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A CONVENIENT SYNTHESIS AND STRUCTURE OF STABILIZED YLIDE COMPLEXES OF PALLADIUM(II)

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Summary

New types of some carbonyl- and cyano-phosphonium ylide complexes of palladium(II) were readily prepared in good yield by treatment of the corresponding bis(phosphonium)hexachlorodipalladate, $[R_3P^+{-}CH_2{-}Z]_2[Pd_2Cl_6]^{2-}$ ($R_3P = Ph_3P$, Z = COMe, COOEt, $CONH_2$ or CN; $R_3P = PhMe_2P$, Z = COPh), with sodium acetate.

Introduction

Recently, we reported [1] a simple preparation of π-allylphosphonium ylide complexes of palladium(II) in high yield by the reaction of bis(allylphosphonium)hexahalogenodipalladates with sodium acetate. This preparation is superior to others [2] because air-sensitive ylides do not need to be handled. NMR studies of such π-allylphosphonium ylide complexes of palladium(II) in dimethylsulfoxide-d_6 suggested that the allyl anion component is coordinated to the palladium atom as a phosphonium-π-allyl ligand, which has a strong σ-interaction with the palladium atom, or as a dynamic allyl ligand. On the basis of these and other chemical and physical studies on the complexes, the structure was concluded to be that of a monomeric phosphonium-π-allyl ylide dihalogenopalladate(II).

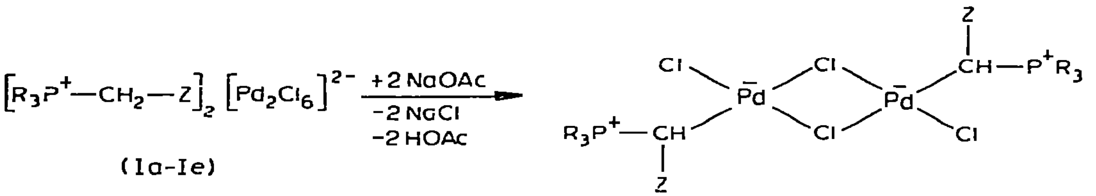
We have applied this convenient technique to prepare in high yield the palladium complexes of stabilized phosphonium ylides involving electron-withdrawing substituents such as acyl, ethoxycarbonyl, carbamoyl, and cyano groups by treating the corresponding bis(phosphonium)hexachlorodipalladates, $[R_3P^+{-}CH_2{-}Z]_2[Pd_2Cl_6]^{2-}$ (Ia, Z = COPh; Ib, Z = COMe; Ic, Z = COOEt; Id, Z = $CONH_2$; Ie, Z = CN) with sodium acetate. The NMR and IR spectral behavior of these stabilized ylide complexes of palladium(II) are compared with the π-allylphosphonium ylide complexes of palladium(II).

Results and discussions

The starting materials, bis(carbonyl or cyanomethylphosphonium)hexachlorodipalladates (Ia-Ie), are readily obtained as brown needles by treating the substituted phosphonium chloride with disodium tetrachloropalladate in methanol at room temperature (eqn. 1). This anion exchange reaction is the same as that used for the preparation of bis(allylphosphonium)hexahalogenodipalladate, $[R_3P^+{-}CH_2{-}CH{=}CH_2]_2[Pd_2X_6]^{2-}$ [1]. In Table 1, yields, melting points, and analyses are listed. It is concluded that the organic part of the original phosphonium salt does not coordinate to the metal, because the NMR and IR spectra of the products were essentially identical with those of the original phosphonium chlorides.

$$2\,[R_3P^+{-}CH_2{-}Z]Cl^- + 2\,Na_2PdCl_4 \xrightarrow[MeOH]{-4\,NaCl} [R_3P^+{-}CH_2{-}Z]_2\,[Pd_2Cl_6]^{2-} \qquad (1)$$

(Ia-Ie)



(2)

(IIa-IIe)

a, $R_3P = PhMe_2P$, $Z = COPh$
b, $R_3P = Ph_3P$, $Z = COMe$
c, $R_3P = Ph_3P$, $Z = COOEt$
d, $R_3P = Ph_3P$, $Z = CONH_2$
e, $R_3P = Ph_3P$, $Z = CN$

The addition of sodium acetate to a methanol suspension of Ia-Ie afforded the corresponding phosphonium ylide complexes of palladium(II) (IIa-IIe) as yellowish-orange solids in 74-85% yield (eqn. 2). Their analyses, melting points, and yields are listed in Table 2 and infrared spectral data are summarized in Table 3.

According to Adams and Chandler [3], *trans*-$[Pd_2L_2Cl_4]$ complexes exhibit one terminal (370-345 cm^{-1}) and two bridging (310-300 and 280-250 cm^{-1} ν(Pd—Cl) stretching bands. The infrared spectra of IIa-IIe in the solid state exhibit one terminal Pd—Cl stretching frequency at 343-320 cm^{-1} and two bridging Pd—Cl stretching vibrations at 318-290 and 260-250 cm^{-1}, suggesting that two terminal chloride ions in Ia-Ie are substituted by the carbanion center of stabilized phosphonium ylides to give a dimer complex, di-μ-chlorobis(trialkylphosphoniumacyl or cyanomethyl)dichlorodipalladate(II) (IIa-IIe). The carbonyl stretching frequencies are shifted to lower region by only 38-50 cm^{-1} in IIa-IId, which excludes the coordination of the carbonyl group to the palladium atom as in IIa'.

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR BIS(PHOSPHONIUM)HEXACHLORODIPALLADATES Ia-Ie

	R_3P	Z	Yield	M.p.	Color	Analysis found (calcd.) (%)		
			(%)	(°C)		C	H	N
Ia	$PhMe_2P$	COPh	79	178.5-179.5	Brown	41.10 (40.97)	3.80 (3.87)	
Ib	Ph_3P	COMe	82	208.0-209.5	Pale-brown	47.66 (47.40)	3.30 (3.01)	
Ic	Ph_3P	COOEt	80	202.0-204.0	Pale-brown	47.00 (47.01)	3.84 (3.94)	
Id	Ph_3P	$CONH_2$	80	194.0-196.0	Brown	45.35 (45.06)	3.58 (3.59)	2.48 (2.63)
Ie	Ph_3P	CN	72	168.5-170.0	Dark-brown	46.88 (46.64)	3.25 (3.33)	2.65 (2.72)

TABLE 2

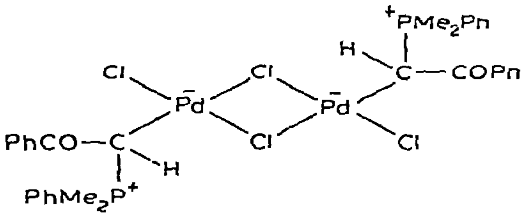
PHYSICAL AND ANALYTICAL DATA FOR PHOSPHONIUM YLIDE COMPLEXES OF DIHALOGENOPALLADATE IIa-IIe

	R_3P	Z	Yield	M.p.	Color	Analysis found (calcd.) (%)		
			(%)	(°C)		C	H	N
IIa	$PhMe_2P$	COPh	85	280 dec.	Pale yellowish-orange	44.77 (44.32)	4.06 (3.95)	
IIb	Ph_3P	COMe	80	194-196 dec.	Pale yellowish-orange	50.80 (50.89)	4.13 (3.86)	
IIc	Ph_3P	COOEt	84	180-182 dec.	Pale yellowish-white	50.20 (50.27)	4.11 (4.03)	
IId	Ph_3P	$CONH_2$	81	270 dec.	Pale yellowish-white	50.42 (50.60)	3.79 (3.66)	2.91 (2.82)
IIe	Ph_3P	CN	74	165 dec.	Orange	50.41 (50.19)	3.28 (3.37)	2.87 (2.93)

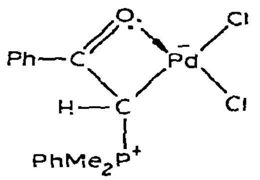
TABLE 3

SELECTED INFRARED DATA (KBr)

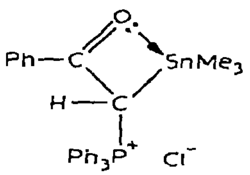
Compound	Absorption (cm^{-1})			
	ν (C=O)	ν (C≡N)	$\Delta\nu$ (C=O)	ν (Pd—Cl)
Ia	1675			330 s
IIa	1637		38	330 m (terminal) 290 (sh) 260 m (bridging)
Ib	1720			329 s
IIb	1673		47	335 m (terminal) 295 (sh) 255 m (bridging)
Ic	1730			330 s
IIc	1683		50	330 m (terminal) 295 (sh) 255 m (bridging)
Id	1698			320 s
IId	1650		48	343 m (terminal) 318 m 260 m (bridging)
Ie		2220 m		325 s
IIe		2195 m 2220 m		320 m (terminal) 290 ~ 250 (br) (bridging)



(IIa)



(IIa')



(III)

The ν(C=O) absorption of [α-(trimethylstannyl)phenacyl]triphenylphosphonium chloride (III) showed a very intense absorption band at 1480 cm^{-1} [4] ($\Delta\nu$(C=O) 185 cm^{-1}; compare with ν(C=O) 1665 cm^{-1} of $[Ph_3P^+—CH_2COPh]Cl^-$) indicative of intramolecular coordination of carbonyl group to a tin atom as an oxy-π-allyl ligand. Recently, Tanaka et al. [5] reported similar sulfur ylide complexes of platinum and palladium in which the coordination of the carbonyl group did not occur [ν(C=O) 1629-1650 cm^{-1}]. This is also confirmed by X-ray and NMR spectroscopic studies [6].

NMR spectral data for Ia-Ie and IIa-IIe are summarized in Table 4. The NMR spectra of Ia-Ie showed a characteristic methylene doublet signal (δ 5.00-5.62) due to coupling with the phosphorus atom. The patterns are identical with those of the original phosphonium chlorides.

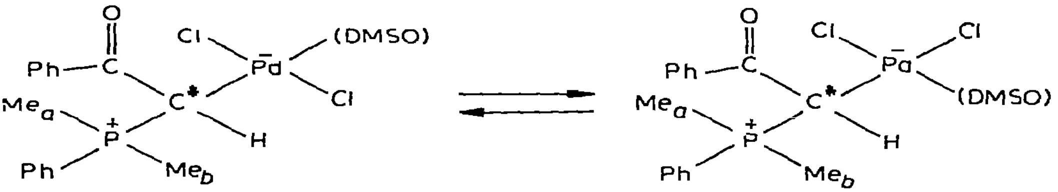
On the other hand, the NMR spectra of the ylide complexes IIa-IIe exhibited characteristic peaks due to methine protons. The appearance of two doublet signals for the methine proton of the phosphonium ylide may be ex-

TABLE 4

NMR SPECTRA OF BIS(PHOSPHONIUM)HEXACHLORODIPALLADATES Ia-Ie AND PHOSPHONIUM YLIDE COMPLEXES OF BIS(DICHLOROPALLADATE) IIa-IIe IN DIMETHYLSULFOXIDE-d_6

Compound	Chemical shift (δ ppm) and [coupling constant (Hz)]					
	P^+—CH_n (n = 2 for I, n = 1 for II)			Other signals		Assignment
Ia	5.00d[14.0]	2H		8.3-7.5m	10H	Ph—P and PhCO
				2.40d[14.0]	6H	CH_3—P
Ib	5.47d[12.0]	2H		8.0-7.5m	15H	Ph—P
				2.37s	3H	CH_3—CO
Ic	5.17d[14.0]	2H		7.8-7.2m	15H	Ph—P
				4.03q[7.0]	2H	CH_2—O—CO
				1.14t[7.0]	3H	CH_3—C
Id	5.00d[15.0]	2H		8.0-7.7m	15H	Ph—P
				7.5(br)	2H	H_2N—CO
Ie	5.62d[15.0]	2H		8.0-7.7m	15H	Ph—P
IIa	5.15d[4.0]	0.6H	1H	8.3-7.5m	10H	Ph—P
	4.15d[5.6]	0.4H		2.43d[10.0]	3H	CH_3(a)—P
				2.20d[10.0]	3H	CH_3(b)—P
IIb	5.41d[3.0]	0.5H	1H	8.0-7.5m	15H	Ph—P
	5.10d[6.0]	0.5H		2.25s	3H	CH_3—CO
IIc	3.94d[8.3]	0.6H	1H	8.0-7.5m	15H	Ph—P
	3.73d[6.0]	0.4H		3.98q[7.0]	2H	CH_2—O—CO
				0.98t[7.0]	3H	CH_3—C
IId	3.90(br)		1H	8.0-7.5m	15H	Ph—P
				6.6(br)	2H	H_2N—CO
IIe	3.82d[4.0]	0.5H	1H	8.2-7.4m	15H	Ph—P
	3.60[4.0]	0.5H				

plained by the monomeric structure of IIa in the solution of DMSO-d_6 including two equilibrium isomers. Moreover, the two methyl groups on the phosphorus atom of the ylide complex (IIa) exhibited two sets of doublet signals in equal intensities [δ 2.20 (J(P—H) 10 Hz) and δ 2.43 (J(P—H) 10 Hz)]. The separation of two methyl protons in IIa is ascribed to the presence of the neighboring asymmetric carbon atom, which is induced by the σ-bond formation between ylidic carbon atom with the palladium atom. The dissociation of IIa-IIe into monomeric structures in polar solvent was supported by the cryoscopic molecular weight determination of IIe in nitrobenzene (monomeric IIe calcd. mol. wt. 476. Found mol. wt. 587).



(3)

TABLE 5

THE PREPARATION OF BIS(PHOSPHONIUM)HEXACHLORODIPALLADATES Ia-Ie AND PHOSPHONIUM YLIDE COMPLEXES OF BIS(DICHLORO-PALLADATE) IIa-IIe

Phosphonium salt mg (mmol)		$PdCl_2$ [a] mg (mmol)	NaCl [a] mg (mmol)	NaOAc [b] mg (mmol)	Time (h)	Product	Yield mg (%)
$(PhMe_2P^+{-}CH_2COPh)Cl^-$	292(1.0) [c]	177(1.0)	177(3.0)		inst.	Ia	371(79)
$(Ph_3P^+{-}CH_2COMe)Cl^-$	354(1.0) [c]	177(1.0)	177(3.0)		inst.	Ib	430(82)
$(Ph_3P^+{-}CH_2COOEt)Cl^-$	384(1.0) [c]	177(1.0)	177(3.0)		inst.	Ic	450(80)
$(Ph_3P^+{-}CH_2CONH_2)Cl^-$	356(1.0) [c]	177(1.0)	177(3.0)		inst.	Id	426(80)
$(Ph_3P^+{-}CH_2CN)Cl^-$	337(1.0) [c]	177(1.0)	177(3.0)		inst.	Ie	371(72)
Ia	469(0.5) [d]			90(1.1)	5	IIa	369(85)
Ib	532(0.5) [d]			90(1.1)	10	IIb	417(84)
Ic	562(0.5) [d]			90(1.1)	10	IIc	422(80)
Id	532(0.5) [d]			90(1.1)	15	IId	432(81)
Ie	515(0.5) [d]			90(1.1)	10	IIe	355(74)

[a] Na_2PdCl_4 was prepared in methanol (10 ml) at room temperature for 5 h. [b] Added as a methanol solution (5 ml). [c] Added as a methanol solution (10 ml). [d] Suspension in methanol (10 ml).

Experimental

IR spectra were measured on a Jasco Model DS 403-G spectrometer in KBr disks. NMR spectra were recorded on a Jeol C-60HL spectrometer in dimethylsulfoxide-d_6 using tetramethylsilane as an internal standard at 25°. All operations of the preparative procedure were performed at room temperature without any precautions to exclude oxygen or moisture. Starting phosphonium chlorides were obtained by the reaction of the corresponding trialkylphosphines with phenacyl chloride, α-chloroacetone, ethyl chloroacetate, α-chloroacetamide, and chloroacetonitrile, respectively.

Preparations of Ia and IIa are described as representative examples, and those of other compounds are listed in Table 5.

Bis(phenacylphenyldimethylphosphonium)hexachlorodipalladate (Ia)

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 phenacylphenyldimethylphosphonium chloride (292 mg, 1.0 mmol) was added dropwise to the above filtrate. Reaction occurred instantaneously giving brown needles of Ia, which were filtered and washed with a large volume of water in order to remove sodium chloride. The Ia was isolated in 79% yield (371 mg).

μ-Dichloro-bis[chloro(phenyldimethylphosphoniumphenacylide)palladium(II) (IIa)

To a methanol (10ml) suspension of Ia (469 mg, 0.5 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 5 h at room temperature. The color of the precipitate changed gradually from brown to yellowish orange. The IIa was isolated by filtration and purified by washing with large volumes of water to remove sodium chloride; yield of IIa was 85% (369 mg).

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