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STABLE UNSYMMETRICAL DIPHOSPHENES

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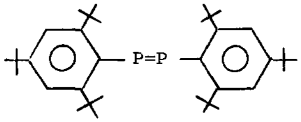
Abstract: Variation of the ortho-alkyl substituents in diaryldiphosphenes revealed that their stability is determined by steric hindrance. By suitable combinations of ortho-substituents, it was therefore possible to prepare the first relatively stable unsymmetrical diphosphenes (3e,f,g) which were characterized by ^{31}P NMR spectroscopy.

The pioneering study of Yoshifuji et al.[1] on bis(2,4,6-tri-tert-butylphenyl)diphosphene (1a), the first stable phosphorus analogue of the well known azo-compounds, has triggered growing activities in the area of stable diphosphenes[2-5]. We wish to report preliminary results concerning the formation of less hindered diphosphenes and of the first stable unsymmetrical representative of this class of compounds.



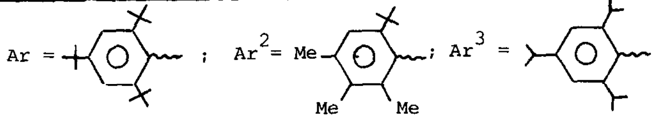
1a

Starting point of our investigations was the recognition of steric hindrance as a necessary requirement for the stabilization of phosphaalkenes RP=CR'R" which are not resonance stabilized[6]. A similar trend seems to hold for the few diphosphenes known so far: those substituted by the 2,4,6-tri-tert-butylphenyl group[1,2b,3,4] or by the $(Me_3Si)_3C$ group[2c,4] are stable at room temperature, while those carrying tert-butyl or mesityl groups polymerize[2a]. In order to define the limits of steric protection more closely, we investigated the formation of diphosphenes for a number of different substituents on phosphorus.

In first instance, we employed Yoshifuji's method of treating aryldihalophosphines with magnesium in THF at room temperature. When the typical deep-orange colour of the diphosphenes had reached a maximum, the solutions were evaporated to dryness at room temperature, the residues extracted with pentane, and the pentane extracts evaporated at room temperature. The residues thus obtained were dissolved in $CDCl_3$ and investigated by ^{31}P NMR spectroscopy. Starting material was no longer present; diphosphenes were unambiguously identified by their characteristic low field ^{31}P chemical shifts[2-4].

$$Ar'PX_2 + Ar''PY_2 \xrightarrow[THF]{Mg} \underset{1}{Ar'P{=}PAr'} + \underset{2}{Ar''P{=}PAr''} + \underset{3}{Ar'P{=}PAr''}$$

Reaction	aryl-dihalophosphine[a]				1 (δ ^{31}P;ppm) [$^1J_{P=P}$;Hz]	2 (δ ^{31}P;ppm) [$^1J_{P=P}$;Hz]	3 (δ ^{31}P;ppm) [$^1J_{P=P}$;Hz]	4 (δ ^{31}P;ppm) [$^1J_{P-P}$;Hz]
	Ar'	X	Ar''	Y				
A	Ar	Cl	-	-	1a(490.6) [0][2b-4]	-	-	{4a}[b]
B	Ar^2	Cl	-	-	1b(509.8) [0]	-	-	{4b}[b]
C	Ar^3	Cl(Br)	-	-	{1c}[b]	-	-	4c(-99.3;-133) [180]
D	Mes	Br	-	-	{1d}[b]	-	-	4d(-109.2;-143.3) [184]
E	Ar	Cl	Ar^2	Cl	1a	2b(=1b)	3e(478;512) [580]	-
F	Ar	Cl	Ar^3	Cl(Br)	1a	{=1c}[b]	3f(470;535) [572]	4c + mixed 4
G	Ar	Cl	Mes	Br	1a	{=1d}[b]	3g(463;541) [571]	4d
H	Ar	Cl	Ph	Cl	1a	{ 2h }[b]	{3h}[b]	
I	Ar^2	Br	Mes	Cl	1b	{=1d}[b]	{3i}[b]	

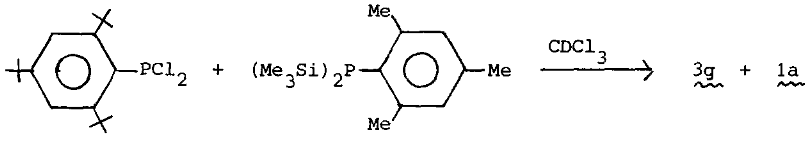
[a] 

; Mes=2,4,6-trimethylphenyl

[b] { } : not observed.

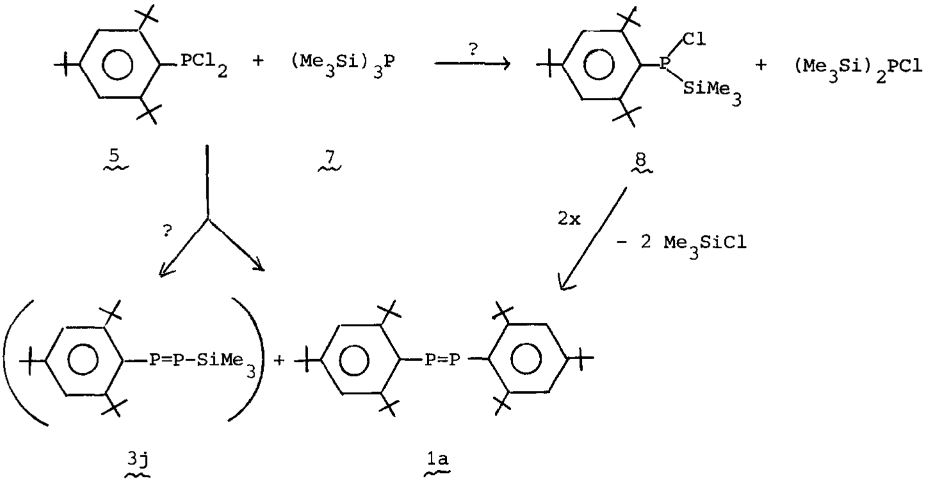
Other products observed were the cyclotriphosphines 4 (PR—PR—PR; 4c: R=Ar^3; 4d: R=Mes) in reactions C,D,F and G; they can be recognized by their high field chemical shift and their typical A_2X coupling pattern[8]. In some cases, unidentified cyclotetra- and/or cyclopentaphosphines were formed as indicated by phosphorus chemical shifts in the range of δ=-30 to -50 ppm[9] (reactions B,C,D,H).

Besides by ^{31}P NMR spectra, new diphosphenes were characterized by mass spectroscopy and, in the case of 3g, by independent synthesis by the method of Satgé[2a]:



5 6

In this reaction, the formation of 1a was unforeseen. Possibly, its formation from 5 is initiated by rapid exchange of one chlorine against a trimethylsilyl group of 6. This mode of reaction is probably also involved when 5 and tris(trimethylsilyl)phosphine (7) are mixed in $CDCl_3$. At room temperature, the reaction was very slow, but at 50-60 °C, 1a was observed. In the reaction mixture a second diphosphene was present; it was not yet identified, but according to the ^{31}P NMR data (δ=486 8 and 628.2 ppm; $^1J_{PP}$=575 Hz) it might be the expected, unsymmetrical 3j.



Although the course of this reaction needs closer investigation, the formation of 1a from 5 and 7 very likely proceeds via the intermediacy of 8.

The following conclusions can be drawn from the results presented in the table.

1) Steric hindrance is indeed the predominant factor in determining the stability of the diphosphenes. This is evidenced by the absence of 1c and 1d (reactions C and D) and of symmetrical or unsymmetrical diphosphenes other than 1a or 1b in reactions H and I.
2) While two *ortho*-isopropyl groups at each benzene ring are not sufficient to stabilize a diaryldiphosphene (1c), the combination of two *ortho*-*tert*-butyl groups plus two *ortho*-methyl groups forms about the limit of stability; it does not matter whether this combination is realized in a symmetrical (1b) or unsymmetrical way (3g). However, 1b and 3g are clearly less stable than 1a, e.g. on TLC and towards air.
3) Cyclotriphosphines 4 were only formed with less bulky substituents (reactions C, D, F and G), but were absent if the substituents were very bulky (reactions A and B). In fact, the formation of diphosphenes and cyclotri- or -oligophosphines seem to be mutually exclusive.
4) One of the most exciting results of the present investigation is the observation of the first relatively stable unsymmetrical diphosphenes: 3e, 3f, 3g and - possibly - 3j.

It is interesting to note that in the all-aryl substituted diphosphenes (1a, 1b, 3e, 3f and 3g) the chemical shifts are spread symmetrically around a value of ca. 490-505 ppm. In the case of 3, P(1) and P(2) are found to be different (assignment of P(1) and P(2) was not yet possible); they show opposite trends in a symmetrical fashion, so that the mean value of δ falls in the range indicated above.

Quite unusual is the coupling constant $^1J_{PP}$=570-580 Hz; it is to our knowledge the highest value observed. It may be considered as evidence for the special bonding situation; the σ-bond between the two sp^2-hybridized phosphorus atoms has very high s-character and is rather short due to the additional π bond (cf. the P=P bond length of 203.4 pm in **1a**[1]). A similar correlation between s-character and $^1J_{CC}$ is well known in ^{13}C NMR spectroscopy[10].

References and Notes

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