DOI: 10.1002/ejoc.200901315

A Theoretical Insight into the Mechanism of the Silver-Catalysed Transsiliranation Reaction

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Keywords: Density functional calculations / Reaction mechanisms / Silanes / Silver / Small ring systems

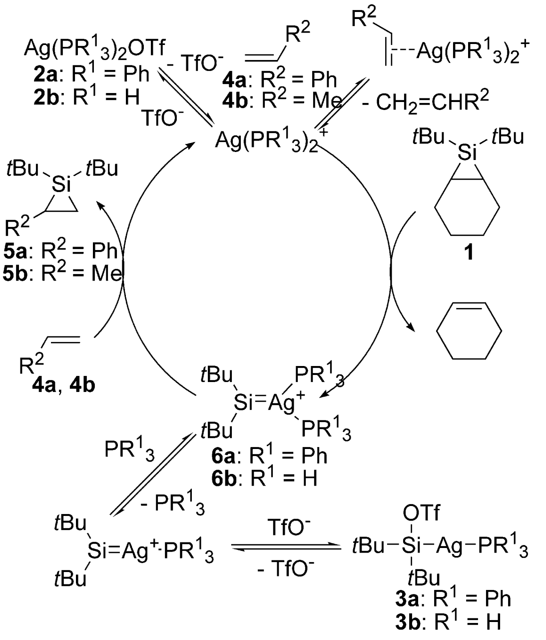
DFT calculations on a silver-catalysed transsiliranation reaction (silylene transfer from a silirane to an alkene) have shown the key role of a silylenesilver ion in the catalytic cycle. Although the corresponding triflate-bound species has previously been detected by NMR and IR spectroscopy, no significant silylene-transfer activity is predicted for such a nonionised structure. Several experimental results can be explained by this new reaction mechanism.

Introduction

Siliranes (also named as silacyclopropanes) can be applied to the stereoselective formation of substituted 2-oxasilolanes in a number of syntheses.[1] Siliranes are usually obtained by the reaction of an alkene with a silylene precursor (such as $t\mathrm{Bu_2SiCl_2}$/Li[2] or hexa-*tert*-butylcyclotrisilane/*hν*).[3] In particular, good results are usually obtained with the di-*tert*-butylsilirane derived from cyclohexene[4] (**1**, see Scheme 1) by using a silver salt as a catalyst.[5] Although such a reaction has usually been named as silacyclopropanation,[6] we propose here the name of transsiliranation, analogously to those of other functional group transfer reactions, such as transacetalisation, transesterification or transthiiranation.

Although some light on the mechanism of the transsiliranation reaction has been shed by an experimental study of Driver and Woerpel,[7] only partial information has been available up to now. Thus, a silylsilver species has been detected by NMR and IR spectroscopy in the reaction between **1** and **2** (Scheme 1). Since the silylsilver compound [**3a** – or a related bis(olefin)-coordinated species, according to the authors] can react with an olefin (**4a**) to yield a new silirane (**5a**), a catalytic cycle involving that species was accordingly proposed.

Whereas neutral species were only considered in the Driver–Woerpel work,[7] analysis of the literature[7–11] has allowed us to propose a new catalytic cycle involving ions in equilibrium with the corresponding nonionic compounds (see Scheme 1). Thus, the reversible dissociation of some triflyloxysilyl-metal compounds (such as ruthenium[8] or osmium[9] derivatives) is well known. Indeed, the presence of a significant amount of ions in a dichloromethane solution of **2a** can be inferred from conductivity measurements.[10] Furthermore, the reported IR spectrum of a mixture of **1** and **2a** in $\mathrm{CD_2Cl_2}$ includes a peak corresponding to bound triflate (1380 $\mathrm{cm^{-1}}$),[7] as well as a smaller one at ca. 1280 $\mathrm{cm^{-1}}$, which we have tentatively attributed to ionic triflate.[11] A rough estimate based on the height of these IR peaks and the corresponding DFT-calculated extinction coefficients provides a ratio [bound triflate]/[ionic triflate] of 7. Instead, the lack of genuine NMR peaks corresponding to **6a** in such a mixture can be attributed to the rapid,



Scheme 1. Mechanism of the transsiliranation reaction.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901315.

reversible triflate dissociation. Finally, we attribute the high experimental activation entropy of the transsiliranation reaction (+129.7 J mol^{-1} K^{-1})[7] to the dissociation of the triflate anion, as a consequence of the equivalence of the oxygen atoms of the triflate anion, as previously argued in a related work.[12]

We present a DFT study (by using B3LYP/6-31G* calculations) of the new mechanism proposed here for the transsiliranation reaction. Whereas an accurate description of the energy differences involved in the transsiliranation reaction would require the use of very high computational requirements (large basis set, modelling of solvent effects), we have focussed on the viability of alternative reaction mechanisms. Accordingly, the original Driver–Woerpel system[7] (**1** + **2a** + **4a**) has been replaced by a more simple reaction model (**1** + **2b** + **4b**).

Results and Discussion

Although dissociation of bis(phosphane)silver(I) triflate (**2a**) is strongly disfavoured (by 350.4 kJ mol^{-1}) according to our calculations, such a value should not be extrapolated to experimental conditions because of the neglect of solvation effects in our study. Thus, single-point PCM calculations (by considering dichloromethane as the solvent) predict a decrease in the free energy for triflate dissociation by 269.0 kJ mol^{-1}, though such a value should only be taken on a semiquantitative basis because of a number of implicit errors (including uncertainty of the cavity boundary for ionic solutes,[13] system simplification, lack of diffuse functions and BSSE). Nevertheless, the similarity in the order of magnitude of both values is consistent with experimental data showing a detectable amount of triflate ion under the reaction conditions.

The occurrence of a pre-equilibrium involving the coordination of an alkene to the bis(phosphane)silver(I) complex allows an explanation of decrease in the rate observed by increasing the olefin concentration;[7] this result is similar to those for copper-catalysed cyclopropanation reactions.[14] Our calculations on the propene coordination predict that such a process is favoured by 0.5 kJ mol^{-1}, though such a low value might be underestimated because of the difference in the ligand properties between the parent phosphane and triphenylphosphane.[15]

The high activity of **1** as a silylene donor can be attributed to the occurrence of intramolecular steric repulsions between a *tert*-butyl group and the flagpole hydrogen atoms of the boat-shaped six-membered ring (see Figure 1). On the other hand, the silylenesilver ion plays a key role in the catalytic cycle. An orthogonal arrangement of the C–Si–C and P–Ag–P sequences is found for **6b** (see Figure 1), similarly to that obtained theoretically for a different silylenesilver complex.[16]

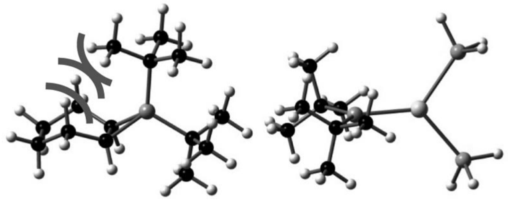
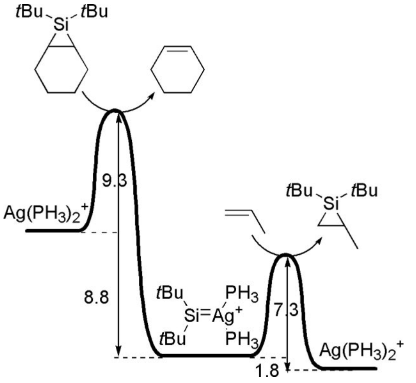


Figure 1. Geometries of **1** (left) and **6b** (right).

The catalytic cycle comprises two steps (see energy profile in Scheme 2). The first elementary reaction involves silylene transfer from a silirane to the bis(phosphane)silver(I) ion to yield an alkene and an activated silylenesilver(I) cation. In the second step, silylene transfer takes place from the silylenesilver ion towards a different olefin. Despite the fact that silylene transfer takes place in a different direction in each step, both processes are thermodynamically favoured (by 36.7 kJ mol^{-1} and 8.1 kJ mol^{-1}), as a consequence of the instability of **1** because of intramolecular steric repulsions. Low activation barriers have been calculated for both silylene-transfer steps [from cyclohexene silirane to bis(phosphane)silver(I) ion, 38.8 kJ mol^{-1}; from silylenesilver(I) ion to propene, 30.2 kJ mol^{-1}].



Scheme 2. Energy profile (in kJ mol^{-1}) for the ionic catalytic cycle.

Some similarities for the geometries of the TSs corresponding to the silylene transfer involving cyclohexene (Figure 2, left) and propene (Figure 2, right) can be observed. Thus, a concerted mechanism can be inferred in both processes; similar to that observed for thiirane desulfuration by triethyl phosphite.[17] The very low asynchronicity of the reaction supports a low charge variation on the vinylic atoms along such a step and provides an explanation for the small experimental magnitude of the Hammett constant for a set of transsiliranation reactions of substituted styrenes ($\rho = -0.62$[7]), analogously to theoretical[18] and experimental ($\rho = -0.85$,[19] -0.79[20]) studies on cyclopropanation reactions catalysed by cationic Cu^{I} complexes.

For a comparison, the analogous catalytic cycle involving the triflate-associated species has also been calculated (energy profile shown in the Supporting Information). Thus, a two-step path is predicted for each silylene transfer through the formation of the corresponding (2-silylalkyl)silver reaction intermediates, with very high activation barriers (up to 249.5 kJ mol^{-1}). The infeasability of the nonionic pathway can be attributed to the violation of the Woodward–Hoffmann rules by apolar four-membered transition

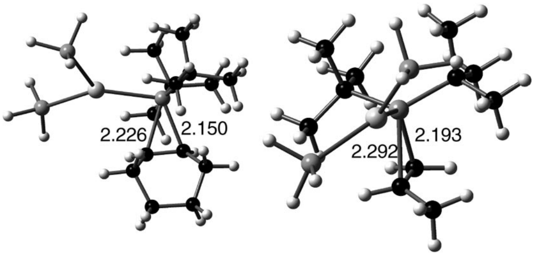


Figure 2. TSs of the silylene transfer between the silylenesilver ion and cyclohexene (left) and propene (right). Some relevant distances (in Å) are also shown.

states,[21] which is similar to that observed in the concerted hydrogenation of ethylene,[22] whereas apparent exceptions of such a ban can be attributed to the participation of vacant d orbitals (catalysed hydrosilylation)[23] or 3-centred geometries (hydroboration).[24]

The silylenesilver complex involved in the ionic reaction mechanism can undergo reversible loss of a phosphane ligand (favoured by 16.5 kJ mol^{-1}), which explains the experimentally observed fast phosphane exchange of the silylsilver complex.[7] The resulting species can reversibly bind a triflate anion to yield a silylsilver compound, which is consistent with spectroscopic data.[7]

Although our theoretical study supports the proposal of a reaction pathway for the transsiliranation reaction with moderate activation barriers, the participation of other alternative mechanistic paths cannot be precluded from a logical point of view.

Conclusions

The nonionic pathway (as proposed in the experimental study) can be disregarded for the transsiliranation reaction on the basis of the very high activation barriers calculated for the corresponding catalytic cycle. Instead, a viable ionic path can be inferred when the cationic species derived from reversible triflate ionisation are considered (related to the nonionic pathway). Thus, a concerted mechanism is predicted for both silylene transfer steps of the catalytic cycle [from cyclohexene silirane to bis(phosphane)silver(I) cation; from silylenesilver(I) ion to the alkene]. The catalytic cycle energetics is favoured by the reduction of the intramolecular steric repulsions of cyclohexene silirane. The new reaction mechanism proposed here is supported by a number of experimental data.

Experimental Section

Calculations were carried out with the Gaussian03 package[25] with B3LYP/SDD,6-31G* basis set, similar to those used in some theoretical studies on silver-carbene complexes.[26] Stationary points were characterised by the right number of negative eigenvalues of the exact Hessian matrix. Gibbs free energies (at 25 °C) are discussed throughout the text.

Supporting Information (see footnote on the first page of this article): Energy profile of the nonionic reaction mechanism, as well as electronic and Gibbs free energies and geometries of the structures involved in both ionic and nonionic reaction mechanisms.

Acknowledgments

We are grateful for the generous financial support of the Spanish Ministerio de Ciencia e Innovación (MICINN) (Projects CTQ2005-08016, CTQ2008-05138-C02-01 and Consolider Ingenio 2010/CSD2006-0003), the European Social Fund (ESF) and the Gobierno de Aragón (Grupo de Excelencia E11). S. R.-R. thanks the Instituto Universitario de Catálisis Homogénea (IUCH) for a grant.

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Received: November 17, 2009