Reactions of a Tungsten−Germylyne Complex with α,β-Unsaturated Ketones: Complete Cleavage of the W≡Ge Bond and Formation of Two Types of η³-Germoxyallyl Tungsten Complexes

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Ⓢ *Supporting Information*

ABSTRACT: Germylyne complex $Cp*(CO)_2W\equiv Ge\{C-(SiMe_3)_3\}$ (**1**) reacted with two molecules of $RC(O)-CH=CH_2$ (R = Me, Et) to give η^3-allyl complexes, in which an oxagermacyclopentene framework was bound to an η^3-allyl ligand through an oxygen atom. In the reaction with α-Me-substituted $MeC(O)C(Me)=CH_2$, **1** reacted with only one molecule of the substrate to give another type of η^3-allyl complex, in which a five-membered oxagermacyclopentenyl ring was coordinated to the W center in an η^3 fashion. Both reactions resulted in unprecedented complete cleavage of a W≡Ge triple bond.

Multiple bonds are more or less intrinsically reactive, and their applications to organic synthesis have been extensively developed in different ways.[1] Carbyne complexes having a transition metal−carbon triple bond, for instance, are reactive toward various organic substrates and are effectively used for transformation of organic molecules.[2] In sharp contrast with carbyne complexes, their heavier analogues have never been utilized for molecular conversion reactions. This is mainly ascribable to the kinetically overstabilized M≡E triple bonds (E = Si,[3] Ge,[4] Sn,[5] Pb[6]) of the known complexes. Reactivity of these triple-bonded complexes has been limited to ligand substitution at the metal center or nucleophilic addition of an anion or a 2e donor to the electropositive E atom.[3,4] There had been no reports on the addition reactions of organic substrates to the M≡E triple bonds until we recently reported such reactions: A germylyne complex $Cp*(CO)_2W\equiv Ge\{C-(SiMe_3)_3\}$ (**1**)[7] reacts with alcohols and aldehydes at room temperature to give products through addition of the substrates to the W≡Ge triple bond with conservation of a tungsten−germanium bond.[8] More recently, Tilley et al. reported the reactions of an unstable cationic osmium−silylyne complex with alkynes, giving products via addition to the Os≡Si triple bond.[9] Here we report new reactions of **1** with α,β-unsaturated ketones that induce complete cleavage of the W≡Ge triple bond and give two types of η^3-germoxyallyl complexes, depending on the substituent at the α position of the ketones. X-ray crystal structures of the products and possible reaction mechanisms featuring initial [2+4] cycloaddition as a key step are also reported.

Treatment of **1** with 2 equiv of $RC(O)CH=CH_2$ (R = Me, Et) in C_6D_6 at room temperature gave η^3-allyl complexes $Cp*(CO)_2W[\eta^3-H_2CCHCROGe\{OC(R)=CHCH_2\}\{C-(SiMe_3)_3\}]$ (**2**, R = Me; **3**, R = Et) in 1 day (Scheme 1).

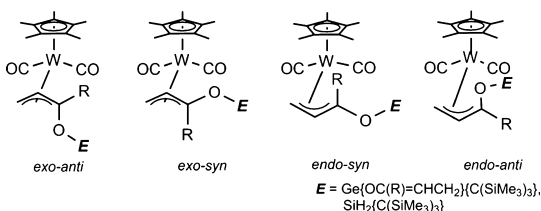**Scheme 1. Reactions of 1 with α,β-Unsaturated Ketones**
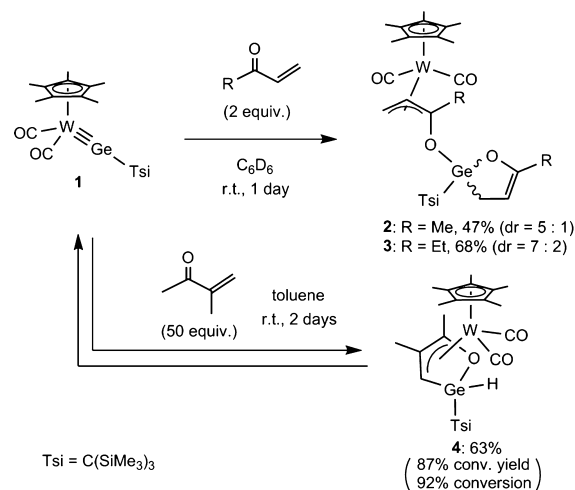
Complexes **2** and **3** were isolated as yellow crystals in 47 and 68% yields, respectively, after recrystallization from hexane at −30 °C. The ^1H NMR spectra of complexes **2** and **3** showed that each of them exists as a mixture of two diastereomers (major:minor = 5:1 for **2**, 7:2 for **3**). These two diastereomers are proposed to be in equilibrium because the ratio of the two diastereomers did not change after recrystallization or purification by alumina column chromatography.[10] The major isomers of complexes **2** and **3** were fully characterized by NMR, mass, and IR spectra as well as by elemental analysis.[11] Because of the relatively weak signals for the minor isomers of **2** and **3**, full assignments of the ^1H and ^{13}C NMR signals were not possible. The existence of η^3-allyl ligands was supported by the ^1H NMR spectra for **2** and **3**: For the major isomer of **2**, the proton signals that appeared at 1.47 ppm (1H) and 2.29 ppm (2H) can be assigned to the protons of the η^3-allyl ligand. $^{13}C\{^1H\}-^1H$ HSQC and HMBC NMR experiments confirmed that the signal at 1.47 ppm is assigned to a terminal methylene proton and the one at 2.29 ppm is the overlap of the other terminal methylene and the central methine proton signals. The protons on the oxagermacyclopentene ring appear at 1.65 and 2.63 ppm (methylene) and 4.90 ppm (methine).

We previously reported that a structurally similar η^3-siloxyallyl complex $Cp*W(CO)_2[\eta^3-H_2CCHCMeOSiH_2\{C-$

Chart 1. Possible Isomers for Z, 2, and 3

exo-anti   *exo-syn*   *endo-syn*   *endo-anti*

E = Ge{OC(R)=CHCH$_2$}{C(SiMe$_3$)$_3$},
SiH$_2${C(SiMe$_3$)$_3$}

(SiMe$_3$)$_3$} (**Z**)[12] was obtained by the reaction of silylene complex Cp*(CO)$_2$W(H)=Si(H){C(SiMe$_3$)$_3$} with MeC(O)-CH=CH$_2$, and the product adopted only the *exo-anti* form among the four possible isomeric forms (Chart 1). In a similar manner, **2** and **3** were also found to take only the *exo-anti* form (*vide infra*), but they exist as mixtures of two diastereomers because each of them has two chiral centers at the W and Ge atoms.

The structure of one of the diastereomers of **3** was confirmed by single-crystal X-ray diffraction analysis (Figure 1),[11] which
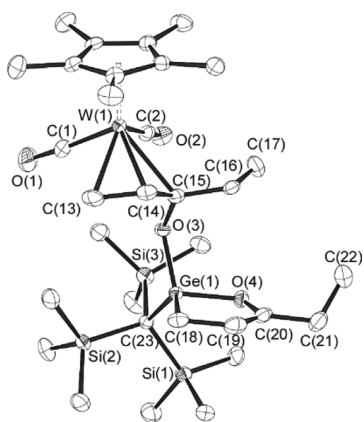

Figure 1. Molecular structure of **3**. The thermal ellipsoids represent 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−C(1) 1.937(6); W(1)−C(2) 1.950(5); W(1)−C(13) 2.304(5); W(1)−C(14) 2.226(5); W(1)−C(15) 2.433(5); C(13)−C(14) 1.420(8); C(14)−C(15) 1.421(7); Ge(1)−O(3) 1.790(3); Ge(1)−O(4) 1.832(4); Ge(1)−C(18) 1.954(5); Ge(1)−C(23) 1.955(5); C(18)−C(19) 1.514(8); C(19)−C(20) 1.316(8); C(1)−W(1)−C(2) 80.4(2); O(4)−C(20)−C(21) 112.5(5); C(21)−C(20)−C(19) 127.2(5); C(19)−C(20)−O(4) 120.3(5).

unambiguously shows that **3** adopts the *exo-anti* structure. The C−C bonds between three allyl carbons [C(13)−C(14) 1.420(8) Å; C(14)−C(15) 1.421(7) Å] are shorter than the normal C−C single bond (~1.54 Å[13]) but longer than the ordinary C−C double bond (~1.33 Å[13]), supporting the η^3-allyl coordination mode. Among the C−C bonds in the oxagermacyclopentene framework, the C(19)−C(20) bond [1.316(8) Å] can be regarded as a double bond and the C(18)−C(19) bond [1.514(8) Å] as a single bond judging from their bond lengths.

In contrast to the reactions with methyl vinyl ketone and ethyl vinyl ketone, only one substrate molecule was incorporated in the reaction of **1** with 3-methyl-3-buten-2-one. Thus, reaction of **1** with 50 equiv of MeC(O)CMe=CH$_2$ in toluene at room temperature for 1 day gave an η^3-allyl complex Cp*(CO)$_2$W[η^3-HCC(Me)C(Me)OGeH{C-(SiMe$_3$)$_3$}] (**4**) in 87% conversion yield (92% conversion), in

which the η^3-allyl ligand forms a part of an oxagermacyclo-pentenyl moiety. Despite the presence of a large excess of substrate (50 equiv), complete conversion of **1** into **4** was not accomplished after further reaction at room temperature for 24 h, indicating the existence of equilibrium between the starting materials (**1** and MeC(O)CMe=CH$_2$) and the product (complex **4**). In fact, when isolated **4** was dissolved in C$_6$D$_6$, nearly complete dissociation of **4** into complex **1** and MeC(O)CMe=CH$_2$ occurred slowly at room temperature in 5 days (Scheme 2). This observation strongly supports that the

Scheme 2. Dissociation of 4 into 1 and 3-Methyl-3-buten-2-one

4
Tsi = C(SiMe$_3$)$_3$

C$_6$D$_6$
r.t., 5 days

1
96% conv. yield
96% conversion

70% conv. yield
96% conversion
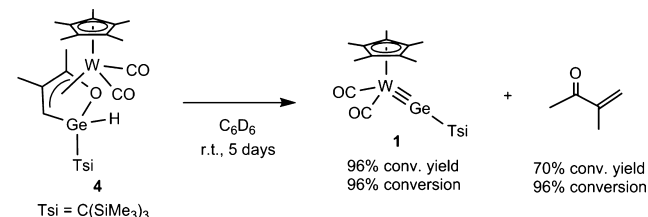
reaction of **1** with 3-methyl-3-buten-2-one is reversible. Complex **4** was isolated as a yellow powder in 63% yield in a large-scale experiment and was fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and elemental analysis. All six ^{1}H NMR signals (SiMe, Cp*, two Me, allyl−H, and Ge−H) for **4** appear at appropriate positions.[11]

Recrystallization of **4** from CH$_2$Cl$_2$ at −30 °C gave single crystals, and one of the crystals was used for X-ray crystallography.[11] The crystal structure of **4** is shown in Figure 2. The C−C bond lengths in the η^3-allyl moiety [C(13)−C(14) 1.439(4) Å; C(14)−C(15) 1.440(4) Å] are nearly identical. Importantly, the distances C(8)···C(17) [3.371 Å] and C(12)···C(17) [3.562 Å] are much shorter than the sum of the van der
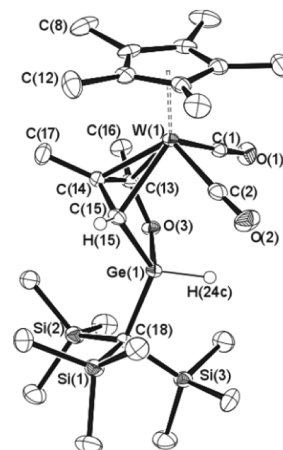

Figure 2. Molecular structure of **4**. The thermal ellipsoids represent 50% probability. H atoms except for H(15) and H(24c) are omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−C(1) 1.947(3); W(1)−C(2) 1.950(3); W(1)−C(13) 2.462(3); W(1)−C(14) 2.227(3); W(1)−C(15) 2.331(3); C(13)−C(14) 1.439(4); C(14)−C(15) 1.440(4); Ge(1)−O(3) 1.831(2); Ge(1)−C(15) 1.937(3); Ge(1)−C(18) 1.981(3); Ge(1)-H(24c) 1.44(4); C(8)···C(17) 3.371; C(12)···C(17) 3.562; C(1)−W(1)−C(2) 85.24(13); O(3)−C(13)−C(16) 111.8(3); C(16)−C(13)−C(14) 123.7(3); C(14)−C(13)−O(3) 117.2(3); C(13)−C(14)−C(17) 124.3(3); C(17)−C(14)−C(15) 123.9(3); C(15)−C(14)−C(13) 109.9(3).

Waals radii of Me groups (4.0 Å[14]), indicating the existence of steric repulsion between these groups. This steric repulsion is expected to be one factor that promotes dissociation of **4** into **1** and $MeC(O)CMe=CH_2$. Though **4** has two chiral centers at the W and Ge atoms, which makes two diastereomers possible, only one diastereomer is observed by ^1H NMR. It is clearly because bulky $Cp*W(CO)_2$ and $C(SiMe_3)_3$ groups cannot occupy positions on the same side of the oxagermacyclo-pentenyl ring.

Possible mechanisms for these reactions are summarized in Scheme 3. In the reactions of **1** with methyl vinyl ketone and

Scheme 3. Possible Mechanisms for the Reactions of 1 with α,β-Unsaturated Ketones
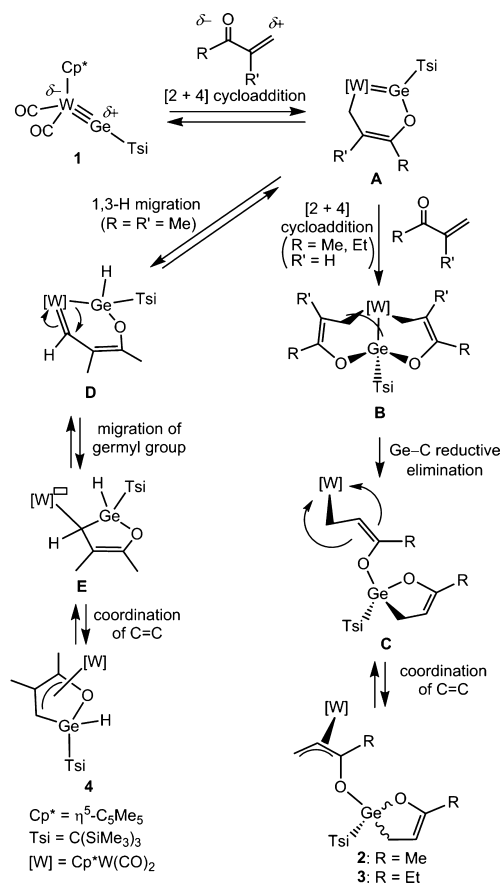
ethyl vinyl ketone, double [2+4] cycloaddition between a W≡Ge triple bond and two O=C—C=C bonds successively occurs to give intermediate **B** with two fused six-membered chelate rings. Intermediate **B** undergoes Ge—C reductive elimination to form η^1-allyl intermediate **C**, and then coordination of the C=C double bond to the right side or the left side of the metal center yields the diastereomeric mixtures of η^3-allyl complexes **2** and **3**. It is proposed that these two diastereomers are converted to each other, probably via η^1-allyl intermediate **C**. In the reaction of **1** with 3-methyl-3-butene-2-one, after a [2+4] cycloaddition of a molecule of the substrate to the W≡Ge triple bond to give **A**, the second [2+4] cycloaddition of the substrate does not occur because the Me group at the α position of 3-methyl-3-butene-2-one sterically prevents the substrate from approaching the W=Ge double bond in the intermediate **A**. Instead of the second cyclo-addition, 1,3-H migration occurs on **A** to give carbene complex

intermediate **D**. Subsequent 1,2-migration of the germyl group to the carbene carbon followed by coordination of the C=C double bond in the oxagermacyclopentenyl ring to the unsaturated W center results in formation of complex **4**.

In conclusion, germylyne complex **1** displays high reactivity toward α,β-unsaturated ketones, leading to complete cleavage of the W≡Ge triple bond to form two types of η^3-germoxyallyl tungsten complexes. The reaction route depends on whether the substituent at the α-position of the α,β-unsaturated ketones exists or not. Mechanisms involving initial single or double [2+4] cycloaddition between the W≡Ge bond and O=C—C=C bond(s) has been proposed for these reactions. To the best of our knowledge, this type of [2+4] cycloaddition reactions with α,β-unsaturated ketones has not been reported for carbyne complexes.

These results imply the specific and diverse reactivity of germylyne complex **1** toward various unsaturated organic compounds. Further investigations on reactivity of **1** toward other unsaturated substrates are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, characterization data, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(10) Further experimental results that support this proposition are described in Supporting Information.

(11) See Supporting Information for details.

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