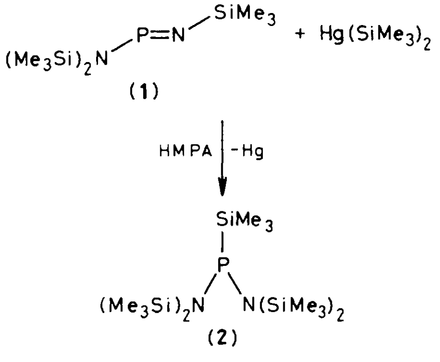
Interaction of *N,N*-Bis(trimethylsilyl)amino-*N'*-trimethylsilyliminophosphine with Bis(trimethylsilyl)mercury: a New Route to Compounds containing the P–Si Linkage

Vadim D. Romanenko, Viktor F. Shul'gin, Viktor V. Scopenko, and Leonid N. Markovski*
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, 252660, Kiev 94, U.S.S.R

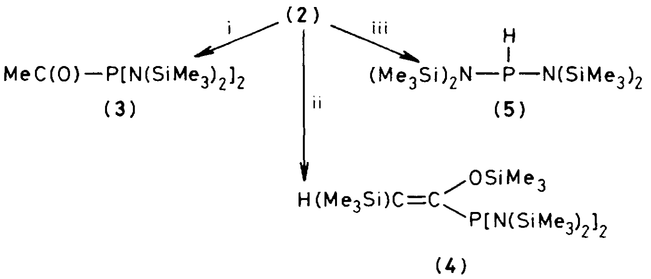
A new route to trimethylsilylaminophosphines and its application to the synthesis of bis[bis(trimethylsilyl)amino]trimethylsilylphosphine (**2**), the first compound containing the N–P^{III}–$SiMe_3$ bonds, are described.

The known syntheses of trimethylsilylphosphines of type $R_{3-n}P(SiMe_3)_n$ (R = H, alkyl, aryl; n = 1—3) normally involve coupling reactions of alkali metal phosphides with silicon halides or reactions of phosphorus halides with organosilyl metallic species.[1] The application of these methods to silylaminophosphines ($R = R'_2N$) is limited to triphenylsilyl-substituted cyclic aminophosphines[2] which are much less reactive than the corresponding trimethylsilyl analogues owing to the specific nature of the interaction between the atoms of the P–$SiPh_3$ system.

We now report the synthesis of the first compound with a N–P^{III}–$SiMe_3$ linkage by a novel route *via* the interaction of dico-ordinated phosphorus compounds with bis(trimethylsilyl)mercury. The aminoiminophosphine (**1**)[3] reacts with $Hg(SiMe_3)_2$[4] in hexamethylphosphoric triamide (HMPA) to produce the diaminophosphine (**2**) in high yield (Scheme 1). Details of the procedure are as follows: (**1**) (0.025 mol) in HMPA (5 ml) was added to a stirred suspension of $Hg(SiMe_3)_2$ (0.025 mol) in HMPA (5 ml) at 40 °C under an argon atmosphere. After 2 h stirring under the same conditions the



Scheme 1



Scheme 2. *Reagents and conditions:* i, MeCOCl, benzene, 20 °C, 3 h; ii, $H(Me_3Si)C=C=O$, diethyl ether, 20 °C, 3 h; iii, MeOH (1 equiv.), diethyl ether, 20 °C, 1 h.

mixture was filtered and concentrated. Distillation of the residue afforded (**2**) (63%), b.p., 130—135 °C at 0.03 mmHg.†

Compound (**2**) is a white, waxy solid which is very sensitive to atmospheric moisture and oxygen, and is thermally stable up to at least 200 °C. The ^{31}P n.m.r. spectrum of (**2**) (in C_6D_6, H_3PO_4 ext.) shows a resonance at 84 p.p.m. The ^1H and $^{13}C\{^1H\}$ n.m.r. spectra at 303 K (in C_6D_6, Me_4Si int.) show the signals expected for free rotation about the P–N bonds.‡

The high lability of the P–Si bond makes (**2**) an extremely interesting synthon. For example, (**2**) reacts smoothly with acetyl chloride and trimethylsilylketene to give the acetyldiaminophosphine (**3**) and the vinyldiaminophosphine (**4**), respectively, while the reaction with methanol gives the diaminophosphine (**5**) (Scheme 2). Compounds (**3**), (**4**), and (**5**) were characterised by elemental analysis and spectroscopy.§

The procedure described (Scheme 1) represents the first example of a potentially general method for preparing compounds containing a P–Si linkage based on the reactions of bis(trimethylsilyl)mercury with low-co-ordinated trivalent phosphorus compounds.

Received, 27th April 1983; Com. 530

References

1 E. A. Chernyshev and E. F. Bugerenko, *Organomet. Chem. Rev.*, 1968, **3**, 469; E. W. Abel and S. M. Illingworth, *ibid.*, 1970, **5**, 143; J. E. Drake and C. Riddle, *Q. Rev., Chem. Soc.*, 1970, **24**, 263.

2 E. E. Nifantiev, S. F. Sorokina, L. A. Vorobieva, and A. A. Borisenko, *Dokl. Akad. Nauk SSSR*, 1982, **263**, 900.

3 E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 585.

4 W. Biffar, H. Nöth, and R. Schwerthöffer, *Liebigs Ann. Chem.*, 1981, 2067. A recent review summarises the current status of the chemistry of the compound: M. G. Voronkov and N. F. Chernov, *Usp. Khim.*, 1979, **48**, 1804.

---

† Satisfactory elemental analyses and cryoscopic molar masses were obtained for all new compounds.

‡ (**2**): ^1H n.m.r. δ 0.34 (d, *J* 7.2 Hz, 9H, Me_3SiP), 0.38 (d, *J* 1.0 Hz, 36H, Me_3SiN); ^{13}C n.m.r. δ 2.48 (d, *J* 24.1 Hz, Me_3SiP), 6.12 p.p.m. (d, *J* 6.88 Hz, Me_3SiN).

§ (**3**): 49% yield, b.p. 100—103 °C at 0.03 mmHg; ^1H n.m.r. (C_6D_6) δ 0.30 (d, *J* 0.6 Hz, 36H, Me_3Si), 2.10 (d, *J* 9.5 Hz, 3H, CH_3CO); ^{31}P n.m.r. (C_6D_6) δ 88.2 p.p.m.; ν(C=O) 1660 cm^{-1}. (**4**) (preferred stereoisomer): 57% yield, b.p. 135—140 °C at 0.03 mmHg; ^1H n.m.r. δ 0.15 (d, *J* 0.75 Hz, 9H, Me_3Si), 0.25 (d, *J* 0.7 Hz, 9H, Me_3SiO), 0.31 (s, 36H, Me_3SiN), 5.50 (d, *J* 3.0 Hz, 1H, CH); ^{31}P n.m.r. (C_6D_6) δ 87.0 p.p.m.; ν(C=C) 1580 cm^{-1}. (**5**): 68% yield, b.p. 90—93 °C at 0.03 mmHg; ^1H n.m.r. (C_6D_6) δ 0.31 (d, *J* 1.14 Hz, 36H, Me_3Si), 6.73 (d, *J* 203.8 Hz, 1H, PH); ^{31}P n.m.r. (C_6D_6) δ 58.8 p.p.m. (d, *J* 204 Hz).