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Efficient Addition Reaction of Dibutylphosphane Oxide with Alkynes: New Mechanistic Proposal Involving a Duo of Palladium and Brønsted Acid

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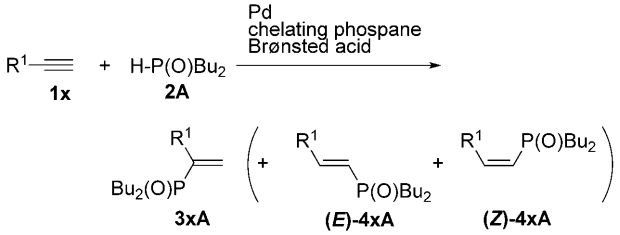
Abstract: The addition reaction of dibutylphosphane oxide [$Bu_2P(O)H$] with alkynes proceeds efficiently in the presence of palladium-chelating phosphane–Brønsted acid catalyst systems. Terminal alkynes afford branched-structured products selectively. On the other hand, the same reaction using monodentate phosphane ligands or the reaction run in the absence of a Brønsted acid affords a much lower yield. A mechanistic study has revealed that Brønsted acids (XOH) interact with oxygen in $M-P(O)R_2$ species (M = Pd, Pt) through hydrogen bonding to transform them to ionic $M^+ \leftarrow PR_2(OH\cdots O^-X)$ species, which was confirmed by NMR spectroscopy and X-ray crystallography. The phosphane-like $PR_2(OH\cdots O^-X)$ moiety is coordinatively labile, as substantiated by the ligand exchange reaction with *tert*-butyl isocyanide. A new mechanism that accommodates these observations has been proposed to rationalize the enhancement of catalytic activity and the regioselectivity induced by the Brønsted acid.

Keywords: alkynes; Brønsted acids; homogeneous catalysis; hydrogen bonding; palladium; phosphorylation

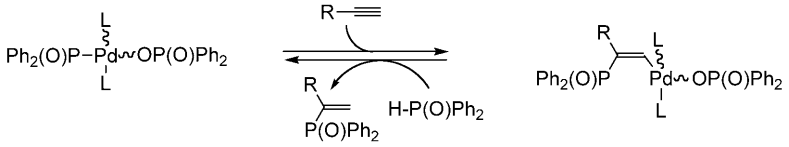
Although metal complex-catalyzed reactions assisted by Brønsted acids (XOH) have long been known, the role of Brønsted acids is usually to generate hydridometal species or to take part in a cascade process comprising metal-catalyzed and acid-catalyzed reactions.[1] Homogeneous catalysis where more intimate metal-acid cooperation plays an indispensable role is still rare.[2]

We and other groups have reported a series of metal complex-catalyzed addition reactions of H–P(O) bonds across C–C unsaturated linkages.[3] As far as the palladium-catalyzed reaction of dialkylphosphane oxides is concerned, there is only one paper published by Toffano and co-workers, disclosing the first examples of the reactions with alkynes.[3u,4] However, the only phosphane oxide they used was a five-membered cyclic one, which might be more reactive than plain dialkylphosphane oxides if we take account of the exceptionally high reactivity of five-membered cyclic hydrogen phosphonates as compared with dimethyl or diethyl phosphonates.[5] In addition, the yields of the adducts were not very high (31–63% ^1H NMR yields). Thus, the process has remained to be further improved in order to generalize the synthetic applicability. In this paper we wish to report a high-yielding general procedure for the addition of dialkylphosphane oxides to C≡C triple bonds by using palladium-chelating phosphane–Brønsted acid catalyst systems (Scheme 1).

Some time ago, one of us reported that the palladium-catalyzed addition of $Ph_2P(O)H$ with terminal alkynes afforded linear compounds as major products,[6] while the same reaction run in the presence of a catalytic quantity of $Ph_2P(O)OH$ under otherwise identical conditions furnished branched-structured prod-



Scheme 1. Addition of dibutylphosphane oxide with alkynes.



Scheme 2. Tentative mechanism proposed in ref.[7] to rationalize the regiochemical reversal induced by addition of a small quantity of $Ph_2P(O)OH$ in PdL_2-catalyzed addition reaction of diphenylphosphane oxide.

ucts.[7] In the mechanistic study on the latter catalysis, $Ph_2P(O)Pd[OP(O)Ph_2](dmpe)$[8] was isolated and this complex was found to display basically the same performance affording the branched products as the catalyst generated *in situ* from $Me_2Pd(dmpe)$ and $Ph_2P(O)OH$ [and also $Ph_2P(O)H$ present as reagent]. On the basis of these findings, a tentative mechanism that involves *phosphopalladation* between $Ph_2P(O)Pd[OP(O)Ph_2]L_2$ and the alkyne was proposed (Scheme 2) although convincing evidence to substantiate the *phosphopalladation* was lacking. With these previous observations in mind, the present finding of the addition of dialkylphosphane oxides being made efficient prompted us to revisit the role of the acid, which also will be disclosed in the present paper.

In a reaction to confirm the necessity of a Brønsted acid, an ethylbenzene (2.0 mL) solution of 1-octyne (**1a**, 1.00 mmol) and $Bu_2P(O)H$ (**2A**, 1.00 mmol) was heated in the presence of $Pd(dba)_2$ (5 mol%), dppben[8] (5 mol%) and $Ph_2P(O)OH$ (5 mol%) at 130 °C for 1 h and the resulting mixture was evaporated. ^{1}H NMR analysis of the residue dissolved in $CDCl_3$ using *p*-dimethoxybenzene as internal standard revealed the formation of 2-dibutylphosphinyl-1-octene (**3aA**) in 92% yield. Very interestingly, another similar reaction run in the absence of $Ph_2P(O)OH$ under otherwise the same conditions resulted in only 5% yield, clearly indicating the dramatically enhanced catalytic performance induced by the addition of $Ph_2P(O)OH$.

Besides $Ph_2P(O)OH$, other Brønsted acids also enhanced the activity as shown in Table 1.[9] When the reaction was run at 110 °C for 1 h using Pd-dppe-acid catalyst systems, $[3,5\text{-}(CF_3)_2C_6H_3]_2P(O)OH$, the most strongly acidic one among those examined, was the best performing (88% yield) while the less acidic $Ph_2P(O)OH$ and the even less acidic (*p-tert*-butyl$C_6H_4)_2P(O)OH$ gave lower yields (75 and 39%, respectively). In another set of reactions (110 °C, 3 h), 2,3,5,6-tetrafluoro-4-toluic acid afforded a 67% yield while the use of plain 4-toluic acid resulted in a 40% yield. Note, however, that these results do not necessarily indicate that stronger acids are always better. What we have to think for successful addition is to use an acid that matches the nature of a particular phosphane oxide (*vide infra*).

Another set of trial experiments shows that the use of chelating phosphanes, dppe and dppben in particular, is an indispensable prerequisite for efficient catalysis.[10] Thus, in the reactions using 1-octyne **1a** (1.00 mmol), $HP(O)Bu_2$ **2A** (1.00 mmol), $Pd(dba)_2$ (5 mol%), and $Ph_2P(O)OH$ (5 mol%) in 2.0 mL toluene at 110 °C for 3 h, the performance of phosphane ligand decreased in the following order: dppe (^{1}H NMR yield of **3aA** = 86%) > dppben (80%) > dppen (53%) = dppp (53%) > $PPhMe_2$ (23%) > dppxy (20%) > dppb (18%) > PPh_2Me (8%) > PPh_3 (~0%) > PMe_3 (0%).

Table 1. Performance of Brønsted acid (XOH) in addition reaction of dibutylphosphane oxide to 1-octyne.[a]

XOH	Time [h]	Yield of **3aA** [%][b]	Selec. [%][c]
$[3,5\text{-}(CF_3)_2C_6H_3]_2P(O)OH$	1	88	94
$Ph_2P(O)OH$	1	75	97
$(p\text{-}t\text{-}BuC_6H_4)_2P(O)OH$	1	39	95
4-toluic acid	3	40	80
$2,3,5,6\text{-}F_4$-4-toluic acid	3	67	93

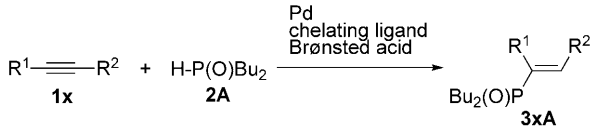
[a] Run using 1-octyne **1a** (1.00 mmol), $HP(O)Bu_2$ **2A** (1.00 mmol), $CpPd(\eta^3\text{-allyl})$ (5 mol%), dppe (5 mol%), and X-OH (5 mol%) in 2.0 mL toluene at 110 °C for 1 h under nitrogen. Conversion of **2A** was 100%.

[b] Determined by ^{1}H NMR spectroscopy.

[c] Selec. = 100 × **3aA**/[**3aA** + (***E***)-**4aA** + (***Z***)-**4aA**].

After these trial experiments, we ran a series of addition reactions of dibutylphosphane oxide with various alkynes using $[3,5\text{-}(CF_3)_2C_6H_3]_2P(O)OH$ as acid and dppe or dppben as ligand (Table 2). Although the reactions were not optimized, all aliphatic and aromatic alkynes (entries 1–8) afforded satisfactory yields. The formation of other regio- and stereoisomers appeared to be negligible in these reactions on the basis of NMR spectroscopy of the crude products run before chromatographic separation. However, a small quantity of a by-product that had come from double bond isomerization appeared to be formed in entries 4 and 5. Cyclohexen-1-ylethyne (**1g**), a conjugated enyne, also reacted normally only at the triple bond and the double bond remained intact (entry 9). In the reaction of methyl 5-hexynoate (**1h**), double bond isomerization of **3hA** took place somewhat extensively to form another isomer in 19% yield, but the ester group was not deteriorated under the conditions (entry 10). In view of our previous results,[7] the new recipe is also envisioned to tolerate other func-

Table 2. Addition reactions of dibutylphosphane oxide with various alkynes.[a]



Entry	**1x**, $R^1=$, $R^2=$	Ligand	Yield of **3xA** [%][b]
1	**1a**, *n*-C_6H_{13}, H	dppe	95 (86)
2	**1a**	dppben	84
3[c]	**1b**, *t*-Bu, H	dppben	86 (74)
4	**1c**, $PhCH_2$, H	dppe	66
5	**1c**	dppben	70 (57)
6	**1d**, *p*-*t*-BuC_6H_4, H	dppben	86 (70)
7	**1e**, Ph, H	dppben	80 (68)
8	**1f**, *p*-FC_6H_4, H	dppben	77 (68)
9	**1g**, 1-cyclohexenyl, H	dppben	96 (81)
10	**1h**, $MeOOC(CH_2)_3$, H	dppben	98[d]
11[e]	**1i**, Ph, Ph	dppben	97 (92)

[a] Run using alkyne **1x** (1.00 mmol), $HP(O)Bu_2$ **2A** (1.00 mmol), $CpPd(\eta^3\text{-allyl})$ (5 mol%), ligand (5 mol%) and $[3,5\text{-}(CF_3)_2C_6H_3]_2P(O)OH$ (5 mol%) in 2.0 mL ethylbenzene at 130 °C for 30 min under nitrogen. Conversion of **2A** was 100%.

[b] Determined by ^1H NMR spectroscopy. The figures in parentheses are isolated yields.

[c] Solvent volume = 3.0 mL.

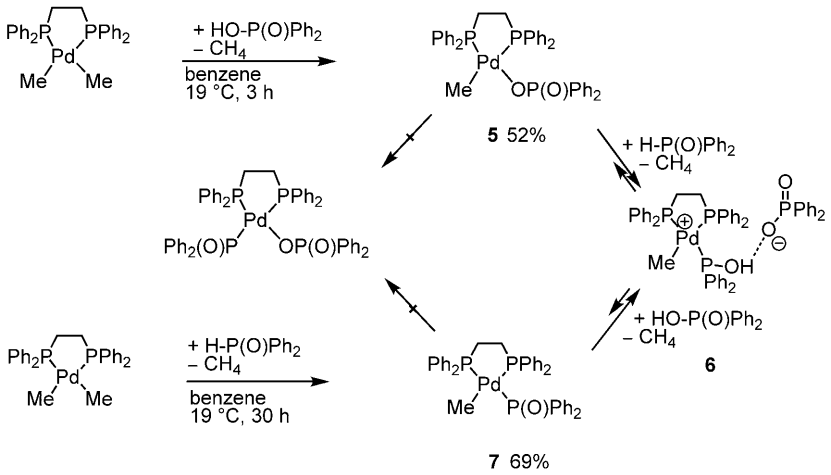
[d] Yield of a mixture of **3hA** (79%) and methyl (*E*)-5-dibutylphosphinyl-4-hexenoate (19%).

[e] Reaction time = 21 h.

tional groups. Finally, diphenylethyne (**1h**), an internal alkyne, also conformed to the reaction to give a nearly quantitative yield although a longer reaction time was required (entry 11).

In our mechanistic study, we examined the reactivity of $Me_2Pd(dppe)$ with diphenylphosphinic acid and diphenylphosphane oxide, in comparison with the reactivity of $Me_2Pd(dmpe)$ reported previously (*vide supra*).[7] When $Me_2Pd(dppe)$ was treated with diphenylphosphinic acid (1 equiv.) at 19 °C for 3 h, $MePd[OP(O)Ph_2](dppe)$ (**5**) was isolated in 52% yield after recrystallization (Scheme 3) and was characterized by X-ray diffraction.[11] However, further treatment of the product with diphenylphosphane oxide (1 equiv.), as opposed to our expectation on the basis of our previous observation using $MePd[OP(O)Ph_2](dmpe)$, did not form $Ph_2P(O)Pd[OP(O)Ph_2](dppe)$, but the product appeared to be a hydrogen-bonded ionic complex **6**. Its structure was supported by ^1H and ^{31}P NMR spectroscopy. FAB-MS analysis also displayed satisfactory data for $[MePd[P(OH)Ph_2](dppe)]^+$ and $[Ph_2P(O)O]^-$, although we were unable to obtain crystalline material suitable for an X-ray diffraction study. The conversion from **5** to **6** is somewhat intuitive. It may involve coordination of $PPh_2(OH)$ and dissociation of $Ph_2P(O)O^-$.[12] However, the mechanism is uncertain at this stage. In another reaction, we treated $Me_2Pd(dppe)$ first with $Ph_2P(O)H$, which afforded $MePd[P(O)Ph_2](dppe)$ (**7**). Further treatment of **7** with $Ph_2P(O)OH$ also gave **6**, but not $Ph_2P(O)Pd[OP(O)Ph_2](dppe)$.

With these unexpected results in hand, we attempted to synthesize $HPd[P(O)Ph_2](dmpe)$ in order to gain more realistic view on the reactivity of its Pd–$P(O)Ph_2$ moiety toward $Ph_2P(O)OH$. However, an attempted reaction to synthesize it starting with $(PhCH{=}CH_2)Pd(dmpe)$ and $Ph_2P(O)H$ (1.2 equiv.) afforded only $Pd[P(OH)Ph_2](dmpe)$ (63% after recrystallization).[12] On the other hand, we could isolate its platinum analogue $HPt[P(O)R_2](dmpe)$ (**8-R**; R = Ph,



Scheme 3. Sequential treatment of $Me_2Pd(dppe)$ with diphenylphosphinic acid followed by diphenylphosphane oxide and *vice versa*.

p-*t*-BuC_6H_4, adamantyl) by mixing Pt(cod)$_2$, dmpe (1 equiv.) and $R_2P(O)H$ (1 equiv.) in toluene, benzene or THF at 20~40 °C for 0.5~17 h. These complexes were fully characterized by NMR spectroscopies, elemental analysis/HR-MS and also by X-ray diffraction for **8-Ph**.[11]

As we anticipated, these complexes, including the one derived from dialkylphosphine oxide, also display hydrogen bonding interaction with phosphinic acids. Thus, when HPt[P(O)Ph$_2$](dmpe) (**8-Ph**) was treated with 1 equiv. of diarylphosphinic acids [Ar$_2$P(O)OH; Ar = Ph, *p*-*t*-BuC_6H_4, 3,5-$(CF_3)_2C_6H_3$], the ^{31}P NMR signals arising from Pd–P(O)Ph$_2$, which appeared at 67.3 ppm (dd) for starting **8-Ph**, was downfield shifted and broadened, indicative of generation of ionic hydridoplatinum complexes (**9-Ph-Ar**) (Figure 1). ^{1}H NMR spectra of these complexes exhibited a (broad) singlet signal due to the proton participating in the O–H···O hydrogen bonding in the range of 8.62–14.4 ppm. Also, a ddd signal accompanied by a satellite band due to ^{195}Pt (997–1034 Hz) was found in a −2.64–−2.32 ppm range, assignable to H–Pt. These spectral features indicate that the resulting species retain their structural integrity except the hydrogen bonding.

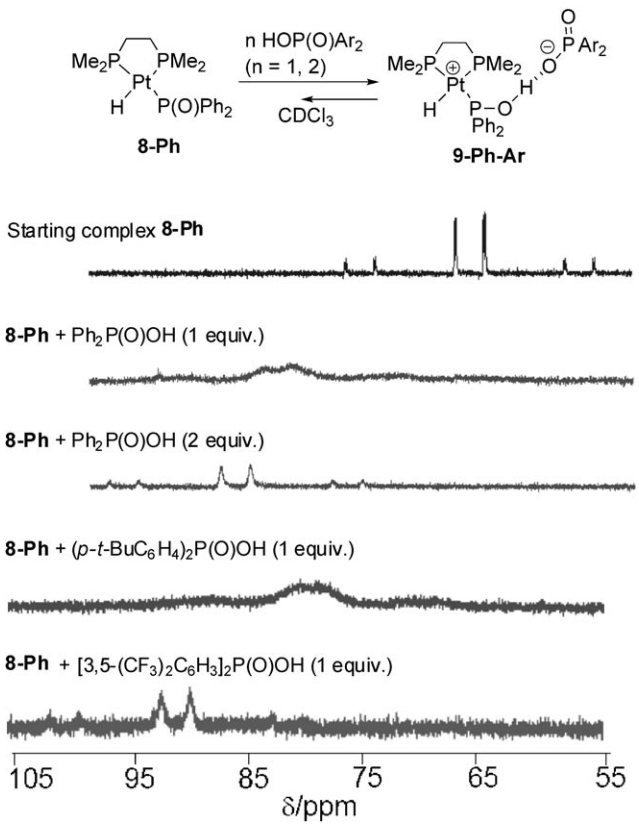


Figure 1. ^{31}P NMR spectral change in the Pt–P(O)Ph$_2$ region upon addition of diarylphosphinic acids to the complex HPt[P(O)Ph$_2$](dmpe) in $CDCl_3$.

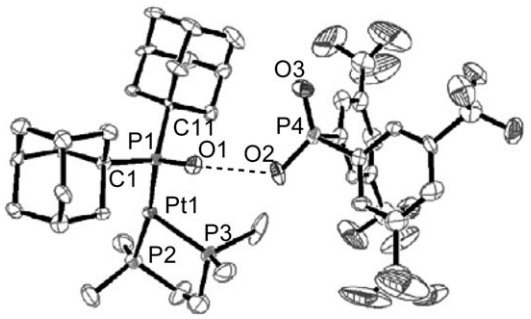
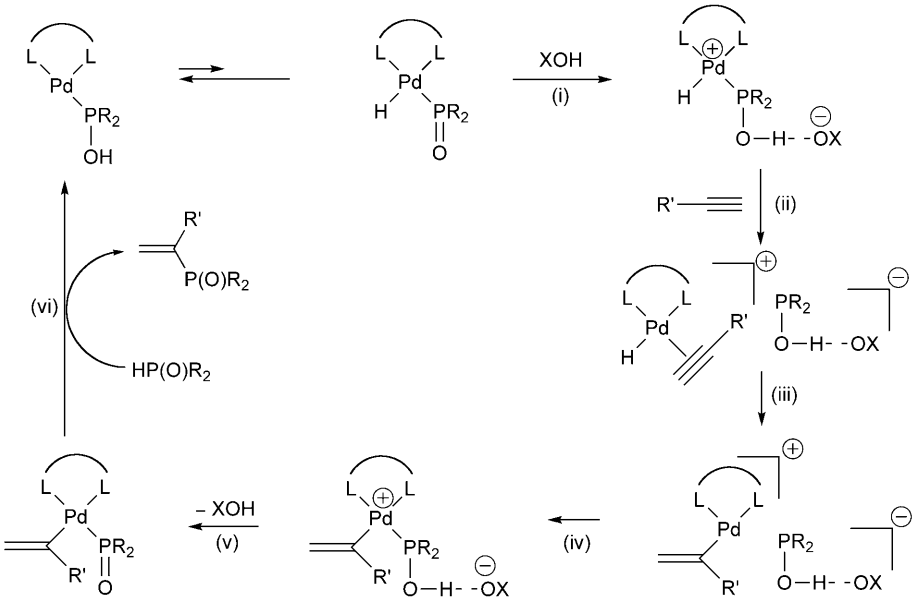


Figure 2. Molecular structure of **9-Ad-[3,5-$(CF_3)_2C_6H_3$]**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvated CH_2Cl_2 molecule are omitted for clarity.

Figure 1 suggests that the hydrogen bonding interaction appears more distinct when a larger quantity of an acid is added as shown by addition of 2 equivalents of Ph$_2$P(O)OH and also when the acidy is higher as substantiated by the addition of [3,5-$(CF_3)_2C_6H_3]_2$P(O)OH (1 equiv.). More decisive evidence came from the treatment of the complex HPt[P(O)Ad$_2$](dmpe) (**8-Ad**; Ad = adamantly) having a more basic dialkyl ligand, P(O)Ad$_2$, with strongly acidic 3,5-$(CF_3)_2C_6H_3)_2$P(O)OH (1.0 equiv.). Upon mixing, the ^{31}P NMR signals due to the Pt[P(O)Ad$_2$] moiety downfield shifted from 106.2 to 137.6 ppm (sharp dd with distinct coupling). The resulting species **9-Ad-[3,5-$(CF_3)_2C_6H_3$]**[13] could be isolated and was fully characterized by NMR and IR spectroscopy, HR-MS, and elemental analysis. Finally the structure was confirmed by X-ray analysis unequivocally (Figure 2).[10]

Very interestingly, ionic species **9-Ad-[3,5-$(CF_3)_2C_6H_3$]** is significantly labile in terms of substitution/dissociation of its *phosphane-like* PAd$_2$[OH···OP(O)(3,5-$(CF_3)_2C_6H_3)_2$]$^-$ ligand. Thus, upon treatment with *tert*-butyl isocyanide (7.0 equiv. in total of incremental additions) at 17 °C for 3 h, **9-Ad-[3,5-$(CF_3)_2C_6H_3$]** was consumed nearly completely to generate the species [HPt(CN-*t*-Bu)$_2$(dmpe)]$^+$ [OP(O)(3,5-$(CF_3)_2C_6H_3)_2$]$^-$ (**10**; *ca.* 60% ^{1}H NMR yield),[14] suggesting that the hydrogen bonding interaction may serve to generate a vacant coordination site, which can be occupied by an alkyne molecule in the catalysis.[15] In contrast, corresponding neutral complex (**8-Ad**) was totally unreactive under the same conditions.

In view of these results, when a Brønsted acid XOH is present, we can think of an alternate mechanistic possibility, such as the one depicted in Scheme 4, in which key steps are dissociation/substitution of the PR$_2$(OH···OX)$^-$ ligand resulting in facile coordination of the C≡C triple bond (step ii), hydropalladation (step iii), recoordination of the PR$_2$(OH···OX)$^-$ ligand (step iv), liberation of XOH



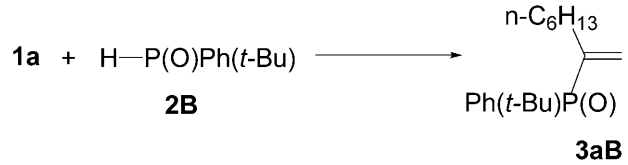
Scheme 4. Alternate mechanism of Pd-chelating phosphane-Brønsted acid-catalyzed addition of secondary phosphane oxide with alkynes.

from hydrogen bonding (step v) and reductive elimination (step vi).[16]

This mechanistic proposal can rationalize the efficient addition of dialkylphosphane oxides disclosed in the present paper and also the following two puzzling observations in the Pd–$Ph_2P(O)OH$-catalyzed addition of diphenylphosphane oxide; (1) the enhanced activity and (2) the provenance of the regiochemical reversal (i.e., selective formation of branched structured products) induced by the addition of $Ph_2P(O)OH$. Given that a coordinatively labile ionic palladium species is generated, an alkyne molecule is envisioned to interact with ionic palladium species more readily than with neutral four-coordinate species and is likely to undergo Markovnikov addition due to the more protonic nature of the cationic "hydridopalladium" species.

Finally it is of importance in consideration of the extension of the recipe to other phosphane oxides that we have to seek the best Brønsted acid for a particular phosphane oxide, as already mentioned. As we have reported in a previous paper, $Ph_2P(O)OH$ appeared to be the best acid among the acids screened as far as diphenylphosphane oxide is concerned.[7] The present paper has already disclosed that [3,5-$(CF_3)_2C_6H_3]_2P(O)OH$, a stronger acid, is the best one for $Bu_2P(O)H$, a more basic phosphane oxide. However, a stronger acid is not necessarily better perfoming, depending on the structure of the phosphane oxide reagent. Table 3 shows that, in the reaction of *tert*-butylphenylphosphane oxide, strongly acidic [3,5-$(CF_3)_2C_6H_3]_2P(O)OH$ (entry 1) afforded the lowest yield among the four acids examined. On the contrary, weaker ones (entries 2–4) were better performing and the best one was *tert*-butylphenylphosphinic acid, the least acidic among the four. These results clearly indicate that acidity is an important factor, but not the only factor that dictates the catalytic activity irrespective of the structure of phosphane oxides. In a scenario based on the acidity, elemental step i (presumably step ii also) in Scheme 4 is envisioned to be facile when the acidity is high. However, a strong acid is not likely to readily dissociate the hydrogen bonding interaction at step v, a prerequisite for reductive elimination, suggesting that stronger acids are not

Table 3. Effect of acids in the reaction of 1-octyne with *tert*-butylphenylphosphane oxide.[a]



Entry[a)]	X-OH	Yield of **3aB**[b]
1	$[3,5\text{-}(CF_3)_2C_6H_3]_2P(O)OH$	25
2	$p\text{-}CH_3C_6F_4COOH$	63
3	$(p\text{-}t\text{-}BuC_6H_4)_2P(O)OH$	68
4	(*t*-Bu)PhP(O)OH	72 (60)

[a] Run using 1-octyne **1a** (1.00 mmol), (*t*-Bu)PhP(O)H **2B** (1.00 mmol), CpPd(η^3-allyl) (5 mol%), dppben (5 mol%) and X–OH (5 mol%) in 2.0 mL ethylbenzene at 130 °C for 4 h under nitrogen.

[b] Determined by ^1H NMR spectroscopy. The figure in parentheses is the isolated yield.

always better than weaker ones. As a separate scenario, we may have to consider the steric effect of the phosphane oxide and acid since the displacement/dissociation (step ii) and recoordination (step iv) of the $PR_2(OH\cdots OX)^-$ ligand are also likely to be affected by its steric demand. Although we have not scrutinized the steric aspect seriously, we believe that we have to seek for an optimum match between the phosphane oxide and the acid, in terms of their electronic and steric factors.

In summary, this communication reports the successful addition of dibutylphosphane oxide to alkynes, both terminal and internal. A new mechanism comprising intimate cooperation of palladium and Brønsted has also been proposed to rationalize the enhancement of the catalysis and the branch selectivity. Full details will be reported shortly.

Experimental Section

Typical Procedure for a Catalytic Reaction and Isolation of Products: Addition Reaction of 1-Octyne (1a) with Dibutylphosphane Oxide (2A) using CpPd(η^3-allyl), Dppe and Bis[3,5-di(trifluoromethyl)-phenyl]phosphinic Acid

To a dried 25-mL Schlenk tube containing CpPd(η^3-allyl) (10.6 mg, 0.05 mmol), dppe (19.9 mg, 0.050 mmol), bis[3,5-di(trifluoromethyl)phenyl]phosphinic acid (24.5 mg, 0.05 mmol) and dibutylphosphine oxide (**2A**, 162 mg, 1.00 mmol) were added toluene (2.0 mL) and 1-octyne (**1a**, 147 μL, 1.00 mmol) under nitrogen at room temperature. The Schlenk tube was then heated in an oil bath kept at 130 °C and the mixture was stirred for 30 min. Evaporation of the solvent yielded the crude mixture, which was added to a solution of *p*-dimethoxybenzene (internal standard, 22.7 mg 0.164 mmol) in $CDCl_3$ (5.0 mL). NMR analysis of the mixture revealed that 2-dibutylphosphinyl-1-octene (**3aA**) was formed in 95% yield together with by-products such as (*E*)-1-dibutylphosphinyl-1-octene (***E*)-4aA** in 3% yield and traces of others. After ^{1}H NMR measurement, the solution was evaporated and the residue was subjected to column chromatography on silica gel (CH_2Cl_2/methanol = 90/1) to allow isolation of **3aA**; yield: 86%; colorless oil; bp 72 °C/0.01 mmHg (Kugelrohr). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.91$ (dd, $J_{H,P} = 18.8$ Hz, $J = 1.2$ Hz, 1H, *trans*-PC=CH), 5.69 (dd, $J_{H,P} = 36.4$ Hz, $J = 1.2$ Hz, 1H, *cis*-PC=CH), 2.04 (dt, $J_{H,P} = 8.8$ Hz, $J = 7.2$ Hz, 2H, $PCCH_2$), 1.76–1.20 [m, 20H, $CH_3(CH_2)_4 + 2P(CH_2)_3CH_3$], 0.87–0.80 (m, 9H, $3CH_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 142.8$ (d, $J = 79.3$ Hz, P*C*=C), 127.0 (d, $J = 5.8$ Hz, PC=*C*H_2), 31.5 (=$CCH_2CH_2CH_2$), 31.0 (d, $J = 10.7$ Hz, =*C*$CH_2CH_2CH_2$), 28.8 [=$C(CH_2)_3CH_2$], 27.6 (d, $J = 5.6$ Hz, =$CCH_2CH_2CH_2$), 27.4 (d, $J = 66.8$ Hz, 2C, $2PCH_2$), 24.0 (d, $J = 14.3$ Hz, 2C, $2PCH_2CH_2CH_2$), 23.3 (d, $J = 3.9$ Hz, 2C, $2PCH_2CH_2CH_2$), 22.4 [=$C(CH_2)_4CH_2$], 13.9 [=$C(CH_2)_5CH_3$], 13.5 [2C, 2P-$(CH_2)_3CH_3$]; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = 42.2$; IR (neat):): $\nu = 1163$ ($\nu_{P=O}$), 1635 cm^{-1} ($\nu_{C=C}$); MS (EI, 70 eV,% relative intensity): $m/z = 272$ (M^+, 7), 257 (8), 243 (25), 229 (24), 215 (27), 201 (100), 187 (19), 161 (14) 104 (10); HR-MS: $m/z = 272.2265$, calcd. for $C_{16}H_{33}OP$: 272.2269.

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[8] The following abbreviations are used in this communication; dmpe = $Me_2P(CH_2)_2PMe_2$, dppe = $Ph_2P(CH_2)_2PPh_2$, dppen = *cis*-$Ph_2PCH{=}CHPPh_2$, dppp = $Ph_2P(CH_2)_3PPh_2$, dppb = $Ph_2P(CH_2)_4PPh_2$, dppben = 1,2-$(Ph_2P)_2C_6H_4$, dppxy = 1,2-$(Ph_2PCH_2)_2C_6H_4$.

[9] In the experiments listed in Table 1, Table 2 and Table 3, CpPd(η^3-allyl) was used as precatalyst in conjunction with a chelating phosphane and a Brønsted acid. It is well established that, upon treatment with phosphane ligands, CpPd(η^3-allyl) generates Pd(0)-phosphane complexes with extrusion of allylcyclopentadiene and its isomers. For the chemistry between CpPd(η^3-allyl) and phosphane ligands, see: a) V. Harder, H. Werner, *Helv. Chim. Acta* **1973**, *56*, 549; b) D. M. Norton, E. A. Mitchell, N. R. Botros, P. G. Jessop, M. C. Baird, *J. Org. Chem.* **2009**, *74*, 6674. This *in situ* procedure has been often utilized in the synthesis of and catalysis by palladium(0) complexes. For selected examples, see: c) P. Leoni, *Organometallics* **1993**, *12*, 2432; d) S. R. Stauffer, N. A. Beare, J. P. Stambuli, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 4641; e) V. P. W. Bohm, W. A. Herrmann, *Chem. Eur. J.* **2001**, *7*, 4191; f) T. Matsumoto, T. Kasai, K. Tatsumi, *Chem. Lett.* **2002**, 346; g) E. Galardon, S. Ramdeehul, J. M. Brown, A. Cowley, K. K. Hii, A. Jutand, *Angew. Chem.* **2002**, *114*, 1838; *Angew. Chem. Int. Ed.* **2002**, *41*, 1760; h) J. H. Kirchhoff, M. R. Netherton, I. D. Hills, G. C. Fu, *J. Am. Chem. Soc.* **2002**, *124*, 13662; i) G. Mann, Q. Shelby, A. H. Roy, J. F. Hartwig, *Organometallics* **2003**, *22*, 2775; j) M. O. Shulyupin, G. Francio, I. P. Beletskaya, W. Leitner, *Adv. Synth. Catal.* **2005**, *347*, 667; k) F. Barrios-Landeros, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 6944; l) D. B. Grotjahn, Y. Gong, L. Zakharov, J. A. Golen, A. L. Rheingold, *J. Am. Chem. Soc.* **2006**, *128*, 438; m) A. G. Sergeev, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* **2008**, *130*, 15549.

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[11] CCDC 795289, CCDC 795290 and CCDC 795291 contain 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.

[12] Secondary phosphine oxides exist in two tautomeric isomers, P(=O)H and P–OH, the former being dominant in the equilibrium. See: a) W. J. Bailey, R. B. Fox, *J. Org. Chem.* **1963**, *28*, 531; b) W. J. Bailey, R. B. Fox, *J. Org. Chem.* **1964**, *29*, 1013; c) L. A. Hamilton, P. S. Landis, in: *Organic Phosphorus Compounds*, (Eds.: G. M. Kosolapoff, L. Maier), Wiley, New York, **1972**, Vol. 4, Chapter 11.

[13] Solvated with a CH_2Cl_2 molecule.

[14] Another species was also formed. See the Supporting Information.

[15] Treatment of **9-Ad-[3,5-$(CF_3)_2C_6H_3$]** with acetonitrile (540 equiv.) in $CDCl_3$ at 17 °C did not induce any reaction to the complex.

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