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Iminophosphanes and Diphosphenes - Recent Developments

E. Niecke^a; O. Altmeyer^a; D. Barion^a; R. Detsch^a; C. Gätner^a; J. Hein^a; M. Nieger^a; F. Reichert^a

^a Anorganisch-Chemisches Institut der Universität Bonn, Bonn 1, FRG

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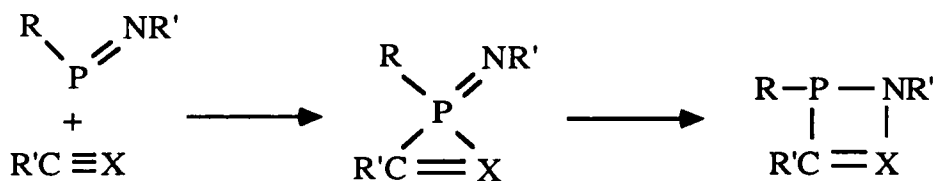
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IMINOPHOSPHANES AND DIPHOSPHENES - RECENT DEVELOPMENTS

E. NIECKE*, O. ALTMEYER, D. BARION, R. DETSCH,
 C. GÄRTNER, J. HEIN, M. NIEGER and F. REICHERT
 Anorganisch-Chemisches Institut der Universität Bonn
 Gerhard-Domagk-Str.1, 5300 Bonn 1, FRG

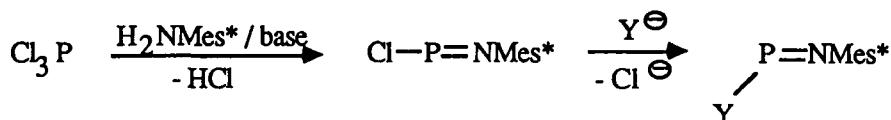
Abstract Novel iminophosphane derivatives are synthesized by nucleophilic displacement from Cl-P=NMe_3^+ . Structures, spectroscopic data, and novel chemical reactions of these compounds are discussed. Furthermore, synthesis of stable cis- and trans isomers of a diphosphene, as well as their mutual interconversion, is reported.

In recent time we have shown that iminophosphanes are capable of carbenic as well as olefinic reaction behaviour^[1]. Carbenic reactivity is impressively demonstrated in the additions of P-alkylated iminophosphanes to alkynes or phosphalkynes, to give λ^5 -phosphirenes or -diphosphirenes, respectively, which further rearrange to the corresponding thermodynamically more stable four membered heterocycles.

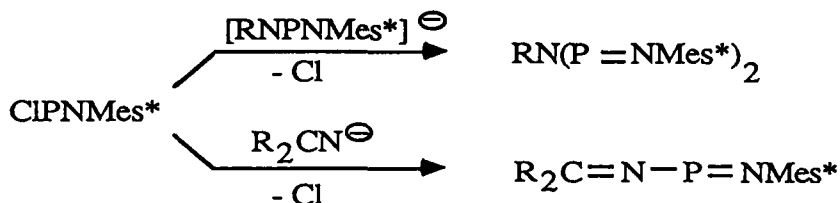


A considerable extension of iminophosphane chemistry became possible with the synthesis of the stable P-chloro-substituted derivative, Cl-P=NMe_3^+ ^[2], which gives access to a variety of new derivatives Y-P=NMe_3^+ via displacement of

the chloride by nucleophiles Y^- (Y^- = alkyl, aryl, $R-C\equiv C^-$, R_2N^- , RO^- , R_2P^- , R_2As^- , RS^- , RSe^- , Br^- , I^- , $CpM(CO)_2^-$, ($M = Fe, Ru$)).

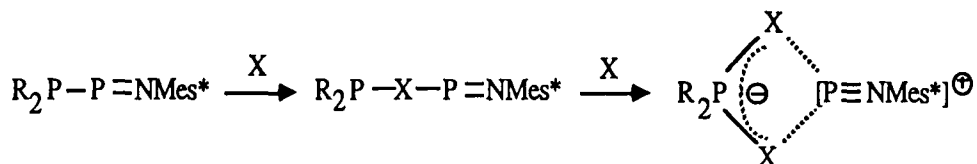


By analogous substitution reactions with diaza-phosphaallyl- or azomethine-anions, respectively, the novel diphospha-pentaazadiene and phospho-diaza-butadiene systems were accessible for the first time.

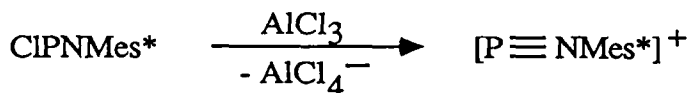


Structural and spectroscopic (NMR, UV/VIS) properties of the new derivatives are discussed. For the ^{31}P -NMR chemical shifts a linear correlation with $n-\pi^*$ optical transition energies is established. Considerable variations of PN bond distances (162-148 pm) and P-N-R bond angles ($107-178^\circ$) in these compounds can be correlated with σ -acceptor and/or π -donor capability of the substituents. The special structural features of the P-iodo-derivative, $I-P=NMe s^*$, are interpreted in terms of description of the bonding situation as a donor-acceptor complex of I^- and $[P NMe s^*]^+$. A similar system, where a formal phospho-diazonium cation is intramolecularly stabilized by a η^2 -donor ligand, is represented by dithio- or diseleno-phosphinato substituted iminophos-

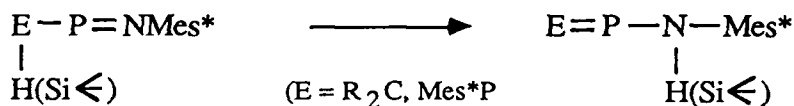
phanes, which are accessible by oxidation of a phosphino-
iminophosphane with excess chalcogene ($X = S, Se$) [3].



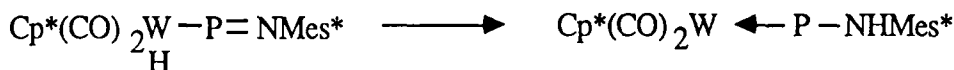
A salt featuring a free phosphadiazonium cation was obtained by chloride abstraction from Cl-P=NMes^* with AlCl_3 [2].



A new type of chemical reaction yet unprecedented for iminophosphanes was discovered in the 1.3-sigmatropic shift of protons or trialkylsilyl groups, with concomitant formation of a new phosphorus-element multiple bond.

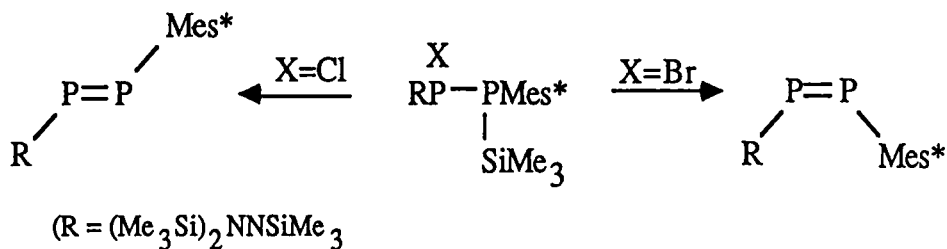


A special case of this reaction, viz. rearrangement of a transition-metal substituted iminophosphane, provides an interesting new route to terminal phosphinidene complexes.



Whereas stable cis-configured iminophosphanes [2, 4] and diphosphenes [5] are known recently, we report for the first

time on a case where both stereoisomers of a diphosphene are stable and may be synthesized selectively. Thus, *trans*-R-P=PMe^s* is obtained as the only product after elimination of halosilane from a functionalized 1-chloro-diphosphine (X=Cl), while the analogous reaction of the bromo-derivative (X=Br) yields exclusively the *cis*-diphosphene. In solution, interconversion of both isomers is observed.



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