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SIMPLE PREPARATION OF π-ALLYLPHOSPHONIUM YLIDE COMPLEXES OF PALLADIUM (II)

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Summary

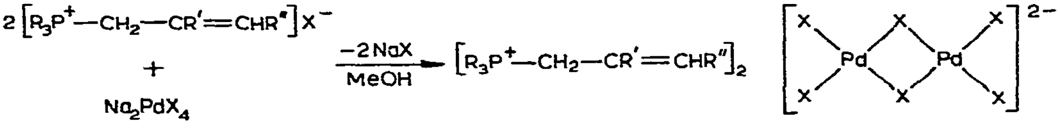
π-Allylphosphonium ylide complexes of palladium(II) were readily prepared by the reaction of the corresponding allylphosphonium hexahalogenodipalladate(I) with sodium acetate in 73—90% yield.

Introduction

Various ylide complexes of transition metals were prepared recently by the direct interaction of transition metal compounds with phosphonium ylides which were generally air-sensitive [1—5]. In this paper, we report a simple and high-yield synthesis of some π-allylphosphonium ylide complexes of palladium(II) by treatment of the corresponding bis (allylphosphonium) hexahalogenodipalladate $[R_3P^+—CH_2—CR'=CHR'']_2\ [Pd_2X_6]^{2-}$ (Ia-Ie), with sodium acetate in methanol.

Results and discussion

Starting bis(allylphosphonium) hexahalogenodipalladates (Ia-Ie) were obtained as red needles according to eqn. 1. Their yields, m.p's., and analyses are summarized in Table 1.


(1)

(Ia-Ie)

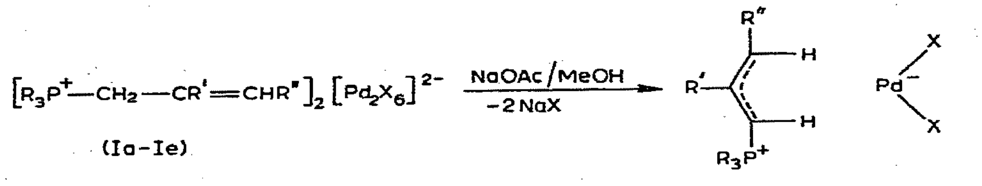
It was concluded that the olefinic part of allylphosphonium salts in Ia-Ie was not coordinated because their NMR and infrared spectra were essentially identical with those of the original allylphosphonium halides.

TABLE 1

PROPERTIES OF BIS(ALLYLPHOSPHONIUM) HEXAHALOGENODIPALLADATES $[R_3P^+—CH_2—CR'{=}CHR'']_2[Pd_2X_6]^{2-}$ (Ia-Ie) AND π-ALLYLPHOSPHONIUM YLIDE COMPLEXES OF DIHALOGENOPALLADATE $R_3P^+—CH{\cdots}CR'{\cdots}CR''\cdot Pd^-X_2$ (IIa-IIe)

Compound	R_3P	R'	R''	X	Yield (%)	M.p. (°C)	Color	Analysis found (calcd.) (%)	
								C	H
Ia	Ph_3P	H	H	Br	100	171—174	Dark-red	39.01 (38.84)	3.17 (3.10)
Ib	$PhMe_2P$	H	H	Br	100	118—120	Dark-red	25.26 (25.15)	3.12 (3.07)
Ic	$PhMe_2P$	CH_3	H	Cl	77	130—133	Pale-red	35.62 (35.50	4.38 (4.47)
Id	Ph_3P	H	CH_3	Cl	72	157—160	Dark-red	49.74 (50.03)	4.16 (4.20)
Ie	$PhMe_2P$	H	CH_3	Cl	60	95—97	Pale-red	35.84 (35.50)	4.35 (4.70)
IIa	Ph_3P	H	H	Br	86	235 (dec.)	Yellow-brown	38.48 (38.41)	2.87 (2.93)
IIb	$PhMe_2P$	H	H	Br	90	225—227	Yellow	29.44 (29.73)	3.32 (3.40)
IIc	$PhMe_2P$	CH_3	H	Cl	77	230 (dec.)	Yellow	38.68 (39.00)	4.51 (3.40)
IId	Ph_3P	H	CH_3	Cl	80	229 (dec.)	Yellow	53.42 (53.52)	4.32 (4.29)
IIe	$PhMe_2P$	H	CH_3	Cl	73	236 (dec.)	Yellow	38.68 (39.00)	4.52 (4.63)

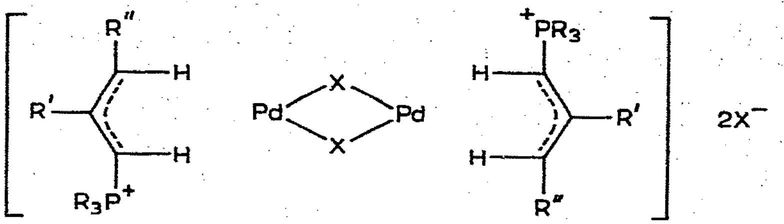
The addition of sodium acetate to a methanol suspension of Ia-Ie resulted in formation of the corresponding π-allylphosphonium ylide complexes of dihalogenopalladate (IIa-IIe) as yellow needles in 73—90% yield (eqn. 2).



(IIa-IIe)

(2)

Analytical and NMR spectroscopic results are summarized in Table 1 and 2, respectively. Another possible structure (III), which involves bridging halogen atoms, was excluded, because both cleavage of bridging halogen atom by thallium(I) acetylacetonate and anion exchange with sodium tetraphenylborate did not take place (but induced decomposition to metallic palladium in the case of IIa). Moreover, cryoscopic molecular weight determination of IIa suggested that it was monomeric in nitrobenzene (IIa mol. wt. calcd.: 569; III mol. wt. calcd.: 1138; found 550). Therefore, the possibility of III was definitely discarded. These facts, infrared spectra and analyses are consistent with the depicted structure II, in which two halogen atoms are bonded to a monomeric dihalogenopalladate(II).



(III)

In this context, π-allylphosphonium tetracarbonylmolybdate has been reported [2], and a recent X-ray structure determination concluded that the allyl ylide component is coordinated to molybdenum as a phosphonium-π-allyl ligand [6]. Schmidbaur [3] reported σ-type gold [3a], copper, mercury, and nickel -ate complexes [3b] of phosphonium ylides.

The NMR spectrum of IIa is shown in Fig. 1 as a representative example. The equivalence of H(3) and H(4) can be explained by IIa either being a dynamic allyl complex or having a strong σ-interaction with the palladium atom at the C(3) position. An extreme representation of the latter possibility is shown as IV. However, the equivalence of H(3) and H(4) can also be explained by V, since NMR spectra were measured in dimethyl sulfoxide-d_6. Results of NMR spectra are summarized in Table 2.

The present method is more convenient than those previously reported [2–5], because air-sensitive ylides do not need to be handled.

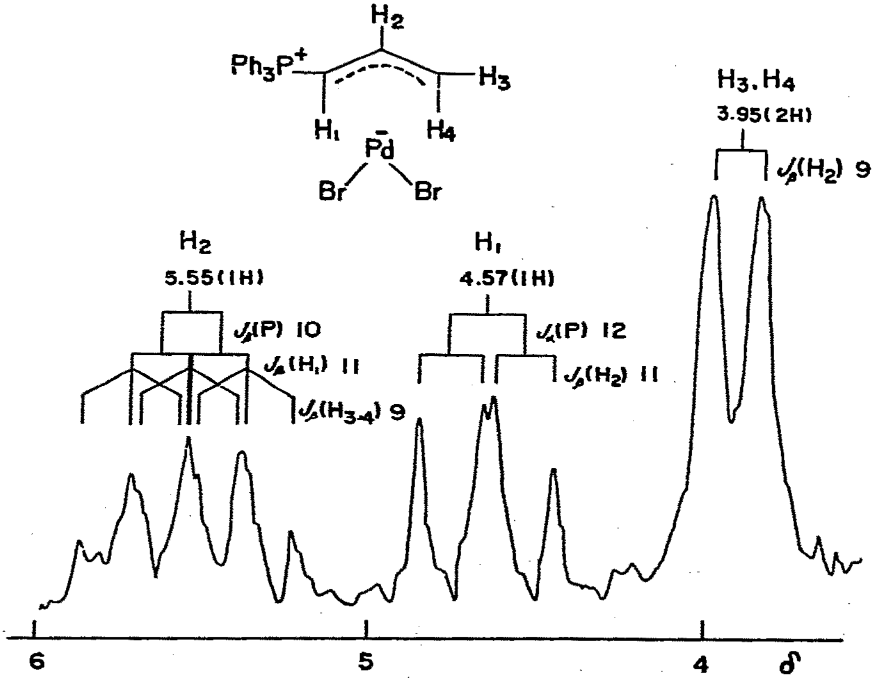


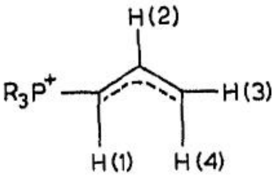
Fig. 1. NMR spectrum of IIa (solvent: dimethyl sulfoxide-d_6) at 25°.

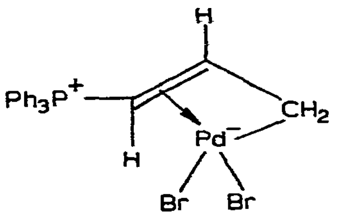
TABLE 2

NMR SPECTRA OF BIS(ALLYLPHOSPHONIUM) HEXAHALOGENODIPALLADATE; $[R_3P^+{-}CH_2{-}CR'{=}CHR'']_2\,[Pd_2X_6]^{2-}$ (Ia-Ie) AND 1-PHOSPHONIUM-π-ALLYL DIHALOGENOPALLADATES $R_3P^+{-}CH{\cdots}CR'{\cdots}CR'' \cdot Pd^-X_2$ (IIa-IIe) IN DIMETHYL SULFOXIDE-d_6[a]

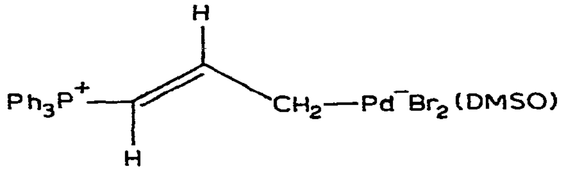
Compound	R_3P	R′	R″	X	Chemical Shift (δ ppm)					Coupling constant (Hz)						
					H(1)	H(2)	H(3,4)	CH_3—C	CH_3—P	J(1,2)	J(1,3)	J(2,3)	J_{1_p}	J_{2_p}	J_{cp}	J(CH_3—H)
Ia	Ph_3P	H	H	Br	4.62 dd		5.52 m[b]			6.8	0	*c*	15.5	*c*		
Ib	$PhMe_2P$	H	H	Br	3.54 dd		5.48 m[b]		2.30 d	6.4	0	*c*	17.0	*c*	14.0	
Ic	$PhMe_2P$	CH_3	H	Cl	3.42 dd		5.10 m	1.53 m	2.23 d		1.5		17.6		14.3	15
Id	Ph_3P	H	CH_3	Cl	4.44 dd		5.35 m[b]	1.58 t		7.0	0	*c*	16.4	*c*	-	6.0
Ie	$PhMe_2P$	H	CH_3	Cl	3.30 dd		5.53 m[b]	1.62 t	2.17 d	6.6	0	*c*	17.0	*c*	14.2	5.0
IIa	Ph_3P	H	H	Br	4.57 dd	5.45 m	3.95 d			11.0	0	9.0	12.0	10.0		
IIb	$PhMe_2P$	H	H	Br	4.90 dd	6.02 m	3.82 d		2.50 d	11.0	0	9.0	12.0	10.0	15.0	
IIc	$PhMe_2P$	CH_3	H	Cl	3.50 dd		3.50 s	1.90 s	2.47 d		0	9.0	12.0		14.3	
IId	Ph_3P	H	CH_3	Cl	4.33 dd	6.25 m	3.27 m	1.36 d		11.7	0	*c*	12.0	11.0		6.7
IIe	$PhMe_2P$	H	CH_3	Cl	4.10 dd	5.73 m	3.30 m	1.37 d	2.43 d	11.6	0	*c*	12.0	11.0	15.0	6.7

[a] The numbering of parent skelton of Ia, Ib and IIa, IIb is as follows:

$R_3P^+{-}CH(1)_2{-}CH(2){=}CH(3)_2$ for Ia, Ib and  for IIa, IIb. This numbering was used when methyl group was introduced in the cases of Ic-Ie and IIc-IIe. [b] Three or two olefinic protons were overlapped at this position. [c] Could not be determined because of complexity of suitable proton signal.



(IV)



(V)

Experimental

General remarks

NMR spectra were measured with a Jeol C-60HL spectrometer using tetramethylsilane as an internal standard. Since both types of complex Ia-Ie and IIa-IIe, are sparingly soluble, NMR spectra were observed in DMSO-d_6. Chemical shifts and coupling constants are summarized in Table 2 for Ia-Ie and IIa-IIe. M.p's, color, and analytical results are shown in Table 1. Experimental procedures only are described in this section.

Bis(allyltriphenylphosphonium) hexabromodipalladate (Ia)

A methanol (5 ml) solution of allyltriphenylphosphonium bromide (383 mg, 1.0 mmol) was added dropwise to a stirred methanol (10 ml) solution of disodium tetrabromopalladate (474 mg, 1.0 mmol). Reaction occurred instantaneously to give dark-red crystalline products, which were separated by filtration followed by washing with large volumes of water in order to remove sodium bromide. Bis(allyltriphenylphosphonium) hexabromodipalladate (Ia) was isolated quantitatively (649 mg).

Bis(allyldimethylphenylphosphonium) hexabromodipalladate (Ib)

This was prepared similarly from allyldimethylphenylphosphonium bromide (259 mg, 1.0 mmol), disodium tetrabromodipalladate (474 mg, 1.0 mmol), and methanol 15 ml) in quantitative yield (520 mg).

Bis(methallyldimethylphenylphosphonium) hexachlorodipalladate (Ic)

A mixture of palladium chloride (177 mg, 1.0 mmol), sodium chloride (177 mg, 3.0 mmol), and methanol (5 ml) was stirred for 5 h at room temperature to give a methanol solution of sodium tetrachloropalladate. Excess sodium chloride was separated by filtration. A methanol (5 ml) solution of methallyldimethylphenylphosphonium chloride (229 mg, 1.0 mmol) was added dropwise to the above filtrate. Reaction occurred instantaneously giving pale red needles of Ic, which was filtered and washed with large volume of water in order to remove sodium chloride; Ic was isolated in 77% yield (284 mg).

Bis(crotyltriphenylphosphonium) hexachlorodipalladate (Id)

This was prepared in a manner similar to Ic from palladium chloride (177 mg, 1.0 mmol), sodium chloride (177 mg, 1.0 mmol), and crotyltriphenylphosphonium chloride (352 mg, 1.0 mmol) in methanol (10 ml) in 72% yield (380 mg).

Bis(crotyldimethylphenylphosphonium) hexachlorodipalladate (Ie)

This was also obtained in a procedure similar to Ic by means of palladium chloride (177 mg, 1.0 mmol), sodium chloride (177 mg, 3.0 mmol), and crotyldimethylphenylphosphonium chloride (229 mg, 1.0 mmol) in methanol (10 ml) in 60% yield (244 mg).

1-Triphenylphosphonium-π-allyl dibromopalladate (IIa)

To a methanol (10 ml) suspension of Ia (649 mg, 0.50 mmol) was added dropwise a methanol (5 ml) solution of sodium acetate (90 mg, 1.1 mmol) with vigorous stirring. The mixture was stirred for 4 h at room temperature. The color of precipitates changed gradually from dark-red to yellowish brown. 1-Triphenylphosphonium-π-allyl dibromopalladate (IIa) was isolated by filtration followed by washing with large volumes of water to remove sodium bromide; yield of IIa was 86% (487 mg). Recrystallization can be achieved using a large volume of chloroform.

1-Dimethylphenylphosphonium-π-allyl dibromopalladate (IIb)

This was prepared in a similar manner to IIa with methanol (10 ml), Ib (520 mg, 0.5 mmol), and sodium acetate (90 mg, 1.1 mmol) in 90% yield (400 mg).

1-Dimethylphenylphosphonium-2-methyl-π-allyl dichloropalladate (IIc)

A methanol (5 ml) solution of sodium acetate (82 mg, 1.0 mmol) was added slowly to a methanol (10 ml) suspension of Ic (406 mg, 0.5 mmol) with vigorous stirring at room temperature. After the addition was complete, the mixture was stirred for 1 h. The color of suspension changed gradually from dark-red to yellow. Solid product was collected by filtration, then was washed with a large volume of water to remove sodium chloride: yield of IIc was 77% (284 mg).

1-Triphenylphosphonium-3-methyl-π-allyl dichloropalladate (IId)

This was prepared in the same manner as IIc, with Id (519 mg, 0.5 mmol) and sodium acetate (82 mg, 1.0 mmol) in methanol (10 ml) in 80% yield (392 mg).

1-Dimethylphenylphosphonium-3-methyl-π-allyl dichloropalladate (IIe)

This was also prepared in a manner similar to IIc, from Ie (406 mg, 0.5 mmol) and methanol (5 ml) solution of sodium acetate (82 mg, 1.0 mmol) in 73% yield (272 mg).

References

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