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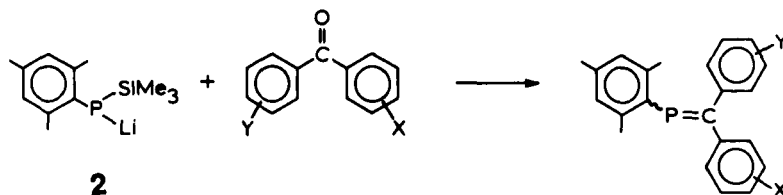
## PROPERTIES OF SUBSTITUTED TRIARYLPHOSPHAALKENES

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**Abstract.** -  $^{31}\text{P}$  NMR spectra of mesityl(diarylmesitylene)phosphines are presented and discussed in terms of the electronic nature and the configurational stability of the phosphorus-carbon double bond.

Substituted phosphaaalkenes (1) were synthesized by the method developed by Becker (2) (Scheme 1).

Scheme 1



Reaction of substituted benzophenones with lithium mesityl(trimethylsilyl)-phosphide 2 leads to phosphaaalkenes with  $^{31}\text{P}$  chemical shifts which correlate with the Hammett values as expected (Table 1): electron donating substituents such as dimethylamino increase the electron density on phosphorus and cause an upfield shift; electron withdrawing substituents such as cyano cause a downfield shift.

In contrast to *para*-methyl groups with an expected upfield shift, *ortho*-methyl groups cause a downfield shift. This unexpected dual behaviour of methyl groups has steric reasons. Mesityl(diarylmethylene)-phosphines are crowded molecules. In the parent compound 1 the *trans*- and *cis*-phenyl rings form angles with the  $\text{P}=\text{C}$  plane of  $36^\circ$  and  $42^\circ$  respectively (1). In the bis-*ortho*-methyl compound, these deviations from

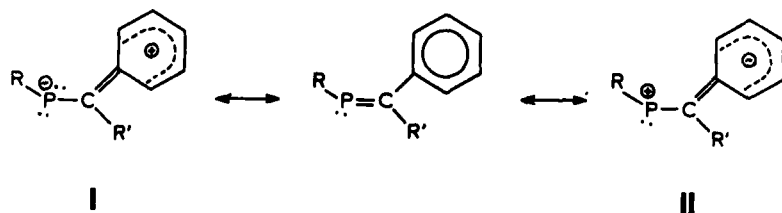
Table 1  $^{31}\text{P}$  NMR chemical shifts of  $\text{Mes-P}=\text{C}(\text{C}_6\text{H}_4\text{X})\text{C}_6\text{H}_4\text{Y}$ 

cpd.	X	Y	$\delta(\text{ppm})$	cpd. E,Z	X	Y	$\delta(\text{ppm})$	
							E	Z
1	H	H	234.5	1g,1g'	H	<i>p</i> -NMe <sub>2</sub>	213.0	214.6
1d	<i>p</i> -NMe <sub>2</sub>	<i>p</i> -NMe <sub>2</sub>	198.7	1h,1h'	H	<i>p</i> -OMe	224.3	226.3
1b	<i>p</i> -OMe	<i>p</i> -OMe	217.1	1j,1j'	H	<i>p</i> -Me	230.1	230.9
1c	<i>p</i> -Me	<i>p</i> -Me	226.7	1k,1k'	H	<i>p</i> -F	233.7	234.5
1d	<i>p</i> -Br	<i>p</i> -Br	241.5	1l,1l'	H	<i>p</i> -Br	238.8	237.4
1e	<i>p</i> -CN	<i>p</i> -CN	261.1	1m,1m'	H	<i>p</i> -CN	251.5	244.3
1f	<i>o</i> -Me	<i>o</i> -Me	250.3	1n,1n'	H	<i>o</i> -Me	235.4	242.6
				1p,1p'	<i>p</i> -Br	<i>p</i> -OMe	230.3	227.1
				1q,1q'	<i>p</i> -Me	<i>p</i> -CN	247.5	239.8

\* tentative assignment

planarity will be even larger, and since mesomeric interactions decrease proportional to the square cosine of the angle between the aryl ring and the double bond, deviations from the Hammett relations may occur. The fact that a larger deviation from planarity causes a downfield shift means that unsubstituted phenyl rings (which can in principle be donating or withdrawing) are electron donating in this case. This behaviour parallels that of aryl ketones and ketimines, but is surprising if one considers that the inherent polarization of the  $\text{P}=\text{C}$  bond is opposite, i.e.  $\delta^+$  on P and  $\delta^-$  on C. Apparently resonance structure I (Scheme 2) in which phosphorus is relieved from double bonding without losing its octet, contributes significantly, while II is not important.

Scheme 2



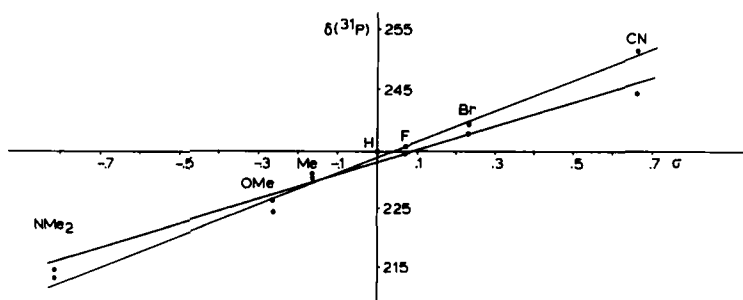


Figure 1

Reaction of **2** with *para*-monosubstituted benzophenones yield mixtures of E- and Z-phosphaalkenes. In the  $^{31}\text{P}$  NMR spectrum two peaks of equal intensity are observed (Table 1).

In Figure 1  $^{31}\text{P}$  shifts are plotted against Hammett values. Two straight lines result, one for the smaller differences  $\Delta\delta$  ( $= \delta(1x) - \delta(1)$ ; ( $\delta(1) = 234.5$  ppm)) and one for the larger  $\Delta\delta$ .  $^{31}\text{P}$  shifts are additive for phosphaalkenes  $\text{MesP}=\text{C}(\text{C}_6\text{H}_4\text{ } p\text{-X})\text{C}_6\text{H}_4\text{ } p\text{-Y}$ . For instance, **1h** and **1h'** have shifts at  $\delta = 224.3$  and  $\delta = 226.3$  ppm, a difference of  $\Delta\delta = -10.2$  and  $\Delta\delta = -8.2$ , respectively; **1l** and **1l'** have  $\Delta\delta = 4.4$  and  $\Delta\delta = 2.9$ . For the mixed compounds **1p'** and **1p** the calculated shifts are  $\delta(1) + \text{larger } \Delta\delta(\text{OMe}) + \text{smaller } \Delta\delta(\text{Br})$  or  $234.5 - 10.2 + 2.9 = 227.2$  ppm and similarly  $234.5 - 8.2 + 4.4 = 230.7$  ppm. These are close to the experimental values ( $\delta = 227.1$  and  $\delta = 230.3$ ).

Configurational assignment was possible when crystallization from pentane at  $-20^\circ\text{C}$  of 1:1 mixture of **1p'** and **1p** yielded crystals with a ratio 12:1. X-ray crystal structure determination revealed the structure shown in Figure 2. It turns out that the isolated crystals of **1p'** ( $\delta(^{31}\text{P}) = 227.1$  ppm) have the Z-configuration, i.e. the *para*-methoxyphenyl group is trans to the P-mesityl group. Because of the aforementioned additivity and Hammett correlation of the phosphorus chemical shifts, one may conclude that it is always the trans-aryl group which has a greater effect on  $\delta(^{31}\text{P})$ , and thus assign the configurations of all phosphaalkenes as

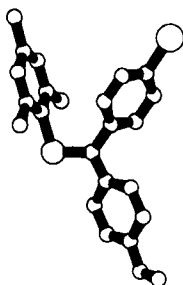


Figure 2

indicated in Table 1. This assignment is in (qualitative) agreement with the expected torsional angles of the aryl groups (*vide supra*).

**1p'** is thermally not stable in solution, but isomerizes to **1p** at room temperature; finally, the 1:1 equilibrium mixture is again obtained. It is expected that in comparison to the analogous ketimines, the barrier of rotation around the P=C double bond will be lower, while inversion at the heteroatom will be more difficult. Preliminary results support a rotation mechanism for the isomerization of **1p'**. The reaction follows first order kinetics, which rules out isomerization via dimers. The energy barrier for this process ( $\Delta G^\ddagger(293) = 23$  kcal/mol) is much lower than the inversion barrier of tri-coordinated phosphines, which in turn is expected to be lower than that of di-coordinated phosphines. Consequently, E/Z isomerization must occur by rotation around the P=C bond. In contrast, ketimines isomerize by an inversion mechanism (3).

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