

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

Ana M. Geer,^[a] Ángel L. Serrano,^[a] Bas de Bruin,^[b] Miguel A. Ciriano,^[a] and Cristina Tejel^{*[a]}

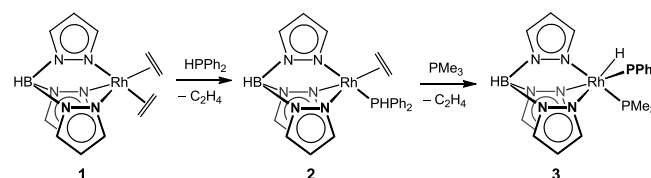
In memory of María Pilar García.

Abstract: Complexes with terminal phosphanido ($M\text{-PR}_2$) functionalities are believed to be crucial intermediates in new catalytic processes involving P–P and P–C bond formation. We showcase here the isolation and characterization of mononuclear phosphanido rhodium complexes ($[\text{RhTp}(\text{H})(\text{PR}_2)\text{L}]$) resulting from the oxidative-addition of secondary phosphanes, a reaction that was also explored computationally. These compounds are active catalysts for the dehydrocoupling of $\text{P}(\text{HPh})_2$ to $\text{Ph}_2\text{P-PPh}_2$. Besides, hydrophosphination of dimethyl maleate and the unactivated olefin ethylene is reported. Reliable evidence for the prominent role of mononuclear rhodium phosphanido species in these reactions is also provided.

Complexes with a terminal phosphanido ($M\text{-PR}_2$) 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] The latter provides an easy way to diphosphanes, phosphacycles and unique oligophosphanes for which interesting properties can be envisaged,^[4] whereas new materials based on phosphorus-boron bonds have 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 methodologies has attracted considerable attention, intensified by the possibility of activate 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 with two notable examples in rhodium chemistry described below.^[9] More recently, main-group reagents such as $[\text{Sn}(\text{C}_5\text{Me}_5)_2\text{Cl}_2]$ have been reported as suitable catalysts for P–P bond formation, although with modest TON values.^[10] Detailed mechanistic information on the dehydrocoupling of phosphanes only exists in few cases, mainly focused on the early transition metal catalysts.^[2b,11] Nonetheless,

a Rh(V) diphosphanide species, $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{H})_2(\text{PR}_2)_2]$, was tentatively hypothesized by Brookhart to mediate in the dehydrocoupling of secondary phosphanes,^[9b] while $[\text{Rh}(\text{dippe})(\text{CH}_2\text{Ph})(\text{H})(\text{P}(\text{H})\text{Ph})]$ ($\text{dippe} = \text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}(\text{H})\text{Pr}_2$) was observed as a transient species in the preparation of the dinuclear $[\{\text{Rh}(\mu\text{-P}(\text{H})\text{Ph})(\text{dippe})\}_2]$ as precatalyst for dehydrocoupling of primary phosphanes.^[9a] A key step postulated in both processes is the activation of the P–H bond, commonly proposed to occur via oxidative addition at late transition metal centres.^[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 for rhodium up to date,^[16] so that proof for 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 type of complexes and give reliable evidence for their participation in catalytic rhodium mediated P–P and P–C bond formation reactions.

Addition of diphenylphosphane to a toluene solution of $[\text{Rh}(\text{Tp})(\text{C}_2\text{H}_4)_2]$ (**1**) led to the immediate replacement of one ethylene ligand to give $[\text{Rh}(\text{Tp})(\text{C}_2\text{H}_4)(\text{P}(\text{H})\text{Ph}_2)]$ (**2**), which was isolated as an orange microcrystalline solid in excellent yield (Scheme 1). Complex **2** was fully characterized as a species of *TBPY-5* geometry with a non-rotating ethylene at the equatorial position. A further reaction of complex **2** with trimethylphosphane in toluene rendered the hydrido-phosphanido complex $[\text{Rh}(\text{Tp})(\text{H})(\text{PMe}_3)(\text{PPh}_2)]$ (**3**), which was 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 rhodium.



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

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. Besides, the hydride (located in the Fourier map) gives a low-field signal at $\delta -15.62$ (ddd) ppm in the ^1H NMR spectrum. Noteworthy, the geometry around the phosphanido phosphorus atom (P1) reveals that the lone pair generated upon oxidative-addition of the P–H bond does not interact with Rh resulting in a Rh–P1 single bond. Thus,

[a] A. M. Geer, A. L. Serrano, Prof. M. A. Ciriano, Dr. C. Tejel, Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC – Universidad de Zaragoza, Pedro Cerbuna 12, 50009-Zaragoza (Spain)

Fax: (+) 34 976761187
E-mail: ctejel@unizar.es

[b] Prof. B. de Bruin, Homogeneous and Supramolecular Catalysis Group, Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam (The Netherlands)

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

the environment of P1 is pyramidal with the sum of the three bond angles amounting $\Sigma^0 = 320.40(2)^\circ$ ($317.03(2)^\circ$ for the second independent molecule), a value somewhat smaller than the expected for a tetrahedron (328.5°) due to the repulsion of the lone-pair.

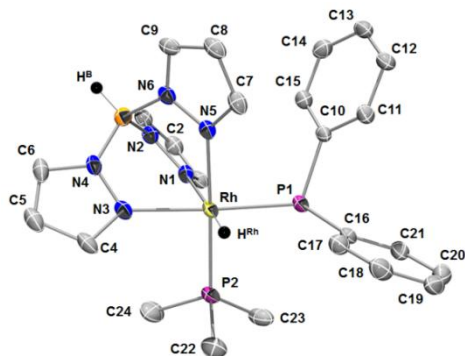


Figure 1. Molecular structure (ORTEP 50%) of complex [Rh(Tp)(H)(PMe₃)(PPh₂)] (**3**). Selected bond distances (Å) and angles (°): Rh–P1, 2.334(1) [2.340(1)]; Rh–P2, 2.248(1) [2.242(1)]; Rh–N1, 2.180(3) [2.180(3)]; Rh–N3, 2.172(3) [2.197(3)]; Rh–N5, 2.100(3) [2.115(3)]; Rh1–H^{Rh}, 1.565(14) [1.564(14)]; 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 between brackets.

Although no intermediates were detected on monitoring the reaction resulting in **3** by NMR, it is reasonable to assume that complex [Rh(Tp)(PPh₂)(PMe₃)] (**A**) is formed initially from the replacement of ethylene by trimethylphosphane followed by cleavage of the P–H bond. Studies of 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]

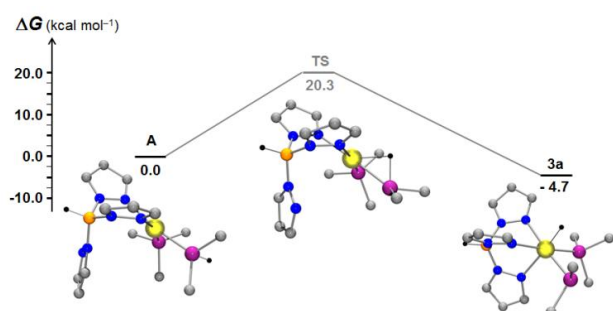
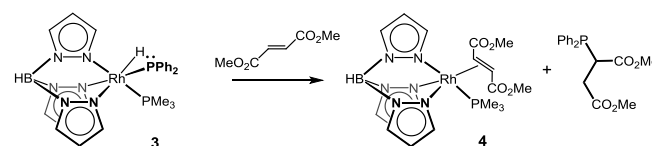


Figure 2. DFT-calculated structures for complexes **A**, **3a** and the connecting transition state (**TS**) at the BP86-def2-TZVP level. ΔG_{298K}° values at the b3lyp-def2-TZVP level relative to **A** are 22.3 kcal mol⁻¹ (**TS**) and -0.5 kcal mol⁻¹ (**3a**).

In the intermediate **A** the rhodium atom adopts a square-planar coordination geometry according to DFT calculations. The Tp ligand was κ^2 -coordinated with a boat conformation for the 'Rh(N–N)₂B' six-membered metallacycle.^[19] This feature agrees with previous observations in 'Rh^I(Tp)' chemistry, which indicate

that the κ^2 -coordination mode becomes stabilized as far as the electronic density on the rhodium atom increases.^[20] Oxidative addition of the P–H bond proceeds via an accessible barrier of ~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 type reactions. 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 easily and cleanly the free functionalized phosphane Ph₂P–CH(CO₂Me)CH₂(CO₂Me) and complex [Rh(Tp)(CO₂MeHC=CHCO₂Me)(PMe₃)] (**4**) (Scheme 2).^[23]

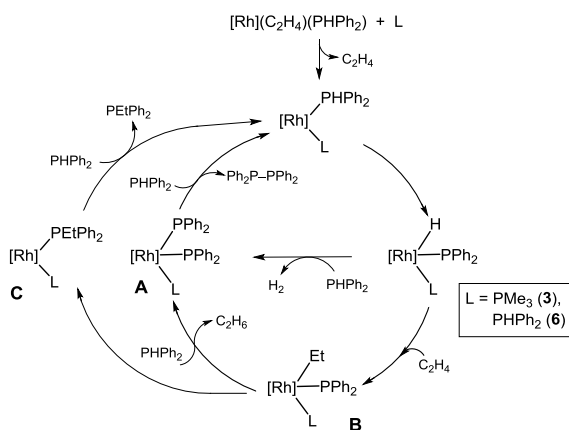


Scheme 2. Synthesis of Ph₂P–CH(CO₂Me)CH₂(CO₂Me) from the hydridophosphanido complex **3**.

According to Glueck,^[21a] a plausible reaction pathway could be an outer sphere mechanism, i.e. nucleophilic attack of the phosphanide 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, i.e., 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, dimethyl fumarate in complex **4** is replaced by PPh₂ to regenerate **3**, which guarantees the viability of a 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.

As mentioned in the introduction, Brookhart and Tilley each 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 type of reactions was tested using PPh₂ as model substrate. Catalytic essays in toluene at 80 °C with 5 mol% of catalyst indicate 51 % conversion after 13 h, while hydrogen was observed by ¹H NMR. A plausible catalytic cycle for this reaction is shown in Scheme 3. Hydrogen could be eliminated from complex **3** on addition of PPh₂ to give the transient species **A** containing 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.



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

While 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 hours 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 well 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 mol of ethane per mol of the diphosphane was simultaneously observed and complex **3** was the sole rhodium complex detected during and at the end of the catalysis.

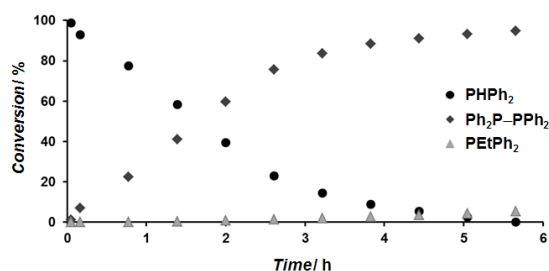


Figure 3. Conversion (%) versus time (h) for the dehydrocoupling of PPh₂ catalyzed by **3**.

It is remarkable that, as the reaction proceeds, PEtPh₂ appears as a product when the conversion into Ph₂P-PPh₂ is over 80 %, so that a mixture of Ph₂P-PPh₂ (95 %) and PEtPh₂ (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 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 formation reactions compete in such a way that a high concentration of phosphane favours the protonation of the ethyl group in **B** and inhibits the P-C reductive elimination to PEtPh₂, which becomes operative at low phosphane concentration.

If equimolecular mixtures (prepared in situ) of **2** and other phosphanes such as PPh₂, PMePh₂, and PMe₂Ph are used as catalyst precursors, the catalysis proceed with identical results in all cases. Under 6 bar of ethylene a full conversion was observed in 7 hours and the products were found to be Ph₂P-PPh₂ (80 %) and PEtPh₂ (20 %). Inspection by NMR of the catalyst precursors revealed the quantitative formation of the hydride phosphanide complexes [Rh(Tp)(H)(L)(PPh₂)] (L = PPh₂, **6**; PMe₂Ph, **7**; PMePh₂, **8**) similar to **3** (see Supporting Information). After addition of the substrate (PPh₂), pressurizing with ethylene and warming at 80 °C, the sole rhodium species present was [Rh(Tp)(H)(PPh₂)(PPh₂)] (**6**), which clearly evidences that the catalysis were performed with **6**.

The catalytic cycle with complex **6** fits with that proposed for **3** (Scheme 3, L = PPh₂). 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** for L = PPh₂ than for L = PMe₃, which favours the reductive elimination of PEtPh₂. Accordingly, the P-C bond formation in **B** would give [Rh(Tp)(L)(PEtPh₂)] (**C**) in which the secondary phosphane replaces PEtPh₂ to close the catalytic cycle. On the other hand, the phosphanido bridged complex [(Tp)(H)Rh(μ-PPh₂)Rh(PPh₂)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 PPh₂, 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 Et₃N. The syntheses and X-ray structures of **9** and [(Tp)(H)Rh(μ-PPh₂)Rh(PPh₂)(PMe₃)] (**10**) can be found in the Supporting Information.^[17]

Primary phosphanes such as PH₂Ph were found to be too reactive to allow the isolation of mononuclear complexes. Reaction of **1** with PH₂Ph in C₆D₆ results immediately in a mixture containing mainly the *trans* diastereoisomers of [(Rh(H)(μ-PHPh)(Tp))₂], as deduced from NMR spectroscopy. Under the catalytic conditions commented above, using either **1** or **3** as catalyst precursors and PH₂Ph as substrate only a 1% of conversion to PhHP-PHPh was observed.

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 [Rh(Tp)(H)(PMe₃)(PPh₂)] (**3**) and DFT calculations. Furthermore, the valuable mechanistic information reported here could help to 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 being developed in our laboratories.

Acknowledgements

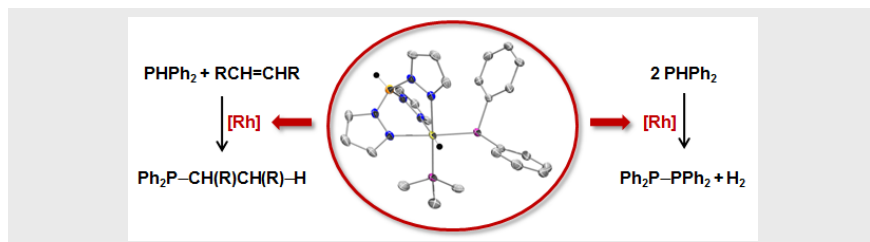
The generous financial support from MICINN/FEDER (Project CTQ2011-22516) and Gobierno de Aragón/FSE (GA/FSE, Inorganic Molecular Architecture Group, E70) and NWO-CW (VICI project 016.122.613; BdB), are gratefully acknowledged. A.M.G. and A.L.S. thank Gobierno de Aragón and MEC, respectively, for a fellowship.

Keywords: rhodium • P–P and P–C • terminal phosphanide • P–H bond • hydrotris(pyrazolyl)borate

- [1] a) b) V. Koshti, S. Gaikwad, S. H. Chikkali, *Coord. Chem. Rev.* **2014**, 265, 52-73; b) P. E. Sues, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2014**, 136, 4746-4760 and references therein; c) L. Rosenberg, *ACS Catal.* **2013**, 3, 2845-2855; d) D. S. Glueck, *Top Organomet. Chem.* **2010**, 31, 65-100 e) R. Waterman, *Dalton Trans.* **2009**, 18-26; f) D. S. Glueck, *Chem. Eur. J.* **2008**, 14, 7108-7117; f) D. S. Glueck, *Dalton Trans.* **2008**, 5276-5286.
- [2] See for example: a) E. M. Leitao, T. Jurca, I. Manners, *Nat. Chem.* **2013**, 5, 817-829; b) R. Waterman, *Chem. Soc. Rev.* **2013**, 42, 5629-5641; c) C. A. Jaska, A. Bartole-Scott, I. Manners, *Dalton Trans.* **2003**, 4015-4021
- [3] I. Wauters, W. Debrouwer, C. V. Stevens, *Beilstein J. Org. Chem.* **2014**, 10, 1064-1096.
- [4] a) M. B. Ghebreab, T. Shalumova, J. M. Tanski, R. Waterman, *Polyhedron* **2010**, 29, 42-45; b) J. D. Masuda, A. J. Hoskin, T. W. Graham, C. Beddie, M. C. Fermin, N. Etkin, D. W. Stephan, *Chem. Eur. J.* **2006**, 12, 8696-8707; c) A. J. Hoskin, D. W. Stephan, *Angew. Chem.* **2001**, 113, 1917-1919; *Angew. Chem. Int. Ed.* **2001**, 40, 1865-1867; d) N. Etkin, M. C. Fermin, D. W. Stephan, *J. Am. Chem. Soc.* **1997**, 119, 2954-2955
- [5] a) M. A. Huertos, A. S. Weller, *Chem. Sci.* **2013**, 4, 1881-1888; b) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, 110, 4023-4078; c) K. Lee, T. J. Clark, A. J. Lough, I. Manners, *Dalton Trans.* **2008**, 2732-2740; d) T. J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* **2006**, 12, 8634-8648; e) T. J. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda, I. Manners, *Chem. Eur. J.* **2005**, 11, 4526-4534; f) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, 122, 6669-6678.
- [6] R. Waterman, *Curr. Org. Chem.* **2012**, 16, 1313-1331.
- [7] a) S. J. Geier, D. W. Stephan, *Chem. Commun.* **2008**, 99-101; b) G. Bai, P. Wei, A. K. Das, D. W. Stephan, *Dalton Trans.* **2006**, 1141-1146.
- [8] a) M. B. Ghebreab, D. K. Newsham, R. Waterman, *Dalton Trans.* **2011**, 40, 7683-7685; b) S. Greenberg, D. W. Stephan, *Chem. Soc. Rev.* **2008**, 37, 1482-1489; c) R. Waterman, *Organometallics* **2007**, 26, 2492-2494; d) D. W. Stephan, *Angew. Chem.* **2000**, 112, 322-338; *Angew. Chem. Int. Ed.* **2000**, 39, 314-329.
- [9] a) L.-B. Han, T. D. Tilley, *J. Am. Chem. Soc.* **2006**, 128, 13698-13699; b) V. P. W. Böhm, M. Brookhart, *Angew. Chem.* **2001**, 113, 4832-4834; *Angew. Chem. Int. Ed.* **2001**, 40, 4694-4696.
- [10] a) R. J. Less, R. L. Melen, D. S. Wright, *RSC Advances* **2012**, 2, 2191-2199; b) V. Naseri, R. J. Less, R. E. Mulvey, M. McPartlin, D. S. Wright, *Chem. Commun.* **2010**, 46, 5000-5002.
- [11] R. Waterman, *Organometallics* **2013**, 32, 7249-7263.
- [12] a) M. Itazaki, Y. Nishihara, K. Osakada, *Organometallics* **2004**, 23, 1610-1621; b) I. Kovacic, D. K. Wicht, N. S. Grewal, D. S. Glueck, C. D. Incarvito, I. A. Guzei, A. L. Rheingold, *Organometallics* **2000**, 19, 950-953.
- [13] Y. S. Ganushevich, V. A. Miluykov, F. M. Polyancev, S. K. Latypov, P. Lönnecke, E. Hey-Hawkins, D. G. Yakhvarov, O. G. Sinyashin, *Organometallics* **2013**, 32, 3914-3919.
- [14] J. B. Bonanno, P. T. Wolczanski, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1994**, 116, 11159-11160.
- [15] R. T. Baker, J. C. Calabrese, R. L. Harlow, I. D. Williams, *Organometallics* **1993**, 12, 830-841.
- [16] The two sole examples of isolated mononuclear rhodium phosphanide complexes known are [Rh(L₃)PR₂] (L₃ = tBuP(CH₂CH₂CH₂PPh₂)₂; R = C₆H₅, C₆H₁₁), prepared by chloride metathesis with LiPR₂. L. Dahlenburg, N. Hock, H. Berke, *Chem. Ber.* **1988**, 121, 2083-2093.
- [17] CCDC 1014724 (**3**) and 1014725 (**10**•C₂H₅N) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [18] Complexes **A**, **3a** and transition state (**TS**) were calculated at the BP86 and b3lyp levels. Geometric parameters by BP86 fit slightly better than those obtained by b3lyp (see Supporting Information).
- [19] C. Tejel, J. M. Villoro, M. A. Ciriano, J. A. López, E. Eguizabal, F. J. Lahoz, V. I. Bakhmutov, L. A. Oro, *Organometallics*, **1996**, 15, 2967-2978.
- [20] C. Slugovc, I. Padilla-Martínez, S. Sirol, E. Carmona, *Coord. Chem. Rev.* **2001**, 213, 129-157.
- [21] a) I. Kovacic, C. Scriban, D. S. Glueck, *Organometallics* **2006**, 25, 536-539; b) C. Scriban, D. S. Glueck, L. N. Zakharov, W. S. Kassel, A. G. DiPasquale, J. A. Golen, A. L. Rheingold, *Organometallics* **2006**, 25, 5757-5767; c) C. Scriban, I. Kovacic, D. S. Glueck, *Organometallics* **2005**, 24, 4871-4874; d) E. Costa, P. G. Pringle, K. Worboys, *Chem. Commun.* **1998**, 49-50; e) E. Costa, P. G. Pringle, M. B. Smith, K. Worboys, *J. Chem. Soc. Dalton Trans.* **1997**, 4277-4282; f) P. G. Pringle, M. B. Smith, *J. Chem. Soc., Chem. Commun.* **1990**, 1701-1702.
- [22] a) S. Sabater, J. A. Mata, E. Peris, *Organometallics* **2013**, 32, 1112-1120; b) K. Chen, S. A. Pullarkat, M. Ma, Y. Li, P.-H. Leung, *Dalton Trans.* **2012**, 41, 5391-5400; c) Y. Huang, S. A. Pullarkat, Y. Li, P.-H. Leung, *Inorg. Chem.* **2012**, 51, 2533-2540; d) M.-J. Yang, Y.-J. Liu, J.-F. Gong, M.-P. Song, *Organometallics* **2011**, 30, 3793-3803; e) Y. Huang, S. A. Pullarkat, Y. Li, P.-H. Leung, *Chem. Commun.* **2010**, 46, 6950-6952; f) Y. Zhang, L. Tang, S. A. Pullarkat, F. Liu, Y. Li, P.-H. Leung, *J. Organomet. Chem.* **2009**, 694, 3500-3505; g) W.-C. Yeo, S.-Y. Tee, H.-B. Tan, G.-K. Tan, L. L. Koh, P.-H. Leung, *Inorg. Chem.* **2004**, 43, 8102-8109.
- [23] Complex **4** was independently prepared by reacting [Rh(Tp)(C₂H₄)₂] (**1**) with PMe₃ and then with dimethyl fumarate. The phosphane Ph₂P-CH(CO₂Me)CH₂(CO₂Me) was characterized by comparison of its spectroscopic data with those reported in the literature: a) K. Heesche-Wagner, T. N. Mitchell, *J. Organomet. Chem.* **1994**, 468, 99-106; b) J. A. Van Doorn, R. L. Wife, *Phosphorus, Sulfur, Silicon Relat. Elem.* **1990**, 47, 253-260.
- [24] Data were obtained with a static NMR tube. If the tube was shaken, the full conversion of PHPh₂ was achieved within 3.5 hours.
- [25] a) M. B. Ghebreab, C. A. Bange, R. Waterman, *J. Am. Chem. Soc.* **2014**, 136, 9240-9243; b) M. O. Shulyupin, M. A. Kazankova, I. P. Beletskaya, *Org. Lett.* **2002**, 5, 761-763.

Entry for the Table of Contents

COMMUNICATION



Mononuclear phosphanido rhodium complexes arising from P-H oxidative addition reactions have been fully characterized for the first time (see Figure). The terminal phosphanides are active catalysts for 'green syntheses' of phosphanes and diphosphanes under mild conditions through phosphane dehydrocoupling and olefin hydrophosphination reactions.

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

Page No. – Page No.

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