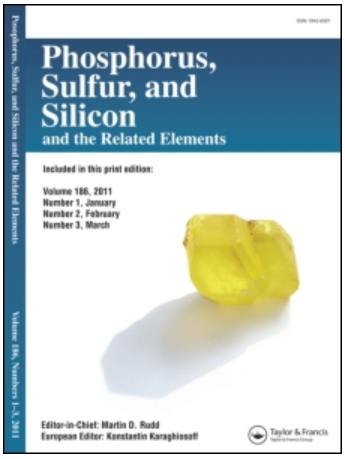

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphorus Carbene and Olefine Analogues

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PHOSPHORUS CARBENE AND OLEFINE ANALOGUES

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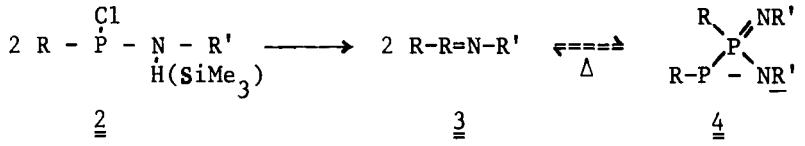
A representative of the yet unknown parent iminophosphane is $Bu^tP{=}NBu^t$ 1 which has been recognized as an carbenic analogue for some time[1]. The unusual properties of 1 prompted our investigations of the synthesis of further phosphorus(III)-(p-p)π-bonds systems with an orbital sequence (HOMO= n(P), LUMO= π* (P=X)) as well as the reaction behaviour of this class of compounds.

The approach of iminophosphanes of type 1 was achieved by chlorosilane elemination or base promoted dehydrochlorination reaction from the aminophosphanes 2[2].



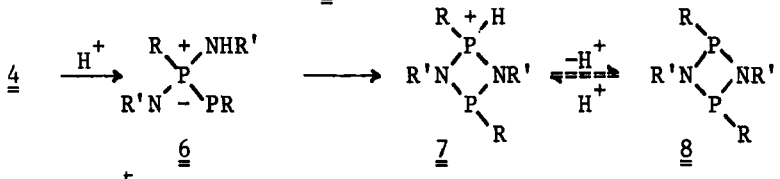
2 3 4

The stability of 3 stronly depends on the steric and electronic demand of the substituents. N-silylated derivatives ($R{=}Bu^t$, $R'{=}SiMe_3$, $SiMe_2Bu^t$) are only accessible in the dimeric form 4, while for N-arylated derivatives ($R{=}Bu^t$, Pr^i, $CH(SiMe_3)_2$; $R'{=}2,4,6\text{-}Bu^t{}_3C_6H_2$) no self dimerisation was observed. Borderline cases are the iminophosphanes ($R{=}Bu^t$, R'=adamanty, mesityl) which exist in both forms[2]. A similar reaction afforded the first iminophosphane with the >P-P=N-skeleton ($Bu^t{}_2P\text{-}P{=}N\text{-}2,4,6\text{-}Bu^t{}_3C_6H_2$; $\delta^{31}P$= 570,99; 430Hz; r_{PN}= 158; ∢ PPN= 106°)[3].

In order to get further insight in the reactivity of carbenic iminophosphanes, the reaction of 1 was studied in comparison with the isovalent olefinic methylenephosphane, $Bu^tP{=}CHBu^t$ 5[4]. The different reaction behaviour of 1 and 5 was confirmed by (4+1)- vs.

(4+2)-cycloadditions with 2,3-dimethylbutadiene and 1,1-oxidative addition vs. 1,2-addition with halogens and carbon tetrachloride[5].

The kinetically favoured (2+1)-cycloadduct of the iminophosphane 1 rearranges in the presence of acids (H^+, BF_3) to the thermodynamically stable diazadiphosphetidine 8; in the reaction with triflate acid two intermediates, the phosphonium salt 6 and the diazadiphosphetidinium ion 7 can be isolated[6].

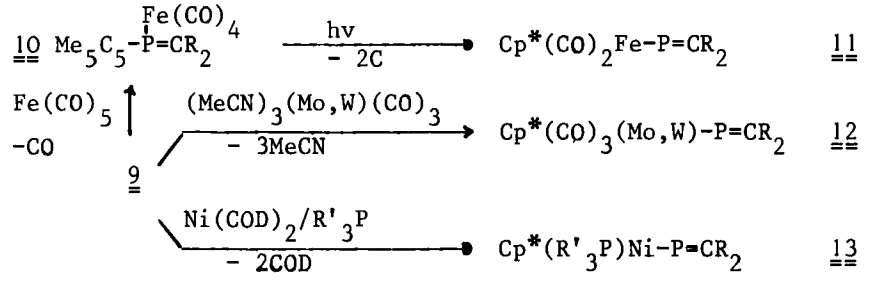


(R=R'=Bu^t)

A novel variety of 1-phosphatriazenes Bu^t-P=N-NR_2 (R=alkyl, phenyl, silyl) were synthesized by elimination reactions from corresponding hydrazophosphanes, $Bu^tP(Cl)$-N(H,$SiMe_3$)-NR_2[5]. Assignment of the order of orbitals (n(P),π(P=N)) in these compounds as well as in aminoiminophosphanes was carried out, utilizing the relationship between u.v. data ((n-π*)-(π-π*)) and ionization potentials (i.p. n(P)- i.p.π(P=N). For alkylated aminoiminophosphanes and 1-phosphatriazenes the π orbital is slighly above σ, while in the case of the silylated derivatives the order of orbitals is reversed[7]. This is in accord with the reaction behaviour towards hexafluoroacetone ((2+2)- vs. (2+1)-cycloaddition reaction[7]).

The ambident reactive behaviour of the iminophosphane system stimulates the synthesis of methylenephosphanes with a frontier orbital sequence (HOMO= n(P), LUMO= π*(P=C)). Suitable derivatives for this should be methylenephosphanes with σ-donor substituents at phosphorus (metal fragments) and π-aceptor substituents (silylgroups).

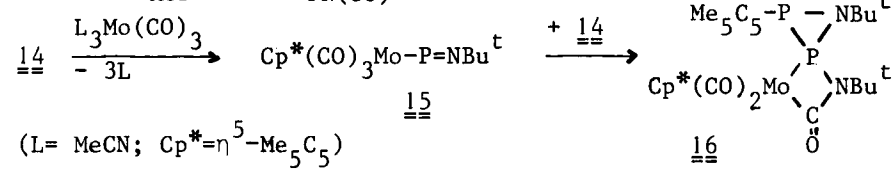
An entry to these compounds is the reaction of Me_5C_5-P=C($SiMe_3$)$_2$ 9 with transition metal complexes, via shift of the cyclopentadienylligand from phosphorus to the metal[8-10].



(R= $SiMe_3$; $Cp^*=\eta^5-C_5Me_5$)

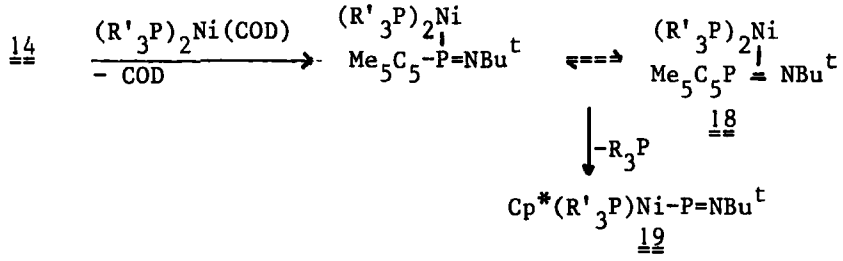
The high nucleophilicity at the phosphorus is evidenced by the spectroscopic investigations ($\delta^{31}P$= 500 - 740 ppm,($n-\pi^*$)= 540 - 640 nm), X-ray crystallographic studies (∢ M-P-C = 123 - 126°) as in the reaction with electrophiles[9,11]. The $Ni(CO)_4$promoted reaction of metallo-methylene-phosphanes is a new approach to metallaphosphaallenes[5].

Realizing that the "ligand shift method" might provide access to the metallo-iminophosphane system, $C_5Me_5-P=NBu^t$ 14 was treated with $(MeCN)_3Mo(CO)_3$. However, this reaction proceeds in a 2:1 molar ratio and affords the spirocyclic compound 16, via a metallo-iminophosphane intermediate 15. The structural investigations of 16 is in accord with a transition metal complex of an aza-$\lambda^3\lambda^3$-azadiphosphiridine[12] (r_{MoP}= 245, $r_{PN(CO)}$= 175 pm).



(L= MeCN; $Cp^*=\eta^5-Me_5C_5$)

Avoiding electrophilic ligands at the metall fragment the approach to metallo-iminophosphanes was accomplished by the reaction of 14 with $(R_3P)_2Ni(COD)$. Based on n.m.r. investigations the primary formed with η^1- and η^2-coordinated complexes 17, 18 rearrange with elemination of phosphane to the novel metallo-iminophosphanes 19[10].



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