Journal of Organometallic Chemistry, 74 (1974) 143—154

PALLADIUM(II) COMPLEXES WITH SULPHONIUM YLIDES*

PIERFRANCESCO BRAVO, GIOVANNI FRONZA, CALIMERO TICOZZI
Istituto di Chimica, Politecnico di Milano, Milan (Italy)
and GIORGIO GAUDIANO
Istituto di Chimica, Università dell'Aquila, L'Aquila (Italy)
(Received January 17th, 1974)

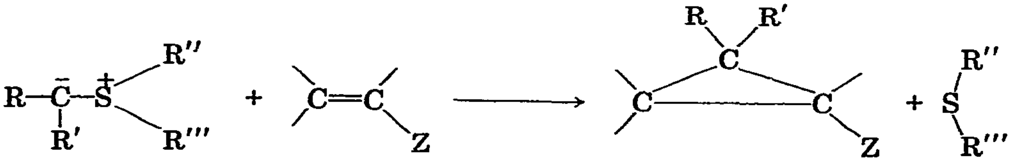
Summary

Keto-stabilized sulphonium ylides displace styrene and benzonitrile from their adducts with $PdCl_2$ to give stable 2/1 ylide—$PdCl_2$ complexes. Evidence is given for epimeric equilibrium between *trans* square-planar structures of these new complexes in solution.

A 1/1 ylide—PdI_2 complex, obtained from dimethylsulphonium methylide, is also described.

Introduction

Sulphonium ylides (I), because of their nucleophilic character, react with a variety of electrophilic substrates, in particular with olefins to give cyclopropanes [2], a reaction (eqn. 1) that has found several interesting applications.



(1)

Z = COOR, COR, CN etc.

Simple olefins however are not attacked by even the most nucleophilic ylides. It is known that normal nucleophilic olefins can be made electrophilic in character by complexation with transition metals, such as Pt and Pd, and nucleophiles such as water, alcohols, amines and carbanions have been made to react with a variety of olefin–metal complexes [3]. To date no report of reaction between ylides and olefins activated by complexation has been recorded**.

Our interest in the chemistry of ylides [4] led us to investigate the reaction between these compounds and complexed olefins, in the hope of promoting

---

[*] A preliminary note on part of this subject has been published [1].

[**] Recently, allylic alkylation of olefinic π-alkyl complexes by means of the anion of methylsulphinylacetate has been reported [3b].

the reaction of the ylide with the olefinic double bond. Our first attempts at reactions of this type, using the easily available styrene—$PdCl_2$ complex, did not afford the expected results; the styrene molecule was displaced by the ylide* and ylide—$PdCl_2$ complexes were always obtained with structures depending on the nature of the ylide.

We report the results of our studies on the synthesis and structure of the palladium—ylide complexes obtained in these preliminary experiments.

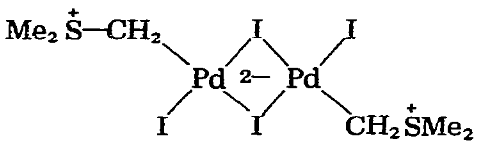
When alkylphosphonium ylides react with transition metal carbonyl complexes, displacement of CO by the ylide or attack on the CO has been reported as usually occurring, with the formation of complexes containing the ylidic moiety [6]. A few complexes of phosphonium and arsonium cyclopentadienylides with transition metal carbonyls have also been reported [7], and various types of phosphonium ylide—metal adducts, complexes and "quasi-complexes" of Ni, Cu, Ag, Au, Zn, Mg, Sn and Pb, have also been reported [8].

Much less information is available on metal complexes of nitrogen [9] and sulphur [10] ylides. For sulphonium ylides, apart from a few organotin sulphonium salts and ylides [10a] only Barney [10b] has reported** the formation of some adducts (possibly complexes) between two cyclopentadienylsulphonium ylides and several metal salts in which the ylides were found to give 1/1 adducts with $PdCl_2$.

Results and discussion

A 1/1 ylide—PdI_2 adduct (II) was obtained from dimethylsulphonium methylide (I) and the styrene—PdI_2 complex in the presence of a DMSO solution of NaI (eqn. 2). A dimeric structure, or the analogous "*cis*" structure,

$$\underset{(I)}{^{-}CH_2-\overset{+}{S}Me_2} + \tfrac{1}{2}[(C_8H_8)\cdot PdCl_2]_2 + 2I^- \rightarrow \underset{(II)}{C_3H_8SPdI_2} + C_8H_8 + 2Cl^- \qquad (2)$$



(II)

is suggested by its stoichiometry. The NMR spectrum, taken in DMSO-d_6, shows two singlets at δ 2.84 and 3.31 ppm in a 3/1 ratio.

When keto-stabilized dimethylsulphonium ylides (III) were reacted with the styrene—$PdCl_2$ adduct in benzene at room temperature, the complexes IV were obtained in very good yields as yellow precipitates. Alternatively the same compounds could be obtained from the ylides and the benzonitrile—$PdCl_2$ adduct in benzene, chloroform or DMSO, or even directly with $PdCl_2$ in DMSO (eqn. 3).

---

[*] Recently the reaction between dimethylsulphonium methylide and some acylferrocenes has been reported in which attack of the ylide occurred at the carbonyl. No displacement of the cyclopentadienyl group by the ylide was observed [5].

[**] Recently Sato and Higuchi [11] have reported the reaction of dimethylsulphonium phenacylides with $CuCl_2$ in MeOH. Under these conditions adducts were formed between $CuCl_2$ and the sulphonium salts corresponding to the ylides. The formation of similar adducts from $PdCl_2$ and dimethylphenacylsulphonium salts has also been observed by us.

$$\underset{\text{(III)}}{2p\text{-}XC_6H_4CO\bar{C}H{-}\overset{+}{S}Me_2} + \left\{\begin{array}{l}\frac{1}{2}[(C_8H_8)\cdot PdCl_2]_2\\ \text{or}\\ (C_6H_5CN)_2\cdot PdCl_2\\ \text{or}\\ PdCl_2\end{array}\right. \longrightarrow$$

$$\underset{\text{(IV)}}{(p\text{-}XC_6H_4COCH\overset{+}{S}Me_2)_2\cdot PdCl_2} + \left\{\begin{array}{l}C_8H_8\\ \text{or}\\ 2C_6H_5CN\end{array}\right. \qquad (3)$$

a, X = H; b, Me; c, MeO; d, Br; e, NO_2.

Compounds IVa-e are crystalline solids, almost insoluble in most organic solvents but slightly soluble in cold and moderately soluble in warm DMSO. They decompose in ethanol, but are thermally quite stable*. They decompose on melting to give the corresponding ω-chloroacetophenone. The analytical data (Table 1) are in accord with a 2/1 ylide—$PdCl_2$ ratio.

X-ray analysis of a single crystal of IVa has shown that it exists in a *d,l-trans* square-planar configuration with the two ylidic ligands bound to palladium through the "anionic" carbon atoms, now sp^3 hybridized (Fig. 1) [13].

IR spectroscopic data of solid state IVa are in accord with this structure, the C=O stretching band appearing at ca. 1630 cm^{-1}, not far from the value observed for the corresponding dimethylphenacylsulphonium chloride (1680 cm^{-1}). The carbanionic character of IIIa is therefore lost on complexation, though a certain degree of polarization in the Pd—C bond is indicated by the lower frequency of the CO band compared to the sulphonium salt. In the free ylide the full negative charge of the anionic carbon atom shifts the C=O band to even lower frequency ("enolate" band at 1508 cm^{-1} [14]). A single Pd—Cl stretching band in the far IR region at 330 cm^{-1} is in accord with a *trans* configuration [15].

TABLE 1

COMPLEXES FROM DIMETHYLPHENACYLSULPHONIUM YLIDES AND $PdCl_2$: $(p\text{-}XC_6H_4CO\bar{C}H{-}\overset{+}{S}Me_2)_2\cdot PdCl_2$ (IV)

Compound	X	M.p. [a] (°C)	Yields (%)	Analyses found (calcd.) (%)				
				C	H	S	Pd	Cl
IVa	H	194	100 [b,c]	44.5 (44.6)	4.1 (4.5)	11.8 (11.9)	19.6 (18.7)	13.7 (13.2)
IVb	Me	188	98 [b]	46.8 (46.7)	5.1 (5.0)	11.3 (11.3)	19.8 (18.9)	12.5 (12.4)
IVc	MeO	190—192	95 [b]	44.3 (44.2)	4.7 (4.7)	10.6 (10.7)	17.5 (17.8)	11.9 (11.9)
IVd	Br	198	95 [b]	34.7 (34.5)	3.5 (3.2)	9.0 (9.2)	14.7 (15.3)	9.9 (10.2) [d]
IVe	NO_2	196	92 [b]	36.6 (38.2)	3.3 (3.5)	9.2 (10.2)	15.6 (16.9)	12.9 (11.3) [e]

[a] From DMSO—water. M.ps are uncorrected. [b] From $(C_6H_5CN)_2PdCl_2$. [c] From $[(C_8H_8)PdCl_2]_2$ and also from $PdCl_2$. [d] Br%: calcd. 23.0; found 22.0. [e] N%: calcd. 4.5; found 5.2.

---

* The great thermal stability which is usually observed for complexes having "onium" groups in the ligands has been rationalized by Ercolani et al. [12] on the basis of internuclear interactions of the charged centers.

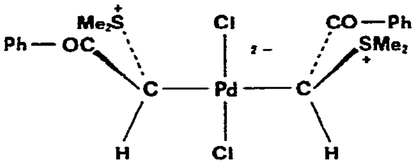


Fig. 1. The structure of IVa from X-ray diffraction.

The UV spectrum of IVa in the solid (reflectance) shows two maxima at ca. 280 and 350 nm, while a single shoulder at 300 nm (log $\epsilon = 3.8$) appears in DMSO solution.

Surprisingly the NMR spectra of IVa (Fig. 5), as well as those of the similar complexes IVb-e, (Figs. 2 and 5) show a pattern rather more complicated than that expected from the solid state structure shown for IVa by X-ray analysis. Because of the low solubilities of IVa-e, "CAT" accumulation was necessary for $CDCl_3$ solutions but with DMSO-d_6 satisfactory concentrations could be obtained by warming for a short time,care being taken to avoid decomposition* by cooling and immediately measuring the spectra. Alternatively relatively high concentrations were obtained even in $CDCl_3$, without heating, by preparing the complexes from stoichiometric amounts of the benzonitrile—$PdCl_2$ adduct and the ylide in the NMR tube. The NMR data are given in Table 2.

A comparison with the NMR parameters of the "free" ylides (Table 3) shows that complexation of ylides with palladium causes a low-field shift for the CH-CO signals of 0.4—0.6 ppm in DMSO-d_6 and 0.7—0.8 ppm in $CDCl_3$, indicative of electron drift from carbon to palladium. However this low-field shift

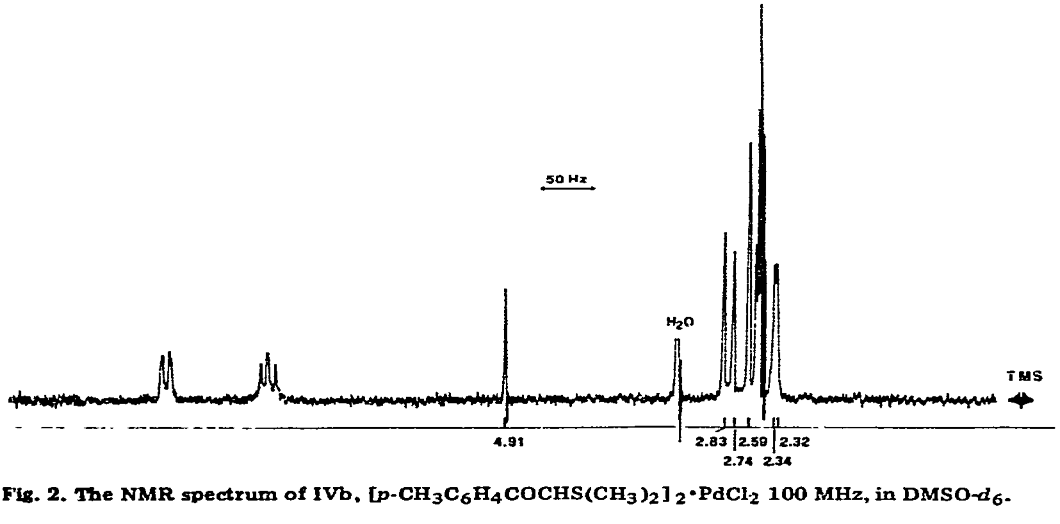


Fig. 2. The NMR spectrum of IVb, $[p\text{-}CH_3C_6H_4COCHS(CH_3)_2]_2 \cdot PdCl_2$ 100 MHz, in DMSO-d_6.

---

* [illegible] discrepancies between the NMR parameters of IVb reported in this paper (Table 2) and those given in the Preliminary Note [1] are probably due to thermal decomposition which occurred in our earlier experiments. Minor discrepancies reported for IVa and IVc can be ascribed to differences in concentration.

TABLE 2

NMR PARAMETERS FOR $(p\text{-XC}_6\text{H}_4\text{CO}\bar{\text{C}}\text{H—}\overset{+}{\text{S}}\text{Me}_2)_2\cdot\text{PdCl}_2$ (IV)[a]

Compound	X	PdCH($\overset{+}{S}$)—CO		$\overset{+}{S}Me_2$[b]		Other Me		Aromatics	
		DMSO-d_6	$CDCl_3$[d]	DMSO-d_6	$CDCl_3$	DMSO-d_6	$CDCl_3$	DMSO-d_6	$CDCl_3$
IVa	H	4.97	5.09	2.60(2)	2.58			7.3-7.5	~7.4
		4.98	5.13	2.71(1)	2.62			8.2-8.3	~8.3
				2.79(1)	2.67				
					2.80				
IVb[e]	Me	4.91	5.02	2.59(2)	2.60 ★	2.34	2.37 ★	7.1-7.2	~7.2
			5.08 ★	2.74(1)	2.62	2.32	2.40	8.1-8.3	~8.3
				2.83(1)	2.70 ★				
					2.86				
IVc	MeO	4.86	4.99	2.61(2)	2.60 ★	3.79	3.82	6.8-7.0	6.95
			5.04 ★	2.78(1)	2.63	3.83	3.87 ★	8.2-8.3	8.38
				2.87(1)	2.75 ★				
					2.94				
IVd	Br	4.98	5.01 ★	2.63(2)	2.62				
		4.99	5.07	2.80(1)	2.64 ★				
				2.86(1)	2.72				
					2.88 ★				
IVe	NO_2	5.15 ★		2.66					
		5.16		2.67 ★					
				2.82					
				2.91 ★					

[a] δ ppm; chemical shifts are slightly dependent on concentration. [b] Relative intensities in parentheses. [c] Ref.: The high field peak of DMSO at 246.0 Hz from TMS. [d] Ref.: $CHCl_3$ (7.26 ppm). [e] See Fig. 2. The most abundant isomer is marked ★.

is small in comparison with the parallel shift observed on protonation of ylides (the CH_2-CO signal of dimethylphenacylsulphonium chloride in DMSO-d_6 is at ca. 5.6 ppm). This trend is qualitatively in accord with the fact that the IR carbonyl frequencies of the complexes are intermediate between those of the ylides and the corresponding sulphonium salts. Tables 2 and 3 show that only minor differences between free and complexed ylides are observed for other proton signals.

Structure

The stoichiometry of the complexes IVa-e and the X-ray analysis of IVa are indicative of square-planar structures. In principle four different isomeric species are possible if the ylide is bound to palladium through the anionic carbon atom: *d,l-trans*, *meso-trans*, *d,l-cis* and *meso-cis*. Since these structures show a plane (*meso*) or a binary (*d,l*) axis of symmetry, in all these possible isomers the two Me_2S^+ and the two CH—Pd groups are equivalent. Therefore all these

TABLE 3

NMR PARAMETERS FOR DIMETHYLSULPHONIUM PHENACYLIDES: $p\text{-XC}_6\text{H}_4\text{CO}\bar{\text{C}}\text{H—}\overset{+}{\text{S}}\text{Me}_2$ (III)[a]

Compound	X	$\bar{C}HCO$		$\overset{+}{S}Me_2$		Other Me	
		DMSO-d_6	$CDCl_3$	DMSO-d_6	$CDCl_3$	DMSO-d_6	$CDCl_3$
IIIa	H	4.33	4.31	2.82	2.94		
IIIb	Me	4.37	4.26	2.81	2.94	2.30	2.33
IIIc	MeO	4.31	4.25	2.81	2.95	3.76	3.80
IIId	Br	4.44	4.27	2.82	2.98		
IIIe	NO_2	4.63	4.28	2.85	3.02		

[a] δ, ppm; conc. 0.25—0.3 *M*. Chemical shifts are slightly dependent on concentration.

isomers should give a unique Pd—CH peak and two Me_2S^+ singlets, due to the anisotropy of the dissymmetric carbon atoms in the NMR spectra[*] [16]. But the experimental data reported in Table 2 show that all the complexes IVa-e exhibit two Pd—CH peaks and four MeS^+ singlets, though overlap often occurs in DMSO-d_6. Moreover *p*-methyls in IVb and *p*-methoxyls in IVc give two different signals, both in DMSO-d_6 and $CDCl_3$ solutions, while only one peak is predicted for a single isomer. The NMR data therefore strongly suggest as does the lack of sharp m.p.'s and IR band-broadening in IVb-e, that complexes IVa-e exist in solution in two forms. Both are probably in a square planar geometry, with palladium bound to the anionic carbon atom of the ylide[**].

The lack of peaks corresponding to the free ylide excludes the possibility of any equilibrium between mono- and binuclear species[***]. For the same reason structures with the ylide as a bidentate or π-allyl-like ligand can be excluded.

It should be noted that the two species in solution must be rapidly interconvertible because IVa, which is unitary when solid, is recovered unchanged (identical IR spectra) from its solutions upon crystallization or precipitation with a non-solvent[‡].

The sum of this and other[‡‡] evidence leads to the conclusion that IVa-e exist in solution as mixtures of *meso-* and *d,l-trans* square-planar structures in equilibrium (Fig. 3). The isomer distribution in solution at equilibrium is different from that observed immediately after the synthesis (see Fig. 4 and the Experimental Section). The isomer distribution at equilibrium in $CDCl_3$ changes widely from compound to compound, but the ratio in DMSO-d_6 is 1/1 for all the complexes but IVe.

Exchange experiments

The interconversion of the two isomeric species implies Pd—C bond fission and means that some "free" ylide has to be present in solution in equilibrium

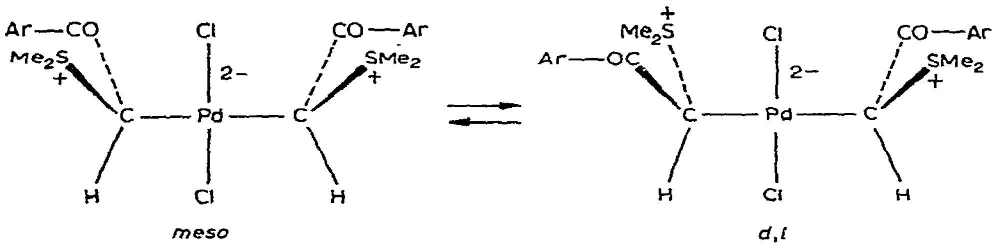


Fig. 3. Equilibrium between *meso* and *d,l* forms of complexes IV in solution.

---

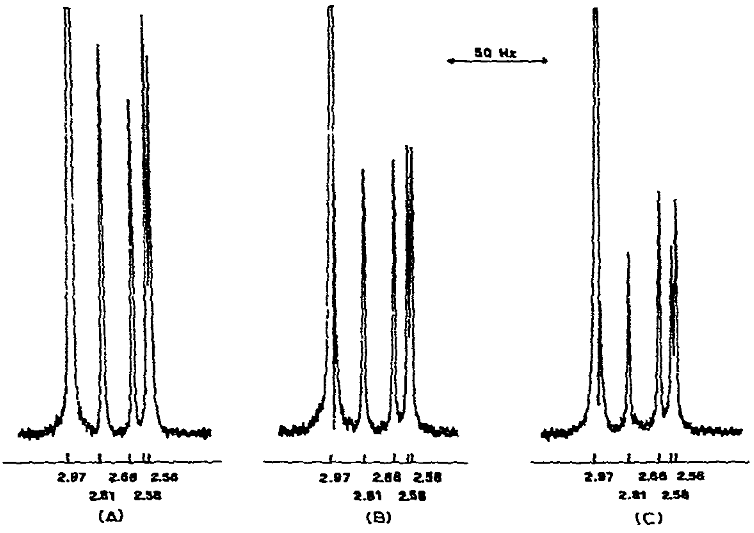
[*] Magnetic non-equivalence of the two methyls of a Me_2S group α to a dissymmetric carbon atom is shown, for instance, by the salt $C_6H_5COCHCl—\overset{+}{S}Me_2\cdot Cl^-$ which, in DMSO-d_6, exhibits two distinct MeS^+ singlets at 2.16 and 3.06 ppm.

[**] Other sites of attachment such as the oxygen of the enolate form of the ylide, or the sulphur atom, apart from any other consideration [10b], are very unlikely, for in both cases the two methyls of the Me_2S^+ groups would probably appear magnetically equivalent.

[***] The peaks of the corresponding sulphonium chlorides are missing in the spectra of IVa-d [dimethylphenacylsulphonium chloride in DMSO-d_6 shows singlets at 3.04 (MeS^+) and 5.62 (CH_2CO) ppm]. The sulphonium chlorides could be formed through protonation of the possible free ylides.

[‡] The same applies for IVb-e.

[‡‡] *cis* structures in Pd(II) square planar complexes are less common than *trans* forms [15a]. The behaviour of IVa in cold pyridine, whereby only one mole of ylide is displaced by pyridine, is also indicative of a *trans* structure.



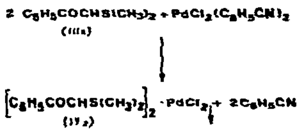


Fig. 4. The isomer distribution for IVa in $CDCl_3$ solution (A) after 10 min, (B) after 20 min, and (C) after 30 min. IVa has been synthesized in the NMR tube from a 2-fold excess of IIIa. Only the $\overset{+}{S}Me$ signals are reported (100 MHz). The peak at 2.97 ppm corresponds to the free ylide in excess. The two pairs of peaks at 2.81—2.58 and 2.66—2.56 ppm correspond to the two epimers of IVa. Details are given in Experimental Section.

with the complex, though in too small a concentration to be revealed by NMR. This has been proved by a successful demonstration of exchange between the ylide bound in IVa and some added free ylide IIIc, in DMSO-d_6 solution. An exchange was observed according to eqn. 4.

$$\underset{\text{(IVa)}}{(C_6H_5CO\overset{-}{C}H\overset{+}{S}Me_2)_2\cdot PdCl_2} + \underset{\text{(IIIc)}}{2p\text{-}MeOC_6H_4CO\overset{-}{C}H\overset{+}{S}Me_2} \rightleftharpoons$$

$$\rightleftharpoons \underset{\text{(IVc)}}{(p\text{-}MeOC_6H_4CO\overset{-}{C}H\overset{+}{S}Me_2)_2\cdot PdCl_2} + \underset{\text{(IIIa)}}{2C_6H_5CO\overset{-}{C}H\overset{+}{S}Me_2} \quad (4)$$

The reaction could best be followed by observing the decrease in the 2.71 ppm peak of IVa, and the appearance of peaks at 2.88, 3.83 and 4.87 ppm due to IVc (Fig. 5).

In spectrum C of Fig. 5 some peaks (e.g. at 4.90 and 4.96 ppm), are clearly different from those of either IVa or IVc and almost certainly originate from mixed complexes of formula IVac. The Me_2S^+ peaks of these mixed complexes probably overlap with the numerous corresponding peaks of IVa and IVc. However, when a 10-fold excess of IIIc was added to the solution of IVa, the peaks corresponding to IVc dominated the spectrum. The experiment was repeated in $CDCl_3$ with a 25-fold excess of IIIc: at the beginning a very complex spectrum was observed, probably due to the presence of several species (IVa, IVc and IVac). After complete equilibration, however, (several hours) only the peaks of IVc could be observed.

$$\underset{\text{(IVac)}}{(C_6H_5COCH\text{—}SMe_2)(p\text{-}MeOC_6H_4COCHSMe_2)\cdot PdCl_2}$$

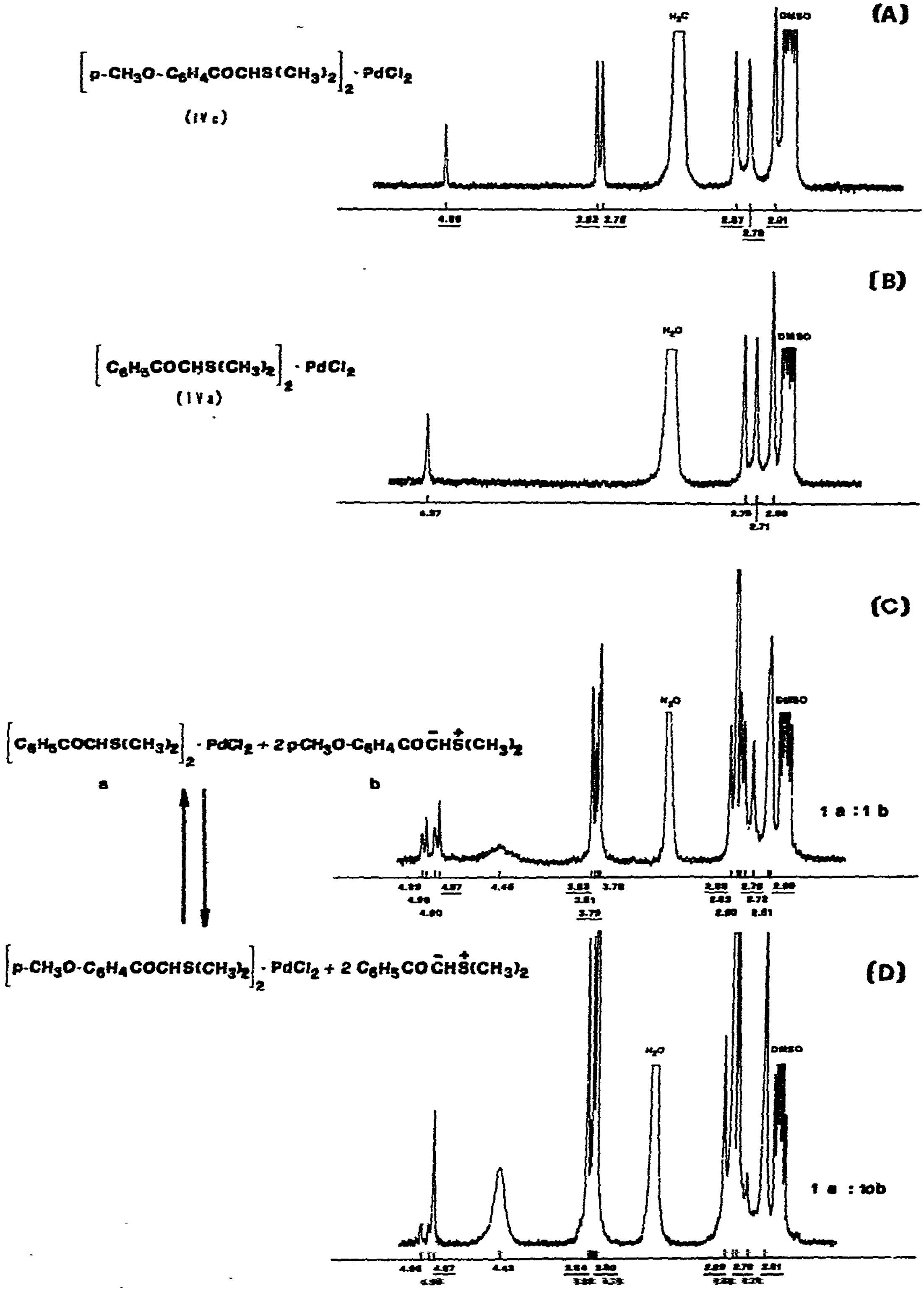


Fig. 5. Ylide exchange in complexes IV in DMSO-d_6 solution. (A) The NMR spectrum of IVc. (B) The NMR spectrum of IVa. (C) The NMR spectrum of a mixture of IVa and the ylide IIIc in a 1/1 molar ratio. (D) The NMR spectrum of a mixture of IVa and IIIc in a 1/10 molar ratio.

Similarly, when the exchange experiment was repeated in DMSO-d_6 between IVa and IIIb in large excess the formation of IVb was indicated. Moreover it was possible to observe the CHCO peak of the displaced ylide IIIa, distinct from the corresponding peak of IIIb in the spectrum, and the amount of IIIa increased when further amounts of IIIb were added.

Displacement of the ylidic ligands in IV by pyridine was also possible: When IVa was dissolved in cold pyridine-d_5 and the NMR spectrum taken, the characteristic peaks of IVa were not observed and instead, peaks appeared in the spectrum corresponding to the free ylide IIIa together with two MeS^+ singlets of equal intensity at 2.86 and 3.42 ppm. This can be explained by the displacement of one mole of ylide from IVa by one mole of pyridine, with the formation of a mixed complex Va.

$(C_6H_5COCH{-}SMe_2)\cdot\text{pyridine-}d_5\cdot PdCl_2$

(Va)

This result supports a *trans* structure for IVa with the *trans* effect of the ylidic ligand greater than that of pyridine. Complete displacement of the ylide from the complex by pyridine-d_5 could only be achieved by heating.

Analogous results were obtained with complexes IVb-e.

Conclusion

The olefinic double bond of the styrene—$PdCl_2$ complex is not attacked by ylides, but instead the olefinic ligand is displaced to give very stable ylide—Pd complexes. Similar behaviour is shown by the benzonitrile—$PdCl_2$ adduct.

Ylides are good ligands for palladium: their complexes with $PdCl_2$ can be readily prepared, even in DMSO, and when complexed are displaced by pyridine only with difficulty.

Experimental

Instrumentation

The IR spectra were taken using a Perkin Elmer model 457 spectrometer; only prominent peaks are reported. The NMR spectra were recorded on a Varian XL-100 spectrometer; chemical shifts (δ, ppm) were measured from TMS as internal standard, unless otherwise specified.

Materials

The keto-stabilized sulphonium ylides were obtained by basic treatment of the corresponding salts (ref. 2, p. 310). They were used after crystallization from benzene.

Compound II

Styrene—$PdCl_2$ complex [17] (1.15 g, 0.02 moles) was added to a solution of dimethylsulphonium methylide (I) obtained [18] from trimethylsulphonium iodide (2.4 g, 0.012 moles) and NaH (0.29 g, 0.012 moles) in DMSO (15 ml). After 24 h standing at room temp. the solution was diluted with water (50 ml). The brown precipitate was collected washed thoroughly with water, dissolved in DMSO and reprecipitated with water. Yield 80% (1.4 g). M.p. 204°. IR (KBr):

2990, 1410, 1400, 1320, 1105, 1060, 1025 and 970 cm^{-1}. Analysis found: C, 8.1; H, 1.8, S, 6.8; Pd, 24.6; I, 58.0. $C_3H_8SPdI_2$ calcd.: C, 8.2; H, 1.8; S, 7.3; Pd, 24.5; I, 58.1%.

General procedure for compounds IVa-e

(A). From $(C_6H_5CN)_2 \cdot PdCl_2$. A solution of the appropriate ylide (IIIa-e, 2 mmoles) in $CHCl_3$ (15 ml) was added to a solution of $(C_6H_5CN)_2 \cdot PdCl_2$ [17] (0.38 g, 1 mmole) in $CHCl_3$ (10 ml). After 24 h standing at room temp. the precipitate was collected, washed with $CHCl_3$, recrystallized from warm DMSO or DMSO-water and dried under vacuum at 50°.

(B). From $[(C_8H_8) \cdot PdCl_2]_2$. A solution of the appropriate ylide (IIIa-e, 4 mmoles) in benzene (15 ml) was added to a solution of $[(C_8H_8) \cdot PdCl_2]_2$ (0.56 g, 1 mmole) in benzene (15 ml). After 24 h standing at room temp. the compound was isolated and purified as described under A.

(C). From $PdCl_2$. A solution of the appropriate ylide (IIIa-e, 2 mmoles) in benzene (15 ml) was added to a solution of $PdCl_2$ (0.18 g, 1 mmole) in DMSO (~ 30 ml). After 12 h standing at room temp. the mixture was diluted and purified as described under A.

IR spectra of compounds IVa-e. IVa: 3020, 2920, 1630, 1580, 1430, 1330, 1320, 1285, 1190, 1020, 885, 750, 695, 640, 480, 410 and 330 cm^{-1}. IVb: 2990, 2920, 1625, 1600, 1570, 1415, 1400, 1315, 1295, 1190, 1180, 1030, 1015, 1000, 930, 920, 820, 750, 740, 595, 460, 440 and 330 cm^{-1}. IVc: 2990, 2840, 1615, 1600, 1570, 1510, 1420, 1290, 1260, 1165, 1030, 1015, 1000, 925, 840, 790, 760, 605, 455 and 330 cm^{-1}. IVd: 2990, 2910, 1630, 1580, 1560, 1480, 1390, 1285, 1190, 1170, 1060, 1030, 1000, 910, 830, 815, 770, 740, 495, 440, 385 and 330 cm^{-1}. IVe: 3010, 1630, 1600, 1520, 1405, 1345, 1310, 1285, 1185, 1030, 1010, 920, 855, 810, 760, 710, 410 and 335 cm^{-1}.

Reaction between dimethylphenacylsulphonium chloride and $PdCl_2$

A solution of dimethylphenacylsulphonium chloride (0.43 g, 2 mmoles) in water (5 ml) was added to a solution of $PdCl_2$ (0.18 g, 1 mmole) in water (15 ml). After a few hours the red precipitate (5.1 g, 84% yield) was collected, washed with water and dried under vacuum, m.p. 192—193°. IR (Nujol): 1680, 1595, 1450, 1410, 1340, 13?5, 1210, 1050, 990, 750 and 680 cm^{-1}. NMR (DMSO-d_6): 3.00 (s, 6, MeS^+), 5.58 (s, 2, CH_2CO). Analysis found: C, 40.3; H, 4.4; S, 10.6; Cl, 23.7; Pd, 18.1. $C_{20}H_{26}O_2S_2Cl_4Pd$ calcd.: C, 39.3; H, 4.3; S, 10.5; Cl, 23.3; Pd, 17.4%.

Thermal decomposition of compounds IV

1 mmole of IV was heated at 200° for 5 min. The molten mixture was taken up with 5 ml of $CHCl_3$. After filtration the mixture was separated by preparative TLC (silica gel, developing solvent hexane—ether 7/3). Upon elution of the appropriate band a 15—30% of the theoretical amount of the ω-chloroacetophenone corresponding to the complex IV was obtained.

The ω-chloroacetophenones have been identified by IR comparison with authentic samples.

Synthesis of compounds IV under NMR control

A solution of $(C_6H_5CN)_2 \cdot PdCl_2$ (0.25 mmoles) in about 0.2 ml of $CDCl_3$ was added to a solution of the ylide III (1 mmole in 0.5 ml of $CDCl_3$) in an NMR tube. A clear solution was obtained and usually two or three spectra could be taken before precipitation of IV occurred. With IVa (see Fig. 4) the signals of the two geometric isomers initially appeared in ca. 2/1 ratio, the more abundant isomer appearing at 2.58, 2.81 (MeS^+) and 5.09 (CH—Pd) ppm. Over half an hour a decrease in intensity was observed for all peaks because of precipitation, while the ratio of the two isomers gradually fell to ca. 1/1. Similar phenomena were observed for IVb, IVc and IVe, where an even greater change in the isomer ratio occurred (e.g. from 10/1 to 3/1 in the case of IVe).

Similar experiments were performed using DMSO-d_6 instead of $CDCl_3$ as solvent.

Acknowledgements

We are grateful to Professor W.A. Fedeli for the data concerning the X-ray analysis of IVa and to Dr. G. Corradini for the IR spectra.

Financial support by the Italian Reserach Council (Contratto N. 71.01586.03 and CT72.00118.03) is acknowledged.

References

1 P. Bravo, G. Fronza, G. Gaudiano and C. Ticozzi, Gazz. Chim. Ital., 103 (1973) 623.
2 A.W. Johnson, Ylid Chemistry, Academic Press, New York, 1966.
3 a. J. Tsuji, in E.C. Taylor and H. Wynberg (Eds.), Advances in Organic Chemistry, Interscience, London, 1969, p. 109;
b. B.M. Trost and T.J. Fullerton, J. Amer. Chem. Soc., 95 (1973) 292.
4 See for instance P. Bravo, G. Gaudiano, P.P. Ponti and C. Ticozzi, Tetrahedron, 28 (1972) 3845, and references therein.
5 J.P. Sevenair, D.H. Lewis and B.W. Ponder, J. Organometal. Chem., 37 (1972) 4061.
6 W. Heiber, E. Winter and E. Schubert, Chem. Ber., 95 (1962) 3070;
H. Bock and H.T. Dieck, Z. Naturforsch. B, 21 (1966) 739;
D.K. Mitchell, W.D. Korte and W.C. Kaska, Chem. Comm., (1970) 1384;
A. Greco, J. Organometal. Chem., 43 (1972) 351;
K.A.O. Starzweski, H.T. Dieck, K.D. Franz and H. Hohmann, J. Organometal. Chem., 42 (1972) C35;
W.C. Kaska, D.H. Mitchell and R.F. Reichelderfer, J. Organometal. Chem., 47 (1972) 391;
D.K. Mitchell and W.C. Kaska, J. Organometal. Chem., 49 (1973) C73;
I.W. Bassi, R. Scordamaglia and A. Greco, Chimica e Ind. (Milano), 55 (1973) 241.
7 E.W. Abel, A. Singh and G. Wilkinson, Chem. Ind. (London) (1959) 1067;
J.C. Kotz and D.G. Pedrotty, J. Organometal. Chem., 22 (1970) 425;
D. Cashmann and F.J. Lalor, J. Organometal. Chem., 32 (1971) 351.
8 G. Wittig and K. Schwarzenbach, Justus Liebigs Ann. Chem., 650 (1961) 1;
D. Seyferth and S.O. Grim, J. Amer. Chem. Soc., 83 (1961) 1610;
N.A. Nesmeyanov, V.M. Novikov and O.A. Reutov, J. Organometal. Chem., 4 (1965) 202;
H. Schmidbaur, Chem. Ber., 101 (1968) 3545;
D.R. Mathiason and N.E. Miller, Inorg. Chem., 7 (1968) 709;
J. Buckle and G.P. Harrison, J. Organometal. Chem., 49 (1973) C17;
S. Kato, T. Kato, M. Misuta, K. Itoh and Y. Ishii, J. Organometal. Chem., 51 (1973) 167;
W. Malish, J. Organometal. Chem., 61 (1973) C15.
H.H. Karsch and H. Schmidbaur, Angew Chem., 85 (1973) 910, and references therein.
9 M. Keeton, R. Mason and D.R. Russell, J. Organometal. Chem., 33 (1971) 259.
10 a. K. Itoh, S. Kato and Y. Ishii, J. Organometal. Chem., 34 (1972) 293;
H. Schmidbaur and G. Kaurmel, Chem. Ber., 104 (1971) 3252.
b. G.S. Barney, Ph.D. Dissertation, 1970; Chem. Abstr., 76 (1972) 9941j.
11 T. Sato and G. Higuchi, Tetrahedron Lett., (1972) 407.

12 C. Ercolani, J.V. Quagliano and L.M. Vallarino, Inorg. Chim. Acta, 3 (1969) 421.
13 W.A. Fedeli, S. Cerrini and M. Colapietro, in preparation.
14 A.W. Johnson and R.T. Amel, Tetrahedron Lett., (1966) 819;
B.M. Trost, J. Amer. Chem. Soc., 89 (1967) 138.
15 a. P.M. Matilis, The Organic Chemistry of Palladium, Academic Press, New York, 1971.
b. W. Kitching, C.J. Moore and D. Doddrell, Inorg. Chem., 9 (1970) 541.
16 L.M. Jackmann and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press, Oxford, 2nd ed., 1969, p. 368.
17 M.S. Kharash, R.C. Seyler and F.R. Mayo, J. Amer. Chem. Soc., 60 (1938) 882.
18 E.J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 87 (1965) 1353.