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INTRAMOLECULAR METALATION OF $PBu^t{}_2Ph$ AND $PBu^t{}_3$ IN PALLADIUM ACETATE COMPLEXES

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Summary

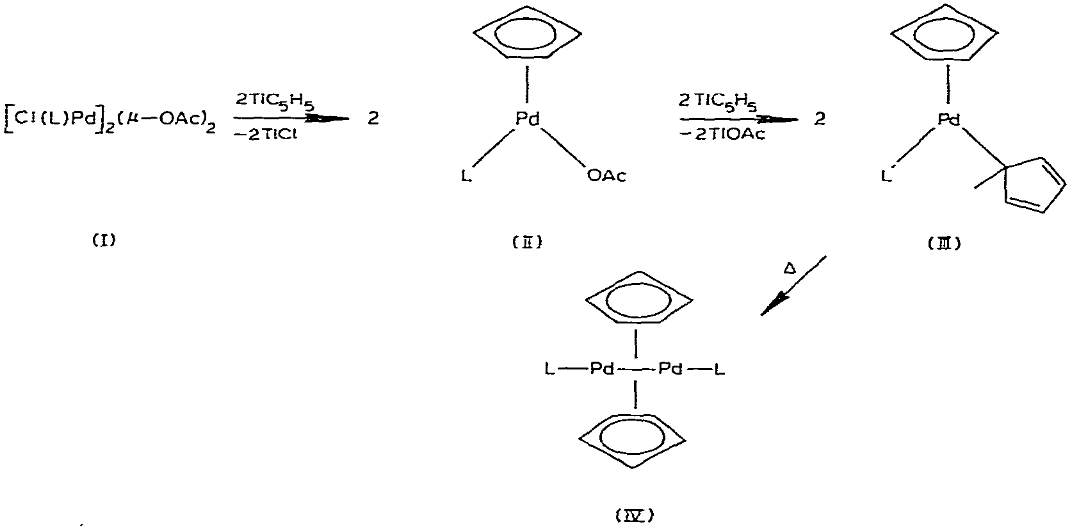
Reaction of $[PdCl_2(PBu^t{}_2Ph)]_2$ with silver acetate gives the internally metalated complex $[\overline{PdCH_2CMe_2P}Bu^tPh]_2(\mu\text{-}Cl)_2$. This reacts with TlC_5H_5 and LiC_5Me_5 with chloride-bridge cleavage to yield $C_5R_5\overline{PdCH_2P}Bu^tPh$ (R = H, Me). The complex $[\overline{PdCH_2CMe_2P}Bu^t{}_2]_2(\mu\text{-}Cl)_2$, prepared from $[PdCl_2(PBu^t{}_3)]_2$ and CH_3COOAg, is analogously converted into $C_5R_5\overline{PdCH_2CMe_2P}Bu^t{}_2$. The chloride complex $C_5H_5Pd(PBu^t{}_2Ph)Cl$ does not eliminate HCl to form $C_5H_5\text{-}\overline{PdCH_2CMe_2P}Bu^tPh$.

Introduction

We recently reported [1] that the reaction of $[Cl(L)Pd]_2(\mu\text{-}OAc)_2$ (I; L = PMe_3, $PPr^i{}_3$, PPh_3) with stoicheiometric amounts of thallium cyclopentadienide produces (via the intermediate II) the complexes $(\eta^5\text{-}C_5H_5)Pd(\eta^1\text{-}C_5H_5)L$ (III) which represent a new class of fluxional molecules. Whereas the bis(cyclopentadienyl)phosphine palladium complexes III are stable at —20° C in the solid state and in solution, at room temperature, in toluene, for example, they react slowly to give the dinuclear sandwiches $(C_5H_5)_2Pd_2L_2$ (IV) [2]. The rate of the intramolecular rearrangement of III and of the reaction of III to give IV sharply increases with the decreasing size of the phosphine ligand, the rate being much greater for L = PMe_3 than for L = $PPr^i{}_3$ [1].

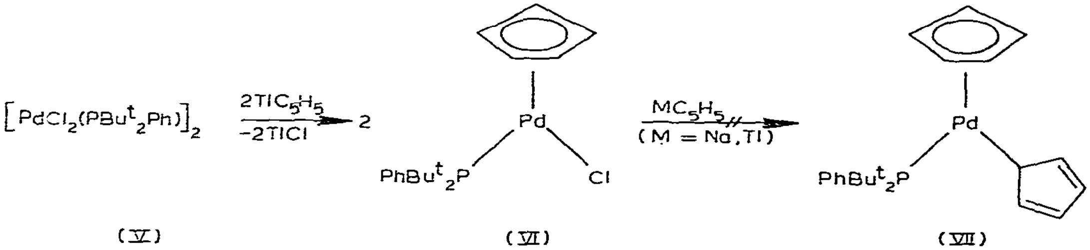
These observations prompted us to prepare palladium complexes of type III and IV with phosphines even more bulky than $PPr^i{}_3$, and in particular with PBu^t_2Ph. During these attempts we observed a very facile intramolecular metalation of this coordinated phosphine, leading to complexes with a four-membered $\overline{PdCCP}$ ring skeleton.

SCHEME 1



Results

The chloro-bridged complex V [3] reacts with TlC_5H_5 to yield $C_5H_5Pd(PBu^t_2Ph)Cl$ (VI). The properties of this green crystalline compound are very similar to those of other cyclopentadienylpalladium complexes of composition $C_5H_5Pd(PR_3)X$ [4]. Further treatment of VI with excess TlC_5H_5 does not lead to substitution of chloride by C_5H_5 to form VII, and this is consistent with the behavior of other $C_5H_5Pd(L)Cl$ complexes towards NaC_5H_5 and TlC_5H_5 [5].



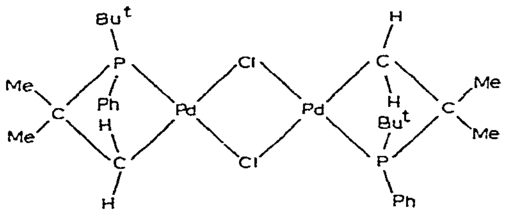
As a result of our experience with the synthesis of the above-mentioned compounds III, we expected that the more appropriate starting material for the preparation of $(\eta^5\text{-}C_5H_5)Pd(\eta^1\text{-}C_5H_5)PBu^t_2Ph$ (VII) would be the acetate complex $C_5H_5Pd(PBu^t_2Ph)OAc$. The proposed synthetic route to this complex was the same as shown in Scheme 1, i.e. reaction of V with AgOAc to give $[Cl(PBu^t_2Ph)Pd]_2(\mu\text{-}OAc)_2$, which on further treatment with TlC_5H_5 should yield $C_5H_5Pd(PBu^t_2Ph)OAc$.

The product of the reaction of V with silver acetate, however, is not complex VIII, but the dinuclear chloro-bridged compound IX, formed by elimination of acetic acid from the intermediate VIII.

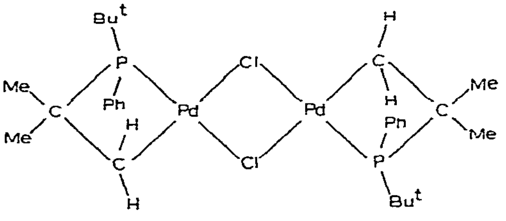
$$V \xrightarrow[-2\ AgCl]{2\ AgOAc} [Cl(PBu^t_2Ph)Pd]_2(\mu\text{-}OAc)_2 \xrightarrow{-2\ HOAc} [\overline{PdCH_2CMe_2P}Bu^tPh]_2(\mu\text{-}Cl)_2$$

(VIII) (IX)

Complex IX forms yellow crystals which are rather air-stable and soluble in most organic solvents. The presence of more than one isomeric form in solution is indicated by the ^{31}P NMR spectrum. This shows three signals, of which the two at lowest and highest field (see Table 1) presumably belong to the *trans* isomers, IX-syn and IX-anti. These signals are nearly of equal intensity. The third, less intense signal, may be tentatively assigned to one of the *cis* isomers.



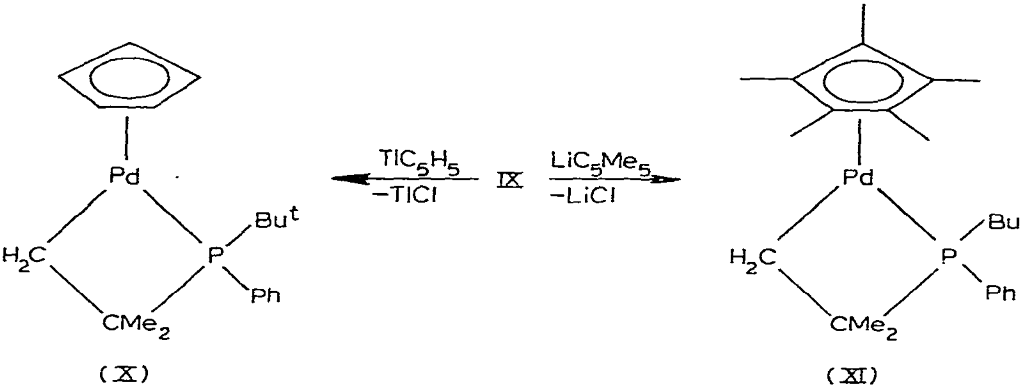
trans – IX – syn



trans – IX – anti

The most characteristic feature of the ^1H NMR spectrum of IX is the presence of two sets of doublets for the methyl protons of the $—CMe_2—$ units in the four-membered rings. The different environment of the two Me groups on the carbon is thus confirmed. The CH_2 protons of the ring also give rise to two signals, one of which is covered by the stronger peaks of the CMe_2 and Bu^t groups.

Reaction of IX with TlC_5H_5 in benzene occurs with chloride-bridge cleavage to give the cyclopentadienyl complex X. Analogously, treatment of IX with LiC_5Me_5 produces the pentamethylcyclopentadienyl complex XI.



Both compounds, X and XI, smoothly react with acetic acid, but not by attack at the $Pd—CH_2$ bond to form $C_5H_5Pd(PBu^t_2Ph)OAc$ (R = H, Me). Although the exact composition of the product has not yet been established, the NMR data indicate that the $\overline{PdCH_2CMe_2P}Bu^tPh$ ring remains intact during the acidolysis, and it is possible that a dinuclear complex containing acetate bridges is formed.

Attempts were made to synthesize the remarkably stable cyclopentadienyl complex X possessing a palladium—carbon σ-bond by an alternative route. Previous work done in our laboratory [6] has shown that the complex C_5H_5Pd-$[P(OC_6H_4\text{-}o\text{-}Me)_3]Cl$ reacts in CH_2Cl_2/pentane solution with Al_2O_3 (on passage

TABLE 1

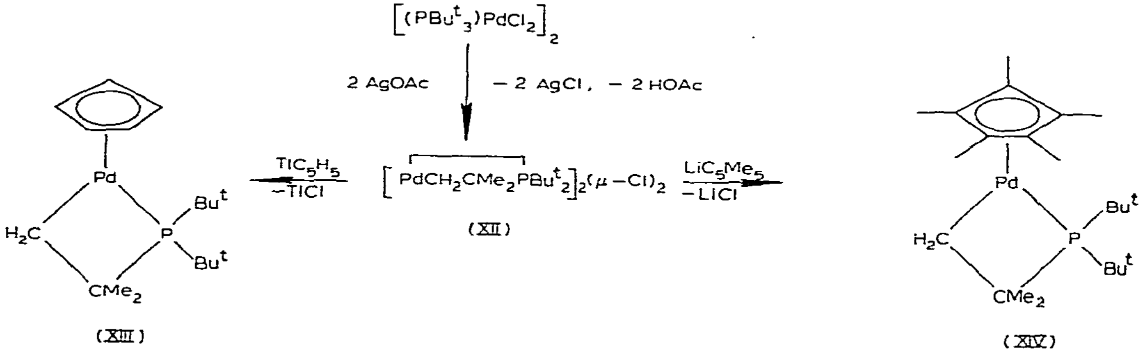
^{1}H AND ^{31}P NMR DATA OF $C_5H_5Pd(PBu^t{}_2Ph)Cl$(VI), $[PdCH_2CMe_2PBu^tPh]_2(\mu\text{-}Cl)_2$(IX), $C_5H_5PdCH_2CMe_2PBu^tR$(X, XIII) AND $C_5Me_5PdCH_2CMe_2PBu^tR$ (XI, XIV), IN C_6D_6 (δ in ppm; J in Hz, ^{1}H: int. TMS; ^{31}P: ext. 85% H_3PO_4)

Complex	^{1}H NMR									^{31}P NMR
	$\delta(C_5R_5)$	J(PH)	$\delta(Bu^t)$	J(PH)	$\delta(CMe_2)$	J(PH)	$\delta(CH_2)$	J(PH)	δ(Ph)	δ
VI	5.50d	2.5	1.37d	14.2					7.78m(2 H)	79.20
									7.12m(3 H)	
IX			1.57d(br)	15.8	1.55d	15.8	1.15d(br)	16.0	7.95m(2 H)	−31.29 [b]
					1.47d	15.8	[a]		7.36m(3 H)	−31.49
										−31.86
X	6.05d	2.1	1.55d	14.9	1.28d	14.9	1.73d	8.2	7.68m(2 H)	−5.92
					0.99d	14.9	1.68d	8.2	7.17m(3 H)	
XI	2.19d	2.5	1.10d	14.0	1.31d	13.5	0.92		7.79m(2 H)	−5.88
					0.97d	14.0	[a]		7.04m(3 H)	
XIII	5.89d	1.9	1.19d	13.0	1.21d	13.6	1.38d	5.8		10.87
XIV	2.18d	2.5	1.35d	12.5	1.42d	12.5	0.97d	7.5		10.58

[a] Signal is hidden by the doublets of the CMe_2 protons. [b] In $CDCl_3$; for explanation see text.

through a chromatographic column) to form the *ortho*-metalated compound $C_5H_5\overline{Pd[OC}_6H_3$-*o*-Me)($OC_6H_4$-*o*-Me)$_2$]. Under exactly the same conditions the analogous elimination of HCl does not occur with $C_5H_5Pd(PBu^tPh)Cl$ (VI). Complex VI is also recovered unchanged after reaction with $NaNH_2$ in THF or with $NaNH_2$ in presence of 15-crown-5. The formation of a five-membered ring (which takes place in the reaction of $C_5H_5Pd[P(OC_6H_4$-*o*-Me)$_3$]Cl) is obviously much more favored than the formation of a four-membered ring which would be involved in the reaction of VI.

The dinuclear metalated complex $[\overline{PdCH_2CMe_2P}Bu^t{}_2]_2(\mu\text{-}Cl)_2$ (XII), which was recently prepared by H.C. Clark et al. [7] from K_2PdCl_4 and tri-tert-butylphosphine in *N,N*-dimethylformamide or from $(PhCN)_2PdCl_2$ and PBu^t_3 in CH_2Cl_2, also reacts with TlC_5H_5 and LiC_5Me_5 to give the compounds XIII and XIV. We found that the method which we used for the synthesis of IX can also be successfully applied to obtain XII; the metalation is even more facile and the yield is quantitative.



The ^1H, ^{31}P and ^{13}C NMR data of XIII and XIV, together with those of complexes VI, IX, X and XI, are shown in Tables 1 and 2.

Discussion

In the past decade several examples of intramolecular metalation reactions of C—H bonds in coordinated phosphine and phosphite ligands have been reported. It has generally been observed that C—H bonds in aromatic rings are more easily substituted by transition metals than those in aliphatic groups. There is also some evidence that the rate of the metalation process is specifically influenced by the transition metal. Shaw and coworkers have found, for example, that platinum complexes of composition *trans*-$[PtX_2L_2]$ where X = Cl, Br, I and L = $PBu^t{}_2R$ or PBu^tR_2 (R = phenyl, *p*-tolyl etc.) are easily metalated, whereas under the same conditions the corresponding palladium complexes *trans*-$[PdX_2L_2]$ show no tendency to form internal metal—carbon bonds [8].

However, Clark [7,9] and Goel [10] have recently shown that it is possible to prepare complexes containing a heterocyclic ring ot the type $\overline{PdCH_2CMe_2P}$-$Bu^t{}_2$. They showed that *trans*-$[PdCl_2(PBu^t{}_3)_2]$ and also the palladium hydrides *trans*-$[PdHX(PBu^t{}_3)_2]$ (X = Cl or CF_3COO) are smoothly converted into the metalated complexes $[\overline{PdCH_2CMe_2P}Bu^t{}_2(PBu^t{}_3)X]$. The chloride-bridged dimer

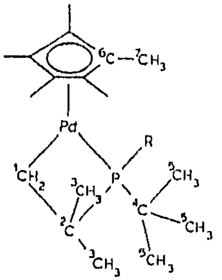
TABLE 2

^{13}C NMR DATA OF $C_5H_5\overline{PdCH_2CMe_2P}Bu^tR$(X, XIII) AND $C_5Me_5\overline{PdCH_2CMe_2P}Bu^tR$(XI, XIV), IN C_6D_6 (δ in ppm; J in Hz; int. TMS)

Complex	δ(^{1}C)	J(PC)	δ(^{2}C)	J(PC)	δ(^{3}C)	J(PC)	δ(^{4}C)	J(PC)	δ(^{5}C)	J(PC)	δ(^{6}C)	J(PC)
X	−6.20d	45.6	33.27d	16.2	29.75d 29.21d	7.0 3.0	47.20d	26.5	28.72d	5.9	94.34d	2.9
XI [a]	6.43d	47.1	34.92d	11.8	31.77d 29.58d	1.5 2.2	48.15d	27.9	28.90d	6.6	103.0d	3.7
XIII	−3.02d	58.9	36.11d	5.2	31.77 [b]		50.87d	20.6	31.68d	4.9	94.18d	2.9
XIV [c]	9.05d	41.9	37.81s		31.87 [b]		51.52d	22.1	31.82d	5.2	102.7d	3.7

[a] Signal of ^{7}C : δ = 11.21d; J(PC) = 1.5. [b] Signal is partly hidden by the doublet of ^{5}C. [c] Signal of ^{7}C : δ = 11.18d; J(PC) = 1.5.

Assignment according to:



$[\overline{\text{PdCH}_2\text{CMe}_2\text{P}}\text{Bu}^t{}_2(\mu\text{-Cl})]_2$ can be obtained either from $[\overline{\text{PdCH}_2\text{CMe}_2\text{P}}\text{Bu}^t{}_2(\text{PBu}^t{}_3)\text{Cl}]$ by phosphine elimination or from $[\text{PdCl}_2(\text{PhCN})_2]$ and $\text{PBu}^t{}_3$ in CH_2Cl_2.

The results of the present work complement those studies in two ways. First, they show that not only palladium complexes of tri-t-butylphosphine but also those of the less bulky di-t-butylphenylphosphine easily undergo intramolecular metalation reactions. Second, they prove that metalation is possible not only by elimination of HCl [7,10] or H_2 [9] but also by elimination of HOAc, and that, at least in the case of the dimeric compounds $[\text{Cl}(\text{PBu}^t{}_2\text{R})\text{Pd}]_2(\mu\text{-X})_2$ (R = Bu^t, Ph), this reaction is even more favored for X = OAc than for X = Cl.

Experimental

NMR spectra were recorded on the following instruments: Varian T 60 (^{1}H), Varian XL 100 (^{31}P), Bruker WH 90-FT (^{13}C). The complexes $[\text{PdCl}_2(\text{PBu}^t{}_2\text{Ph})]_2$ and $[\text{PdCl}_2(\text{PBu}^t{}_3)]_2$ were prepared according to ref. 3. All reactions were carried out under purified nitrogen.

Preparation of $C_5H_5Pd(PBu^t{}_2Ph)Cl$ (VI)

$[\text{PdCl}_2(\text{PBu}^t{}_2\text{Ph})]_2$ (V) (0.5 g, 0.63 mmol) was dissolved in 10 ml THF and TlC_5H_5 (0.37 g, 1.37 mmol) was added. The solution was stirred for 10 min, and the solvent was removed. The residue was extracted with 5 ml toluene and the solution was filtered. After addition of 10 ml pentane, the flask was kept at —78°C for two days. The green crystalline, air-stable precipitate was collected, washed with cold pentane and dried in vacuo. Yield: 0.42 g (79%). M.p. 139—140°C (dec.). (Found: C, 53.18; H, 6.97; Pd, 25.18. $\text{C}_{19}\text{H}_{28}\text{ClPPd}$ calcd.: C, 53.16; H, 6.58; Pd, 24.79%).

Preparation of $[\overline{PdCH_2CMe_2P}Bu^tPh]_2$ (IX)

$[\text{PdCl}_2(\text{PBu}^t{}_2\text{Ph})]_2$ (V) (0.5 g, 0.63 mmol) was dissolved in 10 ml CHCl_3 and AgOAc (0.23 g, 1.38 mmol) was added. The solution was stirred for 12 h in the dark, then filtered and the solvent removed. The residue was recrystallized from CH_2Cl_2/pentane to give yellow crystals. Yield: 0.25 g (55%). M.p. 115°C (dec.). (Found: C, 46.44; H, 6.55; Pd, 29.59. $\text{C}_{28}\text{H}_{44}\text{Cl}_2\text{P}_2\text{Pd}_2$ calcd.: C, 46.30; H, 6.11; Pd, 29.30%).

The complex $[\overline{\text{PdCH}_2\text{CMe}_2\text{P}}\text{Bu}^t{}_2]_2(\mu\text{-Cl})_2$ (XII) was analogously prepared from $[\text{PdCl}_2(\text{PBu}^t{}_3)]_2$ and AgOAc and obtained as pale yellow crystals. The ^{1}H NMR spectrum was identical to that reported in ref. 7. Yield nearly quantitative.

Preparation of $C_5H_5\overline{PdCH_2CMe_2P}Bu^tPh$ (X)

$[\overline{\text{PdCH}_2\text{CMe}_2\text{P}}\text{Bu}^t\text{Ph}]_2(\mu\text{-Cl})_2$ (IX) (0.25 g, 0.34 mmol) was dissolved in 10 ml C_6H_6 and TlC_5H_5 (0.4 g, 1.48 mmol) was added. The solution was stirred for 30 min, and the solvent was removed. The residue was extracted three times with 10 ml pentane, and the filtered solution was concentrated in vacuo. After cooling to —78°C for two days, orange-brown crystals were obtained. Yield: 0.18 g (67%). M.p. 66—68°C (dec.). (Found: C, 57.25; H, 7.02; Pd, 27.51; MW 392 (MS). $\text{C}_{19}\text{H}_{27}\text{PPd}$ calcd.: C, 58.10; H, 6.93; Pd, 27.09%; MW 392.80).

Preparation of $C_5Me_5\overline{PdCH_2CMe_2P}Bu^tPh$ *(XI)*

$[\overline{PdCH_2CMe_2P}Bu^tPh]_2(\mu\text{-}Cl)_2$ (IX) (1.09 g, 1.50 mmol) was dissolved in 10 ml C_6H_6 and LiC_5Me_5 (0.45 g, 3.17 mmol) was added. The solution was stirred for 3 h, and the solvent was removed. The residue was extracted twice with 5 ml pentane, and the filtered solution was concentrated in vacuo. After cooling to −78°C for three days, red crystals were obtained. Yield: 0.54 g (39%). M.p. 145—146°C. (Found: C, 62.02; H, 8.12; Pd, 22.30; MW 462 (MS). $C_{24}H_{37}PPd$ calcd.: C, 62.27; H, 8.06; Pd, 22.98%; MW 462.94).

Preparation of $C_5H_5\overline{PdCH_2CMe_2P}Bu^t{}_2$ *(XIII)*

The complex was prepared from $[\overline{PdCH_2CMe_2P}Bu^t{}_2]_2$ (XII) (0.5 g, 0.73 mmol) and TlC_5H_5 (0.43 g, 1.6 mmol) as for the analogue X. Red crystals. Yield: 0.42 g (77%). M.p. 99—100°C (dec.). (Found: C, 54.14; H, 8.24; Pd, 28.05; MW 372 (MS). $C_{17}H_{31}PPd$ calcd.: C, 54.77; H, 8;38; Pd, 28.54%; MW 372.81).

Preparation of $C_5Me_5\overline{PdCH_2CMe_2P}Bu^t{}_2$ *(XIV)*

The complex was prepared from $[\overline{PdCH_2CMe_2P}Bu^t{}_2]_2(\mu\text{-}Cl)_2$ (XII) (0.7 g, 1.02 mmol) and LiC_5Me_5 (0.32 g, 2.24 mmol) as for the analogue XI. Red crystals. Yield: 0.54 g (60%). M.p. 160°C. (Found: C, 59.56: H, 9.39; Pd, 23.97; MW 443 (MS). $C_{22}H_{41}PPd$ calcd.: C, 59.52; H, 9.54; Pd, 23.97%; MW 443.95).

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