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PHOSPHORUS DIENIC LIKE SYSTEMS [1]

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Summary : P halogenated dicoordinated phosphorus species **1** and **2** react with N or C silylated derivatives leading to phosphorus dienic like systems **6-15**.

Intermolecular elimination of chlorosilane between halogenated and silylated compounds is a classical reaction leading to a variety of substituted species in organic and organometallic chemistry. Phosphorus compounds in particular coordination and bonding were also obtained using this method. Indeed diphospha-2,3 butadienes $(Me_3Si)_2C{=}P{-}P{=}CR_2$ were prepared by mixing the chlorophospha-alkene **1** $(Me_3Si)_2C{=}P{-}Cl$ with $Me_3Si{-}P{=}CR_2$ [2,3] .

We took advantage of such a reaction to prepare new low coordinated phosphorus conjugated dienic like systems by adding to the chlorophospha-alkene **1** [4] or the chlorophospha-imine **2** [5], monosilylated imines **3a**, **b**, **c**, $R^1R^2C{=}N{-}SiMe_3$ (**3a**, R^1= Ph, R^2= H; **3b**, R^1= Me, R^2= $OSiMe_3$; **3c**, R^1=R^2= Ph) monosilylated iminophosphoranes **4a**, **b**, $R_3P{=}NSiMe_3$ (**4a**, R= Ph; **4b**, R= NMe_2)(Scheme I).

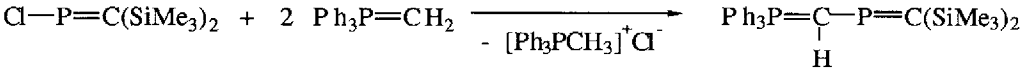
$$\underset{\textbf{1 - 2}}{X{=}P{-}Cl} \quad + \quad \underset{\textbf{3a-c}\ ,\textbf{4a-b}}{Me_3Si{-}N{=}Y} \quad \xrightarrow[-\ Me_3SiCl]{} \quad \underset{\textbf{6 - 14}}{X{=}P{-}N{=}Y}$$

1 : X = $C(SiMe_3)_2$ **2** : X = N-Ar (Ar = $tBu_3C_6H_2$)
3 a : Y = CHPh **3 b** : Y = $C(Me)OSiMe_3$ **3c** : Y = CPh_2
4 a : Y = PPh_3 **4 b** : Y = $P(NMe_2)_3$

Scheme I

In a typical experiment 10^{-2} mol of **1** or **2** in 15 ml of dichloromethane is added over a period of 5 minutes, at room temperature to a dichloromethane solution (15 ml) of the N or C silylated product. As soon as the addition is over, solvent and chlorotrimethylsilane are removed under reduced pressure leading to the expected phosphorus dienes **6-14** in near quantitative yields. **10** can directly be obtained by reacting the lithium derivative $Ph_2C=NLi$ with **1**.

Furthermore easy access to original $R_3P=C-P=CR'_2$ species like **15** was found when 2 equivalents of the ylide $Ph_3P=CH_2$, **5** are treated with one equivalent of the chlorophospha-alkene **1** (Scheme II).



$$Cl-P=C(SiMe_3)_2 + 2\ Ph_3P=CH_2 \xrightarrow[-\ [Ph_3PCH_3]^+Cl^-]{} Ph_3P=\underset{H}{\underset{|}{C}}-P=C(SiMe_3)_2$$

1 **5** **15**

Scheme II

The exact formulation of **6-15** has been mainly established by NMR, IR and mass spectroscopies. For example all these compounds exhibit characteristic ^{31}P chemical shifts (from 234.8 to 359.7 ppm, see Table I) for dicoordinated phosphorus species, while IR spectra show unequivocal absorptions due to $\nu_{(P=N)}$ and $\nu_{(C=N)}$ respectively in the regions 1350-1280 and 1700-1600 cm^{-1}.

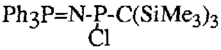
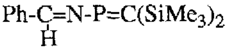
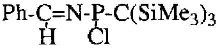
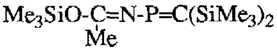
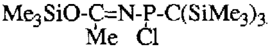
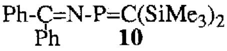
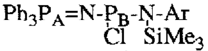
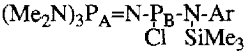
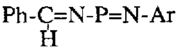
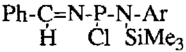
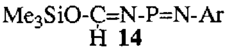
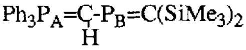
Most of these derivatives are stable at 0°C. If a large number of cyclic dicoordinated phosphorus derivatives stabilized by conjugation are described, the corresponding linear species are not well known: only a few compounds of this type are reported till now [2,3,6].

On the other hand crowded halogenophosphines **16-22** are directly formed when a dichloromethane solution of the starting phospha-alkene **1** or the phospha-imine **2** are mixed and stirred for 2 hours at room temperature with the silylated products **3a, b** and **4a, b**. The formation of chlorophosphines **16-22** result from the 1-2 addition of trimethylchlorosilane either on -P=C or -P=N-fragments.

Indeed these reactions allow to prepare bulky chlorophosphines impossible or difficult to obtain by classical ways. For example the dichlorophosphine $(Me_3Si)_3CPCl_2$ does not react - or react very slowly- with **3a, b** or **4a, b** in the same experimental conditions. Investigations on the reactivity of these new systems are underway.

Table I

^{31}P Chemical shifts of the phosphorus dienic like systems **6-15** and of the chlorophosphines **16-22** in $CHCl_3$.

Compounds	δppm	$^2J_{PP}$(Hz)	Compounds	δppm	$^2J_{PP}$(Hz)
$Ph_3P_A{=}N\text{-}P_B{=}C(SiMe_3)_2$ **6**	$\delta_A=15$ $\delta_B=356$	42	 $Ph_3P{=}N\text{-}\underset{Cl}{P}\text{-}C(SiMe_3)_3$ **16**	$\delta_A=19.1$ $\delta_B=208.9$	75.6
$(Me_2N)_3P_A{=}N\text{-}P_B{=}C(SiMe_3)_2$ **7**	$\delta_A=32.6$ $\delta_B=359.7$	43.4	 $(Me_2N)_3P_A{=}N\text{-}\underset{Cl}{P_B}\text{-}C(SiMe_3)_3$ **17**	$\delta_A=33.9$ $\delta_B=212.8$	79.1
 $Ph\text{-}\underset{H}{C}{=}N\text{-}P{=}C(SiMe_3)_2$ **8**	355.3		 $Ph\text{-}\underset{H}{C}{=}N\text{-}\underset{Cl}{P}\text{-}C(SiMe_3)_3$ **18**	100.7	
 $Me_3SiO\text{-}\underset{Me}{C}{=}N\text{-}P{=}C(SiMe_3)_2$ **9**	328.7		 $Me_3SiO\text{-}\underset{Me}{C}{=}N\text{-}\underset{Cl}{P}\text{-}C(SiMe_3)_3$ **19**	91.1	
 $Ph\text{-}\underset{Ph}{C}{=}N\text{-}P{=}C(SiMe_3)_2$ **10**	322.8				
$Ph_3P_A{=}N\text{-}P_B{=}N\text{-}Ar$ **11**	$\delta_A=5.4$ $\delta_B=237.1$	28.2	 $Ph_3P_A{=}N\text{-}\underset{Cl}{P_B}\text{-}\underset{SiMe_3}{N}\text{-}Ar$ **20**	$\delta_A=12.1$ $\delta_B=173.8$	69
$(Me_2N)_3P_A{=}N\text{-}P_B{=}N\text{-}Ar$ **12**	$\delta_A=27.2$ $\delta_B=234.8$	25	 $(Me_2N)_3P_A{=}N\text{-}\underset{Cl}{P_B}\text{-}\underset{SiMe_3}{N}\text{-}Ar$ **21**	$\delta_A=25.5$ $\delta_B=173.7$	70.7
 $Ph\text{-}\underset{H}{C}{=}N\text{-}P{=}N\text{-}Ar$ **13**	267		 $Ph\text{-}\underset{H}{C}{=}N\text{-}\underset{Cl}{P}\text{-}\underset{SiMe_3}{N}\text{-}Ar$ **22**	133.8	
 $Me_3SiO\text{-}\underset{H}{C}{=}N\text{-}P{=}N\text{-}Ar$ **14**	268.2				
 $Ph_3P_A{=}\underset{H}{C}\text{-}P_B{=}C(SiMe_3)_2$ **15**	$\delta_A=20.4$ $\delta_B=336$	100			

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(2) R. Appel, V. Barth, F. Knoch, *Chem. Ber.*, **116**, 938, 1983

(3) L.N. Markovskii, V.D. Romanenko, L.S. Kachkovskaya, M.I. Povolotskii, I.I. Patsanovskii, Yu.Z. Stepanova, E.A. Ishmaeva, *Zh. Obsch. Khim.* **57**, 901, 1987 ; CA **108**: 204691j (1988)

(4) R. Appel, F. Knoll, I. Ruppert, *Angew. Chem.*, **93**, 771, 1981.
Angew. Chem. Int. Ed. Engl., **20**, 731, 1981.

(5) E. Niecke, M. Nieger, F. Reichert, *Angew. Chem.*, **100**, 1781 1988.
Angew. Chem. Int. Ed. Engl., **27**, 1715, 1988.

(6) R. Appel, V. Kündgen, F. Knoch, *Chem. Ber.*, **118**, 1352, 1985;
L.N. Markovskii, V.D. Romanenko, T.V. Didvanko, *Zh. Obsch. Khim.*, **53**, 1672, 1983;
R. Appel, P. Fölling, W. Schuhn, F. Knoch, *Tetrahedron Lett.*, **27**, 1661, 1986;
R. Appel, F. Knoch, R. Zimmermann, *Chem. Ber.*, **118**, 814, 1985.

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