rh{(*E*)-C(Ph)=C(Bpin)Ph}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**7**), together with a small amount of Rh{(*Z*)-C(Ph)=C(Bpin)Ph}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**8**, 7%), was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. ^1H NMR (400.13 MHz, C_7D_8, 253 K): δ 7.59 (d, $^3J_{H-H}$ = 7.6, 2H, CH Ph), 7.32 (d, $^3J_{H-H}$ = 7.7, 2H, CH Ph), 7.16-7.09 (m, 4H, 2 CH POP + 2CH Ph), 6.99-6.95 (m, 4H, 2 CH POP + 2CH Ph), 6.88 (t, $^3J_{H-H}$ = 7.6, 1H, CH Ph), 6.86 (t, $^3J_{H-H}$ = 7.6, 2H, CH POP), 6.78 (t, $^3J_{H-H}$ = 7.6, 1H, CH Ph), 2.85, 2.22 (both m, 2H, PC*H*$(CH_3)_2$), 1.47 (dvt, $^3J_{H-H}$ = 8.0, *N* = 15.3, 6H, PCH(C*H*$_3)_2$), 1.40 (dvt, $^3J_{H-H}$ = 7.0, *N* = 14.1, 6H, PCH(C*H*$_3)_2$), 1.29 (s, 3H, CH_3), 1.21 (s, 12H, CH_3 Bpin), 1.16-1.07 (m, 12H, PCH(C*H*$_3)_2$), 1.00 (s, 3H, CH_3). $^{13}C\{^1H\}$-apt NMR (100.62MHz, C_7D_8, 253 K plus HSQC and HMBC): δ 191.3 (dt, $^1J_{C-Rh}$ = 42.0, $^2J_{C-P}$ = 8.3, Rh-C=), 155.7 (vt, *N* = 14.4, C-arom POP), 150.5, 148.9 (both s, C Ph), 132.1 (s, CH Ph), 131.2 (s, CH-arom POP), 131.1 (br, C-arom POP), 129.6, 128.8, 127.5, 127.2 (all s, CH Ph), 126.5 (s, CH-arom POP), 124.8 (vt, *N* = 15.4, C-arom POP), 124.0 (s, CH Ph), 123.2 (s, CH-arom POP), 82.2 (s, C Bpin), 35.1 (s, C(*C*$H_3)_2$), 34.3 (s, *C*$(CH_3)_2$), 30.4 (s, C(*C*$H_3)_2$), 25.8 (br, P*C*$H(CH_3)_2$), 25.5 (s, CH_3 Bpin), 25.8 (br, P*C*$H(CH_3)_2$), 19.7, 18.5, 18.0 (all br, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (161.98 MHz, C_7D_8, 253 K): δ 30.4 (d, $^1J_{P-Rh}$ = 189.8). ^{11}B NMR (128.38 MHz, C_7D_8, 253 K): 30.7 (br).

Reaction of Rh(Bpin){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (2) with Diphenylacetylene at Room Temperature: Formation of Rh{(*Z*)-C(Ph)=C(Bpin)Ph}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (8) and Rh{C$_6$H$_4$-2-[*E*-CH=C(Bpin)Ph]}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (9): Diphenylacetylene (27 mg, 0.15 mmol) was added to a solution of **2** (100 mg, 0.15 mmol) in pentane (5 mL) at room temperature. An instantaneous change of the color of the solution from black to red was observed. Immediately, it was concentrated to dryness to afford a red residue. This residue was washed with the minimum amount of pentane (3 x

0.5 mL) to afford a red solid that was dried in vacuo. Yield: 102 mg (80%). The $^{31}P\{^{1}H\}$ NMR spectrum shows a mixture of complexes **8:9** in a ratio 70:30. HRMS (electrospray, *m/z*) calcd. for $C_{47}H_{62}BO_3P_2Rh$ $[M-H]^+$: 849.3247; found 849.3270. IR (cm^{-1}): ν(C=C) 1586 (w), 1513 (w), ν(C-O-C) 1141 (m).

*Spectroscopic data for Rh{(Z)-C(Ph)=C(Bpin)Ph}{κ³-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**8**):* ^{1}H NMR (500.12 MHz, C_6D_6, 298 K): δ 9.26 (d, J_{H-H} = 7.7, 2H, CH Ph), 7.94 (d, J_{H-H} = 7.5, 2H, CH Ph), 7.35 (dd, J_{H-H} = 7.1, J_{H-H} = 7.5, 2H, CH Ph), 7.26 (dd, J_{H-H} = 7.1, J_{H-H} = 7.7, 2H, CH Ph), 7.24-7.02 (m, 4H, 2H CH Ph +2 CH POP), 6.99 (dd, $^{3}J_{H-H}$ = 7.7, J_{H-P} = 1.5, 2H, CH POP), 6.80 (t, $^{3}J_{H-H}$ = 7.6, 2H, CH POP), 2.06 (m, 4H, PC*H*$(CH_3)_2$), 1.22-1.16 (m, 18H, 12H PCH(CH_3)$_2$ + 6H CH_3), 1.09 (s, 12H, Bpin), 1.06-1.02 (m, 12H, PCH(CH_3)$_2$). $^{13}C\{^{1}H\}$-apt NMR (75.48 MHz, C_6D_6, 298 K plus HSQC and HMBC): δ 184.8 (dt, $^{1}J_{C-Rh}$ = 41.7, $^{2}J_{C-P}$ = 11.2, Rh-C=), 155.9 (s, C Ph), 155.2 (vt, *N* = 13.2, C-arom POP), 147.3 (s, C Ph), 131.1 (s, CH-arom POP), 131.0 (vt, *N* = 4.9, C-arom POP), 129.5 (s, CH Ph), 127.6 (s, CH Ph), 127.0 (s, CH Ph), 126.3 (s, CH Ph), 124.6 (vt, *N* = 17.7, C-arom POP), 123.7 (s, CH-arom POP), 123.4 (s, CH Ph), 81.9 (s, C Bpin), 34.0 (s, C(*C*H_3)$_2$), 33.8 (s, *C*$(CH_3)_2$), 31.8 (s, C(*C*H_3)$_2$), 25.4 (s, CH_3 Bpin), 25.1 (m, P*C*H$(CH_3)_2$), 19.9 (vt, *N* = 7.3, PCH(*C*H_3)$_2$), 19.1 (vt, *N* = 8.8, PCH(*C*H_3)$_2$), 17.7, 17.1 (both s, PCH(*C*H_3)$_2$). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 31.6 (d, $^{1}J_{P-Rh}$ = 183.7). ^{11}B NMR (128.38 MHz, C_7D_8, 253 K): 31.0 (br).

*Spectroscopic data for Rh{C_6H_4-2-[E-CH=C(Bpin)Ph]}{κ³-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**9**).* ^{1}H NMR (500.12 MHz, C_6D_6, 298 K): δ 10.86 (s, 1H, =CH), 8.41 (d, J_{H-H} = 6.8, 1H, CH Ph), 7.72 (d, J_{H-H} = 7.2, 1H, CH Ph), 7.24-7.02 (m, 11H, 7 CH Ph + 4 CH POP), 6.85 (t, $^{3}J_{H-H}$ = 7.6, 2H, CH POP), 2.59 (m, 2H, PC*H*$(CH_3)_2$), 2.35 (m, 2H, PC*H*$(CH_3)_2$), 1.39 (s, 3H, CH_3), 1.28 (dvt, $^{3}J_{H-H}$ = 7.7, *N* = 15.7, 6H, PCH(CH_3)$_2$), 1.22-1.16 (m, 18H, 6H PCH(CH_3)$_2$ + 12H Bpin), 1.10 (s, 3H, CH_3), 1.06-1.02 (m, 6H, PCH(CH_3)$_2$), 0.88 (dvt, $^{3}J_{H-H}$ = 7.8, *N* = 15.2, 6H, PCH(CH_3)$_2$). $^{13}C\{^{1}H\}$-apt NMR (75.48 MHz, C_6D_6, 298 K plus HSQC and HMBC): δ 161.4 (dt, $^{1}J_{C-Rh}$ = 42.0, $^{2}J_{C-P}$ = 12.7, Rh-C), 157.4 (vt, *N* = 16.8, C-arom POP), 147.0 (s, C Ph), 142.6 (s, C Ph), 139.8 (s, CH Ph), 136.9 (s, =CH), 132.0 (vt, *N* = 4.7, C-arom POP), 131.1 (s, CH-arom POP), 130.8 (s, CH Ph), 129.1 (s, CH Ph), 127.6 (s, CH-arom POP), 127.0 (s, CH Ph), 126.4 (s, CH Ph), 126.1 (br, C-arom POP), 125.8 (s, CH Ph), 124.3 (s, CH Ph), 123.7 (s, CH-arom POP), 118.7 (s, CH Ph), 83.3 (s, C Bpin), 34.9 (s, C(*C*H_3)$_2$), 34.6 (s, *C*$(CH_3)_2$), 26.4 (s, C(*C*H_3)$_2$), 25.9 (vt, *N* = 17.0, P*C*H$(CH_3)_2$), 25.5 (s, CH_3 Bpin), 24.5 (m, P*C*H$(CH_3)_2$), 19.3 (vt, *N* = 6.9, PCH(*C*H_3)$_2$), 18.6 (vt, *N* = 8.5, PCH(*C*H_3)$_2$), 18.5 (vt, *N* = 10.8, PCH(*C*H_3)$_2$), 17.9 (s, PCH(*C*H_3)$_2$). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 34.2 (d, $^{1}J_{P-Rh}$ = 187.6). ^{11}B NMR (128.38 MHz, C_7D_8, 253 K): 31.0 (br).

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications web site..

General information, crystallographic data, and NMR spectra (PDF)

Accession codes

CCDC 1943084 and 1943085 contain the crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

AUTHOR INFORMATION

Corresponding Author

* maester@unizar.es

Notes

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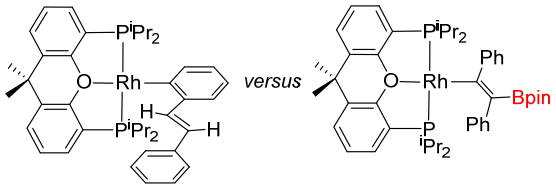
PiPr2
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Rh
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versus
PiPr2
O
Rh
Ph
Bpin
Ph
PiPr2