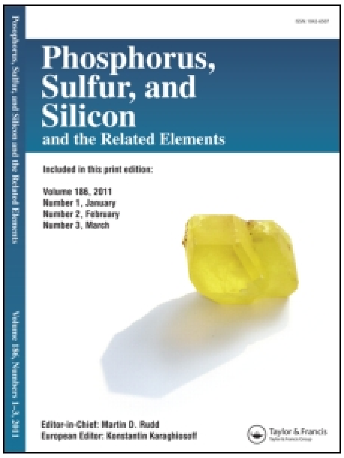

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Synthesis and reactivity of silylated phosphorus compounds

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SYNTHESIS AND REACTIVITY OF SILYLATED PHOSPHORUS COMPOUNDS

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Abstract The preparative and derivative chemistry of several silylated (methylene)phosphines including $(Me_3Si)_2NP{=}CHSiMe_3$, $MesP{=}C(SiMe_3)_2$, and a stable 1-phosphadiene system is reported.

INTRODUCTION

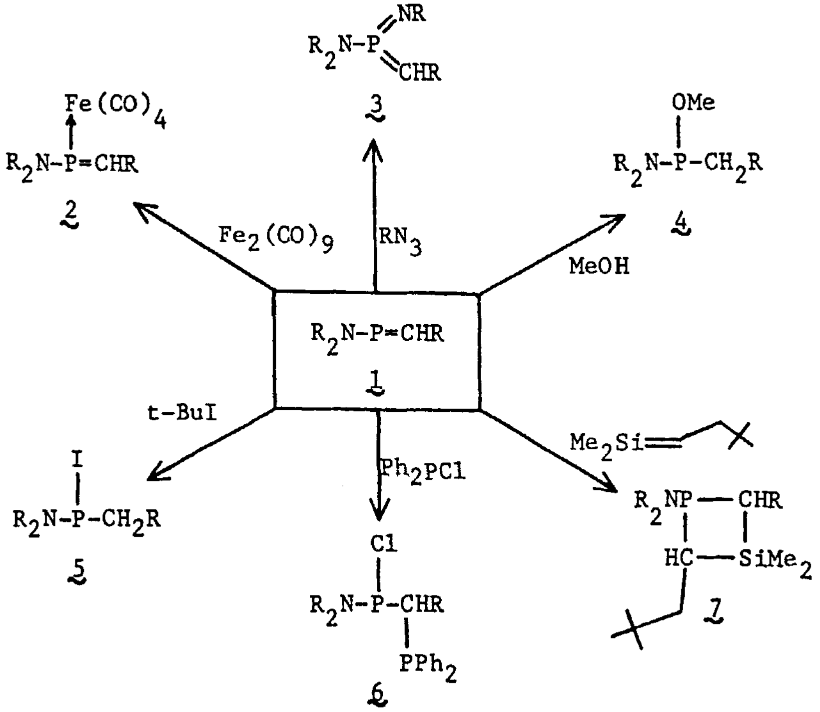
The chemistry of compounds containing the Si-N-P and/or Si-C-P linkages is usually markedly different from that of the nonsilylated analogues. On the one hand, the steric bulk and π-acceptor properties of silyl groups can be used to kinetically stabilize a variety of "low-coordinate" phosphorus systems. Alternatively, the Si-N or Si-C bonds may often serve as reactive sites so that processes such as intramolecular silyl group rearrangements and condensation reactions via silane elimination are commonly found. We report here several illustrative examples from areas of current interest in our laboratory involving silyl-substituted (methylene)phosphines.

REACTIONS OF A SILYLATED AMINO(METHYLENE)PHOSPHINE

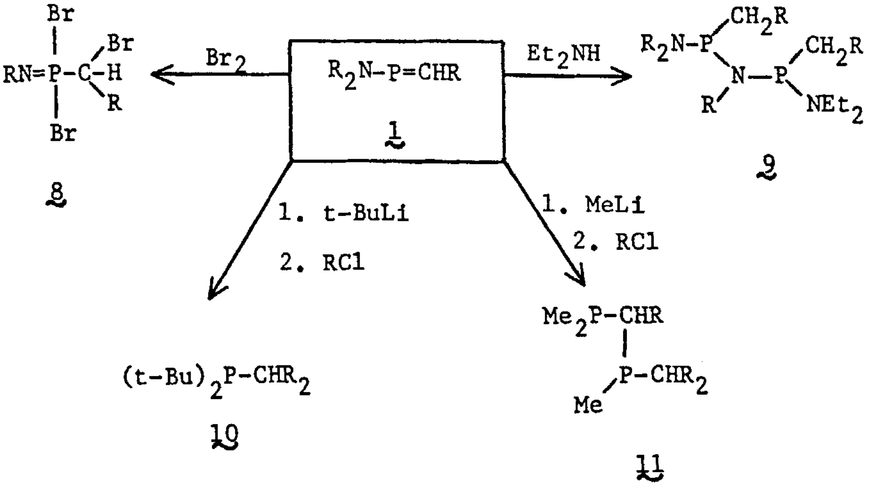
The synthesis of a stable, trisilylated amino(methylene)phosphine 1 has been recently accomplished either by dehydrohalogenation[1] or thermolysis[2] of appropriate chlorophosphine precursors. As an extension of these studies, we are interested in the reactivity of 1 and related compounds including novel phosphadienes.

The modes of reactivity of compound 1 are quite varied but can be divided roughly into two general categories. Among the first type, are relatively straightforward reactions in which the Si_2N-P-C linkage remains intact (Scheme I)[3]. These include: metal complexation via the phosphorus lone pair (2), oxidation to a 3-coordinate phosphorane (3), addition of polar reagents to the P=C bond (4-6), and 2+2 cycloaddition with a silene (7).

SCHEME I (R = $SiMe_3$)



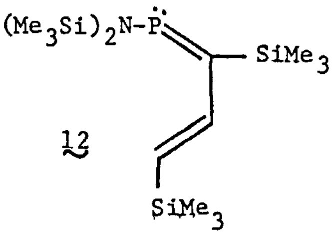
SCHEME II (R = $SiMe_3$)



Reactions of the second type (Scheme II)[3] are more complex processes in which cleavage of the Si-N and/or P-N bonds are involved. These results, while surprising at first, seem to have a common underlying feature. In each case, the initial product, a 3-coordinate phosphine formed by addition to the P=C bond, is apparently more reactive toward the given reagent than is the (methylene)phosphine itself.

SYNTHESIS OF A 1-PHOSPHADIENE

We have also prepared a variety of other amino(methylene)-phosphines, including the stable 1-phosphadiene **12**[3], by the dehydrohalogenation route. Proton, ^{13}C, and ^{31}P NMR data are all consistent with the depicted geometry about the double bonds. Studies of the reactivity of **12** are in progress.

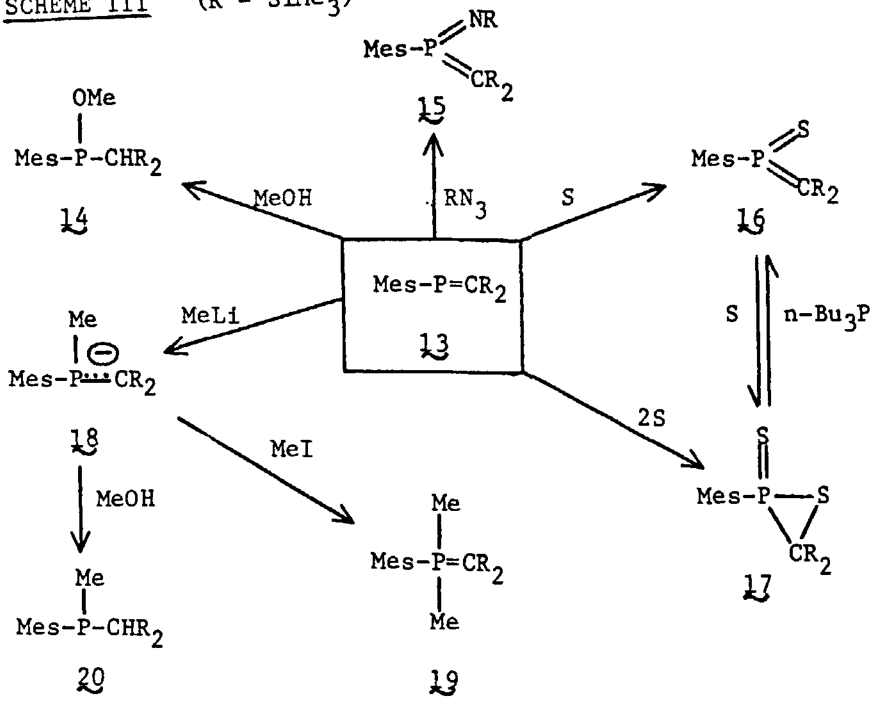


12

P-MESITYL SUBSTITUTED (METHYLENE)PHOSPHINES

The mesityl group is also known to be effective[4], though less so than $(Me_3Si)_2N$[5], in stabilizing various low-coordinate phosphorus systems. We have recently prepared [bis(trimethylsilyl)methylene](mesityl)phosphine **13** and have studied its reactions with several reagents (Scheme III)[3] for comparison with the $(Me_3Si)_2N$-substituted analogues. Noteworthy aspects of this work include: (a) the new, stable 3-coordinate phosphoranes **15** and **16**, (b) the PCS 3-membered ring system **17**, and (c) the anion **18** whose derivatives **19** and **20** illustrate its ambident nature. X-ray crystallographic studies of compounds **16** and **17** are currently being conducted in order to confirm the structural assignments.

SCHEME III (R = SiMe$_3$)



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2. E. Niecke, W.W. Schoeller, and D.-A. Wildbredt, Angew. Chem. Int. Ed. Engl., 20, 131 (1981).
3. Full details of the synthesis and characterization of all new compounds will be reported in forthcoming papers. ^{31}P chemical shifts (in ppm from H_3PO_4). **1**: 309.9; **2**: 305.5; **3**: 102.6; **4**: 157.4; **5**: 173.9; **6**: 154.9, -5.9 (J_{PP} = 227); **7**: 59.9, 61.9; **8**: -51.5; **9**: 36.9, 26.2 (J_{PP} = 287); **10**: 47.4; **11**: -23.3, -38.6 (J_{PP} = 97); **12**: 317.0; **13**: 381.0; **14**: 139.9; **15**: 120.0; **16**: 191.9; **17**: 2.6; **18**: -20.1; **19**: 6.6; **20**: -42.9.
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