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Rhodium-Mediated Functionalization of White Phosphorus: A Novel Formation of C−P Bonds

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*Summary: The rhodium alkyl and aryl complexes [(triphos)Rh(R)(η^2-C_2H_4)] (R = Me (**1**), Et (**2**), Ph (**3**); triphos = $MeC(CH_2PPh_2)_3$) react with white phosphorus in THF at room temperature to give the new complexes [(triphos)Rh(η^1:η^2-P_4R)] (R = Me (**4**), Et (**5**), Ph (**6**)). This reaction represents the first example in which a P−C bond is formed by starting from white phosphorus through the mediation of a transition-metal complex.*

Chemical reactions resulting in the cleavage of C−P bonds are rather common processes which are often promoted by transition-metal complexes.[1] In contrast, the reverse reaction, in which a P−C bond is formed through the intermediacy of a d-block metal, is a very rare process, notwithstanding the ubiquitous role played by phosphines and by phosphorus compounds in both organometallic and coordination chemistry.[2] Examples of metal-mediated P−C bond-forming reactions are limited to the interchange reaction between phosphorus-bound aryl moieties and palladium-bound aryl or alkyl groups,[3] to the Pd-catalyzed coupling of aryl halides with silyl- or stannylphosphines,[4] and to the recently reported catalytic hydrophosphorylation of alkynes[5] and hydrophosphination of olefins.[6] In both of the catalytic processes, the P−C bond-forming step is considered to follow the insertion of the unsaturated substrate into the M−P bond.

Despite the fact that the coordination chemistry of white phosphorus is rich and has been extensively investigated,[7] metal-promoted P−C bond formation starting from white phosphorus is still unknown.[8] This process, however, would be highly desirable, due to the need for an environmentally more acceptable technology for the preparation of organophosphorus compounds.[9,10]

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(1) For recent examples of P−C bond cleavage see: (a) Widenhofer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787. (b) Nakajima, T.; Shimizu, I.; Kobayashi, K.; Koscino, H.; Wakatsuki, Y. *Inorg. Chem.* **1997**, *36*, 6440. (c) Nowotny, M.; Johnson, B. F. G.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1998**, 2223.

(2) Transition-metal ions such as Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} have been shown to act as activators for the phosphonate biosynthesis catalyzed by the phosphoenolpyruvate mutase enzyme. See: Kim, A.; Kim, J.; Martin, B. M.; Dunaway-Mariano, D. *J. Biol. Chem.* **1998**, *273*, 4443 and references quoted therein.

(3) See for example: Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441 and references quoted therein.

(4) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748.

(5) Han, L.-B.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1999**, 395.

(6) (a) Costa, E.; Pringle, P. G.; Worboys, K. *J. Chem. Soc., Chem. Commun.* **1998**, 49. (b) Costa, E.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4277. (c) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *1199*, 55039.

(7) Reviews: (a) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Polyhedron* **1987**, *6*, 351. (b) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104. (c) Scheer, M.; Herrmann, E. *Z. Chem.* **1990**, *29*, 41. (d) Scherer, O. J. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, 1990; Chapter 3. (e) Whitmire, K. H. *Adv. Organomet. Chem.* **1998**, *42*, 2.

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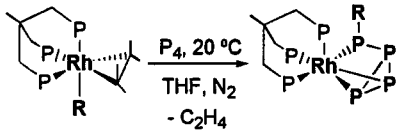
Scheme 1



We have recently shown that Rh and Ir trihydrides containing the ancillary $MeC(CH_2PPh_2)_3$ ligand (triphos) react with white phosphorus in a closed system, undergoing complete hydrogenation of one phosphorus atom of the P_4 molecule.[11] As a result, 1 equiv of PH_3 is formed together with the *cyclo*-triphosphorus complex [(triphos)M(η^3-P_3)] (M = Rh, Ir). A mechanism accounting for the hydrogenation reaction has been proposed in which the complexes [(triphos)M(H)(η^1:η^1-P_4)] and [(triphos)M(η^1:η^2-P_4H)] are intermediates.

Here, we report the first example of a metal-promoted functionalization of P_4 resulting in the formation of a P−C bond which has given us access to unique rhodium complexes containing the unprecedented alkyl- or aryltetraphosphine ligands RP_4^- (R = Me, Et, Ph). Finally, preliminary results concerning the reactivity of these species are also reported.

The reaction of white phosphorus in dry THF under nitrogen with the rhodium alkyl and aryl complexes of formula [(triphos)Rh(R)(η^2-C_2H_4)] (R = Me (**1**), Et (**2**), Ph (**3**))[12] affords the new complexes [(triphos)Rh(η^1:η^2-P_4R)] (R = Me (**4**), Et (**5**), Ph (**6**)), in which the organic group originally bounded to rhodium has been selectively delivered to one of the four phosphorus atoms of the metal-activated P_4 molecule (Scheme 1).[13] During the reaction, 1 equiv of the labile ethene ligand is released, as confirmed by in situ ^{1}H NMR experiments carried out in a sealed NMR tube (singlet at δ 5.50 in THF-d_8).

Monitoring of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy shows that the conversion is rapid even at low temperature (from −30 to −15 °C, depending on the rhodium precursor used), as the solution color quickly changes from light yellow to red-orange after mixing the THF solutions of the two reagents.

When the same reaction was effected using the hydrido−ethene complex [(triphos)Rh(H)(η^2-C_2H_4)] (**7**),[12] the final product of the reaction was not the expected [(triphos)Rh(η^1:η^2-P_4H)] (**8**)[11] but the ethyltetraphosphine complex **5**, which likely was formed by a double metal-assisted insertion process in which the intramolecular insertion of the coordinated ethene into the Rh−H bond was followed by the rhodium-to-phosphorus migration of the ethyl group.[14,15] In keeping with this hypothesis, the exposure of a THF solution of **8** to an ethene atmosphere did not produce **5**, indicating that the insertion of the coordinated ethene molecule into the Rh−H bond precedes the migration of the Rh-bound group to the P_4 ligand.

Although crystals of **4**−**6** suitable for a crystallographic analysis have not yet been obtained, the solution structures of the isolated solid complexes have been unambiguously assigned on the basis of multinuclear and multidimensional NMR spectroscopy. Key experimental evidence was provided by $^{31}P\{^1H\}$ NMR spectroscopy. The ^{31}P spectra were quite similar, irrespective of the electron properties of the organic group on the P_4R ligand and the hybridization of the phosphorylated carbon (sp^2 or sp^3). In agreement with the lack of any symmetry in the molecules, the $^{31}P\{^1H\}$ NMR spectra (THF-d_8) exhibit an ABCDEFGX eight-nuclei spin system (X = ^{103}Rh). The network of connectivities between the seven phosphorus atoms has been rationalized by $^{31}P\{^1H\}$ COSY NMR experiments. The experimental 1D spectra were simulated by computer

(8) The copper-catalyzed formation of halogenophosphines from red phosphorus and alkyl halides has been reported. See: Maier, L. *Angew. Chem.* **1959**, *71*, 574. Maier L. *Helv. Chim. Acta* **1963**, *46*, 2026 and references therein.

(9) The current technology for the preparation of organophosphorus compounds is based in large part on the reactions of phosphorus chlorides. For an alternative "chlorine-free" technology for the catalytic synthesis of organophosphorus compounds, see: Dorfman, Ya. A.; Aleshkova, M. M.; Polimbetova, G. S.; Levina, L. V.; Petrova, T. V.; Abdreimova, R. R.; Doroshkevich, D. M. *Russ. Chem. Rev. (Engl. Transl.)* **1993**, *62*, 877.

(10) The direct synthesis of organophosphorus compounds from white phosphorus has precedents. See, for example: (a) Rauhut, M. M.; Semsel, A. M. *J. Org. Chem.* **1963**, *28*, 471. (b) Rauhut, M. M.; Semsel, A. M. *J. Org. Chem.* **1963**, *28*, 473. (c) Rauhut, M. M.; Bernheimer, R.; Semsel, A. M. *J. Org. Chem.* **1963**, *28*, 478. (d) Rauhut, M. M. In *Topics in Phosphorus Chemistry*; Grayson, M., Griffith, E. J., Eds.; Interscience: New York, 1964; Vol 1, p 1. (e) Maier, L. *Helv. Chim. Acta* **1966**, *49*, 2458. (f) Staendeke, H. *Chem. Ztg.* **1972**, *96*, 494. (g) Brown, C.; Hudson, R. F.; Wartew, G. A. *Phosphorus Sulfur Relat. Elem.* **1978**, *5*, 67. (h) Brandsma, L.; van Doorn, J. A., de Lang, R.-J.; Gusarova, N. K.; Trofimov, B. A. *Mendeleev Commun.* **1995**, 14.

(11) Peruzzini, M.; Ramirez, J. A.; Vizza, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2255.

(12) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226.

(13) Synthesis of [(triphos)Rh(η^1:η^2-P_4R)] (R = Me (**4**), Et (**5**), Ph (**6**)). A solution of the appropriate rhodium complex [(triphos)Rh(R)(η^2-C_2H_4)] (R = Me (**1**), Et (**2**), Ph (**3**)) (1.0 mmol) in THF (30 mL) was stirred at room temperature under nitrogen with a 2-fold excess of white phosphorus (250 mg, 2.02 mmol) dissolved in 10 mL of THF. Immediately the light yellow solution turned deep orange. Stirring was continued for 10 min, and then the solvent and the volatile components were evaporated to dryness under vacuum to leave a red-orange residue, which was washed with *n*-pentane (3 × 5 mL) before being dried at room temperature under a stream of nitrogen. Recrystallization from THF/*n*-hexane (1/3 v/v) may be performed to get analytically pure microcrystals of [(triphos)Rh(η^1:η^2-P_4R)] (R = Me (**4**), Et (**5**), Ph (**6**)) in moderate yield (ca. 60−70%). Compounds **4**−**6** are stable in the solid state under nitrogen but slowly decompose in solution over 10 °C. The decomposition is fast at temperatures higher than 45 °C. All spectroscopic and analytical data for the complexes **4**−**6** have been provided as Supporting Information. As an example, we report here analytical data and selected spectroscopic details for complex **6**. [(triphos)Rh(η^1:η^2-P_4Ph)] (**6**): yield 71%. Anal. Calcd for $C_{47}H_{44}P_7Rh$: C, 60.77; H, 4.78. Found: C, 61.01; H, 4.89. ^{1}H NMR (500.13 MHz, THF-d_8, −7 °C, TMS reference):δ 5.71 (t, *o*-Ph′P_A, 2H), 8.12 (t, *o*-Ph″P_A, 2H), 8.48 (t, *o*-Ph′P_B, 2H), 8.09 (t, *o*-Ph″P_B, 2H), 6.47 (t, *o*-Ph′P_C, 2H), 7.33 (t, *o*-Ph″P_C, 2H), 7.66 (bd, *o*-PhP_D, 2H), 2.59 (t, P_ACH', 1H), 2.01 (dd, P_ACH'', 1H), 2.91 (ddd, P_BCH', 1H), 2.08 (dd, P_BCH'', 1H), 2.24 (dd, P_CCH', 1H), 2.05 (dd, P_CCH'', 1H), 1.46 (s, CH_3(triphos), 3H). $^{13}C\{^1H\}$ NMR (125.76 MHz, THF-d_8, − 7 °C, TMS reference): δ 133.87 (d, $^2J_{CP}$ = 10.8 Hz, *o*-Ph′P_A), 135.96 (t, J = 9.4 Hz, *o*-Ph″P_A), 134.25 (*o*-Ph′P_B), 134.31 (*o*-Ph″P_B), 133.49 (bd, $^2J_{CP}$ = 5.1 Hz, *o*-Ph′P_C), 136.43 (t, J = 10.3 Hz, *o*-Ph″P_C), 137.55 (bd, $^2J_{CP}$ = 12.6 Hz, *o*-PhP_D), 39.50 (t, $^3J_{CP}$ = 9.6 Hz, CCH_3(triphos)), 38.13 (q, $^2J_{CP}$ = 10.1 Hz, CCH_3-(triphos)), 39.70 (ddd, $^1J_{CP}$ = 14.8, $^3J_{CP}$ = 8.2, $^2J_{CRh}$ = 4.4 Hz, P_ACH_2), 32.46 (dd, $^1J_{CP}$ = 16.6, $^3J_{CP}$ = 11.1 Hz, P_BCH_2), 36.69 (dd, $^1J_{CP}$ = 15.0,$^3J_{CP}$ = 8.9 Hz, P_CCH_2). $^{31}P\{^1H\}$ NMR (81.01 MHz, THF-d_8, 20 °C, 85% H_3PO_4 reference; ABCDEFGX spin system (X = ^{103}Rh)): δ 15.68 (m, $^2J_{PAPB}$ = 14.5, $^2J_{PAPC}$ = 32.1, $^2J_{PAPD}$ = 17.0, $^2J_{PAPE}$ = 27.0, $^2J_{PAPF}$ = 5.0, $^3J_{PAPG}$ = 5.0, $^1J_{PARh}$ = 121.5 Hz, P_A), −9.23 (m, $^2J_{PBPC}$ = 55.0, $^2J_{PBPD}$ = 4.0, $^2J_{PBPE}$ = 22.0, $^2J_{PBPF}$ = 17.0, $^3J_{PBPG}$ = 2.0, $^2J_{PBRh}$ = 116.0 Hz, P_B), −4.18 (m, $^2J_{PCPD}$ = 29.3, $^2J_{PCPE}$ = 2.0, $^2J_{PCPF}$ = 2.0, $^3J_{PCPG}$ = 12.2, $^2J_{PCRh}$ = 78.1 Hz, P_C), −209.48 (m, $^2J_{PDPE}$ = 23.0, $^2J_{PDPF}$ = 23.0, $^1J_{PDPG}$ = 160.8, $^1J_{PDRh}$ = 49.9 Hz, P_D), −177.06 (m, $^1J_{PEPF}$ = 327.1, $^1J_{PEPG}$ = 145.4, $^1J_{PERh}$ = 4.0 Hz, P_E), −200.78 (m, $^2J_{PFPG}$ = 145.4, $^1J_{PFRh}$ = 4.0 Hz, P_F), 19.61 (m, $^2J_{PGRh}$ = 6.0 Hz, P_G).

(14) Reaction of [(triphos)Rh(H)(η^2-C_2H_4)] (**7**) with white phosphorus: a THF solution (30 mL) of [(triphos)Rh(H)(η^2-C_2H_4)][12] (700 mg, 0.92 mmol) was treated with an excess of white phosphorus (250 mg, 2.02 mmol) as described in ref 13. Similar workup gave **5** as red microcrystals (yield 61%).

(15) The occurrence of a hydrido(ethene)−ethyl equilibrium has been demonstrated for **7**.[12]

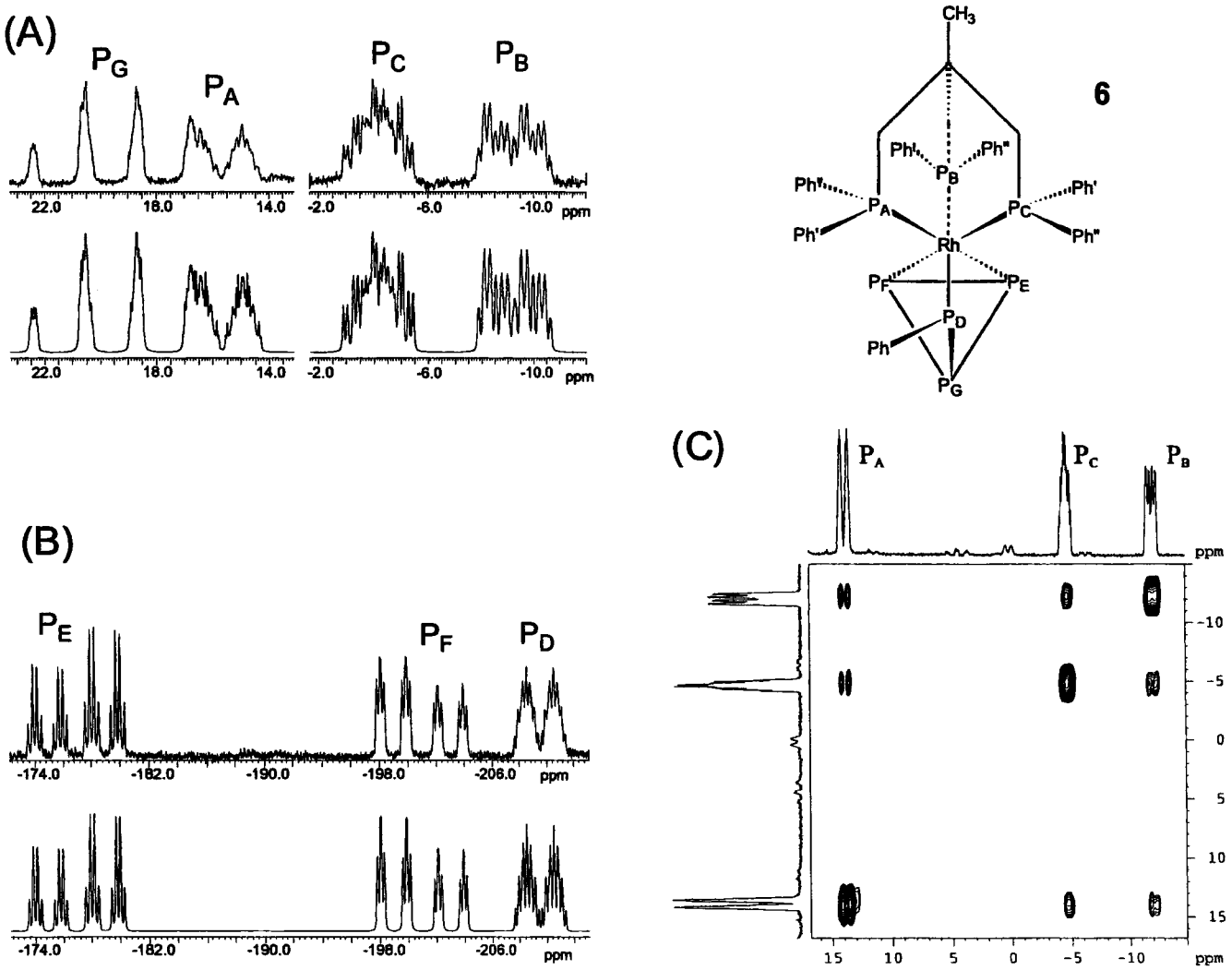
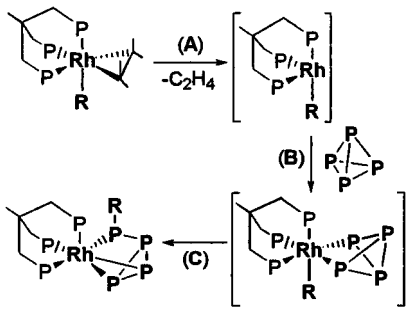


Figure 1. Computed and experimental spectra of [(triphos)Rh(η^1:η^2-P_4Ph)] (**6**) (81.01 MHz, 20 °C, THF-d_8, 85% H_3PO_4 reference): (A) low-field region of the spectrum; (B) high-field part of the spectrum; (C) section of the 2D $^{31}P\{^1H\}$ exchange spectrum of [(triphos)Rh(η^1:η^2-P_4Ph)] (**6**) (202.47 MHz, THF-d_8, −8 °C, τ_m = 0.8 s) in the triphos phosphorus region. No exchange peaks related to the P_4Ph phosphorus atoms have been detected.

techniques (Figure 1 illustrates the computed and the experimental spectrum of [(triphos)Rh(η^1:η^2-P_4Ph)] and includes a sketch illustrating the numbering scheme adopted for the complexes).

The presence of the organic fragment bound to one of the phosphorus atoms was confirmed by the analysis of the ^1H, $^{13}C\{^1H\}$, and $^{13}C\{^1H\}$-DEPT NMR spectra and unambiguously supported by heteronuclear $^1H-^{31}P$ and $^1H-^{13}C$ HMQC and $^1H-^{13}C$ HMBC NMR correlation experiments. With the aim of completely assigning the solution structure and the stereochemistry of the complexes, a series of ^1H-NOESY and *J*-optimized $^1H-^{31}P$ correlation experiments were also performed, which confirmed the suggested structures. In addition, the analysis of ^1H-NOESY and $^{31}P\{^1H\}$ exchange NMR spectra showed also the stereochemical nonrigidity of

Scheme 2



complexes **4**−**6**. Under our experimental conditions, the complexes attain a slow exchange motional regime consistent with the scrambling of the P_4R unit with respect to the (triphos)Rh moiety.[16] A section of the $^{31}P\{^1H\}$ exchange spectrum of **6** is presented in Figure 1C.

Although we do not have mechanistic information, the formation of these complexes is straightforward, in light of the mechanistic studies carried out on the trihydride species.[11] Thus, we are confident that the overall mechanism (Scheme 2) involves a preliminary step in which

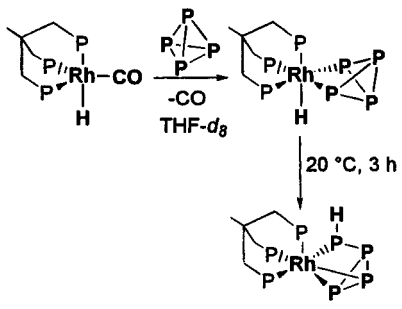
(16) A selective exchange process which does not affect the overall symmetry of the molecule is evident from the 2D-NMR exchange experiment. However, only a relative motion of the P_4R unit with respect to the (triphos)Rh moiety can be envisaged at this stage. A deeper investigation of the process is in progress in order to rationalize the dynamic behavior of these complexes. Fluxionality in highly symmetric [(triphos)M(η^3-P_3)] complexes has been reported previously. See: Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1984**, 359.

the elimination of the ethene molecule[17] and the formation of the transient, highly reactive, coordinatively unsaturated, 16-electron species [(triphos)RhR] (**A**) is followed by the reaction with P_4 to afford the intermediate Rh(III) complex [(triphos)RhR(η^1:η^1-P_4)] (**B**). The final product then is formed following the intramolecular Rh-to-P migration of the organyl ligand and the electronic rearrangement within the P_4R^- ligand (**C**).

Although there are few doubts concerning the mechanism outlined above, it is somewhat surprising that the intermediate species were not detected even when the reactions of the ethene complexes **1**−**3** and **7** with white phosphorus were monitored by in situ ^{31}P NMR spectroscopy at −78 °C. This is particularly puzzling if one considers that the related complex [(triphos)RhH(η^1:η^1-P_4)] (**9**), which is an intermediate in the formation of **8** from [(triphos)RhH_3] and P_4,[11,18] is readily generated when [(triphos)RhH(CO)] is reacted with excess P_4 in THF at −18 °C (Scheme 3).[19]

The reactivity of the compounds [(triphos)Rh(η^1:η^2-P_4R)] with a wide range of substrates is currently under investigation. Preliminary tests demonstrate that a relevant downhill process is the reaction with dihydrogen. We have observed that, on pressurization with H_2, THF solutions of **4**−**6** (P_{H_2} = 20 atm, 60 °C), the expected decomposition to [(triphos)Rh(η^3-P_3)][11] is accompanied not only by the formation of methyl-, ethyl-, or phenylphosphine (GC-MS and ^{31}P NMR, yield <15%)

Scheme 3



but also by the production of several as yet unidentified phosphorus compounds.

In summary, unprecedented alkylation or arylation of the tetrahedral allotrope of elemental phosphorus has been accomplished by reaction of P_4 with rhodium alkyl- or arylethene complexes at a surprisingly low temperature. Our findings clearly demonstrate that a metal-mediated functionalization of the phosphorus molecule can be performed under mild conditions. To our knowledge, this is the first example of such a reaction involving white phosphorus. Studies aimed at developing new protocols for the synthesis of organophosphorus derivatives based on the direct functionalization of white phosphorus in the coordination sphere of a metal can then be foreseen. The catalytic production of organophosphorus compounds is the final target of this research.

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Supporting Information Available: Text giving experimental details describing the preparation and the spectroscopic properties of complexes **4**−**6**, and figures giving computed and experimental ^{31}P{^{1}H} NMR spectra for **4** and **5** (121.42 MHz) and **6** (81.01 MHz), selected 1D NMR (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}) and 2D NMR (^{31}P{^{1}H}-COSY, ^{1}H−^{31}P HMQC, ^{1}H−^{13}C HMQC, ^{1}H−^{1}H COSY) spectra of **5** and **6**, and ^{1}H-NOESY and ^{31}P-{^{1}H} exchange NMR spectra of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) In the reaction of the hydride **7** with P_4, the insertion of ethene into the Rh−H bond is competitive with its elimination and generates the [(triphos)RhEt] fragment for the following reaction with the metal-activated P_4 molecule.

(18) The iridium analogue of **9**, [(triphos)IrH(η^1:η^1-P_4)], has been isolated in the solid state.[11]

(19) [(triphos)RhH(η^1:η^1-P_4)] (**9**) was generated in a 5 mm NMR tube by treating a THF-d_8 solution of the hydrido−carbonyl complex [(triphos)RhH(CO)][20] (30 mg, 0.04 mmol) cooled to −18 °C with 1 equiv of P_4 dissolved in the same solvent (0.5 mL). When the solution was heated to room temperature, **9** transformed quantitatively into **8** within 3 h. Selected spectroscopic data for **9**: ^{1}H NMR (299.94 MHz, THF-d_8, −20 °C, TMS reference): δ −7.03 (brd, $J_{HP_{trans}}$ 144.0 Hz, 1H, RhH); ^{31}P{^{1}H} NMR (121.42 MHz, THF-d_8, 20 °C, 85% H_3PO_4 reference; ABB′CDEE′X spin system (X = ^{103}Rh)) δ 5.89 (m, $^2J_{PAPB}$ = 29.5, $^2J_{PAPB'}$ = 29.5, $^2J_{PAPC}$ = −4.0, $^2J_{PAPD}$ = −4.0, $^3J_{PAPE}$ ≅ $^3J_{PAPE'}$ ≅ 0, $^1J_{PARh}$ = 83.5 Hz, P_A), −5.67 (m, $^2J_{PBPB'}$ ≅ $^2J_{PBPC}$ ≅ $^2J_{PBPD}$ ≅ $^2J_{PB'PC}$ ≅ $^2J_{PB'PD}$ ≅ 0, $^3J_{PBPE}$ ≅ $^3J_{PB'PE'}$ = 15.6, $^3J_{PBPE'}$ ≅ $^3J_{PB'PE}$ = 16.1, $^1J_{PBRh}$ ≅ $^1J_{PB'Rh}$ = 98.2 Hz, P_B and $P_{B'}$), −291.35 (m, $^1J_{PCPD}$ 161.2, $^1J_{PCPE}$ ≅ $^1J_{PCPE'}$ 141.1, $^1J_{PCRh}$ ≅ 0 Hz, P_C), −295.36 (m, $^1J_{PDPE}$ ≅ $^1J_{PDPE'}$ = 146.4, $^1J_{PDRh}$ ≅ 0 Hz, P_D), −309.66 (m, $^1J_{PEPE'}$ = 78.0, $^2J_{PERh}$ ≅ $^2J_{PE'Rh}$ = 33.1 Hz, P_E and $P_{E'}$).

(20) Ott, J.; Venanzi, L. M.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *J. Organmet. Chem.* **1985**, *291*, 89.