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DOI

[10.1002/ange.201407707](https://doi.org/10.1002/ange.201407707)

[10.1002/anie.201407707](https://doi.org/10.1002/anie.201407707)

Publication date

2015

Document Version

Final published version

Published in

Angewandte Chemie

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Geer, A. M., Serrano, Á. L., de Bruin, B., Ciriano, M. A., & Tejel, C. (2015). Terminal Phosphanido Rhodium Complexes Mediating Catalytic P—P and P—C Bond Formation. *Angewandte Chemie*, 127(2), 482–485. <https://doi.org/10.1002/ange.201407707>, <https://doi.org/10.1002/anie.201407707>

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Terminal Phosphanido Rhodium Complexes Mediating Catalytic P–P and P–C Bond Formation**

Ana M. Geer, Ángel L. Serrano, Bas de Bruin, Miguel A. Ciriano, and Cristina Tejel*

In memory of María Pilar García

Abstract: Complexes with terminal phosphanido ($M-PR_2$) functionalities are believed to be crucial intermediates in new catalytic processes involving the formation of P–P and P–C bonds. We showcase here the isolation and characterization of mononuclear phosphanido rhodium complexes ($[RhTp(H)(PR_2)L]$) that result from the oxidative addition of secondary phosphanes, a reaction that was also explored computationally. These compounds are active catalysts for the dehydrocoupling of $PHPh_2$ to Ph_2P-PPh_2 . The hydrophosphination of dimethyl maleate and the unactivated olefin ethylene is also reported. Reliable evidence for the prominent role of mononuclear phosphanido rhodium species in these reactions is also provided.

Complexes with a terminal phosphanido ($M-PR_2$) functionality bound to a single late-transition-metal center seem to be crucial intermediates in relevant processes such as hydrophosphination^[1] and dehydrocoupling reactions.^[2] The former represents an atom-economical route to a very important class of compounds such as organophosphanes.^[3] Dehydrocoupling reactions provide a facile way to diphosphanes, phosphacycles, and unique oligophosphanes, for which interesting properties can be envisaged.^[4] New materials based on phosphorus–boron bonds have already been prepared.^[5] Moreover, safety, selectivity, and “green synthesis” are major advantages of dehydrocoupling and hydrophosphination catalysis.^[6] Consequently, the formation of P–C and P–P bonds using these methods has attracted considerable attention, intensified by the possibility of activating the resulting P–P bonds for the synthesis of new phosphorus-based

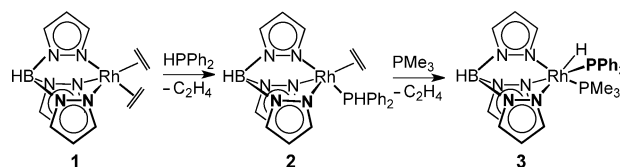
derivatives.^[7] Prevailing catalysts for dehydrogenative P–P coupling are zirconium and titanium complexes,^[8] while the viability of late-transition-metal compounds in this field remains almost unknown, except for the two notable examples based on rhodium that are described below.^[9] More recently, main-group reagents such as $[Sn(C_5Me_5)_2Cl_2]$ have been reported to be suitable catalysts for P–P bond formation, although with modest TON values.^[10] Detailed mechanistic information on the dehydrocoupling of phosphanes only exists in a few cases, mainly concerning early transition-metal catalysts.^[2b,11] Nonetheless, the Rh^V diphosphanide species $[Rh(C_5Me_5)(H)_2(PR_2)_2]$ was tentatively hypothesized by Böhm and Brookhart to mediate in the dehydrocoupling of secondary phosphanes,^[9b] while $[Rh(dippe)(CH_2Ph)(H)(PPh)]$ (*dippe* = $iPr_2PCH_2CH_2P^iPr_2$) was observed as a transient species in the preparation of the dinuclear complex $[[Rh(\mu-PPh)(dippe)]_2]$ as a precatalyst for dehydrocoupling primary phosphanes.^[9a] A key step postulated in both processes is the activation of the P–H bond, commonly proposed to occur by oxidative addition at late-transition-metal centers.^[1c,8b] However, isolated mononuclear hydrido organophosphanido metal complexes from such reactions are known only for platinum,^[12] nickel,^[13] tantalum,^[14] molybdenum, and tungsten,^[15] while none are to date known for rhodium;^[16] thus proof of their involvement in real catalytic P–P and P–C bond-formation processes is warranted. Herein we report the isolation and full characterization of such complexes and give reliable evidence for their participation in catalytic rhodium-mediated P–P and P–C bond-formation reactions.

The addition of diphenylphosphane to a solution of $[Rh(Tp)(C_2H_4)_2]$ (**1**; Tp = hydridotris(pyrazolyl)borate) in toluene led to the immediate replacement of one ethylene ligand to give $[Rh(Tp)(C_2H_4)(PHPh_2)]$ (**2**), which was isolated as an orange microcrystalline solid in excellent yield (Scheme 1). Complex **2** was fully characterized as a species with TBPY-5 geometry and a nonrotating ethylene group at the equatorial position. A further reaction of complex **2** with trimethylphosphane in toluene led to the hydrido-phosphanido complex $[Rh(Tp)(H)(PMe_3)(PPh_2)]$ (**3**), which was

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[**] The generous financial support from MICINN/FEDER (Project CTQ2011-22516), Gobierno de Aragón/FSE (GA/FSE, Inorganic Molecular Architecture Group, E70), and NWO-CW (VICI project 016.122.613; BdB) is gratefully acknowledged. A.M.G. and A.L.S. thank Gobierno de Aragón and MEC, respectively, for fellowships.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201407707>.



Scheme 1. Synthesis of complexes **2** and **3**.

isolated as a yellow solid in high yield after workup. Complex **3** represents the first isolated terminal phosphanido rhodium complex resulting from the formal oxidative addition of a P–H bond to a rhodium center.

The molecular structure of **3**, obtained by single-crystal X-ray diffraction methods (Figure 1),^[17] shows the rhodium atom in the center of a slightly distorted octahedron. Furthermore, the ¹H NMR spectrum showed a high-field signal (ddd) corresponding to the hydride (located in the Fourier map) at δ –15.62 ppm. The geometry around the phosphanido phosphorus atom (P1) reveals that the lone pair of electrons generated upon oxidative addition of the P–H bond does not interact with the Rh center, thus resulting in a Rh–P1 single bond. Thus, the environment at P1 is pyramidal, with the sum of the three bond angles amounting to $\Sigma^0 = 320.40(2)^\circ$ ($317.03(2)^\circ$ for the second independent molecule), a value somewhat smaller than that expected for a tetrahedron (328.5°) because of the repulsion of the lone pair of electrons.

Although no intermediates were detected on monitoring the reaction that resulted in **3** by NMR spectroscopy, it is reasonable to assume that [Rh(Tp)(PPh₂)(PMe₃)] (**A**) is formed initially from the replacement of ethylene by trimethylphosphane followed by cleavage of the P–H bond. Studies on the reaction **A** → **3a** and the geometry of the compounds involved therein by DFT methods (Figure 2) give structural parameters for [Rh(Tp)(H)(PMe₃)(PPh₂)] (**3a**) that correlate with those found in the X-ray structure of **3**.^[18]

According to DFT calculations, the rhodium atom in the intermediate **A** adopts a square-planar coordination geometry. The Tp ligand was κ^2 -coordinated with the “Rh(N–N)₂B” six-membered metallacycle having a boat conformation.^[19] This feature agrees with previous observations involving “Rh^I(Tp)”, which indicate that the κ^2 -coordination mode becomes stabilized as the electronic density on the rhodium

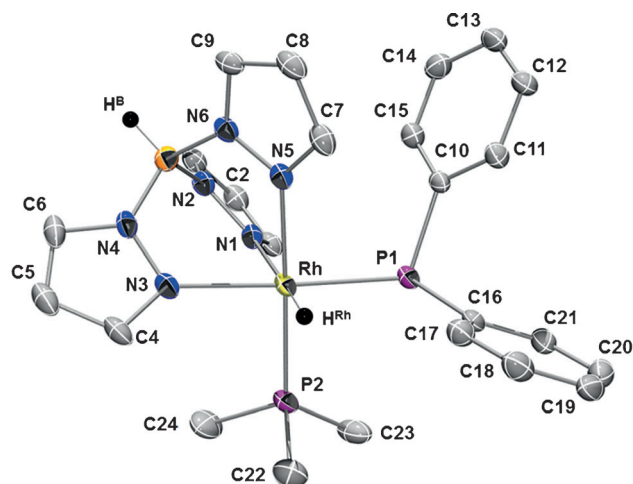


Figure 1. Molecular structure (ORTEP, ellipsoids set at 50% probability) of complex [Rh(Tp)(H)(PMe₃)(PPh₂)] (**3**). Selected bond distances [Å] and angles [°]: Rh–P1 2.334(1) [2.340(1)], Rh–P2 2.248(1) [2.242(1)], Rh–N1 2.180(3) [2.180(3)], Rh–N3 2.172(3) [2.197(3)], Rh–N5 2.100(3) [2.115(3)], Rh1–H^{Rh} 1.565(14) [1.564(14)]; P1–Rh–N3 177.0(1) [174.9(1)]; P2–Rh–N5 173.6(1) [174.5(1)], N1–Rh–H^{Rh} 174.2(2) [175.6(2)]. Data from the second independent molecule in square brackets.

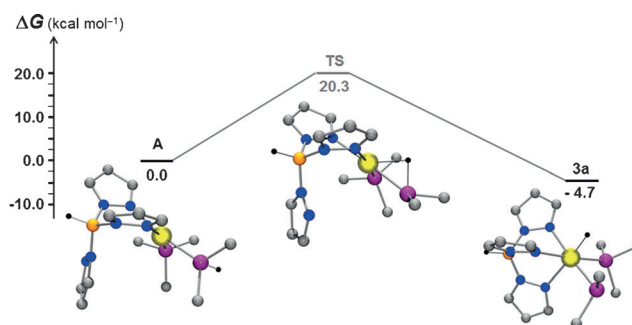
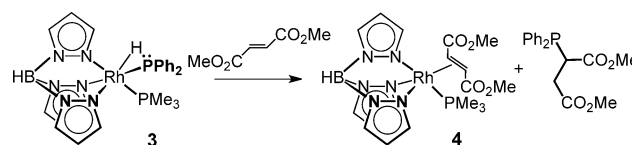


Figure 2. DFT-calculated structures for complexes **A**, **3a**, and the connecting transition state (**TS**) at the BP86-def2-TZVP level. ΔG_{298K}^0 values at the b3Lyp-def2-TZVP level relative to **A** are 22.3 kcal mol^{–1} (**TS**) and –0.5 kcal mol^{–1} (**3a**).

atom increases.^[20] Oxidative addition of the P–H bond proceeds with an accessible barrier of about 20 kcal mol^{–1} (**TS**) to form complex **3** (Figure 2).

The nucleophilicity of the terminal phosphanido group in [Rh(Tp)(H)(PMe₃)(PPh₂)] (**3**) was tested by reaction with dimethyl fumarate (CO₂MeHC=CHCO₂Me), a typical reagent for Michael reactions. The hydrophosphination of a variety of acrylate derivatives mediated by platinum^[21] and palladium^[22] complexes has been widely studied. In our case, the reaction required two molar equivalents of the olefin to reach completion to give cleanly the functionalized phosphane Ph₂P–CH(CO₂Me)CH₂(CO₂Me) and complex [Rh(Tp)(CO₂MeHC=CHCO₂Me)(PMe₃)] (**4**; Scheme 2).^[23]

According to Glueck and co-workers,^[21a] a plausible reaction pathway could be an outer-sphere mechanism, that is, nucleophilic attack of the phosphanido to the external olefin followed by transfer of the hydride to the resulting carbanion to give the rhodium(I) complex [Rh(Tp)(PMe₃)(Ph₂P–CH(CO₂Me)CH₂(CO₂Me))] (**B**). However, based on the observed hydrophosphination of ethylene (see below), a possible inner-sphere mechanism cannot be excluded. Both pathways converge to **B**, in which the functionalized phosphane is replaced by dimethyl fumarate to yield the products. The viability of this step, namely, the replacement of an equatorial phosphane by a good π -acceptor ligand was independently confirmed by the reaction of [Rh(Tp)(PMe₃)₂] (**5**) with dimethyl fumarate, which gives complex **4** cleanly. In addition, the dimethyl fumarate in complex **4** is replaced by PPh₂ to regenerate **3**, which guarantees the viability of the catalytic cycle. Indeed, the functionalized phosphane Ph₂P–CH(CO₂Me)CH₂(CO₂Me) was prepared catalytically in the presence of complex **3**. Catalytic studies (5% cat.) indicated a full and clean conversion after 30 min at room temperature, while complex **4** was the single rhodium compound detected at the end of the catalysis.

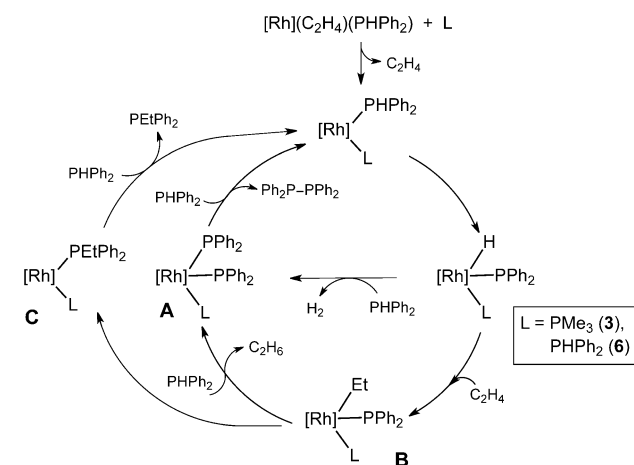


Scheme 2. Synthesis of Ph₂P–CH(CO₂Me)CH₂(CO₂Me) from the hydrophosphanido complex **3**.

As mentioned above, the research groups of Brookhart and Tilley independently reported the catalytic activity of two rhodium complexes for the dehydrocoupling of phosphanes to the corresponding diphosphanes. The catalytic activity of complex **3** for such reactions was tested using PPh_2 as a model substrate in toluene at 80°C with 5 mol% of the catalyst. After 13 h, 51% conversion was observed, while hydrogen was observed by ^1H NMR spectroscopy. A plausible catalytic cycle for this reaction is shown in Scheme 3. Hydrogen could be eliminated from complex **3** by addition of PPh_2 to give the transient species **A**, which contains two *cis*-phosphanide ligands. Reductive elimination of the diphosphane from **A** upon reaction with a new molecule of phosphane would regenerate the catalyst. Nonetheless, other possibilities involving σ -bond metathesis steps cannot be excluded.

Although a hydrogen acceptor is not strictly necessary, the reaction is considerably faster under an ethylene atmosphere (6 bar). Under these conditions, a 100% conversion was achieved within 5 h at 80°C (Figure 3).^[24] Thus, the catalytic activity of **3** under non-optimized conditions is better than that observed for other rhodium compounds.^[9] This reaction could be rationalized if compound **3** engaged in competitive alkene insertion to give the ethyl intermediate **B**. Then, the ethyl ligand could be protonated by the incoming phosphane to give **A** and ethane, thus providing an easier way for the catalysis to proceed (Scheme 3). Indeed, the formation of one mole of ethane per mole of the diphosphane was simultaneously observed and complex **3** was the sole rhodium complex detected during and at the end of the catalysis.

It is remarkable that, as the reaction proceeds, PEtPh_2 appears as a product when the conversion into $\text{Ph}_2\text{P}-\text{PPh}_2$ is over 80%, so that a mixture of $\text{Ph}_2\text{P}-\text{PPh}_2$ (95%) and PEtPh_2 (5%) results at the end of the catalysis. Certainly, complex **3** is a precatalyst for both P–P and P–C bond formation, although the latter reaction is not desirable in this case. However, it is significant that the hydrophosphination of ethylene occurs, since unactivated olefins are essentially absent in this type of reactions.^[1a,13,25] Clearly, P–P and P–C bond-forming reactions compete in such a way that a high concentration of



Scheme 3. Plausible catalytic cycle for the dehydrocoupling of phosphane and hydrophosphination of ethylene mediated by rhodium complexes. $[\text{Rh}] = \text{Rh}(\text{Tp})$.

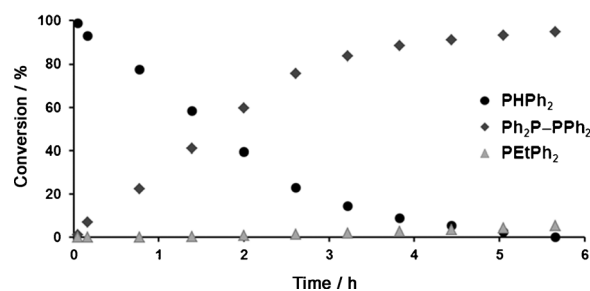


Figure 3. Conversion [%] versus time [h] for the dehydrocoupling of PPh_2 catalyzed by **3**.

phosphane favors the protonation of the ethyl group in **B** and inhibits the P–C reductive elimination to PEtPh_2 , which becomes operative at a low phosphane concentration.

If equimolar mixtures (prepared in situ) of **2** and other phosphanes such as PPh_2 , PMePh_2 , and PMe_2Ph are used as catalyst precursors, the catalysis proceeds with identical results in all cases. Under 6 bar of ethylene, a full conversion was observed in 7 h and the products were found to be $\text{Ph}_2\text{P}-\text{PPh}_2$ (80%) and PEtPh_2 (20%). Inspection of the catalyst precursors by NMR spectroscopy revealed the quantitative formation of hydride phosphanide complexes $[\text{Rh}(\text{Tp})(\text{H})(\text{L})(\text{PPh}_2)]$ ($\text{L} = \text{PPh}_2$, **6**; PMe_2Ph , **7**; PMePh_2 , **8**) similar to **3** (see the Supporting Information). After addition of the substrate (PPh_2), pressurizing with ethylene, and warming at 80°C , the sole rhodium species present was $[\text{Rh}(\text{Tp})(\text{H})(\text{PPh}_2)(\text{PPh}_2)]$ (**6**), which clearly shows that the catalysis was performed with **6**.

The catalytic cycle with complex **6** fits with that proposed for **3** (Scheme 3, $\text{L} = \text{PPh}_2$). An increase in the ethylene hydrophosphination product reduces the selectivity for the dehydrocoupling reaction relative to **3**. This noticeable difference has to be attributed to a more difficult protonation of the ethyl group in **B** with $\text{L} = \text{PPh}_2$ than for $\text{L} = \text{PMe}_3$, which favors the reductive elimination of PEtPh_2 . Accordingly, the P–C bond formation in **B** would give $[\text{Rh}(\text{Tp})(\text{L})(\text{PEtPh}_2)]$ (**C**), in which the secondary phosphane replaces PEtPh_2 to close the catalytic cycle. On the other hand, the phosphanido-bridged complex $[(\text{Tp})(\text{H})\text{Rh}(\mu\text{-PPh}_2)\text{Rh}(\text{PPh}_2)]$ (**9**) was the sole rhodium compound found at the end of the catalysis with **6**. Complex **9** was found to be inactive for the dehydrocoupling of PPh_2 , which also supports the prominent role of mononuclear phosphanide complexes in this reaction.

Complex **9** results from the weak thermal stability of **6**, which was independently found to decompose into **9** and the protonated species HTp , a reaction that cannot be avoided by adding an external base such as Et_3N (the syntheses and X-ray structures of **9** and $[(\text{Tp})(\text{H})\text{Rh}(\mu\text{-PPh}_2)\text{Rh}(\text{PPh}_2)(\text{PMe}_3)]$ (**10**) can be found in the Supporting Information^[17]).

Primary phosphanes such as PH_2Ph were found to be too reactive to allow the isolation of mononuclear complexes. Reaction of **1** with PH_2Ph in C_6D_6 results immediately in a mixture containing mainly the *trans* diastereoisomers of $[\{\text{Rh}(\text{H})(\mu\text{-PPh})(\text{Tp})\}_2]$, as deduced from NMR spectroscopy. Under the catalytic conditions mentioned above, the use of either **1** or **3** as catalyst precursors and PH_2Ph as substrate led to only a 1% of conversion to $\text{PhHP}-\text{PPh}_2$.

In conclusion, we have found that mononuclear hydrido phosphanido rhodium complexes are reliable intermediates in catalytic hydrophosphination and dehydrocoupling reactions. Moreover, they result from the oxidative addition of a P–H bond to the metal, as supported by the full characterization of $[\text{Rh}(\text{Tp})(\text{H})(\text{PMe}_3)(\text{PPh}_2)]$ (**3**) and DFT calculations. Furthermore, the valuable mechanistic information reported here could help in the development of new catalysts for the “green syntheses” of phosphanes and diphosphanes. Further studies on the mechanism and the scope of this reaction as well as the reactivity of the terminal phosphanide ligand are currently underway.

Received: July 29, 2014

Revised: October 29, 2014

Published online: November 19, 2014

Keywords: homogeneous catalysis · hydrotris(pyrazolyl)borate · P–H bonds · P ligands · rhodium

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