Heteroatom Chemistry
Volume 2, Number 5, 1991

Does the *ipso*-Carbon Chemical Shift Tell Us Anything About the Structure of Phenylated Phosphorus Compounds?

Zi-ping Liu and Manfred Schlosser*

Institut de Chimie Organique de l'Université, Rue de la Barre 2, CH-1005 Lausanne, Switzerland

Received 26 February 1991.

ABSTRACT

The nuclear magnetic resonance signals exhibited by the ipso*-carbon atoms of a variety of phenylated phosphorus compounds were found to span over the remarkably wide range of +162 to + 117 ppm. Nevertheless, these changes in chemical shifts have little diagnostic value. They are tentatively attributed to a charge-mediated contraction and expansion of the C,P σ-bond orbital on one hand and to a σ-bond induced deformation of the aromatic π-electron cloud on the other.*

INTRODUCTION

In the course of our nuclear magnetic resonance (NMR) studies of ylid structures [1–3] we noticed an unexpected, though quite characteristic, phenomenon. When an ylid is generated by α-deprotonation of an alkyltriphenylphosphonium salt, the *ortho-*, *meta*, and *para*-carbon nuclei of the phenyl rings change to higher field by approximately 2, 3, and 5 ppm, respectively, while the *ipso*-carbon is shifted downfield by some 15 ppm; this shift is identical to the shift that all of the other aromatic nuclei taken together experience in the opposite direction.

RESULTS AND DISCUSSION

To find out whether or not we are dealing with a general behavior we have compiled the *ipso*-carbon chemical shifts of a variety of other tri-, tetra-, penta-, or hexavalent phosphorus compounds (see Table 1). Actually, the resonances were found to stretch over the remarkably wide range of 45 ppm.

If benzene (δ 129) is taken as the reference, only the *ipso*-carbons of phosphonium salts are shifted upfield; all others shift downfield. At first sight, the deshielding effect appears to correlate with the $C^iPC^{i'}$ valence angles. This must, however, be a coincidence. As a matter of fact, the variation within the family of differently substituted phosphonium halides (Table 1) is very small (δ 118 ± 1) and the counterion effect on the δ_{C^i} shift of methyltriphenylphosphonium can be neglected (δ 119.0 ± 0.4 for the fluoride, chloride, bromide, iodide, and tetraphenylborate). Furthermore, all phosphines investigated resonate in the narrow range of +144 to +138 ppm, no matter whether they are sterically unhindered or carry bulky substituents and whether they have an acyclic, a small ring, or a medium ring structure (see Table 2).

It is more instructive to compare the *ipso*-carbon shifts of phosphorus compounds with isoelectronic species thereof. The signals of lithium tetraphenylaluminate (δ 160) and tetraphenylsilane (δ 134) appear at much lower field than that of their isoperiodic analog tetraphenylphosphonium bromide (δ 118, see Table 3). The differences within a group of isologous compounds is less pronounced. Nevertheless some trends can still be identified. Derivatives of second period elements show up at highest field, while those of the third and fourth row are slightly deshielded and those of the first and fifth row are considerably deshielded (Table 3).

Qualitatively the same relationships are found when we compare phosphines and other neutral

This article is dedicated to Leopold Horner on the occasion of his eightieth birthday.

*To whom correspondence should be addressed.

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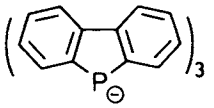
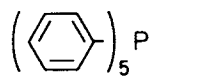
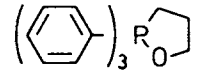
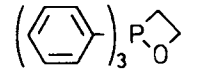
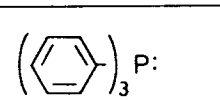
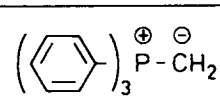
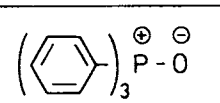
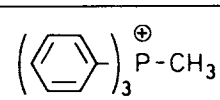
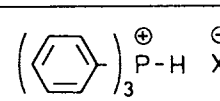
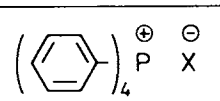
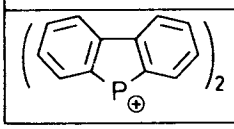
1042-7163/92/$3.50 + .25

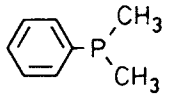
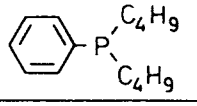
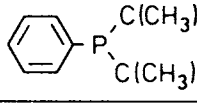
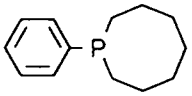
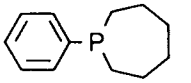
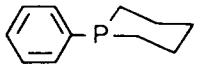
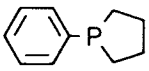
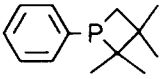
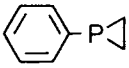
TABLE 1 Tri-, Tetra-, Penta-, and Hexavalent Phosphorus Compounds: Chemical Shifts of *ipso*-Carbon Atoms

phosphorus compound	δ_{C^i}
 [a]	162
	152
	147
	145
	137
	134
	133
 [b]	119
 [b]	118
 [b]	118
 [c]	117

[a] Lithium tris(*o,o'*-biphenylene)phosphate [M = Li].
[b] X = Br.
[c] Bis(*o,o'*-biphenylene)phosphonium iodide [X = I].

derivatives of the fifth main group with fourth group anions and sixth group cations (Table 4) or metal amides and phosphides with sixth group neutral and seventh group cationic analogs (Table 5). In the latter case, however, the third and fourth row species are more shielded than those of the second row.

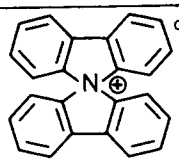
TABLE 2 The Chemical Shifts δ_{C^i} of the *ipso*-Carbon Atoms in a Series of Phenylated Phosphines

phosphine	δ_{C^i}
	144
	140
	138
	143
	142
	141
	143
	141
	139

In addition, the downfield shift turns out to be much smaller if we switch from a neutral species to a di- or trivalent anion (e.g., from triphenylphosphine to triphenylsilyllithium $\Delta\delta$ 8) rather than to an *ate* complex (e.g., from tetraphenylsilane to lithium tetraphenylaluminate, $\Delta\delta$ 26). The attenuation of the deshielding effect may have to do with the resonance delocalization of the negative charge.

Modern computational procedures such as the fascinating IGLO method [4] allow us to predict chemical shift values of carbon or other heavy atom nuclei with an amazing degree of reliability. These techniques are, of course, only applicable to compounds of moderate size and complexity. Even if these practical restrictions did not exist, a mathematical approach may not be fully satisfactory since it does not necessarily provide an intuitive insight into the origin of a given result. Chemists frequently prefer to correlate properties of molecules with more

TABLE 3 Comparison between Isoelectronic Derivatives of Elements Belonging to the Third, Fourth, and Fifth Main Group: Chemical Shifts δ_{C^i} of *ipso*-Carbon Atoms.

$(C_6H_5)_4\overset{\ominus}{B}$ [a] 165	$(C_6H_5)_4C$ 147	 [c] 132
$(C_6H_5)_4\overset{\ominus}{Al}$ [b] 160	$(C_6H_5)_4Si$ 134	$(C_6H_5)_4\overset{\oplus}{P}$ [d] 118
	$(C_6H_5)_4Ge$ 136	$(C_6H_5)_4\overset{\oplus}{As}$ [d] 120
	$(C_6H_5)_4Sn$ 138	
	$(C_6H_5)_4Pb$ 150	

[a] Sodium tetraphenylborate [M = Na].
[b] Lithium tetraphenylaluminate.
[c] Bis(*o,o'*-biphenylene)ammonium iodide [X = I].
[d] Tetraphenylphosphonium and -arsonium tetraphenylborate [X = $B(C_6H_5)_4$].

TABLE 4 Comparison between Isoelectronic Derivatives of Elements Belonging to the Fourteenth, Fifteenth, and Sixteenth Main Groups: Chemical Shifts δ_{C^i} of *ipso*-Carbon Atoms

$(C_6H_5)_3\overset{\ominus}{C}$ [a] 151	$(C_6H_5)_3N$ 149	
$(C_6H_5)_3\overset{\ominus}{Si}$ [a] 145	$(C_6H_5)_3P$ 137	$(C_6H_5)_3\overset{\oplus}{S}$ [b] 124
	$(C_6H_5)_3As$ 140	
	$(C_6H_5)_3Sb$ 138	
	$(C_6H_5)_3Bi$ 155	

[a] Triphenylmethyl- and triphenylsilyllithium [M = Li].
[b] Triphenylsulfonium bromide [X = Br].

qualitative structural or electronic parameters, so-called "effects." Having this in mind, we tentatively account for the observed trends in *ipso*-carbon chemical shifts δ_{C^i} by a σ-induced deformation of the aromatic π-electron cloud ("σ/π interdependence"). [5]

The π-electron density in delocalized molecular systems has been recognized as being an important shielding parameter [6]. Let us start with tetraphenylmethane, the δ_{C^i}-value of which (147) can be considered as normal (for comparison: toluene 137, *tert*-butylbenzene 151) [7]. If the central carbon atom is now replaced by a positively charged nitrogen atom the σ-bond will become polarized, electron excess being accumulated in the vicinity of the heteroelement. As a consequence, the aromatic π-electrons of the aromatic moiety can expand in this direction, where they encounter less σ-repulsion than usual. This leads to an increased shielding of the *ipso*-carbon nucleus. The opposite happens if the carbon center is exchanged against a negatively charged boron atom, a less electronegative element. Now the σ-electron density gradient increases in the direction of the phenyl ring and forces the π-electron cloud to retract. In this way, the *ipso*-carbon becomes deshielded.

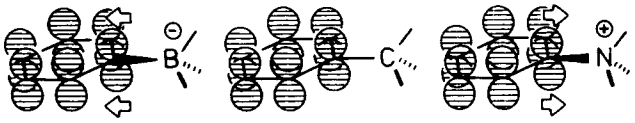


TABLE 5 Comparison between Isoelectronic Derivatives of Elements Belonging to the Fifteenth, Sixteenth, and Seventeenth Main Groups: Chemical Shifts δ_C of *ipso*-Carbon Atoms

$(C_6H_5)_2\overset{\ominus}{N}$ [a] 160	$(C_6H_5)_2O$ 157	
$(C_6H_5)_2\overset{\ominus}{P}$ [a] 156	$(C_6H_5)_2S$ 136	$(C_6H_5)_2\overset{\oplus}{Cl}$ [b] 140
	$(C_6H_5)_2Se$ 131	$(C_6H_5)_2\overset{\oplus}{Br}$ [b] 133
	$(C_6H_5)_2Te$ 115	$(C_6H_5)_2\overset{\oplus}{I}$ [b] 136

[a] Sodium diphenylamide and diphenylphosphide [M = Na].
[b] Diphenylchloronium, -bromonium and -iodonium hexafluorophosphates [X = PF_6].

Derivatives of second and third row elements show the same relationship: Electron-withdrawing positively charged centers cause an upfield shift, and electron-donating negatively charged centers cause a downfield shift. All chemical shifts, however, are smaller than those recorded with isologous first row compounds. This difference may reflect the dilution of σ-electron density because of the increase in bond lengths, which offers a better opportunity for the π-cloud to expand beyond the *ipso*-carbon confinement. If no other factors played a role, shielding and bond lengths should parallel each other. This is not the case, as is evidenced by tetraphenyllead (Table 3) and triphenylbismuth (Table 4), both these derivatives of sixth period elements exhibiting very distinct downfield shifts. A possible reason may be sought in the markedly enhanced polarizibility of the phenyl–metal bond or, in the molecular orbital language, a narrowing of the σ/σ^* gap.

An alternative or complementary explanation may be based on the Karplus-Pople treatment [8] of the paramagnetic contribution to the ^{13}C-chemical shift. The equation contains three types of variables: bond order terms, the reciprocal average volume of the carbon $2p$ orbitals, and, finally, the reciprocal $\sigma \rightarrow \pi^*$ electronic excitation energy. In general, the latter term, like the two others, can be only approximately evaluated. Although one has, therefore, to content oneself with qualitative conclusions, the trend must be considered as unequivocal. Electron-attracting groups make it more difficult to promote a σ-bonded electron into the corresponding more distant π^* orbital, while electron donating groups operate in the opposite sense. As a corollary of this, the nuclear magnetic resonance experiment requires higher or lower field.

EXPERIMENTAL

Generalities

For standard laboratory practice see related articles [2, 4, 9].

NMR Data taken from the Literature

The chemical shifts given in the Tables are only approximately comparable. Several different solvents were used and details of spectra recording are not always specified.

Table 1: 2,2,2-Triphenyloxaphosphetane [10], triphenylphosphine [11], and (triphenylphosphonio)methanide [10].

Table 2: Dimethylphenylphosphine [12], dibutylphenylphosphine [13], di-*tert*-butylphenylphosphine [14], *P*-phenylphosphocane [13], *P*-phenylphosphepane [13], *P*-phenylphosphorinane [13], *P*-phenylphospholane [13], 2,2,3,3-tetramethyl-*P*-phenylphosphetane [13], and *P*-phenylphosphirane [13].

Table 3: Tetraphenylmethane [15], tetraphenylsilane [15], tetraphenylgermane [15], tetraphenylstannane [15], tetraphenylplumbane [15], tetraphenylphosphonium tetraphenylborate [16], and tetraphenylarsonium tetraphenylborate [16].

Table 4: Triphenylmethyllithium [17], triphenylsilyllithium [18], triphenylphosphine [11], triphenylarsine [19], triphenylstibine (triphenylantimony) [19], triphenylbismuthine [19], and triphenylsufonium bromide [20].

Table 5: Sodium diphenylamide [21], sodium diphenylphosphide [21], diphenyl oxide [22], diphenyl sulfide [23], diphenyl selenide [24], diphenyl telluride [25], diphenylchloronium hexafluorophosphate [26], diphenylbromonium hexafluorophosphate [26], and diphenyliodonium hexafluorophosphate [26].

New NMR Data

The ^{13}C-NMR spectra were recorded using a Bruker WH-360 instrument operating at 90.55 MHz. The sweep width was 21,000 Hz, and the acquisition time was 0.38 s allowing for 16 K data points. The chemical shifts refer to tetramethylsilane (δ 0), which served as an internal standard. All samples were investigated twice: first under ^{1}H broad band irradiation and then again without such a decoupling device, both times at 25°C. Roughly 10% solutions were prepared and filled into 10-mm wide tubes. Phosphonium or ammonium salts, triphenylphosphine oxide, or triphenylamine were dissolved in deuterochloroform, all other compounds in perdeuterotetrahydrofuran. Unless commercially available, the samples were prepared according to the literature procedures indicated below.

Table 1: Lithium tris(*o,o'*-biphenylene)phosphate [27], pentaphenylphosphorane [28], 2,2,2-triphenyloxaphospholane [29], triphenylphosphine oxide, methyltriphenylphosphonium bromide [30, 31], triphenylphosphonium bromide [32, 33], tetraphenylphosphonium bromide [34], and bis(*o,o'*-biphenylene)phosphonium iodide [27].

Table 3: Lithium tetraphenylaluminate [35] and bis(*o,o'*-biphenylene)ammonium iodide [36].

ACKNOWLEDGMENT

This work was supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Berne (grant 20-25'577-88). The authors are indebted to Prof. Dieter Hellwinkel, Heidelberg, for a gift of bis(*o,o'*-biphenylene)phosphonium iodide and *o,o'*-diiodobiphenyl samples, and to Prof. Harald Günther, Siegen, for valuable hints.

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