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ATTEMPTED ISOLATION OF MONOMERIC IMINOPHOSPHINES. FORMATION OF A STERICALLY PROTECTED IMINOPHOSPHINE P-SULFIDE AND DETECTION OF IMINOPHOSPHINES

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A monomeric iminophosphine was observed by the desulfurization of the corresponding P-sulfide; the structure of the sulfide was discussed in terms of ab initio calculation; several attempts to isolate sterically protected iminophosphines were described.

Compounds with a multiple bond containing phosphorus(III) have been of current interest because of the unusual chemical and physicochemical properties.[1-3] By introducing a very bulky group into a molecule, we have succeeded in preparation and characterization of bis(2,4,6-tri-t-butylphenyl)diphosphene (**1**)[4,5] as a stable compound, according to the following reaction sequence from the corresponding phosphonous dichloride (**2**).

$$\underset{\mathbf{2}}{ArPCl_2} \quad + \quad Mg \longrightarrow \underset{\mathbf{1}}{Ar\text{-}P\text{=}P\text{-}Ar} \xleftarrow{\text{base}} \underset{\mathbf{8}}{ArPH_2} \quad + \quad \underset{\mathbf{2}}{ArPCl_2}$$

Niecke et al. reported the detection of monomeric di-t-butyliminophosphine at -36 °C,[3] which appeared at 472 ppm in its ^{31}P NMR. Barrans et al.[6] have reported their attempts to isolate iminomesitylphosphines and proposed that such compounds exist as oligomers, whereas very recently, Markovski et al.[7] have succeeded in the isolation of a monomeric trimethylsilyliminophosphine (δ_P 476 ppm). Their reports prompted us to disclose our preliminary results on our several attempts to isolate imino(2,4,6-tri-t-butylphenyl)phosphines (**4**).

$$\underset{\mathbf{2}}{ArPCl_2} \quad + \quad \underset{\mathbf{3}}{H_2NR} \xrightarrow{\text{base}} \underset{\mathbf{5}}{ArPCl(NHR)} \xrightarrow{\text{base}} (\ \underset{\mathbf{4}}{[ArP\text{=}NR]} \longrightarrow\ )\ \underset{\mathbf{7}}{(Ar\overset{|}{P}\text{-}\overset{|}{N}R)_2}$$

Ar = $2,4,6\text{-}Bu^t{}_3C_6H_2$

a: R=Bu^t; **b**: R=Ar; **c**: R=$2,4\text{-}Bu^t{}_2\text{-}6\text{-}MeC_6H_2$; **d**: R=$2,4,6\text{-}Me_3C_6H_2$

2,4,6-Tri-t-butylphenylphosphonous dichloride (**2**) was allowed to react with t-butylamine (**3a**) in the presence of triethylamine. However, attempts to isolate **4a** failed but resulted in the isolation of N-t-butyl-2,4,6-tri-t-butylphenylphosphinic amide (**6a**) as a sole product after the usual work-up. **6a**: mp 192 - 193 °C,

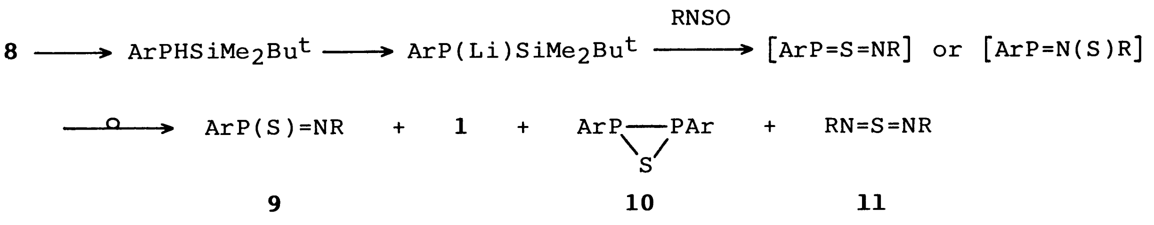
^{31}P NMR $\delta_P(C_6D_6)$ 5.25 ppm; ^1H NMR $\delta(C_6D_6)$ 8.78 (dd, J=545.8, 6.0 Hz, 1H, PH), 7.62 (d, J=5.7 Hz, 2H, arom.), 5.38 (d, J=6.0 Hz, 1H, NH), 1.72 (s, 18H, o-Bu^t), 1.24 (s, 9H, N-Bu^t), and 1.13 (s, 9H, p-Bu^t); IR (KBr) 3220 (NH), 2480 - 2400 (PH), and 1010 (P=O) cm^{-1}; MS (m/z) 365 (M^+); Found: C, 72.01, H, 10.80; N, 3.99%. Calcd for $C_{22}H_{40}NOP$: C, 72.29; H, 11.03; N, 3.83%.

ArP(O)(H)(NHR) **6** (**a**: R=Bu^t; **c**: R=2,4-Bu^t_2-6-MeC_6H_2)

The amide **6a** might be formed from **5a** but not from oligomeric form of **4a**, since the reaction in the presence of a stronger base such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) followed by hydrolysis gave only a small quantity of **6a**: the major reaction product was a dimeric form of **4a** (=**7a**), whose ^{31}P NMR signal appeared at 250.7 ppm (THF). The chemical shift was very close to the reported value for a dimer (trans) of mesityl derivative (**7'a**; Ar = 2,4,6-$Me_3C_6H_2$).$^{6)}$ Similarly, **2** was allowed to react with aromatic amines **3b-d** in the presence of DBU. The observed ^{31}P NMR chemical shifts suggested the formation of dimers; **7b**: 252.4 (PhH); **7c**: 251.7 (THF); **7d**: 250.7 (THF) ppm. The compounds **7a-d** were too sensitive toward air, moisture, or atmosphere of CO_2 to permit isolation and gave intractable materials. Therefore the dimer **7** could be formed directly from **5**. The reactions of aromatic amines in the presence of triethylamine instead of DBU did not proceed at all indicating that the basicity of triethylamine is not strong enough even to give **5**.

On the other hand, when the phosphine (**8**) was converted to lithium (t-butyldimethylsilyl)(2,4,6-tri-t-butylphenyl)phosphide$^{8)}$ and was allowed to react with 1.5 equiv. of N-sulfinyl-2,4-di-t-butyl-6-methylaniline at -78 °C in THF, the corresponding iminophosphine P-sulfide (**9**, 17%) was formed together with diphosphene (**1**, 6%), thiadiphosphirane (**10**, 8%),$^{9)}$ and bis(2,4-di-t-butyl-6-methylphenyl)sulfur diimide (**11**, 62%)$^{10)}$ and **8** was recovered in 33% after chromatographic treatment. **9**: mp 170 °C (decomp); $\delta_P(CDCl_3)$ 109.0 ppm; ^1H NMR $\delta(CDCl_3)$ 7.50 (d, J=7.0 Hz, 2H, ArH), 7.05 (m, 2H, Ar'H), 2.53 (d, J=3.1 Hz, 3H, Me), 1.73 (d, J=0.9 Hz, 18H, o-Bu^t), and 1.33 + 1.17 + 1.29 (s+s+s, 9H+9H+9H, o'+p+p'-Bu^t); UV (hexane) λ_{max} (ε) 238 (13700) and 350 (7000) nm; MS (m/z) 525 (M^+).

The formation of **9** may be explained as follows: first, the formation of sulfur imide phosphinidene after elimination of silyloxy group followed by the cyclization giving thiaphosphaziridine, then resulting in the cleavage to give P-

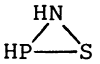
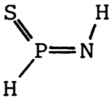
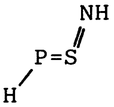
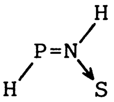


9 **10** **11**

$$\mathbf{9} + P(NMe_2)_3 \xrightarrow{-(Me_2N)_3PS} \underset{\mathbf{4c}}{ArP{=}NR} \xrightarrow{H_2O} \mathbf{6c}$$

R=2,4-Bu^t_2-6-MeC_6H_2

Table 1. Total Energies (hartrees) and Relative Energies (kcal/mol)

Species	HF/3-21G//3-21G	HF/6-31G*//6-31G*	MP2/6-31G*//6-31G*	MP3/6-31G*//6-31G*
	-789.782996 (0.0)[a]	-793.786380 (0.0)[a]	-794.176175 (0.0)[a]	-794.200309 (0.0)[a]
	-789.772428 (6.6)	-793.812422 (-16.3)	-794.209319 (-20.8)	-794.225263 (-15.7)
	-789.703601 (49.8)	-793.735623 (31.9)	-794.151557 (15.4)	-794.167868 (20.4)
	-789.807095 (-15.1)	-793.767445 (11.9)	-794.171413 (3.0)	-794.190808 (6.0)

[a] Values in parentheses are relative energies (thiaphosphaziridine as standard).

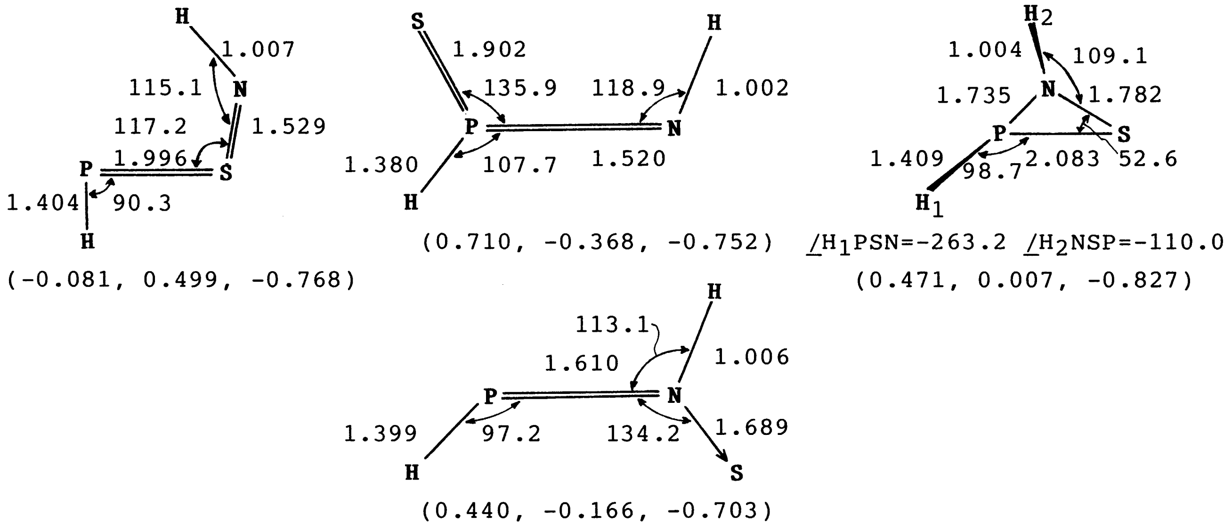


Fig. 1. HF/6-31G* - Optimized Geometries of H_2NPS (Å and degrees). Values in parentheses indicate charge densities at P, S, and N atoms, respectively.

sulfide **9**; alternatively, first, the formation of iminophosphine N-sulfide after elimination of silyloxy group, followed by the migration of sulfur to the P-sulfide **9** (probably via an intermediate of thiaphosphaziridine in a similar fashion); byproducts, **1**, **10**, and **11**, could be formed during the above process.

The compound **9** was desulfurized with tris(dimethylamino)phosphine in benzene at 0 °C for 1 day to give a species of which ^{31}P NMR chemical shift appeared at 420 ppm and the corresponding aminophosphine sulfide (δ_P 81.4 ppm). These results indicated that we detected the generation of monomeric iminophosphine (**4c**). The iminophosphine in the low coordination state thus generated was easily hydrolyzed to give the amide **6c** rather than resulted in the oligomerization to **7c**. **6c**: oil; $\delta_P(CDCl_3)$ 16.89 ppm; ^1H NMR $\delta(CDCl_3)$ 7.76 (dd, J=549.9, 6.2 Hz, 1H, PH), 7.46 (d, J=4.6 Hz, 2H, Ar-arom.), 7.15 + 7.05 (s+s, 1H+1H, Ar'-arom.), 4.24 (dd, J=5.3, 6.2 Hz, 1H, NH), 2.36 (s, 3H, Me), 1.56 (s, 18H, o-Bu^t), and 1.33 + 1.25 + 1.00 (s+s+s, 9H+9H+9H, o'+p+p'-Bu^t); IR(KBr) 2400 (PH) and 1224 (P=O) cm^{-1}; MS (m/z) 511 (M$^+$).

In order to confirm the structure of **9**, Ar and R were replaced with hydrogen atoms and the relative stability of the four possible H_2NPS isomers was calculated by the ab initio method. Geometries were fully optimized at the Hartree-Fock (HF) level with the 3-21G and 6-31G* basis sets.$^{11)}$ Energies were improved at the HF/6-31G* optimized geometries (Fig. 1), using second- and third-order Møller-Plesset perturbation (MP2 and MP3) theories.$^{12)}$ As Table 1 shows, iminophosphine P-sulfide (**9**) is the most stable isomer. This is also supported by the observed ^{31}P NMR chemical shift of **9**. It should be noted that sulfur imide phosphinidene is calculated to be the most unstable.

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