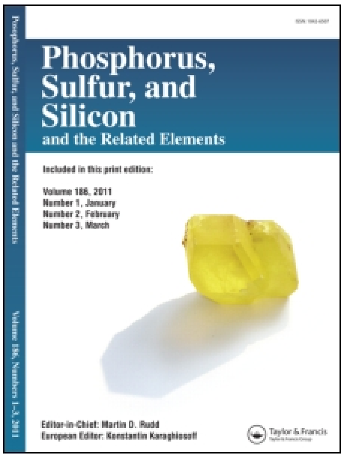

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RECENT DEVELOPMENTS IN THE CHEMISTRY OF CATIONS AND ANIONS CONTAINING LOW VALENT PHOSPHORUS CENTERS

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Iminophosphenium- anmd Methylenephosphenium-Cations

We have already demonstrated that the iminophosphenium ion, $[P{\equiv}NAr]^+$ ($Ar=2,4,6\text{-}t\mathrm{Bu}_3C_6H_2$) **1** is produced by reaction of chloro(aryl)iminophosphine in the presence of the Lewis acid $AlCl_3$[1].

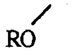
In order to get further insight into the formation of this unique cationic system we studied the structural effects in iminophosphines produced by σ-acceptor substituents at phosphorus and σ-donor substituents at nitrogen, respectively.

Within a series of the oxo-derivatives, RO-P=N-Ar **2**, which has been obtained by nucleophilic displacement reactions from ClP=NAr, we have found that the electronic nature of the substituent R (Me_3Si(**2a**), $t\mathrm{Bu}_2CH$(**2b**), p-Me-C_6H_4-SO_2(**2c**), CF_3SO_2 (**2d**)) exert not only a deformation of the geometry (**A**) → (**B**) (P-N-C(Ar) 144.4(2) (**2a**); 179.1(4) (**2b**)) but also a P-O-bond elongation (**B**) → (**C**) (P-O 162.8(3) (**2b**), 172.8(3) (**2c**), 192.3(3) (**2d**)).

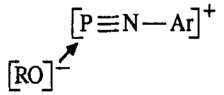
These effects (**A**) → (**C**) are accompanied by a continous PN-bond strengthening as well as a shielding of the ^{31}P nuclei and result in **2d** (P-N 146.7(3), P-N-C(Ar) 176.4(3), $\delta^{31}P$ 55) in a bonding situation similar to that found in **1**.

Similar effects are observed for iminophosphines of the type C_5Me_5-P=NR, **3**, with increasing the σ-donor ability of the nitrogen substituent. While a classical structure (**D**) with a P/C-bond order of unity (188.7(2)) has been observed in the case of R= $(Me_3Si)_2N$, a strong σ-donating substituent ($R=i\mathrm{Pr}_3Si$) results in a η^2-attachment of the planar Me_5C_5-ring to the phosphorus atom (P-C 212.2(4), 216.8(4)[2], so that this species can be regarded as a π-complex between a cyclopentadienyl anion and an azaphospheniun cation (E).

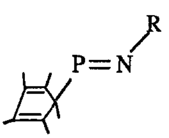
(A)



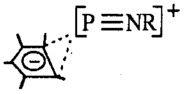
(B)



(C)

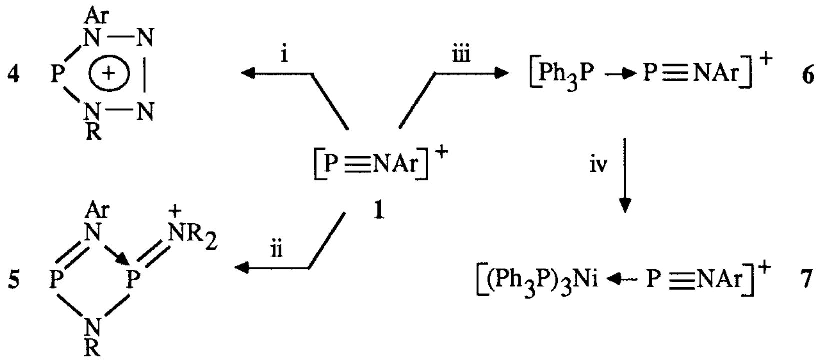


(D)

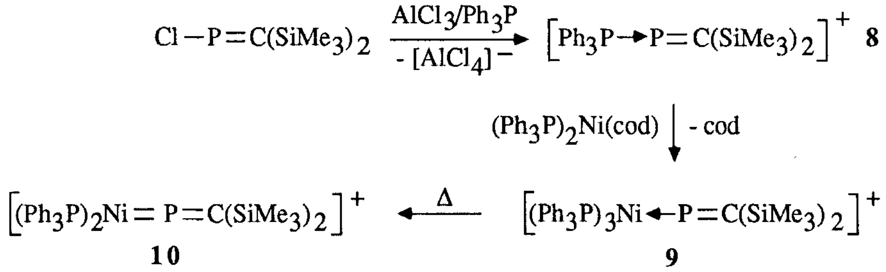


(E)

Reaction of the cation **1** with azides (i) or amino(imino)phosphines (ii) produces the corresponding [2+3]- **4** and [2+2]-cycloadducts **5**, the structures of which were studied by X-ray diffractometry. The averaged bond distances for **4**, are in accord with a delocalized 6π-system, whilst the significant differences in the PN-distances in **5** (e.g. P-N(Ar) 163.6(3), 180.1(3);
P-N(R) 163.2(3), 179.0(3)) are in accord with the formation of an intramolecular donor/acceptor complex one mesomeric structure of which is displayed in **5**. Reaction of **1** with the donor Ph_3P (iii) gives the 1:1 adduct **6** ($\delta^{31}P$ 22, 87, $J_{PP} = 340$ Hz), which by treatment with $(Ph_3P)_2Ni(cod)$ (iv) is transformed into the azaphosphenium complex **7** via ligand shift from the phosphorus to the metal atom ($\delta^{31}P$ 28, 210, $J_{PP} = 69$Hz).



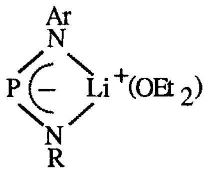
With respect to our investigations on **1** we studied also the interaction of chloro(methylene)phosphines with $AlCl_3$ in the presence of suitable donor molecules and obtained by this route the stable phosphine-adduct **8**. It possess a strong P/C (163.5(4)) and a weak P/P-bond (226.7(4)) and can be used as a suitable precursor for the methylene-phosphenium cation, as it is demontrated by the reaction **8** with $(Ph_3P)_2Ni(cod)$ to give the 18- and 16- electron nickel complexes, **9** ($\delta^{31}P$ 26, 504, $J_{PP} = 77$ Hz) and **10** ($\delta^{31}P$ 29, 309, $J_{PP} = 128$ Hz), respectively.

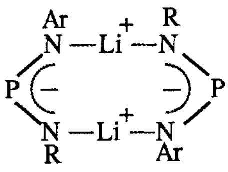


1,3-Diazaphosphaallyl-, 1-Azadiphosphaallyl -, 1,2-Diphosphaallyl- and 1-Phosphaallyl-Anions

Starting from NH-functionalized amino-iminophosphines, RN(H)-P=NAr[3], **11** (R=tBu, 1-Ad, Mes, CPh_3, Ar), the corresponding 1,3-diaza-phosphaallylic systems were obtained by reaction with *n*-butyl lithium.The lithium complexes exhibit a monomeric, **12** or dimeric structure, **13** , depending on the donor properties of the solvent and the steric demand of the substituents[3].
According to the X-ray structure, the bonding situation in the anion is comparable to the bis(amino)phosphenium cation, **14** • $[AlCl_4]^-$ (P-N 161.1, N-P-N 103.7).

12





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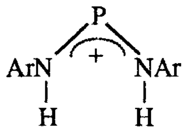


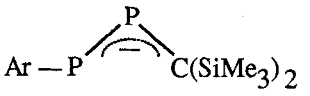
14

PH-functionalized phosphino(iminophosphines (E = NAr) and -methylenephosphines ($E{=}C(SiMe_3)_2$), **15** undergo base catalyzed isomerization into the corresponding diphosphene isomers **16**.

15 $\mathrm{ArP(H){-}P{=}E} \xrightarrow{\text{base}} \mathrm{ArP{=}P{-}E(H)}$ **16**

However, treatment of **15** with *n*-BuLi results in the formation of the lithium salts of 1-azadiphosphaallyl- **17** (δ^{31}P 244, 494, J_{PP} = 544 Hz) and 1,2-diphosphaallyl - anion **18** (δ^{31}P 212, 471, J_{PP} = 534 Hz). Furthermore, the synthesis of a stable 1-azaphosphaallyl system **19** was realized by treatment of ArP(H)Li with tolane. The heteroallylic structure of **17** and **19** is also proven by X-ray crystallographic studies (P-P 206.6(2), P-N 163.2(3), P-P-N 106(1), N····Li 213.9(7) (**17**) ; P-C 175.7(6), C-C 136.6(6), P-C-C 128.7(6), P····Li > 300) (**19**)).

17



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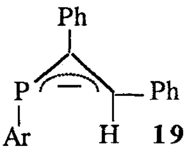
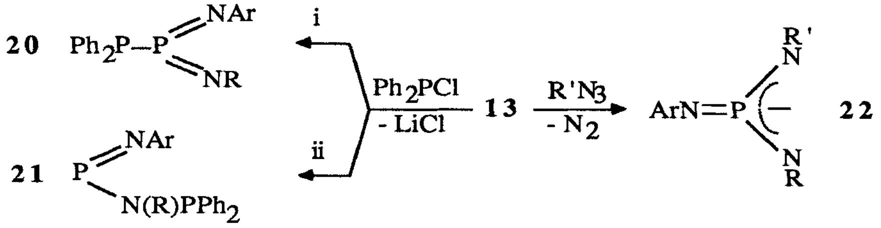
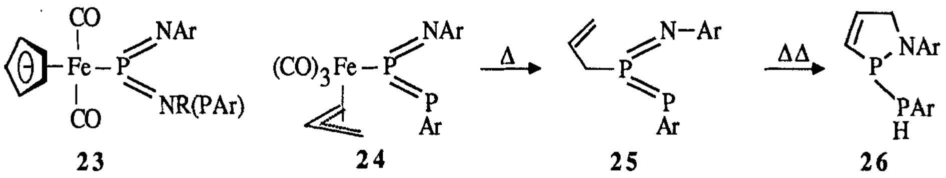


19

Reactions of these novel heteroallyl anions include the ambident reaction behaviour of **13** towards Ph_2PCl to give the isomers **20** or **21** depending on the solvent used (i = ether, ii = pentane)[3]. Reaction with alkyl azide produces the tris(imino)metaphosphate anion **22**, whose allylic bonding situation is evidenced by the ^{31}P- and ^{15}N-n.m.r. data (e.g. R=*t*Bu: δ^{31}P 64.9, δ^{15}N - 234 (NAr), - 281 (NR), J_{NP} = 69 Hz (PNAr), 30 Hz (PNR)). The ferrio-derivatives **23** and **24**, were obtained by the reaction of **13**(**17**) with (η^5-C_5H_5)Fe(CO)$_2$Cl and **17** with (η^3-C_3H_5)Fe(CO)$_3$Cl and it is shown that the latter (**24**) is easilyl transformed into the diphosphene-imine **25** and its phosphino-azaphospholene isomer **26**.





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