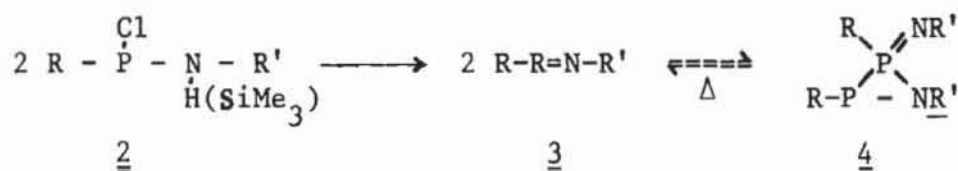


PHOSPHORUS CARBENE AND OLEFINE ANALOGUES

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A representative of the yet unknown parent iminophosphane is $\text{Bu}^t\text{P}=\text{NBu}^t$ 1 which has been recognized as an carbenic analogue for some time¹. 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 elimination or base promoted dehydrochlorination reaction from the aminophosphanes 2².

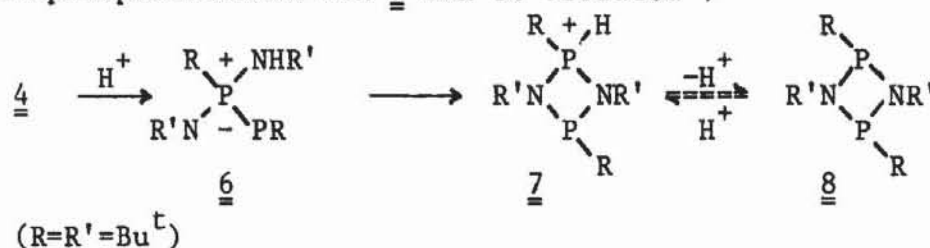


The stability of 3 strongly depends on the steric and electronic demand of the substituents. N-silylated derivatives (R=Bu^t, R'=SiMe₃, SiMe₂Bu^t) are only accessible in the dimeric form 4, while for N-arylated derivatives (R=Bu^t, Prⁱ, CH(SiMe₃)₂; R'=2,4,6-Bu^tC₆H₂) no self dimerisation was observed. Borderline cases are the iminophosphanes (R=Bu^t, R'=adamanty, mesityl) which exist in both forms². A similar reaction afforded the first iminophosphane with the >P-P=N-skeleton (Bu^t₂P-P=N-2,4,6-Bu^t₃C₆H₂; $\delta^{31}\text{P} = 570,99; 430\text{Hz}$; $r_{\text{PN}} = 158; \chi_{\text{PPN}} = 106^{\circ}$)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, $\text{Bu}^t\text{P}=\text{CHBu}^t$ 5⁴. 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 tetrachloride⁵.

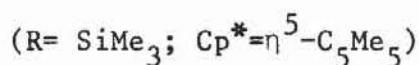
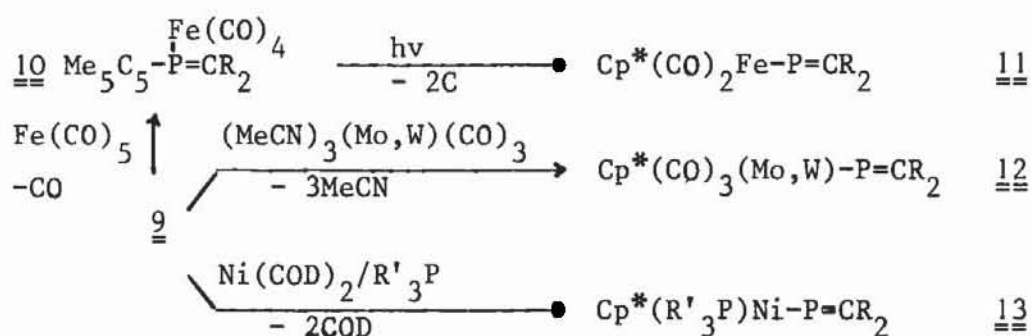
The kinetically favoured (2+1)-cycloadduct of the iminophosphane 1 rearranges in the presence of acids (H^+ , BF_3) to the thermodynamically stable diazadiphosphetidine 8; in the reaction with triflate acid two intermediates, the phosphonium salt 6 and the diazadiphosphetidinium ion 7 can be isolated⁶.



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 ($n(P), \pi(P=N)$) in these compounds as well as in aminoiminophosphanes was carried out, utilizing the relationship between u.v. data ($(n-\pi^*)-(\pi-\pi^*)$) and ionization potentials (i.p. $n(P)$ - i.p. $\pi(P=N)$). For alkylated aminoiminophosphanes and 1-phosphatriazenes the π orbital is slightly above σ , while in the case of the silylated derivatives the order of orbitals is reversed⁷. This is in accord with the reaction behaviour towards hexafluoroacetone ((2+2)- vs. (2+1)-cycloaddition reaction⁷).

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

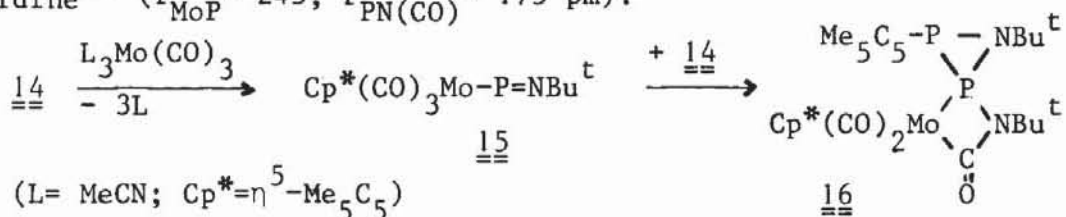
An entry to these compounds is the reaction of $Me_5C_5-P=C(SiMe_3)_2$ 9 with transition metal complexes, via shift of the cyclopentadienylligand from phosphorus to the metal⁸⁻¹⁰.



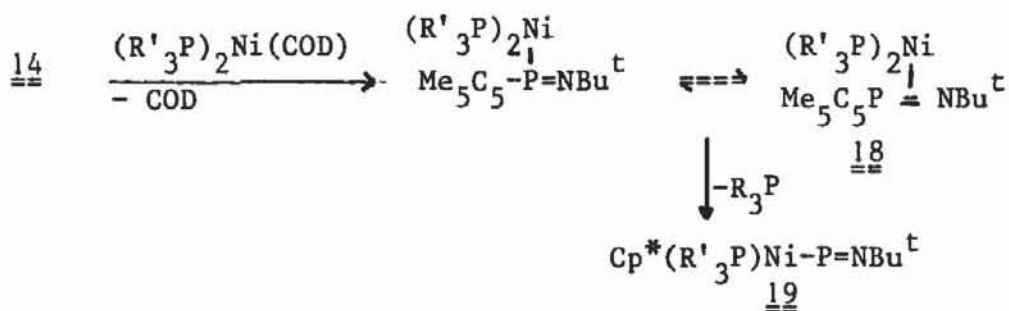
The high nucleophilicity at the phosphorus is evidenced by the spectroscopic investigations ($\delta^{31}\text{P} = 500 - 740$ ppm, $(n-\pi^*) = 540 - 640$ nm), X-ray crystallographic studies ($\angle \text{M-P-C} = 123 - 126^\circ$) as in the reaction with electrophiles^{9,11}. The $\text{Ni}(\text{CO})_4$ promoted reaction of metallo-methylene-phosphanes is a new approach to metallaphosphaallenes⁵.



Realizing that the "ligand shift method" might provide access to the metallo-iminophosphane system, $\text{C}_5\text{Me}_5\text{-P}=\text{NBu}^t$ 14 was treated with $(\text{MeCN})_3\text{Mo}(\text{CO})_3$. 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- $\lambda^3\lambda^3$ -azadiphosphiridine¹² ($r_{\text{MoP}} = 245$, $r_{\text{PN}(\text{CO})} = 175$ pm).



Avoiding electrophilic ligands at the metall fragment the approach to metallo-iminophosphanes was accomplished by the reaction of 14 with $(\text{R}_3\text{P})_2\text{Ni}(\text{COD})$. Based on n.m.r. investigations the primary formed with η^1 - and η^2 -coordinated complexes 17, 18 rearrange with elimination of phosphane to the novel metallo-iminophosphanes 19¹⁰.



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