

Journal of Organometallic Chemistry, 157 (1978) 299–310
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF SOME PHOSPHONIUM, ARSONIUM, SULFONIUM AND PYRIDINIUM KETO-STABILIZED SALTS, AND YLIDES AND OF THEIR PALLADIUM(II) COMPLEXES

GIOVANNI FRONZA, PIERFRANCESCO BRAVO and CALIMERO TICOZZI

C.N.R., Centro Studio Sostanze Organiche Naturali, Istituto di Chimica, Politecnico, Piazza L. da Vinci 32, 20133 Milano (Italy)

(Received March 1st, 1978)

Summary

The ^{13}C chemical shifts, the ^{13}C – ^{31}P coupling constants, and some one-bond ^{13}C – ^1H coupling constants were measured for the title compounds. For the ylides of phosphorus, arsenic and sulfur, the data are consistent with an sp^2 -hybridized ylidic carbon with a strong, localized negative charge, while for the pyridinium ylide this charge is much more delocalized. In the homologous series of salts the electron-withdrawing ability of the groups studied varies in the order: $\text{Ph}_3\text{P}^+ < \text{Ph}_3\text{As}^+ \ll \text{Me}_2\text{S}^+ \ll \text{Me}_2\text{C}_5\text{H}_3\text{N}^+$. The differences in the carbonyl chemical shift between the ylides and the corresponding salts are a measure of the resonance stabilization of the negative charge in the form $\text{X}^+ - \text{C} = \text{C} - \text{O}^-$; this stabilization varies with the groups studied in the order: $\text{Ph}_3\text{P}^+ < \text{Ph}_3\text{As}^+ \approx \text{Me}_2\text{S}^+ \ll \text{Me}_2\text{C}_5\text{H}_3\text{N}^+$. The ylide–palladium(II) complexes contain a bond between the ylidic carbon and the metal: the ylidic carbon is shifted upfield in the complex with respect to the free ligand, while the adjacent carbonyl is shifted strongly downfield. These data suggest that the Pd–C(1) bond is strongly polarized with a high electron density on the C(1) atom which cannot be delocalized through resonance as in the free ligands.

Introduction

In recent years the behaviour of ylides as ligands has been of much interest, particularly for phosphoranes with transition metals. Several complexes with various metals or metal carbonyls have been reported by various authors [1,2]. We have prepared a series of palladium(II) complexes with sulfur ylides which vary in stability [3], as well as with phosphorus arsenic and nitrogen (in pyridine) ylides [4]. The molecular structure of the complex was found to depend mainly on the nature of the ylide; complexes between PdCl_2 and carbonyl

stabilized ylides were very regular in structure. With the series of ylides RCOCH^-X^+ , in which $\text{X} = \text{SMe}_2, \text{PR}_3, \text{AsR}_3$ and $\text{NC}_5\text{H}_3\text{Me}_2$, the complexes were always square planar with the two ylide molecules bound to the metal through the ylidic carbon *trans* to one another.

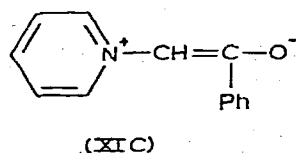
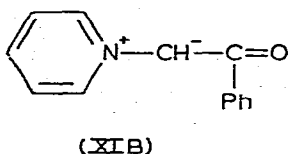
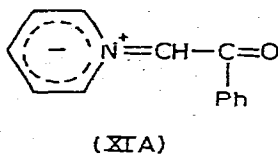
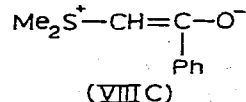
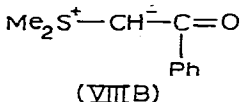
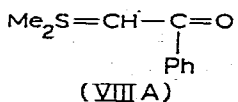
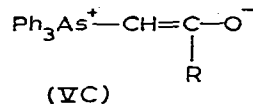
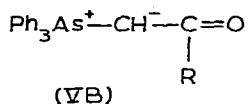
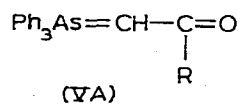
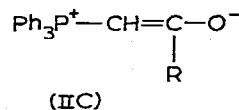
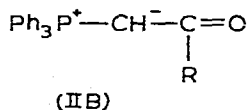
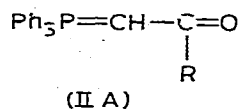
The stabilization of the ylide negative charge by positively charged heteroatoms has been investigated by X-ray analysis [5], photoelectronic spectroscopy [6], nuclear magnetic resonance studies [7–12] and theoretical calculations [13]. Most of these studies involved phosphonium ylides, and led to the following general conclusions: (i) the carbon adjacent to the heteroatom bears a substantial negative charge; (ii) the hybridization of this carbon depends on the nature of the heteroatom and on the presence or absence of stabilizing groups ($\text{C}=\text{C}$, COR , COOR , etc.).

Since the electronic structure of the ylides as free molecules and as ligands in metal complexes is still of actual interest we report here the ^{13}C NMR data for some phosphorus ylide–palladium(II) complexes plus the corresponding ylides and salts, and some more information of the nature of the bonds in the free ylides, mainly on the relative weight on the various resonance structures which contribute to the stabilization of the ylides. Further arsenic, sulfur and nitrogen compounds are included.

Results and discussion

All the compounds studied (salts, ylides and complexes) have been previously reported [3,4]; they are listed in Tables 1 and 2. Table 1 shows the ^{13}C data for all the phosphorus compounds (salts, ylides and palladium chloride complexes); Table 2 shows those for the arsenic, sulfur and nitrogen compounds. Table 3 contains the pertinent data for the aromatic carbons, both in the rings bound to the heteroatom and in those bound to carbonyl. The data for the various ylides will be discussed first, in comparison with the corresponding salts. A discussion of the data for the ylide–palladium chloride complexes will follow.

The three resonance structures contributing to the noteworthy stability of carbonyl-substituted ylides are shown.



The charge-separated structure B is that of a carbanion. Structure A involves the extra stabilization that second and third row elements can provide through π -bonding with the d -orbitals or through a different interaction between the positive sp^3 hybridized heteroatom and the negative sp^2 hybridized carbon, as reported [13]. As a first row element, nitrogen has no d -orbitals available and resonance structures of type A are not possible; however for the pyridinium ylide XI, there are resonance structures in which the negative charge is transferred into the pyridine ring. Structure C represents the stabilization provided by a carbonyl whenever it is adjacent to a carbanion.

The ^{13}C nuclear magnetic resonance spectra of the various ylides may shed light on the relative contribution of A, B and C to the actual structure of the ylides under study.

Phosphonium ylides and salts

As the data in Table 1 show, the one-bond coupling constant $^1J(\text{C}(1)\text{—P})$ varies from about 60 to 110 Hz and the direct carbon—hydrogen coupling constant $^1J(\text{C}(1)\text{—H})$ from about 130 to 164 Hz in passing from the phosphonium salt to the ylide. This large increase in the one-bond coupling constant of the ylide carbon indicates a large increase in s -character in the carbon to phosphorus and carbon to hydrogen bonds. In fact $^1J(\text{C—P})$ and $^1J(\text{C—H})$ have been correlated with the s bond orders $P_{s\text{C}\text{—}\text{H}}^2$ and $P_{s\text{C}\text{—}\text{P}}^2$ of the respective bonds [14a]; recent quantum mechanical calculations have shown these correlations be valid for ylidic carbon to phosphorus bonds as well [10,11].

The chemical shift of the ylide carbon C(1) of the phosphonium compounds varies from about 40 ppm in the salts to about 50 ppm in the ylides; this carbon is very strongly shielded in the ylides with respect to conjugated carbanions. For example, the carbons in phenylcarbanion resonate at 125–170 ppm [14b]. Therefore, a significant negative charge is localized on the ylide carbon.

From the one-bond coupling constants and the chemical shift of the ylide carbon of keto-stabilized phosphonium ylides, this carbon can be assumed to be sp^2 hybridized with a lone pair of electrons in a p orbital. Resonance structure IIb therefore best represents the situation of the ylide carbon, although contributions from IIA and IIC must also be considered.

IIA involves the formation of a $d\pi\text{—}p\pi$ bond between an empty d orbital of phosphorus and a filled p orbital of carbon, which is difficult to evaluate on the basis of ^{13}C NMR data since d orbitals are expected to be diffuse, leaving significant electron density near the C(1) carbon [10]. A comparison between our keto-stabilized ylides and other phosphonium ylides in the literature [11], however, allows a qualitative evaluation of the effect of carbonyl stabilization and thus of the contribution of structure IIC.

The chemical shifts and the C(1)—H coupling constants of the ylide carbon vary greatly as the substituents bound to it change. For example, carbon C(1) in $\text{Ph}_3\text{P=CHCH}_3$ resonates at 2.7 ppm, in $\text{Ph}_3\text{P=CHPh}$ at 27.0 ppm and in $\text{Ph}_3\text{P=CHCOCH}_3$ at 51.3 ppm. And, in non-stabilized ylides, the C(1)—H coupling constants range from 149 to 154 Hz [11], while keto-stabilized systems reach a value of about 164 Hz, for an increase of 10–15 Hz. These variations are too large to be attributed to a steric or inductive effect*. These trends may

* A carbonyl group deshields an α carbon by approximately 15 ppm and increases the coupling constant $^1J(\text{C—H})$ by 1–2 Hz [14c].

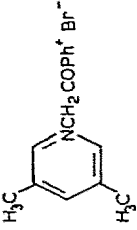
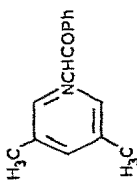
TABLE I

^{13}C CHEMICAL SHIFTS, $^{13}\text{C}-\text{P}$ COUPLING CONSTANTS AND $^{13}\text{C}-^1\text{H}$ ONE BOND COUPLING CONSTANTS FOR PHOSPHONIUM SALTS (I), YLIDES (II) AND COMPLEXES (III) ^a

No	Compound	$^{13}\text{C}-\text{P}-\text{C}-\text{O}-\text{CH}_3$			C(1')	C(S)	C(1)-H	C(3)-H	C(1')-H
		C(1)	C(2)	C(3)					
Ia	$\text{Ph}(\text{CH}_3)_2\text{PCH}_2\text{COPh}^+\text{Br}^-$	37.2 (30.5)	193.0 (6.5)		9.4 (56.5)				
Ib	$\text{Ph}_2\text{CH}_3\text{PCH}_2\text{COPh}^+\text{Br}^-$	37.3 (61.0)	192.2 (6.5)		10.2 (57.5)				
Ic	$\text{Ph}_3\text{PCH}_2\text{COPh}^+\text{Br}^-$	38.8 (62.5)	191.4 (7.0)						
Id	$\text{Ph}(\text{CH}_3)_2\text{PCH}_2\text{COCH}_3^+\text{Br}^-$	39.6 (59.0)	201.7 (7.0)	31.9 (5.5)	8.6 (56.5)	130.5	129.0		135.0
Ie	$\text{Ph}_2\text{CH}_3\text{PCH}_2\text{COCH}_3^+\text{Br}^-$	39.1 (59.5)	201.4 (7.0)	32.0 (6.5)	8.5 (56.0)	130.0	129.0		135.0
If	$\text{Ph}_3\text{PCH}_2\text{COCH}_3^+\text{Br}^-$ ^b	40.1 (58.8)	201.4 (3.0)	32.4 (7.0)					
IIa	$\text{Ph}(\text{CH}_3)_2\text{PCHCOPh}$	51.2 (111.5)	185.5 ^c		12.3 (62.5)				
IIb	$\text{Ph}_2\text{CH}_3\text{PCHCOPh}$	50.7 (112.5)	185.0 (2.5)		11.4 (63.5)				
IIc	$\text{Ph}_3\text{PCHCOPh}$ ^b	50.4 (111.7)	184.9 (3.0)						
IId	$\text{Ph}(\text{CH}_3)_2\text{PCHCOCH}_3$	52.2 (108.0)	191.1 ^c	28.2 (15.0)	12.2 (61.0)	163.0	125.0		131.0
IIf	$\text{Ph}_2\text{CH}_3\text{PCHCOCH}_3$	51.2 (108.5)	190.2 ^c	28.3 (15.0)	10.9 (63.0)	164.5	126.0		131.0
III	$\text{Ph}_3\text{PCHCOCH}_3$ ^b	51.3 (108.0)	190.5 (2.4)	28.4 (16.5)					
IIIa	$[\text{Ph}(\text{CH}_3)_2\text{PCHCOPh}]_2 \cdot \text{PdCl}_2$ ^d	27.3 (56.0)	196.3 ^c		11.1-13.4 (62.0-64.0)				
IIIb	$[\text{Ph}(\text{CH}_3)_2\text{PCHCOCH}_3]_2 \cdot \text{PdCl}_2$ ^d	30.4 (53.0)	205.0 ^c	31.4 (7.0)	11.2-13.6 (60.0-63.0)				
IIIc	$[\text{Ph}_2\text{CH}_3\text{PCHCOCH}_3]_2 \cdot \text{PdCl}_2$ ^e	28.0 (51.0)	204.1 ^c	31.5 (9.5)	10.6-11.0 (60.0-61.0)				

^a Chemical shifts are in ppm from internal TMS and $^{13}\text{C}-\text{P}$ coupling constants (Hz) are listed within the parentheses. ^b Values taken from ref. 10. ^c Unresolved signal. ^d One isomer in solution. The methyl groups are diastereotopic and display two distinct resonances. ^e Two isomers in solution.

TABLE 2
 ^{13}C CHEMICAL SHIFTS AND ^{13}C - ^1H ONE BOND COUPLING CONSTANTS FOR SOME ARSONIUM, SULPHONIUM AND PYRIDINIUM SALTS, YLIDES AND COMPLEXES^a

No.	Compound	$\text{CH}_3\text{-X-C-CO-CH}_3$			C(3)	C(1')	$^1\text{J}(\text{C}(1)\text{-H})$	$^1\text{J}(\text{C}(3)\text{-H})$	$^1\text{J}(\text{C}(1')\text{-H})$
		C(1)	C(2)	C(2')					
IVa	$\text{Ph}_3\text{AsCH}_2\text{COPh}^+\text{Br}^-$	42.6	192.8						
IVb	$\text{Ph}_3\text{AsCH}_2\text{COCH}_3^+\text{Br}^-$	44.2	201.9	31.6		135.0	129.5		
Va	$\text{Ph}_3\text{AsCHCOPh}^b$	57.1	181.8						
Vb	$\text{Ph}_3\text{AsCHCOCH}_3$	56.9	187.0	26.3		173.5	126.0		
Vib	$[\text{Ph}_3\text{AsCHCOCH}_3]_2 \cdot \text{PdCl}_2^c$	41.6	205.5	29.8					
VII	$(\text{CH}_3)_2\text{SCH}_2\text{COPh}^+\text{Br}^-$	41.1	204.9		24.4	144.0		145.5	
VIII	$(\text{CH}_3)_2\text{SCHCOPh}$	52.7	191.5		28.6	178.0		142.0	
IX	$[(\text{CH}_3)_2\text{SCHCOPh}]_2 \cdot \text{PdCl}_2^c$	56.0	179.0		27.2-26.5				
		49.4	<i>d</i>		27.2-25.9				
X		65.9	190.2		18.3 ^e				
XI		98.0	170.0		18.6 ^e				

^a Chemical shifts are in ppm from internal TMS. ^b Values taken from ref. 18b. ^c Two isomers in solution. The methyl groups of IX are diastereotopic and display two distinct resonances. ^d Insufficient signal-to-noise ratio. ^e Methyl chemical shift.

be rationalized in terms of an increasing contribution of resonance structure IIc, so as to approach an sp^2 hybridization for the C(1) carbon atom, and a strong drift of electrons from C(1) toward oxygen. These cause, respectively, an increase in s character of the C—H bond, with the consequent increase in C—H coupling constant, and a low field shift in the resonance of C(1), as observed.

Further evidence for this electron drift from C(1) to carbonyl is provided by the large upfield shift (7–11 ppm) induced by going from the salt to the ylide and by the effects on the groups attached to the carbonyl. For instance, for $\text{CH}_3\text{C}=\text{O}$ vs. $\text{CH}_3\text{C}-\text{O}^-$, the methyl is shifted upfield by approximately 3 ppm and the $^1J(\text{C}(3)-\text{H})$ (see Table 1) decreases from 129 to about 126 Hz as the carbonyl becomes less electron withdrawing*. For a phenyl substituent, part of the charge is transferred to the phenyl, particularly to the *para* carbon, which is shifted approximately 5 ppm upfield.

Groups attached to phosphorus are also affected by going from salt to ylide: for the methyls bound to phosphorus in Ia, IIa; Ib, IIb; Id, IIc and Ie, IIe, $^1J(\text{C}(1')-\text{P})$ increases by ~ 7 Hz while $^1J(\text{C}(1')-\text{H})$ decreases by ~ 4 Hz. These effects may be rationalized by assuming that the phosphorus gains electron density, becoming less electron withdrawing in the ylides. It is known that for the same reason the ^{31}P resonances are shifted upfield in going from the salts to the ylides [10]. The downfield shift of the methyl carbons on going from the salts to the ylides, by approximately 3 ppm, can be attributed to an electric field effect of the negatively charged ylidic carbon, which polarizes the C—H bonds, resulting in decreased electron density at the carbon nucleus** [15].

Further, the aromatic carbons of the phenyl groups attached to phosphorus show a re-distribution of charge: carbon C(1'), directly attached to phosphorus, is shifted downfield 7–8 ppm, while the *para* and *ortho* carbons are shifted upfield 2–3 and ~ 1 ppm, respectively. The *meta* carbon is less affected. Since the *para* carbons are shifted more than the *ortho*, the shifts are probably caused more by a polarization effect of the π electron cloud due to the negative charge on C(1) than by a conjugative effect through the phosphorus [17,18].

One can observe also from the data reported in Tables 1 and 3 that within a series of compounds, some NMR parameters vary systematically as the substituents change. For instance, when a phenyl is substituted for a methyl bound to phosphorus, the *ortho* C(2') carbon shifts downfield 1–1.5 ppm for both the salts and the ylides, although the other chemical shifts and the C—P coupling constants are unchanged. Also, in addition to the expected downfield shift of the carbonyl, the substitution of a COMe for a COPh shifts the ylide carbon about 1 ppm downfield in the ylides and about 2 ppm in the salts; $^1J(\text{C}(1)-\text{P})$ decreases approximately 3 Hz for the ylides and 2 Hz for the salts.

* Direct carbon—hydrogen coupling constants in compounds $\text{X}-^{13}\text{C}-\text{H}$ increase with increasing electronegativity of X. The cause of this increase is generally held to be the increased s character of the C—H bond, due to the increased p character of the C—X bond [16].

** Since a phosphorus less electron withdrawing in the ylides with respect to the salts was expected to shield the methyl carbons, probably this shielding is overcome by the deshielding due to the electric field effect.

Arsonium and sulfonium ylides and salts

The keto-stabilized derivatives of arsenic and sulfur behave in a manner consistent with the corresponding phosphorus compounds. The ylide carbon resonates at 57 ppm for arsenic ylides Va and Vb and at 56 ppm for sulfur ylide VIII; the one-bond C(1)—H coupling constants are 173.5 Hz for Vb and 178 Hz for VIII. As for the phosphoranes, these values show the ylidic carbon in these compounds is planar sp^2 hybridized with a lone pair in a p orbital.

The sizeable increase in the C(1)—H coupling constant in going from phosphorus (164.5 Hz for IIe) to arsenic (173.5 Hz for Vb) to sulfur ylides (178.0 Hz for VIII) shows that the s character of the C(1)—H bond increases in the series. Furthermore the corresponding salts follow the same trend: 130.0 Hz for IIe, 135.0 Hz for IVb, and 144.0 Hz for VII. Since the C(1)—H coupling constants vary in the same way for the two series of ylides and salts, these variations presumably arise more from the different electronegativities [16] of the onium groups ($\text{Ph}_2\text{CH}_3\text{P}^+ < \text{Ph}_3\text{As}^+ < \text{Me}_2\text{S}^+$) than from the changes in geometry of the ylide carbon.

The C(1)—H coupling constant in triphenylphenacylarsonane (Vb) is 173.5 Hz, 43.5 Hz larger than in trimethylmethylenearsonane ($\text{Me}_3\text{As}=\text{CH}_2$); this large increase is due partly to carbonyl stabilization, but probably even more to the change in C(1) hybridization from sp^3 to sp^2 . In fact it is known that the ylide carbon in non-stabilized arsonium ylides is non-planar, as reported by Schmidbaur et al. [12] (The C(1)—H coupling constant in Me_3AsCH_2 is 130 Hz, a typical value for a tetrahedral carbon atom).

In keto-stabilized arsonanes Va and Vb, the carbon C(1) chemical shift in the ylide is 14.5 and 12.7 ppm downfield from that in the salt; the ylide carbonyl is 11 ppm upfield in Va and 15.1 ppm upfield in Vb. These shifts in the arsonanes are greater by approximately one third than those in the corresponding phosphoranes. For sulfur ylide VIII, the C(1) chemical shift in the ylide is only 3.3 ppm downfield from that in the salt VII, whereas the carbonyl is shifted upfield 11.5 ppm as for the arsenic derivatives. We will discuss these data later, when comparing the behaviour of all the different classes of ylides.

Finally, as seen from Tables 2 and 3, the variations in the NMR parameters of the groups bonded to the heteroatoms and to the carbonyl are similar to those seen for the phosphorus derivatives.

Pyridinium ylide and salt

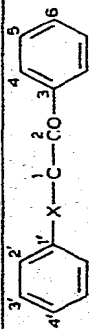
The pyridinium ylide is different from the other ylides discussed so far. As a first row element, nitrogen has no d orbitals available for bond formation; also the number of its substituents and the nature of their bonds to it are different.

The C(1) chemical shift at 99.0 ppm is more than 40 ppm downfield from the other ylides studied and 33.1 ppm downfield from the corresponding salt. Therefore, the negative charge in IX is not concentrated on the ylidic carbon, but rather is strongly delocalized both to the carbonyl and to the pyridine ring, as shown also by the upfield shift of C(2) (20.1 ppm) and of the *ortho* and *para* carbons C(2') and C(4') (12.4 and 14.0 ppm) as compared to the salt. Ylide carbon C(1) is thus sp^2 hybridized: it is part of a π system represented mainly by resonance structures A and C, with structure B of lower importance. Since this ylide is insoluble in benzene, no C(1)—H coupling constants are available.

TABLE 3

^{13}C CHEMICAL SHIFTS AND ^{13}C - ^{31}P COUPLING CONSTANTS FOR AROMATIC RING CARBONS OF PHOSPHONIUM, ARSONIUM SULPHONIUM AND PYRIDINIUM SALTS, YLIDES AND COMPLEXES ^a

No	Compound	C(3)	C(4) ^b	C(5) ^b	C(6)	C(1')	C(2')	C(3')	C(4')
Ia	$\text{Ph}(\text{CH}_3)_2\text{PCH}_2\text{COPh}^+\text{Br}^-$	135.3 (5.0)	129.1	128.8	134.4	120.8 (87.0)	131.7 (11.2)	129.7 (13.0)	134.0 (2.3)
Ib	$\text{Ph}_2\text{CH}_3\text{PCH}_2\text{COPh}^+\text{Br}^-$	135.2 (4.7)	129.4	128.8	134.5	119.6 (88.5)	132.8 (10.5)	129.8 (13.3)	134.4 (1.9)
Ic	$\text{Ph}_3\text{POCH}_2\text{COPh}^+\text{Br}^-$	d	129.9	128.9	134.7	118.8 (89.5)	134.1 (10.6)	130.2 (12.6)	134.7 f
Id	$\text{Ph}(\text{CH}_3)_2\text{PCH}_2\text{COCH}_3^+\text{Br}^-$					120.7 (86.6)	131.7 (10.3)	123.8 (12.6)	134.0 (2.4)
Ie	$\text{Ph}_2\text{CH}_3\text{PCH}_2\text{COCH}_3^+\text{Br}^-$					118.9 (87.4)	132.5 (10.6)	129.7 (13.0)	134.1 f
If	$\text{Ph}_3\text{PCH}_2\text{COCH}_3^+\text{Br}^-$ ^c					119.0 (88.3)	134.2 (10.6)	130.3 (13.2)	134.9 (2.1)
IIa	$\text{Ph}(\text{CH}_3)_2\text{PCHCOPh}$	141.2 (14.0)	127.9	126.8	129.5	d	130.5 (10.1)	129.3 (11.2)	132.1 f
IIb	$\text{Ph}_2\text{CH}_3\text{PCHCOPh}$	141.1 (14.0)	127.7	126.7	129.3	d	131.5 (10.2)	128.9 (12.5)	131.9 f
IIc	$\text{Ph}_3\text{PCHCOPh}$ ^c	141.4 (15.0)	127.7	127.0	129.3	127.1 (91.5)	133.1 (10.3)	128.8 (12.2)	132.0 (2.0)



IIId	Ph(CH ₃) ₂ PCHCOCH ₃				130.2 (10.2)	129.0 (11.7)	131.7 f
IIe	Ph ₂ CH ₃ PCHCOCH ₃				127.9 (88.1)	128.7 (12.2)	131.4 f
IIf	Ph ₃ PCHCOCH ₃ ^c				127.4 (90.3)	128.7 (12.2)	131.8 (2.4)
IIIa	[Ph(CH ₃) ₂ PCHCOPh] ₂ · PdCl ₂	139.2 (10.0)	129.0	128.1	130.4 (10.4)	129.7 (11.8)	132.3 f
IIIId	[Ph(CH ₃) ₂ PCHCOCH ₃] ₂ · PdCl ₂				126.0 (76.0)	129.5 (12.5)	132.6 f
IIIe	[Ph ₂ CH ₃ PCHCOCH ₃] ₂ · PdCl ₂				132.0 (9.0)	129.2 (12.4)	132.5 f
IVa	Ph ₃ AsCH ₂ COPh ⁺ Br ⁻	134.5	130.0	128.9	133.0	130.5	133.7
IVb	Ph ₃ AsCH ₂ COCH ₃ ⁺ Br ⁻				122.2	130.5	133.7
Va	Ph ₃ AsCHCOPh ^e	140.5	127.6	127.1	121.9	129.4	131.6
Vb	Ph ₃ AsCHCOCH ₃				129.9	129.4	131.6
VId	[Ph ₃ AsCHCOCH ₃] ₂ · PdCl ₂				128.9	129.3	131.5
VII	(CH ₃) ₂ SCH ₂ COPh ⁺ Br ⁻	138.9	129.2	128.6	127.8	129.0	131.6
VIII	(CH ₃) ₂ SCHCOPh	141.2	128.6	127.7	133.5		
IX	[(CH ₃) ₂ SCHCOPh] ₂ · PdCl ₂	141.3	128.6	128.2			
X	(CH ₃) ₂ C ₅ H ₃ NCH ₂ COPh ⁺ Br ⁻	133.5	128.9	128.4	143.3	137.8	146.7
XI	(CH ₃) ₂ C ₅ H ₃ NCHCOPh	142.3	127.8	126.0	130.9	135.7	132.7

^a Chemical shifts are in ppm from internal TMS and ¹³C-³¹P coupling constants (Hz) are listed within the parentheses. ^b The assignment of C(4) and C(5) carbons may be reversed. ^c Values taken from ref. 10. ^d Insufficient signal-to-noise ratio. ^e Values taken from ref. 18b. ^f Unresolved signal.

The aromatic phenyl carbons suffer the same changes upon ylide formation as those of preceding series (see Table 3).

Comparison between the different classes of ylides and salts

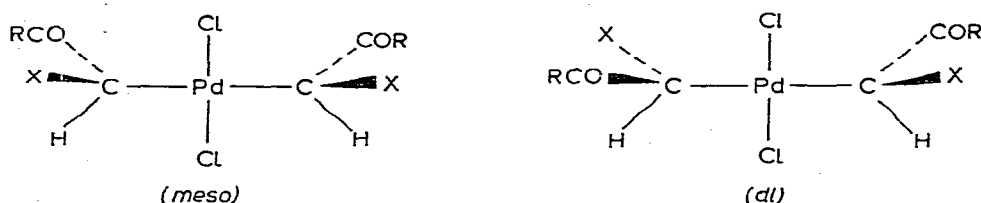
From the C(1) carbon chemical shifts in the series of the salts Ic, IVa, VII and X, one may construct an electronegativity scale for the onium groups as follows: $\text{Ph}_3\text{P}^+ < \text{Ph}_3\text{As}^+ \ll \text{Me}_2\text{S}^+ \ll \text{Me}_2\text{C}_5\text{H}_3\text{N}^+$. The chemical shift of the carbonyl C(2) remains basically unchanged through the series of the same salts.

In the corresponding ylides IIc, Va, VIII and XI, the mesomeric effects of structures A, B, and C add to the inductive effects of the onium groups. Ylide carbon C(1) is deshielded with respect to the salt while carbonyl carbon C(2) is shielded in all the series by a different extent in each series considered (for example, C(1): IIc-Ic, $\Delta = +11.6$; Va-IVa, $\Delta = +14.5$; VIII-VII, $\Delta = +3.3$; XI-X, $\Delta = +33.1$ ppm. C(2); IIc-Ic, $\Delta = -6.5$; Va-IVa, $\Delta = -11.0$; VIII-VII, $\Delta = -11.5$; XI-X, $\Delta = -20.2$ ppm). The different deshielding of the ylide carbon C(1) with respect to the corresponding salt of two series of ylides can be considered as a measure of the different delocalization of the negative charge from C(1) to the rest of the molecule in the two series. Values reported above show that this delocalization increases in the order: $\text{Me}_2\text{S}^+ \ll \text{Ph}_3\text{P}^+ < \text{Ph}_3\text{As}^+ \ll \text{Me}_2\text{C}_5\text{H}_3\text{N}^+ *$.

The carbonyl C(2) shift difference between ylide and salt can be taken as a measure of the stabilization of the ylide negative charge due to resonance structure C, $\text{X}^+-\text{C}=\text{C}-\text{O}^-$; the values reported above show that this stabilization is dependent on the different onium groups, increasing in the order: $\text{Ph}_3\text{P}^+ < \text{Ph}_3\text{As}^+ \approx \text{Me}_2\text{S}^+ < \text{Me}_2\text{C}_5\text{H}_3\text{N}^+$.

Complexes

As previously reported [3,4], these complexes exist in solution as two isomeric species in equilibrium, probably the *meso* and *d,l* forms of the *trans* structure; complexes IIIe, VIb and IX do show double signals. However, the



(III a, III d, X = $\text{Ph}(\text{CH}_2)_2\text{P}$; III e, X = $\text{Ph}_2\text{CH}_2\text{P}$; VI b, X = Ph_3As ;
IX, X = $(\text{CH}_3)_2\text{S}$; XII, X = $(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}$)

spectra of phosphonium ylide complexes IIIa and IIId show one isomer only, evidently the more abundant of the two. In these last two complexes and in sulfur derivative IX, the methyls bonded to the heteroatom show two chemical shifts since they are diastereotopic because of the asymmetric C(1) carbon. The extremely low solubility of some complexes made it impossible to record their

* Other factors which could affect this deshielding as changes in the molecule geometry or long-range effects of the groups linked to the heteroatom should be negligible.

spectra. The spectrum of the pyridinium ylide complex XII is also unavailable because of its slow decomposition in solution.

Formally, these complexes arise from two salt molecules by substituting a palladium atom for one of the methylene hydrogens in each molecule. A comparison of the complexes with the salts is thus of interest. First, there is a large upfield shift for carbon C(1) bonded to the metal in the phosphonium complexes (approximately 10 ppm) and a smaller one in the sulfonium and arsonium derivatives (approximately 3 ppm). In addition, the direct coupling constant C(1)—P in phosphorus complexes is 4–8 Hz less than that in the salt. These observations are consistent with the fact that palladium, as an electron donor, has the effect of localizing a partial negative charge on C(1) and so decreasing the *s* character of the C(1)—P bond.

All the complexes show the carbonyl shifted downfield about 3 ppm from the salt, and 11–15 ppm from the ylide. In the complexes, the carbonyl is adjacent to negatively charged carbon C(1); in contrast to the situation in the ylide, this electron density is localized in the palladium—carbon bond and thus resonance structures like C do not participate. This localized high electron density induces a positive charge on the adjacent carbonyl carbon which is also deshielded with respect to the salt*.

The methyl groups linked to carbonyl in III_d, III_e and VI_b are not much affected by complexation. The phenyl group of complexes III_a and IX shows the C(3) carbon bonded to the carbonyl shifted upfield by 4 and 7 ppm and *para* carbon C(6) shifted downfield by about 3 ppm, whereas the *ortho* and *meta* carbons C(4) and C(5) are less affected. This pattern is consistent with a π polarization effect in which the phenyl π electrons are polarized away from the C(1) [17].

The chemical shifts and the C—P coupling constants of the CH₃ and C₆H₅ groups bonded to heteroatoms P, As and S are basically the same for the ylides and the complexes, both different from that of the salts. This behaviour suggests that the free charge of the ylide C(1) and the high electron density induced by the palladium on the C(1) of the complexes polarize the groups bonded to the heteroatom in the same way.

Conclusions

The chemical shifts and the one-bond coupling constants for the ylidic carbon C(1) in keto-stabilized phosphonium, arsonium and sulfonium ylides show that C(1) has an *sp*² hybridized carbanionic structure with a strong electron drift to the carbonyl. In the pyridinium ylide also, there is a drift of electrons into the pyridine ring through a C(1)—nitrogen bond of partial double bond character. Carbonyl stabilization of the negative charge on C(1) depends in the onium group in the order: Ph₃P⁺ < Ph₃As⁺ \approx Me₂S⁺ \ll Me₂C₃H₃N⁺. In the ylide₂ · PdCl₂ complexes the ¹³C chemical shifts of C(1) confirm that the ylidic carbon is bonded to the metal, and show that the C(1) has a higher electron density than the C(1) carbon in the free ligand.

* Such effect has been already found, for example in piperidinium chloride, where the positive nitrogen causes an upfield shift by 2.5 ppm on the carbon [14d].

Experimental

The compounds studied were prepared as described in ref. 3 and 4, or by other literature methods. When possible, ^{13}C NMR spectra were obtained in CDCl_3 ; because of their low solubility, the sulfur complexes were studied in $\text{DMSO}-d_6$. A ligand exchange reaction precluded the use of pyridine- d_5 and $\text{DMSO}-d_6$ for the other compounds [3]. For the measurement of the one bond coupling constants $^1J(\text{C}-\text{H})$, benzene- d_6 over NaH was used. This approach kept the system anhydrous and stopped chemical exchange reactions. Under these conditions, the NaH does not form metal complexes, ion pairs or bisanions, as shown by the invariance of the $^1J(\text{P}-\text{C})$ upon changing solvent from CDCl_3 to C_6D_6 plus NaH [19]. However, since the solubility was limited, all the compounds could not be examined.

Nuclear magnetic resonance spectra were taken at 25.2 MHz with a Varian XL-15 at 35°C. Broad-band ^1H noise decoupling was used for the carbon chemical shifts, with internal TMS as standard. For the carbon-hydrogen coupling constants, broad-band ^1H gated noise decoupling was used. Uncoupled spectra of ylides and salts were taken with approximately 0.02 M samples, while coupled ones were approximately 0.2 M. Chemical shifts were measured with an accuracy of 0.05 ppm, and C-P and C-H coupling constants with an accuracy of 1 Hz.

Assignments of peaks was based on the multiplicity and intensity of the signals, on the long-range P-C couplings and on the comparison with other reported ylides [10,18].

References

- 1 (a) W.C. Kaska, D.K. Mitchell, R.F. Reichelderfer and W.D. Korte, *J. Amer. Chem. Soc.*, **96** (1974) 2847; (b) L. Weber, *Z. Naturforsch. B*, **31** (1976) 780; (c) E.T. Weleski, J.L. Silver, M.D. Jansson and J.L. Burmeister, *J. Organometal. Chem.*, **102** (1975) 365; (d) H. Koezuka, G. Matsubayashi and T. Tanaka, *Inorg. Chem.*, **15** (1976) 417.
- 2 (a) H. Schmidbaur, *Accounts Chem. Res.*, **8** (1975) 62; (b) H. Schmidbaur, in F.G.A. Stone and R. West (Eds.), *Advan. Organometal. Chem. Vol. 14*, Academic Press, New York, 1976.
- 3 (a) P. Bravo, G. Fronza, C. Ticozzi and G. Gaudiano, *J. Organometal. Chem.*, **74** (1974) 143; (b) 118 (1976) C78.
- 4 P. Bravo, G. Fronza and C. Ticozzi, *J. Organometal. Chem.*, **111** (1976) 361.
- 5 J.C.J. Bart, *J. Chem. Soc. B*, (1969) 350.
- 6 (a) K.A.O. Starzewski, H. tom Dieck and H. Bock, *J. Organometal. Chem.*, **65** (1974) 311; (b) K.A.O. Starzewski, H. Bock and H. tom Dieck, *Angew. Chem., Int. Ed. Engl.*, **14** (1975) 173.
- 7 G.A. Gray, *J. Amer. Chem. Soc.*, **95** (1973) 7736.
- 8 T.A. Albright, W.J. Freeman and E.E. Schweizer, *J. Org. Chem.*, **40** (1975) 3437; **41** (1976) 2716.
- 9 T.A. Albright, W.J. Freeman and E.E. Schweizer, *J. Amer. Chem. Soc.*, **97** (1975) 940; 2942; 2946.
- 10 T.A. Albright, M.D. Gordon, W.J. Freeman and E.E. Schweizer, *J. Amer. Chem. Soc.*, **98** (1976) 6249.
- 11 K.A.O. Starzewski and H. tom Dieck, *Phosphorus*, **6** (1976) 177.
- 12 H. Schmidbaur, W. Richter, W. Wolf and F.H. Köhler, *Chem. Ber.*, **108** (1975) 2649.
- 13 F. Bernardi, H.B. Schlegel, M.-H. Whangbo and S. Wolfe, *J. Amer. Chem. Soc.*, **99** (1977) 5633.
- 14 (a) J.B. Stothers, *Carbon-13 NMR Spectroscopy*, *Organic Chemistry*, Vol. 24, Academic Press, 1972, p. 331; (b) p. 212; (c) p. 146 and 337; (d) p. 273.
- 15 R.L. Willer and E.L. Eliel, *Org. Magn. Res.*, **9** (1977) 285.
- 16 S. Masuda and N. Inamoto, *Chemistry Lett.*, (1973) 655.
- 17 W.F. Reynolds, I.R. Peat, M.H. Freedman and J.R. Lyster, *Can. J. Chem.*, **51** (1973) 1857.
- 18 (a) P. Froyen and D.G. Morris, *Acta Chem. Scand. B*, **31** (1977) 256; (b) **30** (1976) 435.
- 19 T. Bottin-Strzalko, J. Seyden-Penne and M.P. Simonin, *Chem. Commun.*, (1976) 905.