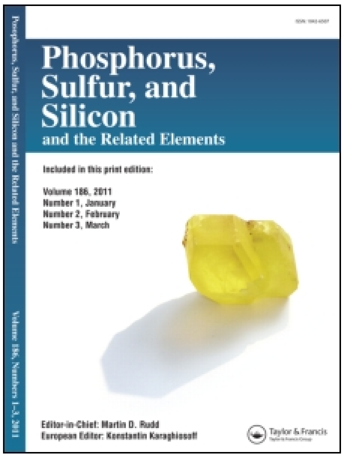

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Palladium Catalyzed Carbon-Phosphorus Bond Activation: Decarbonylation Reaction Of α-Ketophosphonates

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PALLADIUM CATALYZED CARBON-PHOSPHORUS BOND ACTIVATION: DECARBONYLATION REACTION OF α-KETOPHOSPHONATES

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Abstract Various α-ketophosphonates, $RC(O)P(O)(OR')_2$, are catalytically decarbonylated to give phosphonates, $RP(O)(OR')_2$, on treatment with PdR_2L_2 (R=Me, Et; L=tertiary phosphine) or $Pd(PPh_3)_4$. The reaction of trans-$PdEt_2(PMe_3)_2$ with $RC(O)P(O)(OR')_2$ for several minutes under toluene reflux conditions affords trans-$Pd(PMe_3)_2\{C(O)R\}\{P(O)(OR')_2\}$ as yellow crystals. The isolated palladium complexes yield the corresponding phosphonate in toluene at reflux temperature and also serve as a catalyst for the decarbonylation of α-ketophosphonates. The overall catalytic decarbonylation reaction is discussed.

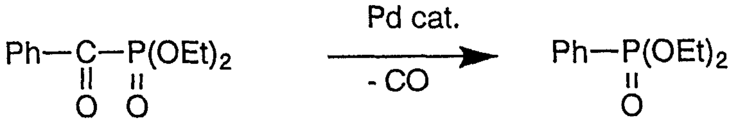
INTRODUCTION

Transition-metal complexes have made significant contributions as a catalysis to industrial and laboratory processes.[1] However, examples of transition-metal complexes activating the carbon-phosphorus bond still remain to be exploited, though they may possess the potential activity. The lack of these studies is presumably a result of the relatively strong carbon-phosphorus bond and thus its less facile cleavage as compared with halogen-, nitrogen-, and hydrogen-phosphorus bonds.[2] Recently, some results concerning carbon-phosphorus bond activation by transition-metal complexes have been reported.[3,4] However, they are stoichiometric reactions and no catalytic C-P bond activation promoted by transition-metal complexes have been reported.

Reported herein are the results of the reaction of a variety of palladium complexes with α-ketophosphonates where unprecedented examples involving catalytic carbon-phosphorus bond scission and formation were found, and the reaction mechanism was elucidated though the isolation of the intermediate Pd complex in the catalytic cycle.

DECARBONYLATION OF α-KETOPHOSPHONATES

The reactions of $PhC(O)P(O)(OEt)_2$ with a various palladium complexes revealed that $PhC(O)P(O)(OEt)_2$ is decarbonylated to give $PhP(O)(OEt)_2$ in toluene reflux conditions in the presence of a catalytic amount of palladium complex such as $Pd(PPh_3)_4$, trans-$PdMe_2(PMe_2Ph)_2$, trans-$PdEt_2(PMePh_2)_2$, and cis-$PdMe_2(PMePh_2)_2$ (eq. 1). In the absence of a palladium complex, $PhC(O)P(O)(OEt)_2$ did not change at all, proving that the decarbonylation is catalyzed by the palladium complexes.



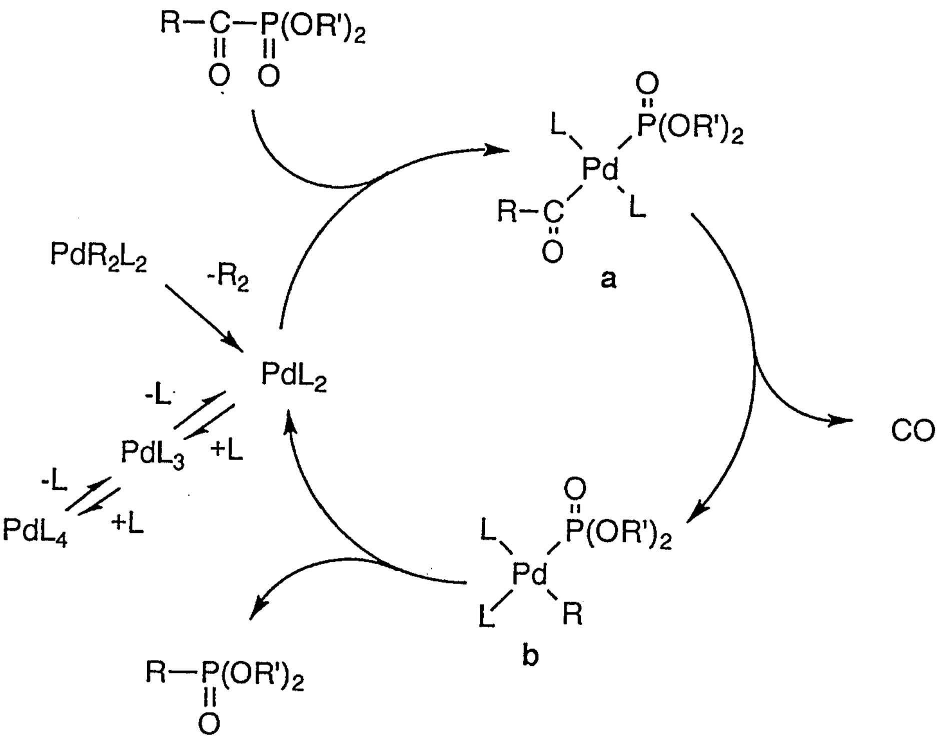
$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{P}(OEt)_2} \xrightarrow[-\,\mathrm{CO}]{\text{Pd cat.}} \mathrm{Ph{-}\underset{\underset{O}{\|}}{P}(OEt)_2} \qquad (1)$$

Concerning α-ketophosphonates, both aroylphosphonates and acetylphosphonates undergo the catalytic decarbonylation and the aroylphosphonates are more readily decarbonylated than acetylphosphonates.

CATALYTIC CYCLE

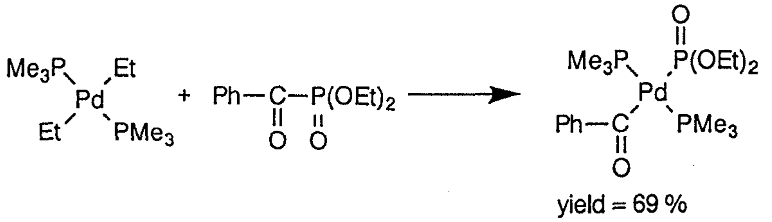
All palladium complexes showing the catalytic ability can readily form a 14-electron Pd(0) species "PdL_2" (L=tertiary phosphine) by equilibrium in solution or on heating. So, "PdL_2" seems to be one of the intermediates of the catalytic cycle. Actually, $Pd(acac)_2$, $PdCl_2(NCPh)_2$ and $PdCl_2(PPh_3)_2$, not being able to change to "PdL_2" species under the reaction conditions employed, did not show catalytic activity. Thus, the overall catalytic reaction is proposed to proceed as shown in Scheme I, which involves oxidative addition of an α-ketophosphonate at a C-P bond to a "PdL_2" species to give **a**, followed by decarbonylation of the aroyl (or the acyl) ligand to give **b** and the subsequent reductive elimination to give the aryl(or alkyl)phosphonate with regeneration of a "PdL_2" species.

Scheme I



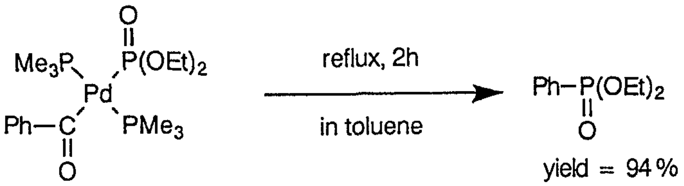
ISOLATION OF CATALYTIC INTERMEDIATE

Refluxing for only several minutes the toluene solution containing trans-$PdEt_2(PMe_3)_2$ and $PhC(O)P(O)(OEt)_2$ followed by cooling the solution in a refrigerator yielded crystalline trans-$Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OEt)_2\}$ (eq. 2), which corresponds to the complex formed by the oxidative addition of $PhC(O)P(O)(OEt)_2$ at a C-P bond toward a "$Pd(PMe_3)_2$" species.

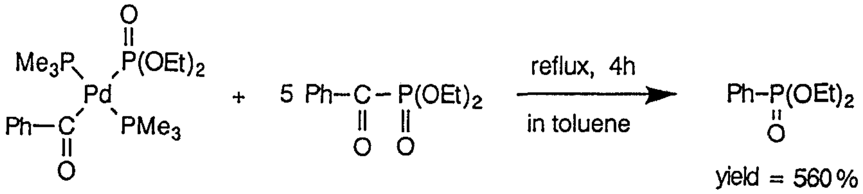


(2)

In order to check whether the isolated complex is one of the complex constituting the catalytic cycle, the thermal reaction was examined in the absence and presence of the corresponding α-ketophosphonate. Reflux for 2 h of a toluene solution of trans-$Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OEt)_2]$ gave $PhP(O)(OEt)_2$ in an almost quantitative yield(eq. 3). Treatment of the complex with 5 equiv of $PhC(O)P(O)(OEt)_2$ yielded $PhP(O)(OEt)_2$ in 560 % yield based on the Pd complex(eq. 4). The results clearly show that the isolated aroyl(phosphonate)palladium complex has the catalytic ability toward decarbonylation of α-ketophosphonates.



(3)



(4)

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