JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 24
1984

Generation of a New, Stable, and Potentially Reactive Diphosphene: Bis[bis(trimethylsilyl)methyl]diphosphene

Jean Escudie, Claude Couret, Henri Ranaivonjatovo, and Jacques Satgé

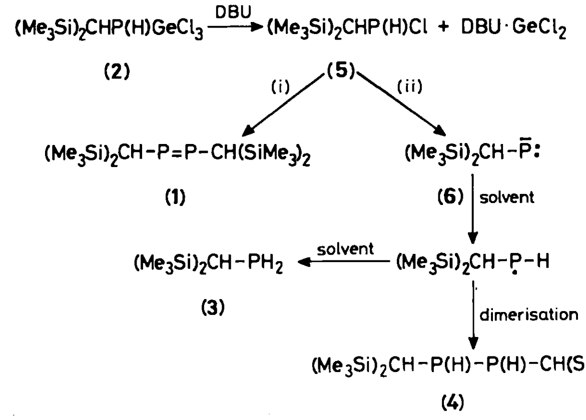
Laboratoire de Chimie des Organominéraux, U.A. 477, C.N.R.S., Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex, France

The reaction of [bis(trimethylsilyl)methyl]trichlorogermylphosphine $(Me_3Si)_2CH{-}P(H)GeCl_3$ with 1,5-diazabicyclo[5.4.0]undec-5-ene affords the new stable and potentially reactive diphosphene $(Me_3Si)_2CH{-}P{=}P{-}CH(SiMe_3)_2$

Most of the diphosphenes synthesized until now are substituted on phosphorus by very bulky groups to prevent cyclic oligomerisation.[1—9] However, this large steric hindrance decreases the reactivity of the –P=P– double bond and, despite the current interest in these compounds, little is known about their reactivity.[1a,3c,6a,10—12]

To extend the synthetic utility of these compounds, we sought a route to a stable and potentially reactive diphosphene, bis[bis(trimethylsilyl)methyl]diphosphene (**1**). Our initial attempts to synthesize (**1**) from $(Me_3Si)_2CHPCl_2$ by classical routes (Mg, Bu^{t}Li, sodium naphthalenide, *etc.*) were unsuccessful: reaction of $(Me_3Si)_2CHPCl_2$ with Bu^{t}Li gave mainly $(Me_3Si)_2CHP(Bu^t)Cl$,† and reaction with magnesium or sodium naphthalenide in tetrahydrofuran (THF) resulted only in oligomerisation to give $[(Me_3Si)_2CH{-}P]_3$ or $[(Me_3Si)_2CH{-}P]_4$.[4c] It was thus clear that a new synthetic route was necessary. It appeared to us that chlorophosphines, RP(H)Cl, would be good precursors of diphosphenes by dehydrochlorination with DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) [equation (1)]. However, as such chlorophosphines are stable only with very bulky substituents, it was necessary, in our case, to use precursors of these compounds. We found that reactions between trichlorogermylphosphines and DBU led to chlorophosphines and the complex DBU·GeCl$_2$ [equation (2)]. The trichlorogermylphosphine (**2**) was easily prepared at room temperature, in nearly quantitative yield, by addition of germanium tetrachloride to bis(trimethylsilyl)methylphosphine (**3**)‡ [equation (3)] [(**2**): n.m.r., ^{1}H (C_6D_6), δ 0.15 (s, 18H, Me$_3$Si) and 3.58 (d, $^1J_{PH}$ 185 Hz, 1H, PH); ^{31}P-{^{1}H} δ (from ext. 85% H_3PO_4), −72.5 p.p.m.; *M*, found 366 (cryoscopy in C_6H_6); calc. 370.1].

Addition of (**2**) in THF to a twofold excess of DBU resulted immediately in the formation of a precipitate of DBU·HCl and the complex GeCl$_2$·DBU which was filtered off. ^{31}P N.m.r. analysis of the supernatant orange solution showed the presence of compounds (**1**), (**3**), and (**4**) in the relative



Scheme 1

$$2RP(H)Cl \xrightarrow[-2DBU\cdot HCl]{2DBU} RP{=}PR \qquad (1)$$

$$R = 2,4,6\text{-}Bu^t_3C_6H_2 \text{ or } (Me_3Si)_3C$$

$$RP(H)GeCl_3 \xrightarrow{DBU} RP(H)Cl + DBU\cdot GeCl_2 \qquad (2)$$

$$\underset{(3)}{(Me_3Si)_2CHPH_2} + GeCl_4 \xrightarrow[-HCl]{THF} \underset{(2)}{(Me_3Si)_2CHP(H)GeCl_3} \qquad (3)$$

$$\underset{(7)}{2,4,6\text{-}Bu^t_3C_6H_2P(H)GeCl_3} \xrightarrow{DBU} \underset{(8)}{2,4,6\text{-}Bu^t_3C_6H_2P(H)Cl} + DBU\cdot GeCl_2 \qquad (4)$$

---

† A small amount of (**1**) (< 5%) was obtained from the reaction of $(Me_3Si)_3SiLi$ with $(Me_3Si)_2CHPCl_2$ by a synthetic route already described.[3a]

‡ Reactions between germanium tetrachloride and primary phosphines provide a general route to trichlorogermylphosphines, and will be developed in a further paper.

proportions 55 : 25 : 20. Rapid distillation using a short column afforded a mixture of (**1**) and (**4**) (70 : 30), b.p. 80—85 °C at 10^{-2} mmHg. The ^{31}P n.m.r. spectrum of (**1**) exhibited an extremely low-field chemical shift, 517 p.p.m., characteristic of a diphosphene structure.[1—9] It was also identified by mass spectroscopy (M^+, m/z 380). The mixture of (**1**) and (**4**) is an orange liquid. This orange coloration must be due to (**1**) since diphosphines such as (**4**) are colourless (refs. 3c, 4a, and refs. cited therein), and diphosphenes orange to red.[1—9] The diphosphene (**1**) is too reactive to permit its isolation in the pure state by column chromatography; slight exposure to air results immediately in the disappearance of (**1**) (^{31}P n.m.r. evidence) with decoloration and the formation of products not yet identified. Its thermal stability is rather good ($t_{\frac{1}{2}} \sim$ 1 week at room temperature in the dark and more than two months at −25 °C). Compound (**3**) was identified as the primary phosphine $(Me_3Si)_2CH-PH_2$, b.p. 78 °C at 20 mmHg [^{31}P n.m.r. (C_6D_6) δ −149 p.p.m.] and compound (**4**) as the disecondary diphosphine $(Me_3Si)_2CH-P(H)-P(H)-CH(SiMe_3)_2$ in its two diastereoisomeric forms [^{31}P n.m.r. (C_6D_6) δ −90 and −98 p.p.m.].

It is presumed that the mechanism of reaction (2) involves the initial formation of (**5**).§ The reaction of (**5**) with an excess of DBU would then give (**1**), (**3**), and (**4**) by the two competitive reactions (i) and (ii) (Scheme 1): reaction (i) intermolecular dehydrochlorination, with formation of the diphosphene (**1**); reaction (ii), intramolecular dehydrochlorination leading to (**3**) and (**4**) probably *via* a triplet[13] phosphinidene intermediate (**6**) which then abstracts hydrogen from the solvent.

Received, 20th July 1984; Com. 1055

---

§ The involvement of chlorophosphine intermediates $RP(H)Cl$[14] in reactions of trichlorogermylphosphines $RP(H)GeCl_3$ with DBU was proved by addition of one equivalent of DBU to (**7**) which afforded quantitative amounts of the stable chlorophosphine (**8**) [equation (4)]

References

1 (a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587; 1982, **104**, 6167; (b) M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, *ibid.*, 1983, **105**, 2495; (c) M. Yoshifuji and N. Inamoto, *Tetrahedron Lett.*, 1983, **24**, 4855.

2 B. Cetinkaya, A. Hudson, M. F. Lappert, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 1982, 609, 691.

3 (a) G. Bertrand, C. Couret, J. Escudie, S. Majid, and J. P. Majoral, *Tetrahedron Lett.*, 1982, **23**, 3567; (b) C. Couret, J. Escudie, and J. Satge, *ibid.*, 1982, **23**, 4941; (c) J. Escudie, C. Couret, H. Ranaivonjatovo, J. Satge, and J. Jaud, *Phosphorus Sulfur*, 1983, **17**, 221.

4 (a) A. H. Cowley, J. E. Kilduff, T. H. Newman, and M. Pakulski, *J. Am. Chem. Soc.*, 1982, **104**, 5820; (b) A. H. Cowley, J. E. Kilduff, M. Pakulski, and C. A. Stewart, *ibid.*, 1983, **105**, 1655; (c) A. H. Cowley, J. E. Kilduff, S. K. Mehrotra, N. C. Norman, and M. Pakulski, *J. Chem. Soc., Chem. Commun.*, 1983, 528.

5 C. N. Smit, T. A. van der Knaap, and F. Bickelhaupt, *Tetrahedron Lett.*, 1983, **24**, 2031.

6 (a) E. Niecke and R. Rüger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 155; (b) E. Niecke, R. Rüger, M. Lysek, S. Pohl, and W. Schoeller, *ibid.*, 1983, **22**, 486; *Angew Chem. Suppl.*, 1983, 639.

7 H. Schmidt, C. Wirkner, and K. Issleib, *Z. Chem.*, 1983, **23**, 67.

8 M. Veith, V. Huch, J. P. Majoral, G. Bertrand, and G. Manuel, *Tetrahedron Lett.*, 1983, **24**, 4219.

9 A. M. Caminade, M. Verrier, C. Ades, N. Paillous, and M. Koenig, *J. Chem. Soc., Chem. Commun.*, 1984, 875.

10 J. Escudie, C. Couret, J. D. Andriamizaka, and J. Satge, *J. Organomet. Chem.*, 1982, **228**, C76.

11 (a) M. Yoshifuji, K. Shibayama, and N. Inamoto, *Chem. Lett.*, 1984, 115, and references cited therein; (b) M. Yoshifuji, I. Shima, K. Shibayama, and N. Inamoto, *Tetrahedron Lett.*, 1984, **25**, 411.

12 (a) A. H. Cowley and M. K. Pakulski, *J. Am. Chem. Soc.*, 1984, **106**, 1491; (b) A. H. Cowley, J. E. Kilduff, N. C. Norman, and M. Pakulski, *ibid.*, 1983, **105**, 4845.

13 G. Trinquier, *J. Am. Chem. Soc.*, 1982, **104**, 6969.

14 Unpublished work.