

## PALLADIUM(II) COMPLEXES WITH KETO-STABILIZED PHOSPHONIUM, ARSONIUM AND PYRIDINIUM YLIDES \*

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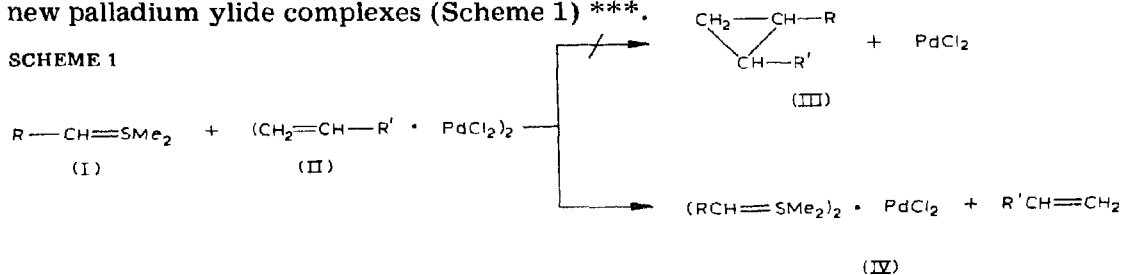
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### Summary

Complexes of the general formula  $(\text{Ylide})_2 \cdot \text{PdCl}_2$  arise in high yields when keto-stabilized alkylphosphoranes ( $\text{XY}_2\text{P}=\text{CHCOR}$ ), arsonanes ( $\text{Ph}_3\text{As}=\text{CHCOR}$ ) and pyridinium ylides ( $\text{C}_5\text{H}_5\text{N}^+-\text{CHCOR}$ ) are treated with styrene- or benzonitrile- $\text{PdCl}_2$  complexes. Evidence is given for a *trans* square planar structure in the solid state and for epimeric equilibrium between *trans* square planar structures in solution for all the new complexes. Cross exchange experiments between ligands of different series are also described.

### Introduction

As already reported, [1] sulphonium ylides were treated with palladium(II) olefin complexes in the hope that ylides would react with such electrophilic olefins to give cyclopropanes. However, both reactive and stabilized sulphonium ylides did not react with the complexed olefins, but rather displaced them to give new palladium ylide complexes (Scheme 1) \*\*\*.

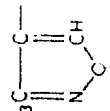
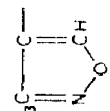


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\*\*\* Allylpalladium complexes also gave IV upon reaction with dimethylsulphonium phenacylide [2], but were alkylated at the  $\alpha$  (allylic) position by the anion of methyl methylsulphonyl acetate [3]. Recently, cyclopropanes were obtained from olefins and sulphonium ylides in the presence of  $\text{Cu}(\text{Acac})_2$ , probably through a Cu-carbene activated species [4].

TABLE I  
 COMPLEXES FROM PHOSPHONIUM YLIDES AND PdCl<sub>2</sub> [R-CO-CH=P(XY<sub>2</sub>)<sub>2</sub> · PdCl<sub>2</sub> (VII)

Compound R	X	Y	M.p. <sup>a,b</sup> (°C)	Yields (%)	Formula	Elemental analyses found (calcd.) (%)			
						C	H	Cl	P
VIIa	CH <sub>3</sub>	Ph	156-157	98	C <sub>42</sub> H <sub>38</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd	61.5 (62.0)	5.6 (4.7)	8.6 (8.7)	7.4 (7.4)
VIIb	CH <sub>3</sub>	Ph	164-166	95	C <sub>32</sub> H <sub>34</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd	57.3 (55.7)	5.1 (4.9)	10.3 (10.3)	9.3 (9.0)
VIIc	CH <sub>3</sub>	Me	176-177	92	C <sub>22</sub> H <sub>30</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd	47.1 (46.7)	5.3 (5.3)	13.0 (12.6)	11.3 (11.0)
VIIId	C <sub>6</sub> H <sub>5</sub>	Ph	216-218	98	C <sub>57</sub> H <sub>42</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd	66.1 (66.4)	4.4 (4.5)	7.9 (7.6)	6.9 (6.6)
VIIe	C <sub>6</sub> H <sub>5</sub>	Me	215-217	98	C <sub>42</sub> H <sub>38</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd	61.5 (61.9)	4.7 (4.5)	9.0 (8.7)	7.9 (8.2)
VIIIf	C <sub>6</sub> H <sub>5</sub>	Ph	221-222	94	C <sub>32</sub> H <sub>34</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Pd	56.0 (55.7)	5.0 (4.9)	10.0 (10.3)	8.7 (9.0)
VIIg		Ph	195-197	95	C <sub>38</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Pd	55.0 (55.4)	4.5 (4.4)	8.7 (8.6)	7.6 (7.5)
VIIh		Ph	160	90	C <sub>38</sub> H <sub>32</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Pd <sub>2</sub>	38.0 (38.3)	3.9 (3.7)	16.5 (16.2)	7.4 <sup>d</sup> (7.1)

<sup>a</sup> Uncorrected. <sup>b</sup> Partial decomposition often occurred some 10-20° C before melting. <sup>c</sup> A dimeric, halogen-bridged structure is suggested by its stoichiometry.

<sup>d</sup> N: found 3.5%; calcd. 3.2%. Pd: found 24.3%; calcd. 24.2%.

It was of interest to extend this work by studying the reaction of other ylides (nitrogen, phosphorus or arsenic) with palladium(II) olefin complexes. Therefore, some stabilized phosphonium ylides and a few arsenic and nitrogen ylides were treated with both styrene- and benzonitrile-palladium chloride complexes.

Reported reactions between phosphonium ylides and metal complexes fall into two groups. All cases where the ylide reacts with an activated ligand to give rise to a new species form the first group, while the second includes all reactions where one or more ligands of the reacting complex are displaced by one or more moles of the ylide. To the first class belong the reactions between Cr, Mo, and W carbonyls and alkyl phosphonium ylides to form complexes of general formula  $[(\text{Ph}_3\text{PCHCO})\text{M}(\text{CO})_5]^- [\text{HX}]^+$ , in analogy to the betaines of the Wittig reaction [5]. In other cases, the Wittig reaction goes to completion \*, as when hexaphenylcarbodiphosphorane is treated with  $\text{Mn}(\text{CO})_5\text{Br}$  [6], or certain triphenylphosphines with  $\text{Mo}(\text{CO})_6$  or  $\text{Ir}(\text{CO})_5$  [7]. To the second class belong the reactions between alkyl phosphoranes [5,9] or other special phosphoranes [10,11] and Cr, Mo, V, W, Fe carbonyls to form complexes of general formula  $(\text{CO})_{x-n}\text{M}(\text{ylide})_n$ .  $\alpha_1\beta$ -Unsaturated phosphoranes [12] can displace two ligands from metalcarbonyl complexes and cyclopentadienyl triphenylphosphoranes [13] can displace three ligands.

A number of Cu, Ag, Au, Ni and Cr complexes with phosphonium diylides as ligands are also reported [14]. In the case of keto-stabilized phosphoranes, two different types of complexes can arise, depending on carbon-metal or oxygen-metal bond formation [15,16]. Much less information is available on the reactions of arsenic ylides or nitrogen ylides with metal complexes [17].

## Results and discussion

### *Complexes with phosphonium ylides*

When triphenylphosphonium phenacylide (VI<sub>d</sub>) was treated with the styrene-PdCl<sub>2</sub> adduct in benzene or chloroform at room temperature, the complex VII<sub>d</sub> was obtained as a yellow precipitate and styrene was liberated into the solution. The same complex could be obtained also upon reaction of VI<sub>d</sub> with PdCl<sub>2</sub> · (PhCN)<sub>2</sub> or directly upon reaction of VI<sub>d</sub> with PdCl<sub>2</sub> in a DMSO solution. Analysis of the reaction mixture revealed no reaction between styrene or benzonitrile and the ylide (see Experimental). Complexes VII<sub>a</sub>–h could similarly be obtained by reacting the corresponding ylides VI<sub>a</sub>–h with an olefin-PdCl<sub>2</sub> adduct or with the benzonitrile-PdCl<sub>2</sub> adduct. The carbonyl and phosphorus substituents in the ylides were chosen to give easily identifiable NMR signals to facilitate spectroscopic study of the solution phenomena. Phosphonium salts V also react readily with (PhCN)<sub>2</sub> · PdCl<sub>2</sub> in chloroform to give stable adducts VIII, which are transformed by a base into the corresponding more stable complexes VII (Scheme 2).

All complexes VII<sub>a</sub>–h are very stable yellow crystalline compounds, moderately soluble in DMSO, and slightly soluble in CHCl<sub>3</sub>. Solubility depends mainly on the phosphonium group; it is higher for the dimethylphenylphosphonium than

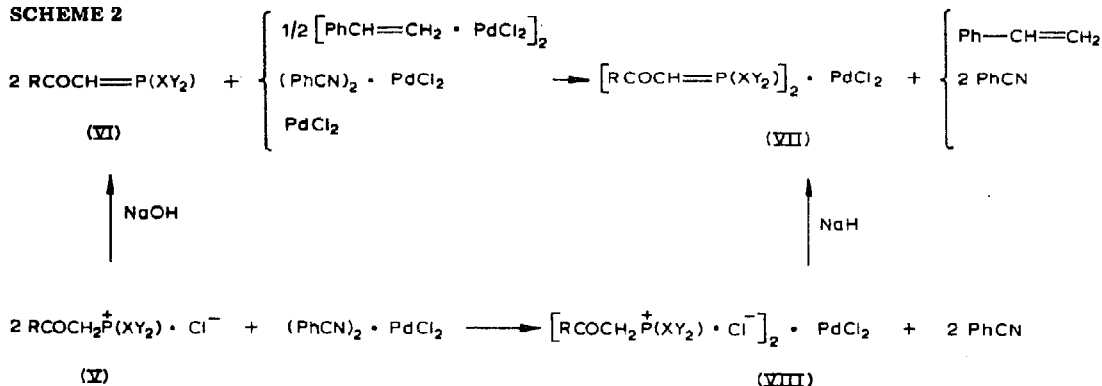
\* Casey [8] reported that an olefination reaction, involving the metal carbon bond, occurred when some phosphoranes were treated with carbene metal complexes. Alkenes or 1,4-dicarbonyls were formed in low yields when alkyl or carbonyl stabilized phosphoranes were refluxed with iron pentacarbonyl [9].

TABLE 2  
NMR PARAMETERS <sup>a</sup> FOR [RCOCH=P(XY<sub>2</sub>)<sub>2</sub>]<sub>2</sub> · PdCl<sub>2</sub> (VII)

Compound R	X	Y	CH		R	X		Y		CH(ylide)		CH <sub>2</sub> (salt) <sup>c</sup>			
			δ(J)	δ(J)		δ(J)	δ(J)	δ(J)	δ(J)	δ(J)	δ(J)	δ(J)	δ(J)		
VIIa CH <sub>3</sub>	Ph	Ph	5.14	2.53	2.53										
			(s)	(2.0)											
VIIb CH <sub>3</sub>	Me	Ph	5.18	2.63	2.63										
			(s)	(2.0)											
			4.58	2.18		2.68									
			(s)	(2.5)			(14.0)								
			4.62	2.26	2.68										
			(s)	(2.5)		(14.0)									
VIIc CH <sub>3</sub>	Ph	Me	4.32	2.34	2.34										
			(s)	(2.5)		(13.5)									
VIIe C <sub>6</sub> H <sub>5</sub>	Me	Ph	4.34	2.38	2.38										
			(s)	(2.5)											
VIIe C <sub>6</sub> H <sub>5</sub>	Me	Ph	5.24	2.48	2.48										
			(s)	(14.0)											
			5.33	2.67		2.67									
			(s)	(14.0)											
VIIe C <sub>6</sub> H <sub>5</sub>	Ph	Me	4.92	2.08	2.08										
			(s)	(14.0)		(14.0)									
VIIe C <sub>6</sub> H <sub>5</sub>	Ph	Me	4.99	1.71	1.71										
			(s)	(14.0)		(14.0)									
<sup>b</sup> VIIg	CH <sub>3</sub> C	Ph	4.82	2.44	2.44										
			(2)	(s)		(s)									
<sup>b</sup> VIIg	CH <sub>3</sub> C	Ph	4.92	2.46	2.46										
			(2)	(s)		(s)									
<sup>b</sup> VIIh	CH <sub>3</sub> C	Ph	4.56	2.47	2.47										
			(2)	(s)		(s)									
<sup>b</sup> VIIh	CH <sub>3</sub> C	Ph	4.64	2.47	2.47										
			(2)	(s)		(s)									

<sup>a</sup> The spectra were taken at 35° C, CDCl<sub>3</sub> sol. (0.05–0.1 mol/l). Values for the most abundant isomer are reported in the first line for each compound. <sup>b</sup> measured in ppm, <sup>c</sup> *J* in Hz (all *J* refer to doublets due to coupling with phosphorus). <sup>d</sup> Prepared from stoichiometric amounts of (PhCN)<sub>2</sub> · PdCl<sub>2</sub> and ylides in the NMR tube. In the last two columns values for methine protons of some corresponding ylides and for methylene protons of some salts are reported. See also ref. 21. <sup>e</sup> Broad signals; see ref. 20 for a possible explanation.

## SCHEME 2

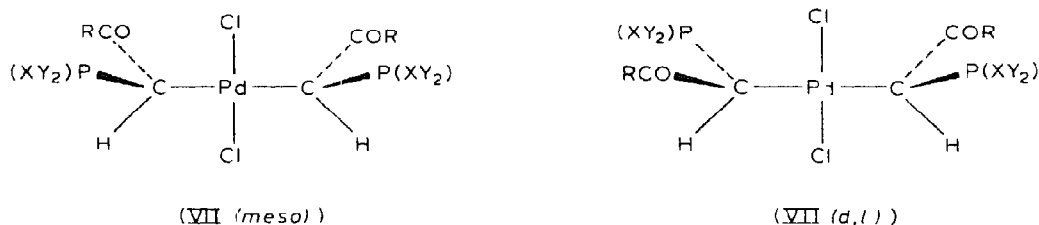


for the triphenylphosphonium group. The complexes precipitate from benzene or chloroform solutions in a fairly pure state; they can be recrystallized from DMSO/water mixtures. Yields, analytical and physico-chemical data are reported in Table 1, NMR data in Table 2 and IR data in Table 3.

The general structure  $(\text{ylide})_2 \cdot \text{PdCl}_2$  is in agreement with analytical data for all complexes except VIIh, for which a dimeric structure  $(\text{ylide} \cdot \text{PdCl}_2)_2$  with two chlorines bridging the palladium atoms is suggested.

In the IR spectra (nujol mulls), the carbonyl stretch at  $1625\text{--}1645 \text{ cm}^{-1}$  and the absence of the enolate band at  $1520\text{--}1530 \text{ cm}^{-1}$  suggest bonding of the ylides to palladium through the  $sp^3$  carbon rather than the enolate oxygen. In fact, in certain alkyltin chloride complexes with triphenylphosphonium acetyl, benzoyl or carbethoxy methylides, a strong enolate band ( $1465\text{--}1510 \text{ cm}^{-1}$ ) is present, in agreement with an X-ray analysis showing tin bound to oxygen. In other complexes of the same series with a tin-carbon bond, and also in  $(\text{PhCOCH}=\text{SMe}_2)_2 \cdot \text{PdCl}_2$  with a Pd-carbon bond, the carbonyl stretching band appears at  $1675\text{--}1740 \text{ cm}^{-1}$ . In the far IR region (solid state), a single palladium chlorine band centered at  $320\text{--}330 \text{ cm}^{-1}$  is indicative of a *trans* configuration for complexes VIa-g [18].

The data reported above are in agreement with both a *meso* and a *d, l trans* square planar structure for complexes VIIa-g.



### Complexes with arsonium and pyridinium ylides

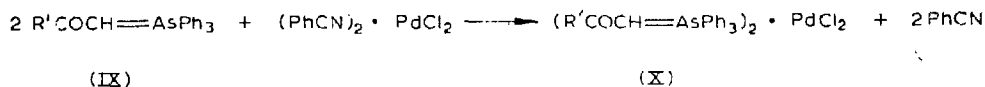
Triphenylarsonium acetyl methylide IXa and phenacylide IXb smoothly react with the benzonitrile-palladium chloride adduct in benzene. Complexes Xa and Xb slowly precipitate as crystalline compounds while benzonitrile is liberated.

Also pyridinium ylides XIa and XIb react similarly to give the corresponding complexes XIIa and XIIb in high yields. The stable crystalline compounds derived

TABLE 3  
 PROMINENT PEAKS IN THE IR SPECTRA OF COMPLEXES OF THE TYPE (YLIDE)<sub>2</sub> · PdCl<sub>2</sub><sup>a</sup>

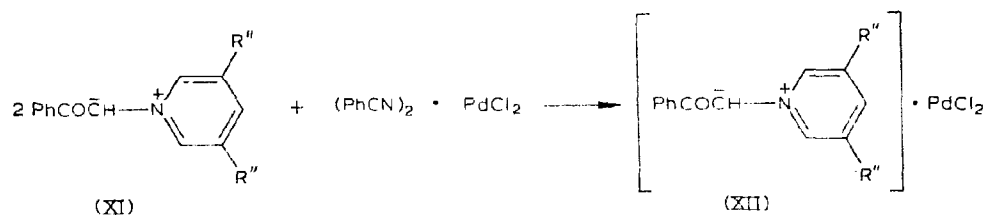
Compound	IR peaks (cm <sup>-1</sup> )																		
VIIa	3050	1665	1470	1430	1280	1140	1100	740	710	680	515	500	330	470	460	420	340	315	
VIIb	3050	2990	2915	1635	1430	1340	1300	1285	1145	1110	910	770	730	500	470	435	320	270	
VIIc	3050	2980	2920	1640	1430	1340	1280	1140	1105	920	830	745	680	470	435	320	270		
VIIId	3050	1625	1480	1430	1290	1180	1100	1015	740	710	680	510	395	325					
VIIe	3050	2920	1625	1570	1430	1320	1290	1180	1100	1015	890	740	680	490	390	325			
VIIIf	3050	2980	2910	1620	1570	1430	1320	1300	1290	1180	1110	1020	930	740	680	500	470	415	325
VIIg	3080	3050	2990	2920	1630	1435	1400	1315	1125	1100	1020	900	810	735	680	505	490	370	325
VIIh	3080	3050	2980	2910	1645	1575	1400	1305	1130	1105	950	925	740	680	485	470	330		
Xa	3050	2905	1635	1470	1430	1265	1130	1075	990	840	730	680	460	405	350	330			
Xb	3050	1620	1480	1430	1280	1175	1010	740	720	680	485	470	460	335	285				
XIIa	3050	2960	1650	1630	1470	1440	1205	990	760	675	580	560	460	320					
XIIb	3050	2920	1655	1630	1595	1440	1260	1210	910	680	460	320							

<sup>a</sup> The spectra were divided into three portions: 3200–2800; 1700–500 and 500–250. Only prominent peaks of each portion are reported. Nujol mull for the portion 3200–500 cm<sup>-1</sup> and solid state for 500–250 cm<sup>-1</sup>.



(Xa) R' = Me ; m.p. = 174–175 °C ; yield 98%

(Xb) R' = Ph ; m.p. = 201 °C ; yield 95%



(XIIa) R'' = H ; m.p. 222–225 °C ; yield 95%

+ 2 PhCN

(XIIb) R'' = Me ; m.p. = 149 °C ; yield 90%

from arsonium ylides (Xa, b) are pale yellow, while complexes derived from pyridinium ylides (XIIa, b) are orange-yellow. As for phosphonium ylide complexes VIIa–g, analytical data (see Experimental) are in accord with a general formula (ylide)<sub>2</sub> · PdCl<sub>2</sub> for both type of complexes. In the IR spectra (nujol mulls), carbonyl stretching bands are present at 1635 and 1620 cm<sup>-1</sup> respectively for Xa and Xb and at 1650 cm<sup>-1</sup> for XIIa and XIIb. In the far IR region (solid state), bands attributable to Cl–Pd–Cl bonds in a *trans* configuration appear at 330 and 335 cm<sup>-1</sup> for Xa and Xb and at 320 cm<sup>-1</sup> for XIIa and XIIb. These data show that the complexes with arsonium and pyridinium ylides, as those with phosphonium and sulphonium [1] ylides, exist in a *trans* square planar structure with the two ylidic units bound to palladium through the sp<sup>3</sup> carbon atom.

### Complexes in solution

According to the NMR spectra (see Table 2) all new complexes exist in solution as two isomeric species in equilibrium, most probably the two *trans* forms: *meso* and *d, l*. In both these structures the two ylidic ligands are exchangeable through a symmetry operation and they are therefore isochronous and must give rise to the same signals. Furthermore NMR spectra of both forms depend upon the substituents attached to a single onium atom (phosphorus or arsenic). When the three substituents at the onium atom are equal to each other (X = Y), they are magnetically equivalent; while when X ≠ Y, the two Y substituents are diastereotopic because of the dissymmetric ylidic carbon atom and therefore should give rise to two different signals.

Two characteristic spectra of these complexes are reported in Fig. 1 (A and B). In case A, the two Y substituents (two phenyl groups) form an unresolved multiplet, while X, (a methyl group) gives rise to signals at δ 2.69 and 2.72 (<sup>2</sup>J<sub>(PCH)</sub> = 14 Hz) due to the presence of two stereoisomers in solution in 56 : 44 ratio. Two distinct signals for the CH bound to palladium at δ 4.82 and 4.92 (<sup>2</sup>J<sub>(PCH)</sub> = 2 Hz) and two singlets for the CH<sub>3</sub> and the CH of the isoxazole nucleus appear at δ 2.44 and 2.46 and at δ 9.27 and 9.60 respectively. In case B, the two diastereo-

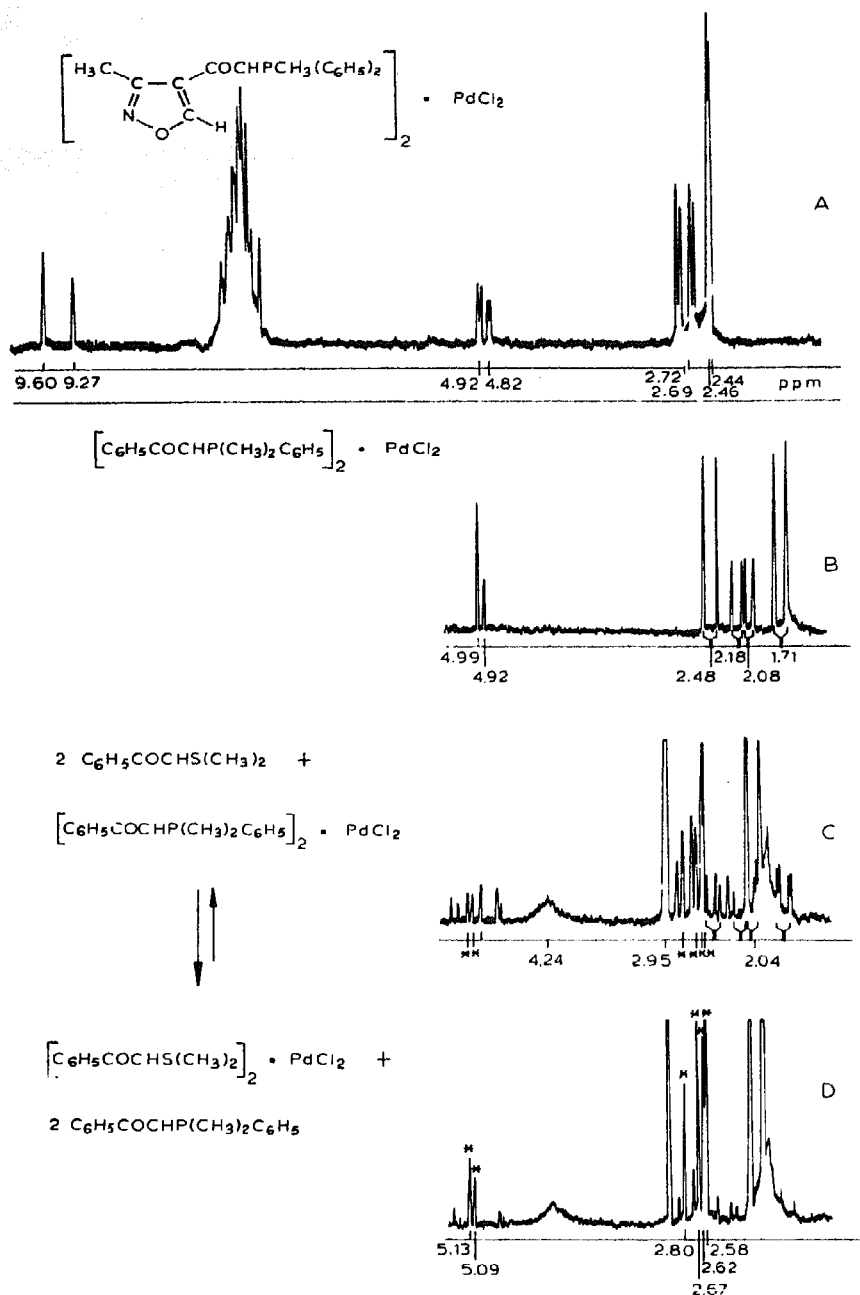


Fig. 1: NMR spectra (CDCl<sub>3</sub>) of complexes VIIg (A) and VIIf (B), Ylide exchange in complexes in CDCl<sub>3</sub>: the NMR spectrum of a mixture of complex VIIf and ylide I in a 1 : 2 molar ratio taken after 15 min (C) and after 1 h (complete equilibration) (D).

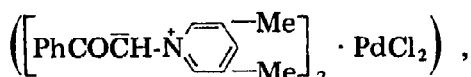
topic groups (Y = Me) of the most abundant isomer (73%) give rise, as expected, to two distinct signals at  $\delta$  1.71 and 2.48, ( $^2J_{(\text{PCH})} = 14$  Hz) while the methine proton appears as a singlet at  $\delta$  4.99. The corresponding signals for the less abun-



dant isomer (27%) appear at  $\delta$  2.08 and 2.18, ( ${}^2J_{\text{PCH}} = 14$  Hz) and  $\delta$  4.92 respectively.

Some interesting conclusions can be drawn from analysis of the data reported on Table 2, in particular regarding the chemical shifts and coupling constants of the methine protons. Complexation of phosphoranes with palladium causes a low field shift of  $\sim 1$  ppm, indicative of an electron drift from carbon to metal. Protonation of the ylide causes an even greater low field shift (1.7 ppm); the difference between the two indicates a certain polarization of the C—Pd bond, probably due to a back donation. Also,  ${}^2J_{\text{PCH}}$  for the methine varies widely from the ylide (20–24 Hz) to the salt (12–13 Hz) to the complex (0–2 Hz), while  ${}^2J_{\text{PCH}}$  for other groups attached to phosphorus remains practically unchanged. Since values of  ${}^2J_{\text{PCH}}$  in phosphonium salts are assumed to be negative\*, the variation observed in our case from salts (12–13 Hz) to complexes (0–2 Hz) shows a strong positive contribution upon substitution of hydrogen by palladium. The observed positive contribution is consistent with the higher *s* character of the carbon-to-phosphorus bond orbital in the complexes caused by the increased *p* character of the carbon-to-palladium bond orbital.

The complexes from arsonium ylides (X) and pyridinium ylides (XII) reveal similar trends. They exist in solution as mixtures of two stereoisomers in equilibrium, as shown by the NMR spectra of Xa,  $(\text{CH}_3\text{COCH}=\text{AsPh}_3)_2 \cdot \text{PdCl}_2$ , (singlets at  $\delta$  2.51 and 2.42 ( $\text{CH}_3\text{CO}$ ) and singlets at  $\delta$  5.32 and 5.26 ( $\text{CH}=\text{As}$ ) and of XIIb,

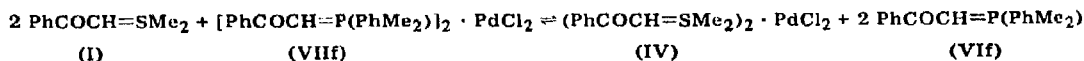


(singlets at  $\delta$  2.52 and 2.40 (Me) and singlets at  $\delta$  6.49 and 6.51 (CH-N)). The ratio of the isomers is 60 : 40 in the first case and 1 : 1 in the second. In the case of complex Xa the chemical shift of the methine proton is intermediate between that of the starting ylide ( $\delta$  3.97) and the corresponding salt ( $\delta$  6.15) while for XIIb the difference between the chemical shifts of the ylide ( $\delta$  6.62), complex and salt ( $\delta$  6.54) is negligible.

### Exchange experiments

All synthesized complexes of the type (ylide) $_2 \cdot \text{PdCl}_2$  exchange ligands in solution. The reaction can be easily followed by NMR and can be used to compare the ligand-capacity of ylides.

One such experiment is illustrated in Fig. 1 (B, C, D). The equilibrium:



is considered. After 15 min a solution containing stoichiometric amounts of I and VIIIf shows (Fig. 1, C) displaced phosphonium ylide (Me—P at  $\delta$  2.04) and the new complex (a mixture of two stereoisomers; Me—S at  $\delta$  2.58, 2.62, 2.67 and 2.80 and CH=S at  $\delta$  5.09 and 5.13). Complete equilibration occurred after 1 h.

\* It has been observed [19] that the algebraic value  ${}^2J_{\text{PCH}}$  in a series of phosphonium compounds increases with increasing *s*-character of the carbon-to-phosphorus bond.

The equilibrium (Fig. 1, D) is shifted in favour of complex IV, and so indicates a higher ligand capacity of sulphonium compared to phosphonium ylide.

Other equilibria were also studied by mixing stoichiometric amounts of ylides and complexes in  $\text{CDCl}_3$ . In  $2 \text{ VI}f + \text{VII}c \rightleftharpoons \text{VII}f + 2 \text{ VI}c$ , almost equal amounts of the two complexes, plus minor amounts of new compounds (probably mixed complexes) were present when the equilibrium was reached (1 h). The equilibrium  $2 \text{ VI}c + \text{VII}a \rightleftharpoons \text{VII}c + 2 \text{ VI}a$  is completely shifted to the right ( $>95 : 5$ ), while  $2 \text{ XI}b + \text{VII}f \rightleftharpoons \text{XII}b + 2 \text{ VI}f$  is shifted in favour of the pyridinium ylide complex ( $\sim 70 : 30$ ). Further, equilibrium  $2 \text{ IX}a + \text{VII}c \rightleftharpoons \text{X}a + 2 \text{ VI}c$  is slightly shifted to the left ( $60 : 40$ ) and contains a large amount of mixed complexes. Finally,  $2 \text{ IX}a + \text{VII}a \rightleftharpoons \text{X}a + 2 \text{ VI}a$  is completely shifted ( $\sim 95 : 5$ ) in favour of the arsonium ylide.

These results show that the stability of complexes in solution depends both on the hetero atom of the onium group and on the kind of substituents attached to it. Onium groups with similar substitution give rise to complexes of relative stability  $\text{S} > \text{P}$ ,  $\text{As} \gg \text{P}$  and  $\text{N}(\text{pyridinium}) \geq \text{P}$  [22].

## Conclusions

Reactions between sulphonium, phosphonium, arsonium and pyridinium keto-stabilized ylides and benzonitrile- or styrene- $\text{PdCl}_2$  adducts are very similar. All cases result in complexes of general formula  $(\text{ylide})_2 \cdot \text{PdCl}_2$  which exist in a *trans* square planar structure in the solid state and in two isomeric structures in equilibrium in solution.

## Experimental

### Instrumentation

The NMR spectra were recorded on Varian A-60 and XL-100 spectrometers; chemical shifts  $\delta(\text{ppm})$  were measured from TMS as internal standard. The IR spectra were taken using Perkin-Elmer mod. 137 and 457 spectrometers; only prominent peaks are reported. Microanalyses of complexes were performed by A. Bernhardt Mikroanalytisches Laboratorium.

### Materials

The haloketones were obtained by standard halogenation of the corresponding ketones. The phosphonium salts Va-h were obtained in yields ranging from 85 to 95% by refluxing a benzene solution equimolar in the proper haloketone and the appropriate phosphine (Meybridge Chemical, England). The crystalline salts were collected and recrystallized from ethanol/ether mixtures. The phosphonium ylides VIa-h were obtained by basic treatment of an aqueous solution of the corresponding salt and crystallized from benzene before use. Salts Va-f and ylides VIa-f have already been described [20-23]. Arsonium ylides XIa, b were prepared according to the literature [24]. Pyridinium ylides XIa, b were prepared according to Kröhnke [24a] and used immediately.

### Synthesis of phosphoranes VIg and VIh

A solution of 4-bromoacetylloxazole (4.1 g, 0.02 mol) and diphenylmethyl-

phosphine (4.0 g, 0.02 mol) in benzene (50 ml) was left 48 h at room temperature. The resulting precipitate solidified after scratching and was crystallized from ethanol/ether: Vh (7.3 g, 91% yield); m.p. 210–212°C; IR (nujol): 1680, 1570, 1145, 980, 925, 745  $\text{cm}^{-1}$ .

To a solution of the phosphonium bromide Vh (4.5 g, 0.01 mol) in water (40 ml), NaOH 10% (15 ml) was added dropwise with stirring and cooling with an ice-water bath. The mixture was extracted with chloroform, the extracts dried over  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The ylide VIg (3.05 g, 95% yield) was obtained and crystallized from benzene; m.p. 109–111°C. IR (nujol): 1685, 1530, 1510, 1400, 1200, 1105, 1120, 985, 910, 750  $\text{cm}^{-1}$ . NMR( $\text{CDCl}_3$ ): 2.39 (3H, d,  $J = 14$  Hz,  $\text{CH}_3\text{-P}$ ); 2.50 (3H, s,  $\text{CH}_3\text{-C=N}$ ); 8.60 (1H, s,  $\text{CH-ON}$ ). Mass Spectrum: 323, base peak ( $\text{M}^+$ ); 241 ( $\text{Ph}_2\text{MePCHCO}^+$ ), 216 ( $\text{Ph}_2\text{MePO}^+$ ), 183  $m/e$  ( $\text{C}_{12}\text{H}_8\text{P}^+$ ).

The same procedure gave the phosphonium bromide Vh (m.p. 113–114°C from ethanol/ether; 85% yield; IR (nujol): 1680, 1575, 1140, 965, 955  $\text{cm}^{-1}$ ) and the phosphorane VIh (m.p.  $\sim 100^\circ\text{C}$  (dec.) from benzene; 88% yield; IR (nujol): 1590, 1520, 1410, 1120, 1080, 965  $\text{cm}^{-1}$ ).

#### General procedure for compounds VIIa–h

(A) From  $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$ . A solution of  $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$  [25] (1.15 g, 0.3 mmol) in chloroform (15 ml) was added dropwise to a solution of the appropriate ylide (6 mmol) in chloroform or benzene (30 ml). Complexes VIIa–h start to separate as microcrystalline precipitates within a few minutes. After 24 h standing at room temperature the precipitate was collected washed with chloroform and dried 2 h at 60–70°C under vacuum. Those complexes which are quite soluble in chloroform were collected after diluting the solutions with benzene. Sometimes recrystallization from DMSO/water (cautiously dissolving in DMSO at 40–50°C and diluting with water) was necessary to obtain analytically pure samples.

(B) From  $(\text{C}_6\text{H}_5\text{CH=CH}_2 \cdot \text{PdCl}_2)_2$ . A solution of the appropriate phosphorane (4 mmol) in benzene (15 ml) was added to a solution of  $(\text{C}_6\text{H}_5\text{CH=CH}_2 \cdot \text{PdCl}_2)_2$  [25] (0.56 g, 1 mmol) in benzene (15 ml). After 24 h standing at room temperature the complex was isolated and purified as described under (A). \*

(C) From  $\text{PdCl}_2$ . A solution of phosphorane VIc (0.39 g, 2 mmol) in benzene (15 ml) was added to a solution of  $\text{PdCl}_2$  (0.18 g, 1 mmol) in DMSO ( $\sim 30$  ml). After diluting with water ( $\sim 30$  ml) the mixture was left 24 h at room temperature. VIc was collected and purified as described under (A) (0.49 g, 86%).

#### Reaction of dimethylphenylacetyl phosphonium chloride Vc and $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$

A solution of phosphonium chloride Vc (0.5 g, 2.1 mmol) in chloroform (20 ml) was added dropwise to a solution of  $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$  (0.39 g, 1 mmol)

\* A GLC analysis at oven temperature of 100°C of the mother liquors of the reaction showed the presence of styrene (98%, calculated by using  $\omega$ -methyl styrene as internal standard). A second analysis performed at oven programmed temperature of 100–240°C,  $\Delta t = 8^\circ\text{C min}^{-1}$ , showed no higher boiling products to be present ( $\text{Ph}_3\text{PO}$  maximum limit). A Hewlett–Packard gas chromatograph mod. 5751 equipped with a flame ionization detector, and a 2 m  $\times$  2 mm i.  $\phi$  pyrex column, packed with 10% silicone-gum rubber UCCW-982 on chrom. W-AW DMCS 100–120 mesh was used.

in chloroform (10 ml). A brown-yellow precipitate separated immediately which was collected, washed thoroughly with chloroform and dried at 60°C under vacuum:  $(\text{CH}_3\text{COCH}_2\text{PPhMe}_2 \cdot \text{Cl}^-)_2 \cdot \text{PdCl}_2$  (0.59 g, 92% yield); m.p. 208–209°C. Anal.: Found: C, 41.4; H, 5.1; P, 9.8; Cl, 22.2.  $\text{C}_{22}\text{H}_{32}\text{O}_2\text{P}_2\text{Cl}_4\text{Pd}$  calcd.: C, 41.2; H, 5.0; P, 9.7; Cl, 22.2%. NMR (DMSO): 2.25 (3H, d,  $J_{(\text{HP})} = 2$  Hz;  $\text{CH}_3\text{CO}$ ); 2.28 (6H, d,  $J_{(\text{HP})} = 15$  Hz;  $\text{CH}_3\text{P}$ ); 4.42 (2H, d,  $J_{(\text{HP})} = 14$  Hz;  $\text{CH}_2\text{P}$ ).

*Reaction of  $(\text{CH}_3\text{COCH}_2\text{PPhMe}_2 \cdot \text{Cl}^-)_2 \cdot \text{PdCl}_2$  with  $\text{NaH}$*

To a solution of  $(\text{CH}_3\text{COCH}_2\text{PPhMe}_2 \cdot \text{Cl}^-)_2 \cdot \text{PdCl}_2$  (0.32 g, 0.5 mmol) in DMSO (8 ml), NaH (0.11 mmol) was added with stirring. The brownish-yellow solution turned orange-yellow. After dilution with water (20 ml) a yellow precipitate slowly separated. It was collected (0.26 g, 93% yield) and shown to be identical to the complex VIIc by comparing the IR spectrum with that of an authentic sample.

*Reaction of arsonium ylides IXa, b with  $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$*

A solution of  $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$  (2.3 g, 6 mmol) in chloroform (20 ml) was added dropwise to a solution of triphenylarsonium acetylmethylide (4.3 g, 12 mmol) in benzene (40 ml). The mixture was left 24 h at room temperature and the resulting  $(\text{CH}_3\text{COCH}=\text{AsPh}_3)_2 \cdot \text{PdCl}_2$  (Xa) was collected, washed with chloroform and dried under vacuum at 70°C (5.2 g, 98% yield). Anal.: Found: C, 55.6; H, 4.3; As, 16.9; Cl, 8.1.  $\text{C}_{42}\text{H}_{38}\text{O}_2\text{As}_2\text{PdCl}_2$  calcd.: C, 55.9; H, 4.21; As, 16.6; Cl, 7.9%. In a similar fashion  $(\text{PhCOCH}=\text{AsPh}_3)_2 \cdot \text{PdCl}_2$  (Xb) was obtained (95% yield). Anal.: Found: C, 60.5; H, 4.0; As, 14.8; Cl, 7.1; Pd, 10.8.  $\text{C}_{52}\text{H}_{42}\text{O}_2\text{As}_2\text{PdCl}_2$  calcd.: C, 60.8; H, 4.1; As, 14.6; Cl, 6.9; Pd, 10.4%.

*Reaction of pyridinium ylides XIa, b with  $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$*

A solution of  $(\text{C}_6\text{H}_5\text{CN})_2 \cdot \text{PdCl}_2$  (2.3 g, 6 mmol) in chloroform (20 ml) was added to a solution of pyridinium ylide XIa (2.2 g, 12 mmol) in benzene (30 ml). After 24 h at room temperature, the complex XIIa was collected (6.5 g, 95% yield). Anal.: Found: C, 54.3; H, 4.3; N, 4.5.  $\text{C}_{26}\text{H}_{22}\text{O}_2\text{N}_2\text{Cl}_2\text{Pd}$  calcd.: C, 54.6; H, 3.9; N, 4.2%. In the same way complex XIIb (90% yield) was obtained. Anal.: Found: C, 57.2; H, 4.8; N, 4.5; Cl, 11.2.  $\text{C}_{30}\text{H}_{30}\text{O}_2\text{N}_2\text{Cl}_2\text{Pd}$  calcd.: C, 57.4; H, 4.8; N, 4.5; Cl, 11.3%.

*Exchange experiments monitored by NMR*

In an NMR tube, a solution of the appropriate ylide (0.04–0.1 mmol) in  $\text{CDCl}_3$  (0.5 ml) was added to a solution of the complex (0.02–0.05 mmol) in  $\text{CDCl}_3$  (0.5 ml). The spectra were registered immediately and every 15 min thereafter. The relative amounts of the two complexes at equilibrium were deduced from the integration of their methine protons. Care was taken to have clear solutions throughout the experiment. Because of the persistence in the equilibrium mixtures of minor quantities of other different complexes (probably mixed or dimeric complexes), the data recorded have only an approximate value.

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