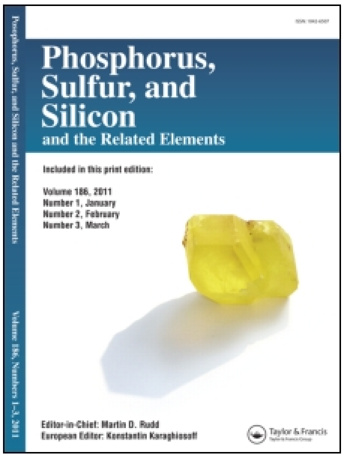

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P-FUNCTIONALIZED λ^3-IMINOPHOSPHINES AND DIPHOSPHENES

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Abstract The synthesis of P-functionalized iminophosphines and diphosphenes is discussed. The reactivity and the coordination chemistry of selected compounds have been explored.

INTRODUCTION

Previously we have described the synthesis and characterization of N-(2,4,6-tri-tert-butylphenyl)-substituted iminophosphines, R-P=NTtb (R = Alk,Ar; Ttb = 2,4,6-t-$Bu_3C_6H_2$).[1] These compounds have an unusual high thermal stability and undergo many interesting and synthetically useful reactions. In extension of this work we turned to the P-functionalized λ^3-iminophosphines (X-P=NTtb) the properties and synthetic potential of which remains nearly unexplored.

RESULTS AND DISCUSSION

We have found in 1987/88 that aminoiminophosphine Me_2N-P=N-Ttb (1a) has a cis-geometry not previously observed for compounds with a PN double bond.[2] This finding stimulated our further research on the series of aminoiminophosphines R_2N-P=N-Ttb (1). Detailed study of these compounds has shown that their conformation depends on the size of the phosphorus substituent (R_2N). Whereas Me_2N-, Et_2N- and $(CH_2)_5N$-derivatives (1a-c) exist as cis isomers, the sterically more hindered aminoiminophosphines (1d-f) are present only in the form of trans isomers. Some spectral and structural data for the aminoiminophosphines 1a, 1c and 1e are summarized below: (1a), δ_P 203, P=N 153.9(3), The ^{31}P chemical shifts of the oxy-substituted iminophosphines <u>3a-i</u> (δ_P 180-145) occur at a significantly higher field than analogous P-alkylated iminophosphines (δ_P 415-490). This markedly upfield ^{31}P shift can be explained in terms of a dipolar structure, $R\overset{\delta-}{O}\cdots P\overset{\delta+}{\equiv} N$-Ttb. The molecular geometry of <u>3c</u> (Fig.1) is in accord with such an interpretation. The O-P-N-C has a cis planar conformation. The angle of 164.1° at nitrogen atom is significantly larger than the range found for trans-iminophosphines (114-130°). The P=N (149.7 pm) and P-O (164.1 pm) bond lengths are in good agreement with expectations based on bond orders. Note that the same trend in bond lengths and angles is apparent in the structures of cis-ClP=NTtb (5a)[5] and cis-BrP=NTtb (5b) (Fig.2; P=N 149.8, Br-P 233.7 pm, PNC 159.5°).

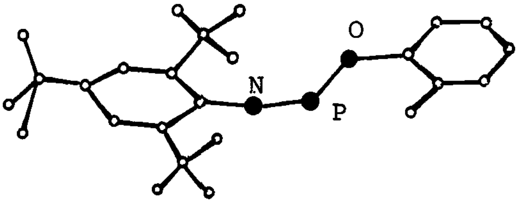


Fig.1. Molecular structure of 2-MeC_6H_4OP=NTtb (<u>3c</u>)

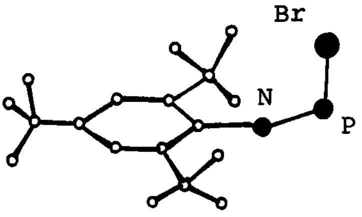


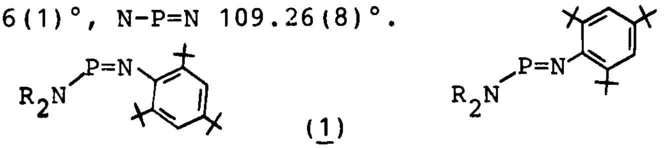
Fig.2. Molecular structure of BrP=NTtb (<u>5b</u>)

As could be expected <u>3</u> proved to be good substrates for nucleophilic substitution reactions.[4] For example, trearment of the aryloxyiminophosphine <u>3c</u> with t-BuSLi or t-Bu_2PLi results in the quantitative formation of new λ^3-iminophosphines: cis-t-BuS-P=NTtb (P=N 154.9, S-P 209.8 pm, SPN 109.0°, PNC 131.3°) and trans-t-Bu_2P-P=NTtb (P=N 157.0, P-P 219.1 pm, PPN 105.9°, PNC 120.2°).

The interaction of <u>5a</u> with TtbP(Li)H affords the iminophosphine TtbP(H)-P=NTtb wich undergoes rearrangement to diphosphene Ttb-P=P-N(H)Ttb. This is first example of structural isomerization of iminophosphine to diphosphene.

The P-Chloroiminophosphine <u>5a</u> is an easily accessib-

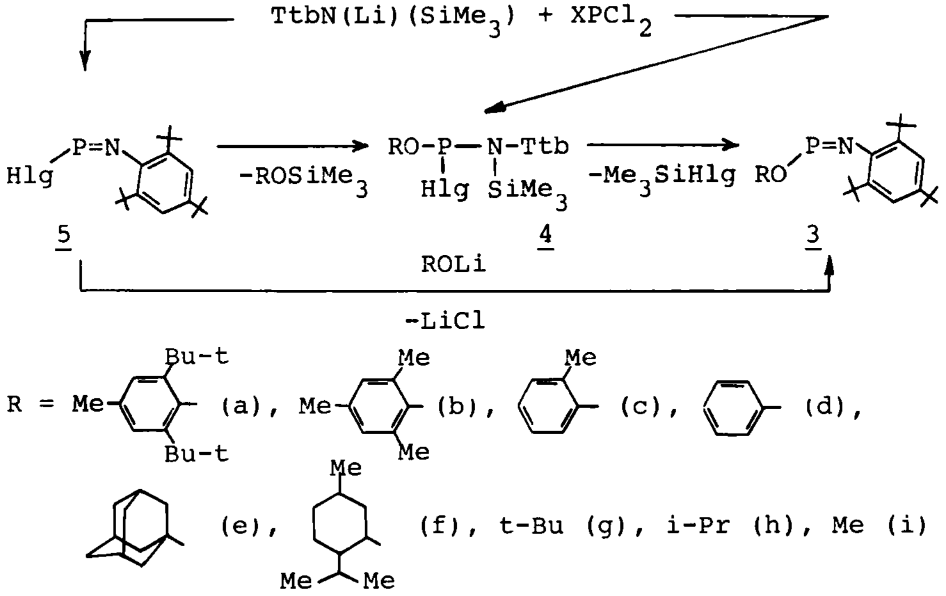
P-N 165.1(3) pm, P=N-C 140.7(4)°, N=P-N 115(3)°; (1d), δ_P 268.1, P=N 155.5(2), P-N 165.6(2) pm, P=N-C 129.6(1)°, N-P=N 105.6(1)°; (1e), δ_P 327, P=N 156.6(2), P-N 166.8(2)pm, P=N-C 117.6(1)°, N-P=N 109.26(8)°.



cis-Isomer (1) trans-Isomer

$$R = \overbrace{\text{Me (a), Et (b)}}^{\text{cis}}, \underbrace{\text{i-Pr (c), t-Bu (d), Me}_3\text{Si (e)}}_{\text{trans}}$$

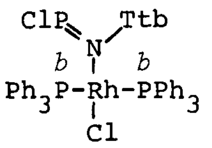
The extraordinary geometry of aminoiminophosphine Me_2N-P=NTtb (1a) promted us to synthesize of P-aryl(alkyl)-oxy-substituted λ^3-iminophosphines (3). We have developed two methods for preparing these compounds. The first one involves the elimination of Me_3SiCl from suitably substituted phosphites 4.[3] The second one relies on the nucleophilic displacement reactions at the dicoordinated phosphorus atom in λ^3-iminophosphines.



5: Hlg = Cl (a), Br (b)

le[5,6] key compounds for the synthesis of complicated molecules including P=N π-bond. Thus, condensation of 5a with $(R_2N)_2C{=}ESiMe_3$ (E=N,P) provides a new route to the 2,3-diphosphabutadienes $(R_2N)_2C{=}E{-}P{=}NTtb$. In analogous way, the 1,3-diaza-$2\lambda^3,4\lambda^5$-diphosphabutadienes $X_3P{=}N{-}P{=}NTtb$ (X = Alk, Ar, R_2N) have been obtained. Structural details for cis(s-trans)-$Ph_3P^2{=}N^1{-}P^1{=}N^2Ttb$ are summarized below: $P^1{-}N^1$ 156.3, $P^1{-}N^2$ 159.7, $P^2{-}N^2$ 155.2 pm; $N^1P^1N^2$ 112.3°, $P^1N^1C^1$ 132.8°, $P^1N^2P^2$ 159.7°.

Of special interest are the reactions of P-functionalized iminophosphines with transition metal derivatives. Treatment of 5 with $RhCl(PPh_3)_3$ yields compound 6, the first example of complexes of this structural type. Alternatively the iminophosphine PhP=NTtb reacts with $RhCl(PPh_3)_3$ to give 7.



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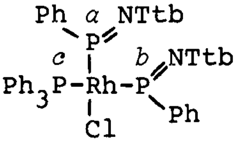

7

6: $\delta(P^a)$ 326.5, $\delta(P^b)$ 27.6, $^2J(P^aRh)$ 74.3, $^1J(P^bRh)$ 106; $\delta(^{15}N)$ -90.9 (rel.CH_3NO_2), $^1J(NP^a)$ 87, $^2J(NP^b)$ 3.1, $^1J(NRh)$ 3.6 Hz. 7: $\delta(P^a)$ 90.7, $\delta(P^b)$ 133.7, $\delta(P^c)$ 26.9, $^2J(P^aP^c)$ 352, $^2J(P^aP^b)$ 66, $^2J(P^bP^c)$ 36, $^1J(P^aRh)$ 146, $^1J(P^bRh)$ 281, $^1J(P^cRh)$ 133 Hz.

REFERENCES

1. L.N.Markovsky, V.D.Romanenko, A.V.Ruban et al., Zh. Obshch. Khim., 56, 2231 (1986).
2. V.D.Romanenko, A.V.Ruban, A.N.Chernega et al., Zh. Obshch. Khim., 58, 948 (1988).
3. L.N.Markovsky, V.D.Romanenko, A.V.Ruban et al., Zh. Obshch. Khim., 58, 291 (1988).
4. V.D.Romanenko, A.V.Ruban, A.N.Chernega and L.N.Markovsky, Zh. Obshch. Khim., 58, 2802 (1988).
5. E.Niecke, M.Nieger and F.Reichert, Angew. Chem., 100, 1781 (1988).
6. V.D.Romanenko, A.V.Ruban, G.V.Reitel et al., Dok. Akad. Nauk SSSR, in press.