Unexpected Zwitterionic Allenyls from Silylenes and a Fischer Alkynylcarbene: A Remarkable Silylene-Promoted Rearrangement


Abstract: The silylenes Si(Bu3bzam)R (Bu3bzam = N,N-bis((tertbutyl)benzamidinate; R = Mes, CH2SiMes) attack the carbene atom of the Fischer alkynyl(ethoxy)carbene complex [W(CO)5(CH2Et)(2)] to give, after a striking rearrangement, zwitterionic α-allenyl complexes in which the original carbene C atom forms part of the allene C2 fragment and also of a CNCNSi five-membered ring (inserted into a Si–N bond of the original amidinatosilylene). These remarkable allenyl products, which contain two stereogenic groups, are selectively formed as single diastereoisomers.

Silylenes are currently receiving an increasing interest from the chemical community not only because of their unique fundamental chemistry but also due to their rising use as ligands in coordination complexes. Additionally, it has been recently found that some silylenes, particularly those stabilized by donor groups, have a stronger electron-donor capacity than the most basic phosphines and even N-heterocyclic carbene (NHCs). This is a key factor of their newly reported behavior as steering ligands in homogeneous catalysis but, despite their strong nucleophilicity, their use as nucleophiles for the formation of Si–C bonds is still little developed.

Within the family of donor-stabilized silylenes, those having an amidinato fragment are being increasingly used because their syntheses are relatively easy and their electronic and steric properties can be easily tuned. In this context, we have recently achieved the first insertion of a carbene fragment into an N–Si bond by treating an amidinatosilylene with a tungsten Fischer methyl(ethoxy)carbene complex at room temperature (Scheme 1). In contrast, similar reactions using phosphines or NHCs afford carbonyl- and/or carbene-substituted products. Noteworthy, although group 6 metal Fischer carbene complexes are frequently used as precursors of carbene synthons, the transfer of the carbene fragment requires catalysts or harsh reaction conditions (> 120°C).

We now report that, studying reactions of amidinatosilylenes with group 6 metal Fischer alkynyl(ethoxy)carbene complexes, we have unexpectedly obtained zwitterionic α-allenyl complexes in which the original carbene C atom forms part of the allene fragment and also of a CNCNSi five-membered ring. These remarkable products, which contain two stereogenic groups, are selectively formed as single diastereoisomers through a striking rearrangement that follows an initial attack of the silylene to the carbene atom.

Scheme 1. Reaction of an amidinatosilylene with a tungsten Fischer methyl(ethoxy)carbene complex.

Scheme 2. Reactions of amidinatosilylenes 1mes and 1tmsm with the Fischer alkynyl(ethoxy)carbene complex 2 (isolated yields are given in parenthesis).

Supporting information for this article is given via a link at the end of the document.
The XRD structures of 3max and 3'tmsm (Figure 1)\[16] show that both compounds are based on an allene C5 moiety that has one end (C25 in 3max and C20 in 3'tmsm) attached to a W(CO)5 fragment and a phenyl group and the other end (C27 in 3max and C22 in 3'tmsm) forming part of a CSiNCN five-membered ring. In addition, these structures also show a number of novel and unexpected features: (a) the original Ccarbene atom of complex 2 (Cα; see Greek labelling in Scheme 2) has ended inserted into a Si–N bond of the original amidinatosilylene reagent, (b) the OEt group has been transferred from the C atom of 2 to the Si atom, (c) the W(CO)5 fragment has moved from Cα to Cβ, and (d) both 3max and 3'tmsm have two new stereogenic groups, i.e., the allene group and the Si atom, but, maintaining in both compounds a common stereochemistry for the allene group, they differ in the stereochemistry of the Si atom, since the arrangement of the W(CO)5 and OEt groups is syn in 3max but anti in 3'tmsm. Therefore, the reactions that lead to 3max and 3'tmsm, being completely diastereoselective, have opposite stereoselectivity.

The most distinctive features of the NMR spectra of 3max and 3'tmsm are the 13C signals of their allene C5 skeleton (δ 80.3 (Cα), 162.5 (Cβ) and 114.2 (Cγ) for 3max and 82.2 (Cα), 164.6 (Cβ) and 111.8 (Cγ) for 3'tmsm) and the fact that their OEt methylene protons are diastereotopic in their 1H spectra, as expected for a OEt group attached to a stereogenic atom. The 13C NMR data of Cα and Cβ are comparable to those previously obtained for other α-alkenyl complexes.\[16] The 29Si(1H) spectra of 3max and 3'tmsm show singlets at δ −21.47 (3max) and 1.29 and −8.99 (3'tmsm).

Regarding the IR spectra of 3max and 3'tmsm, the strong decrease of their νCO absorptions (Supporting Information), compared to those of the starting carbene complex 2,\[16] suggests that the allenylic ligands are more electron donating than the carbene.

NBO calculations (B3LYP-D3/def2-SVP/toluene) confirmed the zwitterionic character of the allenylic complexes, as the highest positive charge is located on the ring Si atom (+2.14 au (3max) and +2.19 au (3'tmsm)), whereas there is a concentration of negative charge on the metallic moiety (W atom and carbonyl O atoms), the charge of the W atom being −0.51 (3max) and −0.50 au (3'tmsm).

The novelty of the reactions shown in Scheme 2 led us to undertake a mechanistic DFT study (B3LYP-D3/def2-SVP/toluene) of the synthesis of complex 3max.\[17] In order to shed light on the origin of the stereoselectivity of this reaction, the reaction pathway that would lead to the unobserved diastereoisomer (3'tmsm), which has a stereochemistry analogous to that of 3'tmsm, was also modelled. Scheme 3 shows that the Ccarbene atom of 2 is easily attacked (energy barrier 3.3 kcal mol⁻¹) by the Si atom of 1max to give intermediate I1. An easy migration (energy barrier 5.0 kcal mol⁻¹) of the ethoxy group to the Si atom leads to the key intermediate I2, in which both N atoms are equally close to the Ccarbene atom (Cδ), of the just reformed carbene fragment. From I2, the migration of the rear (in Scheme 3) N atom to the Ccarbene atom (attack from the rear side of the planar carbene ligand, TS3) leads to the selective formation of intermediate I3, which contains the W(CO)5 and OEt groups at the same side (syn arrangement) of the newly formed five-membered ring (this step...
fixes the stereochemistry of the two stereogenic centers. A subsequent “walking” (1,3-shift\textsuperscript{16a,16b}) of the W(CO)\textsubscript{5} fragment from C\textsubscript{4} to C\textsubscript{5} (energy barrier 14.9 kcal mol\textsuperscript{-1}; rate determining step) leads to the experimentally observed complex 3\textsubscript{max}. TS4 has structural similarities with other calculated transition states for 1,3-M(CO)\textsubscript{5} migrations\textsuperscript{[16a,16b]} Thus, TS4 shows C–W distances of about 3 Å (C-W 3.02 Å, C-W 3.04 Å) and a C–M–C angle of about 50° (51.5°). The C–C\textsubscript{C\textsubscript{4}} (1.40 Å) and C–C\textsubscript{C\textsubscript{5}} (1.24 Å) distances indicate that TS4 still has a strong alkynyl character, which, to allow the 1,3-metal shift, bends the C–C\textsubscript{C\textsubscript{4}}–C\textsubscript{5} angle by 169° by approaching the central C\textsubscript{C} atom to the metal (C-W 2.62 Å).

The alternative reaction pathway (depicted in Figure S8 of the Supporting Information) that would lead to the experimentally unobserved complex 3'\textsubscript{max}, which contains the W(CO)\textsubscript{5} and OEt groups in an anti arrangement, involves a higher energy barrier for the rate determining 1,3-migration of the W(CO)\textsubscript{5} fragment (20.2 kcal mol\textsuperscript{-1} of T4' vs. 14.9 kcal mol\textsuperscript{-1} of T4).

Although the stereochemistries of 3\textsubscript{max} and 3'\textsubscript{max} are fixed in the I2 \rightarrow I3 and I2 \rightarrow I3' steps, respectively, the reverse processes I3 \rightarrow I2 and I3' \rightarrow I2 have low energy barriers (7.9 and 9.9 kcal mol\textsuperscript{-1}, respectively). Therefore, the step responsible for the observed stereoselectivity of 3\textsubscript{max} is the rate determining metal “walking” step, because the energy barrier to the transformation of I3 into 3\textsubscript{max} (TS4) is 5.3 kcal mol\textsuperscript{-1} lower than that to the transformation of I3' into 3'\textsubscript{max} (TS4'). Interestingly, a close view of TS4 (Figure 2) reveals that there is an interaction between two ring C atoms of the mesityl group and one phenyl H atom. Such a CH\textsubscript{α}-arene stabilizing interaction\textsuperscript{[16c]} is not found in TS4', should be (at least in part) responsible for the greater stability of TS4 (compared with that of TS4'). A similar CH\textsubscript{α}-arene interaction is also observed in 3\textsubscript{max} (Figure S6 of the Supporting Information), which is 5.9 kcal mol\textsuperscript{-1} more stable than 3'\textsubscript{max}.

The above computational study also suggests that the minor unidentified products observed by NMR in the room temperature reaction of 1\textsubscript{max} with 2 may be intermediates I3 and I3', as they evolve to 3\textsubscript{max} at higher temperatures.

The mechanisms of the processes that would lead to diastereoisomers 3\textsubscript{min} and 3'\textsubscript{min}, although not calculated\textsuperscript{[17]} should be closely related to those described above for 3\textsubscript{max} and 3'\textsubscript{max}, respectively. However, as 3'\textsubscript{max} is the final product of the reaction of 1\textsubscript{max} with 2, its formation should be kinetically more favoured than that of 3\textsubscript{max} (the rate-limiting step should have a lower barrier). The fact that the CH\textsubscript{3}SiMes group lacks the aryl fragment necessary to form the CH\textsubscript{α}-arene stabilizing interactions observed in TS4 might be responsible for this difference.

These results contrast with those previously known for reactions of phosphines\textsuperscript{[20]} and NHCs\textsuperscript{[6]} with group 6 metal Fischer alkynyl(alkoxy)carbenes, which render products resulting from the simple conjugate addition of the nucleophile to the remote C atom (C\textsubscript{3}) of the alkyl fragment (the phosphonium alkynyl derivatives are quite unstable in solution\textsuperscript{[20]}). Similar C\textsubscript{3}-addition of nucleophiles has also been observed in reactions of less electrophilic Fischer alkynyl(aryl)carbenes of manganese\textsuperscript{[21]} and rhenium.\textsuperscript{[22]} Nucleophilic addition to the C\textsubscript{3} atom of Fischer carbene complexes requires small and/or very strong (anionic) nucleophiles.\textsuperscript{[23]}

To conclude, two remarkable zwitterionic \textalpha-allyl complexes (3\textsubscript{max} and 3'\textsubscript{max}), having the remote C atom of their alkynyl moiety forming part of a NCN\textsubscript{Si} five-membered ring, have been prepared by treating a Fischer alkynyl(ethoxy)carbene complex (2) with two amidinatosiylene (1\textsubscript{max} and 1\textsubscript{min}). A theoretical (DFT) study has shed light on the mechanism of these reactions, which, starting with a nucleophilic attack of the silylene to the C\textsubscript{carbene} atom, involves a striking rearrangement that implies a transfer of the OEt group to the Si atom, a transfer of the carbene C atom into a Si–N bond (ring expansion of the original amidinatosiylene group), and a 1,3-shift of the metal fragment (metal “walking” on the unsaturated C\textsubscript{C} moiety). This mechanistic study has also explained the total stereoselectivity of the reactions, which, generating two new stereogenic groups, lead to only one diastereomeric product.

No doubt, the very strong nucleophilicity of the silylenes used in this work is a key factor responsible for the unique results described in this contribution, which open new avenues toward novel reactivity modes unattainable for conventional nucleophiles, such as phosphines or NHCs.

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COMMUNICATION


Entry for the Table of Contents

Nucleophilic silylenes

A striking stereoselective rearrangement, which ends in unprecedented zwitterionic allenyls having one end of the allene C₃ fragment inserted into a Si–N bond, takes place in reactions of an amidinatosilylene with Fischer alkynylcarbenes.

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