Synthesis of a phosphine imide bearing a hydrosilane moiety, and its water-driven reduction to a phosphine†‡

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Organosilanes bearing a phosphine imide moiety were synthesized and crystallographically characterized. Reaction of the pentacoordinated hydrodiphenylsilyl derivative with water gave [2-(diphenylphosphino)-phenyl]diphenylsilanol accompanied by both reduction of the phosphine imide moiety and hydrolytic oxidation of the Si–H moiety.

Hydrosilanes, R₃Si–H, are useful for hydrosilylation of multiple bonds,¹ reduction of various functional groups,² reductive aldol reactions,³ and preparation of a silanol, R₃Si–OH, by hydrolysis.⁴ In some hydrosilanes, the silicon-bound hydrogen migrates intramolecularly through the 1,2-shift of the dyotropic rearrangement,⁵ 1,3-shift,⁶ and 1,5-shift.⁷ As represented by the 1,3-hydride shift, the hypercoordinated hydrosilanes show hydride reducing reactivity without catalysis.⁸ Some neutral pentacoordinated hydrosilanes react easily with alcohols, carboxylic acids, and water in the absence of a catalyst and evolve hydrogen gas,⁹,¹⁰ whereas tetracoordinated hydrosilanes react with them quite slowly even under harsh reaction conditions.¹¹ In these pentacoordinated hydrosilanes, the intramolecular coordination of a tertiary amino group with a suitable tether to the silicon atom is crucial for the pentacoordinated state of silicon and enhancement of the hydride reactivity. If a hydrosilyl group is located in the neighborhood of a phosphine imide, R₃P=NR¹², the intramolecular N···Si coordination, which should increase its hydride reactivity, is expected. This expectation is based on the reports in which some phosphine imides have been used as a chelating ligand for several transition metal complexes.⁹ As far as we know, amongst the few reported silicon compounds bearing a phosphine imide ligand, no such hydrosilane has been reported.¹⁰

We report here the synthesis and structure of a hydrosilane bearing a phosphine imide moiety and a unique conversion of its triarylphosphine imide moiety to the triarylphosphine moiety by hydride transfer from the hydrosilane moiety triggered by the reaction with water without any catalyst.

Phosphine imide 1 was lithiated with methylthiolium in Et₂O at room temperature,⁹,¹¹,¹² and then treated with chlorosilanes to give the corresponding silylated phosphine imides 2a–c in 56, 59 and 64% yields, respectively, from 1 (Scheme 1). Compounds 2a–c are thermally stable at room temperature in contrast to the phosphorus ylide analogue of 2a which was reported to undergo 1,4-silyl migration at 0°C.¹³ Compounds 2a and 2b are not sensitive to water. However, in contrast, compound 2c is very sensitive to moisture. Treatment of 2c with water at room temperature gave [2-(diphenylphosphino)phenyl]diphenylsilanol (3) quantitatively, based on the monitoring of the reaction using 3¹³P NMR spectroscopy and it was isolated in 87% yield (Scheme 2). The structure of 3 was determined using ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectroscopy, IR spectroscopy and mass spectrometry. The ³¹P NMR spectrum (δP = −10.1 ppm) established the existence of a triarylphosphine moiety in 3, instead of the corresponding triarylphosphine oxide moiety. Formation of the other product, tert-butylamine, which was derived from the imino moiety of 2c, was confirmed using GC-MS.

Interestingly, the reaction of 2c with water resulted in the conversion from a hydrosilane and a triarylphosphine imide to a silanol and a set of a triarylphosphine and an amine, respectively. Therefore, this is not a usual hydrolysis of an iminophosphorane to give the corresponding phosphine oxide.

In order to reveal the causes of the reactivity of 2c, we analyzed the structure in detail. The ¹H, ¹³C, ²⁹Si, and ³¹P NMR...
Hydride transfer from silicon to phosphorus generates an amino(hydro)phosphorane intermediate, and its facile reductive deamination gives 3 and tert-butylamine as the final products. In another possible reaction mechanism, the phosphine imide moiety, which may work as a base, is hydrolyzed to a phosphine oxide and tert-butylamine before the conversion of the hydroxilane moiety to silanol. We carried out three experiments to determine the reaction mechanism: (i) monitoring of the reaction solution using VT-NMR spectroscopy, (ii) a labeling experiment using D₂O instead of H₂O, and (iii) a reaction of 2c with methanol. In experiment (i), however, the formation of 3 from 2c was so fast that no intermediate could be observed using ¹H and ³¹P NMR spectroscopy even at −20 °C. In experiment (ii), quantitative formation of 2(Ph₂P)₅C₆H₄Si(OH)Ph₃ (3-d) and BuNH₂ in the reaction of 2c with D₂O was confirmed using ¹H and ³¹P NMR spectroscopy. The GC-MS measurement also supported the formation of BuNH₂ (m/z = 74, M⁺). Therefore, silicon-bound hydrogen in 2c was used for the quantitative formation of BuNH₂ but not for the formation of hydrogen gas in the reaction with water. The experimental result is consistent with the proposed reaction mechanism in Scheme 2. Combination of the characteristics of both pentacoordinated silicon and phosphorus should be a key for this reaction of 2c. In experiment (iii), the reaction of 2c with methanol gave methoxysilane 4 in 64% yield (Scheme 2). Therefore, even though OH⁻ or MeO⁻ may attack the phosphorus in any of the steps, the intermediate should give 2c back and finally give 3 or 4. Experiments (ii) and (iii) rule out other reaction mechanisms involving the hydrolysis of the phosphine imide moiety.

In the previous reports, phosphine imides were reduced with strong reductants such as lithium aluminum hydride and trichlorosilane, which react vigorously with water. In contrast, the reduction of the phosphine imide of 2c to phosphine was promoted by...
the reaction with water and it proceeded quickly at room temperature. Simultaneously, the hydrosilane moiety was converted to the silanol moiety. In association with this reactivity of 2c to give 3 and 4, dehydrogenative condensation of hydrosilanes with alcohols or amines without additional catalyst has been reported by combination of a triarylborane moiety in a single molecule, although condensation with water was not mentioned.\(^{20}\) In addition, some hypercoordinated silanes evolve hydrogen gas in the condensation with alcohols, carboxylic acids and water.\(^ {21a/d} \) Therefore, it is notable that the conversion of 2c to 3 and 4 proceeds at room temperature without any catalyst evolving hydrogen gas.

In summary, three organosilicon compounds 2a–c bearing a phosphine imide moiety were synthesized. The hydrosilane moiety of the hydrodiphenylsilyl derivative 2c was hydrolyzed without any catalyst to the corresponding silanol accompanied by the reduction of the iminophosphorane moiety to triarylphosphine imide moiety were synthesized. The hydrosilane 2c, without any catalyst evolving hydrogen gas.

Notes and references


