Untypical Regioselectivity of Carbon Dioxide Coupling with Titanocene Complexes of Phenyl(trimethylsilyl)acetylene by Using the *meso*-1,2-Ethylene-1,1′-bis(η^5-tetrahydroindenyl) Ligand System

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The reaction of [*meso*-(ebthi)$TiCl_2$] [ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] with magnesium in the presence of the alkynes $Me_3SiC{\equiv}CSiMe_3$ and $PhC{\equiv}CSiMe_3$ resulted in the formation of the complexes [*meso*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] (**1**) and [*meso*-(ebthi)Ti(η^2-PhC_2SiMe_3)] (**2a** and **2b**), which were isolated and then characterized by their NMR spectra. Due to incomplete reduction the Ti^{III} complex [*meso*-(ebthi)Ti(THF)Cl] (**3**) was also obtained as a by-product of these reactions. By insertion into the Ti–CPh bond carbon dioxide reacted with the titanacyclopropene structure of the alkyne complex [*meso*-(ebthi)Ti(η^2-PhC_2SiMe_3)] (**2a**), with untypical regioselectivity to yield the α-silyl-substituted *meso*-(ebthi)titanafuranone **6a**. In the analogous reactions of the complexes [$(thi)_2$Ti(η^2-PhC_2SiMe_3)] (thi = η^5-tetrahydroindenyl), [*rac*-(ebthi)Ti(η^2-PhC_2SiMe_3)], and [Cp^*_2Ti(η^2-PhC_2SiMe_3)] with carbon dioxide typical regioselectivity (insertion into the M–CSi bond of the titanacyclopropene) was observed, yielding the β-silyl-substituted titanafuranones **7**, **8a**, and **9**. These results show that insertion of carbon dioxide into the M–C bond of the titanacyclopropene structure of the alkynemetallocene complexes is governed by the substitution pattern of the alkyne and the steric enviroment around the metal center. The complexes **3**, **6a**, and **7** were investigated by X-ray crystal structure analysis.

A large number of reviews concerning the cooordination chemistry, the stoichiometric reactions, and the catalytic activation of carbon dioxide have been published.[1] In this series of publications little has been reported concerning insertion reactions of carbon dioxide into the metallacyclopropene structure of alkynetitanocene and -zirconocene complexes, although the nature of the observed products shows a strong dependence on the different Cp substituents, the alkynes, and the metals used. To the best of our knowledge Scheme 1 summarizes all the different types of reaction products previously described.

The first results of this chemistry came from Vol′pin et al.[2] who trapped the benzyne complex [Cp_2Ti(η^2-*o*-C_6H_4)] during the thermal decomposition of Cp_2TiPh_2 by a reaction with CO_2 to give the titanabenzofuranone complex **I**. The titanafuranone **VI** as well as the dimeric carboxylate complex **XI** (not isolated or characterized) were said to be the result of the interaction of a solution of [$CpCp^*Ti$(η^2-PhC_2CPh)] with CO_2.[3] Recently, we have shown that dimeric compounds such as **VIII** and **X** are the primary products in the reactions of alkynetitanocene complexes [Cp_2Ti(η^2-RC_2R)] (R = Ph, Me_3Si) with CO_2[4] and that only after subsequent interaction with oxygen the titanafuranone complexes **II** and **III**[4] are formed. In the first step a coupling of only half the amount of the alkynes with CO_2 occurs, and not the direct coupling of all the alkyne to metallafuranones. Other complexes of this type **IV** and **V** were also described.[5]

The chemoselectivity for coupling of the alkyne and CO_2, as well as the structures of the products obtained, depends strongly on the substituents of the Cp ligands and the alkynes. In the reaction of CO_2 with the permethyltitanocene complex [Cp^*_2Ti(η^2-$Me_3SiC_2SiMe_3$)] the alkyne is not coupled and the carbonate-bridged complex **XII**[6a][6b] was obtained. When [Cp^*_2Ti(Me)Ph] was thermolyzed in the presence of CO_2 the benzyne complex [Cp^*_2Ti(η^2-*o*-C_6H_4)] was trapped, and the complex **VII** formed.[6c] In the reaction of [Cp_2Ti(η^2-Me_3SiC_2tBu)] and CO_2[4d] the products obtained are another carbonate-bridged complex **XIII**, the carbon monoxide complex [$Cp_2Ti(CO)_2$], and the free alkyne.

In the reaction of the alkynezirconocene complex [Cp_2Zr(THF)(η^2-$Me_3SiC_2SiMe_3$)] with CO_2 only the zirconafuranone **XIV** was obtained, which has a dimeric structure.[7]

Whereas, e.g. for nickel(0) complexes with unsymmetrically substituted alkynes, the regioselectivity of the carbon dioxide coupling reaction was studied both theoretically[1r] and experimentally[1s][1t], fewer results have been reported on the regioselectivity of these reactions with titanocene

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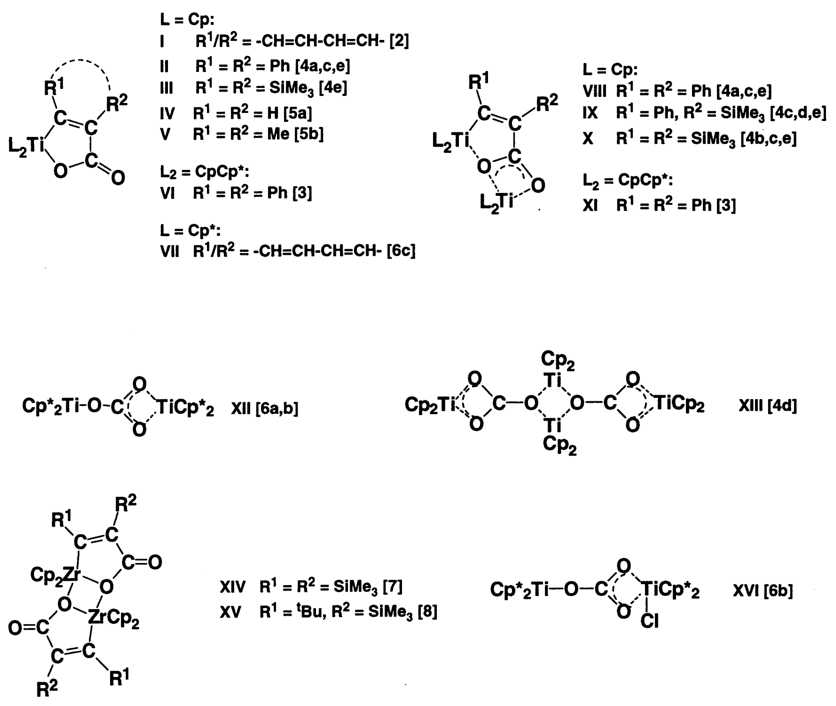
Scheme 1



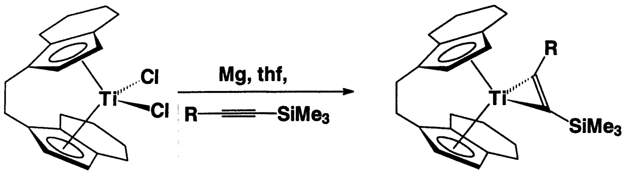
and zirconocene complexes. Using the unsymmetrically disubstituted alkynes $PhC{\equiv}CSiMe_3$ and $tBuC{\equiv}CSiMe_3$, an insertion of carbon dioxide at the silicon-substituted carbon atom is typical for titanocene as well as zirconocene, yielding the (vinylcarboxylato)titanium complex **IX**[4d] and the dimeric zirconocene compound **XV**,[8] respectively (see explanation below).

Here we report on a strategy to change the regioselectivity of the insertion of carbon dioxide into titanocene complexes, using $PhC{\equiv}CSiMe_3$, by the use of different ligand systems.

Results

Complex Syntheses

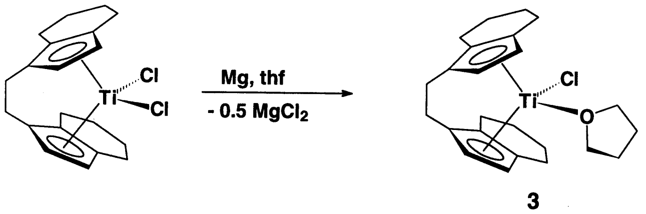
Starting Materials: The preparation of the complexes $[Cp_2Ti(\eta^2\text{-}PhC_2SiMe_3)]$,[4c][11] $[(thi)_2Ti(\eta^2\text{-}PhC_2SiMe_3)]$ (thi = tetrahydroindenyl),[12] and [*rac*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)][13] has been described recently. In order to investigate the influence of the ligand system on the regiochemistry of insertion reactions we prepared the alkyne complexes [*meso*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] (**1**) and [*meso*-(ebthi)Ti(η^2-PhC_2SiMe_3)] (**2**) by the same procedure (Eq. 1).



1 R= SiMe3
2a R= Ph

As a consequence of the *meso*-ebthi ligand we obtained the complex **2** as a mixture (3:1) of the two diastereomeric products **2a** (major isomer) and **2b** (minor isomer), which could not be seperated by crystallization. The ratio in which the two diastereomers are formed can be explained if one considers the different steric requirements of the alkyne substituents. In the major isomer the bulky trimethylsilyl group could be located at the less hindered side of the molecule, while the flat phenyl group could be situated between the two saturated rings. This assumption was proven by ^1H-NOESY NMR investigations (see below).

One by-product in the reaction of [*meso*-(ebthi)$TiCl_2$] with magnesium in THF in the presence of $Me_3SiC{\equiv}CSiMe_3$ is the Ti^{III} complex **3**, as the result of an incomplete reduction (Eq. 2).



3

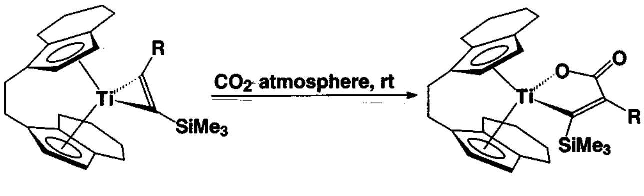
Regioselectivity: Three general questions must be kept in mind when determining the regioselectivity of the coupling of carbon dioxide with phenyl(trimethylsilyl)acetylene:

(i) What is the overall regioselectivity in the raw material (before the workup)?

(ii) Is the regioisomer identified by the X-ray crystal structure determination identical with the bulk product, as determined by NMR investigations?

(iii) Is there any cycloreversion of one regioisomer leading to the “opposite” product?

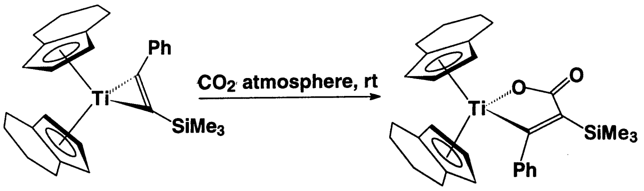
Complex **1** with the symmetrically substituted bis(trimethylsilyl)acetylene reacts with CO_2 to give the titanafuranone **5**, where the bulky Me_3Si groups are located at the sterically less hindered side of the complex, while the CO_2 is situated between the two saturated rings, as verified by NOE experiments. For **2a** an unusual insertion reaction was observed at the phenyl-substituted carbon atom and the complex **6a** was isolated in a high yield of 87% (Eq. 3). No other isomers were detected by NMR investigation of the raw material. The structure of the unexpected product **6a,** with the Me_3Si group in α-position, was proven by NMR investigations (NOE experiments) and confirmed by an X-ray crystal structure analysis (see below).



1 R = SiMe3
2a R = Ph

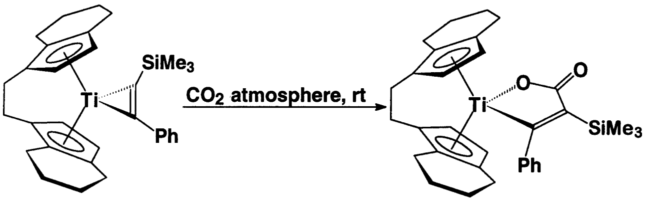
5 R = SiMe3
6a R = Ph

The opposite regioselectivity was observed in the reaction of the corresponding alkyne complex [(thi)$_2$Ti(η^2-PhC_2SiMe_3)] with CO_2. The titanafuranone **7** was formed by insertion of CO_2 at the silicon-substituted carbon atom (Eq. 4). A by-product, detected by NMR and in a very low yield (5%), is presumed to be the titanafuranone resulting from CO_2 insertion at the Ti−CPh bond.



7

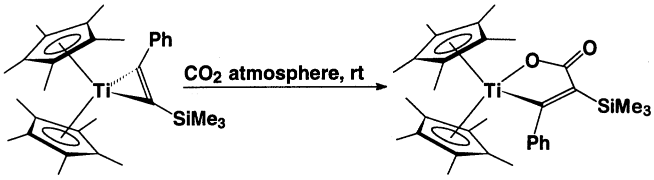
The opposite regioselectivity, compared to the reaction course from complex **2a** to **6a**, was also found in the reaction of the bridged alkyne complex [*rac*-(ebthi)Ti(η^2-Me_3SiC_2Ph)] **4** with carbon dioxide to yield the complex **8a** (Eq. 5).



4

8a

This regioselectivity is identical to that obtained in the reaction of the (alkyne)permethyltitanocene complex [$Cp^*_2Ti(\eta^2$-$Me_3SiC_2Ph)$][4c] with carbon dioxide, which gives the complex **9** as the sole product (Eq. 6).



9

NMR and Structural Investigations: The regio- and stereochemistry of the reactions were investigated by ^1H- and ^{13}C-NMR methods. The ^1H-NOESY spectra of the isomer **2a** feature NOE cross peaks from the CH protons of ebthi (^1H: $\delta = 4.88$, d, $^3J = 3.0$ Hz, 2 H, CH ebthi; $\delta = 7.28$, d, $^3J = 3.0$ Hz, 2 H, CH ebthi) to the trimethylsilyl group. This clearly indicates that the Me_3Si group is located at the sterically less hindered side of the complex. For the minor isomer **2b** the analogous NOE signals could not be observed. Similarly, a strong NOE is found at the cyclopentadienyl doublets for titanafuranone **6a** upon irradiation of the $SiMe_3$ protons, proving a close proximity, and hence silyl substitution, at C_α relative to Ti.

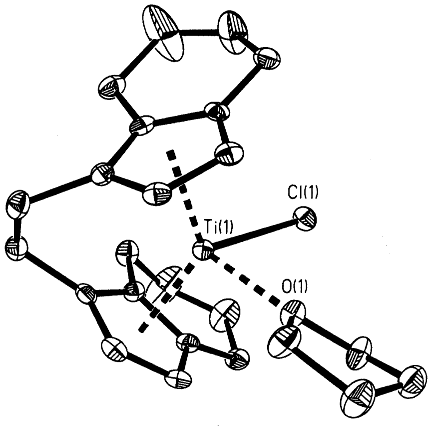
The position of the silyl group at the metallafuranone (α or β) can also be determined from proton-coupled ^{13}C-NMR spectra, where characteristic and clearly distinguishable patterns occur for the trimethylsilyl- and phenyl-substituted carbon atoms. The C_α signal appears at very low field ($\delta > 230$); the C_β and the carbonyl signals are found at $\delta \approx 160$ (see Experimental Section). Surprisingly, there is no clear influence of the substituents on the chemical shifts, and the C_α signal of the product with the "opposite" regiochemistry (**6a**) exhibits a very similar shift compared to that of the other titanafuranones (**6a**: C_α-$SiMe_3$: $\delta = 237.4$; **7**: C_α-Ph: $\delta = 239.2$; **8a**: C_α-Ph: $\delta = 236.2$), and the same observation is made for the shifts of C_β. This is not understood because Me_3Si groups very often give a more extended low-field shift for signals of C atoms in the β position to the silicon atom (see also complex **5**: C_α: $\delta = 264.9$).[8] Complex **3** was investigated by X-ray crystal-structure analysis (see Figure 1). To clarify the regioselectivity and to understand it from the perspective of the structures of the products obtained, the complexes **6a** and **7** were investigated by X-ray crystal-structure analysis (see Figures 2 and 3).

Discussion

Preparation of Starting Complexes

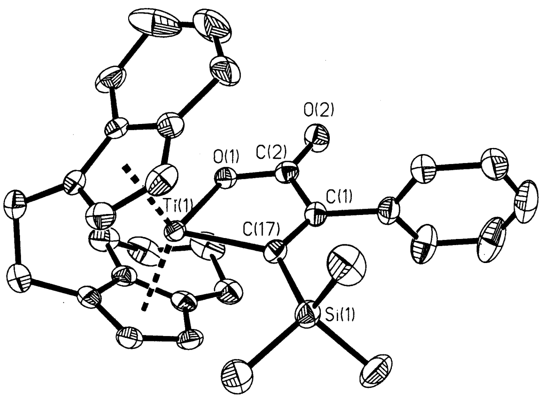
The complex [*rac*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] was recently prepared in high yield by the reduction of [*rac*-(ebthi)$TiCl_2$] with magnesium in THF at room temp. in the presence of bis(trimethylsilyl)acetylene.[13] Using the same procedure to prepare [*meso*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] (**1**), the titanium(III) complex **3** is obtained as a by-product. The incomplete reduction seems to be the consequence of

Figure 1. Molecular structure of **3**[a]



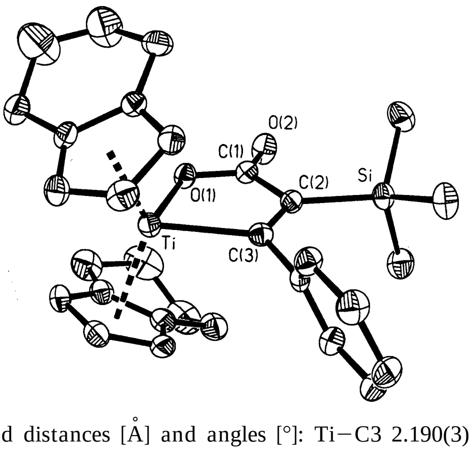
[a] Selected distances [Å] and angles [°]: Ti1−Cl1 2.447(1), Ti1−O1 2.257(3); Cl1−Ti1−O1 83.10(8), Cp′−Ti1−Cp′ 130.8(1).

Figure 2. Molecular structure of **6a**[a]



[a] Selected distances [Å] and angles [°]: Ti1−O1 1.950(2), Ti1−C17 2.184(3), C1−C17 1.348(4), C1−C2 1.499(4); O1−Ti1−C17 80.2(1), C1−C17−Si1 122.7(2), C17−C1−C21 127.0(3), Cp′−Ti1−Cp′ 130.9(1).

Figure 3. Molecular structure of **7**[a]



[a] Selected distances [Å] and angles [°]: Ti−C3 2.190(3), Ti−O1 1.938(2), C2−C3 1.362(4), C1−C2 1.490(4); O1−Ti−C3 77.96(9), C22−C3−C2 121.7(3), Si−C2−C3 128.6(2), Cp′−Ti−Cp′ 134.5(1).

the steric situation in the *meso*-ebthi isomer, where the ligand shields one face of the molecule. Detailed investigations concerning the reduction of [Cp_2TiCl_2] by magnesium in THF without the alkyne had shown the chlorine-bridged Ti−(μ-Cl)$_2$−Mg species to be formed in one of the first steps of the reactions.[14] It seems reasonable to assume that steric reasons influence the reaction pathway and lead to the formation of Ti^{III} complexes such as **3**. A similar complex [$Cp^*_2Ti(THF)Cl$] was also indicated as a by-product during the preparation of [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$]. The reaction of the mother liquor with CO_2 gave not only **XII** but also **XVI** (see Scheme 1), apparently formed due to the presence of incompletely reduced Ti^{III} complex in the solution.[6b] Interestingly, **3** is a monomer and coordinates a THF ligand. In a series of well-known complexes [$(C_5H_{5-n}Me_n)TiX$] (n = 0, 1, 3−5; X = Cl, Br, I) it was shown that an increase in n in the range $n = 3-5$ is connected with an increasing tendency to monomerize and to coordinate THF. This was explained primarily by considering the electron-donating properties of the Me groups.[15] Additionally, in **3** the threefold substituted Cp ligand is fixed in such a position that a dimerization seems to be unfavourable. The complexes with an unsymmetrically substituted alkyne, [*meso*-(ebthi)Ti(η^2-$PhSiC_2SiMe_3$)] (**2**), and the corresponding racemic compound **4** were prepared by the same procedure.

Regioselectivity

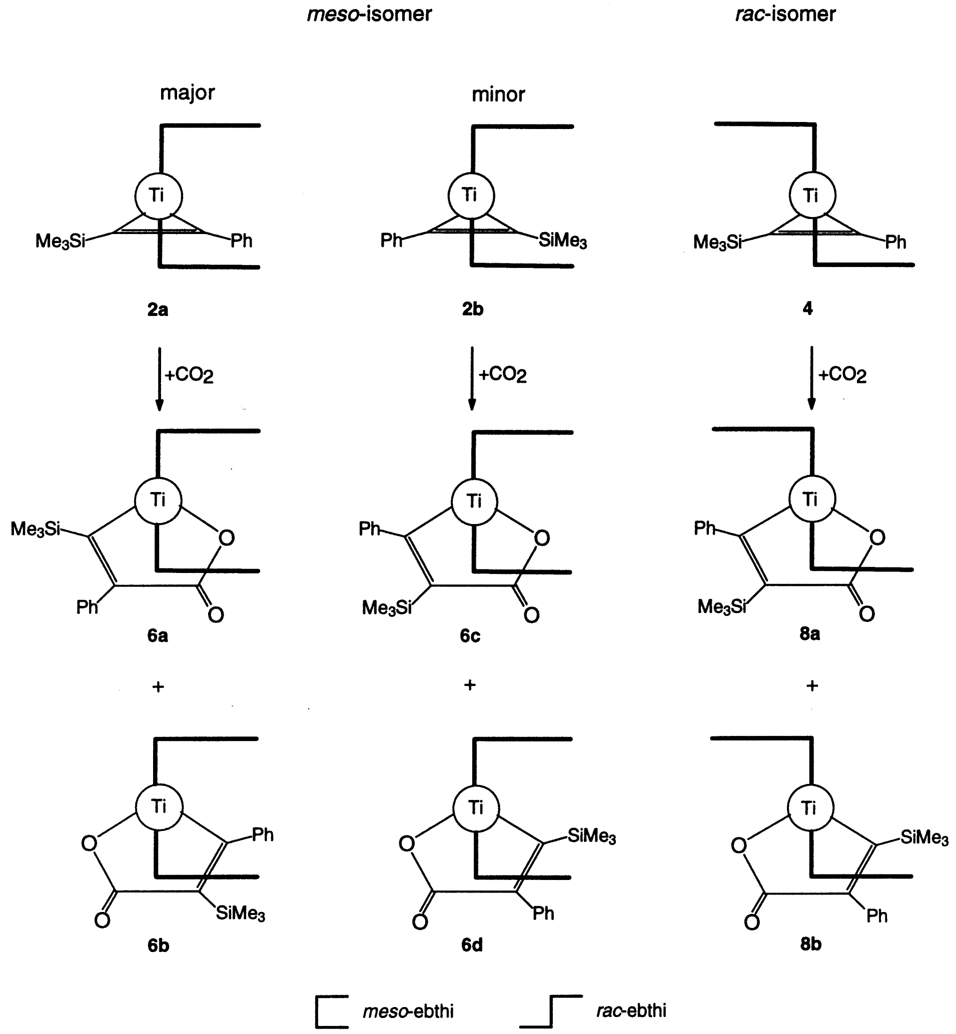
All titanocene and zirconocene complexes with unsymmetrically disubstituted alkynes of the type [$Cp_2Ti(\eta^2\text{-}RC_2SiMe_3)$] or [$Cp_2Zr(thf)(\eta^2\text{-}RC_2SiMe_3)$] are characterized by longer M−CSi than M−CR distances.[4d][8] This is explained electronically by assuming a (d-p)-π interaction of silyl groups, which reduces the electron density from the alkyne resulting in a positive charge on the CR group and a shorter M−CR bond, or by steric reasons resulting from the bulky $SiMe_3$ groups. The result of these effects is a kinetically favored reaction at the M−CSi bond to give the β-silyl-substituted metallacycles. In some cases a subsequent cycloreversion in solution to the thermodynamically more stable α-silyl product[4d][8] was observed.

The regioselectivity of the CO_2 insertion, influenced by the alkyne substituents, is characterized by insertions into the M−CSi bond (e.g as found. in **IX** and **XV**). For these complexes no cycloreversion could be observed. In this respect, the regioselectivity found in **6a** is unexpected and opposite: insertion into the M−CPh bond.

Regarding the stereochemical possibilities for the CO_2 insertion into the metallacyclopropene structure of the diastereomers **2a** and **2b,** in total four reaction products were expected, as indicated in Scheme 2.

For the major complex **2a** the attack of CO_2 occurs at the M−C−Ph bond to give the complex **6a**, and the other regioisomer, **6b,** was not found. There are three different explanations for the observed regioselectivity shown by the product obtained:

Scheme 2



(i) In the starting complex [*meso*-(ebthi)Ti(η^2-PhC_2SiMe_3)] the larger $SiMe_3$ groups are preferentially located at the nonsubstituted sides of the Cp′s, whereas the flat phenyl groups are between the cyclohexanediyl substituents (a similar situation is verified in complex **3** with the smaller chlorine atom and larger THF molecule). The insertion of CO_2 occurs in the M−CPh bond in order to minimize the steric restrictions between the saturated ring units and the phenyl group.

(ii) The Me_3Si group comes into the α position to the metal center which is in many metallacycles thermodynamically favoured (after cycloreversion) as shown by a number of coupling reactions of silylalkynes.[4d][8]

(iii) It seems possible that in the starting complex **2a** the M−CPh distances become nearly identical or longer, compared to the M−CSi bonds, due to the steric interactions of the phenyl groups and the cyclohexanediyl substituents. This could be the reason for the other regioselectivity, since all Cp complexes show longer M−CSi than M−CPh bonds.

Complex **2b** seems to form two insertion products, **6c** and **6d**. This is surprising because the steric repulsion between the bulky Me_3Si group and the tetramethylene unit should lead to a uniform reaction and only one product (**6c**). So far the separation and unambiguous characterization of the insertion products formed has failed and a stereochemical statement is not possible.

Compared to this "unusual" regioselectivity, the "normal" insertion of carbon dioxide into the complexes [$(thi)_2Ti(\eta^2$-$PhC_2SiMe_3)$], [*rac*-(ebthi)Ti(η^2-Me_3SiC_2Ph)], and [$Cp^*{}_2Ti(\eta^2$-$Me_3SiC_2Ph)$] follows the rules discussed above, with insertions at the M−CSi bond to the β-silyl-substituted metallacycles.

The reaction product **9** of the (alkyne)permethyltitanocene complex [$Cp^*{}_2Ti(\eta^2$-$Me_3SiC_2Ph)$] with carbon dioxide, differs from the dinuclear complex **IX**[4c][4d][4e] (Scheme 1) which was observed in the reaction of the corresponding titanocene complex [$Cp_2Ti(\eta^2$-$Me_3SiC_2Ph)$] with carbon dioxide. Interestingly, in the reaction of the corresponding permethylzirconocene complex [$Cp^*{}_2Zr(\eta^2$-$Me_3SiC_2Ph)$][16] with carbon dioxide a 1:1 mixture of the two possible regioisomers was obtained.[17]

Conclusion

The regioselectivity of the carbon dioxide insertion into titanocene complexes with unsymmetrically disubstituted alkynes of the type $[L_2Ti(\eta^2\text{-}PhC_2SiMe_3)]$ is influenced by the nature of the ligands L used. With $L_2 = Cp_2, Cp^*_2$, thi$_2$ or *rac*-ebthi the "normal" reaction at the M−CSi bond to give the β-silyl-substituted titanafuranones was observed. With L_2 = *meso*-ebthi the opposite regioselectivity gives, after insertion into the M−CPh bond, the α-silyl-substituted titanacycle.

In all reactions investigated, the regioselectivity identified by X-ray crystal structure determination is consistent with the results of NMR investigations. In most reactions only one regioisomer was obtained. There are no hints of any cycloreversion leading to the "opposite" regioisomeric titanafuranone, as e.g. found in corresponding metallacyclic compounds.[4d][8]

Steric interactions seem to be the reason for the different regioselectivity and, after these considerations, the fixation of the tetrahydroindenyl units in a certain position by the *ansa* bridge is the most important feature in understanding the unusual regioselectivity for carbon dioxide insertion.

Experimental Section

General Remarks: All operations were carried out under argon with standard Schlenk techniques. Prior to use, solvents were freshly distilled from sodium tetraethylaluminate under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. − NMR: Bruker ARX 400 at 9.4 T (chemical shifts given in ppm relative to TMS; the signals of the aliphatic ebthi protons have not been analyzed). − Melting points: Sealed capillaries with a Büchi 535 apparatus. − Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of [meso-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] (**1**): 0.03 g (1.5 mmol) of magnesium cuttings and 0.34 ml (1.5 mmol) of bis(trimethylsilyl)acetylene were added to a suspension of 0.53 g (1.4 mmol) of [*meso*-(ebthi)TiCl$_2$] in 15 ml of THF. The mixture was stirred at 45°C until the color changed from red to black/brown. After that, the solution was stirred at room temp. for 2 h, the solvent removed in vacuo and the brown solid residue dissolved in 15 ml of *n*-hexane. After filtration and repeated removal of the solvent, brown/yellow needles of **1** crystallized from the oil at −78°C. The crystals were collected by filtration after washing with *n*-hexane at −78°C. Yield: 0.42 g (62%); m.p. 142−145°C. − ^{1}H NMR ([D$_6$]benzene): δ = −0.20 (s, 9 H, SiMe$_3$), 0.09 (s, 9 H, SiMe$_3$), 4.32 (d, ^3J = 3.0 Hz, 2 H, CH ebthi), 7.83 (d, ^3J = 3.0 Hz, 2 H, CH ebthi). − ^{13}C NMR ([D$_6$]benzene): δ = 1.1, 4.4 (SiMe$_3$), 23.5, 23.6, 24.4, 26.3, 26.7 (CH$_2$ ebthi), 113.8, 114.3 (CH ebthi), 122.7, 126.0, 129.0 (C ebthi), 242.1, 254.3 (C alkyne). − $C_{28}H_{42}Si_2Ti$ (482.7): calcd. C 69.67, H 8.77; found C 68.69, H 8.56. − IR (Nujol): ṽ = 1589 cm^{-1}.

Preparation of the Complexes [meso-(ebthi)Ti(η^2-Me_3SiC_2Ph)] (**2a** and **2b**): As described above for **1**, 0.37 g (0.96 mmol) of [*meso*-(ebthi)TiCl$_2$], 24 mg (1.0 mmol) of magnesium cuttings, and 0.20 ml (1.0 mmol) of phenyl(trimethylsilyl)acetylene yielded the red/brown alkynemetallocene complexes **2a** and **2b**, as indicated by both NMR and IR. The product was isolated in the same manner as described for **1**, but only a red brown oil was obtained which was a mixture (3:1) of the diastereomeric products **2a** (major) and **2b** (minor). Yield: 0.21 g of **2a** and **2b** (45%). − ^{1}H NMR ([D$_6$]benzene) of major isomer **2a**: δ = −0.02 (s, 9 H, SiMe$_3$), 4.88 (d, ^3J = 3.0 Hz, 2 H, CH ebthi), 6.6−7.5 (m, 5 H, Ph), 7.29 (d, ^3J = 3.0 Hz, 2 H, CH ebthi). − ^{1}H NMR ([D$_6$]benzene) of minor isomer **2b**: δ = 0.19 (s, 9 H, SiMe$_3$), 4.38 (d, ^3J = 3.0 Hz, 2 H, CH ebthi), 6.6−7.5 (m, 5 H, Ph), 7.44 (d, ^3J = 3.0 Hz, 2 H, CH ebthi). − ^{13}C NMR ([D$_6$]benzene) of major isomer **2a**: δ = 0.6 (SiMe$_3$), 23.4, 23.4, 23.7, 25.5, 27.3 (CH$_2$ ebthi), 112.1, 114.5 (CH ebthi), 122.5, 123.5, 125.2 (C ebthi), 127.6, 131.2 (CH Ph, *para* not found), 139.7 (C Ph), 220.1, 224.9 C(alkyne). − ^{13}C NMR([D$_6$]benzene) of minor isomer **2b**: δ = 3.9 (SiMe$_3$), 23.4, 23.8, 24.3, 25.9, 27.2 (CH$_2$ ebthi), 112.5, 113.2 (CH ebthi), 145.7 (C Ph, further ebthi and Ph signals not unambiguously identified), 210.3, 227.9 C(alkyne). − $C_{31}H_{38}SiTi$ (486.6): calcd. C 76.52, H 7.87; found C 76.04; H 7.72.

Preparation of [meso-(ebthi)Ti(THF)Cl] (**3**): The method used was as described above for **1** {starting with 0.31 g of [*meso*-(ebthi)TiCl$_2$]} but after the reaction a second extraction of the brown solid with 20 ml of THF yielded a dark blue solution, which was reduced to ca. 5 ml and stored at −30°C. After 72 h at −30°C, blue crystals (57 mg, 17%) formed, which were washed with cold *n*-hexane and isolated by filtration. M.p. decomposition, loss of THF in vacuo. − $C_{24}H_{32}ClOTi$ (419.9): calcd.C 68.66, H 7.68; found: C 68.02; H 7.63.

Preparation of [rac-(ebthi)Ti(η^2-Me_3SiC_2Ph)] (**4**): The method used was as described above for **1**. 0.32 g (0.84 mmol) of [*rac*-(ebthi)TiCl$_2$], 21 mg (0.86 mmol) of magnesium cuttings, and 0.17 ml (0.86 mmol) of phenyl(trimethylsilyl)acetylene yielded the alkynemetallocene complex **4**, which was isolated as a black oil. After standing for one week, the oil solidified as black crystals (0.29 g, 90%), which were washed with cold *n*-hexane (−30°C) to obtain analytical pure material, m.p. 156°C. − ^{1}H NMR ([D$_6$]benzene): δ = 0.15 (s, 9 H, SiMe$_3$), 4.23 (d, ^3J = 3.0 Hz, 1 H, CH ebthi), 4.54 (d, ^3J = 3.2 Hz, 1 H, CH ebthi), 6.66 (2 H, Ph *ortho*), 6.92 (1 H, Ph *para*), 7.07 (2 H, Ph *meta*), 8.10 (d, ^3J = 3.2 Hz, 1 H, CH ebthi), 8.50 (d, J = 3.0 Hz, 1 H, CH ebthi). − ^{13}C NMR ([D$_6$]benzene): δ = 2.1 (SiMe$_3$), 22.9, 23.2, 23.4, 23.7, 23.7, 23.9, 25.3, 25.3, 26.5, 26.6 (CH$_2$ ebthi), 111.7, 112.8, 113.8, 114.0 (CH ebthi), 128.0, 130.2 (CH Ph, *para* not found), 124.6, 124.8, 124.8, 126.0, 126.1, 127.5 (C ebthi), 141.2 (C Ph), 213.8, 220.8 C(alkyne). − $C_{31}H_{38}SiTi$ (486.6): calcd. C 76.52, H 7.87; found C 75.97, H 7.81. − IR (Nujol): ṽ = 1638 cm^{-1}.

Preparation of **5**: 0.48 g (1.0 mmol) of [*meso*-(ebthi)Ti(η^2-Me$_3$SiC$_2$SiMe$_3$)] was dissolved in a mixture of THF/*n*-hexane (3:1) (ca. 10 ml) which was exposed to CO$_2$. The color of the solution changed from red/brown to orange. After standing 24 h at −78°C, 0.37g (0.70 mmol, 70%) of red needles of complex **5** precipitated from the solution; m.p. > 240°C. − ^{1}H NMR ([D$_8$]THF): δ = 0.05 (s, 9 H, α-SiMe$_3$), 0.17 (s, 9 H, β-SiMe$_3$), 5.83 (d, ^3J = 3.1 Hz, 2 H, CH ebthi), 6.54 (d, ^3J = 3.1 Hz, 2 H, CH ebthi). − ^{13}C NMR ([D$_8$]THF): δ = 3.0, 3.6 (SiMe$_3$), 22.1, 22.9, 23.6, 24.7, 29.3 (CH$_2$ ebthi), 113.0, 115.3 (CH ebthi), 129.9, 132.5, 133.8 (C ebthi), 161.5, 171.7 (C$_β$ titanacycle), 264.9 (C$_α$ titanacycle). − $C_{29}H_{42}O_2Si_2Ti$ (526.7): calcd. C 66.13, H 8.03. found C 66.32, H 7.98. − IR (Nujol): ṽ = 1610 cm^{-1}.

Preparation of **6a**: 200 mg (0.41 mmol) of [*meso*-(ebthi)Ti(η^2-Me$_3$SiC$_2$Ph)] was dissolved in 10 ml of a mixture of THF/*n*-hexane (3:1) which was exposed to CO$_2$. The color of the solution changed from red/brown to orange. After standing 36 h at −30°C, light red crystals of **6a** crystallized from the solution which were then isolated by filtration to yield 137 mg (63%); m.p. >240°C. − ^{1}H NMR ([D$_8$]THF): δ = −0.25 (s, 9 H, SiMe$_3$), 5.86 (d, ^3J = 3.0 Hz, 2 H, CH ebthi), 6.66 (d, ^3J = 3.0 Hz, 2 H, CH ebthi), 7.08 (2 H, Ph *ortho*), 7.15 (3 H, Ph *meta*/*para*). − ^{13}C NMR ([D$_8$]THF): δ = 2.4 (SiMe$_3$), 22.1, 22.8, 23.8, 24.6, 29.4 (CH$_2$ ebthi), 112.8, 115.7 (CH ebthi), 130.0, 132.3, 133.4 (C ebthi), 126.5 (*p*-Ph), 127.3, 130.5 (CH Ph), 144.4 (*i*-Ph), 158.1 (*C*-Ph), 162.6 (CO), 237.4 (*C*-SiMe$_3$). − $C_{32}H_{38}O_2TiSi$ (530.62): calcd. C 72.43, H 7.22. found C 71.95, H 7.29. − IR (Nujol): ν̃ = 1240 cm^{-1}.

Preparation of **7**: 200 mg (0.43 mmol) of [(thi)$_2$Ti(η^2-Me$_3$Si-C$_2$Ph)][12] was dissolved in 5 ml of a mixture of THF/*n*-hexane (3:1) which was exposed to CO$_2$. The color of the solution changed from dark red to orange. After standing 24 h at 0°C, light red crystals crystallized from the solution. Filtration yielded 188 mg of **7** (87%); m.p. 185°C. − ^{1}H NMR ([D$_8$]THF): δ = −0.16 (s, 9 H, SiMe$_3$), 1.58 (m, 4 H, thi), 1.74 (m, 2 H, thi), 1.88 (m, 2 H, thi), 1.98 (ddd, ^2J = 16 Hz, ^3J = 5 and 7 Hz, 2 H, α-CH$_2$ thi), 2.47 (dt, ^2J = 16 Hz, ^3J = 6 Hz, 2 H, α-CH$_2$ thi), 2.77 (dt, ^2J = 17 Hz, ^3J = 6 Hz, 2 H, α-CH$_2$ thi), 2.92 (dt, ^2J = 17 Hz, ^3J = 6 Hz, 2 H, α-CH$_2$ thi), 5.20 (t, *J* = 3 Hz, 2 H, β-CH thi), 6.44 (dd, *J* = 2 and 3 Hz, 2 H, α-CH thi), 6.57 (dd, *J* = 2 and 3 Hz, 2 H, α-CH thi), 6.92 (2 H, Ph *ortho*), 6.97 (1 H, Ph *para*), 7.16 (2 H; Ph *meta*). − ^{13}C NMR ([D$_8$]THF): δ = 1.0 (SiMe$_3$) 22.8, 22.8, 25.3, 25.4 (CH$_2$ thi), 110.2, 111.8, 119.9 (CH thi), 124.9 (*o*-Ph), 125.5 (*p*-Ph), 128.2 (*m*-Ph), 131.4, 134.7 (C thi), 150.5 (*i*-Ph) 155.5 (*C*-SiMe$_3$), 164.8 (CO), 239.2 (*C*-Ph). − MS (70eV); *m/z* (%): 504.6 [M$^+$], 286 [(thi)$_2$Ti$^+$]. $C_{30}H_{36}O_2SiTi$ (504.6): calcd. C 71.41, H 7.19; found C 71.45, H 7.04.

Preparation of **8a**: As described above for **6a**, 143 mg [*rac*-(ebthi)$_2$Ti(η^2-Me$_3$SiC$_2$Ph)] yielded, after exposure to CO$_2$ and recrystallization from THF/*n*-hexane (1:1) (ca. 3 ml), 112 mg (72%) of **8a** as orange needles, m.p. 268°C (decomposition). − ^{1}H NMR ([D$_8$]THF) δ = −0.10 (s, 9 H, SiMe$_3$), 5.35 (d, ^3J = 2.8 Hz, 1 H, CH ebthi), 5.57 (d, ^3J = 3.2 Hz, 1 H, CH ebthi), 6.40 (d, ^3J = 3.2 Hz, 1 H, CH ebthi), 6.89 (2 H, Ph *ortho*), 7.07 (1 H, Ph *para*), 7.18 (2 H, Ph *meta*), 7.55 (d, ^3J = 2.8 Hz, 1 H, CH ebthi). − ^{13}C NMR ([D$_8$]THF): δ = 1.8 (SiMe$_3$), 21.6, 22.2, 22.3, 22.7, 23.9, 24.3, 24.3, 24.6, 28.7, 28.9 (CH$_2$ ebthi), 111.4, 114.7, 117.0, 123.3 (CH ebthi), 126.1, 129.7, 133.0, 133.8, 134.6, 136.2 (C ebthi), 126.9 (*p*-Ph), 127.9, 128.2 (CH Ph), 147.7 (*i*-Ph), 156.4 (*C*−SiMe$_3$), 164.6 (CO), 236.2 (*C*−Ph). − $C_{32}H_{38}O_2TiSi$ (530.62): calcd. C: 72.43, H: 7.22; found C: 72.04, H: 7.04.

Preparation of **9**: 344 mg (0.70 mmol) of [Cp*$_2$Ti(η^2-Me$_3$Si-C$_2$Ph)][4c] was dissolved in 15 ml of *n*-hexane under argon and the resulting solution filtered. Argon was then carefully removed in vacuo, and the flask with the solution filled with CO$_2$ at 20°C. After standing 24 h at 20°C, dark red crystals had formed, which were filtered, washed with cold *n*-hexane and dried in vacuo. Yield 266 mg of **9** (71%); m.p. 173−174°C. − ^{1}H NMR ([D$_8$]THF): δ = 0.01 (s, 9 H, SiMe$_3$), 1.86 (s, 30 H, C$_5$Me$_5$), 6.58 (m, 2 H, *o*-Ph), 7.04 (m, 1 H, *p*-Ph), 7.15 (m, 2 H, *m*-Ph). − ^{13}C NMR ([D$_8$]THF): δ = 2.0 (SiMe$_3$), 12.3 (C$_5$*Me*$_5$), 126.9 (*C*$_5$Me$_5$), 126.6 (*p*-Ph), 127.8 (*m*-Ph), 129.8 (*o*-Ph), 146.5 (*i*-Ph), 154.7 (*C*−SiMe$_3$), 166.1 (CO), 244.1 (*C*−Ph). − IR (Nujol): ν̃ = 1620 (CO), 1237 (SiMe$_3$) cm^{-1}. − MS (70eV); *m/z* (%): 537 [M$^+$]. − $C_{32}H_{44}O_2SiTi$ (536.7): calcd. C 71.62, H 8.62; found C 71.76, H 8.63.

X-ray Crystallographic Study of Complexes **3**, **6a**, *and* **7**: Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-86)[9] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93)[10]. The hydrogen atoms were included at calculated positions. All other nonhydrogen atoms were refined anisotropically. Cell constants and other experimental details were collected and are recorded in Table 1. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Further details of the crystal-structure investigations are available on request from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC-101470.

Table 1. Crystallographic data of **3**, **6a**, and **7**

	3	**6a**	**7**
cryst. color, habit	green, prism	red-orange, prism	red, prism
cryst. system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	*Pbca*
lattice constants			
a [Å]	8.161(1)	11.482(2)	15.027(3)
b [Å]	16.512(2)	16.295(2)	17.111(3)
c [Å]	15.114(2)	14.874(2)	20.612(4)
β [°]	97.370(11)	92.700(11)	
Z	4	4	8
T [K]	200(2)	293(2)	293(2)
μ(Mo-K_α) [mm^{-1}]	0.568	0.378	0.393
θ range [°]	1.83−24.34	1.85−24.33	1.98−24.33
no. of rflns. (measd.)	5942	8187	12238
no. of rflns. (indep.)	3235	4388	3564
no. of rflns. (obsd.)	2139	3272	2809
no. of parameters	244	325	307
*R*1 [$I > 2\sigma(I)$]	0.056	0.047	0.041
*wR*2 (all data)	0.165	0.128	0.119

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