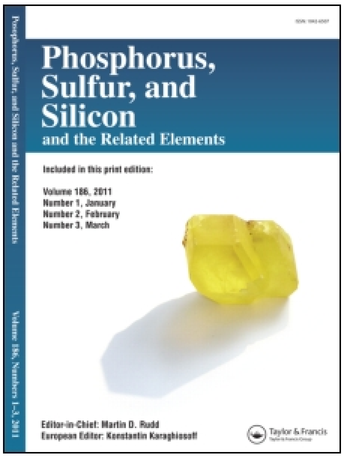

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Heterobifunctional Phosphorus-Nitrogen Compounds: Iminophosphoranophosphines and Their Complexes

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HETEROBIFUNCTIONAL PHOSPHORUS-NITROGEN COMPOUNDS: IMINOPHOSPHORANOPHOSPHINES AND THEIR COMPLEXES.

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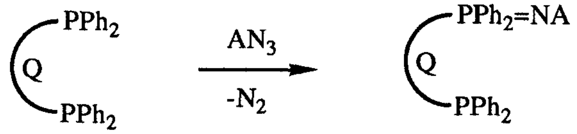
T6G 2G2

Abstract Heterobifunctional phosphorus compounds have been prepared by oxidizing one phosphorus atom of a bis(phosphine) with azides. A variety of backbone structures have been used with one and two carbon chains, saturated and unsaturated structures and RN. Some degree of steric control appears to limit the extent of oxidation in *cis* bis(phosphines) with rigid backbones. Trimethylsilyl azide gives silylated iminophosphoranes with a reactive functionality on the imine nitrogen which can be replaced *via* metathetical elimination of Me_3SiX or converted to the trimethylsiloxy metal derivative by rearrangement of the trimethylsilyl group to terminal oxygen of a highly oxidized metal oxo precursor. Structural features of several examples of the heterobifunctional phosphorus compounds and their derivatives are described.

A variety of heterobifunctional imino-phosphoranophosphines of the general type $AN{=}PR_2QPR_2$ [A is H, $SiMe_3$, fluoroaromatics, nitroaromatics, etc., R is typically phenyl, and Q is *o*-C_6H_4 (**1a**), CH_2, C_2H_2 (**1b**, cis), N(R') (**3**) etc.] can be obtained by controlled azide oxidation of one phosphorus of a bis(phosphine). The saturated backbones typically tend to oxidize fully but careful control of conditions can produce the desired mono-oxidized product. Certain backbones however favor mono-oxidation through either electronic or steric control. As examples, the geometrically constrained *cis* substituted backbones represented by the *ortho*-phenylene and *cis*-ethylene bis(phosphines) yields only the mono-oxidized iminophosphoranophosphines **1a** and **1b** even under vigorous conditions of azide oxidation (eq. 1). This presumably arises as a result of steric constraints on the transition state involved.



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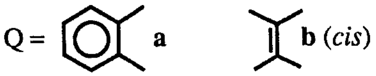
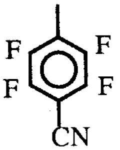
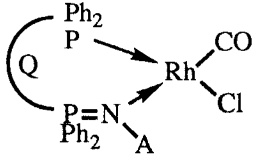


A = $SiMe_3$, $O{=}P(OPh)_2N$-,



The crystal structure of **1a** ($A{=}SiMe_3$) shows that the geometry in the region between the phosphorus centers is such that approach to the lone pair of the trivalent phosphorus is blocked by the imine functionality of the oxidized center so that it appears that the lone pair on phosphorus is thus shielded from attack by additional azide. If however the *trans* bis(phosphine) analog is used, azide oxidation of both phosphorus centers occurs readily and the mono-oxidized species cannot be obtained cleanly. The parameters obtained from the structure of **1a** give a bond length of 1.53Å and a N-Si bond length of 1.67Å. The Si-N-P angle is 152.7°.

In spite of the apparent interference of the lone pairs on P(III) and the imine nitrogen, compounds of the type **1** readily form complexes of the type **2** thus the lone pairs are accessible for complexation reactions. The Rh complex of **1a** is typical and the trimethyl silyl substituted compound of **1a** has been structurally characterized.



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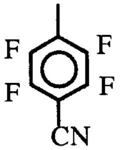
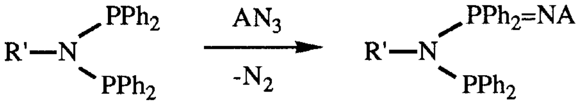
Q = as above

A = $SiMe_3$, $O{=}P(OPh)_2N$-,



The amino bis(phosphines) $[R_2P]_2N(R')$ (R = Ph, R' = Ph, Et, Me) can also be oxidized by azides at one phosphorus center to produce stable, acyclic linear phosphazenes, (3) [(**3a**) A = Me_3Si, R' = ^{n}Pr, (**3b**) A = p-CN-C_6F_4, R' = Et, (**3c**) A = $(PhO)_2P(O)$, R = Et] (eq. 2). These compounds in general have shown a tendency to undergo only limited



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(2)

(mono) oxidation. We have also observed during the slow reaction of azide (e.g. p-$CNC_6F_4N_3$) the formation of an intermediate species which appears to be the phosphazide. This species then decomposes slowly to the imine **3**. Interestingly the reaction shows initially (by ^{31}P nmr) that the bis amine(phosphine) is converted completely to the phosphazide. This phosphazide then decomposes (with some evidence that the imine nitrogen interacts with the P(III) center) to produce the iminophosphoranophosphine **3** along with some small amounts of doubly oxidized bis(phosphine) *and* (equal amounts of) the bis amino(phosphine). Crystal structures of two examples of compounds of type **3** illustrate the notable features of this backbone; the P(III)-N-P(V) angles are close to 120° and this bridging nitrogen is very nearly planar. The P(V)-N(bridge) bonds (*ca.* 1.68Å) are shorter than the P(III)-N(bridge) bond (*ca.* 1.73Å) and longer than the P(V)=N(terminal) (*ca.* 1.57Å) imine bonds.

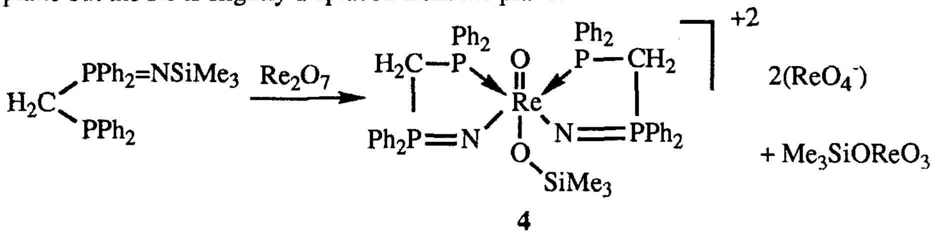
Substitutional Chemistry

When trimethyl silyl azide is used as oxidant, the imine nitrogen developed contains a reactive functionality, the $SiMe_3$ group, which can be replaced by means of metathetical reactions with halides with elimination of Me_3SiX or by a migration of the Me_3Si group to a terminal oxygen thereby creating a siloxy derivative. By the first route, pentafluorobenzonitrile reacts with the silyl imine in many, but not all cases, to form the tetrafluorobenzonitrile iminophosphorane. This opens a versatile route to substitution at nitrogen which allows varied substituents to be placed on the imine nitrogen without requiring that the azide be obtained. The halogen on the fluoroaromatic must be activated for this route to be viable.

Of considerable interest also are reactions of the silyl imine with metal halides and oxides to form derivatives which contain metal-nitrogen σ bonds. Two reactions have proven to be especially useful for the formation of these M-N σ bonds. The first is the elimination of Me_3SiCl from a metal chloride (eq. 3):

$$R_2P\text{-}N(R')\text{-}PR_2\text{=}NSiMe_3 + CpTiCl_3 \rightarrow R_2P\text{-}N(R')\text{-}PR_2\text{=}N\text{-}Ti(Cp)Cl_2 + Me_3SiCl \quad (3)$$

An alternative route of some interest is provided by highly oxidized metal oxides such as Re(VII) which react with silylated iminophosphorano-phosphines with Me_3Si migration from nitrogen of the ligand to the oxygen of the metal thus forming a siloxy derivative. As a novel example of this reaction, an unexpected dication of Re(VII) (**4**), containing two Re-N bonds, was obtained from the reaction of $Ph_2PCH_2P(Ph)_2NSiMe_3$ with Re_2O_7 (eq. 4). The cation has been positively identified by X-ray crystallography and is apparently stabilized by the chelation of the phosphines to the Re center. The structure shows clearly the *cis* relationship of the phosphines (and the nitrogens) to each other. The O=Re bond length is 1.68Å, the Re-O($SiMe_3$) bond length is 1.93Å and the Re-O-$SiMe_3$ angle is 149°. The O=Re-O angle is 168°. The Re-N bond lengths average 2.08Å and the central planar core is defined by the two P(III) and the N atoms. The P(V) of one ligand also lies in that plane but the Re is slightly displaced from the plane.



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Summary

The examples shown herein illustrate the versatility of this series of compounds toward the formation of metal derivatives by migration or elimination reactions. Considerable versatility is also demonstrated by these compounds with the formation of chelate and monodentate complexes with metals. Development of these heterobifunctional bis(phosphorus) compounds has also provided some interesting features of the compounds themselves and we expect additional features of interest to arise as work progresses.

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