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Palladium-catalyzed hydrophosphorylation of 1,3-dienes leading to allylphosphonates

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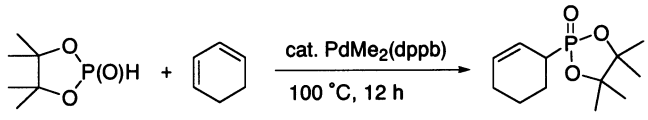
Abstract—Palladium-catalyzed 1,4-hydrophosphorylation of 1,3-dienes efficiently takes place with 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide HP(O)($OCMe_2CMe_2O$) to afford the corresponding allylphosphonates selectively in high yields. Mechanistic studies have revealed that the reaction proceeds through addition of intermediate H–Pd species to 1,3-diene generating a π-allylpalladium complex, which affords the adduct via subsequent reductive elimination. © 2000 Elsevier Science Ltd. All rights reserved.

The interest in the transition metal-catalyzed addition of heteroatom compounds across unsaturated carbon linkages is rapidly growing as one of the most attractive and clean methods for the construction of carbon–heteroatom bonds.[1] Over the last few years we have been involved in the development of palladium-catalyzed P–H bond addition reactions with alkynes, alkenes and allenes.[2] As for 1,3-dienes, Hirao and coworkers have very briefly claimed in their paper on the coupling of hydrogen phosphonates with organic halides (Hirao coupling)[3] that a hydrogen phosphonate adds to isoprene.[3c,4] However, the efficiency is not satisfactory (10% yield, 150°C, 20 h). We now wish to disclose that hydrophosphorylation of 1,3-dienes with 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide **1** readily takes place in the presence of a palladium catalyst to selectively afford allylphosphonates in high yields. Allylphosphonates are valuable synthetic intermediates.[5,6]

Heating a mixture of 1,3-cyclohexadiene (93 μL, 1.0 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide **1** (164 mg, 1.0 mmol), and $PdMe_2$(dppb)[7] [28 mg, 5 mol%; dppb = 1,4-bis(diphenylphosphino)butane] in 1,4-dioxane (1.5 mL) at 100°C for 12 h under nitrogen resulted in a complete disappearance of **1** to selectively afford the corresponding 1,4-addition product, allylphosphonate **2a**, in 97% GC yield. Evaporation of the solvent followed by recrystallization of the residue using hexane gave pure **2a** in 76% isolated yield as white solid (Eq. (1)).[8]



1 **2a** (1)

As demonstrated in Table 1, the same procedure could be successfully applied to 2,3-dimethyl-1,3-butadiene to form **2b** as the sole product in 87% yield (entry 2). The reaction of 1,3-butadiene by using $PdMe_2$(binap) [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] gave **2c** quantitatively with a *E*/*Z* ratio of 83/17 (entry 3). Similar selectivities but somewhat low activities were found with $PdMe_2$(dppb) (100°C, 19 h, 96% yield; *E*/*Z* = 82/18) and $PdMe_2$(dppf) (dppf = 1,1′-bis(diphenylphosphino)ferrocene; 100°C, 12 h, 71% yield; *E*/*Z* = 81/19). However, the reactions catalyzed by $PdMe_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were non-selective resulting in the *E*/*Z* ratios of approximately 1/1. The results were more complicated in the reactions of 1,3-pentadiene and isoprene, which respectively formed the regioisomeric 1,4-adducts **2d**/**2e** and **2f**/**2g** besides their *cis*/*trans* stereoisomers. Both of these reactions were most selective when effected by $PdMe_2$(dppf) [dppf = 1,1′-bis(diphenylphosphino)ferrocene] as shown in Table 1; the regioisomers formed via the attack of the phosphoryl group at the sterically less hindered carbon (**2d** and **2f**) were favored over the other regioisomers with the phosphoryl group attached to the more congested carbon (**2e** and **2g**).[9]

Keywords: addition reactions; catalysis; dienes; hydrophosphorylation; palladium.

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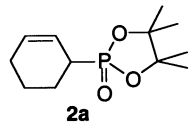
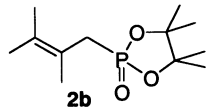
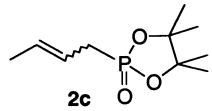
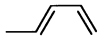
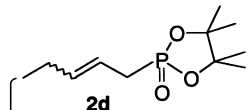
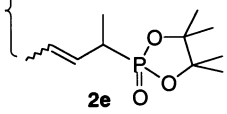
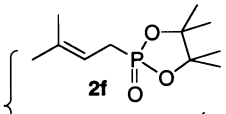
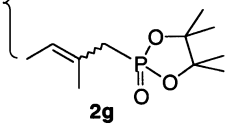
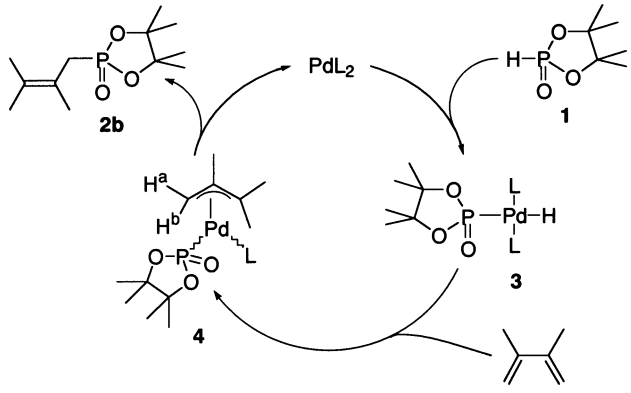
Table 1. Hydrophosphorylation of 1,3-dienes[a]

Entry	Diene	Conditions	Adduct	GC yield/%
1		cat. $PdMe_2$(dppb) 100 °C, 12 h	 **2a**	97 (76)[b]
2		cat. $PdMe_2$(dppb) 100 °C, 12 h	 **2b**	87 (80)[b]
3		cat. $PdMe_2$(binap) 100 °C, 12 h	 **2c**	98 (*E*/*Z* = 83/17)
4		cat. $PdMe_2$(dppf)[c] 80 °C, 16 h	 **2d**  **2e**	89 (*E*/*Z* = 93/7) 7 (*E*/*Z* = 96/4)
5		cat. $PdMe_2$(dppf) 60 °C, 12 h	 **2f**  **2g**	82 16 (*E*/*Z* = 81/19)

[a] Run by heating a mixture of **1**, a diene (1~10 equiv) and a palladium catalyst (5 mol%) in 1,4- dioxane (~0.7 M).
[b] Figures in parentheses are isolated yields.
[c] $PdMe_2$(binap) performed similarly.

We believe the hydrophosphorylation proceeds through the events shown in Scheme 1 (illustrated for 2,3-dimethyl-1,3-butadiene), which accommodates the following observations. As reported previously,[2e] the oxidative addition of **1** (0.087 mmol) with $Pd(PCy_3)_2$ (1 equiv.) readily proceeded at room temperature in toluene to generate the hydridopalladium complex (**3**; L = PCy_3) as the sole product in 15 min. When 2,3-dimethyl-1,3-butadiene (5 equiv.) was added to this solution, π-allyl complex (**4**; L = PCy_3) was found by ^{1}H NMR spectroscopy to be formed very cleanly; the *syn* proton H^a was observed at δ 3.27 (d, J_{HP} = 12.0 Hz) as a doublet, while the *anti* proton H^b appeared at δ 2.39 (d, J_{HP} = 16.0 Hz), which was also a doublet due to the phosphorus at the *trans* position.[10] Its ^{31}P NMR spectrum also displayed the emergence of new signals assignable to **4** [δ 102.5 (P(O), d, $J_{P(O)P}$ = 77.0 Hz), 44.5 (PCy_3, d, $J_{P(O)P}$ = 77.0 Hz)], as the signals due to **3** [δ 113.1 (P(O), t, $J_{P(O)P}$ = 41.0 Hz), 46.0 (PCy_3, d, $J_{P(O)P}$ = 41.0 Hz)][2e] gradually diminished. Conversion of **3** to **4**, as estimated based on the intensity of ^{1}H NMR signals, was approximately 11% after 30 min and was complete after 17 h. Finally, heating the resulting solution at 80°C for 1 h, reductive elimination of **2b** (δ 37.2) from **4** readily took place in a quantitative yield with concomitant regeneration of $Pd(PCy_3)_2$ (δ 39.2).



Scheme 1.

Acknowledgements

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8. Data for **2a**: white powder, mp 80°C. ^{1}H NMR ($CDCl_3$) δ 5.83–5.90 (m, 1H), 5.63–5.72 (m, 1H), 2.59–2.64 (m, 1H), 1.94–2.00 (m, 6H), 1.48 (s, 3H), 1.46 (s, 3H), 1.32 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 131.3, 121.1, 87.8, 36.5 (J_{CP} = 132.2 Hz), 25.1, 24.9, 24.5, 24.4, 22.8, 20.5; ^{31}P NMR ($CDCl_3$) δ 42.6. HRMS for $C_{12}H_{21}O_3P$, calcd: 244.1228, found: 244.1252. Anal. calcd for $C_{12}H_{21}O_3P$: C, 59.00; H, 8.67. Found: C, 59.12; H, 8.00.
9. The following observation suggests that the predominant formation of the *E*-isomers of **2c**, **d**, **e** and **g** appears to result from the kinetic control during the product forming process, rather than from possible *Z*-to-*E* isomerization due to the thermodynamic control. Thus, a mixture of separately prepared *Z*-rich **2e** (0.27 mmol; $E/Z = 27/73$), 2,3-dimethyl-1,3-diene (5 mmol), **1** (1.0 mmol), and $PdMe_2$(dppb) (28 mg, 5 mol% relative to **1**) in dioxane (1.5 mL) was heated at 100°C for 12 h to give **2b** in 71% GC yield. The *E*/*Z* ratio of **2e**, however, was retained unchanged within the error of GC.
10. The correlation of H^a and H^b was also unambiguously confirmed by ^{1}H–^{13}C COSY NMR spectroscopy. In ^{13}C NMR, the terminal carbon of **4** appeared at δ 58.0 (d, J_{CP} = 52.7 Hz). For NMR studies on π-allylpalladiums, see: (a) Powell, J.; Shaw, B. L. *J. Chem. Soc. (A)* **1967**, 1839. (b) Vrieze, K.; Praat, A. P.; Cossee, P. *J. Organomet. Chem.* **1968**, *12*, 533.