

# Reversible Carbene Insertion into a Ge–N Bond and New Insights into CO- and Carbene-Substitution Reactions Involving Amidinatogermylenes and Fischer Carbene Complexes

Lucía Álvarez-Rodríguez,<sup>[a]</sup> Javier A. Cabeza,<sup>\*[a]</sup> Pablo García-Álvarez,<sup>[a]</sup> Mar Gómez-Gallego,<sup>[b]</sup>  
Laura González-Álvarez,<sup>[a]</sup> Alba D. Merinero,<sup>[b]</sup> and Miguel A. Sierra<sup>\*[b]</sup>

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[a] L. Álvarez-Rodríguez, Prof. Dr. J. A. Cabeza, Dr. P. García-Álvarez, L. González-Álvarez  
Centro de Innovación en Química Avanzada (ORFEO-CINQA)  
Departamento de Química Orgánica e Inorgánica  
Universidad de Oviedo, 33071 Oviedo, Spain  
E-mail: jac@uniovi.es

[b] Prof. Dr. M. Gómez-Gallego, A. D. Merinero, Prof. Dr. M. A. Sierra  
Centro de Innovación en Química Avanzada (ORFEO-CINQA)  
Departamento de Química Orgánica  
Universidad Complutense, 28040 Madrid, Spain  
E-mail: sierraor@ucm.es

Supporting Information and the ORCID identification numbers for the authors of this article can be found at the end of the document.

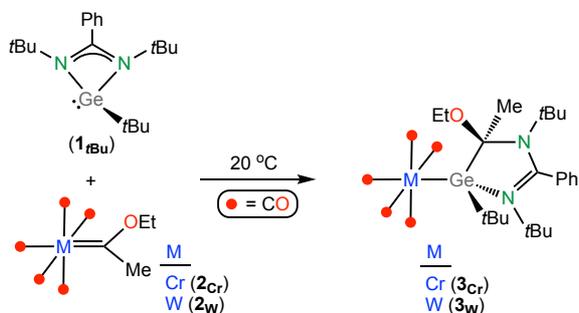
## Abstract

The formation of the 5-membered-ring germylene complexes  $[M(\text{CO})_5\{\text{Ge}(\text{tBu}_2\text{bzamC}(\text{OEt})\text{Me})\text{tBu}\}]$  ( $\mathbf{3}_M$ ;  $M = \text{Cr}, \text{W}$ ), which occurs readily at room temperature from the germylene  $\text{Ge}(\text{tBu}_2\text{bzam})\text{tBu}$  ( $\mathbf{1}_{\text{tBu}}$ ) and the Fischer carbenes  $[M(\text{CO})_5\{\text{C}(\text{OEt})\text{Me}\}]$  ( $\mathbf{2}_M$ ;  $M = \text{Cr}, \text{W}$ ), has been found to be reversible. Upon heating at 60 °C, complexes  $\mathbf{3}_M$  undergo epimerization to an equilibrium mixture of  $\mathbf{3}_M$  and  $\mathbf{3}'_M$ . At that temperature, the chromium epimers (but not the tungsten ones) release CO to end in the mixed germylene-Fischer carbene complexes  $[\text{Cr}(\text{CO})_4\{\text{C}(\text{OEt})\text{Me}\}\{\text{Ge}(\text{tBu}_2\text{bzam})\text{tBu}\}]$  (*cis*- $\mathbf{4}_{\text{Cr}}$  and *trans*- $\mathbf{4}_{\text{Cr}}$ ). The latter decompose at 120 °C to  $[\text{Cr}(\text{CO})_5\{\text{Ge}(\text{tBu}_2\text{bzam})\text{tBu}\}]$  ( $\mathbf{6}_{\text{Cr}}$ ). As the formation of *cis*- $\mathbf{4}_{\text{Cr}}$  and *trans*- $\mathbf{4}_{\text{Cr}}$  from  $\mathbf{3}_M$  requires the presence of free  $\mathbf{1}_{\text{tBu}}$  and  $\mathbf{2}_M$  in the reacting solutions, the reactions of  $\mathbf{1}_{\text{tBu}}$  with  $\mathbf{2}_M$  to give  $\mathbf{3}_M$  (and  $\mathbf{3}'_M$  at 60 °C) should be reversible. This proposal has been proven by germylene-exchange crossover reactions in which free  $\mathbf{1}_{\text{tBu}}$  and  $[M(\text{CO})_5\{\text{Ge}(\text{tBu}_2\text{bzamC}(\text{OEt})\text{Me})\text{CH}_2\text{SiMe}_3\}]$  ( $\mathbf{5}'_M$ ;  $M = \text{Cr}, \text{W}$ ) were formed when complexes  $\mathbf{3}_M$  were treated at room temperature with the germylene  $\text{Ge}(\text{tBu}_2\text{bzam})\text{CH}_2\text{SiMe}_3$  ( $\mathbf{1}_{\text{tmsm}}$ ). A clear differential behavior between NHCs and amidinatogermylenes ( $\mathbf{1}_{\text{tBu}}$  and  $\mathbf{1}_{\text{tmsm}}$ ) in their reactivity against group 6 metal Fischer carbene complexes is demonstrated. The higher electron-donor capacity of amidinatogermylenes with respect to NHCs and the bias of the former to get involved in ring expansion processes are responsible for this differential behavior.

## Introduction

The fundamental chemistry of heavier tetrylenes (HTs),<sup>[1]</sup> *i.e.*, compounds containing a heavier group 14 element in the +2 oxidation state, their use as ligands in coordination chemistry,<sup>[2]</sup> and the fact that they are an entry into the exciting and little explored chemistry of these elements in very low oxidation states (+1, 0)<sup>[3,4]</sup> are currently vivid research themes. A relevant feature of some HTs, in particular of those that are stabilized by donor groups, that has been recognized as a key factor of their recently reported behavior as steering ligands in homogeneous catalysis,<sup>[5,6]</sup> is that their electron-donor capacity (nucleophilicity) can be very strong, even stronger than that of the most basic phosphanes and N-heterocyclic carbenes.<sup>[6h,j,m,7]</sup> Within the family of HTs that are intramolecularly stabilized by a donor group, those containing an amidinato<sup>[1a,2b]</sup> (or guanidinato<sup>[1a]</sup>) fragment have been recently chosen by many researchers because their syntheses are easy and their electronic and steric properties can be easily tuned.

On the other hand, insertion reactions of carbene fragments into C–C, C–H and N–H bonds are key processes in modern organic and organometallic syntheses.<sup>[8–10]</sup> Group-6 metal (Fischer) carbene complexes have been extensively used for this purpose as carbene sources, although they require high temperatures<sup>[9]</sup> or catalysis<sup>[10]</sup> to transfer their carbene fragment. In this regard, we have communicated unprecedented room-temperature insertions of Fischer carbene ligands into a Ge–N bond of an amidinatogermylene (Scheme 1).<sup>[11]</sup> Remarkably, the final products (**3<sub>M</sub>**), despite containing two stereogenic atoms, were obtained as single diastereoisomers. A mechanistic DFT study of these reactions revealed that they start with a nucleophilic attack of the germylene Ge atom to the carbene C atom, proceed through a totally stereoselective insertion of the carbene fragment into a Ge–N bond of the amidinatotetrylene, and end in  $[M(CO)_5L]$  complexes (**3<sub>M</sub>**), in which L belongs to an unprecedented family of HT ligands featuring a GeCNCN five-membered ring.



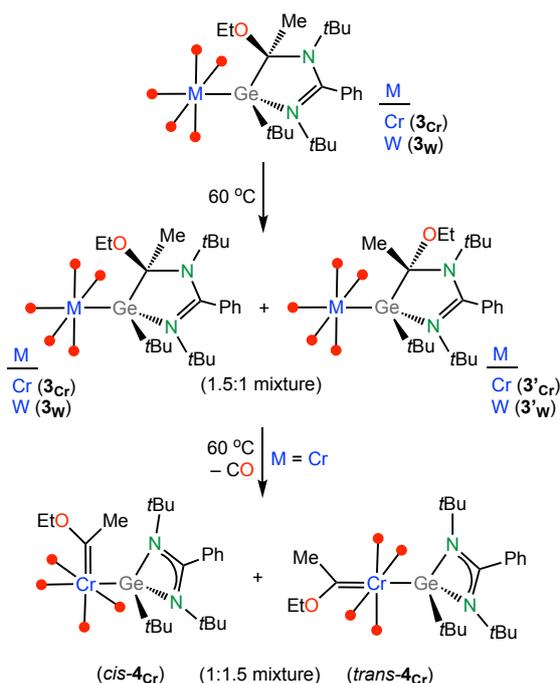
**Scheme 1.** Reactions of germylene **1<sub>tBu</sub>** with the Fischer carbene complexes **2<sub>M</sub>** (M = Cr, W).

We now report a series of experiments that irrefutably prove that the reactions shown in Scheme 1 are equilibria (they can be reversed) and provide new insights into CO- and carbene-

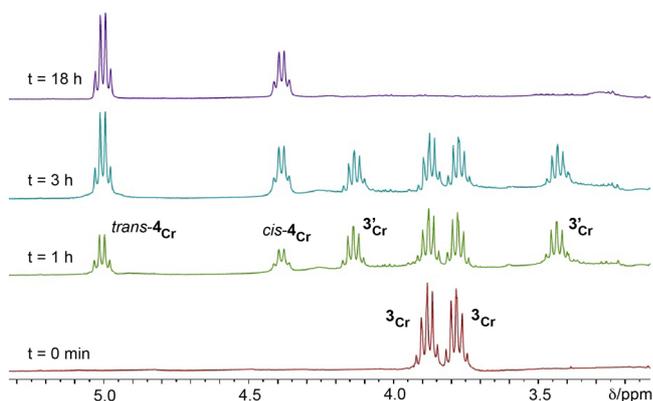
substitutions reactions on Fischer carbene complexes. In these experiments, all of them starting from complexes  $\mathbf{3}_M$ , we have observed epimerization, carbonyl substitution and carbene substitution processes. To our knowledge, this reactivity has no precedent in the chemistry of HTs and Fischer carbenes.

## Results and Discussion

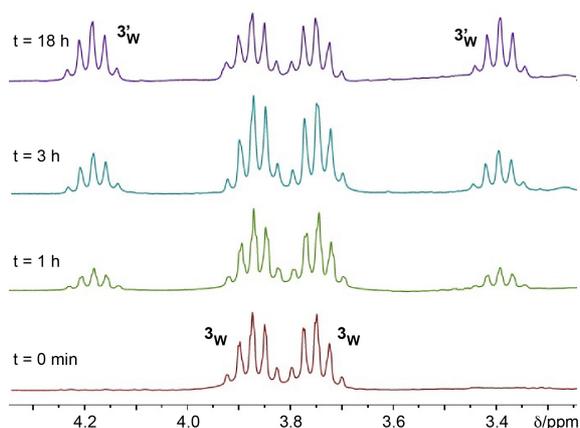
The thermolysis (60 °C, 18 h, argon atmosphere) of a toluene solution of the chromium complex  $\mathbf{3}_{Cr}$  led to a 1:1.5 mixture (mole ratio,  $^1H$  NMR integration) of *cis*- and *trans*-[Cr(CO)<sub>4</sub>C(OEt)Me]{Ge(*t*Bu<sub>2</sub>bzam)*t*Bu}] (*cis*- $\mathbf{4}_{Cr}$  and *trans*- $\mathbf{4}_{Cr}$ ; Scheme 2). Monitoring by  $^1H$  NMR a reaction carried out in C<sub>6</sub>D<sub>6</sub> (Figure 1), we observed the initial formation of an equilibrium mixture of  $\mathbf{3}_{Cr}$  and its epimer  $\mathbf{3}'_{Cr}$  (ca. 1.5:1 mole ratio) and that both diastereoisomers slowly evolved toward the final mixture of *cis*- $\mathbf{4}_{Cr}$  and *trans*- $\mathbf{4}_{Cr}$ . A similar  $^1H$  NMR monitoring of the thermolysis of the tungsten complex  $\mathbf{3}_W$  in C<sub>6</sub>D<sub>6</sub> (Figure 2) also revealed the occurrence of an analogous epimerization process, since an equilibrium mixture of  $\mathbf{3}_W$  and  $\mathbf{3}'_W$  (ca. 1.5:1 mole ratio) was formed, but, in this case, no further evolution of these species was observed.



**Scheme 2.** Thermally-induced transformations of compounds  $\mathbf{3}_M$  (M = Cr, W).



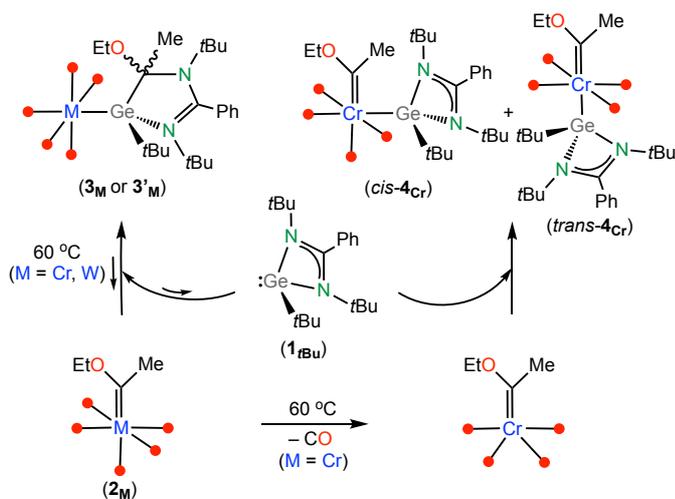
**Figure 1.** Room temperature (20 °C)  $^1\text{H}$  NMR spectra (400.5 MHz; region containing the resonances of the methylene protons of the OEt group) of samples obtained after heating a  $\text{C}_6\text{D}_6$  solution of complex  $\mathbf{3}_{\text{Cr}}$  in a sealed NMR tube at 60 °C for 1 h, 3 h, and 18 h (the spectrum at 0 min was taken prior to start heating), showing the initial epimerization of  $\mathbf{3}_{\text{Cr}}$  into  $\mathbf{3}'_{\text{Cr}}$  and the final transformation of both epimers into *cis*- $\mathbf{4}_{\text{Cr}}$  and *trans*- $\mathbf{4}_{\text{Cr}}$ .



**Figure 2.** Room temperature (20 °C)  $^1\text{H}$  NMR spectra (400.5 MHz; region containing the resonances of the methylene protons of the OEt group) of samples obtained after heating a  $\text{C}_6\text{D}_6$  solution of complex  $\mathbf{3}_{\text{W}}$  in a sealed NMR tube at 60 °C for 1 h, 3 h, and 18 h (the spectrum at 0 min was taken prior to start heating), showing the epimerization of  $\mathbf{3}_{\text{W}}$  into  $\mathbf{3}'_{\text{W}}$ .

The characterization of  $\mathbf{3}'_{\text{Cr}}$  and  $\mathbf{3}'_{\text{W}}$  as the species shown in Scheme 2 is based on the pattern (number and multiplicity) of their  $^1\text{H}$  NMR signals, which is similar to those of their parent compounds of  $\mathbf{3}_{\text{Cr}}$  and  $\mathbf{3}_{\text{W}}$ , as well as in the greater separation of the  $^1\text{H}$  NMR signals of the diastereotopic  $\text{CH}_2$  protons of the ethoxy group (two doublets of quartets) of  $\mathbf{3}'_{\text{M}}$  (in comparison to those of compounds  $\mathbf{3}_{\text{M}}$ ; Figures 1 and 2), which indicates that the ethoxy group of  $\mathbf{3}'_{\text{M}}$  is now placed *anti* to the *GetBu* group.<sup>[11]</sup> Regarding the final products of the thermolysis of the chromium compound  $\mathbf{3}_{\text{Cr}}$  at 60 °C, the  $^{13}\text{C}\{^1\text{H}\}$  resonances of their carbene ( $\delta$  356.7 and 351.5 for *cis*- and *trans*- $\mathbf{4}_{\text{Cr}}$ , respectively) and carbonyl ligands ( $\delta$  233.8, 229.2 and 225.6 for *cis*- $\mathbf{4}_{\text{Cr}}$ ; 227.0 for *trans*- $\mathbf{4}_{\text{Cr}}$ ) and the fact that their ethoxy  $\text{CH}_2$  protons are no longer diastereotopic (they appear as just a quartet in the  $^1\text{H}$  NMR spectra; Figure 1) clearly indicate that they are the tetracarbonyl derivatives *cis*- $\mathbf{4}_{\text{Cr}}$  and *trans*- $\mathbf{4}_{\text{Cr}}$  (Scheme 2).

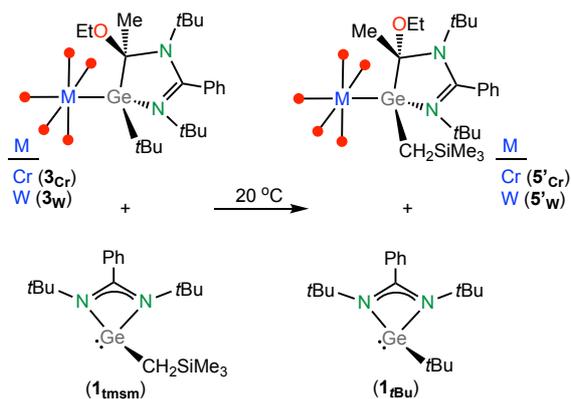
All the above experimental data suggested that, unexpectedly, the formation of  $\mathbf{3}_M$  ( $M = \text{Cr}, \text{W}$ ) from germylene  $\mathbf{1}_{\text{tBu}}$  and the corresponding Fischer carbene complex  $\mathbf{2}_M$  should be reversible, since the formation of *cis*- $\mathbf{4}_{\text{Cr}}$  and *trans*- $\mathbf{4}_{\text{Cr}}$  from the corresponding complex  $\mathbf{3}_M$  requires the presence of free  $\mathbf{1}_{\text{tBu}}$  and  $\mathbf{2}_M$  in the reacting solutions. Scheme 3 displays a simple mechanistic proposal that, in accordance with the previous statement, accounts for (a) the thermally-induced transformation of  $\mathbf{3}_M$  ( $M = \text{Cr}, \text{W}$ ) into an equilibrium mixture of the epimers  $\mathbf{3}_M$  and  $\mathbf{3}'_M$  and (b) the final formation of the tetracarbonyl derivatives *cis*- $\mathbf{4}_{\text{Cr}}$  and *trans*- $\mathbf{4}_{\text{Cr}}$  in the case of the chromium system. If  $\mathbf{1}_{\text{tBu}}$  and  $\mathbf{2}_M$  are present to some extent in solutions of  $\mathbf{3}_M$  (and  $\mathbf{3}'_M$ ), the Fischer carbene complexes  $\mathbf{2}_M$  can react with  $\mathbf{1}_{\text{tBu}}$  to reform  $\mathbf{3}_M$  at room temperature, or give both  $\mathbf{3}_M$  and  $\mathbf{3}'_M$  at higher temperatures (the formation of both epimers is indeed possible at 60 °C<sup>[11]</sup>). In the case of the thermolysis of  $\mathbf{3}_{\text{Cr}}$ , the Fischer carbene complex  $\mathbf{2}_{\text{Cr}}$  can alternatively undergo a thermally-induced decarbonylation to give a transient tetracarbonyl species that rapidly alleviates its unsaturation reacting with  $\mathbf{1}_{\text{tBu}}$  to give the tetracarbonyl derivatives *cis*- $\mathbf{4}_{\text{Cr}}$  and *trans*- $\mathbf{4}_{\text{Cr}}$  as the final products. It is well known that carbonyl substitutions on electrophilic Fischer carbene complexes by phosphanes, arsanes and stibanes can lead to mixtures of *cis*- and *trans*-tetracarbonyl derivatives<sup>[12]</sup> and that carbonyl substitutions are easier for Cr than for W.<sup>[13]</sup>



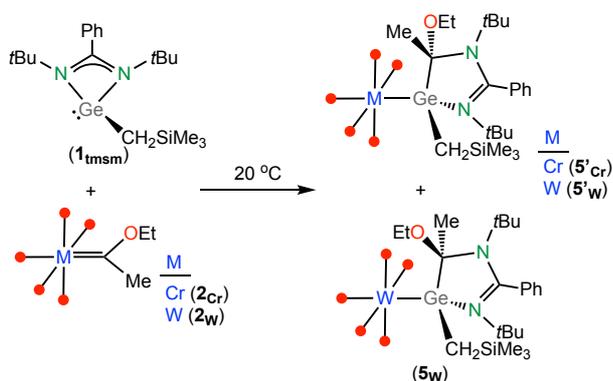
**Scheme 3.** Proposed reaction pathway for the epimerization and carbonyl substitution reactions discussed in this work.

The reversibility of the insertion reactions shown in Scheme 1 was additionally and unambiguously demonstrated by means of crossover experiments in which complexes  $\mathbf{3}_M$  were treated with a germylene other than  $\mathbf{1}_{\text{tBu}}$ , reasoning that  $\mathbf{2}_M$ , if formed, it could react with the new germylene to give a new product. The exchange product  $\mathbf{5}'_{\text{Cr}}$  and free germylene  $\mathbf{1}_{\text{tBu}}$  were formed upon mixing the chromium complex  $\mathbf{3}_{\text{Cr}}$  with the germylene  $\text{Ge}(\text{tBu}_2\text{bzam})\text{CH}_2\text{SiMe}_3$  ( $\mathbf{1}_{\text{tmsm}}$ ) in  $\text{C}_6\text{D}_6$  at room temperature (ca. 100% conversion after 18 h, NMR analysis, Scheme 4). The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $\mathbf{5}'_{\text{Cr}}$  in the reaction mixture were identical to those of an authentic sample prepared by treating  $\mathbf{2}_{\text{Cr}}$  with  $\mathbf{1}_{\text{tmsm}}$  at room temperature (Scheme 5). In a similar manner, the germylene exchange experiment with the tungsten complex  $\mathbf{3}_{\text{W}}$  and  $\mathbf{1}_{\text{tmsm}}$  led to the exchange product  $\mathbf{5}'_{\text{W}}$  and

free  $1_{tBu}$  (ca. 50% conversion after 18 h, NMR analysis, Scheme 4). A small amount (< 5%) of epimer  $5_W$  was also observed in this case in the reaction mixture. In an independent experiment, we confirmed that  $2_W$  reacts with  $1_{tmsm}$  at room temperature to give a mixture of epimers  $5'_W$  and  $5_W$  (Scheme 5) in ca. 10:1 ratio, from which  $5'_W$  was satisfactorily separated and characterized. Germylene  $1_{tmsm}$ , being smaller than  $1_{tBu}$ ,<sup>[6a]</sup> but with a similar basicity, is able to displace the equilibrium towards the formation of the corresponding exchange products. Undoubtedly, these results demonstrate the presence of free Fischer carbene complex  $2_M$  and germylene  $1_{tBu}$  in solutions of  $3_M$ .

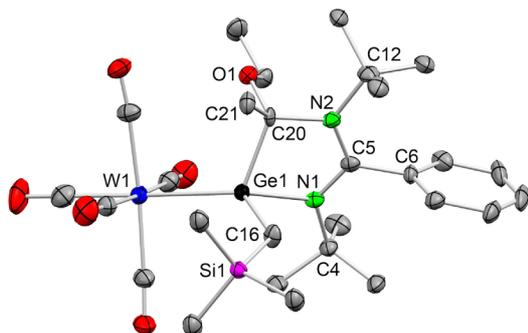


**Scheme 4.** Germylene exchange reactions.



**Scheme 5.** Reactions of  $1_{tmsm}$  with  $2_M$  (M = Cr, W).

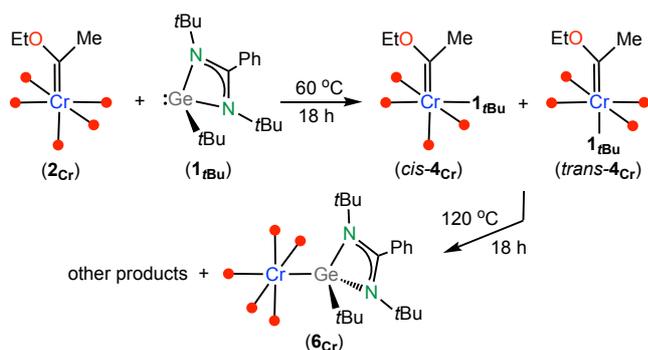
The IR  $\nu_{CO}$  absorptions and the  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra of the new complexes  $5'_{Cr}$  and  $5'_W$  are similar to those of  $3_{Cr}$  and  $3_W$ , respectively, in agreement with their structural similarities (the latter were crystallographically characterized<sup>[11]</sup>). The stereochemistries of  $5'_{Cr}$ ,  $5'_W$  and  $5_W$  (Scheme 5) were established by NOE  $^1H$  NMR measurements, which indicated that the Me and  $CH_2SiMe_3$  groups are close to each other (*syn* arrangement) in  $5'_{Cr}$  and  $5'_W$  but not in  $5_W$ . The molecular structure of  $5'_W$  was also confirmed by X-ray diffraction (XRD; Figure 3). The fact that the stereochemistry of the stereogenic C atom of  $3_{Cr}$  and  $3_W$  (products of the room temperature reactions of  $2_M$  with  $1_{tBu}$ ; Scheme 1) is opposite to that of  $5'_{Cr}$  and  $5'_W$  (major or only products of the room temperature reactions of  $2_M$  with  $1_{tmsm}$ ; Scheme 5) indicates that the volume of the R group of germynes  $1_R$  (R = Mes,  $CH_2SiMe_3$ ) has a decisive influence on the stereoselectivity of their reactions with Fischer carbene complexes  $2_M$ .



**Figure 3.** XRD molecular structure of compound **5'w** (thermal ellipsoids drawn at 30% probability; H atoms omitted for clarity). Only one of the two positions occupied by the disordered  $\text{CH}_2\text{SiMe}_3$  group is shown. Selected bond lengths (Å): W1–Ge1 2.6479(8), Ge1–C16 2.027(9), Ge1–C20 1.993(6), Ge1–N1 2.022(5), C5–N1 1.317(8), C5–N2 1.373(8), C20–N2 1.501(8).

Complexes *cis*-**4<sub>Cr</sub>** and *trans*-**4<sub>Cr</sub>** are mixed germylene-Fischer carbene compounds formed by a CO ligand replacement reaction. Interestingly, structurally related complexes have been rarely observed with N-heterocyclic carbenes (NHCs) in place of germylenes and their syntheses have never been achieved by reacting NHCs with chromium Fischer carbene complexes of the type  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OR})\text{R}'\}]$ .<sup>[14]</sup> Depending on the R' group, the NHC prefers conjugate addition (R' = alkenyl<sup>[14a]</sup> or alkynyl;<sup>[15]</sup> room temperature reactions) or carbene replacement (R' = Me, Bu or Ph; reactions at 70 °C), the latter leading to pentacarbonyls of the type  $[\text{Cr}(\text{CO})_5(\text{NHC})]$  in low to medium yields.<sup>[16]</sup> It is also known that the pentacarbonyl germylene complex  $[\text{Cr}(\text{CO})_5\{\text{Ge}(\text{tBu}_2\text{bzam})\text{tBu}\}]$  (**6<sub>Cr</sub>**) can be prepared in 40% yield by treating the Fischer styrylcarbene complex  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OEt})\text{CHCHPh}\}]$  with germylene **1<sub>tBu</sub>** in toluene at 80 °C,<sup>[11]</sup> but the mechanisms of these reactions have not been investigated.

To check whether complex **6<sub>Cr</sub>** could also be prepared by replacing the carbene ligand of **2<sub>Cr</sub>** by germylene **1<sub>tBu</sub>**, these reagents (1:1 molar ratio) were thermolyzed in  $\text{C}_6\text{D}_6$  in a sealed NMR tube. As described above (Figure 1), a 1:1.5 mixture of *cis*-**4<sub>Cr</sub>** and *trans*-**4<sub>Cr</sub>** was formed after 18 h at 60 °C. The NMR tube was then heated at 120 °C for 36 h. The corresponding <sup>1</sup>H NMR spectrum indicated the presence of complex **6<sub>Cr</sub>** as the major component (ca. 60%) of a mixture of products that did not contain *cis*-**4<sub>Cr</sub>** and *trans*-**4<sub>Cr</sub>** (Scheme 6). This experiment demonstrates that the tetracarbonyl complexes *cis*-**4<sub>Cr</sub>** and *trans*-**4<sub>Cr</sub>** are intermediates in the thermolytic synthesis of complex **6<sub>Cr</sub>** from **2<sub>Cr</sub>** and germylene **1<sub>tBu</sub>**. Therefore, similar tetracarbonyl complexes of the type *cis/trans*- $[\text{Cr}(\text{CO})_4\{\text{C}(\text{OR})\text{R}'\}(\text{L})]$  might be intermediates in the previously-reported preparation of complex **6<sub>Cr</sub>** from  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OEt})\text{CHCHPh}\}]$  and germylene **1<sub>tBu</sub>** at 80 °C<sup>[11]</sup> and of the NHC complexes  $[\text{Cr}(\text{CO})_5(\text{NHC})]$  from  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OMe})\text{R}'\}]$  and free NHCs at 70 °C.<sup>[16]</sup>



**Scheme 6.** Thermal synthesis of **6<sub>Cr</sub>** from **2<sub>Cr</sub>** and **1<sub>tBu</sub>**.

## Conclusions

This work demonstrates that the insertion of a carbene ligand into a Ge–N bond, a process that was observed for the first time studying the room temperature reactions of the amidinatogermylene **1<sub>tBu</sub>** with the electrophilic Fischer carbenes **2<sub>M</sub>** (M = Cr, W),<sup>[11]</sup> can be reversible. The existence of an equilibrium between the inserted germylene complexes [M(CO)<sub>5</sub>{Ge(tBu)<sub>2</sub>bzamC(OEt)Me}tBu] (**3<sub>M</sub>**), germylene **1<sub>tBu</sub>** and the corresponding Fischer carbene **2<sub>M</sub>** explains the epimerization of the former in solution (at 60 °C) and the unexpected thermally-induced transformation of compounds **3<sub>Cr</sub>** and **3'<sub>Cr</sub>** to the mixed germylene-Fischer carbene complexes [Cr(CO)<sub>4</sub>{C(OEt)Me}{Ge(tBu)<sub>2</sub>bzam}tBu] (*cis*-**4<sub>Cr</sub>** and *trans*-**4<sub>Cr</sub>**). In addition, through the isolation of the *cis*-**4<sub>Cr</sub>** + *trans*-**4<sub>Cr</sub>** mixture and its subsequent transformation into complex **6<sub>Cr</sub>** by thermolysis, this work has also shown that tetracarbonylchromium species of the type [Cr(CO)<sub>4</sub>{C(OR)R'}(L)] are intermediates in the synthesis of [Cr(CO)<sub>5</sub>(L)] complexes from [Cr(CO)<sub>5</sub>{C(OR)R'}] and 2-electron donors L.

It should also be noted that the behavior of germylenes **1<sub>tBu</sub>** and **1<sub>tmsm</sub>** in their reactions with group 6 metal Fischer carbene complexes (Schemes 1 and 5) was quite unexpected because other nucleophiles of high basicity, such as N-heterocyclic carbenes, do not attack the C<sub>carbene</sub> atom of group 6 metal Fischer carbene complexes.<sup>[14a,15,16]</sup> The extraordinarily high electron-donor capacity of the amidinatogermylenes **1<sub>tBu</sub>**<sup>[7c]</sup> and **1<sub>tmsm</sub>**,<sup>[6a]</sup> which makes them behave as very strong nucleophiles, and the tendency of amidinatotetraylenes to get involved in ring expansion processes,<sup>[1a,2a,7e,17]</sup> should be responsible for their remarkable reactivity with Fischer carbene complexes.

## Experimental Section

**General Experimental Data:** Solvents were dried over appropriate desiccating reagents and were distilled under argon immediately before use. All reactions were carried out under argon in a drybox. The germylenes  $\mathbf{1}_{tBu}^{[7c]}$  and  $\mathbf{1}_{tmsm}^{[6a]}$ , the Fischer carbene complexes  $\mathbf{2}_M$  ( $M = Cr, W$ ),<sup>[18]</sup> the ring-expanded products  $\mathbf{3}_M^{[11]}$  and the germylene complex  $\mathbf{6}_{Cr}^{[11]}$  were prepared following reported procedures. All these reagents and all reaction products were stored at  $-20\text{ }^\circ\text{C}$  under argon in a dry box. All remaining reagents were purchased from commercial sources. The reaction products were vacuum-dried for several hours prior to being weighted and analyzed. Elemental analyses were obtained with an Elementar Vario EL microanalyzer. IR spectra were recorded in solution using a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run in  $C_6D_6$  on a Bruker AV-300 and AV-400 instruments, using as standards the solvent residual protic resonance for  $^1H$  [ $\delta(C_6HD_5) = 7.16\text{ ppm}$ ] and the solvent resonance for  $^{13}C$  [ $\delta(C_6D_6) = 128.10\text{ ppm}$ ]. HRMS were obtained with a Bruker Impact II mass spectrometer operating in the ESI-Q-ToF positive mode; data given refer to the most abundant isotopomer of the molecule or the fragment with the greatest mass.

**Thermolysis of  $[Cr(CO)_5\{Ge(tBu_2bzamC(OEt)Me)tBu\}]$  ( $\mathbf{3}_{Cr}$ ):** In a drybox, a J. Young NMR tube was loaded with  $\mathbf{3}_{Cr}$  (94 mg, 0.151 mmol) and  $C_6D_6$  (0.3 mL). The resulting yellow solution was heated at  $60\text{ }^\circ\text{C}$  for 18 h outside the drybox to give a ca. 1:1.5 mixture of *cis*- and *trans*- $[Cr(CO)_4\{C(OEt)Me\}\{Ge(tBu_2bzam)tBu\}]$  (*cis*- $\mathbf{4}_{Cr}$  and *trans*- $\mathbf{4}_{Cr}$ ). The reaction progress was monitored by  $^1H$  NMR (Figure 1).

**Thermolysis of *cis*- $\mathbf{4}_{Cr}$  and *trans*- $\mathbf{4}_{Cr}$ :** The NMR tube of the above reaction was heated at  $120\text{ }^\circ\text{C}$  for 36 h to give complex  $\mathbf{6}_{Cr}$  as the major component (ca. 60%) of the reaction mixture. The reaction progress was monitored by  $^1H$  NMR (Figure S3 of the Supporting Information).

**Thermolysis of  $[W(CO)_5\{Ge(tBu_2bzamC(OEt)Me)tBu\}]$  ( $\mathbf{3}_W$ ):** In a drybox, a J. Young NMR tube was loaded with  $\mathbf{3}_W$  (114 mg, 0.151 mmol) and  $C_6D_6$  (0.3 mL). The resulting yellow solution was heated at  $60\text{ }^\circ\text{C}$  for 18 h to give a ca. 1.5:1 mixture of  $\mathbf{3}_W$  and  $\mathbf{3}'_W$ . The reaction progress was monitored by  $^1H$  NMR (Figure 2).

**Synthesis of  $[Cr(CO)_5\{Ge(tBu_2bzamC(OEt)Me)CH_2SiMe_3\}]$  ( $\mathbf{5}'_{Cr}$ ):** In a drybox, toluene (1 mL) was added to a mixture of germylene  $\mathbf{1}_{tmsm}$  (71 mg, 0.18 mmol) and Fischer carbene complex  $\mathbf{2}_{Cr}$  (48 mg, 0.18 mmol). The resulting orange solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was washed with hexane (0.5 mL) to give  $\mathbf{5}'_{Cr}$  as a yellow solid (87 mg, 74 %). Anal. (%): Calcd for  $C_{28}H_{42}CrGeN_2O_6Si$  (655.35 amu) C, 51.32; H, 6.46; N, 4.27; found C, 51.36; H, 6.53; N, 4.22. (+)-ESI HRMS:  $m/z$  657.1131 [ $M + H$ ]<sup>+</sup>. IR (toluene):  $\nu_{CO}$  2036 (m), 1949 (w, sh), 1909 (vs, br)  $cm^{-1}$ .  $^1H$  NMR ( $C_6D_6$ , 400.1 MHz, 298 K):  $\delta$  7.18 (m, 1 H, CH of Ph), 7.05–6.92 (m, 2 H, 2 CH of Ph), 6.85–6.82 (m, 2 H, 2 CH of Ph), 3.82 (m, 1 H, CH of  $OCH_2CH_3$ ),

3.45 (m, 1 H, *CH* of  $\text{OCH}_2\text{CH}_3$ ), 2.22 (s, 3 H,  $\text{CCH}_3$ ), 1.25–1.12 (m, 5 H,  $\text{CH}_3$  of  $\text{OEt}$  +  $\text{CH}_2$  of  $\text{CH}_2\text{SiMe}_3$ ), 1.04 (s, 18 H, 6  $\text{CH}_3$  of 2 *t*Bu), 0.42 (s, 9 H, 3  $\text{CH}_3$  of  $\text{CH}_2\text{SiMe}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.6 MHz, 298 K):  $\delta$  226.5 (CO), 223.4 (COs), 161.2 (NCN), 134.1 ( $\text{C}_{\text{ipso}}$ ), 131.8–126.7 (CHs of Ph), 96.7 (CGe), 65.6 ( $\text{CH}_2$  of  $\text{OEt}$ ), 60.7 (C of *t*Bu), 51.4 (C of *t*Bu), 34.2 (3  $\text{CH}_3$  of *t*Bu), 34.0 (3  $\text{CH}_3$  of *t*Bu), 28.9 ( $\text{CCH}_3$ ), 17.6 ( $\text{CH}_2$  of  $\text{CH}_2\text{SiMe}_3$ ), 15.4 ( $\text{CH}_3$  of  $\text{OEt}$ ), 2.7 (3  $\text{CH}_3$  of  $\text{CH}_2\text{SiMe}_3$ ) ppm.

**Synthesis of  $[\text{W}(\text{CO})_5\{\text{Ge}(\text{tBu}_2\text{bzamC}(\text{OEt})\text{Me})\text{CH}_2\text{SiMe}_3\}]$  ( $\mathbf{5}'_w$ ):** In a drybox, toluene (1 mL) was added to a mixture of germylene  $\mathbf{1}_{\text{tmsm}}$  (32 mg, 0.081 mmol) and Fischer carbene complex  $\mathbf{2}_w$  (32 mg, 0.081 mmol). The resulting yellow solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. A  $^1\text{H}$  NMR spectrum of the solid residue indicated the presence of  $\mathbf{5}'_w$  and  $\mathbf{5}_w$  in a *ca.* 10:1 mole ratio. The dry solid was washed with hexane (0.5 mL) to give pure  $\mathbf{5}'_w$  as a yellow solid (46 mg, 72 %). Anal. (%): Calcd for  $\text{C}_{28}\text{H}_{42}\text{GeN}_2\text{O}_6\text{SiW}$  (787.20 amu) C, 42.72; H, 5.38; N, 3.56; found C, 42.76; H, 5.41; N, 3.51. (+)-ESI HRMS:  $m/z$  809.1625 [ $M + \text{Na}$ ] $^+$ . IR (toluene):  $\nu_{\text{CO}}$  2050 (m), 1954 (w, sh), 1914 (vs, br)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400.1 MHz, 298 K):  $\delta$  7.01 (m, 1 H, *CH* of Ph), 6.94–6.88 (m, 2 H, 2 *CH* of Ph), 6.80–6.74 (m, 2 H, 2 *CH* of Ph), 3.77 (m, 1 H, *CH* of  $\text{OCH}_2\text{CH}_3$ ), 3.48 (m, 1 H, *CH* of  $\text{OCH}_2\text{CH}_3$ ), 2.13 (s, 3 H,  $\text{CCH}_3$ ), 1.21–1.16 (m, 5 H,  $\text{CH}_3$  of  $\text{OEt}$  +  $\text{CH}_2$  of  $\text{CH}_2\text{SiMe}_3$ ), 1.04 (s, 9 H, 3  $\text{CH}_3$  of *t*Bu), 1.02 (s, 9 H, 3  $\text{CH}_3$  of *t*Bu), 0.42 (s, 9 H, 3  $\text{CH}_3$  of  $\text{CH}_2\text{SiMe}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.6 MHz, 298 K):  $\delta$  202.7 (COs), 201.7 (CO), 168.2 (NCN), 134.1 ( $\text{C}_{\text{ipso}}$ ), 131.4–126.3 (CHs of Ph), 96.5 (CGe), 65.1 ( $\text{CH}_2$  of  $\text{OEt}$ ), 60.4 (C of *t*Bu), 60.1 (C of *t*Bu), 34.1 (3  $\text{CH}_3$  of *t*Bu), 33.5 (3  $\text{CH}_3$  of *t*Bu), 29.4 ( $\text{CCH}_3$ ), 17.3 ( $\text{CH}_2$  of  $\text{CH}_2\text{SiMe}_3$ ), 15.5 ( $\text{CH}_3$  of  $\text{OEt}$ ), 2.6 (3  $\text{CH}_3$  of  $\text{CH}_2\text{SiMe}_3$ ) ppm.

**Reaction of  $\mathbf{3}_{\text{Cr}}$  with  $\mathbf{1}_{\text{tmsm}}$ :** In a drybox, a J. Young NMR tube was loaded with complex  $\mathbf{3}_{\text{Cr}}$  (30 mg, 0.048 mmol), germylene  $\mathbf{1}_{\text{tmsm}}$  (19 mg, 0.048 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). The resulting yellow solution was stirred at room temperature for 18 h. A  $^1\text{H}$  NMR spectrum of the resulting solution showed the complete conversion of the starting reagents into a mixture of  $\mathbf{5}'_{\text{Cr}}$  and  $\mathbf{1}_{\text{tBu}}$ .

**Reaction of  $\mathbf{3}_w$  with  $\mathbf{1}_{\text{tmsm}}$ :** In a drybox, a J. Young NMR tube was loaded with complex  $\mathbf{3}_w$  (50 mg, 0.066 mmol), germylene  $\mathbf{1}_{\text{tmsm}}$  (26 mg, 0.066 mmol) and  $\text{C}_6\text{D}_6$  (0.3 mL). The resulting yellow solution was stirred at room temperature for 18 h. A  $^1\text{H}$  NMR spectrum of the resulting solution showed a *ca.* 50 % conversion of the starting reagents into a mixture that, in addition to the major products  $\mathbf{5}'_w$  and  $\mathbf{1}_{\text{tBu}}$ , also contained a very small amount (< 5%) of  $\mathbf{5}_w$ .

**X-Ray Diffraction Analysis:** A crystal of  $\mathbf{5}'_w$  was analyzed by X-ray diffraction. A selection of crystal measurement and refinement data is given in Table S1. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.<sup>[19]</sup> The structure was solved using SIR-97.<sup>[20]</sup> Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.<sup>[21]</sup> All non-H atoms were refined anisotropically. H atoms set in calculated positions

and were refined riding on their parent atoms. The CH<sub>2</sub>SiMe<sub>3</sub> moiety was found disordered over two positions with a 80:20 occupancy ratio, requiring restraints on its geometrical and thermal parameters. The WINGX program system<sup>[22]</sup> was used throughout the structure determinations. The molecular plot was made with MERCURY.<sup>[23]</sup> CCDC deposition number 1870987.

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## Conflict of interest

The authors declare no conflict of interest.

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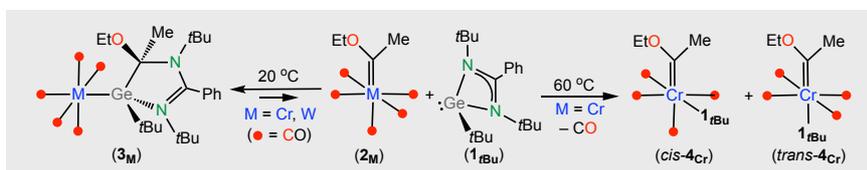
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FULL PAPER



**A reversible ring expansion:** The formation of the 5-membered-ring germylene complexes 3<sub>M</sub> (M = Cr, W) from germylene 1<sub>tBu</sub> and electrophilic Fischer carbenes (2<sub>M</sub>) is reversible. In fact, complex 3<sub>Cr</sub> leads to the CO-substitution products *cis*-4<sub>Cr</sub> and *trans*-4<sub>Cr</sub> when it is heated at 60 °C.

L. Álvarez-Rodríguez, J. A. Cabeza,\*  
P. García-Álvarez, M. Gómez-Gallego,  
L. González-Álvarez, A. D. Merinero,  
and M. A. Sierra\*

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**Reversible Carbene Insertion into a Ge–N Bond and New Insights into CO- and Carbene-Substitution Reactions Involving Amidinatogermylenes and Fischer Carbene Complexes**

ORCID Identifiers

L. Álvarez-Rodríguez:	<a href="http://orcid.org/0000-0003-3176-3855">http://orcid.org/0000-0003-3176-3855</a>
J. A. Cabeza:	<a href="http://orcid.org/0000-0001-8563-9193">http://orcid.org/0000-0001-8563-9193</a>
P. García-Álvarez:	<a href="http://orcid.org/0000-0002-5024-3874">http://orcid.org/0000-0002-5024-3874</a>
M. Gómez-Gallego	<a href="http://orcid.org/0000-0002-8961-7685">http://orcid.org/0000-0002-8961-7685</a>
L. González-Álvarez	<a href="http://orcid.org/0000-0002-1354-8396">http://orcid.org/0000-0002-1354-8396</a>
A. D. Merinero	<a href="http://orcid.org/0000-0003-1088-413X">http://orcid.org/0000-0003-1088-413X</a>
M. A. Sierra	<a href="http://orcid.org/0000-0002-3360-7795">http://orcid.org/0000-0002-3360-7795</a>