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# Stereoselective insertion of $GeCl_2$ into tungsten–chlorine bonds of aminomethylene and aminocarbyne complexes

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Dedicated to Professor Dr H. Brunner on the occasion of his 65th birthday on 4.10.2000

## Abstract

Treatment of $Cp^*(CO)_2W{\equiv}CNEt_2$ (**1**) ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) with HCl affords the aminomethylene complex *cis*-$Cp^*(Cl)(CO)_2W{=}C(H)NEt_2$ (**2**). Complex **2** inserts stereoselectively $GeCl_2$ into the tungsten–chlorine bond to afford *cis*-$Cp^*(GeCl_3)(CO)_2W{=}C(H)NEt_2$ (**3**). Complex **3** can also be obtained directly from **1** and $GeCl_2$(diox) (diox = 1,4-dioxane) in $CH_2Cl_2$. Similarly, treatment of $Cp^{**}(CO)_2W{\equiv}CNEt_2$ (**1a**) ($Cp^{**} = \eta^5$-ethyltetramethylcyclopentadienyl) with $GeCl_2$(diox) in toluene affords *cis*-$Cp^{**}(GeCl_3)(CO)_2W{=}C(H)NEt_2$ (**3a**). An isomerization equilibrium is established between **3** and *trans*-$Cp^*(GeCl_3)(CO)_2W{=}C(H)NEt_2$ (**4**) in the melt (208°C), which favors the *trans* isomer (**3**:**4** ratio = 1:6). The aminocarbyne complex *cis*-$Cp^*(Cl)_2(CO)W{\equiv}CNEt_2$ (**5**) reacts with $GeCl_2$(diox) to yield stereoselectively *spy*-5-14-$Cp^*(Cl)(GeCl_3)(CO)W{\equiv}CNEt_2$ (**6**). Complexes **2**–**6** were fully characterized and the crystal structures of the complexes **2**, **3**, **4** and **6** are presented. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Germylenes; Insertion; Carbene complexes; Carbyne complexes; Tungsten

## 1. Introduction

Germylenes, the heavier Group 14 homologues of carbenes, have been shown to insert into σ-bonds providing an easy access to tetravalent germanium compounds [1]. We have shown previously, that $GeCl_2$(diox) is a useful source of $GeCl_2$ reacting fast and selectively with various chloro and hydrido complexes of molybdenum and tungsten to afford respectively trichlorogermyl and dichlorogermyl complexes of the general formula $(\eta^5\text{-}C_5R_5)M(CO)_{3-n}L_n(GeCl_{3-m}H_m)$ (R = H, Me; M = Mo, W; $n = 0$–2; L = EtNC, $PMe_3$; $m = 0$, 1) [1,2]. These complexes contain two reactive sites for further functionalization, that are the transition metal and the germanium center. This has been demonstrated recently by the high-yield syntheses of the dimetallagermanes $[(\eta^5\text{-}C_5R_5)M(CO)_3]_2GeX_2$ (R = H, Me; M = Mo, W; X = H, Cl) [3] and the triazidogermyl complexes *trans*-$(\eta^5\text{-}C_5R_5)W(CO)(PMe_3)_2Ge(N_3)_3$ (R = H, Me) [4].

Several features of the above mentioned $GeCl_2$ insertion reactions are not consistent with pathways involving radicals or ionic intermediates. These are the lack of evidence for the formation of escape products and the increase in rate observed, when the reaction is carried out in poorly coordinating solvents, when the metal complex becomes more electron-rich, or when the ligand sphere becomes less crowded. These features suggest instead the intermediate formation of an adduct, in which the metal complex acts as a Lewis base and $GeCl_2$ as a Lewis acid [5]. Additional support for the latter pathway is given by the stereoselectivity of these reactions. For example the chloro complexes $(\eta^5\text{-}C_5R_5)M(CO)_2(PMe_3)Cl$ (R = H, Me; M = Mo, W), which exist exclusively as *cis* isomers in solution at room temperature, afford with $GeCl_2$(diox) stereoselectively the *cis* trichlorogermyl complexes $(\eta^5\text{-}C_5R_5)M(CO)_2(PMe_3)GeCl_3$. These isomerize either in solution or in the solid-state to the thermodynamically more stable *trans* isomers [1,6]. In continuation of this work, we report here on stereoselective insertions of $GeCl_2$ into tungsten-chlorine bonds of aminomethylene and aminocarbyne complexes.

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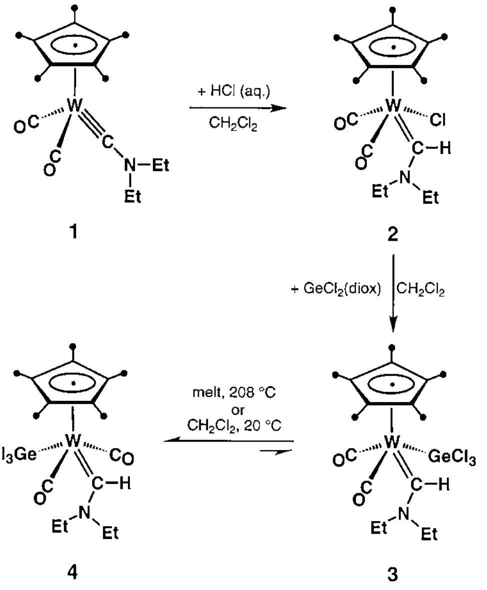

Scheme 1. Synthesis of the tungsten aminomethylene complexes **2**–**4** starting from the aminocarbyne complex **1** (the dots at the five-membered rings denote methyl groups).

## 2. Results and discussion

Starting material for the reactions described below was the aminocarbyne complex $Cp^*(CO)_2W{\equiv}CNEt_2$ (**1**) [7]. Addition of HCl to the metal–carbon triple bond of **1** affords selectively the aminomethylene complex *cis*-$Cp^*(Cl)(CO)_2W{=}C(H)NEt_2$ (**2**), which was isolated as a carmine-red, slightly air-sensitive solid in 87% yield (Scheme 1) [8][1]. Complex **2** is readily soluble in $CH_2Cl_2$, insoluble in pentane and melts at 137°C.

The IR spectrum of **2** in $CH_2Cl_2$ displays two $\nu(CO)$ absorptions at 1929 and 1830 $cm^{-1}$ (Table 1). The higher energy absorption of the symmetric CO stretching vibration is more intense than the lower energy absorption of the antisymmetric CO stretching vibration, which indicates the presence of the *cis* isomer in agreement with the NMR data of this compound. Both absorptions appear at lower wavenumbers than those of *cis*-$Cp^*W(CO)_2(PMe_3)Cl$ ($\nu(CO)$ in $CH_2Cl_2$: 1931 and 1837 $cm^{-1}$) [6] or *cis*-$Cp^*W(CO)_2(CNEt)Cl$ ($\nu(CO)$ in $CH_2Cl_2$: 1947 and 1868 $cm^{-1}$) [1], which suggests that the σ-donor/π-acceptor ratio of the aminomethylene ligand is higher than that of $PMe_3$ and EtNC in these complexes. In addition, the IR spectrum of **2** in $CH_2Cl_2$ shows one weak absorption band at 1536 $cm^{-1}$, which can be assigned to the $\nu$ ($C_{carbene}\overset{\cdots}{=}N$) stretching vibration. This band suggests in valence bond terms a strong contribution of the resonance formula **B** to the metal–carbene bond (Fig. 1) [9] and is characteristic of tungsten(II) aminomethylene complexes (Table 1)[2] [10].

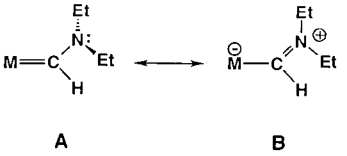

Fig. 1. Resonance formulas for the tungsten–aminomethylene bond of complexes **2**–**4**.

Table 1
Selected IR absorptions and NMR resonances of tungsten(II) aminomethylene complexes bearing a Cp* ligand [a]

| Complex | $\nu(CO)$ | $\nu(C_{carbene}\overset{\cdots}{=}N)$ | $\delta(W{=}CH)$ | $\delta(W{=}C)$ |
|---|---|---|---|---|
| *cis*-$Cp^*(Cl)(CO)_2W{=}C(H)NEt_2$ (**2**) | 1929 (vs), 1830 (s) | 1536 (w) | 10.60 | 243.8; $^1J(W,C) = 104$ Hz |
| *cis*-$Cp^*(Br)(CO)_2W{=}C(H)NEt_2$ | 1929 (vs), 1831 (s) | 1534 (w) | 10.63 | 242.7; $^1J(C,H) = 130$ Hz |
| *cis*-$Cp^*(I)(CO)_2W{=}C(H)NEt_2$ | 1927 (vs), 1833 (s) | 1527 (w) | 10.71 | 240.6; $^1J(W,C) = 101$ Hz |
| *cis*-$Cp^*(GeCl_3)(CO)_2W{=}C(H)NEt_2$ (**3**) | 1950 (vs), 1874 (s) | 1528 (w) | 10.45 | 237.7; $^1J(W,C) = 92$ Hz, $^1J(C,H) = 139$ Hz |
| *cis*-$Cp^{**}(GeCl_3)(CO)_2W{=}C(H)NEt_2$ (**3a**) | 1950 (vs), 1874 (s) | 1529 (w) | 10.45 | 237.5; $^1J(W,C) = 92$ Hz |
| *trans*-$Cp^*(GeCl_3)(CO)_2W{=}C(H)NEt_2$ (**4**) | 1955 (m), 1878 (vs) | 1518 (w) | 10.56 | 234.3; $^1J(W,C) = 95$ Hz |
| *cis*-$[Cp^*(CO)_2(EtNC)W{=}C(H)NEt_2](PF_6)$ | 1969 (vs), 1905 (vs) | 1543 (w) | 10.49 | 232.6; $^1J(W,C) = 85$ Hz |
| *cis*-$[Cp^*(CO)_2({}^tBuNC)W{=}C(H)NEt_2](PF_6)$ | 1969 (vs), 1905 (vs) | 1542 (w) | 10.50 | 233.5; $^1J(W,C) = 87$ Hz, $^1J(C,H) = 137$ Hz |
| $Cp^*(Br)(CO)(EtNC)W{=}C(H)NEt_2$ | 1801 (vs) | 1508 (w) | 10.54 | 248.7 |
| $Cp^*(I)(CO)(EtNC)W{=}C(H)NEt_2$ | 1805 (vs) | 1506 (w) | 10.58 | 246.8; $^1J(C,H) = 128$ Hz |
| $Cp^*(Br)(CO)({}^tBuNC)W{=}C(H)NEt_2$ | 1801 (vs) | 1508 (w) | 10.56 | 249.5; $^1J(W,C) = 104$ Hz |
| $Cp^*(I)(CO)({}^tBuNC)W{=}C(H)NEt_2$ | 1805 (vs) | 1507 (w) | 10.62 | 247.3 |
| *cis*-$[Cp^*(CO)(EtNC)_2W{=}C(H)NEt_2]I$ | 1881 (vs) | 1518 (w) | 10.30 | 238.7; $^1J(W,C) = 88$ Hz |

[a] IR absorptions in $cm^{-1}$ in $CH_2Cl_2$, relative intensities in parentheses. $^1H$- and $^{13}C$-NMR chemical shifts in ppm in $CD_2Cl_2$ at 25°C.

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[1] A similar reaction has been reported for $Cp(CO)_2W{\equiv}CNEt_2$.

[2] The oxidation state of tungsten is formally +II in the aminomethylene complexes listed in Table 1, if the aminomethylene group is considered as a neutral two-electron donor ligand, the Cp* group as an anionic six-electron donor ligand and the halo and $GeCl_3$ group as an anionic two-electron donor ligand. The oxidation state of tungsten in the aminocarbyne complexes **5** and **6** is formally +II, if the aminocarbyne ligand is considered as a cationic two-electron donor ligand bearing a pair of orthogonal empty molecular orbitals of π-symmetry.

Further evidence for this is given by the $^{1}$H-NMR spectrum (300 MHz) of **2** in $CD_2Cl_2$ at 298 K, which displays a double set of resonances for the inequivalent ethyl groups indicating that rotation of the diethylamino group about the $C_{carbene}$–N bond is slow on the NMR time scale (Section 4.2). Furthermore, the $^{1}$H-NMR spectrum shows one singlet for the proton attached to the carbene–carbon atom at a position ($\delta$ 10.60) typical of tungsten(II) aminomethylene complexes (Table 1). The $^{13}C\{^{1}H\}$-NMR spectrum displays at 298 K a carbene-carbon resonance at $\delta$ 243.8 and two carbonyl-carbon resonances at $\delta$ 249.4 and 254.4 indicating unambigously the *cis* configuration of **2**.

This is also confirmed by the solid-state structure of **2**, which was determined by a single-crystal X-ray diffraction study. Suitable red single crystals of **2** were obtained upon slow evaporation of a $CH_2Cl_2$ solution at ambient temperature. The molecular structure of complex **2** with the atom-labeling scheme adopted is depicted in Fig. 2, and selected bond lengths and angles are listed in Table 2.

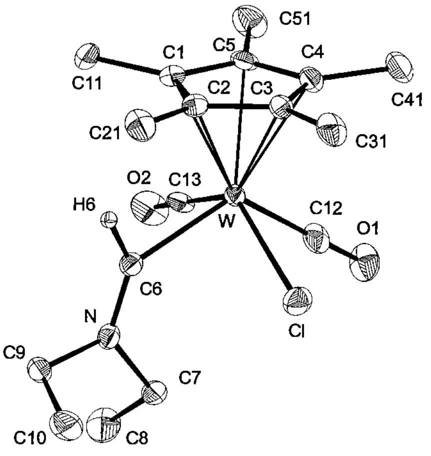


Fig. 2. DIAMOND plot of the molecular structure of **2** with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity reasons except that bonded to the carbene carbon atom C6.

Table 2
Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **2**[a]

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| W–C(1) | 229.7(6) | W–$C_f$ [a] | 201.1 |
| W–C(2) | 238.3(6) | W–C(12) | 196.5(7) |
| W–C(3) | 242.6(6) | W–C(13) | 196.2(9) |
| W–C(4) | 236.9(7) | W–Cl | 250.8(2) |
| W–C(5) | 228.9(6) | C(6)–N | 128.9(5) |
| W–C(6) | 214.1(3) | C(7)–N | 147.9(4) |
| W–$C_g$ [a] | 201.7 | C(9)–N | 146.5(7) |
| *Bond angles* | | | |
| Cl–W–C(6) | 78.73(9) | C(12)–W–C(13) | 74.7(3) |
| Cl–W–C(12) | 79.6(2) | W–C(6)–N | 134.32(8) |
| Cl–W–C(13) | 131.0(2) | C(6)–N–C(7) | 123.2(3) |
| C(6)–W–C(12) | 120.9(2) | C(6)–N–C(9) | 120.6(3) |
| C(6)–W–C(13) | 79.8(2) | C(7)–N–C(9) | 115.8(3) |

[a] $C_g$ denotes the center of the Cp* ring and $C_f$ the foot of the normal from tungsten to the Cp* ring plane.

Complex **2** shows 'four-legged piano-stool' coordination geometry [1,11], which can conveniently be described as tetragonal pyramidal with the Cp* ligand occupying one coordination site at the apex of the pyramid. The tungsten atom is located at a distance of 201.1 pm from the Cp* ring plane and a distance of 96.1 pm from the basal plane of the pyramid defined by the ligating atoms Cl, C(6), C(12) and C(13). The dihedral angle between these planes is 6.3°. The carbonyl ligands are *cis* positioned in agreement with the IR and NMR spectra in solution, and have a mean W–CO bond length of 196.4(8) pm, which is similar to that of other 'four-legged piano-stool' tungsten(II) dicarbonyl complexes bearing a Cp* ligand, e.g. **3** (average W–CO = 196.8(8) pm), **4** (197.3(6) pm), *cis*-$Cp^*W(CO)_2(PMe_3)GeCl_3$ (195.5(6) pm) [6] and *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$ (197.4(10) pm) [6]. The W–Cl bond length of 250.8(2) pm is similar to that of other half-sandwich tungsten(II) chloro complexes, such as $CpW(CO)_3Cl$ (Cp = $\eta^5$-cyclopentadienyl) (249.0(2) pm) [12], ($\eta^5$-$C_5H_4CH_2OAc$)$W(CO)_3Cl$ (251.0(4) pm) [13], *cis*-($\eta^5$-$C_9H_7$)$W(CO)_2(PPh_3)Cl$ (249.2(2) pm) [14], *cis*-$CpW(CO)_2\{P(H)(Ph)[N(SiMe_3)_2]\}Cl$ (250.1(1) pm) [15] and $CpW[PPh_2C(O)N(Et)PPh_2](CO)Cl$ (250.6(3) pm) [16]. The aminomethylene ligand is arranged almost perpendicular to the Cp* ligand as evidenced by the dihedral angle of 88.9° between the least-squares plane passing through the atoms N, C(6), (C7) and C(9) and the Cp* ring plane. Only one conformer is found in the solid state, in which the diethylamino group points away from the Cp* ligand avoiding the steric repulsion between these groups. The W–$C_{carbene}$ bond of 214.1(3) pm compares favorably with that of the tungsten(II) complexes **3** (213.8(8) pm) and **4** (211.5(6) pm) (Table 3). It is, however, longer than that of the W(IV) aminomethylene complexes $Cp^*(Cl)_3W{=}C(H)NEt_2$ (206.5(7) pm) [17] and $Cp^*(Cl)(bdt)W{=}C(H)NEt_2$ (207.9(7) pm) ($bdt^{2-}$ = 1,2-benzenedithiolato) [18], which is probably due to the larger $W^{II}$ covalent radius. The W–$C_{carbene}$ bond of **2** is also longer than that of related tungsten(II) carbene complexes, in which the carbene-carbon atom does not bear any π-donor substituents, e.g. *trans*-$Cp(SnPh_3)(CO)_2W{=}C(H)(C_6H_4\text{-}4\text{-}Me)$ (203.2(7) pm) [19], *trans*-$Cp(I)(CO)_2W{=}C(H)(C_6H_4\text{-}4\text{-}Me)$ (205.5(17) pm) [20] and $Cp_2W{=}C(H)Ph$ (205(2) pm) [21]. This indicates the strong π-interaction between the amino group and the carbene–carbon atom in **2,** which is also shown by the IR and NMR spectra of this compound (vide supra). Additional evidence for this is

Table 3
Selected structural data of tungsten(II) aminomethylene and trichlorogermyl complexes bearing a Cp* or a Cp ligand [a]

| Complex | W–$C_{carbene}$ | $C_{carbene}$–N | W–Ge | Ge–Cl [b] | Cp*/carbene [c] | Cl–Ge–Cl [b] | W–Ge–Cl [b] | Ref. |
|---|---|---|---|---|---|---|---|---|
| *cis*-Cp*(Cl)$(CO)_2$W=C(H)$NEt_2$ (**2**) | 214.1(3) | 128.9(5) | | | 88.9 | | | This work |
| *trans*-CpW(CO)$(PMe_3)_2GeCl_3$ [d] | | | 253.2(1) | 223.3(2) | | 95.1(1) | 121.66(7) | [2b] |
| *spy*-5-14-Cp*W(CO)(CNEt)-$(PMe_3)GeCl_3$ [e] | | | 254.68(9) | 222.5(2) | | 96.72(8) | 120.18(6) | [31] |
| *spy*-5-13-Cp*W(CO)(CNEt)-$(PMe_3)GeCl_3$ | | | 249.3(2) | 222.1(4) | | 97.6(2) | 119.6(1) | [31] |
| *cis*-Cp*W$(CO)_2(PMe_3)GeCl_3$ | | | 255.90(5) | 220.6(2) | | 98.01(6) | 119.27(4) | [6] |
| *cis*-Cp*$(GeCl_3)(CO)_2$W=C(H)-$NEt_2$ (**3**) | 213.8(8) | 129.0(10) | 252.69(9) | 220.4(2) | 73.6 | 98.53(9) | 118.95(7) | This work |
| *trans*-Cp*$(GeCl_3)(CO)_2$-W=C(H)$NEt_2$ (**4**) | 211.5(6) | 131.2(7) | 251.96(8) | 220.2(2) | 87.9 | 98.65(7) | 118.84(5) | This work |
| *cis*-Cp*W$(CO)_2$(CNEt)$GeCl_3$ | | | 254.4(2) | 219.6(6) | | 99.1(3) | 118.5(2) | [1] |
| Cp*W$(CO)_3GeCl_3$ [e] | | | 256.2(2) | 217.9(5) | | 100.2(2) | 117.6(2) | [1] |
| CpW$(CO)_3GeCl_3$ | | | 254.37(9) | 217.8(3) | | 101.3(1) | 116.80(8) | [31] |

[a] Bond lengths are given in pm, angles in degrees and estimated standard deviations in parentheses.

[b] The mean values of the Ge–Cl bond lengths and the Cl–Ge–Cl and W–Ge–Cl bond angles are listed.

[c] Cp*/carbene denotes the dihedral angle between the least square planes of the Cp* ligand (ring-carbon atoms) and the aminomethylene ligand ($C_{carbene}$, N and $C_{methylene}$ atoms).

[d] Four crystallographically independent molecules were found in the crystal structure; the average bonding parameters of the four molecules are listed.

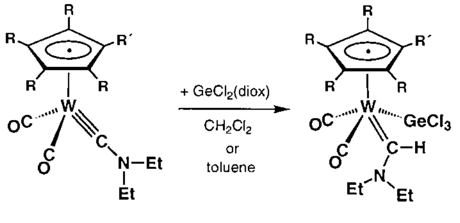
[e] Two crystallographically independent molecules were found in the crystal structure; the average bonding parameters of the two molecules are listed.

given by the $C_{carbene}$–N bond length of 128.9(5) pm, which is considerably smaller than that of a C($sp^2$)–N($sp^2$) single bond (144 pm) and very close to that of a C–N double bond (127 pm) [22], by the sum of the bond angles around the amino nitrogen atom of 359.6° indicating $sp^2$ hybridization, and by the planarity of the carbene ligand, which is shown by the dihedral angle of 8.4° between the least squares plane defined by the atoms C(6), N, C(7) and C(9) and the W–C(6)–N plane.

Complex **2** reacts with $GeCl_2$(diox) in $CH_2Cl_2$ at ambient temperature to give exclusively the trichlorogermyl complex *cis*-Cp*$(GeCl_3)(CO)_2$W=C(H)$NEt_2$ (**3**) (Scheme 1). This was isolated in 90% yield as an orange, slightly air-sensitive solid, that is soluble in $CH_2Cl_2$ and THF, slightly soluble in diethyl ether and insoluble in pentane. Insertion of $GeCl_2$ into the metal–chlorine bond of **2** to afford **3** is a fast and stereoselective reaction. Thus, no intermediates or other products than **3** were observed on IR monitoring of the insertion reaction at ambient temperature, which revealed a gradual replacement of the $\nu$(CO) absorptions of **2** (1929 and 1830 $cm^{-1}$) by those of **3** (1950 and 1874 $cm^{-1}$) and showed that the reaction was completed within 1h. Furthermore, the NMR spectra of the isolated product showed only the presence of the *cis* isomer **3**. Complex **3** is the product of kinetic reaction control and isomerizes to the thermodynamically more stable *trans* isomer **4** (Scheme 1). Isomerization was found by $^1$H-NMR spectroscopy to be very slow in $CD_2Cl_2$ solution at ambient temperature and reaches only after several weeks the thermodynamic equilibrium, which favors the *trans* isomer **4** (molar ratio **3**:**4** = 1:3.6, calculated from the integration of the W=C*H* signals). Simultaneous thermal analysis (TG-DTA) of **3** reveals that isomerization occurs also in the melt at 198°C to afford a mixture of **3** and **4**. Thus, when a sample of the pure *cis*-isomer **3** was heated, only one endothermic transition at $T_e = 198$°C was observed. This transition was shown by visual inspection and IR spectroscopic investigation of the cooled sample ($\nu$(CO) and $\nu$($C_{carbene}$–N) absorptions) to involve melting of **3** and concomitant *cis–trans* isomerization. Further evidence for this was given by a separate experiment, in which a sample (171 mg) of the pure *cis* isomer **3** was heated at 208°C in a Schlenk tube under static vacuum for 40 min. The resulting homogeneous dark green melt was quenched to −20°C to avoid *cis–trans* re-equilibration and the resulting glass-like solid was purified to give in 80% yield a dark yellow solid, which was shown by $^1$H- and $^{13}$C-NMR spectroscopy to be a mixture of **3** and **4** in the molar ratio of 1:6. The product was contaminated to 5% with a Cp* containing complex of unknown composition, which shows that some decomposition also takes place during the isomerization process in the melt at 208°C. The resulting isomeric mixture of **3** and **4** was shown by $^1$H-NMR spectroscopy to change it's composition in $CD_2Cl_2$ solution at ambient temperature, until the same thermodynamic equilibrium had been established, which was set up starting from the pure *cis* isomer (**3**:**4** molar ratio = 1: 3.6).

A *cis–trans* isomerization equilibrium in the molten state, as that observed for the aminomethylene complexes **3** and **4**, has been reported previously for the structurally related ethylisocyanide complexes *cis*- and *trans*-$CpW(CO)_2(CNEt)GeCl_3$ [6]. In comparison, the trimethylphosphane derivatives *cis*-$(\eta^5\text{-}C_5R_5)M(CO)_2(PMe_3)GeCl_3$ (R = H, Me; M = Mo, W) were shown to undergo a unidirectional thermal isomerization in the solid-state to afford the *trans* isomers [6]. These results indicate, that subtle changes in the ligand sphere of these 'four-legged piano-stool' molybdenum and tungsten trichlorogermyl complexes have a strong influence on their thermal behavior. Similar phenomena have been recently reported for a variety of 'four-legged-piano-stool' rhenium cyclopentadienyl complexes [23].

In an attempt to add $GeCl_2$ across a metal–carbon triple bond, the aminocarbyne complex **1** was treated with $GeCl_2$(diox) in $CH_2Cl_2$. However, IR monitoring of the reaction revealed the intermediate formation of the aminomethylene complex **2** and a rapid and clean conversion of the starting material to the *cis*-trichlorogermyl complex **3**. After addition of 1.5 equivalents of $GeCl_2$(diox), the starting material **1** and the intermediate product **2** had been consumed and the reaction mixture was worked up to afford the trichlorogermyl complex **3** in 41% yield (Eq. (1)).



(1)

**1, 1a** **3, 3a**

**1**, **3** : R, R′ = Me; **1a**, **3a** : R = Me, R′ = Et

These results show unambigously, that a source of HCl is generated in solution during the reaction and converts **1** into the aminomethylene complex **2**. The latter reacts with $GeCl_2$(diox) to give the final product **3** (Scheme 1). The origin of HCl is presently obscure. An obvious way to form HCl would involve hydrolysis of $GeCl_2$(diox), however, the solvent used was thoroughly dried. Another possibility would be contamination of $GeCl_2$(diox) with HCl, the latter being a product of the reaction of $GeCl_4$ with $SiEt_3H$, which was used to prepare $GeCl_2$(diox) [24,25]. This can be however excluded, since the reagent $GeCl_2$(diox) was found to be analytically pure and was further shown by IR and NMR spectroscopy to be free of HCl. A reaction of $GeCl_2$(diox) with $CH_2Cl_2$ to generate HCl can be also excluded. Thus, $^1$H and $^{13}C\{^1H\}$-NMR spectra of a solution of $GeCl_2$(diox) in $CH_2Cl_2 + CD_2Cl_2$ show only the signals of $GeCl_2$(diox) and remain unchanged at ambient temperature for at least four days. In addition, no side products resulting from protonolysis were observed in various reactions of substrates with $GeCl_2$(diox) in $CH_2Cl_2$, in which the products isolated in high yield are sensitive towards HCl. Examples for this type of reactions are the preparation of Cp*GeCl from $GeCp^*_2$ and $GeCl_2$(diox) and the synthesis of the dichlorogermyl complexes $(\eta^5\text{-}C_5R_5)M(CO)_{3-n}(PMe_3)_n(GeCl_2H)$ from $(\eta^5\text{-}C_5R_5)M(CO)_{3-n}(PMe_3)_nH$ (R = H, Me; M = Mo, W; $n = 0$, 1) and $GeCl_2$(diox) [2a]. Finally, treatment of $Cp^{**}(CO)_2W{\equiv}CNEt_2$ (**1a**) with $GeCl_2$(diox) in toluene affords via the aminomethylene complex *cis*-$Cp^{**}Cl(CO)_2W{=}C(H)NEt_2$ (**2a**) the trichlorogermyl complex *cis*-$Cp^{**}(GeCl_3)(CO)_2W{=}C(H)NEt_2$ (**3a**), which reveals that the same type of product is formed also in the absence of $CH_2Cl_2$ (Eq. (1)).

Complexes **3**, **3a** and **4** were fully characterized. Thus, the IR spectra display in $CH_2Cl_2$ one weak $\nu(C_{carbene}\overset{...}{=}N)$ absorption band at 1528 (**3**), 1529 (**3a**) and 1518 $cm^{-1}$ (**4**), which is typical of tungsten(II) aminomethylene complexes and indicates the high double-bond character of the $C_{carbene}$–N bond (Table 1). All compounds show two $\nu$(CO) absorptions, which appear at considerably higher wavenumbers than those of the chloro complex **2** (Table 1). This reveals that insertion of $GeCl_2$ into the tungsten–chlorine bond causes a reduction of the electron density at the tungsten center and weakens thereby the W–CO back bonding [1,2,6]. The relative intensity of the $\nu$(CO) absorptions is a sensitive spectroscopic probe to distinguish between the *cis* isomers **3**, **3a** and the *trans* isomer **4**, since for the *cis* isomers the higher energy absorption of the symmetric $\nu$(CO) vibration is more intense than the lower energy absorption of the antisymmetric $\nu$(CO) vibration, while the opposite is true for the *trans* isomer (Table 1) [2a,6,23a,26]. The $^1$H-NMR spectra display the expected low-field resonance for the carbene-proton at $\delta$ 10.45 (**3**, **3a**) and 10.56 (**4**), and a double set of resonances for the inequivalent ethyl groups of the carbene ligand (Table 1, Sections 4.3, 4.4 and 4.5). This shows that rotation of the diethylamino group about the $C_{carbene}$–N bond is too slow on the NMR time scale and gives additional evidence of extensive $\pi$-bonding between the carbene-carbon and the amino-nitrogen atom. Due to the $C_1$ symmetry of complexes **3** and **3a** the methylene protons of the diethylamino group are diastereotopic and give rise to doublet of quadruplet signals (**3** in $CD_2Cl_2$: $\delta$ 3.64, 3.79, 3.81 and 3.95), whereas the methylene protons of **4** are enantiotopic, because of the $C_s$ symmetry of this compound, and appear as quadruplets at $\delta$ 3.73 and 3.94 (Sections 4.3, 4.4 and 4.5). The carbene–carbon resonances are observed in the $^{13}C\{^1H\}$-NMR spectra at low field (**3**: $\delta = 237.7$; **3a**: $\delta = 237.5$; **4**: $\delta = 234.3$) and are flanked by tungsten satellites due to coupling with the $^{183}W$ nucleus (Table 1). The $^1J(W,C_{carbene})$ coupling constants of 92 Hz (**3**, **3a**), and 95 Hz (**4**) have values close to those of other tungsten(II) aminomethylene complexes (85–104 Hz) (Table 1). These are however considerably smaller than those observed for high oxidation-state tungsten alkylidene complexes, e.g. $W(NPh)[C(H)SiMe_3](CH_2SiMe_3)_2$: $^1J(W,C) = 127$ Hz [27], $W(O)[C(H)^tBu](PEt_3)_2Cl_2$: 148 Hz [28], $W(NPh)[C(H)^tBu](CH_2^tBu)_2$: 163 Hz [27], $W(O)[C(H)^tBu](PEt_3)Cl_2$: 176 Hz [29], $W(O)[C(H)^tBu](PMe_2Ph)(O^tBu)_2$: 186 Hz [28] and $W[C(H)^tBu](NAr')(OR)_2$ ($Ar' = C_6H_3$-2,6-$Me_2$; $R = {}^tBu$, $CMe_2(CF_3)$, $CMe(CF_3)_2$): 196–202 Hz [30], which suggests the presence of a weaker $W-C_{carbene}$ bond in **2**–**4**.

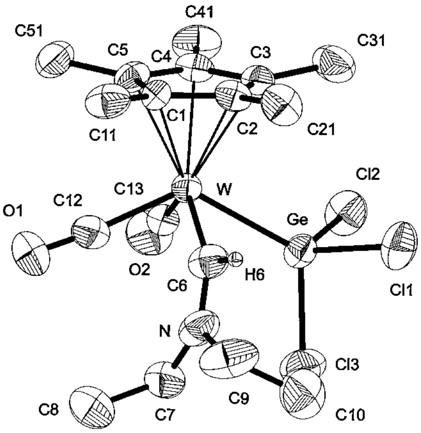


Fig. 3. DIAMOND plot of the molecular structure of **3** with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity reasons except that bonded to the carbene carbon atom C6.

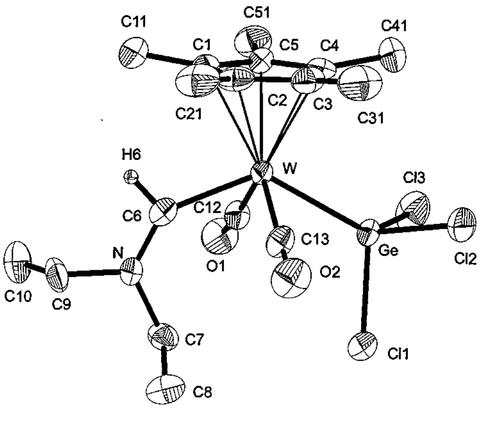


Fig. 4. DIAMOND plot of the molecular structure of **4** with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity reasons except that bonded to the carbene carbon atom C6.

Table 4
Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **3**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| W–C(1) | 230.2(6) | W–C(13) | 199.0(8) |
| W–C(2) | 238.1(6) | W–Ge | 252.69(9) |
| W–C(3) | 240.0(7) | Ge–Cl(1) | 221.2(2) |
| W–C(4) | 235.8(7) | Ge–Cl(2) | 220.3(2) |
| W–C(5) | 229.0(7) | Ge–Cl(3) | 219.7(2) |
| W–C(6) | 213.8(8) | C(6)–N | 129.0(10) |
| $W-C_g$ [a] | 200.6 | C(7)–N | 147.4(11) |
| $W-C_f$ [a] | 200.3 | C(9)–N | 151.4(10) |
| W–C(12) | 194.6(8) | | |
| *Bond angles* | | | |
| Ge–W–C(6) | 77.1(2) | C(7)–N–C(9) | 115.9(7) |
| Ge–W–C(12) | 125.1(2) | W–C(12)–O(1) | 174.7(7) |
| Ge–W–C(13) | 75.6(2) | W–Ge–Cl(1) | 118.67(7) |
| C(6)–W–C(12) | 81.4(4) | W–Ge–Cl(2) | 115.89(7) |
| C(6)–W–C(13) | 122.8(3) | W–Ge–Cl(3) | 122.28(7) |
| C(12)–W–C(13) | 75.0(3) | Cl(1)–Ge–Cl(2) | 99.77(9) |
| W–C(6)–N | 140.3(7) | Cl(1)–Ge–Cl(3) | 98.22(10) |
| C(6)–N–C(7) | 122.5(7) | Cl(2)–Ge–Cl(3) | 97.61(9) |
| C(6)–N–C(9) | 121.3(8) | | |

[a] For $C_g$ and $C_f$ notation see Table 2.

The solid-state structures of complexes **3** and **4** were determined by single-crystal X-ray diffraction. Suitable orange (**3**) and yellow (**4**) single crystals were grown upon diffusion of pentane into a $CH_2Cl_2$ solution at − 30°C. The molecular structures of **3** and **4** with the atom-labeling schemes used are depicted in Figs. 3 and 4, respectively. Selected bond lengths and angles are collected in Tables 4 and 5.

Both complexes show as **2** tetragonal pyramidal coordination geometry. The aminomethylene and trichlorogermyl ligands are *cis* arranged in **3** and *trans* arranged in **4**. The tungsten atom lies at a distance of 200.3 pm (**3**) and 200.5 pm (**4**) from the Cp* ring plane and a distance of 99.6 pm (**3**) and 103.1 pm (**4**) from the basal plane of the pyramid defined by the ligating atoms Ge, C(6), C(12) and C(13) (Figs. 3 and 4). The dihedral angle between these planes is 7.2° (**3**) and 6.1° (**4**). The aminomethylene ligand is in both compounds planar, as shown by the dihedral plane of 1.9° (**3**) and 5.7° (**4**) between the least squares plane defined by the atoms C(6), N, C(7) and C(9) and the W–C(6)–N plane, and has the same bonding characteristics as in **2**, i.e. a comparatively long $W-C_{carbene}$ bond, a short $C_{carbene}-N$ bond and a planar amino group (see molecular structure of **2** and Table 3). All these structure data suggest in agreement with the spectroscopic data a strong contribution of the resonance formula **B** to the metal–aminomethylene bond in **3** and **4** (Fig. 1). Furthermore, the C(6)–N–C(7)–C(9) plane of the aminomethylene ligand and the Cp* ring plane are in **4**, as in **2**, almost orthogonal to each other (dihedral angle = 87.9°), whereas in **3** the aminomethylene ligand deviates slightly from the 'upright' conformation (dihedral angle = 73.6°) (Table 3). Only one rotamer with respect to the $M–C_{carbene}$ bond is observed for both compounds in the solid-state, in which the diethylamino group points away from the Cp* ligand. A steric repulsion between the diethylamino group and the Cp* methyl groups is expected to evolve in the other possible 'upright' conformer, in which the diethylamino group points towards the Cp* ligand, and makes apparently this conformer thermodynamically less stable (see also molecular structure of **2**). The W–Ge bond lengths of 252.69(9) pm (**3**) and 251.96(8) pm (**4**) and the mean Ge–Cl bond lengths of 220.4(2) pm (**3**) and 220.2(2) pm (**4**) are in the range observed for other Cp* substituted tungsten(II) trichlorogermyl complexes (Table 3) [31]. The tetrahedral coordination geometry of the germanium atom is strongly distorted, as shown by the mean Cl–Ge–Cl bond angles of 98.53(9)° (**3**) and 98.65(7)° (**4**), which are considerably more acute than the mean W–Ge–Cl angles of 118.95(7)° (**3**) and 118.84(5)° (**4**) (Table 3). A comparison of the bonding parameters of the trichlorogermyl complexes in Table 3 shows that successive substitution of CO by weaker π-acceptor ligands results in a decrease of the W–Ge bond lengths. This is revealed for example in the complex series $Cp^*W(CO)_3GeCl_3 >$ *cis*-$Cp^*W(CO)_2(CNEt)GeCl_3 >$ *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3 \approx$ *trans*-$Cp^*(GeCl_3)(CO)_2W{=}C(H)NEt_2 >$ *spy*-5-13-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$ [6]. A steric influence on the W–Ge bonds is also observed. Thus, the W–Ge bond lengths increase as the steric demand of the ligands in proximity to the $GeCl_3$ group is enhanced. This becomes evident on comparison of the following pairs of complexes $Cp^*W(CO)_3GeCl_3 > CpW(CO)_3GeCl_3$, *cis*-$Cp^*W(CO)_2(PMe_3)GeCl_3 >$ *cis*-$Cp^*(GeCl_3)(CO)_2W{=}C(H)NEt_2$ and *spy*-5-14-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3 >$ *spy*-5-13-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$ [32][3]. The Ge–Cl bond lengths are larger than that of $GeCl_4$ (211.3(3) pm) [33], and increase in general as the electron density at the tungsten center is enhanced. This increase is accompanied by a decrease of the Cl–Ge–Cl bond angles and an enlargement of the W–Ge–Cl bond angles (Table 3). All these structural trends can be rationalized using the atom rehybridization model of Bent [34] and/or suggesting the presence of a tungsten–trichlorogermyl π-back bonding [1,2b,6].

Table 5
Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **4**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| W–C(1) | 234.2(5) | W–C(13) | 197.3(6) |
| W–C(2) | 231.5(5) | W–Ge | 251.96(8) |
| W–C(3) | 233.4(6) | Ge–Cl(1) | 220.4(2) |
| W–C(4) | 235.8(6) | Ge–Cl(2) | 221.3(2) |
| W–C(5) | 236.3(6 | Ge–Cl(3) | 219.0(2) |
| W–C(6) | 211.5(6) | C(6)–N | 131.2(7) |
| $W–C_g$ [a] | 200.6 | C(7)–N | 147.8(7) |
| $W–C_f$ [a] | 200.5 | C(9)–N | 148.0(7) |
| W–C(12) | 197.2(5) | | |
| *Bond angles* | | | |
| Ge–W–C(6) | 130.5(2) | C(7)–N–C(9) | 115.2(5) |
| Ge–W–C(12) | 75.14(14) | W–C(12)–O(1) | 175.0(5) |
| Ge–W–C(13) | 74.96(14) | W–Ge–Cl(1) | 116.17(5) |
| C(6)–W–C(12) | 77.7(2) | W–Ge–Cl(2) | 119.27(5) |
| C(6)–W–C(13) | 78.1(2) | W–Ge–Cl(3) | 121.08(5) |
| C(12)–W–C(13) | 112.0(2) | Cl(1)–Ge–Cl(2) | 98.84(6) |
| W–C(6)–N | 137.7(4) | Cl(1)–Ge–Cl(3) | 97.96(7) |
| C(6)–N–C(7) | 124.6(5) | Cl(2)–Ge–Cl(3) | 99.14(7) |
| C(6)–N–C(9) | 120.0(5) | | |

[a] For $C_g$ and $C_f$ notation see Table 2.

The outcome of the reaction of **2** with $GeCl_2$(diox) prompted us to examine whether also other compounds would stereoselectively insert $GeCl_2$ into their M–Cl bonds. The aminocarbyne complex *cis*-$Cp^*(Cl)_2(CO)W\equiv CNEt_2$ (**5**) was chosen as substrate containing two different W–Cl bonds. IR monitoring of the reaction of **5** with $GeCl_2$(diox) revealed a fast and stereoselective conversion of the starting material into the trichlorogermyl complex *spy*-5-14-$Cp^*(Cl)(GeCl_3)(CO)W\equiv CNEt_2$ (**6**) [32][3], which was isolated as a red solid in 81% yield and was fully characterized (Eq. (2)). No intermediates or other products could be detected by IR spectroscopy at ambient temperature, which let us suggest that the stereoselectivity of this reaction is controlled kinetically. However, at this stage we cannot exclude the possibility that also other stereoisomers of $Cp^*(Cl)(GeCl_3)(CO)W\equiv CNEt_2$ are formed during the reaction, which isomerize too fast to **6** to be detected by IR spectroscopy. In this case, the stereoselectivity of the $GeCl_2$ insertion would be under thermodynamic control.

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[3] Two isomers of $Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$ were isolated, the one bearing the $GeCl_3$ and the $PMe_3$ ligand in *trans* position (*spy*-5-13) and the other bearing the $GeCl_3$ and the CO ligand in *trans* position (*spy*-5-14). Both isomers were assigned a polyhedron symbol (*spy*-5) and a configuration index (13 or 14) following the IUPAC Recommendations on the Nomenclature of Inorganic Compounds: W. Liebscher, J. Neels (Eds.), Nomenklatur der Anorganischen Chemie, Deutsche Ausgabe der IUPAC Empfehlungen 1990, VCH, Weinheim, 1994. The Cp* ligand was considered as the group of highest priority (priority number 1), which after application of the Cahn–Ingold–Prelog rules leads to the configuration indices 13 and 14 for the two isomers of $Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$ and to the configuration index 14 for the aminocarbyne complex **6**. In an earlier publication [2b] the Cp* ligand was assigned the lowest priority (priority number 5) resulting in the configuration index 52 for the isomer of $Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$, in which the $GeCl_3$ and $PMe_3$ ligands are *trans* arranged.

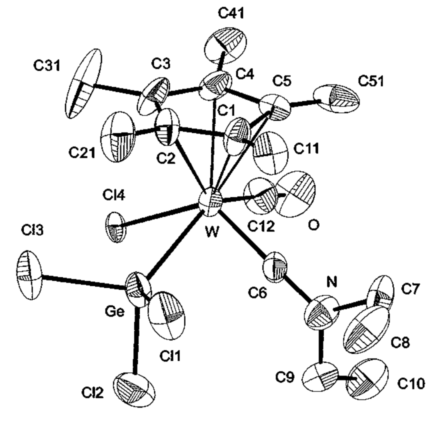
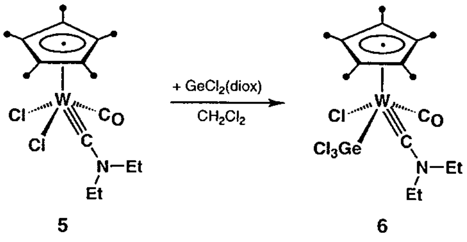


Fig. 5. DIAMOND plot of the molecular structure of **6** with the thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms are omitted for clarity reasons.

Table 6
Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **6**[a]

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| W–C(1) | 227.7(14) | W–Ge | 257.84(16) |
| W–C(2) | 239.6(15) | W–Cl(4) | 266.6(2) |
| W–C(3) | 243.5(15) | Ge–Cl(1) | 220.6(4) |
| W–C(4) | 235.2(13) | Ge–Cl(2) | 219.0(5) |
| W–C(5) | 235.9(11) | Ge–Cl(3) | 220.2(4) |
| W–C(6) | 187.1(12) | C(6)–N | 131.0(18) |
| W–$C_g$ [a] | 201.0 | C(7)–N | 147(2) |
| W–$C_f$ [a] | 200.5 | C(9)–N | 150(2) |
| W–C(12) | 198.9(14) | | |
| *Bond angles* | | | |
| Ge–W–C(6) | 79.3(4) | C(7)–N–C(9) | 118.9(14) |
| Ge–W–C(12) | 136.4(5) | W–C(12)–O | 175.4(15) |
| Ge–W–Cl(4) | 78.26(7) | W–Ge–Cl(1) | 117.42(13) |
| Cl(4)–W–C(6) | 117.8(4) | W–Ge–Cl(2) | 117.82(15) |
| Cl(4)–W–C(12) | 77.1(5) | W–Ge–Cl(3) | 121.01(15) |
| C(6)–W–C(12) | 81.2(7) | Cl(1)–Ge–Cl(2) | 99.4(2) |
| W–C(6)–N | 177.2(12) | Cl(1)–Ge–Cl(3) | 99.02(19) |
| C(6)–N–C(7) | 119.2(14) | Cl(2)–Ge–Cl(3) | 98.0(2) |
| C(6)–N–C(9) | 121.9(14) | | |

[a] For $C_g$ and $C_f$ notation see Table 2.



(2)

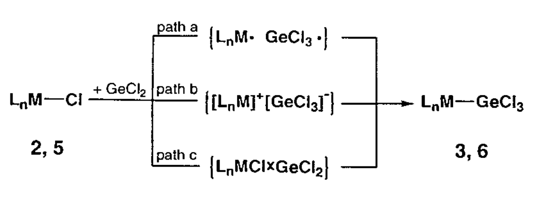
Complex **6** is soluble in $CH_2Cl_2$, sparingly soluble in diethylether and insoluble in pentane and decomposes upon melting at 143°C. It shows in the IR spectrum in $CH_2Cl_2$ one very strong $\nu$(CO) absorption at 2018 $cm^{-1}$, which is shifted by 32 $cm^{-1}$ to higher wavenumbers than that of the aminocarbyne complex **5** [17,18]. This indicates as in the case of the aminomethylene complexes **3** and **4**, that insertion of $GeCl_2$ into the tungsten–chlorine bond reduces the electron density at the tungsten center and weakens the W–CO back bonding [1,2,6]. The IR spectrum of **6** displays also one strong absorption at 1599 $cm^{-1}$, which is assigned to the $\nu(C_{carbyne}\overset{\cdots}{-}N)$ vibration and suggests in valence bond terms a strong contribution of the resonance formula **D** to the metal–aminocarbyne bond {M≡C–$NEt_2$ (**C**)↔$M^{(-)}$=C=$N^{(+)}Et_2$ (**D**)}. The position of this absorption is almost identical to that of **5** ($\nu(C_{carbyne}\overset{\cdots}{-}N)$ in $CH_2Cl_2$ = 1600 $cm^{-1}$) [17] and characteristic of 18-electron tungsten(II) aminocarbyne complexes bearing one carbonyl ligand [18]. Complex **6** is also distinguished in the $^{13}C\{^1H\}$-NMR spectrum in $CD_2Cl_2$ by a low-field resonance for the carbyne-carbon nucleus at $\delta$ 301.2, and displays in the $^1H$-NMR spectrum in $CD_2Cl_2$ at 25°C one set of resonances for the ethyl groups, which shows that rotation of the diethylamino group about the $C_{carbyne}$–N bond is too fast on the NMR time scale under these conditions [17,18]. Furthermore, the methylene protons are diastereotopic because of the $C_1$ symmetry of the complex and give rise in the $^1H$-NMR spectrum to two doublets of quadruplets at $\delta$ 3.50 and 3.72.

The molecular structure of **6** was determined by X-ray diffraction on dark red single crystals, which were obtained upon slow evaporation of the $CD_2Cl_2$ solution used for the NMR studies. The molecular structure is shown in Fig. 5 and selected bond lengths and angles are summarized in Table 6.

Complex **6** is like **2**–**4** tetragonal pyramidal. The trichlorogermyl and carbonyl ligand occupy *trans* positions at the basal plane of the pyramid, which forms a dihedral angle of 10° to the Cp* ring plane. The tungsten atom resides at a distance of 200.5 pm from the Cp* ring plane and a distance of 97.1 pm from the basal plane of the pyramid. The W–Cl bond of **6** is with 266.6(2) pm considerably longer than that of **2** (250.8(2) pm) and other half-sandwich tungsten(II) chloro complexes [13–16] (vide supra)[2], which suggests that the aminocarbyne ligand exerts a strong *trans* influence. The aminocarbyne ligand has in **6** the same bonding characteristics as in other 18-electron tungsten(II) aminocarbyne complexes bearing a carbonyl ligand [18], i.e. a comparatively long W–$C_{carbyne}$ bond of 187.1(12) pm and short $C_{carbyne}$–N bond of 131.0(18) pm, a trigonal planar geometry at the amino-nitrogen atom and an almost orthogonal arrangement to the Cp* ligand (the dihedral plane between the carbyne ligand plane defined by the atoms C(6), N, C(7) and C(9) and the Cp* ring plane is 86.9°). The trichlorogermyl ligand has similar bonding parameters to those found in the complexes **3** and **4**, with a mean Ge–Cl bond length of 219.9(4) pm and mean Cl–Ge–Cl and W–Ge–Cl bond angles of 98.8(2)° and 118.75(14)°, respectively (Tables 3 and 6). However, the

W–Ge bond of **6** is with 257.84(16) pm longer than that of **3** and **4,** which is probably a consequence of the reduced electron density at the tungsten center in **3**. The Ge–Cl(4) distance of 331.0 pm is considerably larger than that found in $GeCl_4$ (211.3(3) pm) [33], but slightly shorter than the sum of the van der Waals radii of the two atoms (370 pm) ($r_w$(Ge) = 195 pm, $r_w$(Cl) = 175 pm) [35]. This is constrained by the complex geometry and is not the result of an intramolecular donor–acceptor interaction between the chloro ligand and the germanium atom of the trichlorogermyl ligand. The bonding parameters of the trichlorogermyl ligand also do not provide any evidence for such an interaction. In comparison, the complex $[(MeSCH_2CH_2SMe)Mo(CO)_3(SnCl_3)Cl] \cdot CH_2Cl_2$ reveals an intramolecular donor–acceptor interaction between the chloro ligand and the tin atom of the trichlorostannyl ligand with a Sn–Cl distance of 278.1(4) pm, which is by only 19% longer than the Sn–Cl bonds in the $SnCl_3$ ligand ((Sn–Cl)$_{av.}$ = 233.7(5) pm) [36]. Furthermore, the intramolecular donor–acceptor interaction results in this case in a distorted trigonal bipyramidal coordination of the tin atom and an elongation by 6.6 pm of that one Sn–Cl bond in the $SnCl_3$ ligand, which is located in *trans* position to the donor–acceptor Sn–Cl bond [36,37].

Three reaction mechanisms can be discussed for the $GeCl_2$ insertion reactions of **2** and **5** in view of the suggested pathways for the insertion of germylenes into carbon–halogen bonds [38]. The first mechanism involves a chlorine atom abstraction from **2** or **5** to give intermediately a 17-electron tungsten complex and the $GeCl_3$ radical [39], the radical pair then collapsing to the insertion product **3** or **6** (Scheme 2, path a). The second pathway involves the transient formation of the ion pair $[ML_n]^+[GeCl_3]^-$ bearing an electrophilic 16-electron complex cation [40][4]. Rapid recombination of the ions would be therefore expected to occur subsequently to give the insertion product (Scheme 2, path b). The third mechanism involves the intermediate formation of a donor–acceptor adduct, in which **2** (**5**) acts as an organometallic Lewis base [41][5] and $GeCl_2$ as a Lewis acid, which then rearranges to yield the insertion product **3** (**6**) (Scheme 2, path c). The first two pathways should be accompanied by loss of configuration at the tungsten center and lead to a mixture of stereoisomers. This is at least not compatible with the stereochemical outcome of the $GeCl_2$ insertion reaction of **2**, in which the exclusive formation of the *cis* stereoisomer **3** is controlled kinetically (vide supra). In addition, an abstraction-recombination pathway involving radicals should also lead to escape products [38], such as $GeCl_4$ and $Ge_2Cl_6$ [42]. This is also not consistent with the observed exclusive formation of the insertion products **3** and **6**.



Scheme 2. Possible mechanisms for the $GeCl_2$ insertion reaction of complex **2** and **5**.

We therefore suggest path c to be the most plausible for the $GeCl_2$ insertion reactions of **2** and **5** (Scheme 2). Additional support for this is provided by the reaction of *cis*-$Cp^*W(CO)_2(PMe_3)Cl$ with $GeCl_2$(diox) to give the insertion product *cis*-$Cp^*W(CO)_2(PMe_3)GeCl_3$. In this reaction, an intermediate can be detected by IR spectroscopy, which displays two $\nu$(CO) absorptions at considerably higher energy (2081 and 2007 $cm^{-1}$) than those of the starting material (1931 and 1837 $cm^{-1}$) or the product (1953 and 1878 $cm^{-1}$) [6,31], as would be expected for a donor–acceptor adduct of $Cp^*W(CO)_2(PMe_3)Cl$ and $GeCl_2$ [41]. Studies are currently in progress to find further direct or indirect evidence for the intermediate formation of donor–acceptor adducts in the $GeCl_2$ insertion reactions of molybdenum(II) and tungsten(II) chloro and hydrido complexes.

## 3. Conclusion

Stereoselective insertion of $GeCl_2$ into the W–Cl bond of the aminomethylene complex *cis*-$Cp^*(Cl)(CO)_2W{=}C(H)NEt_2$ and the aminocarbyne complex *cis*-$Cp^*(Cl)_2(CO)W{\equiv}CNEt_2$ is observed to afford exclusively the trichlorogermyl complexes *cis*-$Cp^*(GeCl_3)(CO)_2W{=}C(H)NEt_2$ and *spy*-5-14-$Cp^*(Cl)(GeCl_3)(CO)W{\equiv}CNEt_2$, respectively. Stereoselectivity of the $GeCl_2$ insertion is in the case of *cis*-$Cp^*(Cl)(CO)_2W{=}C(H)NEt_2$ under kinetic control, the *cis* stereoisomer formed isomerizing either in solution or in the melt to the thermodynamically more stable *trans* stereoisomer. Possible pathways of the $GeCl_2$ insertion reaction are discussed, the most plausible one involving the transient formation of a donor–acceptor adduct, in which the tungsten chloro complex acts as a Lewis base and $GeCl_2$ as a Lewis acid.

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[4] Numerous salts containing the trichlorogermanate(II) anion have been structurally characterized.

[5] Several transition metal complexes have been shown to act as Lewis bases forming adducts with Lewis acids.

## 4. Experimental

### *4.1. General*

Standard inert-gas atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane over $CaH_2$, diethyl ether over Na/benzophenone, $CH_2Cl_2$ over Sicapent and Na/Pb alloy), distilled under nitrogen and stored over 4 Å molecular sieves. The compounds **1** [7], **5** [17] and $GeCl_2$(diox) [24,25] were prepared as described previously. Complex **1a** was obtained following the method described for **1** in Ref. [7]. Elemental analyses were obtained from the Central Analytical Group of the Chemistry Department of the Humboldt-Universität zu Berlin. Solution IR spectra were recorded in the region of 2200–1500 $cm^{-1}$ on a Bruker IFS-55 spectrometer using a NaCl cell; the intensities of the absorption bands are given in parentheses (vs = very strong, s = strong, m = medium, w = weak). All $^{1}H$-NMR (300 MHz) and $^{13}C\{^{1}H\}$-NMR spectra (75.5 MHz) were recorded on a Bruker AM-300 spectrometer in dry deoxygenated methylene-$d_2$ chloride or chloroform-$d_1$. The $^{1}H$ and $^{13}C\{^{1}H\}$-NMR spectra were calibrated against the internal residual proton and natural abundance $^{13}C$ resonances of the deuterated solvent (methylene-$d_2$ chloride, $\delta_H$ 5.32 and $\delta_C$ 53.8 ppm; chloroform-$d_1$, $\delta_H$ 7.24 and $\delta_C$ 77.0 ppm). The following abbreviations were used for the signal multiplicities: s = singlet, t = triplet, q = quadruplet, dq = doublet of quadruplets, m = multiplet. Mass spectra were obtained with a Hewlett–Packard 5995A or a Varian MAT 311A spectrometer using an ionization energy of 70 eV; $m/z$ values are given relative to the $^{184}W$, $^{35}Cl$ and $^{74}Ge$ isotopes. Melting points were determined using a Büchi 530 melting point apparatus and are corrected. The samples were sealed under vacuum in capillary tubes and heated slowly until the samples melted. IR spectra of the molten samples were recorded and compared with those of authentic samples to determine whether the compounds had decomposed. The simultaneous thermal analysis (STA) of **3** was carried out as described in Ref. [6].

### *4.2. Synthesis of cis-Cp*(Cl)(CO)$_2$W=C(H)NEt$_2$ (**2**)*

A yellow solution of 502 mg (1.09 mmol) of **1** in 30 ml of $CH_2Cl_2$ was cooled to −78°C and treated with 0.10 ml (1.16 mmol) of an aqueous solution of HCl (36% w/w). The mixture was allowed to warm to ambient temperature and stirred for 2 h. During this time the colour of the solution turned to red. Completion of the reaction was confirmed by IR spectroscopy. The solution was concentrated in vacuo to ca. 1 ml and the product precipitated upon addition of 10 ml of diethyl ether and then 20 ml of pentane. The supernatant solution was decanted off and the carmine-red precipitate was washed twice with 5 ml of pentane and dried in vacuo at ambient temperature. M.p.: 137°C. Yield: 470 mg (87%). — Anal. Calc. for $C_{17}H_{26}ClNO_2W$ (495.68): C, 41.19; H, 5.29; Cl, 7.15; N, 2.83; W, 37.09. Found: C, 41.14; H, 5.46; Cl, 7.01; N, 2.73; W, 36.82%. — IR ($CH_2Cl_2$): $\tilde{\nu}$ ($cm^{-1}$) = 1929 (vs) and 1830 (s) [$\nu$(CO)], 1536 (w) [$\nu(C_{carbene}\overset{\cdots}{-}N)$]. — $^{1}H$-NMR ($CD_2Cl_2$, 298 K): $\delta$ = 1.26 (t, $^{3}J(H,H) = 7.3$ Hz, 3H, $CH_2CH_3$), 1.32 (t, $^{3}J(H,H) = 7.3$ Hz, 3H, $CH_2CH_3$), 1.96 (s, 15H, $C_5Me_5$), 3.66 (m, 3H, $C(H_A)(H_B)CH_3$ and $C(H_{A'})(H_{B'})CH_3$), 3.95 (dq, $^{2}J(H,H) = 13.6$, $^{3}J(H,H) =$ 7.3 Hz, 1H, $C(H_A)(H_B)CH_3$), 10.60 (s, 1H, W=CH). — $^{13}C\{^{1}H\}$-NMR ($CD_2Cl_2$, 298 K): $\delta$ = 10.9 ($C_5Me_5$), 13.8 ($CH_2CH_3$), 15.3 ($CH_2CH_3$), 53.4 ($CH_2CH_3$), 56.2 ($CH_2CH_3$), 105.9 ($C_5Me_5$), 243.8 (W = C, $^{1}J(W,C) =$ 104 Hz), 249.4 (CO, $^{1}J(W,C) = 153$ Hz), 252.4 (CO, $^{1}J(W,C) = 142$ Hz). — EI-MS: $m/z = 495$ [$M^+$], 467 [$M^+ - CO$], 459 [$M^+ - HCl$], 439 [$M^+ - 2CO$].

### *4.3. Synthesis of cis-Cp*(GeCl$_3$)(CO)$_2$W=C(H)NEt$_2$ (**3**)*

#### *4.3.1. Method 1*

A sample of **2** (218 mg, 0.44 mmol) and 102 mg (0.44 mmol) of $GeCl_2$(diox) were mixed in a Schlenk tube, the mixture cooled to −78°C and suspended in 20 ml of $CH_2Cl_2$. The suspension was allowed to warm to ambient temperature and stirred for 1 h. During this time all $GeCl_2$(diox) dissolved and the colour of the solution turned from red to orange. Completion of the reaction was confirmed by IR spectroscopy. The slightly cloudy solution was concentrated in vacuo, filtered and the clear orange filtrate was concentrated to ca. 1 ml. The resulting suspension was treated with 5 ml of diethyl ether and 10 ml of pentane to complete precipitation of the product. The orange supernatant solution was decanted off and the precipitate was dried for 8 h under high vacuum at ambient temperature to afford **3** as an orange, microcrystalline solid. M.p.: 198°C (isomerization to **4**). Yield: 253 mg (90%). — Anal. Calc. for $C_{17}H_{26}Cl_3GeNO_2W$ (639.19): C, 31.94; H, 4.10; Cl, 16.64; N, 2.19. Found: C, 31.95; H, 4.17; Cl, 17.04; N, 2.19%. — IR ($CH_2Cl_2$): $\tilde{\nu}$ ($cm^{-1}$) = 1950 (vs) and 1874 (s) [$\nu$(CO)], 1528 (w) [$\nu(C_{carbene}\overset{\cdots}{-}N)$]. — $^{1}H$-NMR ($CD_2Cl_2$, 298 K): $\delta$ = 1.35 (t, $^{3}J(H,H) = 7.3$ Hz, 3H, $CH_2CH_3$), 1.37 (t, $^{3}J(H,H) = 7.3$ Hz, 3H, $CH_2CH_3$), 2.10 (s, 15H, $C_5Me_5$), 3.64, 3.79, 3.81 and 3.95 (dq each, $^{2}J(H,H) = 13.9$, $^{3}J(H,H) = 7.3$ Hz, 1H each, $2 \times C(H_A)(H_B)CH_3$), 10.45 (s, 1H, W=CH). — $^{13}C\{^{1}H\}$-NMR ($CD_2Cl_2$, 298 K): $\delta$ = 10.9 ($C_5Me_5$), 14.0 ($2 \times CH_2CH_3$), 54.9 ($CH_2CH_3$), 57.9 ($CH_2CH_3$), 105.2 ($C_5Me_5$), 231.1 (CO, $^{1}J(W,C) = 148$ Hz), 235.0 (CO, $^{1}J(W,C) = 127$ Hz), 237.7 (W=C, $^{1}J(W,C) = 92$, $^{1}J(C,H) = 139$ Hz). — EI-MS: $m/z = 639$ [$M^+$], 604 [$M^+ - Cl$], 467 [$M^+ - GeCl_2 - CO$], 439 [$M^+ - GeCl_2 - 2CO$], 411 [$M^+ - GeCl_2 - 2CO - C_2H_4$], 383 [$M^+ - GeCl_2 - 2CO - 2C_2H_4$].

### *4.3.2. Method 2*

$\mathrm{GeCl_2}$(diox) was added in small portions at ambient temperature to a yellow solution of 123 mg of **1** (0.27 mmol) in 30 ml of $\mathrm{CH_2Cl_2}$. After each addition a colour change to red–brown was observed, which then disappeared. IR spectra of the solution were recorded to monitor the progress of the reaction. These showed a gradual decrease in intensity of the $\nu$(CO) absorptions of **1** at 1930 and 1841 $\mathrm{cm^{-1}}$ and a concomitant increase in intensity of two $\nu$(CO) absorptions at 1950 and 1874 $\mathrm{cm^{-1}}$ due to the formation of **3**. Furthermore, the $\nu$(CO) absorption of **1** at 1841 $\mathrm{cm^{-1}}$ was found to shift gradually to 1830 $\mathrm{cm^{-1}}$ as the amount of added $\mathrm{GeCl_2}$(diox) increased, which indicated the intermediate formation of **2** (the second $\nu$(CO) absorption of **2** is masked by the $\nu$(CO) absorption of **1** at 1930 $\mathrm{cm^{-1}}$). A total amount of 90 mg (0.39 mmol) of $\mathrm{GeCl_2}$(diox) had to be added until complexes **1** and **2** had been consumed. Some minor products of unknown composition were also formed after addition of the last portion of $\mathrm{GeCl_2}$(diox) as evidenced by the presence of few, weak IR bands in the range of 2100–2000 $\mathrm{cm^{-1}}$. The resulting cloudy, orange solution was filtered, and the filtrate was evaporated to dryness. The residue was washed twice with 10 ml of diethyl ether and the ether washings containing **3** to a small extent (IR evidence) were discarded. The residue was dried in vacuo at ambient temperature to give an orange–brown solid consisting mainly of **3**. Yield of crude product: 155 mg (92% relative to **1**). The solid was treated with 30 ml of THF, the solution filtered and the filtrate concentrated in vacuo to 2 ml. Addition of 20 ml of diethyl ether caused precipitation of an orange solid, which was filtered off. The orange filtrate was evaporated to dryness and the residue washed with pentane and dried in vacuo at ambient temperature to afford **3** as an orange powder. Yield: 69 mg (41% relative to **1**). Anal. Calc. for $\mathrm{C_{17}H_{26}Cl_3GeNO_2W}$ (639.19): C, 31.94; H, 4.10; Cl, 16.64; N, 2.19. Found: C, 31.49; H, 4.18; Cl, 17.18; N, 2.03%. — $^1$H-NMR ($\mathrm{CDCl_3}$, 298 K): $\delta = 1.35$ (t, $^3J(\mathrm{H,H}) = 7.3$ Hz, 3H, $\mathrm{CH_2C}H_3$), 1.36 (t, $^3J(\mathrm{H,H}) = 7.3$ Hz, 3H, $\mathrm{CH_2C}H_3$), 2.08 (s, 15H, $\mathrm{C_5}Me_5$), 3.61, 3.78, 3.80 and 3.96 (dq each, $^2J(\mathrm{H,H}) = 13.9$, $^3J(\mathrm{H,H}) = 7.3$ Hz, 1H each, $2 \times \mathrm{C}(H_\mathrm{A})(H_\mathrm{B})\mathrm{CH_3}$), 10.46 (s, 1H, W=C$H$). — $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{CDCl_3}$, 298 K): $\delta = 10.7$ ($\mathrm{C_5}Me_5$), 13.7 ($\mathrm{CH_2}C\mathrm{H_3}$), 13.8 ($\mathrm{CH_2}C\mathrm{H_3}$), 54.4 ($C\mathrm{H_2CH_3}$), 57.5 ($C\mathrm{H_2CH_3}$), 104.6 ($C_5\mathrm{Me_5}$), 230.8 ($C$O), 233.4 ($C$O), 238.0 (W=$C$, $^1J(\mathrm{W,C}) = 92$, $^1J(\mathrm{C,H}) = 139$ Hz).

### *4.4. cis-Cp**(GeCl$_3$)(CO)$_2$W=C(H)NEt$_2$ (**3a**)*

A mixture of 63 mg (0.13 mmol) of **1a** and 42 mg (0.18 mmol) of $\mathrm{GeCl_2}$(diox) was suspended in 30 ml of toluene at −78°C. The suspension was allowed to warm to ambient temperature and stirred for 1.5 h. During this time the color of the solution changed from yellow to orange and a red–brown, oily precipitate was formed. IR monitoring of the reaction revealed a gradual decrease in intensity of the $\nu$(CO) absorptions of **1a** at 1936 and 1856 $\mathrm{cm^{-1}}$, a concomitant increase in intensity of the $\nu$(CO) absorptions of the product **3a** at 1948 and 1876 $\mathrm{cm^{-1}}$ and the intermediate formation of **2a** (one $\nu$(CO) absorption at 1836 $\mathrm{cm^{-1}}$; the other $\nu$(CO) absorption is masked by that of **1a** at 1936 $\mathrm{cm^{-1}}$). After 1.5 h stirring at ambient temperature the relative intensity of the $\nu$(CO) absorptions of **1a**, **2a** and **3a** had stopped to change and 21 mg (0.09 mmol) of $\mathrm{GeCl_2}$(diox) were added to the mixture, which was stirred for additional 1.5 h to complete the conversion of the complexes **1a** and **2a** into **3a**. The suspension was then evaporated to dryness, the residue washed with 10 ml of pentane and treated with 2 ml of THF. Addition of 10 ml of diethyl ether caused precipitation of a yellow–brown solid, which was filtered off. The clear orange filtrate was evaporated to dryness and the residue washed with 5 ml of pentane and dried in vacuo to afford **3a** as an orange powder. Yield: 70 mg (80% relative to **1a**). IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ ($\mathrm{cm^{-1}}$) = 1950 (vs) and 1874 (s) [$\nu$(CO)], 1529 (w) [$\nu(\mathrm{C_{carbene}}\overset{\cdots}{-}\mathrm{N})$]; IR (toluene): $\tilde{\nu}$ ($\mathrm{cm^{-1}}$) = 1948 (vs) and 1876 (s) [$\nu$(CO)], 1524 (w) [$\nu(\mathrm{C_{carbene}}\overset{\cdots}{-}\mathrm{N})$]. — $^1$H-NMR ($\mathrm{CD_2Cl_2}$, 298 K): $\delta = 1.08$ (t, $^3J(\mathrm{H,H}) = 7.5$ Hz, 3H, $\mathrm{CCH_2C}H_3$), 1.35 (t, $^3J(\mathrm{H,H}) = 7.3$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 1.37 (t, $^3J(\mathrm{H,H}) = 7.3$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 2.09, 2.10 and 2.12 (s each, 6:3:3, 12H, $\mathrm{C_5}Me_4\mathrm{Et}$), 2.42 (m, 2H, $\mathrm{CC}(H_\mathrm{A})(H_\mathrm{B})\mathrm{CH_3}$), 3.64, 3.80 and 3.94 (dq each, $^2J(\mathrm{H,H}) = 13.9$ Hz, $^3J(\mathrm{H,H}) = 7.3$ Hz, 1:2:1, 4H, $2 \times \mathrm{NC}(H_\mathrm{A})(H_\mathrm{B})\mathrm{CH_3}$), 10.45 (s, 1H, W=C$H$). — $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{CD_2Cl_2}$, 298 K): $\delta = 10.6$, 10.7, 10.8 and 10.9 (1C each, $\mathrm{C_5}Me_4\mathrm{Et}$), 14.0 ($2 \times \mathrm{NCH_2}C\mathrm{H_3}$), 15.2 ($\mathrm{CCH_2}C\mathrm{H_3}$), 19.6 ($\mathrm{C}C\mathrm{H_2CH_3}$), 54.8 ($\mathrm{N}C\mathrm{H_2CH_3}$), 57.9 ($\mathrm{N}C\mathrm{H_2CH_3}$), 104.3, 104.4, 106.0, 106.1 and 109.8 (1C each, $C_5\mathrm{Me_4Et}$), 231.0 ($C$O, $^1J(\mathrm{W,C}) = 148$ Hz), 235.0 ($C$O, $^1J(\mathrm{W,C}) = 127$ Hz), 237.5 (W=$C$, $^1J(\mathrm{W,C}) = 92$ Hz).

### *4.5. Isomerization equilibrium of cis-Cp*(GeCl$_3$)(CO)$_2$W=C(H)NEt$_2$ (**3**) and trans-Cp*(GeCl$_3$)(CO)$_2$W=C(H)NEt$_2$ (**4**)*

A Schlenk tube was charged with 171 mg (0.27 mmol) of the *cis*-isomer **3**, evacuated and heated in an oil bath at 208°C for 20 min. During this time the orange–yellow solid melted. The Schlenk tube was cooled rapidly to ambient temperature and an IR spectrum of a small sample of the dark-green solidified melt was recorded in $\mathrm{CH_2Cl_2}$. This revealed the presence of a new $\nu(\mathrm{C_{carbene}}\overset{\cdots}{-}\mathrm{N})$ absorption at 1518 $\mathrm{cm^{-1}}$ (**4**) in addition to that of **3** at 1528 $\mathrm{cm^{-1}}$. Furthermore, the $\nu$(CO) absorptions of **3** at 1950 and 1874 $\mathrm{cm^{-1}}$ had shifted to 1955 and 1878 $\mathrm{cm^{-1}}$, respectively, and their relative intensity had changed, the higher energy $\nu$(CO) absorption being less intense than the other one. All these observations indicated the formation of the *trans* isomer **4**. The solidified melt was heated for additional 20 min at 208°C to ensure complete equilibration of the system (IR monitoring) and the melt was quenched to −20°C. The green residue was dissolved at ambient temperature in 15 ml of $CH_2Cl_2$, the solution was filtered and the filtrate concentrated to ca. 1 ml in vacuo. Addition of 10 ml of diethyl ether and 10 ml of pentane caused precipitation of a dark-yellow solid, which was washed with pentane and dried in vacuo. Yield: 136 mg (80%). The product was shown by $^1H$- and $^{13}C$-NMR spectroscopy in $CD_2Cl_2$ to be a mixture of the isomers **3** and **4** (ratio 1:6) contaminated to 5% with a Cp* containing complex of unknown composition. Spectroscopic data of **4**: — IR ($CH_2Cl_2$): $\tilde{\nu}$ ($cm^{-1}$) = 1955 (m) and 1878 (vs) [$\nu$(CO)], 1518 (w) [$\nu(C_{carbene}\cdots N)$]. — $^1H$-NMR ($CD_2Cl_2$, 298 K): $\delta = 1.32$ (t, $^3J$(H,H) = 7.3 Hz, 3H, $CH_2CH_3$), 1.36 (t, $^3J$(H,H) = 7.3 Hz, 3H, $CH_2CH_3$), 2.13 (s, 15H, $C_5Me_5$), 3.73 (q, 2H, $^3J$(H,H) = 7.3 Hz, 2H, $CH_2CH_3$), 3.94 (q, 2H, $^3J$(H,H) = 7.3 Hz, 2H, $CH_2CH_3$), 10.56 (s, 1H, W=CH). — $^{13}C\{^1H\}$-NMR ($CD_2Cl_2$, 298 K): $\delta = 10.6$ ($C_5Me_5$), 13.8 ($CH_2CH_3$), 15.7 ($CH_2CH_3$), 52.2 ($CH_2CH_3$), 56.9 ($CH_2CH_3$), 105.0 ($C_5Me_5$), 226.9 (2 × CO, $^1J$(W,C) = 144 Hz), 234.3 (W=C, $^1J$(W,C) = 95 Hz).

### 4.6. *spy-5-14-Cp*(Cl)(GeCl$_3$)(CO)W≡CNEt$_2$* (**6**)

A mixture of 470 mg (0.94 mmol) of **5** and 217 mg (0.94 mmol) of $GeCl_2$(diox) was suspended in 20 ml of $CH_2Cl_2$ and stirred for 1 h at ambient temperature. During this time all $GeCl_2$(diox) dissolved and the colour of the solution changed from violet to red. Completion of the reaction was confirmed by IR spectroscopy (replacement of the $\nu$(CO) absorption of **5** at 1986 $cm^{-1}$ by that of **6** at 2018 $cm^{-1}$). The solution

Table 7
Summary of crystallographic data of the complexes **2**, **3**, **4** and **6**

| | 2 | 3 | 4 | 6 |
|---|---|---|---|---|
| Empirical formula | $C_{17}H_{26}ClNO_2W$ | $C_{17}H_{26}Cl_3GeNO_2W$ | $C_{17}H_{26}Cl_3GeNO_2W$ | $C_{16}H_{25}Cl_4GeNOW$ |
| Molecular weight | 495.68 | 639.19 | 639.19 | 645.62 |
| Crystal color | Red | Orange | Yellow | Dark red |
| Crystal size (mm) | 0.38 × 0.19 × 0.19 | 0.38 × 0.38 × 0.19 | 0.46 × 0.38 × 0.19 | 0.65 × 0.38 × 0.15 |
| Temperature (K) | 210(2) | 180(2) | 200(2) | 293(2) |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/n$ (no. 14) | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) | $Pn$ (no. 7) |
| Unit cell dimensions | | | | |
| $a$ (Å) | 9.2773(14) | 8.1643(11) | 8.537(2) | 9.240(4) |
| $b$ (Å) | 13.145(3) | 29.462(4) | 9.438(2) | 10.225(4) |
| $c$ (Å) | 15.684(2) | 10.0855(12) | 15.281(3) | 12.217(3) |
| $\alpha$ (°) | 90 | 90 | 92.68(2) | 90 |
| $\beta$ (°) | 104.342(13) | 113.76(1) | 92.81(2) | 99.93(4) |
| $\gamma$ (°) | 90 | 90 | 114.27(2) | 90 |
| $V$ (Å$^3$) | 1853.0(5) | 2220.3(5) | 1118.0(4) | 1137.0(7) |
| $Z$ | 4 | 4 | 2 | 2 |
| $\rho_{calc}$ (g $cm^{-3}$) | 1.777 | 1.912 | 1.899 | 1.886 |
| $\mu$(Mo–$K_\alpha$) ($mm^{-1}$) | 6.141 | 6.647 | 13.199 | 6.601 |
| $F$(000) | 968 | 1232 | 1232 | 620 |
| $2\Theta$ min./max. (°) | 4.10/48.68 | 4.62/48.68 | 4.74/48.86 | 3.98/50.06 |
| $hkl$ range | −10, 10/−15, 15/0, 17 | −9, 8/0, 34/0, 11 | −9, 9/−10, 10/0, 17 | −10, 10/−12, 12/−14, 14 |
| Total data | 12731 | 12136 | 9524 | 5610 |
| Data unique [$I > 2\sigma(I)$] | 2955 ($R_{int} = 0.0435$) | 3464 ($R_{int} = 0.1864$) | 3395 ($R_{int} = 0.0896$) | 4016 ($R_{int} = 0.0326$) |
| Absorption correction, min./max. | | DIFABS [a] 0.806/1.307 | | $\psi$-scan, 0.0356/0.1606 |
| Res. el. density min./max. (e Å$^{-3}$) | −2.275/2.590 | −1.341/0.955 | −1.954/1.653 | −1.056/2.823 |
| Parameters refined | 192 | 230 | 230 | 217 |
| Absolute structure parameter $\chi$ [b] | | | | 0.032(16) |
| Extinction coefficient, $x$ [c] | 0.0029(4) | | | |
| $R_1$ [d] [$I > 2\sigma(I)$] | 0.0448 | 0.0405 | 0.0288 | 0.0453 |
| $wR_2$ [e] [$I > 2\sigma(I)$] | 0.1106 | 0.1043 | 0.0759 | 0.1286 |
| Goodness-of-fit [f] | 1.052 | 1.093 | 1.062 | 1.067 |

[a] Ref. [50a]

[b] Ref. [50b]

[c] $F_c^* = kF_c[1 + 0.001F_c^2x\lambda^3/\sin(2\theta)]^{-1/4}$.

[d] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.

[e] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[f] $GOF = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

was filtered and the red filtrate evaporated to dryness. The oily residue was washed four times with 15 ml of diethyl ether to afford **6** as a red solid. Yield: 488 mg (81%). M.p.: 143°C (dec.). — Anal. Calc. for $C_{16}H_{25}Cl_4GeNOW$ (645.62): C, 29.77; H, 3.90; Cl, 21.96; N, 2.17. Found: C, 28.86; H, 3.87; Cl, 21.52; N, 2.08%. — IR ($CH_2Cl_2$): $\tilde{\nu}$ [cm$^{-1}$] = 2018 (vs) [$\nu$(CO)], 1599 (s) [$\nu(C_{\text{carbyne}} \overset{\cdots}{=} N)$]. — $^1$H-NMR ($CD_2Cl_2$, 298 K): $\delta = 1.36$ (t, $^3J$(H,H) = 7.3 Hz, 6H, $N(CH_2CH_3)_2$), 2.24 (s, 15H, $C_5Me_5$), 3.50 (dq, $^2J$(H,H) = 13.5, $^3J$(H,H) = 7.3 Hz, 2H, $N[C(H_A)(H_B)CH_3]_2$), 3.72 (dq, $^2J$(H,H) = 13.5, $^3J$(H,H) = 7.3 Hz, 2H, $N[C(H_A)(H_B)CH_3]_2$). — $^{13}C\{^1H\}$-NMR ($CD_2Cl_2$, 298 K): $\delta = 11.7$ ($C_5Me_5$), 14.0 ($N(CH_2CH_3)_2$), 49.3 ($N(CH_2CH_3)_2$), 107.9 ($C_5Me_5$), 216.8 (CO), 301.2 ($W\equiv C$).

### 4.7. Crystal structure determination of 2, 3, 4 and 6

A summary of the crystal data, data collection and refinement is given in Table 7.

The data collection for **2, 3** and **4** was performed on a STOE IPDS area detector equipped with a low temperature device and for **6** on a STOE STADI4 four-circle diffractometer at ambient temperature. Graphite-monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å) was used. The lattice parameters were derived from the setting angles of 44 reflections in the range of $27.1 \leq 2\Theta \leq 28.7°$ for **6** and from 2000 reflections after data collection for **2**, **3** and **4**.

The data on the crystals **2**, **3** and **4** were collected in the $\phi$-rotation mode in 2.4, 1.3 and 1.7° steps leading to 92, 154 and 153 exposures and each of them was exposed for 2.4, 2.6 and 1.7 min, respectively. Intensity data were integrated and converted into a SHELX *hkl*-file with the STOE IPDS software [43]. The data for **6** were collected in the $\omega$–$2\Theta$ scan mode. After every 2 h three standard reflections were monitored and the crystal was reoriented in case of deviation between 0.1 and 0.15°. Intensity data were corrected for Lorentz and polarisation effects.

The input files for the SHELX programs were prepared with the program UTILITY [44]. Structure solution was performed with the Patterson Method (SHELXS-86) [45] and a subsequent difference-Fourier-synthesis (SHELXL-93 and SHELXL-97) [46]. Refinement on $F^2$ was carried out by full-matrix least-squares techniques (SHELXL-93 and SHELXL-97). Non hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms H(6) connected to the carbene-carbon atoms in complexes **2**, **3** and **4** were found in the difference-Fourier map and were refined isotropically. $U_{eq}$ was found to be 36(19), 89(35) and 45(17), respectively. All other hydrogen atoms were included using a riding model ($U_{eq} = 80$). Neutral atom scattering factors were taken from Cromer and Mann [47]. Geometrical calculations were carried out with PLATON [48] and illustrations with DIAMOND [49].

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 162116 (**2**), 162114 (**3**), 162115 (**4**) and 162117 (**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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