PREPARATION AND STRUCTURE OF NEW PHOSPHONIUM SALT TYPE PALLADIUM(II) η^3-ALLYL YLIDE COMPLEXES *

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Summary

New palladium allyl ylide complexes, $[(\eta^3\text{-}R_3^1PCHCR^2CHR^3)_2Pd_2X_2][Y]_2$ (II), ($R^1 = C_2H_5$ or Ph; $R^2 = H$ or CH_3; $R^3 = H$ or CH_3; $X = Cl$ or Br; $Y = PF_6$, BF_4, or CF_3SO_3) are obtained from $(\eta^3\text{-}R_3^1PCHCR^2CHR^3)PdX_2$ (I) and silver hexafluorophosphate, tetrafluoroborate or trifluoromenthanesulfonate in acetone. The phosphonium allyl ylide is coordinated as a η^3-ligand as indicated by the variable temperature NMR spectrum of a typical complex $[(\eta^3\text{-}Ph_3PCHCHCH_2)_2Pd_2Br_2][PF_6]_2$.

Introduction

A number of η^1-ylide transition metal complexes have been synthesized in the last decade. They can be classified into two groups, the onium metallate ylide complexes on the one hand [1], and the onium salt type ylide complexes [2] on the other. Numerous η^1-ylide complexes so far reported belong to the former type. η^2-Phosphonium salt type complexes were reported by Kaska et al. [3] in the case of the ylide $Ph_3P=C=PPh_3$, in a zerovalent platinum skeleton $(CO)_3[(EtO)_3PC=CPh][PPh_2]Fe(CO)_3$ by Carty et al. [4] and in $(\pi\text{-}Cp)NiPPh_3(C_2R)Fe(CO)_3$ by Yasufuku et al. [6]. There are a few examples of η^3- [6] and η^5- [7] onium metallate ylide complexes, but none of η^3- and η^5-onium salt type ylide complexes.

Recently, we published about the transformation from onium metallate ylide complexes to the onium salt type ylide complexes; briefly, the formal charge of
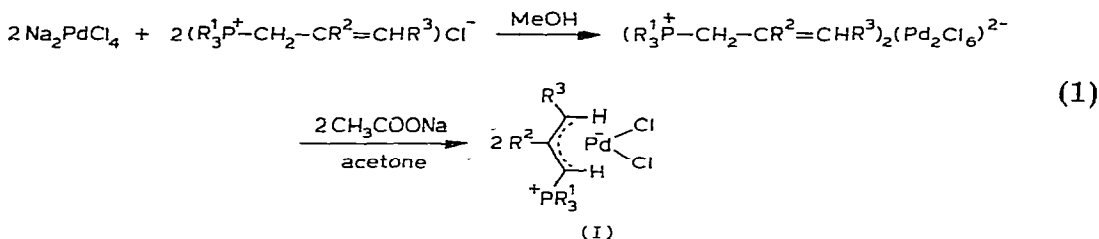
the central metal decreased from —1 to neutral; in other words, two chloride anions of dimeric [PhMe$_2$PCH(SiMe$_3$)PdCl$_2$]$_2$ were abstracted by an appropriate cation (eg. Ag$^+$) in the presence of a bidentate ligand which coordinates to the two unsaturated sites thus generated [8]. Saito et al. [9] also prepared the chelated phosphonium salt ylide type complexes with sodium cation as abstracting agent.

In this paper, new η^3-phosphonium salt type neutral palladium dinuclear complexes are reported, which were prepared from dihalo-η^3-phosphonium allyl ylide palladate I and silver hexafluorophosphate, tetrafluoroborate or trifluoromethanesulfonate. Structures were determined by NMR and IR spectra and conductivities compared with the corresponding palladate complexes.

Results and discussion

Modified preparative procedure of η^3-phosphonium palladate complexes

Zwitterionic starting complexes were prepared in high yield without handling an unstable phosphonium allyl ylide as in our previous paper [6b]. However, any attempt to prepare dichloro palladate complexes was unsuccessful because they were unstable in a methanolic sodium acetate solution and decomposed easily. In order to generalize this convenient procedure, reactions between onium salt complexes and sodium acetate in acetone were carried out (eq. 1).

$$2\,Na_2PdCl_4 + 2(R^1_3\overset{+}{P}-CH_2-CR^2=CHR^3)Cl^- \xrightarrow{\text{MeOH}} (R^1_3\overset{+}{P}-CH_2-CR^2=CHR^3)_2(Pd_2Cl_6)^{2-}$$

(1)

$$\xrightarrow[\text{acetone}]{2\,CH_3COONa} 2\,R^2 \cdots$$

(I)

This modification was successful; yield, m.p. and color of the resulting zwitterionic complexes are summarized in Table 1, and proton NMR data are in Table 2. Low temperature NMR spectra of Ia at —60°C in DMSO-d_6 show no change of its spectral pattern, compared with the room temperature spectrum.

TABLE 1

PHYSICAL DATA FOR DIHALO-(1-PHOSPHONIUM-η^3-ALLYL YLIDE) PALLADATE COMPLEXES (R$^1_3$PCHCR^{2}CHR^3)PdX$_2$ (Ia—Ie)

No.	R^1	R^2	R^3	X	Yield (%)	M.p. (°C) (dec.)	Color
Ia [a]	Ph	H	H	Br	86	235	Yellow brown
Ib	Ph	H	H	Cl	83	201—202	Yellow
Ic	Ph	Me	H	Cl	82	198—201	Yellow
Id	Ph	H	Me	Cl	85	168—170	Yellow
Ie	Et	H	H	Cl	86	201—204	Yellow

[a] Ref. 6b.

TABLE 2

PROTON NMR SPECTRA OF $(R_3^1PCH^1CR^2CH^3R^3)PdX_2$ (Ia—Ie) in DMSO-d_6 (int. TMS)

No.	Structure	δ (ppm)	J (Hz)
Ia	[structure]	H^1 4.57 (d of d) H^2 5.55 (d of d of t) H^3, $H^{3'}$ 3.95(d)	$J(H^1-H^2)$ 11.0 $J(H^1-P)$ 12.0 $J(H^2-P)$ 10.0 $J(H^2-H^3)$ 9.0
Ib	[structure]	H^1 4.70 (d of d) H^2 5.51 (d of d of t) H^3, $H^{3'}$ 3.68(d)	$J(H^1-H^2)$ 12.0 $J(H^1-P)$ 14.9 $J(H^2-P)$ 11.0 $J(H^2-H^3)$ 9.2
Ic	[structure]	H^1 H^2 (complex pattern at H^3 3.5 and 5.5) CH_3 1.63 and 2.30	
Id	[structure]	H^1 4.20 (m) H^2 5.23 (m) H^3 4.20 (m) CH_3 1.33(d)	
Ie	[structure]	H^1 3.55(m) H^2 5.90 (d of d of t) H^3, $H^{3'}$ 3.67(d) $P-CH_2$ 2.44 (d of q) $P-C-CH_3$ 1.19 (d of t)	$J(H^1-H^2)$ 11.1 $J(H^1-P)$ 9.0 $J(H^2-P)$ 28.5 $J(H^2-H^3)$ 9.0 $J(CH_2-CH_3)$ 7.5 $J(P-CH_2)$ 21.0 $J(P-C-CH_3)$ 18.5

Preparation of μ,μ-dihalobis(1-phosphonium-η^3-allyl ylide) dipalladium salt

When silver hexafluorophosphate, tetrafluoroborate or trifluoromethanesulfonate was added to an acetone suspension of the above mentioned zwitterionic η^3-allyl ylide complexes at room temperature, the elimination of silver halide occurred readily to yield the title complexes IIa—IIh in good yields (eq. 2).

$$(Y = PF_6, BF_4, CF_3SO_3)$$
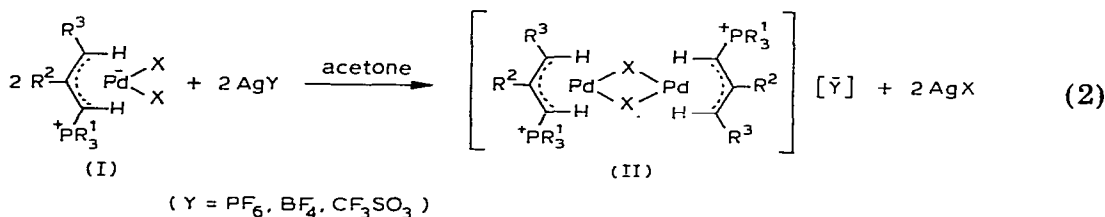
Preparative and analytical results are summarized in Table 3, and spectral data in Table 4.

Complexes IIa—IIh gradually decompose in solution at room temperature, and especially they decompose spontaneously in a methanolic solution. There

TABLE 3

PHYSICAL AND ANALYTICAL DATA FOR NEUTRAL DINUCLEAR PALLADIUM COMPLEXES [(R$_3^1$PCHCR^{2}CHR^3)$_2$Pd$_2$X$_2$](Y)$_2$ (II) HAVING AN η^3-ALLYL YLIDE LIGAND

No.	R^1	R^2	R^3	X	Y	Yield (%)	M.p. (°C) (dec.)	Analysis found (calcd.) (%)		Conductivity (ohm^{-1} cm^2 mol^{-1})	Concentration (M) (solv.)
								C	H		
IIa	Ph	H	H	Br	PF$_6$	59	165–170	39.81 (40.09)	3.01 (3.02)	319	1.16 × 10^{-4} (acetone)
IIb	Ph	H	H	Cl	PF$_6$	62	174–178	42.66 (42.81)	3.43 (3.25)	298	6.61 × 10^{-4} (acetone)
IIc	Ph	H	H	Cl	BF$_4$	73	183–185	47.43 (47.50)	3.91 (3.61)		
IId	Ph	H	H	Cl	CF$_3$SO$_3$	79	200–203	44.36 (44.54)	3.22 (3.23)		3.73 × 10^{-4} (acetone)
IIe	Ph	Me	H	Cl	PF$_6$	81	168–169	44.01 (43.81)	3.51 (3.51)	274	
IIf	Ph	H	Me	Cl	PF$_6$	83	180–181	43.52 (43.81)	3.76 (3.51)	285	3.76 × 10^{-4} (acetone)
IIg	Et	H	H	Cl	PF$_6$	78	92–93	24.76 (24.29)	4.48 (4.30)		
IIh	Et	H	H	Cl	BF$_4$	82	201–204	28.09 (27.94)	4.98 (4.95)		
Ia										8.68	6.03 × 10^{-4} (DMF) [a]
III [b]										158	2.09 × 10^{-3} (acetone)
										69.7	4.92 × 10^{-4} (DMF)
IV [c]						72	130–133	55.92 (56.07)	4.58 (4.88)	124	2.09 × 10^{-3} (acetone)

[a] DMF, dimethyl formamide. [b] [PhMe$_2$PCH(SiMe$_3$)PdCl(1,5-cyclooctadiene)][PF$_6$]. [c] [(Ph$_3$PCHCHCH$_2$)(Ph$_3$P)PdCl][PF$_6$].

is a marked contrast between I and II; the palladate complex Ia could be prepared in methanol, but the neutral complexes II are more reactive to nucleophiles than the palladate one. They have been recrystallized from acetone and benzene or dichloromethane and ether. Suitable crystals of neither compound could be obtained for X-ray analysis, because of their spongy nature when separated from the solvent. However, IIg and IIh were stable and they could be recrystallized from acetonitrile without decomposition. Electron releasing ethyl groups stabilize the phosphonium center, as well as the allylic C(1) and C(3) atoms. In these complexes, IIa—IIh, a nucleophile attacks stereochemically and regio-specifically at the C(3) site. As shown in Table 4, the chemical shifts of H^3 of complexes IIg and IIh appear at higher field than any other of the complexes II. This is consistent with the fact that complexes IIg and IIh are stable.

The chemical shifts of the protons of the η^3-allyl ligand of complexes II, for example, in IIa are deshielded downfield (H^1; δ 4.57 → 4.89, H^2; 5.55 → 5.92, H^3; 3.95 → 4.27 ppm, respectively). As a consequence, the electron density around the central palladium atom is decreased from Ia to IIa. Since the η^3-allyl ylide ligand of Ia is more shielded by its higher electron density than that of IIa, the allyl proton signals of IIa are shifted downfield. From the H^1 *syn* location it is reasonable to assume that the H^1 proton is affected by the variation in the charge of the palladium atom in the same way as H^3.

Conductivities of complexes in acetone suggest the dinuclear phosphonium salt ylide complex structure. These data are shown in Table 3 together with a comparable complex in which substituted phosphonium salt ylide and cyclic diolefin are involved as ligands, [PhMe$_2$PCH(SiMe$_3$)PdCl(1,5-cyclooctadiene)]-[PF$_6$] (III). Its structure has already been determined as a monomeric one-to-one electrolyte by NMR, IR, molecular weight determination and X-ray analysis [10]. The palladate complex Ia shows low conductivity (8.68 ohm^{-1} cm^2 mol^{-1}), and complex III is a one-to-one electrolyte (158 ohm^{-1} cm^2 mol^{-1}). IIa shows a value of 319 ohm^{-1} cm^2 mol^{-1} which is twice that of III. Since IIa is a two-to-two electrolyte, it is a dimeric complex with two phosphonium salt ylides.
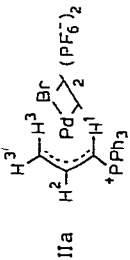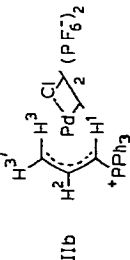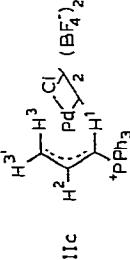
The dimeric structure of II was also supported by the formation of the mono-meric complex IV on cleavage of the bridging chloride with triphenylphosphine in the case of IIb (eq. 3).
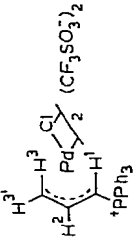

$$[\ \ \text{Pd} \ \ ]_2 [\text{PF}_6^-] \ + \ 2\,\text{PPh}_3 \ \xrightarrow{72\%} \ 2\ [\ \ \text{Pd}\ ] [\text{PF}_6^-] \qquad (3)$$
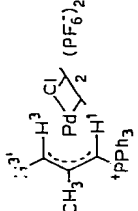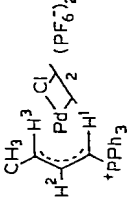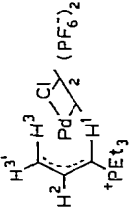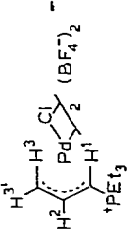
(IIb)　　　　　　　　　　　　(IV)
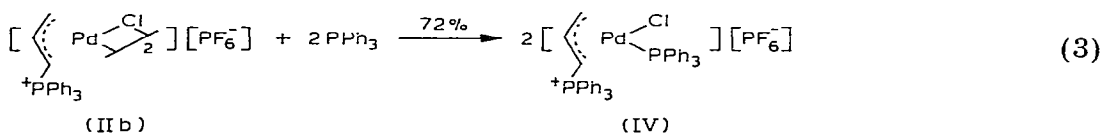
With respect to the new phosphonium allyl ylide ligand structure in the complexes IIa—IIh, the two protons at C(3) are equivalent from NMR spectra at room temperature (Table 4) indicating that the allyl ylide ligand has either a C(3) σ-bonded structure of a dynamic η^3-bonded structure. Therefore, we have measured the variable temperature NMR spectra of IIa as a typical case. The results are also listed in Table 4, and detailed NMR spectral patterns are illustrated in Fig. 1. At low temperatures the *syn* ($H^{3'}$) and *anti* (H^3) protons are definitely separated at δ 4.70 and 3.89 ppm respectively (coalescence temperature +3°C). This strongly supports a η^3-allyl structure which is similar to that of the behaviour

TABLE 4

PROTON NMR SPECTRA OF COMPLEXES $[(R^1_3PCHCR^2CHR^3)_2Pd_2X_2](Y)_2$ (II)

No. Structure	Temp. (°C)	δ (ppm)	J (Hz)	Solvent	$\nu(Y)$ (cm^{-1})
IIa	r.t.	H^1 4.89 (d of d) H^2 5.92 (d of d of t) $H^{3'}$, H^3 4.27 (d)	$J(H^1\!-\!H^2)$ 12.0 $J(H^1\!-\!P)$ 12.0 $J(H^2\!-\!P)$ 26.2 $J(H^2\!-\!H^3)$ 9.5	Acetone-d_6	836
	−40	H^1 4.95 (d of d) H^2 5.92 (d of d of d) H^3 3.89 (d) $H^{3'}$ 4.70 (d)	$J(H^1\!-\!H^2)$ 12.0 $J(H^1\!-\!P)$ 12.0 $J(H^2\!-\!P)$ 20.1 $J(H^2\!-\!H^3)$ 4.5 $J(H^2\!-\!H^{3'})$ 12.0		
	+50	H^1 4.87 (d of d) H^2 5.90 (d of d of t) $H^{3'}$, H^3 4.27 (d)	$J(H^1\!-\!H^2)$ 12.0 $J(H^1\!-\!P)$ 12.0 $J(H^2\!-\!P)$ 26.2 $J(H^2\!-\!H^3)$ 9.5		
IIb	r.t.	H^1 5.18 (d of d) H^2 5.98 (d of d of t) $H^{3'}$, H^3 4.13 (d)	$J(H^1\!-\!H^2)$ 12.0 $J(H^1\!-\!P)$ 12.8 $J(H^2\!-\!P)$ 26.2 $J(H^2\!-\!H^3)$ 9.0	DMSO-d_6	835
IIc	r.t.	H^1 4.32 (d of d) H^2 5.58 (d of d of t) $H^{3'}$, H^3 4.13 (d)		CD$_3$CN	1055

|	Structure	Temp.	NMR data	Solvent	
IId	Pd structure with H1, H2, H3, H3', Cl, +PPh3, (CF3SO3−)2	r.t.	H1 4.38 (d of d) H2 5.59 (m) H3', H3 4.17 (d)	CD3CN	1265
IIe	Pd structure with H1, H2, H3, CH3, Cl, +PPh3, (PF6−)2	r.t.	H1 4.90 and 5.77 (m and m) H3', H3 4.24 (d) CH3 1.77 and 2.52 (s and s)	DMSO-d_6	835
IIf	Pd structure with H1, H2, H3, CH3, Cl, +PPh3, (PF6−)2	r.t.	H1 4.60 (m) H2 5.62 (m) H3 4.69 (m) CH3 1.33 (d)	DMSO-d_6	840
IIg	Pd structure with H1, H2, H3, H3', Cl, +PEt3, (PF6−)2	r.t.	H1 3.86 (d of d) H2 6.23 (m) H3', H3 4.10 (br, s) P—CH2 2.56 (d of q) P—C—CH3 1.40 (d of t)	Acetone-d_6	840
IIh	Pd structure with H1, H2, H3, H3', Cl, +PEt3, (BF4−)2	r.t.	H1 3.70 (d of d) H2 6.00 (m) H3', H3 4.10 (br, s) P—CH2 2.53 (d of q) P—C—CH3 1.34 (d of t)	Acetone-d_6	1055
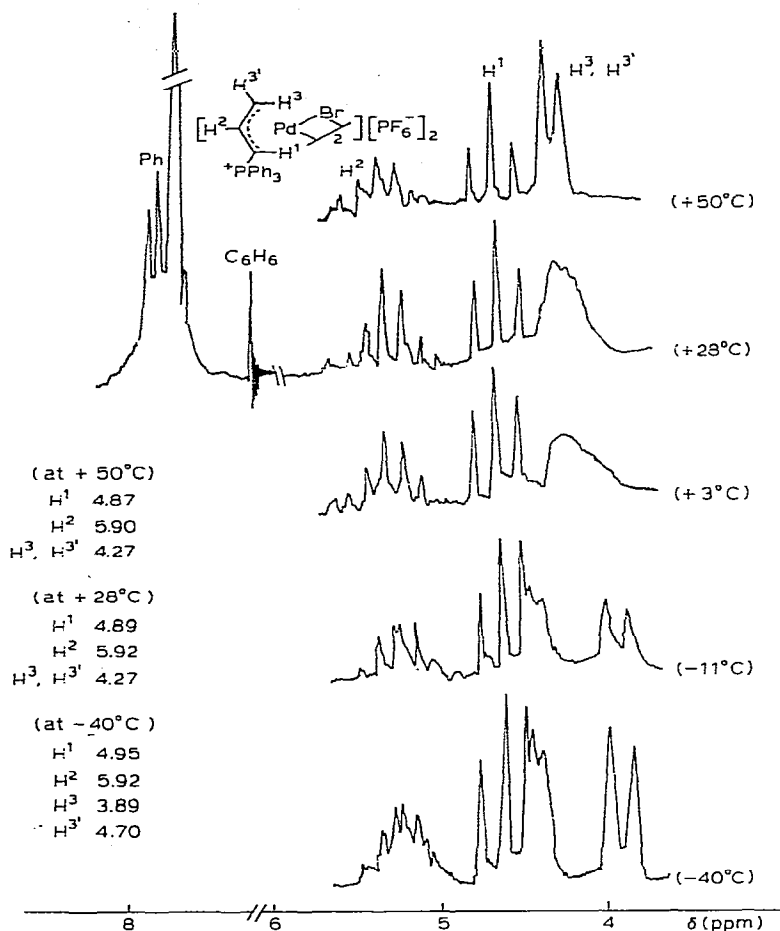
Fig. 1. Variable temperature spectra of complex IIa.

of π—σ interconversion in di-μ-chlorobis(η^3-crotyl)dipalladium [11]. From this evidence, the phosphonium allyl ylide ligand coordinates as a dynamic η^3-structure rather than a C(3) σ-bonded structure. Although we could not obtain direct evidence from variable temperature NMR spectra, the coordination of the allyl ylide ligand to the palladate complexes I may be as a dynamic η^3-structure, because of a similarity of their NMR spectra at room temperature. In complexes IIg and IIh, H^3 and $H^{3'}$ appeared as a broad singlet at room temperature which resembles the coalescence spectral pattern of IIa at +3°C.

Experimental

General remarks

All the preparative procedures and variable temperature NMR sampling were undertaken under argon or dinitrogen. The proton NMR and infrared spectra were recorded on a JEOL C-60HL spectrometer, and on a JASCO

DS-403G spectrometer, respectively. Conductivity was measured on a TOA Electronics CM-5B equipment.

Preparation of 1-triphenylphosphonium-η^3-allyl dibromopalladate (Ia). This complex was prepared according to ref. 6.

Preparation of 1-triphenylphosphonium-η^3-allyl dichloropalladate (Ib). The onium salt complex $(Ph_3PCH_2CH=CH_2)_2(Pd_2Cl_6)$ was prepared by the same method as Ia [6b].

To an acetone (40 ml) suspension of $(Ph_3PCH_2CH=CH_2)_2(Pd_2Cl_6)$ (1.5 g, 1.5 mmol) was added sodium acetate (262 mg, 3.2 mmol) with vigorous stirring. The mixture was stirred for 10 h at room temperature. The color of the reaction mixture changed gradually from dark-red to yellow. The yellow precipitate was isolated by filtration followed by washing with a large volume of water to remove sodium chloride and excess sodium acetate. The complex Ib was obtained in 83% yield.

Preparation of 1-triphenylphosphonium-η^3-methallyl dichloropalladate (Ic). Ic was prepared in the same manner as Ib with $[Ph_3PCH_2C(CH_3)=CH_2]_2(Pd_2Cl_6)$ (241 mg, 0.23 mmol) and sodium acetate (39.7 mg, 0.48 mmol) in acetone (20 ml) in 82% yield.

Preparation of 1-triphenylphosphonium-η^3-crotyl dichloropalladate (Id). Id was prepared in a similar manner to Ib with $[Ph_3PCH_2CH=C(CH_3)H]_2(Pd_2Cl_6)$ (334 mg, 0.32 mmol) and sodium acetate (56.6 mg, 0.69 mmol) in acetone (20 ml) in 85% yield.

Preparation of 1-triethylphosphonium-η^3-allyl dichloropalladate (Ie). Ie was obtained by a procedure similar to Ib by means of $(Et_3PCH_2CH=CH_2)_2(Pd_2Cl_6)$ (19.3 g, 0.02 mol) and sodium acetate (1.23 g, 0.015 mol) in acetone (100 ml) for 2 h in 86% yield. Recrystallization from acetonitrile and ether gave pale yellow needles of Ie. Anal. Found: C, 32.32; H, 5.76. $C_9H_{19}Cl_2PPd$ calcd.: C, 32.31; H, 5.71%.

Preparation of μ,μ-dibromobis(1-triphenylphosphonium-η^3-allyl)dipalladium bis(hexafluorophosphate) (IIa). Preparation of IIa is described as a representative example. Preparation of the other compounds II is listed in Table 5.

To an acetone (20 ml) suspension of $(Ph_3PCHCHCH_2)PdCl_2$ (Ia; 152 mg, 0.27

TABLE 5

DATA FOR THE SYNTHESIS OF $[(R_3^1PCHCR^2CHR^3)_2Pd_2X_2](Y)_2$ (II)

Palladate complex		Acetone (ml)	AgY [a]		T ($^{\circ}$C)	t (min)	Product	Yield (%)
No.	mg(mmol)		Y	mg(mmol)				
Ia	152(0.27)	20	PF$_6$	67(0.27)	r.t.	10	IIa	59
Ib	129(0.27)	20	PF$_6$	67(0.27)	−30	10	IIb	73
Ib	378(0.79)	30	BF$_4 \cdot$ H$_2$O	165(0.78)	0	10	IIc	62
Ib	388(0.81)	30	CF$_3$SO$_3$	208(0.81)	r.t.	10	IId	79
Ic	493(1.00)	30	PF$_6$	253(1.00)	−30	10	IIe	83
Id	161(0.33)	20	PF$_6$	83(0.33)	−30	10	IIf	81
Ie	192(0.57)	20	PF$_6$	143(0.56)	−30	10	IIg	78
Ie	474(1.41)	30	BF$_4 \cdot$ H$_2$O	300(1.40)	−30	10	IIh	83

[a] Added as an acetone solution (10 ml).

mmol), was added an acetone (10 ml) solution of $AgPF_6$ (67 mg, 0.27 mmol) under dinitrogen at room temperature. The reaction occurred instantaneously giving a yellow solution of IIa and a gray precipitate of silver bromide. The mixture was stirred at room temperature for 10 min, and was filtered quickly under vacuum because of its instability through a No. 4C filter or through a No. 5C filter paper under dinitrogen. The solution was evaporated under reduced pressure. The product was obtained in 59% yield. Recrystallization was achieved using acetone and benzene or dichloromethane and ether.

Preparation of 1-triphenylphosphonium-η^3-allyl(triphenylphosphine)chloro-palladium hexafluorophosphate (IV). To a THF (15 ml) suspension of the complex IIb, $[(Ph_3PCHCHCH_2)_2Pd_2Cl_2](PF_6)_2$ (140 mg, 0.12 mmol) was added a THF (5 ml) solution of triphenylphosphine (62 mg, 0.24 mmol). The reaction occurred instantaneously giving an orange-yellow solution after stirring for 1 h at room temperature. The solution was evaporated under reduced pressure. The product was recrystallized from THF by adding ether to give orange-yellow crystals containing 1 mol THF as solvate in 72% yield. NMR ($CDCl_3$) (δ, ppm): 4.20 (d, of d, 1H, H^1), 5.50 (m, 1H, H^2), 3.68 (d, 2H, H^3) and 1.8 and 4.7 (m, each 4H, THF). IR (KBr): 837 cm^{-1} ($\nu(PF_6)^-$. The solvent-free yellow powder was obtained from dichloromethane by adding a large volume of ether.

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