DOI: 10.1002/chem.201001054

Nucleophilic Silylenoid Character of Stable Phosphonium Sila–ylides

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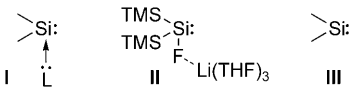
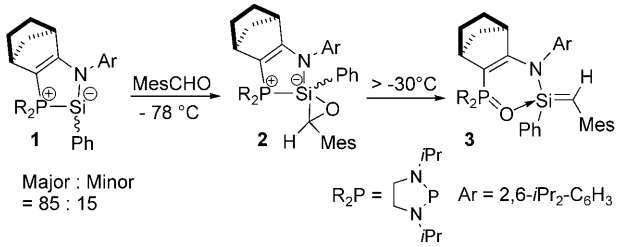
Donor-stabilised silylenes **I** or silylenoids **II** are attractive stable sources of highly reactive transient silylenes **III**.[1] Moreover, their highly modulable structure, by changing the substituents and donor ligands, to modify the reactivity of the silicon(II) centre, is also of great interest.[2] Indeed, several stable, complexed silylenes **I** with different donor ligands have been synthesised.[3–5] Even, the highly reactive dihalogenosilylene has been recently isolated as an N-heterocyclic carbene complex, demonstrating the effectiveness of the stabilisation system.[4a,b] However, the ligand effect on the chemical properties of the low-valent silicon centre in derivatives **I** has been poorly investigated.



One of the typical reactions of transient silylenes is the concerted [2+1] cycloaddition reaction with olefins,[6] in the case of singlet silylenes.[7] In contrast, the reaction with carbonyl compounds, leading to silaoxiranes, does not proceed through a [2+1] cycloaddition, but rather involves the transient formation of a silacarbonyl ylide,[8] which can be trapped by dipolarophiles, such as olefins, to afford the corresponding oxasilacyclopentanes.[9] Although several reactions of silylene–base adducts (base: imine or amine) with diphenylacetylene, affording 1,2-disilacyclobutene derivatives (2:1 silylene/acetylene adduct) have been described, in the case of donor-stabilised silylenes direct observation of [2+1] cycloaddition reactions has never been achieved.[10] Herein we report clear experimental and theoretical evidence for [2+1] cycloadditions involving a phosphine-coordinated silylene, the stable phosphonium sila–ylide **1**.[11] In contrast to the case for free silylene species, its reaction with an aldehyde gives rise to a pentacoordinate oxasilirane by a concerted [2+1] cycloaddition with a very low energy barrier, demonstrating its behaviour as a nucleophilic silylenoid.

Recently, we have shown that phosphonium sila–ylide **1** reacts with carbonyl compounds as a heavier silicon homologue of the Wittig reagent.[11] To gain more insight into the mechanism of this reaction, the process with mesitylaldehyde was monitored by NMR spectroscopy at low temperature. The main product detected was the pentacoordinate oxasilirane **2**, as a pair of diastereomers (85:15),[12] which transforms into the silene **3** at temperatures higher than −30 °C (Scheme 1). The ^{29}Si NMR spectrum shows two sets of doublets at very high field ($\delta = -120$ and -123 ppm). In good agreement with a pentacoordinate silicon centre in **2**,[14,15] these values are drastically shifted upfield compared with those of tetracoordinate silaoxiranes.[13] In the ^{31}P NMR



Scheme 1. The Wittig reaction of **1** with an aldehyde.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001054.

spectrum, the signals appear in the typical region for tetracoordinate phosphonium functions ($\delta = 43$ and 39 ppm), and the large coupling constants (J (P,Si) = 87.7 and 71.3 Hz; J (P,C) = 86.8 and 22.7 Hz) provide strong evidence for the P–Si bond. Oxasilirane **2** was isolated in crystalline form from a concentrated THF solution at −60 °C, and its structure was unambiguously established by single-crystal X-ray diffraction analysis (Figure 1).[16]

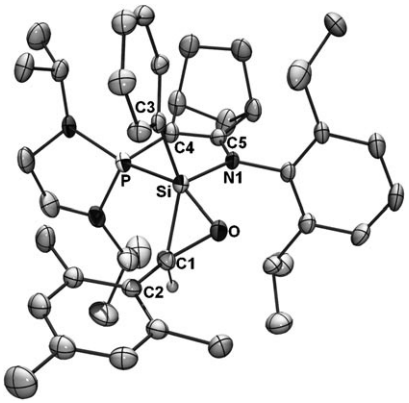
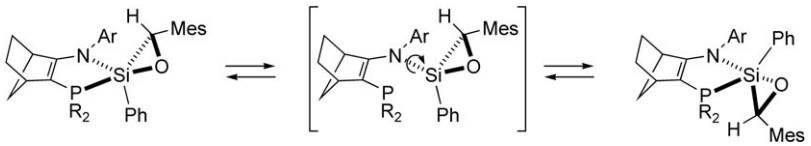


Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. H atoms (except for that on C1) are omitted for clarity. Selected bond lengths [Å] and angles [°] for **2**: Si–O 1.687(2), Si–C1 1.850(3), O–C1 1.512(4), Si–C3 1.875(3), Si–P 2.4905(13), Si–N1 1.816(3); O-Si-C1 50.37(12), O-C1-Si 59.22(14), Si-O-C1 70.42(16), O-Si-P 153.25(9), C1-Si-C3 118.56(16), C1-Si-N1 127.15(14), N1-Si-C3 110.11(13), O-Si-N1 98.06(12), O-Si-C3 106.48(14), N1-Si-P 84.44(9), C1-Si-P 107.42(11), C3-Si-P 97.45(11).

Oxasilirane **2** presents a strongly deformed trigonal bipyramidal (TBP) geometry with the phosphorus and oxygen atoms in apical positions (O-Si-P: 153.25°). The sum of the three equatorial angles (355.8°) is very close to the ideal TBP (360°). The P–Si apical bond is significantly elongated (P–Si: 2.491 Å) compared with the corresponding value in **1** (2.304 Å),[11] and it is longer than that in other pentacoordinate silicon compounds with phosphine ligands (2.41 Å).[17] The geometric parameters of the silaoxirane fragment are similar to those observed for previously reported tetracoordinate silaoxiranes except for the slightly elongated Si–O apical bond (1.687 and 1.668 Å, respectively).[18]

The oxasilirane **2** presents a P,O-apical structure with an inverted stereochemistry at the silicon centre relative to that of the major diastereomer of sila–ylide **1**.[11] This is probably due to the isomerisation of **2** (P,C-apical to P,O-apical TBP) through Si–N bond rotation after the dissociation of the P–Si bond of **2** and suggests a facile dissociation–association of this bond in spite of its rigid cyclic structure (Scheme 2). The substantially elongated Si–P bond in **2** is in good agreement with a weak P–Si interaction.

To gain a deeper understanding of these experimental results, we performed a theoretical study on the sila-Wittig reaction between the model ylide **4a** (X = NMe) and formaldehyde (Figure 2) at the B3LYP/6-31+G*+ΔZPVE level of theory.[19] All of our attempts to find a reaction pathway through a [2+2] cycloaddition reaction, which is similar to the classical Wittig reaction, failed. Instead, the calculations predict that the first step of the process is a [2+1] cycloaddition reaction at the silicon centre to afford the P,C-apical oxasilirane **5a**. The model reaction, including less bulky substituents, proceeds exothermically in a concerted mechanism without an internal energy barrier. At 298 K the calculated Gibbs activation energy is 10.6 kcal mol^{-1}, thus indicating that most of the activation free energy stems from entropic contributions. These results are consistent with the experimental observation of the quasi-immediate reaction of **1** with mesityl aldehyde at low temperature (−78 °C) in spite of the highly elevated steric congestion.[20] Moreover, the geometrical parameters in **TS1** clearly indicate that this low-barrier cycloaddition reaction takes place not on the dissociated free silylene centre, but on the tricoordinate silicon(II) centre. Silaoxaphosphetane **6a**, the precursor of silene **7**,



Scheme 2. Possible mechanism for the isomerisation of **2**.

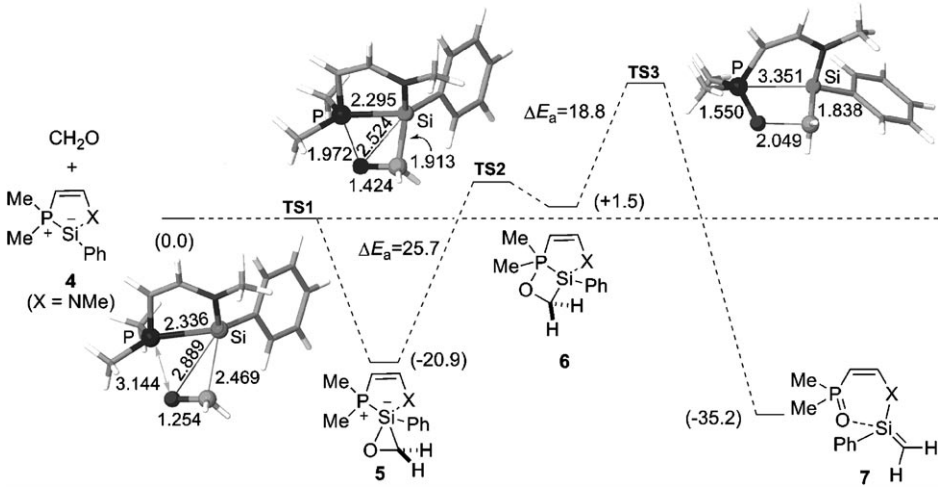


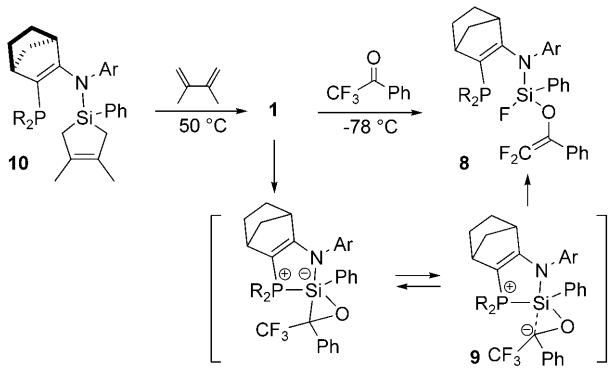
Figure 2. Energy profile for the reaction of **4a** (X = N-Me) with formaldehyde (B3LYP/6-31+G*+ΔZPVE).

can only form from the oxasilirane **5a** by isomerisation. The higher energy of **6** than **5a** ($\Delta E_{\mathbf{6-5a}} = 22.4$ kcal mol^{-1}) is in agreement with the experimental observations. In the case of an ylide with more electronegative amino groups (NH_2) on the phosphorus atom, this energy gap is smaller ($\Delta E_{\mathbf{6-5a}} = 15.0$ kcal mol^{-1}).

The low energy barrier for the [2+1] cycloaddition is a general feature of phosphonium sila–ylides. Indeed, similar calculations for the reaction with a cyclic ylide **4b** (X = CH_2) as well as with an acyclic one (**4c**: $Me_3P \rightarrow SiMePh$) predict that they proceed by a barrier-free (in terms of internal energy) concerted mechanism ($E_a = 0$ kcal mol^{-1}).[21] These results indicate a nucleophilic silylenoid character of the phosphonium sila–ylides, rather than the α,β-ambiphilic character[22,23] as postulated by Seyferth and Lim.[24]

Due to the transient formation of the labile pentacoordinate oxasilirane, the pathway of the reaction is strongly influenced by the nature of the substituents. Indeed, a Wittig-type reaction was observed with mesitylaldehyde (Si–O bond cleavage), while the reaction of **1** with trifluoroacetophenone affords exclusively fluorosilane **8** (Scheme 3, Figure 3). The latter pathway can be rationalised by the transient formation of a betaine species **9**, which features a carbanion centre stabilised by two electron-withdrawing groups (Si–C bond cleavage).[25] These results suggest the high reactivity of the transient oxasiliranes and behaviour, in some cases, similar to the intermediate of the Brook rearrangement.[26] Furthermore, ylide **1** also reacts with classical silylene trapping agents such as 2,3-dimethylbutadiene to give the corresponding [1+4]-cycloadduct **10**.[6]

In summary, we have clearly demonstrated that tricoordinate divalent silicon species react with unsaturated derivatives by a concerted low-energy-barrier [2+1] cycloaddition process, affording labile pentacoordinate silicon intermediates. Furthermore, the first persistent pentacoordinate oxasilirane **2**, which behaves like an intermediate of the Brook rearrangement, has been isolated and fully characterised. Thanks to the high stability of phosphonium sila–ylides, a precise mechanistic study with detection of fragile reactive intermediates was possible, and these ylides can be used as precursors to prepare new reactive species. Other reactions of phosphonium sila–ylides, extending their nucleophilic silylenoid character, particularly with poorly reactive unsaturated compounds, are under active investigation.



Scheme 3. The reaction of **1** with 2,3-dimethylbutadiene and trifluoroacetophenone.

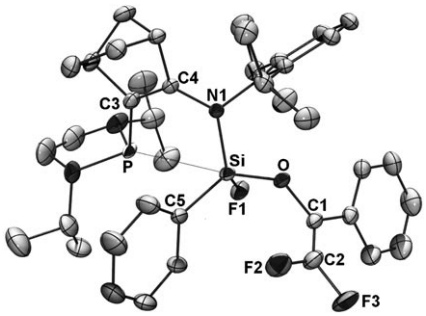


Figure 3. Molecular structures of **8**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] : C3–C4 1.353(2), C3–P 1.794(3), Si–N1 1.7193(14), P–Si 3.401(3), Si–F1 1.5888(12), Si–O 1.6480(13), Si–C5 1.839(2), O–C1 1.381(2), C1–C2 1.320(3); C4-C3-P 126.80(16), F1-Si-O 103.42(6), F1-Si-N1 115.25(7), O-Si-N1 101.53(6), F1-Si-C5 109.63(8), O-Si-C5 109.42(8), N1-Si-C5 116.32(8), C1-O-Si 125.48(11), C4-N1-Si 126.82(11), C3-C4-N1 130.63(15).

Acknowledgements

We are grateful to the CNRS and Ingenio-Consolider (CSD2007-00006) for financial support of this work.

Keywords: cycloaddition · phosphorus · silicon · silylenes · ylides

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Received: April 21, 2010
Published online: June 25, 2010

