COMMUNICATION

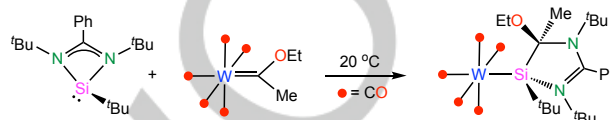# Unexpected Zwitterionic Allenyls from Silylenes and a Fischer Alkynylcarbene: A Remarkable Silylene-Promoted Rearrangement

Javier A. Cabeza,*[a] Pablo García-Álvarez,[a] Mar Gómez-Gallego,[b] Laura González-Álvarez,[a] Alba D. Merinero,[b] and Miguel A. Sierra*[b]

Abstract: The silylenes Si(^{t}Bu$_2$bzam)R (^{t}Bu$_2$bzam = N,N'-bis(tertbutyl)benzamidinate; R = Mes, CH$_2$SiMe$_3$) attack the C$_{carbene}$ atom of the Fischer alkynyl(ethoxy)carbene complex [W(CO)$_5${C(OEt)C$_2$Ph}] to give, after a striking rearrangement, zwitterionic σ-allenyl complexes in which the original carbene C atom forms part of the allene C$_3$ 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[1] but also due to their rising use as ligands in coordination complexes.[2,3] 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 phosphanes and even N-heterocyclic carbenes (NHCs).[4,5] This is a key factor of their newly reported behavior as steering ligands in homogeneous catalysis,[3,4] but, despite their strong nucleophilicity, their use as nucleophiles for the formation of Si–C bonds is still little developed.[1a,f,k,6]
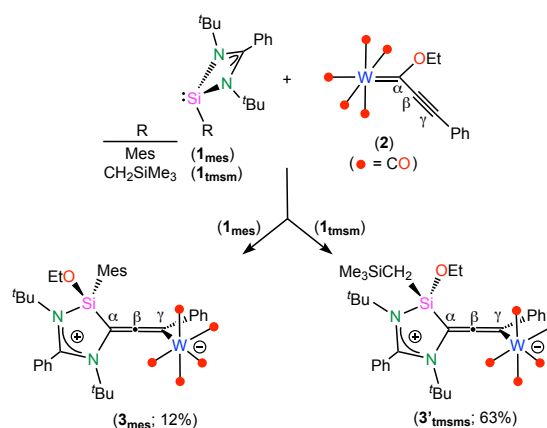
Within the family of donor-stabilized silylenes, those having an amidinato fragment are being increasingly used because their syntheses are relatively easy and their electronic and steric properties can be easily tuned.[1a,2b] In this context, we have recently achieved the first insertion of a carbene fragment into an N–Si bond by treating an amidinatosilylene with a tungsten Fischer methyl(ethoxy)carbene complex at room temperature (Scheme 1).[7] In contrast, similar reactions using phosphanes[8] or NHCs[9] afford carbonyl- and/or carbene-substituted products. Noteworthy, although group 6 metal Fischer carbene complexes are frequently used as precursors of carbene synthons,[10,11] the transfer of the carbene fragment requires catalysts[11h-m] or harsh reaction conditions (> 120 °C).[11a–g]

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

We now report that, studying reactions of amidinatosilylenes with group 6 metal Fischer alkynyl(ethoxy)carbene complexes, we have unexpectedly obtained zwitterionic σ-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 C$_{carbene}$ atom.

The silylenes Si(^{t}Bu$_2$bzam)R (^{t}Bu$_2$bzam = N,N'-bis(tertbutyl)benzamidinate; R = Mes (**1$_{mes}$**),[12] CH$_2$SiMe$_3$ (**1$_{tmsm}$**)[13]) reacted with the Fischer alkynyl(ethoxy)carbene [W(CO)$_5${C(OEt)C$_2$Ph}] (**2**)[14] in C$_6$D$_6$ at 40–60 °C to give the zwitterionic σ-allenyl complexes [W(CO)$_5${C(Ph)CC(^{t}Bu$_2$bzamSi(OEt)R)}] (R = Mes (**3$_{mes}$**), CH$_2$SiMe$_3$ (**3'$_{tmsm}$**)) (Scheme 2). Room temperature reactions led to mixtures in which **3$_{mes}$** and **3'$_{tmsm}$** were accompanied by minor unidentified products that disappeared (almost completely for the reaction with **1$_{mes}$** or completely for reaction with **1$_{tmsm}$**) when the reacting solutions were heated at 40–60 °C.

Scheme 2. Reactions of amidinatosilylenes **1$_{mes}$** and **1$_{tmsm}$** with the Fischer alkynyl(ethoxy)carbene complex **2** (isolated yields are given in parenthesis).
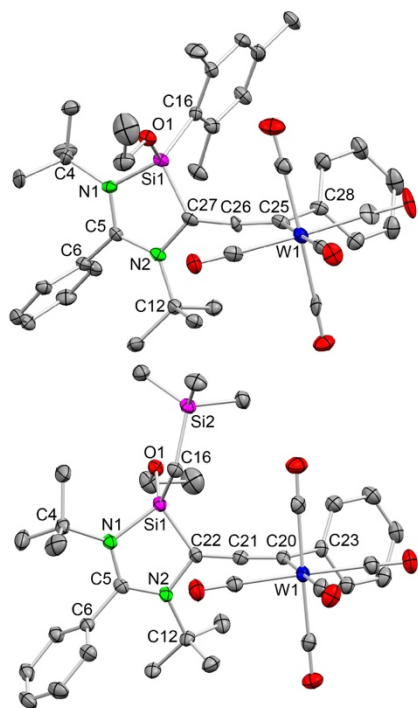
Figure 1. XRD molecular structures of 3_{mes} (top) and $3'_{tmsm}$ (bottom). Selected bond distances (Å) and angles (°): 3_{mes}: W1−C25 2.28(1), C25−C26 1.31(2), C25−C28 1.50(2), C26−C27 1.32(2), C27−N2 1.43(2), C27−Si 1.83(1), Si1−N1 1.79(1), N1−C5 1.35(1), C5−N2 1.38(1), C25−C26−C27 171(1); $3'_{tmsm}$: W1−C20 2.306(3), C20−C23 1.491(4), C20−C21 1.286(4), C21−C22 1.329(4), C22−N2 1.460(4), C22−Si1 1.819(3), Si1−N1 1.801(3), N1−C5 1.361(4), C5−N2 1.340(4), C20−C21−C22 174.2(3).

The XRD structures of 3_{mes} and $3'_{tmsm}$ (Figure 1)[15] show that both compounds are based on an allene C_3 moiety that has one end (C25 in 3_{mes} and C20 in $3'_{tmsm}$) attached to a $W(CO)_5$ fragment and a phenyl group and the other end (C27 in 3_{mes} 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 $C_{carbene}$ atom of complex **2** (C_α; 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_α atom of **2** to the Si atom, (c) the $W(CO)_5$ fragment has moved from C_α to C_γ, and (d) both 3_{mes} 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 3_{mes} but *anti* in $3'_{tmsm}$. Therefore, the reactions that lead to 3_{mes} and $3'_{tmsm}$, being completely diastereoselective, have opposite stereoselectivity.

The most distinctive features of the NMR spectra of 3_{mes} and $3'_{tmsm}$ are the ^{13}C signals of their allene C_3 skeleton (δ 80.3 (C_α), 162.5 (C_β) and 114.2 (C_γ) for 3_{mes} and 82.2 (C_α), 164.6 (C_β) and 111.8 (C_γ) 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 ^{13}C NMR data of C_α and C_β are comparable to those previously obtained for other σ-allenyl

complexes.[16] The $^{29}Si\{^1H\}$ spectra of 3_{mes} and $3'_{tmsm}$ show singlets at δ −21.47 (3_{mes}) and 1.29 and −8.99 (3_{mes}).

Regarding the IR spectra of 3_{mes} and $3'_{tmsm}$, the strong decrease of their ν_{CO} absorptions (Supporting Information), compared to those of the starting carbene complex **2**,[14] suggests that the allenyl ligands are more electron donating than the carbene.

NBO calculations (B3LYP-D3/def2-SVP/toluene) confirmed the zwitterionic character of the allenyl complexes, as the highest positive charge is located on the ring Si atom, +2.14 au (3_{mes} and $3'_{tmsm}$), 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 (3_{mes}) and −0.50 au ($3'_{tmsm}$).
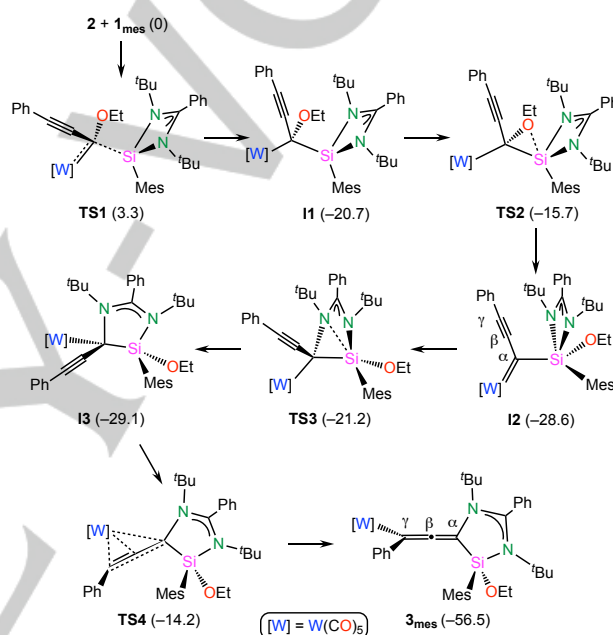
Scheme 3. DFT-Calculated mechanism of the reaction that leads to 3_{mes} from 1_{mes} and complex **2**. Gibbs energies (kcal mol^{-1}; relative to the sum of those of 1_{mes} and **2**) of intermediates (**I**), transition states (**TS**) and final product (3_{mes}) are given in parenthesis.

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 3_{mes}.[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 ($3'_{mes}$), which has a stereochemistry analogous to that of $3'_{tmsm}$, was also modelled. Scheme 3 shows that the $C_{carbene}$ atom of **2** is easily attacked (energy barrier 3.3 kcal mol^{-1}) by the Si atom of 1_{mes} 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 $C_{carbene}$ atom (C_α) of the just reformed carbene fragment. From **I2**, the migration of the rear (in Scheme 3) N atom to the $C_{carbene}$ 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[16a,18]) of the $W(CO)_5$ fragment from C_α to C_γ (energy barrier 14.9 kcal mol⁻¹; rate determining step) leads to the experimentally observed complex **3mes**. **TS4** has structural similarities with other calculated transition states for 1,3-$M(CO_5)$ migrations.[16a,18b] Thus, **TS4** shows C–W distances of about 3 Å (C_α–W 3.02 Å, C_γ–W 3.04 Å) and a C_α–M–C_γ angle of about 50° (51.5°). The C_α–C_β (1.40 Å) and C_β–C_γ (1.24 Å) distances indicate that **TS4** still has a strong alkyne character, which, to allow the 1,3-metal shift, bents the C_α–C_β–C_γ angle to 169° by approaching the central C_β atom to the metal (C_β–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'mes**, which contains the $W(CO)_5$ and OEt groups in an *anti* arrangement, involves a higher energy barrier for the rate determining 1,3-migration of the $W(CO)_5$ fragment (20.2 kcal mol⁻¹ of **T4'** *vs.* 14.9 kcal mol⁻¹ of **T4**).
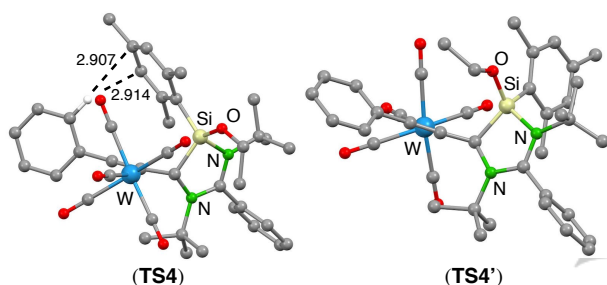

Figure 2. Comparative views of the diastereomeric transition states **TS4** and **TS4'** (most H atoms omitted for clarity), showing the close contacts (Å) found between two mesityl C atoms and a phenyl H atom in **TS4**.

Although the stereochemistries of **3mes** and **3'mes** are fixed in the **I2 → I3** and **I2 → I3'** steps, respectively, the reverse processes **I3 → I2** and **I3' → I2** have low energy barriers (7.9 and 9.9 kcal mol⁻¹, respectively). Therefore, the step responsible for the observed stereoselectivity of **3mes** is the rate determining metal "walking" step, because the energy barrier to the transformation of **I3** into **3mes** (**TS4**) is 5.3 kcal mol⁻¹ lower than that to the transformation of **I3'** into **3'mes** (**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–π-arene stabilizing interaction,[19] 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–π-arene interaction is also observed in **3mes** (Figure S6 of the Supporting Information), which is 5.9 kcal mol⁻¹ more stable than **3'mes**.

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

The mechanisms of the processes that would lead to diastereoisomers **3tmsm** and **3'tmsm**, although not calculated,[17] should be closely related to those described above for **3mes** and **3'mes**, respectively. However, as **3'tmsm** is the final product of the reaction of **1tmsm** with **2**, its formation should be kinetically more

favoured than that of **3tmsm** (the rate-limiting step should have a lower barrier). The fact that the CH_2SiMe_3 group lacks the aryl fragment necessary to form the CH–π-arene stabilizing interactions observed in **TS4** might be responsible for this difference.

These results contrast with those previously known for reactions of phosphanes[20] and NHCs[16] 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_γ) of the alkynyl fragment (the phosphonium allenyl derivatives are quite unstable in solution[20]). Similar C_γ-addition of nucleophiles has also been observed in reactions of less electrophilic Fischer alkynyl(aryl)carbenes of manganese[21] and rhenium.[22] Nucleophilic addition to the C_α atom of Fischer carbene complexes requires small and/or very strong (anionic) nucleophiles.[23]

To conclude, two remarkable zwitterionic σ-allenyl complexes (**3mes** and **3'tmsm**), having the remote C atom of their allenyl moiety forming part of a CNCNSi five-membered ring, have been prepared by treating a Fischer alkynyl(ethoxy)carbene complex (**2**) with two amidinatosilylenes (**1mes** and **1tmsm**). A theoretical (DFT) study has shed light on the mechanism of these reactions, which, starting with a nucleophilic attack of the silylene to the $C_{carbene}$ atom, involves a striking rearrangement that implies a transfer of the OEt group to the Si atom, a insertion of the carbene C atom into a Si–N bond (ring expansion of the original amidinatosilylene group), and a 1,3-shift of the metal fragment (metal "walking" on the unsaturated C_3 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 phosphanes or NHCs.
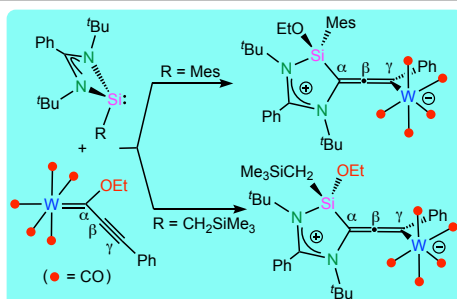
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COMMUNICATION

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