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P–H activation

Rhodium Complexes in P–H Bond Activation Reactions

Víctor Varela-Izquierdo,[a] Ana M. Geer,*[b] Bas de Bruin,[c] José A. López,[a] Miguel A. Ciriano,[a] and Cristina Tejel*[a]

Abstract: The feasibility of oxidative addition of the P–H bond of PHPh3 to a series of rhodium complexes to give mononuclear hydrido-phosphanido complexes has been analyzed. Three main scenarios have been found depending on the nature of the L ligand added to [Rh(Tp)(C5H5)(PHPh3)]. (Tp = hydridotris(pyrazolyl)borate): (i) clean and quantitative reactions to terminal hydrido-phosphanido complexes [Rh(Tp)(P)(PHPh3)] (L = PMe3, PMePh and PHPh3); (ii) equilibria between RhIII and RhII species: [Rh(Tp)(P)(PHPh3)] (L) = [Rh(Tp)(PHPh3)(L)] (L = PMe3, PPh3 and PHPh3) and (iii) a simple ethylene replacement to give the rhodium(i) complexes [Rh(c5-Tp)(L)(PHPh3)] (L = NHCS-type ligands). The position of the P–H oxidative addition–reductive elimination equilibrium is mainly determined by steric influencing the entropy contribution of the reaction. When ethylene was used as a ligand, the unique rhodaphosphacyclobutane complex [Rh(Tp)(η1-Et)(c5-C5H4CH2PPh3)] was obtained. DFT calculations revealed that the reaction proceeds through the rate limiting oxidative addition of the P–H bond, followed by a low-barrier sequence of reaction steps involving ethylene insertion into the Rh–H and Rh–P bonds. In addition, oxidative addition of the P–H bond in OPPh3 to [Rh(Tp)(C5H5)(PHPh3)] gave the related hydride complex [Rh(Tp)(OPPh3)(PHPh3)], but ethyl complexes resulted from hydride insertion into the Rh–ethylene bond in the reaction with [Rh(Tp)(C5H5)].

Introduction

P–H bond activation at a single metal center is a critical step in metal-catalyzed transformations involving the formation of P–C and P–P bonds, such as hydrophosphination, hydrophosphonylation, dehydrocoupling, and polymerization reactions.[1] In this reaction, the P–H bond transforms into a terminal phosphano ligand (M–P) thus enhancing its nucleophilic character and consequently its reactivity.[2]

Among the different approaches to this reaction, one of the most popular involves proton transfer from phosphines or phosphine oxides to an internal base, that is, a proton acceptor group coordinated to the metal. Relevant examples include protonolysis at alkyl,[3] and acetate palladium complexes,[4] nickel silanolate,[5] and silylamides,[6] and iron complexes with an Fe–CH2SiMe3 motif.[7] In addition, metals with formal d0 electron count such as lanthanides, early transition metals and some actinides engage in α-bond metathesis as reported for complexes with alkyls,[8] silylamides,[9] amides,[10] and more recently alkoxy groups.[11]

Moreover, P–H bond activation through metal-ligand cooperation has been recently reported for ruthenium and iridium complexes bearing carbene-type ligands,[12] whereas chelated assisted P–H bond cleavage has been described for diphosphane-phosphane oxides,[13] and diphosphane-phosphane compounds,[14] which results in a phosphanido functionality embedded within a tripodal ligand.

Another interesting methodology that does not require any previous functionalization of the metal center is the oxidative addition reaction, that is, insertion of the metal into a P–H bond, which eventually results in hydrido-phosphanido compounds. However, isolated complexes from such reactions have only been reported in a few instances. As a matter of fact, pioneering work from Schunn[15] and Ebsworth,[16] showed the preparation of iridium(III) complexes derived from the oxidative addition of PH3, whereas diphenylphosphane has been successfully added to iridium(I) complexes only recently.[17]

Moreover, tri-coordinated complexes of platinum(0)[18] and nickel(0)[19] react with secondary phosphines to render mononuclear complexes with a H–M–PR3 moiety. However, a similar reaction with a related nickel(II) complex bearing a β-diketiminate ancillary ligand stops at the coordination level, simply leading to [Ni(nacnac)(PHPh3)].[20] Furthermore, the strong influence of the ancillary ligands in the course of the reactions is
In these circumstances, the reactivity of the complexes were characterized in solution and also from electronically saturated $J_{\text{Tp}}(\mu-\text{PPh}_3)$, which gives [Co(dtbpe)(H)(PHDmp)].

Hydrido-phosphanido complexes of early and middle transition metals have also been prepared from oxidative addition reactions of the coordinatively and electronically unsaturated complex $\text{TaF}_5(\text{SiO})_3$,[23] and also from electronically saturated complexes $\text{Mo}(\text{Cp}^*)\text{Cl}(\text{PMe}_3)$,[24] and $\text{W}(\text{dppe})_2\text{N}$_3[25] with HPPh3. The later require light irradiation to dissociate dihydrogen and thus generate the required coordination vacancy.

There are few examples of P–H bond activation with rhodium complexes. Particularly pertinent to the present work are the rhodium(III) hydrido-phosphanido intermediates observed by Tilley[26] in the synthesis of dinuclear bis(phosphanido) bridged complexes and a rhodium(V) bis(hydrido-phosphanido) complex proposed by Brookhart in the catalytic dehydrocoupling of secondary phosphines.[27] More recently, Grützmacher reported a terminal rhodium(I)-phosphanido complex with a bulky tetradentate ligand, which contains an unusually long Rh–P bond,[28] whereas we have isolated mononuclear hydrido-phosphanido rhodium complexes and demonstrated that they are intermediates in catalytic hydrophosphanation and dehydrocoupling reactions.[29]

In this paper we showcase the feasibility for the oxidative addition reaction of the P–H bond of PPh3 and OPPh2 to a series of rhodium complexes that give cleanly new mononuclear hydrido-phosphanido complexes, a rhodaphosphacyclobutane complex or ethyl complexes depending on the ancillary ligands and the reaction conditions. Some clues to account for the different reactivity observed, supported by DFT studies are also provided.

Results and Discussion

Reactions with PMe$_2$, PMe$_3$Ph and PPh$_2$

We have previously reported that upon addition of diphenylphospine to $[\text{Rh}(\text{Tp})(\text{C}_2\text{H}_4)]_2$ (1; $\text{Tp} = \text{hydridotris(pyrazol-1-yl)borate}$) one ethylene ligand is replaced to give $[\text{Rh}(\text{Tp})(\text{C}_2\text{H}_4)](\text{PPh}_3)_2$ (2), which was isolated as a yellow microcrystalline solid in excellent yield (Scheme 1).[29] Complex 2 was fully characterized as a species with TBPY-5 geometry with a non-rotating ethylene at the equatorial position. Slow addition of PPh3 under vigorous stirring is required to obtain pure samples of complex 2; otherwise this compound is contaminated with variable amounts of the dinuclear complex $[[\text{Tp}(\text{H})\text{Rh}(\mu-\text{PPh}_3)]_2$ (3) (Scheme 1).

Addition of P-donor ligands such as PMe$_2$, PMe$_3$Ph, and even PPh$_3$ to 2 promotes the oxidative addition of the P–H bond to give the hydrido-phosphanido complexes $[\text{Rh}(\text{Tp})(\mu-\text{L})(\text{PPh}_3)]_2$ (L = PMe$_2$, PMe$_3$Ph 5, and PPh$_3$ 6). These reactions were found to be immediate and quantitative by $^1$H and $^3$P($^1$H) NMR spectroscopy,[29] and complexes 5–6 have now been isolated as yellow microcrystalline solids after workup (Scheme 2).

These complexes represent the first isolated terminal phosphanido rhodium complexes resulting from the formal oxidative addition of a P–H bond to a rhodium center. According to the formulation, complex 6 can be directly prepared by adding two molar equivalents of PPh$_2$ to the bis(ethylene) complex 1.

Complexes 4 and 5 were characterized in solution as single static species by the signal of the hydride ligand at high field ($\delta = -15.62$ and $-15.44$ ppm, respectively) in their $^1$H NMR spectra and two doublets of doublets for the two inequivalent phosphorus atoms in the $^3$P($^1$H) NMR spectra. Interestingly, the values of $J(\text{P},\text{Rh})$ for the terminal phosphido ligand (63 and 62 Hz) were found to be smaller than those corresponding to the phosphane ligands (136 and 138 Hz). It can be attributed to a substantial reduction in the $\sigma$-orbital character of the Rh–P$_2$ bond as compared to the Rh–phosphane,[17a] and thus provides a useful tool for the identification of the terminal phosphanido ligand.

Complex 6 proved to be a fluxional species, since a single resonance ($^3$P($^1$H) NMR) and broad signals ($^1$H NMR) were observed at room temperature, but it gives sharp NMR signals at $-70$ °C in $\text{D}_2$toluene. The most relevant resonances at this temperature were the hydride ligand ($\delta = -14.79$ ppm) and the PH proton ($\delta = 6.46$ ppm) showing a large $J(\text{H},\text{P}) = 391.0$ Hz coupling in the $^1$H NMR spectrum.

This fluxionality can be ascribed to a prototropic shift of the PH proton from the phosphane to the phosphanido and, in good agreement, a low-barrier transition state of $+16.7$ kcal...
mol$^{-1}$ for this shift was calculated with DFT methods (Figure 1).

Complex 6 contains an intact diphenylphosphane ligand that could be appropriate for the study of the oxidative addition reaction of the P–H bond in the presence of a second rhodium center. A bimetalloc system might work more efficiently for bond activation due to the cooperation of two metal centers.$^{[19]}$ However, on mixing equimolar amounts of [Rh(Tp)(H)(PHPh$_2$)]$\text{6}$ and [Rh(Tp)(C$_2$H$_4$)(PHPh$_2$)]$\text{2}$ (1) the immediate formation of [Rh(Tp)(C$_2$H$_4$)(PHPh$_2$)]$\text{2}$ was observed instead. Simultaneously, the bis(hydrido) dinuclear complex [(TP)(H)Rh$_2$P$_2$]$_\text{3}$ was isolated as an orange microcrystalline solid in good yield.

This reaction occurs with the concomitant extrusion of one Tp ligand as HTp (1H NMR evidence). On a preparative scale, 7 was isolated as an orange microcrystalline solid in good yield after workup.

The molecular structure of 7, displayed in Figure 2, shows two rhodium atoms bridged by two phosphane ligands. The Rh$^\text{III}$ atom, labelled as Rh1, completes a distorted octahedral geometry with the three N atoms of the Tp and the hydride ligand, whereas the Rh$^\text{I}$ center, labelled as Rh2, shows a square-planar environment with four P atoms (two from the phosphane bridges and two from two diphenylphosphane ligands). The Rh1–P1 and Rh1–P2 bond distances are slightly shorter than the related Rh2–P1 and Rh2–P2, which is expected from the different oxidation states Rh1 (Rh$^\text{III}$) and Rh2 (Rh$^\text{II}$).

Reactions with PMePh$_2$ and PH$_2$

Interestingly, the reaction of [Rh(Tp)(C$_2$H$_4$)(PHPh$_2$)]$\text{2}$ with the slightly less basic and more sterically demanding phosphate PMePh$_2$ resulted in an equilibrium distribution of the rhodium(III) species [Rh(Tp)(H)(PMePh$_2$)]$\text{3}$ (8a) and the rhodi-
dm(1) species [Rh(κ^2-Tp)(PMePh_2)(PHPh_2)] (8b) in solution, which are formed in a 70:30 ratio at room temperature (Schemes 2 and 4). This ratio corresponds to a value of $K_{eq} = 2.33 (8b \leftrightarrow 8a)$ and $\Delta G_{298} = -0.50$ kcal mol$^{-1}$.

In addition, small amounts of [Rh(Tp)(H)(PHPh_2)(PHPh_2)] (6) and [Rh(κ^2-Tp)(PMePh_2)] (9) were also involved in the equilibrium (Scheme 4). They are the result of a phosphane exchange reaction undergone by the rhodium(I) complex 8b.

Such equilibria were easily detected from the $^1H-^1H$ NOESY spectrum (Figure 3) because of the chemical exchange of the hydride ligand in 8a and the PH proton of 8b (left) as well as that of the methyl group of PMePh_2 in complexes 8a, 8b, and 9 (right).

From these solutions a yellow solid (8) was isolated after workup in very good yield. The IR (ATR) spectrum shows bands at 2457 and 2082 cm$^{-1}$, assignable to the B–H and Rh–H stretching vibrations, respectively, so most probably complex 8 is the hydrido-phosphanido complex 8a in the solid state.

A similar result occurred on addition of triphenylphosphane to [Rh(Tp)(C_6H_4)(PHPh_2)] (2). Thus, monitoring the reaction by NMR spectroscopy, the complexes [Rh(Tp)(H)(PHPh_2)(PHPh_2)] (10a), [Rh(κ^2-Tp)(PMePh_2)(PHPh_2)] (10b), [Rh(Tp)(H)(PHPh_2)(PHPh_2)] (6) as well as [(Tp)(H)Rh(μ-PPh_2)]_2 (3), [Rh(Tp)(C_6H_4)(PHPh_2)] and free PPh_2, were identified in solution (see Supporting Information). In this case, complexes 10a/10b were found to be formed in a 28:72 ratio at room temperature, which corresponds to a value of $K_{eq} = 0.39 (10b \leftrightarrow 10a)$ and $\Delta G_{298} = +0.56$ kcal mol$^{-1}$.

DFT calculations (B3LYP-D3, 6–311G(d,p)/LanL2TZ(f)) on the rhodium(I) complexes [Rh(κ^2-Tp)(L)(PHPh_2)] (L = PMePh_2 8b, PPh_2 10b) showed that they are square-planar species with the Tp ligand bonded to rhodium in a κ^2-fashion and with the six-membered metallacycle Rh(NN)B showing a boat conformation (Figure 4).

In Scheme 4, Equilibrium between complexes 8a, 8b, 6, and 9.

Figure 3. Two selected regions of the $^1H-^1H$-noeys spectrum of 8 showing the negative cross-peaks due to the chemical exchange. Color code: [Rh(Tp)(H)(PMePh_2)(PHPh_2)] (8a, black), [Rh(κ^2-Tp)(PMePh_2)(PHPh_2)] (8b, red) and [Rh(κ^2-Tp)(PMePh_2)] (9, green).

Figure 4. Selected region of the VT-$^1H$ NMR spectra of the reaction [Rh(Tp)(C_6H_4)(PHPh_2)] (2) with PPh_2 in [D_6]toluene showing conformers 10b-Pz-in and 10b-Pz-out. Color code: [Rh(Tp)(H)(PHPh_2)(PHPh_2)] (10a, black), [Rh(Tp)(PMePh_2)(PHPh_2)] (10b, red) and [Rh(Tp)(H)(PHPh_2)(PHPh_2)] (6, blue).

This puckered structure leads to two conformers depending on the location of the uncoordinated pyrazolate ring, either inside or outside the pocket of the complex. Both conformers were clearly observed in the $^31P-^1H$ NMR spectra at $-60$ °C for 8b and 10b, and the equilibrium between them accounts for the intriguing spectra at room temperature, in which only one signal of the phosphorus atoms of 8b and 10b was clearly observed, whereas the second one is very broad and hard to distinguish from the baseline (Figure 4).

Comments on phosphane ligands promoting P–H bond activation reactions.

At first glance, one could argue that the oxidative addition reaction of the P–H bond in complexes [Rh(κ^2-Tp)(L)(PHPh_2)] would be favored by increasing the electron density at the rhodium center. As the electron richness of the metal in this series is given by the donor ability of the ligand L, this magnitude can be evaluated from the r(CO) stretching frequencies in complexes that only differ in the L ligand. For such purpose, the complexes [Rh(acac)(CO)(L)] (acac = acetylacetonate) that show a unique r(CO) band were chosen. The observed frequencies, collected in Table 1, give the following order of electronic parameters: PMe_3 > PMe_2Ph > PMePh_2 > PPh_3 > PPHPh_2, which fit fairly well with the TEPs (Tonman electronic parameters) previously reported.

Table 1. IR r(CO) bands for the rhodium(I) complexes [Rh(acac)(CO)(L)] in toluene and computed cone angles.

<table>
<thead>
<tr>
<th>L</th>
<th>PMe_3</th>
<th>PMe_2Ph</th>
<th>PMePh_2</th>
<th>PPh_3</th>
<th>PPHPh_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(CO) [cm$^{-1}$]</td>
<td>1968</td>
<td>1971</td>
<td>1975</td>
<td>1980</td>
<td>1982</td>
</tr>
<tr>
<td>cone angles [°]</td>
<td>118</td>
<td>122</td>
<td>136</td>
<td>145</td>
<td>128</td>
</tr>
</tbody>
</table>

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From these data is clear that electronic effects are not the most relevant factor to account for the above-described results. In particular, the richest (PMe$_3$) and poorest (PPh$_3$) rhodium centers give both the corresponding rhodium(III) hydrophosphanido complexes cleanly. In both cases, the reactions were found to be almost instantaneous, achieving completion in less than 5 min.

Interestingly, a nice fit is found if steric effects are considered instead. Indeed, according to the cone angle: PMe$_3$ < PMePh < PPh$_3$, whereas with the bigger ligands, PMePh$_2$ and PPh$_3$, the equilibrium [Rh(x$^2$-Tp)(L)(PPh$_3$)] $\rightleftharpoons$ [Rh(Tp)(H)(L)(PPh$_3$)] was observed. In other words, it can be concluded that an increase in the size of the ligand diminishes the stability of the rhodium(III) oxidation state relative to the rhodium(I) counterpart, in such a way that an equilibrium between them is observed.

Since for complexes with the phosphanes PMePh$_2$ and PPh$_3$, both species are clearly observable by NMR, the thermodynamic parameters for the P–H oxidative addition reactions:

$$[\text{Rh}(x^2\text{-Tp})(L)(\text{PPh}_3)] = [\text{Rh}(\text{Tp})(\text{H})(L)(\text{PPh}_3)]$$

could be estimated from the Van’t Hoff plots (see Supporting Information). In both cases, a straight line was obtained giving values of $\Delta H = -2.12 \pm 0.02$ (8), $-2.64 \pm 0.01$ kcal mol$^{-1}$ (10) and $\Delta S = -5.77 \pm 0.06$ (8), $-10.74 \pm 0.05$ u.e. (10), which lead to $\Delta G$ at 298 K of $-0.40$ (8) and $-0.56$ kcal mol$^{-1}$ (10).

Although both reactions are exothermic, with similar values of enthalpy, the entropic contribution, more negative for the more sterically demanding ligand (PPh$_3$), is the key factor that determines the lower stability of the rhodium(III) hydrophosphanido complex. Indeed, the change in the environment of rhodium from square-planar to octahedral, associated to the P–H bond activation reaction, produces more crowded complexes, which are more destabilized as the size of the ligand increases. Accordingly, complexes with the less demanding ligands PMe$_3$, PMePh, and PPh$_3$ are expected to be obtained as hydrophosphanido complexes as observed experimentally.

**Reactions with N-heterocyclic carbenes**

The ability of N-heterocyclic carbenes to promote P–H bond activation reactions was also tested by reacting [Rh(Tp)(C$_3$H$_4$)(PPh$_3$)] (2) with IMes (1,3-dimesitylimidazol-2-ylidene) and BzIme (1,3-dimethylbenzimidazol-2-ylidene). The products from the reactions were found to be the rhodium(I) complexes [Rh(x$^2$-Tp)(L)(PPh$_3$)] ($\text{L} = \text{IMes}$ 11, BzIme 12), which were isolated as yellow solids in good yields (Scheme 5).

**Analytical and spectroscopic data of 11–12** agree with the proposed formulation. In particular, the PH proton was observed as a doublet of doublets at $\delta = 5.95$ (11) and 6.16 ppm (12) with large $J(\text{PH}) = 332.5$ and 322.7 Hz and small $J(\text{H}, \text{Rh}) = 3.3$ and 1.1 Hz coupling constants, respectively, at low temperature. In addition, the abnormally large $J(\text{PH})$ coupling constants of 195 and 192 Hz, respectively, would be related with a square-planar environment of rhodium, further confirmed by a X-ray diffraction study of complex 11. Moreover, complex 11 was found to adopt the boat conformation in the solid state, with the uncoordinated pyrazolate ring dangling outside the pocket of the complex (11-Pz-out, Figure 5).

**Figure 5. Molecular structure (ORTEP, ellipsoids set at 50% probability) of complex [Rh(x$^2$-Tp)(IMes)(PPh$_3$)] (11-Pz-out).** Selected bond lengths [Å] and angles [$^\circ$]: Rh–P 2.1985(5), Rh–N 2.0957(14), Rh–N5 2.1014(14), Rh–C22 1.9903(16), P–Rh–N3 1.7664(4), N5–Rh–C22 1.7378(6).

**Scheme 5. Reactions of [Rh(Tp)(C$_3$H$_4$)(PPh$_3$)] (2) with IMes and BzIme.**

DFT calculations (B3LYP-D3, 6–311G(d,p)/LanL2TZ(f)) on the conformer found in the solid state (11-Pz-out) as well as on that with the pyrazolate ring inside the pocket of the complex (11-Pz-in) revealed the former to be more stable than the latter by 3.9 kcal mol$^{-1}$. On the contrary, for complex 12 having the less demanding BzIme ligand, the conformer 12-Pz-in was found to be more stable than 12-Pz-out by 4.1 kcal mol$^{-1}$.

Complexes 11 and 12 were found to be fluxional species in solution. The analysis of the $^1$H–$^1$H NOESY spectrum of 11 at room temperature revealed the presence of a dynamic process, in which the three pyrazolate rings, the four methyl groups at the ortho position of the IMes ligand, and the phenyl groups of the PPh$_3$ exchange. This process is slightly faster in the case of complex 12, since at this temperature the $^1$H NMR spectrum is close to that expected for the fast-exchange region. Such exchange could take place through the participation of pentacoordinated TBPY-5 species (the turnstile motion), as generally accepted for Tp-complexes. However, in the particular case of complex 11, first a boat-to-boat inversion of the six-membered metallacycle Rh(NN)$_3$B is required to achieve the suitable conformer (11-Pz-in) to undergo $\kappa^2$–$\kappa^3$ isomerism.

The lack of a further P–H bond oxidative addition in the case of complexes 11 and 12 cannot be attributed to electronic effects as commented before. Indeed, they contain the more donating ligands (NHCS), with v(CO) stretching frequencies in
the complexes [Rh(acac)(CO)(L)] (L = IMes, BzMe) of 1955 and 1962 cm\(^{-1}\), respectively. Most probably, the particular steric requirements of these ligands that place the steric demand in a specific direction account for their lack of further reactivity.

**Reaction with ethylene**

Heating a solution of [Rh(Tp)(C\(_2\)H\(_5\))(PHPh\(_3\))] (2) in the presence of ethylene (6 bar) at 60 °C for six days resulted in the novel rhodaphosphacyclobutane complex [Rh(Tp)(n\(^1\)-Et)(\(\kappa\)\(^2\)-C\(_2\)\text{-CH}_3\text{-CH}_2\text{PPH}_3\))] (13, Scheme 6), which was isolated as an orange microcrystalline solid in good yields.


Control of the temperature and pressure of ethylene was crucial to get pure samples of 13 in such a way that complex 13 was contaminated with variable amounts of [[Tp(H)Rh(μ-PPh\(_3\))]\(_2\)] (3) under lower pressures of ethylene and/or higher temperatures. As an example, this reaction was completed in 3 h at 105 °C in D\(_6\)toluene under an atmosphere of ethylene (2 bar), but the yield of 13 decreased up to 45%.

Complex 13 was identified as the rhodaphosphacyclobutane compound shown in Scheme 6 by its analytical and spectroscopic data. Thus, the \(^1\)H NMR spectrum showed the diastereotopic CH\(_3\) protons of ethyl group as two multiplets coupled to a triplet corresponding to the methyl group (Figure 6, in blue). In addition, the large coupling constant of the methylenic carbon to rhodium (\(J(C,\text{Rh}) = 24\) Hz) clearly evidences the presence of a direct Rh–C bond.\(^{[19]}\)

Signals due to the protons and carbons of the rhodaphosphacyclobutane moiety were clearly identified in the \(^1\)H, \(^13\)C(\(^1\)H), and \(^31\)P(\(^1\)H) NMR spectra (red and green, Figure 6). The methylenic protons and carbon directly attached to rhodium (\(H_1\), \(C_3\), in red) were upfield shifted relative to that bonded directly to phosphorus (\(H_3\), \(C_1\), in green). In particular, the signal at \(δ = −9.5\) ppm, with a large coupling constant to rhodium of 20 Hz, can be attributed to the CH\(_3\) group directly attached to the rhodium atom (C\(_3\)), whereas that at \(δ = 36.0\) ppm (\(J(C,\text{Rh}) = 4\) Hz) corresponds to C\(_3\) directly bonded to phosphorus. A characteristic feature of the rhodaphosphetane moiety was present in the \(^{31}\)P(\(^1\)H) NMR spectrum, which showed a doublet at \(δ = −36.1\) ppm (\(J(P,\text{Rh}) = 122\) Hz) shifted upfield in about 70 ppm relative to 2 (48.1 ppm). Such a shift is diagnostic of a phosphorus atom in a four-membered metalacycle.\(^{[40]}\)

Repetitive attempts to grow single crystals of complex 13 under different conditions gave systematically very small and gminated microcrystals; thus, preventing further crystallographic structure determination. Hence, DFT geometry optimization was used to get structural information. An energy minimum was found for [Rh(Tp)(n\(^1\)-Et)(\(\kappa\)\(^2\)-C\(_2\)\text{-CH}_3\text{-CH}_2\text{PPH}_3\))] (13') (Figure 7), with rhodium in an almost octahedral environment.

The strong trans influence of the alkyl carbons (C1 and C2) is clearly demonstrated by the considerable elongation of the Rh–N1 and Rh–N5 bond distances (2.240 and 2.211 Å, respectively) in comparison with the other Rh–N3 bond (2.118 Å), which is trans to the phosphate. The four-membered ring slightly deviates from planarity (P-C-Rh torsion angle of 12.55°). Among the endocyclic angles, the P-Rh-C angle is the most acute (71.24°).

The formation of the rhodaphosphacyclobutane 13 is remarkable as there are very few examples of metallaphosphacyclobutanes, mainly limited to ruthenium\(^{[41]}\) and palladium\(^{[42]}\) complexes. Rhodium phosphacyclobutanes are also known, however they have mainly been obtained from ortho metalation of phosphanes.\(^{[43]}\) To our knowledge, this is the first example of a rhodaphosphacyclobutane derived from an alkene, as well as the first example of insertion of a non-activated olefin (ethylene) into a Rh–P bond. Moreover, reactions leading to P–C bond formation with non-activated olefins such as ethylene are essentially absent in the literature.\(^{[1b,d,f]}\) Notable examples include a nickel phosphenamide complex that can undergo ethylene insertion leading to an organic phosphirane via an intermediate four-membered nickel phosphacycle,\(^{[44]}\) the nickel-mediated reaction of a primary phosphate to a functionalized phosphate through ethylene insertion,\(^{[1c]}\) and a ruthenium...
phosphide species which reacts with olefins, including ethylene and 1-hexene, to yield metallaphosphacyclobutanes.\[41\]

The most plausible mechanistic pathways to 13 are shown in Scheme 7 and involve two inner-sphere ethylene insertions into the Rh–H and the Rh–P bonds. In both cases, the first step is the oxidative addition of diphenylphosphane to give intermediate A. In the next step, insertion of the coordinated ethylene can occur into either the Rh–H (Scheme 7, in green) or the Rh–P bond (Scheme 7, in red). Coordination of ethylene on the resulting intermediates (B1/B2) would produce C1/C2, suitable for the second ethylene insertion into the Rh–P/Rh–H bonds, respectively.

The first step in both pathways is the oxidative addition of the P–H bond of complex 2 to form intermediate A. This reaction has a relative high barrier of \( +28.7 \text{ kcal mol}^{-1} \) according to DFT calculations (Figure 8). This seems to be the rate-determining step for the formation of 13. Experimentally the reaction requires heating to 60 °C for six days to reach completion, from which one can estimate an activation barrier of about \( +27.3 \text{ kcal mol}^{-1} \) using the Eyring equation,\[40\] which is in reasonable agreement with the slightly overestimated DFT barrier.

The two most logical pathways for the formation of complex 13 from A were both computed with DFT calculations. The green pathway through intermediates B1 and C1 is clearly the preferred pathway, and has low-barrier and very accessible transition states once A is formed (Figure 9). The alternative red pathway via intermediates B2 and C2 has much higher barriers (Figure 10), and the formation of intermediate B2’ from B2 involving dissociation of the Rh–P bond of the rhodium-phosphacyclobutane ring (\( \approx 31.3 \text{ kcal mol}^{-1} \)) is even more endergonic than TS1 (Figure 8).

It is therefore clear that the reaction to form complex 13 should follow the green pathway (through intermediates B1 and C1) as shown in Figure 9. The mechanism described herein is distinct from the ruthenium chemistry described by Rosenberg et al., in which the ruthenium species undergoes a 2+2 cycloaddition through a Ru phosphaneidene (Ru–P) intermediate,\[41\] whereas the chemistry reported here occurs through the rhodium hydrido-phosphaneido intermediate A.

Our results indicate a preference for ethylene insertion into the Rh–H bond and are in agreement with related DFT studies\[40\] on alkene insertion into metal-phosphaneide bonds for which calculations showed that alkene insertion into a M–H bond should be much easier compared to a M–P bond (M = Pd, Ni, Pt, and Rh).
Attempts to eliminate ethane and PEtPPh₂ from 13 aimed to close a hypothetical dual hydrophosphonation/hydrogenation catalytic cycle were tested using HPPPh₂ as proton source. Therefore, complex 13 was heated in the presence of PHPh₂ (20 mol equiv) at 80 °C under an atmosphere of ethylene (6 bar). PEtPPh₂ (20%) and ethane were observed as products, but the major component of the reaction mixture was found to be PH₃P·PHPh₂ (80%), the product from the dehydrocoupling reaction. Even after prolonged heating of 13 (105 °C for a week) no evidence for ethylene deinsertion was observed. Other ligands were also added to 13 to favor reductive elimination. However, no reaction was observed with CO (1 atm., 80 °C, 48 h) by ¹H and ³¹P NMR spectroscopy.

Reactions with OPHPh₂

Diphenylphosphane oxide reacts with [Rh(Tp)(C₅H₅)](PHPh₂) (2) to give [Rh(Tp)(H)(POPPh₂)(PHPh₂)] (14), which was fully characterized by analytical and spectroscopic methods, including a X-ray crystallographic study (Figure 11).

![Figure 11. Molecular structure (ORTEP, ellipsoids set at 50% probability) of complex [Rh(Tp)(H)(POPPh₂)(PHPh₂)] (14). Selected bond lengths [Å] and angles [°]: Rh–P1 2.238(2), Rh–P2 2.268(2), Rh–N1 2.162(4), Rh–N2 2.164(4), Rh–N3 2.122(4), P2–Oa 1.511(6), P1–Rh–N5 174.5(2), P2–Rh–N3 179.0(2), N1–Rh–Hb 105.1(3). Only the C⁷⁷ of the phenyl rings are shown for clarity.](image)

Its molecular structure shows the rhodium atom in the center of a slightly distorted octahedron bound to the three nitrogen atoms of theTp ligand, two phosphorus atoms coming from the phosphanido and the phosphane oxide, respectively, and the hydride ligand. The remaining proton is bound to a phosphorus atom, as deduced by its signal at δ = 7.17 ppm (J(H,P) = 410.2, ²J(H,P) = 10.5 Hz) in the ¹H NMR spectrum, but it could not be located in the structure due to the disorder of the oxygen atom over the two phosphorus atoms (75.3(14) and 24.7(14)% relative abundance).

Spectroscopic data of 14 in solution agreed with the structure shown in Figure 11. Thus, the ³¹P(¹H) NMR spectrum showed two doublets of doublets at δ = 75.7 and 33.5 ppm; the peak at high field has been assigned to the phosphane PHP₂ ligand. The hydride ligand resonates at δ = 13.74 ppm as a doublet of doublets of doublets by coupling to the two cis P atoms (²J(H,P) = 23.2 and 20.4 Hz) and to the ¹⁰³Rh nuclei (³J(H,Rh) = 16.0 Hz), whereas the PH proton was observed at δ = 7.17 ppm in the ¹H NMR spectrum. Moreover, ¹H–³¹P HMBC NMR experiments (with J(H,P) = 10 and 400 Hz) showed that this proton was strongly coupled to the phosphane ligand (³J(H,P) = 410.1) and in less extension to the POPPh₂ ligand (³J(H,P) = 10.5 Hz). These observations along with its molecular structure (Figure 11, in which both phosphorus atoms are coordinated to rhodium) definitively confirm that the hydride ligand comes from the phosphane oxide (OPHPh₂) instead of the phosphane PHP₂.

A plausible sequence of reactions in the synthesis of 14 is shown in Scheme 8. The red pathway starts with the coordination of diphosphane oxide to render intermediate A, followed by the activation of P–H bond. This step requires decoordination of one of the pyrazolate arms to allow the approaching of the P–H bond to rhodium. The participation of the tautomer hydroxydiphosphane would give intermediate B followed by an easy O–H bond activation reaction (green pathway). Although both possibilities could be operative, we believe that the pathway marked in green is more plausible, in spite of the smaller abundance of the hydroxy tautomer in the equilibrium, because of the type of bonds involved. Indeed, such activations through the tautomer phosphinous acid have been previously proposed for ruthenium complexes on the basis of DFT calculations.

Interestingly, the reaction of OPHPh₂ with the bis(ethylen) complex [Rh(Tp)(C₅H₅)] (1) (in 1:1 molar ratio) did not give the mononuclear complex [Rh(Tp)(C₅H₅)(OPHPh₂)] (analogous to 2), but the bis(μ-ethyl) dinuclear complex [[(Tp)(μ-1-Et)Rh(μ-OPHPh₂)]₂ (15) along with the mononuclear complexes [Rh(Tp)(μ-1-R)(POPPh₂)(POPPh₂)] (R = Et, 16 and H, 17) (Scheme 9). From these solutions, complex 15 was isolated.
after work-up, whereas a mixture of complexes 16 and 17 was isolated in high yield if solutions of 15 in the presence of two molar equivalents of OPHPh₂ were heated for 14 h at 60 °C in toluene.

The dinuclear nature of 15 is evident from the 31P(1H) NMR, which shows a multiplet corresponding to the AA' part of an AA'XX' spin system (A, A' = 31P; X, X' = 103Rh) for the two equivalent phosphorus nuclei. The ethyl group was clearly observed as three signals (1:1:1 ratio) in the 1H NMR spectrum with the methylenic protons strongly coupled to the phosphorus atom according to the 1H-13P HMBC spectrum.

Complexes 16 and 17 could not be separated because of their high tendency to crystallize together in a disordered manner. Indeed, all single crystals studied by X-ray methods revealed that they contained both complexes in an approximate 1:1 ratio. Nonetheless, spectroscopic data of the isolated solid agrees with a mixture of 16 and 17 in a 2:1 molar ratio. Thus, a broad signal, corresponding to the hydrogen interacting with the two oxygens, was found at δ = 18.34 ppm in the 1H NMR spectrum. The methylenic protons of the ethyl ligand in 16 were observed at δ = 2.22 ppm as a quartet of triplets of doublets because of the coupling with the three protons of the adjacent methyl group (J(H,H) = 7.5 Hz), the two equivalent phosphorus atoms (J(1H,1P) = 4.1 Hz) and 103Rh (J(1H,1Rh) = 1.9 Hz). The hydride ligand in 17 was detected at δ = −12.99 ppm as a triplet of doublets because of the coordination with the two equivalent phosphorus atoms (J(1H,1P) = 21.7 Hz) and 103Rh (J(1H,1Rh) = 16.7 Hz).

Scheme 10 shows a plausible sequence of reactions that accounts for the synthesis of 15–17 from the reactions of [Rh(Tp)₂(C₆H₄)₂] (1) with OPHPh₂. The first part of the reaction would consist in the coordination of the hydroxydiphenylt au-tomer to give intermediate A, followed by the oxidative addition reaction of the O–H bond to give species B, as previously commented for complex 14.

From B, ethylene replacement by a new molecule of OPHPh₂ would give the hydride complex [Rh(Tp)(H)(OPPh₂)(OPPh₂)] (17), but a competitive insertion reaction of the hydride ligand into the Rh–ethylene bond would lead to intermediate C. From C, a dimerization would render the dinuclear complex [[(Tp)ₙ-Et(Rh-μ-OPPh₂)]₂] (15), whereas coordination of OPHPh₂ would produce the mononuclear complex [Rh(Tp)(η¹-Et)(OPPh₂)(OPPh₂)] (16).

The proposed equilibrium between complex 15 and intermediates B and C has been verified by the reaction of 15 with OPHPh₂ (in 1:2 molar ratio), which systematically gives a mixture of the mononuclear complexes 16 and 17 in a 2:1 ratio. Since no change of this ratio was observed on heating this mixture for prolonged time, complexes 16 and 17 are not in equilibrium and, most probably, they arise from intermediates B and C, respectively. This ratio could represent the relative rates for OPHPh₂ coordination to B/C (assuming a fast equilibrium B+·C), or alternatively the ratio of B and C in the equilibrium if coordination of OPHPh₂ were faster. However, considering the low ΔG values for hydride insertions into Rh–ethylene bonds, the first possibility seems to be more plausible.

Conclusions

The combination of tridentate hydridotris(pyrazolyl)borate and phosphane ligands on rhodium provides a useful platform for the selective oxidative addition reaction of the P–H bond in diphenyolphosphane to give the new hydrido-phosphane complexes [Rh(Tp)(H)(L)(PPh₂)] (L = PMe₃, PMePh, PPh₂). Increasing the steric bulk of the phosphane by using PMePh₂ or PPh₂ also results in the corresponding hydrido-phosphane complexes, but in these cases they establish an equilibrium with the corresponding square-planar rhodium(II) complexes with a k⁺-coordinatedTp ligand. The thermodynamic parameters for such equilibria: [Rh(n²-Tp)(L)(PPh₂)] ≈ [Rh(Tp)(H)(L)(PPh₂)] (L = PMePh₂, PPh₂), obtained from the Van ‘t Hoff plots, indicate both reactions to be slightly exothermic (∆H = (−2.12 ± 0.02) and (−2.64 ± 0.01) kcal mol⁻¹) with a negative entropic contribution; larger for the bulkier PPh₂ than for PMePh₂ (∆S = (−10.74 ± 0.05) and (−5.77 ± 0.06) u.e., respectively). These results strongly support that steric factors, over electronic effects, govern the formation of the final products. Indeed, both the richest (with PMe₃) and poorest (with PPh₂) rhodium centers give the corresponding rhodium(III) hydrido-phosphane complexes cleanly. However, complexes with the highly donating NHCS ligands IMes and BzIIMe remained in the rhodium(II) oxidation state under similar conditions. In this case, the lack of reactivity can be attributed to the particular steric requirements of these ligands that direct the steric demands in a specific direction, hindering the access to the P–H bond activation transition state.

The reaction of [Rh(Tp)(C₆H₄)(PPh₂)] with ethylene leads to the unique rhodophosphacyclobutane complex [Rh(Tp)(η¹-Et)(C₆H₄CH₂PPh₂)]. It is the result of a double ethylene insertion into the Rh–H and Rh–P bonds. Computational studies provided insights into the reaction mechanism, revealing that the lowest energy pathway involves oxidative addition of the P–H bond in 2 to form intermediate A, followed by low-barrier reaction steps involving ethylene insertion into the formed Rh–H and Rh–P bonds.

A formal P–H bond activation of phosphane oxide also takes place to give the related hydrido complex...
[RhTp(H)(PPh3)(POPh3)], in the reaction of [RhTp(C3H5)2(PPh3)] with OPOPh3, but ethyl complexes result from hydride insertion into Rh=ethylene bond in the reaction with [RhTp(C3H5)2]. In these reactions, the participation of the phosphinous acid tautomer is proposed, firstly coordinating to the metal through the phosphorous atom, and then transferring the O=H proton to the rhodium.

We believe that the results reported here expand the knowledge on oxidative addition reactions of secondary phosphanes to rhodium, which can be useful for the design of catalyzed processes leading to green syntheses of phosphanes.

Experimental Section

All the operations were carried out under an argon atmosphere using standard Schlenk techniques as well as dry-box facilities. The complexes [RhTp(C3H5)2] (1),[RhTp(C3H5)(PPh3)] (2), and [RhTp(H)(PMe3)(PPh3)] (3) were prepared according to literature methods. Diphenylphosphane purchased from Aldrich was found to contain about 4% of diphenylphosphine oxide. The oxide was removed by silica gel column chromatography using diethyl ether as eluent. Diethyl ether was then evaporated under vacuum. Elemental analyses (carbon, hydrogen, and nitrogen) were carried out with a PerkinElmer 2400 CHNS/O microanalyzer. Mass spectra and high-resolution mass spectra of complexes were acquired on a Bruker Esquire3000 plus (ESI+) and a Bruker MicroTOF-Q (ESI+) spectrometers, respectively. NMR spectra were recorded on a Bruker AV300, AV400 and AV500 spectrometers operating at 300.13, 400.13 and 500.13 MHz, respectively, for 1H. Chemical shifts are reported in ppm and referenced to SiMe4 using the internal signal of the deuterated solvent (1H and 13C) and external H2PO4, 85% in water ([P,P] and HBF4, 15% in [D3]benzene ([B]). IR spectra of solid samples were recorded with a PerkinElmer 10 FT-IR spectrometer (4000-400 cm-1) equipped with attenuated total reflectance (ATR). For the labeling of protons and carbons see the Supporting Information.

Synthesis of the complexes

([Tp][H]+[PPh3]+[PPh3]) (3): An NMR tube was charged with [RhTp(C3H5)2] (1, 9.0 mg, 0.024 mmol) and [RhTp(H)(PPh3)] (6, 16.6 mg, 0.024 mmol) and then [D3]benzene (0.5 mL) was added. The reaction was monitored by 1H and 31P-[H] NMR showing the immediate formation of [RhTp(C3H5)(PPh3)] (2) while a white solid corresponding to complex 3 precipitated. The resulting suspension was centrifuged, decanted and the remaining solid was washed with hexane (3-5 mL) and dried under vacuum. Yield: 7.5 mg (63%). IR(ATR): v(=B-H) 2485 cm⁻¹ (m), v(=R-H) 2064 cm⁻¹ (m); 1H NMR (400.13 MHz, [D3]benzene, 25 °C): δ = 0.91 (3H, s, PPh3), 7.68 (3H, J(3-P, B) = 1.8 Hz, 2H, PPh3), 7.52 (3H, J(3-P, B) = 7.4 Hz, 2H, PPh3), 7.38 (3H, J(3-P, B) = 7.2 Hz, 2H, PPh3). 7.28 (3H, J(3-P, B) = 8.0 Hz, 2H, PPh3), 7.17 (2H, J(3-P, B) = 2.7 Hz, 2H, PPh3), 7.07 (2H, J(3-P, B) = 6.8 Hz, 2H, PPh3), 7.01 (3H, J(3-P, B) = 3.4 Hz, 2H, PPh3), 6.81 (3H, J(3-P, B) = 1.8 Hz, 2H, PPh3), 6.76 (3H, J(3-P, B) = 7.4 Hz, 2H, PPh3), 6.65 (3H, J(3-P, B) = 0.7 Hz, 4H, PPh3), 6.46 (3H, J(3-P, B) = 0.7 Hz, 4H, PPh3), 6.40 (3H, J(3-P, B) = 7.7 Hz, 4H, PPh3), 5.78 (3H, J(3-P, B) = 2.1 Hz, 2H, PPh3), 5.67 (3H, J(3-P, B) = 2.2 Hz, 4H, PPh3), 12.54 ppm (td, 4H, J(3-P, B) = 22.3, J(H,B) = 17.8 Hz, 1H, Rh-H). 13C[NMR (161.3 MHz, [D3]benzene, 25 °C): δ = -48.99 ppm (t, J(P, H) = 92 Hz); 13C[NMR (128.4 MHz, [D3]benzene, 25 °C): δ = -3.38 ppm (s, BH). Elemental analysis calc % for C18H14N4P3Rh: 50.24% C, 4.43% H, 17.02%.
**Reaction of [Rh(Tp)(C₅H₅)(PPh₃)] (2) with PMe₅:** Methylidyne-porphyrinylphosphine (22 μL, 0.11 mmol) was added to a solution of [Rh(Tp)(C₅H₅)(PPh₃)] (2, 57.0 mg, 0.11 mmol) in toluene (5 mL).

After stirring for 20 min, the solution was evaporated to 0.5 mL, washed with hexane (6 mL) and left steady overnight. The orange microcrystals that precipitated were separated by decantation, washed with cold hexane (1 x 2 mL) and dried under vacuum.

Yield: 68.0% (80 mg). IR (ATR): ν(ν-B) 2451 cm⁻¹ (m), ν(RH-H) 2082 cm⁻¹ (m); NMR: m/z calc for C₂₅H₂₃N₂P₂Rh [M⁺]+ 703.1547, found: 703.1561 (error (m/D) = -0.43); elemental analysis calc (%) for C₂₅H₂₃N₂P₂Rh: 58.14, H 4.88, N 11.97; found: C 57.41, H 4.89, N 12.22.

**NMR data for [Rh(Tp)(PMe₅)(PPh₃)(P)] ([8a, 70%]):**

- ¹H NMR (500.13 MHz, δ = 0.85, δ = 0.1, δ = 1.2, δ = 0.7, 2H, PH₅), 7.62 (δ = 0.7, δ = 1.1, δ = 1.4, 2H, PMe₅), 7.59 (δ = 0.7, δ = 0.9, δ = 1.0, 2H, PMe₅), 7.38 (δ = 0.9, δ = 1.1, δ = 1.2, 2H, PMe₅), 7.26 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 7.18 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 7.05 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.90 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.79 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.67 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.61 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.57 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 5.91 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 5.52 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 4.62 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 1.94 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 1.30 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 0.83 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 0.41 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅), 0.19 (δ = 0.9, δ = 1.0, δ = 1.0, 2H, PMe₅).

**Selected NMR resonances for [Rh(Tp)(PMe₅)(PPh₃)(P)] ([8a, 70%]):**

- ¹H NMR (400.13 MHz, δ = 0.5, δ = 0.1, δ = 0.7, 2H, PH₅), 7.59 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 7.58 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 7.26 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 7.18 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 7.05 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.90 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.79 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.67 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.61 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 6.57 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 5.91 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 5.52 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 4.62 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 1.94 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 1.30 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 0.83 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 0.41 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅), 0.19 (δ = 0.7, δ = 1.0, δ = 1.0, 2H, PMe₅).

**Reaction of [Rh(Tp)(C₅H₅)(PPh₃)] (2) with PPh₃:** An NMR tube was charged with equimolar amounts of complex 2 (15.6 mg, 0.03 mmol) and PPh₃ (9.1 mg, 0.03 mmol) and left steady overnight. The orange microcrystals that precipitated were separated by decantation, washed with hexane (2 mL) and dried under vacuum. The yield was 84 mg (71%), IR (ATR): ν(ν-B) 2433 cm⁻¹ (m), ν(RH-H) 2082 cm⁻¹ (m); NMR: m/z calc for C₂₅H₂₃N₂P₃Rh [M⁺]+ 703.1547, found: 703.1561 (error (m/D) = -0.43); elemental analysis calc (%) for C₂₅H₂₃N₂P₃Rh: 58.14, H 4.88, N 11.97; found: C 57.41, H 4.89, N 12.22.
for 6 days to give a cloudy light-yellow solution. Then, toluene (2 mL) was added and the suspension was filtered off to remove small amounts of complex 3. The filtrate was dried under vacuum, washed with hexane (2 × 0.5 mL) and dried under vacuum. Yield: 22.0 mg (78%). IR(ATR): ν(B–H) 2460 cm⁻¹ (m); ¹H NMR (500.13 MHz, [D₈]benzene, 25 °C): δ = 7.74 (d, J(H,H) = 1.5 Hz, 1H, Pz²), 7.652 (d, J(H,H) = 2.2 Hz, 2H, Pz²), 7.651 (d, J(H,H) = 2.1 Hz, 1H, Pz³), 7.56 (dd, J(H,H) = 2.3 Hz, J(H,J) = 0.7 Hz, 1H, Pz³), 7.51 (ddd, J(H,J) = 0.9 Hz, J(J,H) = 7.5 Hz, 1H, J(J,H) = 1.7 Hz, 2H, PPh²), 7.49 (d, J(J,J) = 1.7 Hz, 1H, Pz³), 7.19 (dd, J(J,J) = 10.6 Hz, J(J,J) = 7.0 Hz, 2H, PPh²), 7.04 (m, 3H, PPh³), 6.87 (d, J(J,J) = 1.5 Hz, 1H, Pz³), 6.84 (t, J(J,J) = 7.5 Hz, 1H, PPh), 6.71 (t, J(J,J) = 6.9 Hz, 2H, PPh³), 6.09 (t, J(J,J) = 2.1 Hz, 1H, Pz³), 5.94 (br, 1H, Pz³), 5.77 (t, J(J,J) = 2.1 Hz, 1H, Pz³), 3.95 (dd, J(J,J) = 15.0 Hz, J(J,J) = 10.9 Hz, J(J,J) = 6.4 Hz, 1H, H²), 3.64 (dd, J(J,J) = 15.0 Hz, J(J,J) = 10.9 Hz, J(J,J) = 6.4 Hz, 1H, H³), 2.23 (dd, J(J,J) = J(J,Rh) = 7.8 Hz, J(J,J) = 3.8 Hz, 1H, H⁴); 0.042 mmol) in toluene (6 mL). After stirring for 14 hours at 60 °C, the light-yellow solution was evaporated, and the residue was washed with hexane (5 × 1 mL) and dried under vacuum. Yield: 60.9 mg (98%; ratio = 16.17:1). NMR data for [Rh(Tp)[η²-R(PPh₃)(PPh₃)]] (16, 66.6%): ¹H NMR (500.13 MHz, [D₈]benzene, 25 °C): δ = 18.34 (brs, 1H, POH), 7.92 (dd, J(J,J) = 7.9 Hz, J(J,J) = 5.7, J(J,J) = 3.7 Hz, J(J,J) = 1.6 Hz, 4H, PPh³); 7.55 (d, J(J,J) = 2.3 Hz, 4H, Pz²); 7.36 (d, J(J,J) = 2.3 Hz, 1H, Pz³), 7.12 (m, 4H, PPh³); 7.09 (m, 2H, POH), 6.91 (ddd, J(J,J) = 6.8 Hz, J(J,J) = 5.2, J(J,J) = 3.8 Hz, J(J,J) = 1.4 Hz, 4H, PPh³), 6.83 (m, 4H, PPh³), 6.75 (m, 2H, POH), 6.74 (d, J(J,J) = 2.3 Hz, 1H, POH), 5.84 (t, J(J,J) = 2.2 Hz, 1H, POH), 5.21 (t, J(J,J) = 2.1 Hz, 1H, POH), 2.22 (quad, J(J,J) = 7.5 Hz, 2J(J,J) = 4.1 Hz, J(J,J) = 1.9 Hz, 2H, CH₂); 0.52 ppm (t, J(J,J) = 7.5 Hz, 3H, Me); ¹P[H] NMR (202.5 MHz, [D₈]benzene, 25 °C): δ = −0.882 ppm (d, J(J,P) = 140 Hz, 2P); ¹B[H] NMR (160.5 MHz, [D₈]benzene, 25 °C): δ = −4.42 ppm (s, BH).

**DFT geometry optimizations**

The DFT geometry optimizations and thermochemical calculations were carried out with the Gaussian 09 program package,[31] using the B3LYP-D3 hybrid functional.[32] Geometry optimizations were performed in the gas phase with the Lanl2TZ(f) effective core potential basis set for the metal atoms, and the 6-311G(dp) basis set for the remaining atoms.
Profiles for reactions in Figures 8–10 were computed with the Turbomole program[47] coupled to the POS Baker optimizer[24] by the BOpt package.[50] Geometries were fully optimized as minima or transition states using the BP86 functional,[51] the Turbomole def2-TZVP basis set[52] and a small grid size (m4). To reduce computation time, the resolution-of-identity (r) approximation[58] was applied. Grimme’s dispersion corrections (version D3, disp3, ‘zero damping’) were applied to include Van der Waals interactions.[52a]

X-ray diffraction studies on complexes [(Tp)(H)Rh(μ-
PPh2)2Rh(PPh3)]0.5H2O (7-0.5H2O), [Rh(Tp)(Mes)(PPh2)] (11) and [Rh(Tp)(H)POPh3] (14)

Intensity measurements were collected with a Bruker Smart Apex-II (7 and 11) or a Bruker Smart Apex (14) diffractometers, with graphite-monochromated MoKα radiation at 100 K (ω scans of 0.3°). A semi-empirical absorption correction was applied to the data set with the multi-scan[20] methods. The structures were solved by direct methods with SHELXS-2013[20] (7 and 14) or SHELXL-2014[20] (11) and refined by full-matrix least-squares on F2 with the program SHELXL-2016,[20] in the WINGX[20] package. In the 24.7(14)% of the crystal of 14 the phosphanido and the phosphane oxide ligands are swapped. All non-hydrogen atoms were refined with anisotropic displacement parameters, and their hydrogen atoms were geometrically calculated and refined by the riding mode, including the isotropic displacement parameters. The hydride ligands were located in difference-Fourier maps and refined with a geometrical restraint (DFIX) card. The hydrogens bonded to phosphorus (7 and 11) or boron atoms (7) were also located in a difference-Fourier map and refined with some degree of freedom. Hydrogen atoms of the water solvent (7) were not included in the model. For selected crystallographic data see the Supporting Information.

CCDC 1949932 (7-0.5H2O), 1949933 (11), and 1949934 (14) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: insertion · oxidative addition · P–H activation · rhodaphosphacyclobutane · rhodium


Complexes \([\text{Rh}(\text{acac})(\text{L})(\text{CO})]\) were prepared in situ by addition of the appropriate ligand to solutions of \([\text{Rh}(\text{acac})(\text{CO})]\) in toluene. The related \([\text{Rh}(\text{TP})(\text{L})(\text{CO})]\) complexes were not used in this study since the \(\delta^2\)-selective process is not irreversible.


H. Geissler, P. Gross, B. Hucke, New palladophospho-cyclobutane com-
ounds obtained by reacting special tri-organopalladium compounds with palladium salts palladium complexes or alkali palladate salts in or-


For a first order reaction \((\ln \theta = -k t)\) reaching 99% conversion in six days, the rate constant \(k\) is approximately \(8.9 \times 10^{-6} \text{s}^{-1}\), which trans-
lates to a free energy barrier \(\Delta G^\ddagger\) of approximately \(+27.3 \text{ kcal mol}^{-1}\) by using the Eyring–Polanyi equation \((k = \frac{\tau}{h} \exp(-\Delta G^\ddagger/k_B T))\) with \(\tau =\) Boltzmann constant, \(R =\) gas constant, \(h =\) Planck constant, and assuming a trans-
mission coefficient of 1.


J. A. López, private communication.


See the Supporting Information for a complete reference.


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