Ruthenium-Catalyzed Addition Reaction of Diphenylphosphinic Acid to Terminal Alkynes: Regioselective Synthesis of Alkenyl Diphenylphosphinates

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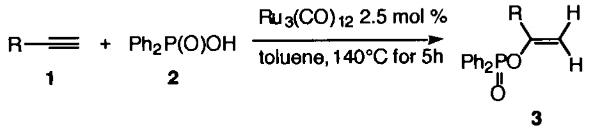
Diphenylphosphinic acid adds across the triple bond of terminal alkynes in the presence of $Ru_3(CO)_{12}$, leading to regioselective formation of alkenyl diphenylphosphinates $CH_2=C(R)[OP(O)Ph_2]$.

In the previous paper we reported successful addition of diphenylphosphine oxide to terminal alkynes to synthesize (1-alken-1-yl)diphenylphosphine oxides.[1] However, an addition of a catalytic quantity of diphen-ylphosphinic acid induced a reversal of regioselectivity to result in selective formation of (1-alken-2-yl)diphenylphosphine oxides.[2] This unexpected reversal of regioselectivity prompted us to further investigate the interaction of diphenylphosphinic acid with transition metal complexes. We now wish to report ruthenium-catalyzed addition reaction of diphenylphosphinic acid with terminal alkynes. Although metal complex-catalyzed addition reactions of O-H bonds of carboxylic acids[3] and alcohols[4] with alkynes have been actively studied, analogous reactions of phosphinic acids have never been explored. Alkenyl phos-phinates, the products of the new addition reaction, are of potential use in organic synthesis[5] and as monomers and co-monomers for fire-retardant (co)polymers.[6]

When a mixture of oct-1-yne (0.1 mmol), diphenylphosphinic acid (0.12 mmol; sparingly soluble at room temperature) and $Ru_3(CO)_{12}$ (2.5 mol% relative to oct-1-yne) in toluene-d_8 (0.5 ml) was heated in a sealed NMR tube at 140 °C for 5 h, 1-hexen-2-yl diphenylphosphinate (**3a**), the Markovnikov adduct, was found by ^1H NMR spectroscopy to be formed as a sole product (Scheme 1). In a preparative scale experiment using oct-1-yne (0.4 mmol), diphenylphosphinic acid (0.48 mmol) and $Ru_3(CO)_{12}$ (2.5 mol%) in toluene (3 ml), the resulting mixture was filtered to remove a pale yellow solid material (a mixture of diphenylphosphinic acid and catalyst residue) and was evaporated. Column chromatography of the residue on silica gel (hexane/acetone = 5/1-5/5 gradient) gave pure 1-hexen-2-yl diphenylphosphinate (**3a**) in 88% yield. The structure was fully characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy.[7]



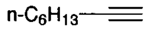
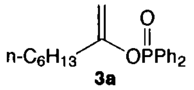
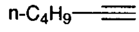
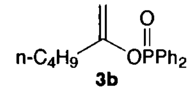
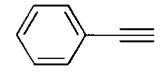
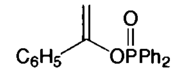
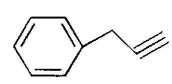
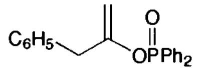
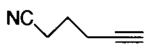
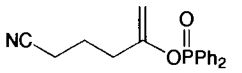
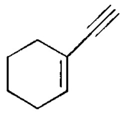
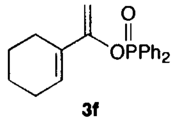
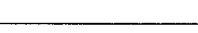
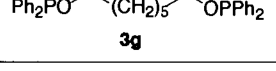
a R = n-C_6H_{13}, **b** R = n-C_4H_9, **c** R = C_6H_5, **d** R = $CH_2C_6H_5$, **e** R = $(CH_2)_3CN$, **f** R = c-C_6H_9

Scheme 1.

Catalytic activity of several complexes was also briefly examined for the reaction of oct-1-yne. The results (NMR yield of **3a** after 5 h at 140 °C) were as follows; $Ru_3(CO)_{12}$ (90%) > $RuCl_2$(*p*-cymene)(PPh_3) (53%) > RhCl(1,5-cod)(PPh_3) (21%) > $RuH_2(CO)(PPh_3)_3$ (18%) > $[RhCl(1,5\text{-cod})]_2$ (10%). Thus $Ru_3(CO)_{12}$ proved to be the catalyst of choice.

As summarized in Table 1, various terminal alkynes, independent of the nature of alkynes, reacted similarly with $Ph_2P(O)OH$ to give corresponding Markovnikov adducts in good yields with high regioselectivities. The reaction of phenylacetylene with $Ph_2P(O)OH$ afforded **3c** in 70% isolated yield. 3-Phenylprop-1-yne also reacted similarly with $Ph_2(O)OH$ to furnish **3d**. 5-Hexynonitrile reacted only at the C–C triple bond and the C–N triple bond remained intact. The olefinic bond was unreactive under the conditions. Accordingly the reaction of 1-ethynylcyclohexene with $Ph_2P(O)OH$ gave the product coming from the selective addition to the triple bond. Introduction of two phosphinate groups readily occurred when 1,8-nonadiyne was allowed to react with 2.2 equivalens of $Ph_2P(O)OH$. The

Table 1. The reaction of terminal alkynes with $Ph_2P(O)OH$ in the presence of $Ru_3(CO)_{12}$[a]

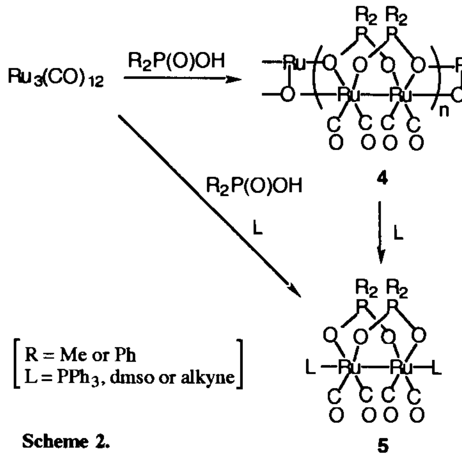
Entry	Alkyne	Product	Yield %[b]
1		 **3a**	88
2		 **3b**	67[c]
3		 **3c**	70
4		 **3d**	79
5		 **3e**	82
6		 **3f**	65
7		 **3g**	86

[a] Alkyne (0.4 mmol), diphenylphosphinic acid (0.48 mmol), $Ru_3(CO)_{12}$ (2.5 mol%), toluene (3 ml), 140 °C, 5 h.
[b] Isolated yield based on the alkynes used.
[c] $RuCl_2$(*p*-cymene)(PPh_3) was used as catalyst.

$^{31}P\{H\}$ NMR spectum of **3g** displayed only one resonance at 28.3 ppm, confirming the high regioselectivity.

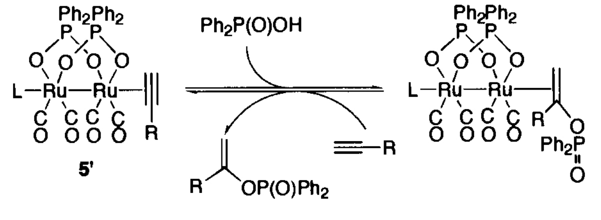
In the preliminary experiments, however, the procedure could not be successfully applied to internal alkynes (diphenylacetylene and 1-phenylprop-1-yne). They reacted very sluggishly to give only traces of the corresponding adducts (as characterized by GC-MS). Attempted reactions of dimethylphosphinic acid and dibutyl phosphate used in place of diphenylphosphinic acid did not work either. Diphenyl phosphate did react with oct-1-yne but a messy mixture resulted. Obviously further study is needed to generalize the new addition reaction.

The mechanism of the addition reaction is not clear at the present time. With the mechanism described for the relevant addition of carboxylic acids[3a,d] in mind we propose dimeric ruthenium species being involved as depicted in Scheme 2.



Scheme 2.

The following observations partly substantiate the proposal. When a toluene solution (5 ml) of $Ru_3(CO)_{12}$ (0.1 mmol) and $Ph_2P(O)OH$ (5 equiv.) was refluxed for 30min, a homogeneous orange solution was formed. Further heating for additional 3 h gave a pale yellow precipitate. The precipitate is formulated as polymeric dinuclear species $[Ru_2(\mu_2{:}\mu_2{:}\eta^2\text{-}O_2PPh_2)_2(CO)_4]_n$ (**4**); elemental analysis was satisfactory for the formula[8] and the species displayed CO stretching bonds at 2040, 1988 and 1959 cm^{-1}, which appeared reasonable as compared with the known methyl analogue.[9a] Species **4** was found to catalyze the addition reaction, albeit sluggishly presumably because of its extremely low solubility; the reaction of phenylacetylene with $Ph_2P(O)OH$ at 140 °C for 5 h in the presence of **4** (5 mol% as the dimeric structure) formed **3c** in 10% yield. This suggests that **4** could partly depolymerize with alkynes to generate active species. Similar depolymerization of the methyl analogue of **4** is known to proceed upon treatment with ligands such as PPh_3 and dimethyl sulfoxide to afford corresponding dimeric adducts (**5**, R = Me, L = PPh_3, dmso).[9a] Indeed, when a mixture of **4** and an excess of phenylacetylene (2 equiv relative to the dimeric formula) in toluene was heated at 140 °C for 2 h, complex **4** partly dissolved to generate an orange solution, although we were unable to identify the new species due to the low conversion. In addition, complex **5** (L = dmso) was found to catalyze the addition reaction to give **3a** in 54% yield (3.7 mol% catalyst, 140 °C, 5 h). Based on these observations and precedent, species like **5'** (R = Ph, L = alkyne), possibly generated directly from $Ru_3(CO)_{12}$, $Ph_2P(O)OH$ and the alkyne, carries the catalysis in the real reaction system. Besides the indirect route via the depolymerization with a ligand (*vide supra*), dimeric adduct **5** (R = Ph, L = PPh_3) is also known to be obtained directly from $Ru_3(CO)_{12}$, $Ph_2P(O)OH$ and PPh_3.[9b] As to the event after the formation of **5'**, one can think of various possibilities.[10] Scheme 3 depicts a possibility; although we are unable to provide any evidence, an external attack of the phosphinic acid may follow the generation of **5'** to result in the formation of **3**, as in the addition of carboxylic acids to alkynes.[3a,d]



Scheme 3. Possible reaction mechanism.

In conclusion, the present paper discloses the first examples of addition of diphenylphosphinic acid to terminal alkynes. The reaction proceeds with high selectivities and in good yields. Extension to other phosphorus-bound O-H bond is under way.

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References and Notes

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7 **3a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.85-7.79 (m, 4H), 7.52-7.40 (m, 6H), 4.76 (s, 1H), 4.37 (s, 1H), 2.16 (t, 2H, *J* 7.5), 1.51-1.44 (m, 8H), 0.85 (t, 3H, *J* 7.0); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7 ($J_{C\text{-}P}$ 9.2), 132.2 ($J_{C\text{-}P}$ 2.7), 131.7 ($J_{C\text{-}P}$ 10.3), 128.5 ($J_{C\text{-}P}$ 13.4), 97.6 ($J_{C\text{-}P}$ 5.2), 35.3 ($J_{C\text{-}P}$ 4.3), 31.6, 28.5, 26.4, 22.6, 14.1; $^{31}P\{H\}$ NMR (121 MHz, $CDCl_3$) δ 28.2 ppm; GC-MS *m/z* (relative intensity) 328 (5, M^+), 219 (100); HRMS: calc. for $C_{20}H_{25}O_2P$: 328.1590. Found: 328.1580.

8 **4**: Anal. Calcd for $C_{28}H_{20}O_8P_2Ru_2$: C, 44.92; H, 2.67%. Found: C, 44.98; H, 2.56%.

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10 The very low reactivity of internal acetylenes and rapid H/D exchange between $n\text{-}C_6H_{13}C{\equiv}CH$ and $Ph_2P(O)OD$ hampered the invenstigation into the stereochemistry of the addition reaction.