Catalytic Carbon–Phosphorus Bond Activation by Palladium Complexes. Decarbonylation and Metathesis Reactions of α-Ketophosphonates and Isolation of Aroyl(phosphonato)palladium Complexes as Intermediates

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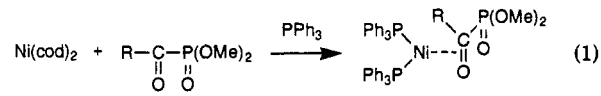
Various α-ketophosphonates, $RC(O)P(O)(OR')_2$, are catalytically decarbonylated to give phosphonates, $RP(O)(OR')_2$, on treatment with PdR_2L_2 (R = Me, Et; L = tertiary phosphine), $Pd(PPh_3)_4$, or $Pd(PCy_3)_2$. Crossover experiments on two kinds of α-ketophosphonates revealed that a metathesis reaction at a C–P bond of an α-ketophosphonate takes place prior to the decarbonylation in the presence of a catalytic amount of palladium complex ($R^1C(O)P(O)(OR^2)_2 + R^3C(O)P(O)(OR^4)_2 \rightleftharpoons R^1C(O)P(O)(OR^4)_2 + R^3C(O)P(O)(OR^2)_2$). 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 and metathesis reactions of α-ketophosphonates. The overall catalytic decarbonylation reaction is proposed to consist of oxidative addition of $RC(O)P(O)(OR')_2$ at the C–P bond to a "PdL_2" species generated from PdR_2L_2 or PdL_4 to give *trans*-$PdL_2\{C(O)R\}\{P(O)(OR')_2\}$, followed by decarbonylation of the C(O)R ligand to give $PdL_2R\{P(O)(OR')_2\}$ and subsequent reductive elimination to give $RP(O)(OR')_2$ with regeneration of a "PdL_2" species. The mechanism of the α-ketophosphonate metathesis reaction is also discussed.

Introduction

Transition-metal complexes have made significant contributions as catalysts in industrial and laboratory processes.[1] However, examples of transition-metal complexes activating the carbon–phosphorus bond still remain to be exploited, though these complexes may possess 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] Most of them include aryl carbon–phosphorus bond breaking in triarylphosphines,[4,5] and only a limited number of examples with non-aryl carbon–phosphorus bond cleavage have been found.[6] All of them are stoichiometric reactions, and to our knowledge, no catalytic C–P bond activation promoted by transition-metal complexes has been reported.

We have been studying the reactions of α-ketophosphonates, $RC(O)P(O)(OR)_2$, with some transition-metal complexes and found that $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) reacts with $RC(O)P(O)(OMe)_2$ in the presence of PPh_3 to give $(PPh_3)_2Ni(\eta^2(CO)\text{-}RC(O)P(O)\text{-}(OMe)_2)$, where the α-ketophosphonate coordinates to a $Ni(PPh_3)_2$ moiety in an η^2-CO mode[7] (see eq 1).



(1)

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Table I. Decarbonylation of $PhC(O)P(O)(OEt)_2$ Catalyzed by Various Palladium Complexes[a]

Pd complex	reactn time, h[b]	yield of $PhP(O)(OEt)_2$, %[c]
$Pd(PPh_3)_4$ (1)	48	52
$Pd(PCy_3)_2$ (2)	75	60
trans-$PdMe_2(PMe_2Ph)_2$ (3)	2	69
trans-$PdEt_2(PMePh_2)_2$ (4)	0.2	100
cis-$PdMe_2(PMePh_2)_2$ (5)	0.2	100
$Pd(styrene)(PMePh_2)_2$ (6)	0.2	100
$PdMe_2(dppe)$ (7)	5	60

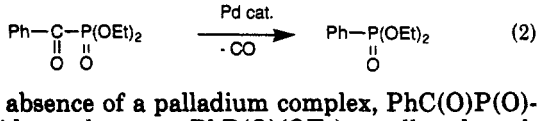
[a] Reaction conditions: $PhC(O)P(O)(OEt)_2$/Pd complex = 5/1 (molar ratio); at toluene reflux temperature. [b] Time required to complete the reaction; confirmed by following the amount of $PhC(O)P(O)(OEt)_2$ and $PhP(O)(OEt)_2$ by GLC. [c] Based on $PhC(O)P(O)(OEt)_2$.

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 through the isolation of the intermediate Pd complex in the catalytic cycle. A portion of this study has been communicated.[8]

Results and Discussion

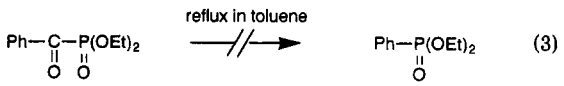
Reaction of Palladium Complexes with α-Ketophosphonates. The reactions of $PhC(O)P(O)(OEt)_2$ with a variety of palladium complexes were examined. After a palladium complex was dissolved in toluene and an equimolar amount of $PhC(O)P(O)(OEt)_2$ was added, the solution was refluxed for several hours. Then, the products were detected by gas chromatography and ^{31}P NMR measurements. The results revealed that $Pd(acac)_2$, $PdCl_2(NCPh)_2$, and $PdCl_2(PPh_3)_2$ did not react at all with $PhC(O)P(O)(OEt)_2$; i.e., $PhC(O)P(O)(OEt)_2$ remained unreacted, whereas the Pd complexes listed in Table I converted $PhC(O)P(O)(OEt)_2$ into $PhP(O)(OEt)_2$ in 100% yield when equivalent amounts of these Pd complexes were used.

Next, we examined whether the decarbonylation of $PhC(O)P(O)(OEt)_2$ promoted by the Pd complexes listed in Table I was stoichiometric or catalytic. Each of the palladium complexes was treated with 5 molar equiv of $PhC(O)P(O)(OEt)_2$ under toluene reflux conditions. The amount of $PhP(O)(OEt)_2$ formed was followed by GLC at suitable time intervals. The final amount of $PhP(O)(OEt)_2$ formed and the time required to complete the reaction are listed in Table I. In all cases, the yields of $PhP(O)(OEt)_2$ were much more than 20% based on the reactant, $PhC(O)P(O)(OEt)_2$, indicating that these palladium complexes serve as catalysts for the decarbonylation reaction (eq 2).



(2)

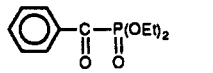
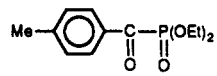
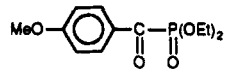
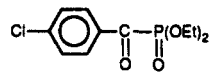
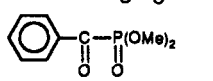
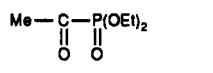
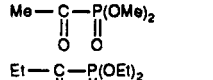
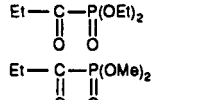
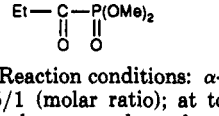
In the absence of a palladium complex, $PhC(O)P(O)(OEt)_2$ did not change to $PhP(O)(OEt)_2$ at all under toluene reflux conditions (eq 3), proving that the decarbonylation is catalyzed by the palladium complexes.



(3)

Next we examined the decarbonylation of various α-ketophosphonates by using **5** as a catalyst, which is one of the most effective complexes among the palladium complexes examined in this work. The time required to complete the reaction and the yield of phosphonates formed are listed in Table II. The results prove that aroylphosphonates and acetylphosphonates undergo catalytic decarbonylation and that aroylphosphonates are more readily decarbonylated than acetylphosphonates (a shorter time of reaction and a higher yield were obtained for the former). In contrast, propionylphosphonates are converted into ethylphosphonates in less than 10% yield; the reaction is not catalytic in this case. The reason will be mentioned later.

Table II. Decarbonylation of Various α-Ketophosphonates Catalyzed by *cis*-$PdMe_2(PMePh_2)_2$ (5)[a]

α-ketophosphonate	reactn time, h[b]	yield of phosphonate, %[c]
	0.2	100
	0.2	100
	1.0	72
	3.0	35
	0.2	76
	72	55
	76	43
	95	9
	96	5

[a] Reaction conditions: α-ketophosphonate/*cis*-$PdMe_2(PMePh_2)_2$ = 5/1 (molar ratio); at toluene reflux temperature. [b] Time required to complete the reaction; confirmed by following the amount of α-ketophosphonate and phosphonate by GLC. [c] Based on α-ketophosphonate.

The decarbonylation of α-ketophosphonates catalyzed by a transition metal involves C(O)–P bond activation. Decarbonylation is known for aldehydes, acyl halides,[9] acyl cyanides,[10] and thiol esters,[11] which involve C(O)–H, C(O)–halogen, C(O)–CN, and C(O)–S bond cleavage, respectively. Decarbonylation via C(O)–P bond fission has not, however, been reported so far even in stoichiometric reactions. The results reported here represent the first such examples.

Catalytic Cycle of Decarbonylation of α-Ketophosphonates. The palladium complexes listed in Table I which show catalytic activity for the decarbonylation of α-ketophosphonates are considered to serve as catalyst precursors. All of them can readily form the 14-electron

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Table III. Decarbonylation of $PhC(O)P(O)(OEt)_2$ Catalyzed by *cis*-$PdMe_2(PMePh_2)_2$ in the Absence and in the Presence of 5 Equiv of $PMePh_2$[a]

	yield of $PhP(O)(OEt)_2$, %[b]	
reactn time, h	without $PMePh_2$	with $PMePh_2$
0.2	100	15
5	100	64
72	100	65

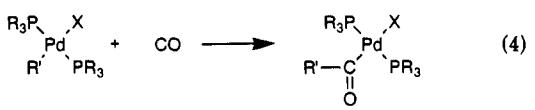
[a] Reaction conditions: $PhC(O)P(O)(OEt)_2$/*cis*-$PdMe_2(PMePh_2)_2$ = 5/1; at toluene reflux temperature. [b] Based on $PhC(O)P(O)(OEt)_2$.

Pd(0) species "PdL_2" (L = tertiary phosphine) by equilibrium in solution (for **1**) or on heating (for **3–7**). Complex **2** is a "PdL_2" form by itself. In contrast, $Pd(acac)_2$, $PdCl_2(NCPh)_2$, 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. Complexes **4–6**, yielding the same "$Pd(PMePh_2)_2$" species, showed identical, and relatively high, activities. Complexes **3** and **7**, yielding different "PdL_2" species, i.e., $Pd(PMe_2Ph)_2$ and Pd(dppe), respectively, showed relatively low activity. Complex **1** required a long time (48 h) to drive the reaction to completion and resulted in a 52% conversion yield, which may be due to the low concentration of the catalytically active species "$Pd(PPh_3)_2$" being in equilibrium with $Pd(PPh_3)_4$ and $Pd(PPh_3)_3$. Complex **2**, having sterically bulky ligands, exhibited a relatively low catalytic activity. These results indicate that the 14-electron Pd(0) species "PdL_2" is one of the members constituting the catalytic cycle.

In order to obtain additional support, the reaction of **5** with 5 equiv of $PhC(O)P(O)(OEt)_2$ was carried out in the presence of 5 equiv of $PMePh_2$. The results are shown in Table III, together with the results in the absence of $PMePh_2$. The presence of tertiary phosphine ligands in the system decreases the catalytic activity appreciably, consistent with the assumption that coordinatively unsaturated "PdL_2" is the catalytic species.

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 subsequent reductive elimination to give the aryl-(or alkyl-)phosphonate with regeneration of a "PdL_2" species.

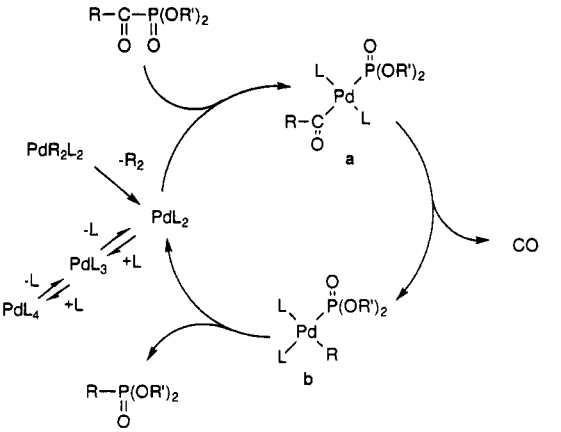
As shown in Table II, the decarbonylation takes a longer time to complete for acylphosphonates than for aroylphosphonates. Although decarbonylation rates of acyl–palladium complexes and aroyl–palladium complexes have not been compared directly, the carbonylation rates of a variety of palladium complexes of the type $Pd(X)(R')(PR_3)_2$ (eq 4) have been reported.[13] Generally, electron-



(4)

withdrawing groups attached directly to the palladium (an R′ group in eq 4) decrease the reaction rate and electron-supplying groups increase it. The alkyl complexes are considerably more reactive than the aryl complexes. According to the results, the reaction from **a** to **b** in Scheme I, corresponding to the reverse reaction of eq 4, is expected to be more favorable for aroyl(phosphonato)palladium complexes than for the acyl(phosphonato)palladium complexes, which is consistent with our observations.

Scheme I



The considerably low yields of $EtP(O)(OR)_2$ (R = Et, Me) in the decarbonylation reaction of $EtC(O)P(O)(OR)_2$ (R = Et, Me) is also explained according to Scheme I. In these cases, **b** is an ethyl–phosphonato complex for which it is likely that β-hydrogen abstraction from the ethyl ligand precedes reductive elimination, causing the low yield of the reductive-elimination product, $EtP(O)(OR)_2$.

Isolation of $PdL_2\{C(O)R\}\{P(O)(OR')_2\}$. In order to elucidate the details of the catalytic cycle, we attempted to isolate a palladium complex as a catalytic intermediate. The conversion of **a** into **b** may occur by dissociation of one of the L ligands in **a** to give a 14e species, $PdL\{C(O)R\}\{P(O)(OR')_2\}$, R migration to the vacant site on the palladium to yield $PdL(CO)(R)\{P(O)(OR')_2\}$, and then L/CO replacement to form **b**. A bulky and less basic tertiary phosphine ligand is considered to favor dissociation of the ligand from **a**. Thus, we reasoned that use of a small and basic tertiary phosphine ligand such as PMe_3 would render the PMe_3-coordinated aroyl-(or acyl-) phosphonato complex stable enough to allow its isolation against the R migration followed by the reductive elimination of R and $P(O)(OR')_2$. This assumption led to the successful isolation of *trans*-aroyl(phosphonato)palladium complexes with PMe_3 ligands.

After the toluene solution containing *trans*-$PdEt_2(PMe_3)_2$ and $RC(O)P(O)(OR')_2$ (R = Ph, tol (tol stands for a *p*-tolyl group); R′ = Et, Me) was refluxed for only a few minutes, cooling the solution in a refrigerator yielded yellow crystals. The spectroscopic data are shown in Table IV.

The ^{31}P NMR spectra show two resonances mutually coupled with a J value of about 75 Hz; one is a doublet at about −18 ppm and the other is a triplet at about 89 ppm. The former resonance is due to PMe_3, and the latter is attributed to $P(O)(OR')_2$. ^{31}P NMR chemical shifts of transition-metal phosphonato complexes (L_nM–$P(O)(OR')_2$) depend on the kind of transition metals and the substituents on the phosphorus, but values for L_nM–$P(O)(OMe)_2$ have been observed between 75 and 126 ppm for various kinds of transition metals.[14] The values of the Pd complexes isolated here fall in this range.

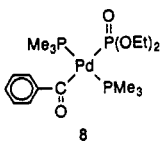
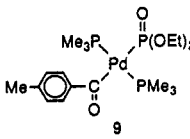
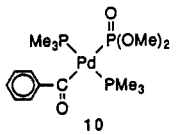
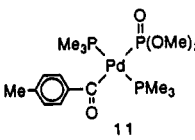
The methyl proton in the PMe_3 ligands was observed as a virtual triplet with P–H coupling (J = 3.9 Hz). In ^{13}C NMR spectra, the carbonyl carbon was observed as a doublet of triplets with coupling constants of 198 and 3 Hz at about 258 ppm.

In the IR spectra, strong absorptions at 1604–1620 cm^{-1} are assigned to ν_{CO} of the aroyl group coordinated to the palladium. The two ν_{CO} bands for **8**, **10**, and **11** are presumably due to Fermi resonance.

(13) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

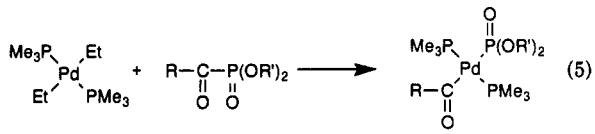
(14) Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577.

Table IV. Spectroscopic Data

complex	IR (ν_{CO}), cm^{-1} [a]	^1H NMR, ppm[b]	^{13}C NMR, ppm[b]	^{31}P NMR, ppm[c]
 8	1619 1604	8.16 (d, J = 7.32 Hz, 2 H, C_6H_5) 7.16 (m, 3 H, C_6H_5) 4.33 (dquin, J = 9.77, 7.32 Hz, 2 H, OCH_2) 4.10 (dquin, J = 10.25, 6.83 Hz, 2 H, OCH_2) 1.28 (t, J = 6.84 Hz, 6 H, OCH_2CH_3) 1.13 (t, J = 3.91 Hz, 18 H, PCH_3)	258.35 (d, J = 193.7 Hz, CO) 145.44 (dt, J = 52.8, 8.8 Hz, ϵC_6H_5) 131.57 (s, p C_6H_5) 128.89 (s, o C_6H_5) 128.59 (s, m C_6H_5) 56.26 (d, J = 8.8 Hz, OCH_2CH_3) 17.67 (s, OCH_2CH_3) 15.68 (dt, J = 14.7, 5.9 Hz, PCH_3)	−18.74 (d, J_{PP} = 74.2 Hz, PMe_3) 88.18 (t, J_{PP} = 74.2 Hz, $P(O)(OEt)_2$)
 9	1604	8.10 (d, J = 7.81 Hz, 2 H, C_6H_4Me) 7.00 (d, J = 7.32 Hz, 2 H, C_6H_4Me) 4.34 (dquin, J = 10.25, 7.57 Hz, 2 H, OCH_2) 4.12 (dquin, J = 10.26, 7.08 Hz, 2 H, OCH_2) 2.04 (s, 3 H, $C_6H_4CH_3$) 1.29 (t, J = 7.08 Hz, 6 H, OCH_2CH_3) 1.17 (t, J = 3.91 Hz, 18 H, PCH_3)	257.33 (d, J = 196.6 Hz, CO) 143.67 (dt, J = 52.9, 10.3 Hz, ϵ C_6H_4Me) 141.81 (s, p C_6H_4Me) 129.54 (s, o C_6H_4Me) 128.76 (s, m C_6H_4Me) 56.14 (d, J = 5.8 Hz, OCH_2CH_3) 21.34 (s, $C_6H_4CH_3$) 17.71 (s, OCH_2CH_3) 15.72 (dt, J = 14.7, 5.8 Hz, PCH_3)	−18.68 (d, J_{PP} = 75.7 Hz, PMe_3) 88.98 (t, J_{PP} = 75.7 Hz, $P(O)(OEt)_2$)
 10	1620 1605	8.14 (d, J = 7.81 Hz, 2 H, C_6H_5) 7.16 (m, 3 H, C_6H_5) 3.70 (d, J = 10.26 Hz, 6 H, OCH_3) 1.11 (t, J = 3.66 Hz, 18 H, PCH_3)	257.72 (d, J = 196.3 Hz, CO) 145.30 (dt, J = 53.8, 8.1 Hz, ϵ C_6H_5) 131.60 (s, p C_6H_5) 128.91 (s, o C_6H_5) 128.52 (s, m C_6H_5) 47.63 (d, J = 8.1 Hz, OCH_3) 15.59 (t, J = 13.4 Hz, PCH_3)	−18.35 (d, J_{PP} = 75.7 Hz, PMe_3) 89.22 (t, J_{PP} = 75.7 Hz, $P(O)(OMe)_2$)
 11	1619 1605	8.10 (d, J = 7.81 Hz, 2 H, C_6H_4Me) 6.99 (d, J = 7.81 Hz, 2 H, C_6H_4Me) 3.72 (d, J = 10.25 Hz, 6 H, OCH_3) 2.03 (s, 3 H, $C_6H_4CH_3$) 1.13 (t, J = 3.91 Hz, 18 H, PCH_3)	256.56 (d, J = 196.6 Hz, CO) 143.59 (dt, J = 53.8, 10.7 Hz, ϵ C_6H_4Me) 141.90 (s, p C_6H_4Me) 129.59 (s, o C_6H_4Me) 128.76 (s, m C_6H_4Me) 47.67 (d, J = 8.8 Hz, OCH_3) 21.34 (s, $C_6H_4CH_3$) 15.72 (t, J = 14.7 Hz, PCH_3)	−18.39 (d, J_{PP} = 76.9 Hz, PCH_3) 90.73 (t, J_{PP} = 76.9 Hz, $P(O)(OMe)_2$)

[a] In C_6H_6. [b] In C_6D_6. [c] In $C_6H_5CH_3$.

These observations confirmed the formation of *trans*-$Pd(PMe_3)_2\{C(O)R\}\{P(O)(OR')_2\}$ (eq 5), which corresponds to the complex formed by the oxidative addition of $RC(O)P(O)(OR')_2$ at the C–P bond to a "$Pd(PMe_3)_2$" species.

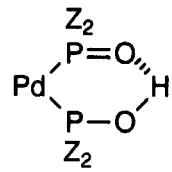


(5)

R =	R' =		yield = 69 %
Ph	Et	8	
tol	Et	9	82
Ph	Me	10	79
tol	Me	11	71

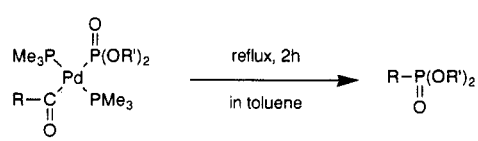
The isolated complexes are fairly stable in the solid state and in organic solvents. No reaction takes place when these complexes are allowed to stand in benzene at room temperature for a few days.

Some Pd–$P(O)Z_2$ (Z = R, OR) type complexes have already been reported, but all of them have an additional $P(OH)Z_2$ ligand cis to the $P(O)Z_2$ ligand, and an intramolecular hydrogen bond as shown is formed between the two ligands:[6h,15]



Our complexes are, to our knowledge, the first Pd–$P(O)Z_2$-type example without such a hydrogen bond at the phosphoryl oxygen.

Catalytic Properties of $Pd(PMe_3)_2\{C(O)R\}\{P(O)(OR')_2\}$ toward Decarbonylation of $RC(O)P(O)(OR')_2$. In order to check whether the isolated complexes are one of the complexes constituting the catalytic cycle, the thermal reaction of these isolated complexes was examined in the absence and presence of the corresponding α-ketophosphonate. Reflux for 2 h of a toluene solution of the aroyl(phosphonato)palladium complex gave the corresponding phosphonate in an almost quantitative yield, as confirmed by GLC and ^{31}P NMR spectroscopy (eq 6).

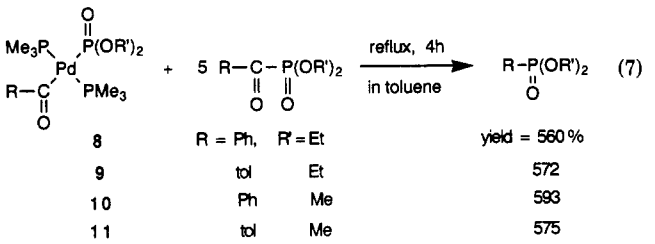


(6)

8	R = Ph,	R' = Et	yield = 94 %
9	tol	Et	100 %
10	Ph	Me	100 %
11	tol	Me	98 %

(15) (a) Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* **1970**, 2080. (b) Dixon, K. R.; Rattray, A. D. *Can. J. Chem.* **1971**, *49*, 3997. (c) Cornock, M. C.; Gould, R. O.; Jones, C. L.; Stephenson, T. A. *J. Chem. Soc. A* **1977**, 1307. (d) Nifant'ev, E. E.; Kukhareva, T. S.; Antipin, M. Y.; Struchkov, Y. T.; Klabunovsky, E. I. *Tetrahedron* **1983**, *39*, 797.

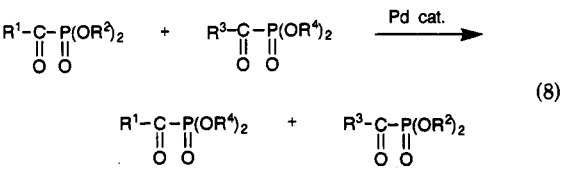
Treatment of these complexes with 5 equiv of the corresponding α-ketophosphonate in toluene at reflux temperature for 4 h yielded the corresponding phosphonate in 560–600% yield based on the Pd complex, as confirmed by GLC and ^{31}P NMR spectroscopy (eq 7).



(7)

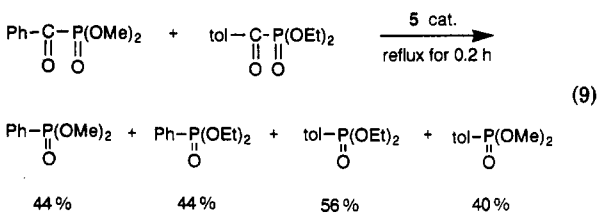
The results clearly show that the isolated aroyl(phosphonato)palladium complexes have catalytic activity toward decarbonylation of α-ketophosphonates.

Metathesis Reactions between α-Ketophosphonates at a C-P Bond Catalyzed by a Palladium Complex. It has been shown in this work that α-ketophosphonates undergo decarbonylation catalyzed by a palladium complex, and the catalytic cycle involves aroyl (or acyl) carbon–phosphorus bond cleavage and also aryl (or alkyl) carbon–phosphorus bond formation. During the course of this study, we have also found that a palladium complex catalyzes an α-ketophosphonate metathesis reaction, generally expressed by eq 8, prior to the observed decarbonylation.



(8)

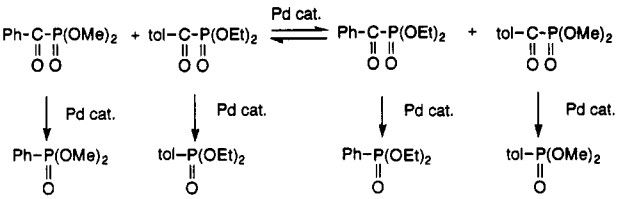
A toluene solution containing equimolar amounts of $PhC(O)P(O)(OMe)_2$ and $tolC(O)P(O)(OEt)_2$ and 20 mol % of **5** based on $PhC(O)P(O)(OMe)_2$ was refluxed for 0.2 h, and the products were identified by GLC and ^{31}P NMR measurements. Four kinds of phosphonates were detected in almost equal yields. (See eq 9. The percentage expresses the percent yield of the phosphonates. If the two kinds of α-ketophosphonates are completely converted into the four kinds of phosphonates with equal distribution, the expression should be 50%:50%:50%:50%.)



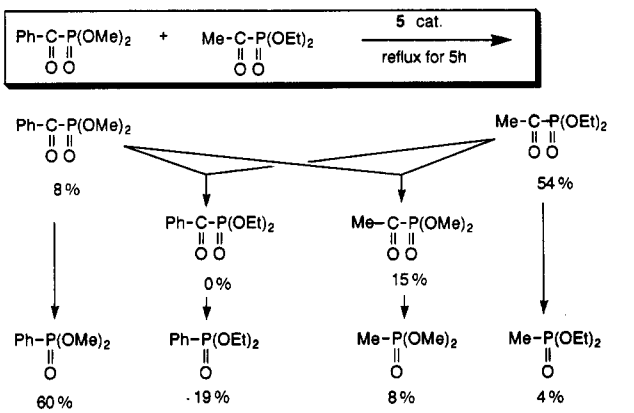
(9)

$PhP(O)(OEt)_2$ and $tolP(O)(OMe)_2$ should not be formed by simple decarbonylation of the respective α-ketophosphonates used in eq 9. One possible route to form them is the recombination of $PhP(O)(OMe)_2$ and $tolP(O)(OEt)_2$ formed by simple decarbonylation of the respective α-ketophosphonates. Thus, we examined the reaction of $PhP(O)(OMe)_2$ and $tolP(O)(OEt)_2$ prepared separately under 5-h toluene reflux conditions in the presence of the Pd catalyst and found that no reaction takes place (eq 10); in other words, 100% of $PhP(O)(OMe)_2$ and $tolP(O)(OEt)_2$ were recovered. The results indicate

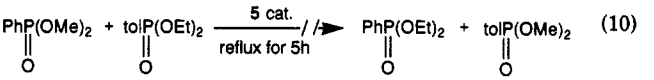
Scheme II



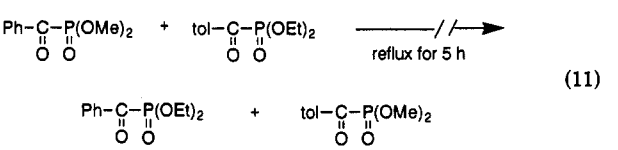
Scheme III



that a metathesis process between phosphonates at the C-P bond can be ruled out. We also examined the reaction



(10)

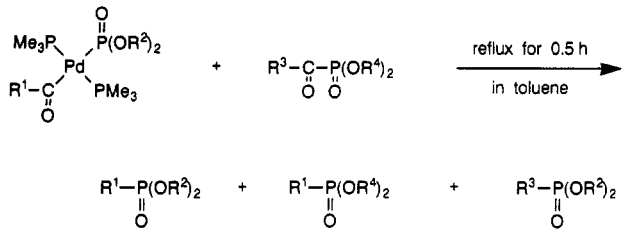


(11)

of $PhC(O)P(O)(OMe)_2$ with $tolC(O)P(O)(OEt)_2$ in the absence of a palladium complex and found that no reaction takes place (eq 11). Therefore, the plausible mechanism to explain the result of eq 9 is the scrambling of α-ketophosphonates at the C-P bond catalyzed by the palladium complex followed by decarbonylation (Scheme II), though the metathesized α-ketophosphonates $PhC(O)P(O)(OEt)_2$ and $tolC(O)P(O)(OMe)_2$ were not detected because they had been completely converted into the corresponding phosphonates under our present experimental conditions.

The treatment of the mixture of equimolar amounts of $PhC(O)P(O)(OMe)_2$ and $MeC(O)P(O)(OEt)_2$ with 20 mol % of **5** was attempted in toluene. After a 5-h reflux, the components in the solution were examined by GLC and ^{31}P NMR measurements (Scheme III). The amount of phenylphosphonates formed is greater than that of methylphosphonates, and the amount of benzoylphosphonate unreacted is smaller than that of acetylphosphonate unreacted; these findings are consistent with a greater decarbonylation rate for aroylphosphonates than for acylphosphonates (vide supra). It was noteworthy in this experiment that $MeC(O)P(O)(OMe)_2$ formed from $PhC(O)P(O)(OMe)_2$ and $MeC(O)P(O)(OEt)_2$ by the metathesis reaction was detected. The other metathesized product, $PhC(O)P(O)(OEt)_2$, was not detected presumably due to fast decarbonylation to give $PhP(O)(OEt)_2$. The amount of $PhP(O)(OEt)_2$ (19%) is close to the sum of those of $MeC(O)P(O)(OMe)_2$ (15%) and $MeP(O)(OMe)_2$ (8%), indicating that $PhC(O)P(O)(OMe)_2$ and $MeC(O)P(O)(OEt)_2$ undergo scrambling promoted by a palladium complex to give $PhC(O)P(O)(OEt)_2$ and $MeC(O)P(O)(OMe)_2$, but the

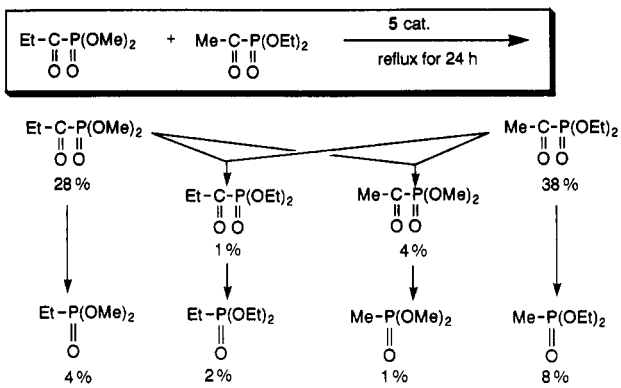
Table V. Product Distribution in the Reaction



				yield, %[a]			
R^1	OR^2	R^3	OR^4	$R^1P(O)(OR^2)_2$	$R^1P(O)(OR^4)_2$	$R^3P(O)(OR^2)_2$	$R^3P(O)(OR^4)_2$
Ph	OEt	tol	OMe	56	44	40	50
tol	OEt	Ph	OMe	60	40	26	53
Ph	OMe	tol	OEt	65	15	35	48
tol	OMe	Ph	OEt	70	28	30	25

[a] The yield is based on the palladium complex.

Scheme IV



latter is so much less reactive toward decarbonylation that it remains partially unreacted.

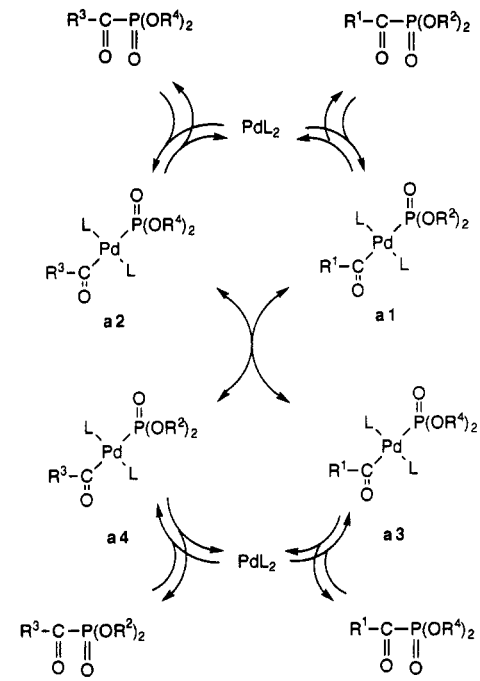
A crossover experiment was also performed involving equimolar amounts of two kinds of acylphosphonates and 20 mol % of **5**. The result in the case of the mixture of $EtC(O)P(O)(OMe)_2$ and $MeC(O)P(O)(OEt)_2$ after 24-h reflux in toluene is shown in Scheme IV.

In this case, all phosphorus-containing products predicted from the metathesis and decarbonylation reactions were detected, though these amounts were low compared with those of the starting α-ketophosphonates. Thus, it is reasonable to suppose that $EtP(O)(OEt)_2$ and $MeP(O)(OMe)_2$ are derived from $EtC(O)P(O)(OEt)_2$ and $MeC(O)P(O)(OMe)_2$, respectively, which are generated by the metathesis reaction between $EtC(O)P(O)(OMe)_2$ and $MeC(O)P(O)(OEt)_2$.

Reaction of $Pd(PMe_3)_2\{C(O)R^1\}\{P(O)(OR^2)_2\}$ with $R^3C(O)P(O)(OR^4)_2$. In order to obtain more detailed information about the α-ketophosphonate metathesis reaction, the reactions of the isolated aroyl(phosphonato)palladium complex $Pd(PMe_3)_2\{C(O)R^1\}\{P(O)(OR^2)_2\}$ with $R^3C(O)P(O)(OR^4)_2$ were examined. A toluene solution containing equimolar amounts of $Pd(PMe_3)_2\{C(O)R^1\}\{P(O)(OR^2)_2\}$ and $R^3C(O)P(O)(OR^4)_2$ was refluxed for 0.5 h, and the product distribution was examined. The results are shown in Table V. In all four cases, the four expected phosphonates were observed in almost equal amounts. The results show that $Pd(PMe_3)_2\{C(O)R^1\}\{P(O)(OR^2)_2\}$ serves as a catalyst for the α-ketophosphonate metathesis reaction and the random scrambling at a C–P bond of α-ketophosphonates goes essentially to completion prior to the effective decarbonylation of α-ketophosphonates.

Two mechanisms are conceivable to explain the results shown in Table V. One is shown in Scheme V. There is

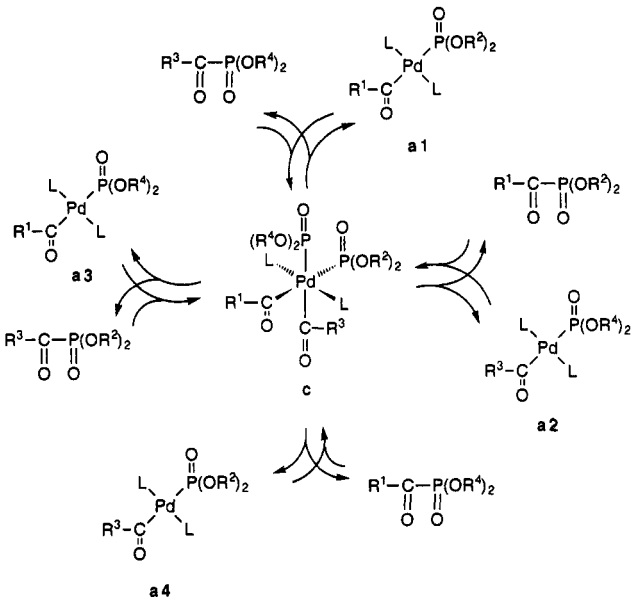
Scheme V



an equilibrium between *trans*-$Pd(PMe_3)_2\{C(O)R^1\}\{P(O)(OR^2)_2\}$ (**a1**) and $PdL_2 + R^1C(O)P(O)(OR^2)_2$ in favor of the former. $R^3C(O)P(O)(OR^4)_2$ oxidatively adds to PdL_2 to give *trans*-$Pd(PMe_3)_2\{C(O)R^3\}\{P(O)(OR^4)_2\}$ (**a2**). Aroyl ligand exchange or phosphonato ligand exchange takes place readily between complexes **a1** and **a2** to give **a3** and **a4**. Both of them are also in equilibrium with $R^1C(O)P(O)(OR^4)_2$ and $R^3C(O)P(O)(OR^2)_2$. The four complexes thus formed, **a1**, **a2**, **a3**, and **a4**, then undergo decarbonylation, followed by reductive elimination according to the cycle shown in Scheme I to give four kinds of phosphonates. If we suppose that the equilibrium and the ligand exchange are achieved faster than the decarbonylation, the amounts of **a1**–**a4** are almost equally distributed, leading to four kinds of phosphonates in almost equal yields.

The alternative mechanism is shown in Scheme VI. $R^3C(O)P(O)(OR^4)_2$ undergoes oxidative addition toward **a1** at a C–P bond to give the Pd(IV) complex **c**. The configuration around the Pd metal is not clear, but the configuration formed by the trans addition is tentatively depicted here. Reductive elimination of an aroyl group and a phosphonato group from **c** leads to four kinds of aroyl(phosphonato)palladium complexes (**a1**, **a2**, **a3**, and

Scheme VI



a4) and four kinds of α-ketophosphonates. If we suppose that the formation of phosphonates from **a1**–**a4** according to the catalytic cycle shown in Scheme I is slower than the formation of four kinds of α-ketophosphonates from **a1** and $R^3C(O)P(O)(OR^4)_2$, almost equimolar amounts of four kinds of phosphonates should be expected.

Several examples of oxidative-addition–reductive-elimination reactions that involve Pd(IV) complexes have been documented. The reactions of organopalladium diamine complexes with alkyl halides have been successful in the isolation of Pd(IV) complexes.[16] In contrast, organopalladium(IV) phosphine complexes have not yet been observed, though such Pd(IV) complexes are proposed as intermediates in several reactions.[17]

No $R^1C(O)C(O)R^3$, $R^1C(O)R^3$, R^1–R^3, or $(R^2O)_2P(O)P(O)(OR^4)_2$ was detected in our reactions. The result, however, does not rule out the mechanism shown in Scheme VI if an aroyl group and a phosphonato group on **c** undergo selective reductive elimination.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk-tube techniques. Toluene and hexane were distilled from sodium metal and stored under a nitrogen atmosphere. Palladium complexes used here, $Pd(acac)_2$,[18] $PdCl_2(PPh_3)_2$,[19] $PdCl_2(NCPh)_2$,[20] $Pd(PPh_3)_4$,[21] $Pd(PCy_3)_2$,[22] $PdMe_2(dppe)$,[23] *trans*-$PdEt_2(PMePh_2)_2$,[12] *cis*-$PdMe_2(PMePh_2)_2$,[12] *trans*-$PdMe_2(PMe_2Ph)_2$,[24] *trans*-$PdEt_2(PMe_3)_2$,[25] and Pd(styrene)$(PMePh_2)_2$,[26] were prepared according to the literature methods. α-Ketophosphonates were prepared from the corresponding acid chlorides and trialkyl phosphites by the Arbuzov reaction according to the literature methods.[27] Phosphonates as authentic samples were synthesized by published procedures.[28]

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60, FX-100, GSX-270, and GSX-500 instruments were used to obtain ^1H, ^{13}C, and ^{31}P NMR spectra. ^1H and ^{13}C NMR data were referenced to $(CH_3)_4Si$, and ^{31}P NMR data were referenced to 85% H_3PO_4.

Preparation of *trans*-Pd$(PMe_3)_2${C(O)Ph}{P(O)$(OEt)_2$} (8). $PhC(O)P(O)(OEt)_2$ (0.20 mL, 242 mg, 1.00 mmol) was added to a solution of *trans*-$PdEt_2(PMe_3)_2$ (157 mg, 0.50 mmol) in 2 mL of toluene. After the solution was refluxed until the color changed from yellow to reddish purple (about 5 min), hexane (20 mL) was added, and the solution was put in a refrigerator for several hours. The resulting yellow crystals were collected by filtration, washed with hexane, and dried in vacuo to give **8** (173 mg, 0.35 mmol, 69%). Anal. Calcd for $C_{17}H_{33}O_4P_3Pd$: C, 40.77; H, 6.64. Found: C, 40.52; H, 6.60.

Preparation of *trans*-Pd$(PMe_3)_2${C(O)tol}{P(O)$(OEt)_2$} (9). $tolC(O)P(O)(OEt)_2$ (0.19 mL, 212 mg, 0.83 mmol) was added to a solution of *trans*-$PdEt_2(PMe_3)_2$ (128 mg, 0.40 mmol) in 2 mL of toluene. Procedures similar to those for **8** were applied to obtain **9** as yellow crystals (170 mg, 0.33 mmol, 82%). Anal. Calcd for $C_{18}H_{35}O_4P_3Pd$: C, 42.00; H, 6.85. Found: C, 41.85; H, 6.73.

Preparation of *trans*-Pd$(PMe_3)_2${C(O)Ph}{P(O)$(OMe)_2$} (10). $PhC(O)P(O)(OMe)_2$ (0.18 mL, 240 mg, 1.12 mmol) was added to a solution of *trans*-$PdEt_2(PMe_3)_2$ (178 mg, 0.56 mmol) in 2 mL of toluene. Procedures similar to those for **8** were applied to obtain **10** as yellow crystals (209 mg, 0.44 mmol, 79%). Anal. Calcd for $C_{15}H_{29}O_4P_3Pd$: C, 38.11; H, 6.18. Found: C, 38.22; H, 6.15.

Preparation of *trans*-Pd$(PMe_3)_2${C(O)tol}{P(O)$(OMe)_2$} (11). $tolC(O)P(O)(OMe)_2$ (0.27 mL, 332 mg, 1.46 mmol) was added to a solution of *trans*-$PdEt_2(PMe_3)_2$ (229 mg, 0.72 mmol) in 2 mL of toluene. Procedures similar to those for **8** were applied to obtain **11** as yellow crystals (248 mg, 0.51 mmol, 71%). Anal. Calcd for $C_{16}H_{31}O_4P_3Pd$: C, 39.48; H, 6.42. Found: C, 39.29; H, 6.38.

Thermolysis of *trans*-Pd$(PMe_3)_2${C(O)R}{P(O)$(OR')_2$}. The thermolysis was carried out in an identical manner for the four aroyl(phosphonato)palladium complexes isolated here. The details are described here for *trans*-$Pd(PMe_3)_2${C(O)Ph}{P(O)$(OEt)_2$} (**8**). A solution of **8** (27 mg, 0.053 mmol) and CH_2Ph_2 (8.9 μL, 9.0 mg, 0.053 mmol) used as the internal standard for GLC analysis in 2 mL of toluene was refluxed for 1.5 h. Then, the resulting solution was subjected to GLC analysis to determine the amount of $PhP(O)(OEt)_2$ formed.

Reaction of *trans*-Pd$(PMe_3)_2${C(O)R}{P(O)$(OR')_2$} with $RC(O)P(O)(OR')_2$. In a typical procedure, $PhC(O)P(O)(OEt)_2$ (61 μL, 74 mg, 0.305 mmol) and CH_2Ph_2 (25 μL, 25 mg, 0.151 mmol) were added to a solution of *trans*-$Pd(PMe_3)_2${C(O)Ph}{P(O)$(OEt)_2$} (**8**) (31 mg, 0.061 mmol). After being refluxed for 6 h, the solution was subjected to GLC analysis to determine the amount of $PhP(O)(OEt)_2$ formed.

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Registry No. 1, 14221-01-3; 2, 33309-88-5; 3, 82916-00-5; 4, 75172-21-3; 5, 60885-30-5; 6, 70316-76-6; 7, 63455-39-0; 8, 138695-22-4; 9, 138695-23-5; 10, 138695-24-6; 11, 138695-25-7; $PhC(O)P(O)(OEt)_2$, 3277-27-8; $tolC(O)P(O)(OEt)_2$, 2942-54-3; MeC_6H_4-*p*-$C(O)P(O)(OEt)_2$, 16703-95-0; ClC_6H_4-*p*-$C(O)P(O)(OEt)_2$, 10570-46-4; $PhC(O)P(O)(OMe)_2$, 18106-71-3; $MeC(O)P(O)(OEt)_2$, 919-19-7; $MeC(O)P(O)(OMe)_2$, 17674-28-1; $EtC(O)P(O)(OEt)_2$, 1523-68-8; $EtC(O)P(O)(OMe)_2$, 51463-65-1; $PhP(O)(OEt)_2$, 1754-49-0; $tolP(O)(OEt)_2$, 1754-46-7; $MeOC_6H_4$-*p*-$P(O)(OEt)_2$, 3762-33-2; ClC_6H_4-*p*-$P(O)(OEt)_2$, 2373-43-5; $PhP(O)(OMe)_2$, 2240-41-7; $MeP(O)(OEt)_2$, 683-08-9; $MeP(O)(OMe)_2$, 756-79-6; $EtP(O)(OEt)_2$, 78-38-6; $EtP(O)(OMe)_2$, 6163-75-3; $tolC(O)P(O)(OMe)_2$, 33493-30-0; $tolP(O)(OMe)_2$, 6840-25-1; *trans*-$PdEt_2(PMe_3)_2$, 124717-55-1.

Notes

Double Insertion of Methylene into Nickel–Phosphorus Bonds: Synthesis and Structure of $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$

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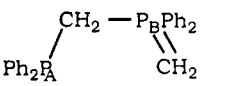
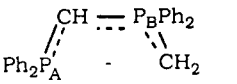
Summary: The new nickel phosphorus ylide complex, $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$ (**1**) has been prepared by the reaction of $Ni(COD)_2$, dppm (bis(diphenylphosphino)-methane), and CH_2Br_2. The complex crystallizes from DMSO as **1**·2DSMO: triclinic space group $P\bar{1}$, a = 9.972 (2) Å, b = 12.061 (2) Å, c = 12.675 (2) Å, α = 114.19 (1)°, β = 100.71 (1)°, γ = 91.45 (1)°, V = 1357.6 Å^3 (Z = 1). Complex **1** can be reversibly deprotonated by 2 equiv of $NaNH_2$ to afford $Ni(CH_2PPh_2CHPPh_2)_2$ (**2**) and reprotonated by HBr.

Nickel complexes with chelating phosphorus ylide ligands are of considerable interest as catalysts for olefin homologation and polymerization.[1] A nickel ylide complex reported by Keim and co-workers[2] is a highly active catalyst for the Shell higher olefins process (SHOP).[3] A variety of different synthetic routes to modified chelating phosphorus ylide nickel catalysts have been described.[4-8] We now report a remarkably straightforward preparation of a new nickel ylide complex $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$ (**1**). Complex **1** can be reversibly deprotonated to afford the neutral product $Ni(CH_2PPh_2CHPPh_2)_2$ (**2**), which was prepared earlier via a different procedure by Schmidbaur.[4] Results of an X-ray crystallographic study of **1** provide the opportunity to compare the characteristics of (methylenediphenylphosphino)(diphenylphosphino)methane (A) and its deprotonated ylide anion (B) as chelating ligands to the same metal.

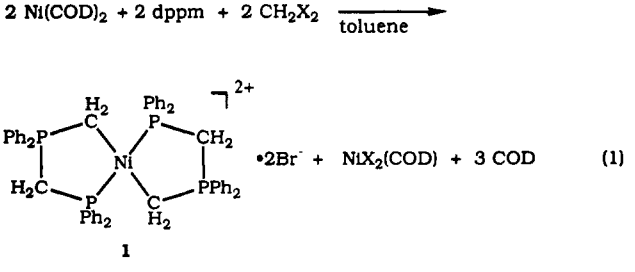


(A)



(B)

The complex $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$ (**1**) was prepared by addition of 2 equiv of dppm (bis(diphenylphosphino)methane) to 1 equiv $Ni(COD)_2$[9,10] (COD = 1,5-cyclooctadiene) at −20 °C in toluene, followed by addition of 2 equiv of CH_2Br_2. The yellow solid was filtered out, washed with diethyl ether, and dried under vacuum to obtain **1** in yields approaching the theoretical limit of 50% based on $Ni(COD)_2$ (1 equivalent of $Ni(COD)_2$ is oxidized by CH_2Br_2) (eq 1). The $^{31}P\{^1H\}$ NMR spectrum



(1)

(X = Br, I)

of **1** in DMSO-d_6 consists of two approximate triplets centered at 47.87 and 32.31 ppm with $J(AB) \approx J(AB')$ =

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