Synthesis and Reactions with Carbon Dioxide of Mono(σ-alkynyl) Titanocene(III) Complexes Cp*₂Ti(C≡CR) (R = Me, *t*-Bu) and the Corresponding "Ate" Complexes [Cp*₂Ti(C≡CR)₂Li(THF)$_n$] (R = SiMe₃, *t*-Bu, Ph)

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The reactions of the titanium(III) complex Cp*₂TiCl with lithium acetylides RC≡CLi depend strongly on the solvents used. In THF only the lithium tweezer compounds [Cp*₂-Ti(C≡CR)₂Li(THF)$_n$] (Cp* = η^5-C₅Me₅; R = SiMe₃, $n = 1$ (**1**); R = *t*-Bu, $n = 1$ (**2**); R = Ph, $n = 2$ (**3**)), not the expected mono(σ-alkynyl) titanocene(III) complexes, were obtained, whereas in *n*-hexane these complexes Cp*₂Ti(C≡CR) were isolated for R = Me (**4**), *t*-Bu (**5**). The reaction of the complex [Cp*₂Ti(C≡CSiMe₃)₂Li(THF)] (**1**) with carbon dioxide results in the titanafuranone **6**, which presumably is formed by insertion of carbon dioxide into the η^2-butadiyne complex Cp*₂Ti(η^2-Me₃SiC≡CC≡CSiMe₃). The complex [Cp*₂Ti(C≡C-*t*-Bu)₂Li-(THF)] (**2**) reacts with carbon dioxide to yield the permethyltitanocene carboxylate Cp*₂Ti(O₂CC≡C-*t*-Bu) (**7**) via insertion into the σ-acetylide bond of the in situ formed titanium(III) intermediate [Cp*₂Ti−C≡C-*t*-Bu]. Compound **7** was also obtained in the reaction of the isolated titanium(III) complex Cp*₂Ti−C≡C-*t*-Bu (**5**) with carbon dioxide. The interaction of [Cp*₂Ti(C≡CPh)₂Li(THF)₂] (**3**) with carbon dioxide gives the stable bis(σ-acetylide) permethyltitanocene Cp*₂Ti(C≡CPh)₂ (**8**) without coupling of the σ-acetylide groups (as found for **1**) and without insertion into the σ-acetylide bond (as found for **2**). The syntheses and reactions of these compounds are compared to those of similar complexes of unsubstituted titanocene compounds. Complexes **1**, **5**, and **7** were investigated by X-ray crystal structure analysis.

Introduction

Do monomeric σ-alkynyl titanocene(III) complexes L₂-Ti(C≡CR) really exist? The answer to this question is of relevance in some catalytic reactions, and such a compound has never been structurally characterized. Teuben et al. investigated the reaction of [Cp₂TiCl]₂ with NaC≡CPh and did not obtain the expected monomeric complex [Cp₂TiC≡CPh] but rather a binuclear complex with a bridging butadiyne ligand, [Cp₂Ti]₂[μ-η^2(1,3): η^2(2,4)-PhC₂C₂Ph].[1] Since then, there has been, to the best of our knowledge, only one example of such a monomeric species: Cp*₂TiC≡CMe, reported as the product of the reaction of Cp*₂TiCl with LiC≡CMe, but without structural characterization.[2]

We became aware of the question of the synthesis of monomeric σ-alkynyl titanocene(III) complexes such as L₂Ti(C≡CSiMe₃) when we considered the mechanism of our recently described C−C single-bond metathesis of 1,4-disubstituted 1,3-butadiynes.[3] The interaction of butadiynes with titanocenes and zirconocenes can give, via metallacyclocumulenes,[4] a cleavage of, or a coupling

to butadiynes by, the metallocene cores.[4] The course of reaction can be formulated in such a way that the titanocene reacts with the diyne to give a dimeric complex which subsequently dissociates to produce the extremely unstable monomeric Ti(III) complex [Cp₂Ti-(σ-C≡CR)], which then dimerizes to either the respective starting complex or, in the desired way, to a differently substituted binuclear complex.[4] This view recently also was supported by dynamic NMR investigations in which we could show that dinuclear C−C-cleaved complexes, e.g., [Cp₂Ti]₂[(μ-C≡CSiMe₃)(μ-C≡C-*t*-Bu)] very likely are present in solutions of the uncleaved complexes [Cp₂-Ti]₂[μ-η^2(1,3):η^2(2,4)-*t*-BuC₂−C₂SiMe₃].[5] With regard to the metal compound Cp₂Ti(Me₃SiC≡CSiMe₃) that is used as the titanocene source, this metathesis could not be conducted catalytically, because an excess of the diyne favors, instead of the cleavage, the coupling reactions of diynes. This makes the complexes with

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coupled diyne, e. g., titanacyclopentadienes, dominant in the product range. It is well-known that sterically demanding ligands prevent undesired coupling reactions of the substrates. We therefore replaced the cyclopentadienyl ligand (Cp) in our starting compounds by the pentamethylcyclopentadienyl ligand (Cp*).[6] Because the unstable monomeric Ti(III) complexes [Cp$_2$Ti(σ-C≡CR)] are assumed to play such an important role in the reaction sequence of our metathesis reaction, we were interested in synthesizing the corresponding permethyltitanocene complexes Cp*$_2$Ti(σ-C≡CR).

Additionally, species such as L$_2$Ti(C≡CSiMe$_3$) could also be important in catalytic oligomerization reactions of 1-alkynes.[7] Cleavage of Me$_3$SiC≡CC≡CSiMe$_3$ by the system Cp$_2$TiCl$_2$/magnesium gives the dimeric titanium-(III) complex [Cp$_2$Ti(C≡CSiMe$_3$)]$_2$.[8] The system Cp*$_2$-TiCl$_2$/magnesium/Me$_3$SiC≡CC≡CSiMe$_3$ under the same conditions, via cleavage of the central C−C single bond of the diyne and coupling of the acetylide with another diyne, yields the complex Cp*$_2$Ti[μ-η^2(1,2):η^1(3)-Me$_3$-SiC≡CC=C(SiMe$_3$)C≡CSiMe$_3$], displaying a hex-3-ene-1,5-diyn-3-yl ligand.[9] The initial formation of the mono-(alkynyl)titanium(III) complex L$_2$Ti(C≡CSiMe$_3$) in both systems is assumed, which for L = Cp dimerizes quickly to [Cp$_2$Ti(C≡CSiMe$_3$)]$_2$. Alternatively for R = Cp*, it can react with a diyne to yield the complex Cp*$_2$Ti[μ-η^2(1,2):η^1(3)-Me$_3$SiC≡CC=C(SiMe$_3$)C≡CSiMe$_3$]. The Cp* ligands prevent dimerization of the mono(alkynyl) complexes.

We report here that the expected complexes Cp*$_2$Ti-(σ-C≡CR) (R = Me, t-Bu) were obtained by the salt elimination reaction of Cp*$_2$TiCl with LiC≡CR in n-hexane, whereas in THF with R= Ph, t-Bu, SiMe$_3$ the titanium(III) "ate" complexes [Cp*$_2$Ti(C≡CR)$_2$Li(THF)$_n$] were formed. These complexes are compared with [Cp$_2$Ti(C≡C-t-Bu)$_2$Li(THF)$_2$] in the reactions with carbon dioxide.

Results and Discussion

Reactions of the Permethyltitanocene Complexes. The reactions of the titanium(III) complex Cp*$_2$-TiCl with lithium acetylides RC≡CLi depend strongly on the solvents used. In THF the expected Cp*$_2$Ti(C≡CR) complexes could not be prepared by reacting Cp*$_2$-TiCl with 1 or 2 equiv of RC≡CLi. Only the lithium tweezer compounds [Cp*$_2$Ti(C≡CR)$_2$Li(THF)$_n$] (Cp* = η^5-C$_5$Me$_5$; R = SiMe$_3$, n = 1 (**1**), R = t-Bu, n = 1 (**2**); R = Ph, n = 2 (**3**)) were isolated (Scheme 1).

These results are in good agreement with recent results of Mach et al. in studies of similar systems.[10a] Whether the "ate" complexes are thermodynamic or kinetic products was a question of interest. Their

formation in THF does not depend on the experimental procedure: adding the Cp*$_2$TiCl to an excess of RC≡CLi or vice versa. Also, warming of the mixtures for some time gave no different results.

Scheme 1


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1 : R = SiMe₃, n = 1
2 : R = tBu, n = 1
3 : R = Ph, n = 2
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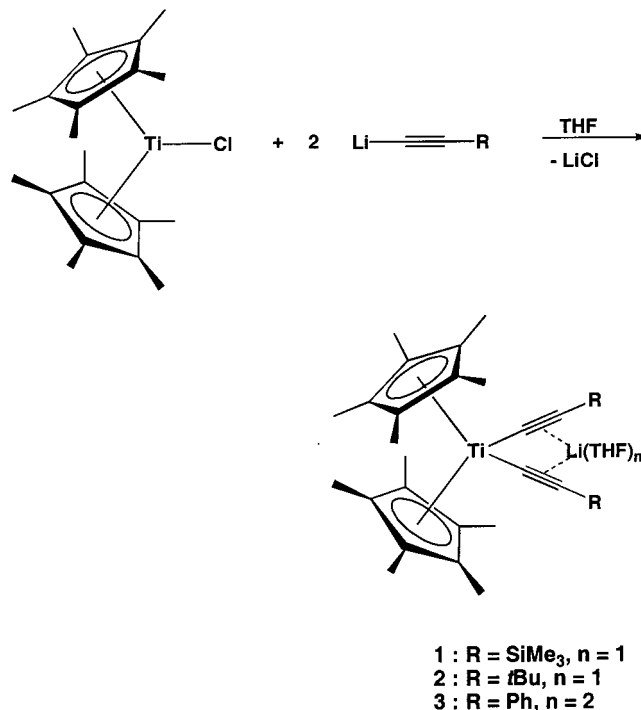
Complexes of the type [L$_2$Ti(C≡CR)$_2$ML$_n$], with M = alkali metal, are very rare in the titanocene system.[11] There are only a few examples of partially methylated analogues such as [(Me$_4$HC$_5$)$_2$Ti(C≡CSiMe$_3$)$_2$M(THF)$_n$] (M = Li, Na, K, Cs) that were prepared by the reaction of (Me$_4$HC$_5$)$_2$Ti(C≡CR)$_2$ complexes with alkali metals[12a,b] and the complex [(Me$_4$HC$_5$)$_2$Ti(C≡CC≡CSiMe$_3$)$_2$Li-(THF)$_2$] synthesized from (Me$_4$HC$_5$)$_2$TiCl and LiC≡CC≡CSi-Me$_3$.[12c] They were reported also for permethylmetallocene systems; e.g., the complex [Cp*$_2$Ti(C≡CSiMe$_3$)$_2$-MgCl(THF)] was prepared by the scission of Me$_3$SiC≡CC≡CSiMe$_3$ by the system Cp*$_2$TiCl$_2$ and magnesium.[10] Complexes **1**−**3** are extremely sensitive to air and moisture. They are readily soluble in n-hexane and more so in THF and toluene. As titanium(III) complexes they are paramagnetic. In their IR spectra the absorptions due to the complexed triple bond are in the same range (e.g., **1**: 1954 cm^{-1}) as those of the partially methylated analogues that contain the same alkynyl substituent R = Me$_3$Si, [(Me$_4$HC$_5$)$_2$Ti(C≡CSiMe$_3$)$_2$M(THF)$_n$] (M = Li, 1948 cm^{-1}; M = Na, 1945 cm^{-1}; M = K, 1944 cm^{-1}; M = Cs, 1948 cm^{-1}).[12a,b] For R = t-Bu, compared to the free complex (Cp*$_2$Ti(C≡CR)$_2$, 2075 cm^{-1} [6b]), the coordination shift for **2** (2030 cm^{-1}) is in the typical range.

The X-ray crystal structure of complex **1** confirmed the connectivity shown in Scheme 1.

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Conducting the reactions of $Cp*_2TiCl$ with acetylides $RC\equiv CLi$ in *n*-hexane for R = Ph and $SiMe_3$ gave only mixtures of complexes, but for R = Me (**4**) and *t*-Bu (**5**) the well-defined titanium(III) complexes $Cp*_2Ti(C\equiv CR)$ were isolated (Scheme 2).

Scheme 2

4 : R = Me
5 : R = *t*Bu
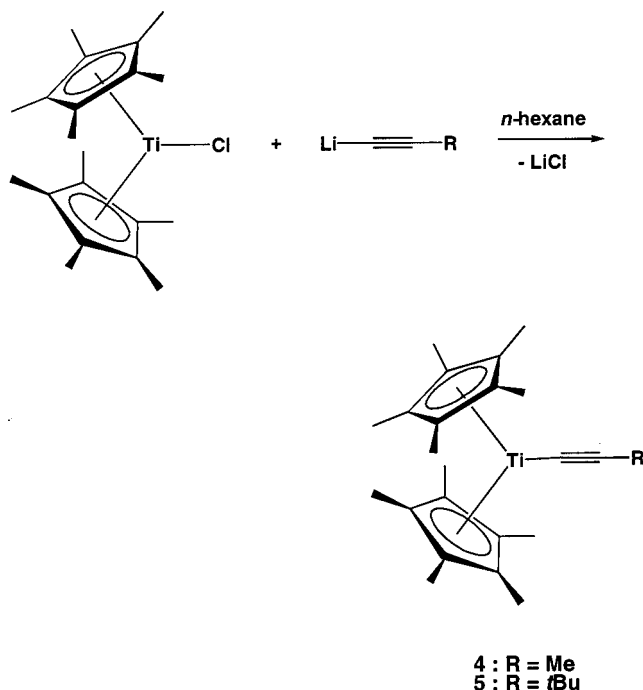
Complexes **4** and **5** are extremely sensitive to air and moisture. As mentioned above, complex **4** was reported earlier, but not its structure.[2] Both complexes are soluble in *n*-hexane and very soluble in THF and toluene. The paramagnetic titanium(III) complexes show in their infrared spectra the absorptions due to the triple bond in the expected range (e.g. **4**, 2080 cm^{-1};[2] **5**, 2071 cm^{-1}).

Scheme 3
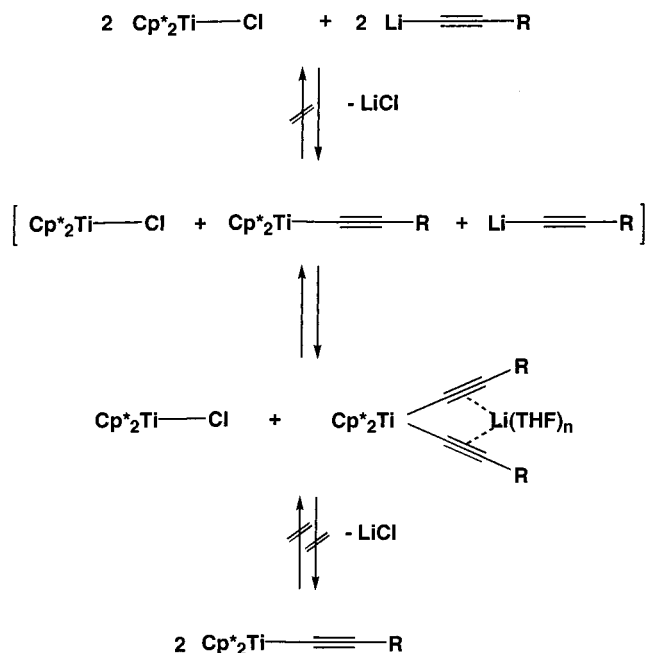
Complex **5** was investigated by X-ray diffraction. It is the first example of the structure of a monomeric titanocene(III) monoacetylide (see below).

For the formation of the "ate" complexes instead of the titanium(III) monoacetylides according to Scheme 1, one can assume that the reaction of $Cp*_2TiCl$ with 2 equiv of $LiC\equiv CR$ gives the tweezer "ate" complexes $[Cp*_2Ti(C\equiv CR)_2Li(THF)_n]$ together with unreacted $Cp*_2$-TiCl. In THF, possibly due to kinetic reasons, the reaction stops here. On the other hand, it seems more likely that $LiC\equiv CR$ reacts more rapidly with the initially formed $Cp*_2Ti(\sigma\text{-}C\equiv CR)$ than with $Cp*_2TiCl$ (Scheme 3).

Starting from complexes **1**–**3**, we were interested in preparing the monomeric Ti(III) monoacetylides $Cp*_2$-$Ti(\sigma\text{-}C\equiv CR)$ by dissociation of $LiC\equiv CR$ and in their subsequent reactions with substrates. Additionally we tried to prepare the corresponding Ti(IV) diacetylides $Cp*_2Ti(\sigma\text{-}C\equiv CR)_2$ by oxidation with oxygen and elimination of lithium oxides. These complexes can give by coupling of the alkynyl units the five-membered titanacyclocumulenes $Cp*_2Ti(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$.[3,4] Such an oxidation by air is a well-established method of preparing titanium(IV) complexes starting from titanium(III) "ate" complexes.[13]

However, in all conducted experiments such an alkynyl coupling was found only for complex **1** (Scheme 4): the reaction with an excess of carbon dioxide leads to the well-known titanafuranone **6**,[6a,14] which presumably is formed by insertion of carbon dioxide into the η^2-butadiyne complex $[Cp*_2Ti(\eta^2\text{-}1,2\text{-}Me_3SiC\equiv CC\equiv CSiMe_3)]$ (Scheme 4).[6a,14]

This η^2-butadiyne complex was prepared and isolated before by two different methods, the reduction of $Cp*_2$-$TiCl_2$ by magnesium in the presence of $Me_3SiC\equiv CC\equiv CSiMe_3$ and, additionally, by irradiation of isolated $Cp*_2Ti(C\equiv CSiMe_3)_2$.[6a] It seems reasonable to assume an oxidation from Ti(III) to Ti(IV) by carbon dioxide, similar to what has been found when employing oxygen from air,[13] which was excluded carefully in our experiments described herein. Complex **6** was formed in a yield of only 40%, in addition to a mixture of unidentified side products. This can be ascribed to the three different steps of the formation of **6** (oxidation, coupling, insertion), not all proceeding quantitatively altogether. The data of the titanafuranone **6**, obtained by reaction of **1** with carbon dioxide, are identical with those of samples obtained by reactions of $[Cp*_2Ti(\eta^2\text{-}1,2\text{-}Me_3\text{-}SiC\equiv CC\equiv CSiMe_3)]$ with carbon dioxide.[6a,14]

The complex $[Cp*_2Ti(C\equiv C\text{-}t\text{-}Bu)_2Li(THF)]$ (**2**) reacts with carbon dioxide to give the permethyltitanocene carboxylate $Cp*_2Ti(O_2CC\equiv C\text{-}t\text{-}Bu)$ **7** (Scheme 5), via insertion into the σ-acetylide bond of the assumed titanium(III) intermediate $Cp*_2TiC\equiv C\text{-}t\text{-}Bu$, which could be formed by the dissociation of complex **2**.

Complex **7** could be also prepared by reacting the isolated complex **5** with carbon dioxide (Scheme 6).

A similar compound, $Cp*_2TiO_2CH$, was obtained by Teuben et al.[2] in the salt elimination reaction of $Cp*_2$-TiCl and NaO_2CH and, alternatively, by the carbon dioxide insertion and a subsequent olefin elimination of $Cp*_2TiCH_2CH_2R$.[15]

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Scheme 4

1

+ 2 CO$_2$
- [Li]
- THF

6

+ CO$_2$ - [Li]
- THF

+ CO$_2$
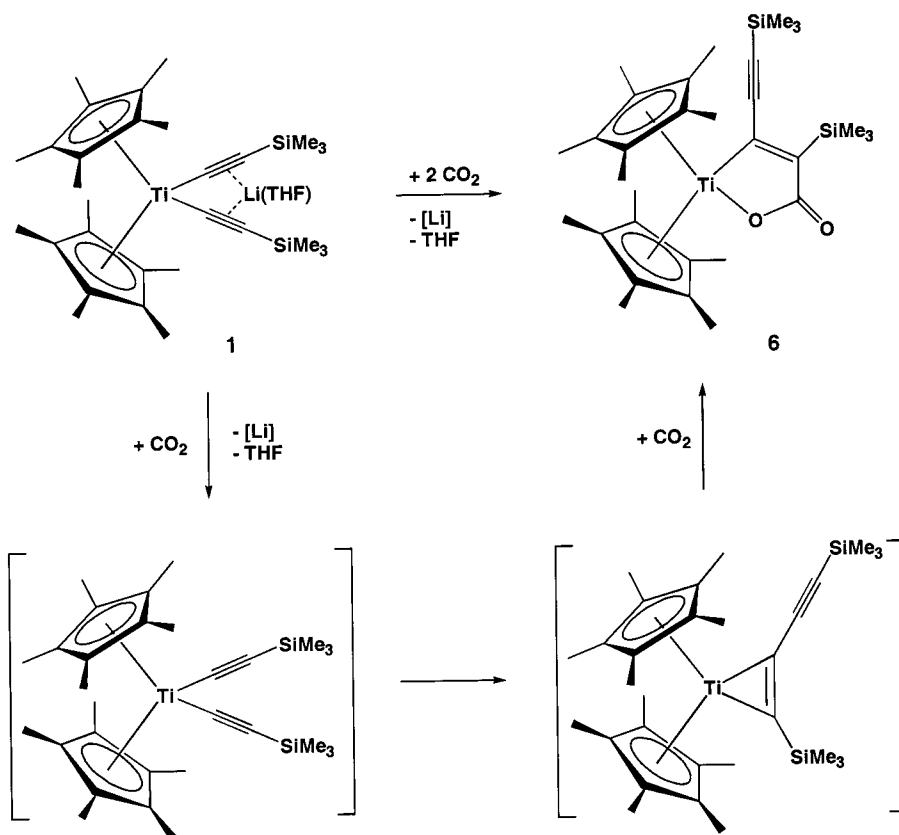
Under an atmosphere of carbon dioxide the titanium-(III) "ate" complex [Cp*$_2$Ti(C≡CPh)$_2$Li(THF)$_2$] **3** reacts, without any coupling as found for **1** and **2**, to the titanium(IV) bis(acetylide) Cp*$_2$Ti(C≡CPh)$_2$ (**8**) (Scheme 7).

The yield of complex **8** was only 32%, the rest being a mixture of unidentified further products. The titanium is oxidized during the reaction from Ti(III) to Ti(IV) by carbon dioxide, as found in the reaction of **1** to **6**. Again air was excluded carefully. The salt elimination reaction from Cp*$_2$TiCl and LiO$_2$CC≡CR, according to Teuben et al.,[17] worked also very well to prepare complex **9** (R = Ph, Scheme 8), similarly as found for complex **7** (R = *t*-Bu), but failed for R = SiMe$_3$.

The comparison of the reactions of **1**–**3** with carbon dioxide illustrates the fact that the stability of the bis-(acetylides) depends on the substituents. Compounds **1** and **3** initially are oxidized followed by an insertion of carbon dioxide into the intermediates, as shown in the

reaction of **1**. Complex **2** reacts directly, after dissociation and without being oxidized, with carbon dioxide.

Motivated by these results in the reactions of the "ate" complexes **1**–**3** with carbon dioxide, which are strongly differentiated by the substituents R used, the corresponding reactions of the unsubstituted Cp analogues and of similar compounds were considered as well.

Reactions of Related Titanocene Complexes. The Ti(IV) complex Cp$_2$Ti(C≡CSiMe$_3$)$_2$[8] very easily gives, upon standing under an atmosphere of argon, a reduction to the diyne Me$_3$SiC≡CC≡CSiMe$_3$ together with the well-known dimeric diamagnetic Ti(III) compound [Cp$_2$-Ti(C≡CSiMe$_3$)]$_2$.[8] The same reaction is observed under carbon dioxide. Neither a η^2 complex of the formed diyne nor a compound incorporating carbon dioxide is formed, as found for the corresponding pentamethylcyclopentadienyl complex.

When using the unsubstituted Cp compound [Cp$_2$Ti-

Scheme 5

2

- THF

+ 2 CO$_2$

7

+

Li———*t*Bu

+

LiO$_2$C———*t*Bu

Scheme 6

5

7
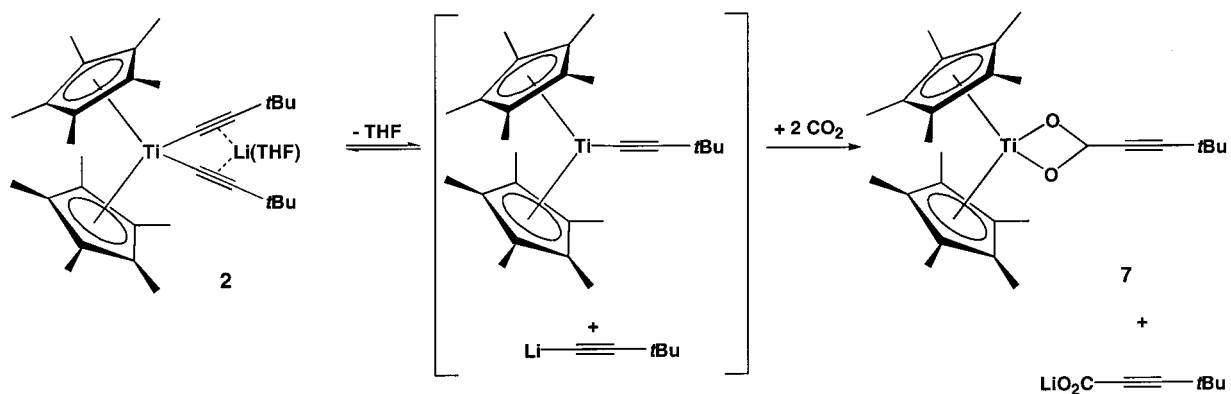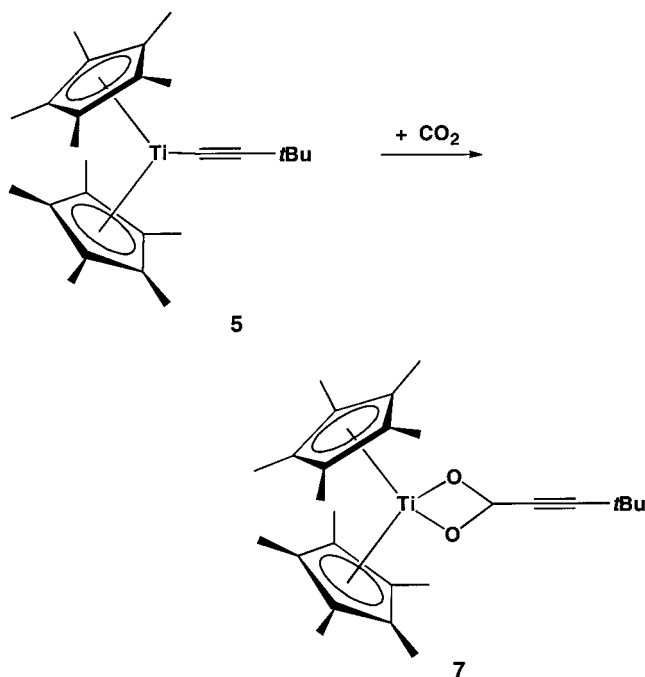
(C≡C-*t*-Bu)$_2$Li(THF)$_2$], which corresponds to the Cp* complex **2**, in the reaction with carbon dioxide at room temperature, no insertion product such as complex **7** was observed. Instead, a binuclear complex with a bridging butadiyne, [Cp$_2$Ti]$_2$[μ-η^2(1,3):η^2(2,4)-*t*-BuC$_2$C$_2$*t*-Bu],[16] was obtained (Scheme 9).

Scheme 7

3

8
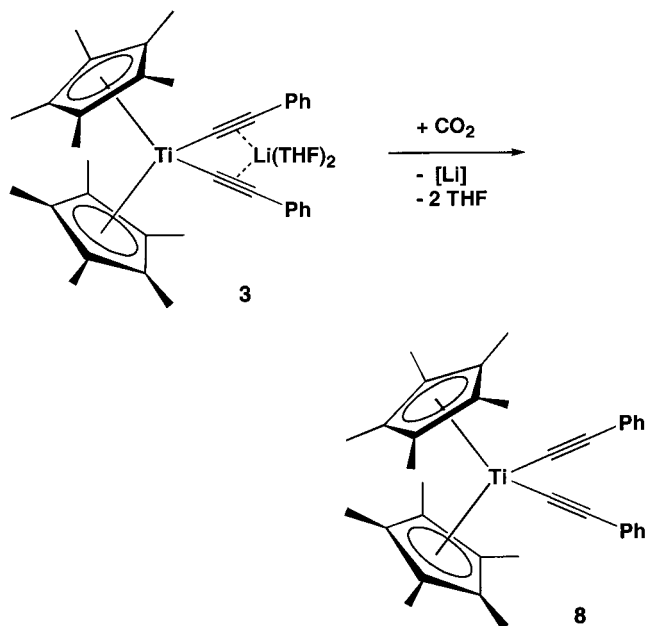
This complex previously has been prepared by the reaction of *t*-BuC≡CC≡C-*t*-Bu with 2 equiv of "Cp$_2$Ti"[16a] or by the dimerization of the titanium(III) complex [Cp$_2$-TiC≡C-*t*-Bu].[17] The different reactions of the titanocene complex [Cp$_2$Ti(C≡C-*t*-Bu)$_2$Li(THF)$_2$] and the above-mentioned permethyltitanocene complex [Cp*$_2$Ti(C≡C-*t*-Bu)$_2$Li(THF)] (**2**) with carbon dioxide may result from different stabilities and reactivities of the titanium(III) species Cp$_2$TiC≡C-*t*-Bu and Cp*$_2$TiC≡C-*t*-Bu. After

dissociation, the lifetime of the Cp complex is too short to give a reaction with carbon dioxide. An alternative reasoning point could be that the Ti−C bond is more activated in the case of Cp*$_2$Ti(C≡C-*t*-Bu).

In all of these reactions the influence of the substituents on the reactions of the complexes [Cp*$_2$Ti(C≡CR)$_2$Li(THF)$_n$] (R = SiMe$_3$ (**1**), *t*-Bu (**2**), Ph (**3**)) with carbon dioxide is well documented. Additionally, the influence of the ligands Cp and Cp*, used in these and other similar systems, can be compared.

Structural Investigations. The complex [(Cp*$_2$Ti-(C≡CSiMe$_3$)$_2$Li(THF)] (**1**) was investigated by X-ray diffraction.[18] However, the poor quality of the crystals made it impossible to discuss bond lengths and angles in detail. Nevertheless, connectivity has been established. The same applies to the complex [Cp$_2$Ti(C≡C-*t*-Bu)$_2$Li(THF)$_2$].[19] Interestingly, the Cp* compound **1** contains only one THF molecule coordinated to the lithium, while there are two for the Cp analogue. Steric interactions between the THF molecules and the Cp* ligands seem to be obvious reasons for this observation. Still, the comparable complex [(η^5-C$_5$HMe$_4$)$_2$Ti(C≡CSiMe$_3$)Li(THF)$_2$] contains two THF ligands again.[12d]

The complexes Cp*$_2$Ti(C≡C-*t*-Bu) (**5**) and Cp*$_2$Ti(O$_2$-CC≡C-*t*-Bu) (**7**) were also investigated by X-ray diffraction. Table 1 lists crystallographic data. The molecular structures are shown in Figures 1 and 2.

The structure of complex **5** consists of a bent metallocene in which the titanium atom is coordinated by the midpoints of the pentamethylcyclopentadienyl rings and the carbon atom of the acetylide unit. The Ti−C bond length in the alkynyl complex **5** (2.108(6) Å) is shorter than that found in the corresponding alkyl compound Cp*$_2$Ti(CH$_2$-*t*-Bu) (2.231(5) Å).[2]

The structure of complex **7** consists of a bent metallocene in which the titanium atom is tetracoordinated by the midpoints of the pentamethylcyclopentadienyl rings and the two carboxylate oxygens. The TiO bond lengths (Ti−O1 = 2.178(2) Å, Ti−O2 = 2.185(3) Å) are longer compared to those in complex Cp*$_2$TiO$_2$COTiCp*$_2$,[20] where distances between 2.144(4) and 2.151(4) Å are found.

The triple bonds are different in both molecules (**5**, 1.204(6) Å; **7**, 1.173(5) Å). The shortening in **7** is very likely caused by the influence of the carboxylate groups. The triple bond is, as expected, almost linear in both

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(17) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem.* **1996**, *108*, 1175; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112.

(18) Crystal data for **1** (crystals were obtained from a solution of *n*-hexane/THF): 0.3 × 0.2 × 0.2 mm, dark red prisms, space group *Cmc*2$_1$, orthorhombic, *a* = 12.969(3) Å, *b* = 16.121(3) Å, *c* = 18.053(4) Å, *V* = 3774(1) Å^3, *Z* = 4, ρ_{obsd} = 1.041 g cm^{-3}, 5543 reflections measured, 1653 were independent of symmetry, of which 1034 were observed (*I* ≥ 2σ(*I*)), R1 = 0.095, wR2(all data) = 0.310, 131 parameters. The Cp* ligands, the SiMe$_3$ groups, and the coordinated THF molecule are disordered.

(19) Crystal data for [Cp$_2$Ti(C≡C-*t*-Bu)$_2$][Li(THF)$_2$] (crystals were obtained from a solution of *n*-hexane/THF): 0.2 × 0.1 × 0.1 mm, brown prisms, space group *P*2$_1$/*c*, monoclinic, *a* = 10.761(1) Å, *b* = 17.698(2) Å, *c* = 30.727(3) Å, *β* = 92.287(9)°, *V* = 5847.2(10) Å^3, *Z* = 4, ρ_{obsd} = 1.117 g cm^{-3}, 7638 reflections measured, 7174 were independent of symmetry, of which 4176 were observed (*I* ≥ 2σ(*I*)), R1 = 0.079, wR2 (all data) = 0.327, 614 parameters.

(20) Burlakov, V. V.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T.; Shur, V. B.; Rosenthal, U.; Thewalt, U. *J. Organomet. Chem.* **1996**, *522*, 241.

Scheme 8

7: **R** = *t*Bu
9: **R** = Ph
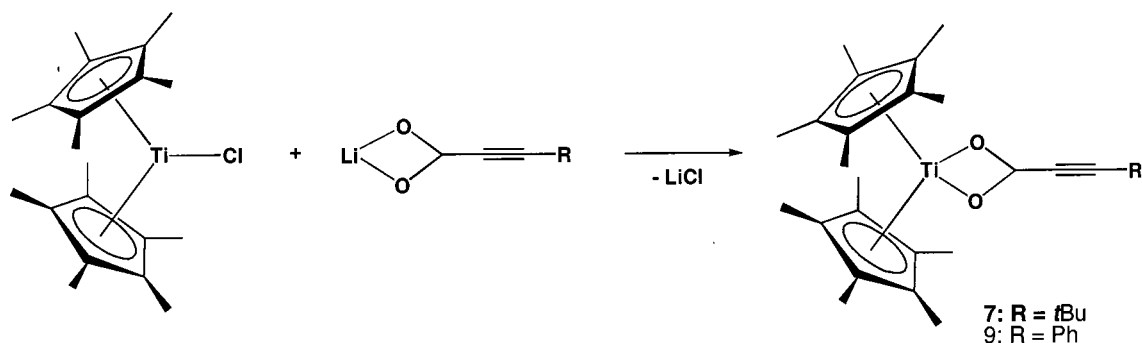
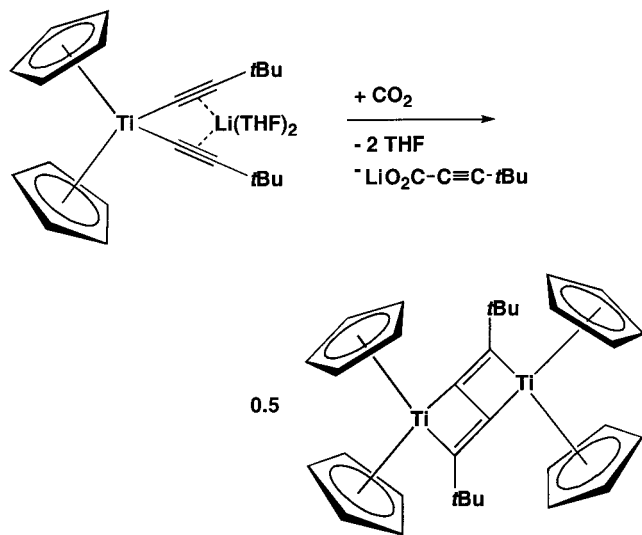complexes (**7**, C21−C22−C23 = 175.5(5)°; **5**, Ti−C13−C14 = 176.1(5)°, C13−C14−C15 = 177.8(5)°).

Conclusions

The course of the reaction of Cp*$_2$TiCl with lithium acetylides is governed by the solvents used. The Ti(III) complexes Cp*$_2$Ti(σ-C≡CR) are formed only in *n*-hexane. In THF the corresponding "ate" complexes [Cp*$_2$-Ti(C≡CR)$_2$Li(THF)$_n$] were obtained.

The reactions of the titanocene complex [Cp$_2$Ti(C≡C-*t*-Bu)$_2$Li(THF)$_2$] and the corresponding permethylti-tanocene complex [Cp*$_2$Ti(C≡C-*t*-Bu)$_2$Li(THF)] (**2**) with carbon dioxide epitomize the different stabilities and

Scheme 9

Table 1. Crystallographic Data of 5 and 7

	5	7
cryst color, habit	brown, prism	green, prism
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$
lattice constants		
a (Å)	14.556(3)	10.192(2)
b (Å)	12.015(2)	9.713(2)
c (Å)	14.685(3)	14.011(3)
β (deg)	108.45(3)	110.14(3)
Z	4	2
cell vol (Å^3)	2436.3(8)	1302.2(5)
density (g cm^{-3})	1.089	1.131
temp (K)	200(2)	293(2)
μ(Mo Kα) (mm^{-1})	0.358	0.347
no. of rflns (measd)	7157	7039
no. of rflns (indep)	3734	4121
no. of rflns (obsd)	1743	3499
no. of params	241	269
R1($I > 2\sigma(I)$)	0.066	0.044
wR2(all data)	0.167	0.113

reactivities of the Ti(III) intermediates [Cp$_2$TiC≡C-*t*-Bu] and Cp*$_2$TiC≡C-*t*-Bu, formed by dissociation of the starting materials. Only the permethyltitanocene com-plex Cp*$_2$TiC≡C-*t*-Bu could be isolated in *n*-hexane, and it was trapped in THF in the reaction of **2** with carbon dioxide by isolating Cp*$_2$Ti(O$_2$CC≡C-*t*-Bu) (**7**). The lifetime of the corresponding titanocene derivative [Cp$_2$-TiC≡C-*t*-Bu] is shorter, and it seems to be so unstable
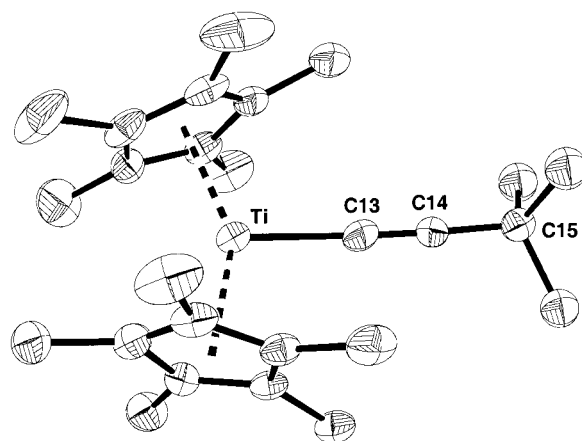

Figure 1. ORTEP view of **5** (30% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the second part of the disordered *t*-Bu group have been omitted. Selected bond lengths (Å) and angles (deg): Ti−C13 = 2.108(6), C13−C14 = 1.204(6), C14−C15 = 1.474(7); Ti−C13−C14 = 176.1-(5), C13−C14−C15 = 177.8(5).
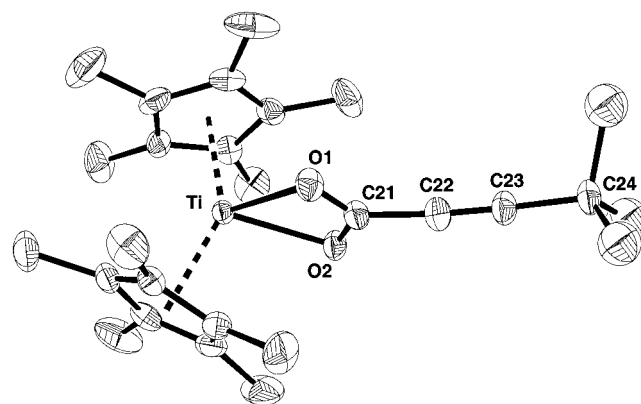

Figure 2. ORTEP view of **7** (30% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the second part of the disordered *t*-Bu group have been omitted. Selected bond lengths (Å) and angles (deg): Ti−O1 = 2.178(2), Ti−O2 = 2.185(3), C21−C22 = 1.471(5), C22−C23 = 1.173(5), C21−O1 = 1.257(4), C21−O2 = 1.256(4); O1−Ti−O2 = 59.94(9), O1−C21−O2 = 120.3(3), Ti−C21−C22 = 177.8(3), C21−C22−C23 = 175.5(5).

that it dimerizes very quickly with formation of [Cp$_2$-Ti]$_2$[μ-η^2(1,3):η^2(2,4)-t-BuC$_2$C$_2$$t$-Bu] before reacting with carbon dioxide.

An additional observation which supports these conclusions comes from the cleavage of Me$_3$SiC≡CC≡CSiMe$_3$ in the system Cp$_2$TiCl$_2$/magnesium, which gives the dimeric titanium(III) complex [Cp$_2$Ti(C≡CSiMe$_3$)]$_2$.[8] The system Cp*$_2$TiCl$_2$/magnesium/Me$_3$SiC≡CC≡CSiMe$_3$ yields, via a cleavage of the central C−C single bond of the diyne and coupling with another diyne, the complex Cp*$_2$Ti[μ-η^2(1,2):η^1(3)-Me$_3$SiC≡CC=C(SiMe$_3$)C≡CSiMe$_3$].[9] In both cases the formation of mono(alkynyl)-titanium(III) complexes L$_2$Ti(C≡CSiMe$_3$) is assumed, which for L = Cp dimerizes quickly to [Cp$_2$Ti(C≡CSiMe$_3$)]$_2$ or alternatively for R = Cp* can insert an diyne to yield the complex Cp*$_2$Ti[μ-η^2(1,2):η^1(3)-Me$_3$SiC≡CC=C(SiMe$_3$)C≡CSiMe$_3$].

In both of the described examples the Cp* ligands stabilize the mono(alkynyl) complexes and prevent their dimerization.

Experimental Section

All operations were carried out under an inert atmosphere (argon) using 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. Infrared spectra were recorded with a Nicolet Magna 550 (Nujol mulls using KBr plates). Mass spectrometer: AMD 402 (EI: electron impact measurements). NMR: Bruker ARX 400 at 9.4 T (chemical shifts given in ppm relative to TMS). Melting points were measured in sealed capillaries on a Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of [Cp*$_2$Ti(C≡CSiMe$_3$)$_2$Li(THF)] (1). A 0.86 mL amount (6.2 mmol) of trimethysilylacetylene was dissolved in 5 mL of THF. The colorless solution was cooled to −78 °C, and 2.48 mL (6.2 mmol) of n-butyllithium (2.5 M/n-hexane) was added. After the mixture was warmed to room temperature, 1.1 g (3.1 mmol) of Cp*$_2$TiCl was added and the deep blue solution was stirred for 24 h. The solvents were distilled in vacuo, and the brown residue was suspended in 10 mL of n-hexane. After filtration and crystallization at −78 °C, 0.980 g (54%) of **1** was obtained, which was filtered and dried in vacuo: brown crystals; mp >265 °C. Anal. Calcd for C$_{34}$H$_{56}$LiOTiSi$_2$ (591.81): C, 69.00; H, 9.54. Found: C, 68.66; H, 9.19. IR (Nujol; ν (cm^{-1})): 1954 vs, 1922 sh, 1243 vs, 1036 s, 882 sh, 837 vs, 755 s, 691 s. MS (70 eV; m/z (u)): 519 [M − THF]$^+$, 512 [M − THF]$^+$, 415 [M − LiTHF − C$_2$SiMe$_3$]$^+$, 318 [Cp*$_2$-Ti]$^+$.

Preparation of [Cp*$_2$Ti(C≡C-t-Bu)$_2$Li(THF)] (2). A solution of 1.30 mL of 3,3-dimethylbutyne-2 (10.6 mmol) in 15 mL of THF was cooled to −78 °C and treated with 4.24 mL (10.6 mmol) n-butyllithium (2.5 M/n-hexane). After 15 min the solution was warmed to room temperature and 1.89 g (5.3 mmol) of Cp*$_2$TiCl was added. The solution was stirred for 24 h, the solvent was removed in vacuo, and the residue was suspended in 10 mL of n-hexane. After filtration and crystallization at −78 °C, 2.001 g (68%) of green crystals was obtained, which was filtered and dried in vacuo: mp 178−179 °C. Anal. Calcd for C$_{36}$H$_{56}$LiOTi (559.66): C, 77.26; H, 10.09. Found: C, 77.24; H, 9.85. IR (Nujol; ν (cm^{-1})): 2030 s, 1237 vs, 1199 m, 1036 s, 883 m. MS: (70 eV; EI m/z (u)): 399 [M − LiTHF − C$_2$-t-Bu]$^+$, 318 [Cp*$_2$Ti]$^+$.

Preparation of [Cp*$_2$Ti(C≡CPh)$_2$Li(THF)$_2$] (3). A solution of 0.30 mL of phenylacetylene (2.7 mmol) in 15 mL of THF was cooled to −78 °C and treated with 1.1 mL (2.7 mmol) of n-butyllithium (2.5 M/n-hexane). After 15 min the solution was

warmed to room temperature and 0.477 g (1.35 mmol) of Cp*$_2$-TiCl was added. The solution was stirred for 24 h, the solvent was removed in vacuo, and the residue was suspended in 10 mL of n-hexane. After filtration and crystallization at −78 °C, 0.560 g (63%) of blue crystals was obtained, which was filtered and dried in vacuo: mp >270 °C. Anal. Calcd for C$_{44}$H$_{56}$LiO$_2$-Ti (671.75): C, 78.67; H, 8.40. Found: C, 78.55; H, 8.19. IR (Nujol; ν (cm^{-1})): 2013 s, 1591 m, 1585 m, 1038 m, 1025 m, 890 m, 688 m. MS (70 eV; EI m/z (u)): 671 [M]$^+$, 520 [M − 2LiTHF]$^+$, 419 [M − 2LiTHF − C$_2$Ph]$^+$, 318 [Cp*$_2$Ti]$^+$.

Preparation of Cp*$_2$Ti(C≡CMe) (4). A 0.70 mL amount (1.74 mmol) of n-butyllithium (2.5 M/n-hexane) was dissolved in 10 mL of n-hexane under Ar. The argon was carefully removed in vacuo, and the flask was filled with propyne. The solution was stirred for 1 h at room temperature, and the resulting suspension was slowly added to the deep blue solution of 0.617 g (1.74 mmol) of Cp*$_2$TiCl in 10 mL of n-hexane. The mixture was stirred for 2.5 h, and the resulting brown-green solution was concentrated to 7−8 mL. After filtration and 1 day at −78 °C, 0.411 g (66%) of dark green complex **4** had formed, which was separated from the mother liquor, washed with cold n-hexane, and dried in vacuo: mp 163−165 °C. Anal. Calcd for C$_{23}$H$_{33}$Ti (357.40): C, 77.30; H, 9.31. Found: C, 77 0.24; H, 8.98. MS (70 eV; EI m/z (u)): 357 [M]$^+$, 318 [Cp*$_2$Ti]$^+$, 317 [Cp*$_2$Ti − H]$^+$. The analytical and spectroscopic data of the sample are identical with those described in ref 2.

Preparation of Cp*$_2$Ti(C≡C-t-Bu) (5). A solution of 0.21 mL of 3,3-dimethylbutyne (1.7 mmol) in 10 mL of n-hexane was cooled to −78 °C and treated with 0.68 mL (1.7 mmol) of n-butyllithium (2.5 M/n-hexane). After 15 min the solution was warmed to room temperature and the resulting white suspension was added to the deep blue solution of 0.606 g (1.7 mmol) of Cp*$_2$TiCl in 10 mL of n-hexane. The mixture rapidly changed from blue to brown. After filtration and concentration of the solution to 5 mL, the crystallization at −78 °C gave greenish brown crystals which were separated from the mother liquor, washed with cold n-hexane, and dried in vacuo to give 0.430 g (63%) of complex **5**: mp 129−131 °C. Anal. Calcd for C$_{26}$H$_{39}$Ti (399.48): C, 78.18; H, 9.84. Found: C, 78.24; H, 9.75. IR (Nujol; ν (cm^{-1})): 2721 w, 2071 s. MS (70 eV; EI m/z (u)): 399 [M]$^+$, 317 [Cp*$_2$Ti − H]$^+$.

Preparation of 6. A 220 mg amount (0.37 mmol) of **1** was dissolved in 10 mL of THF. The solution was stirred for 3 h under an atmosphere of CO$_2$ at room temperature. The solvent was removed, and the residue was extracted with 3 mL portions of n-hexane. Cooling for 48 h at −78 °C afforded 83 mg (40%) of a brown crystalline product, which was separated from the mother liquor by filtration and dried in vacuo: mp 208 °C. Anal. Calcd for C$_{31}$H$_{48}$O$_2$Si$_2$Ti (556.77): C, 66.87; H, 8.69. Found: C, 67.02; H, 8.89. IR (Nujol; ν (cm^{-1})): 2095 m, 2076 m, 1627 vs, 1491 m, 1233 s, 1022 m, 853 vs, 837 vs. MS (70 eV; CI, m/z (u)): 556 [M]$^+$, 541 [M − CH$_3$]$^+$, 513 [M − CH$_3$ − CO]$^+$, 422 [M − Cp* + H]$^+$, 318 [Cp*$_2$Ti]$^+$. ^{1}H NMR (THF-d_8, 297 K): δ 0.14 (s, 9 H, SiMe$_3$); 0.24 (s, 9 H, SiMe$_3$), 1.92 (s, 30 H, Cp*). ^{13}C NMR (THF-d_8, 297 K): δ −0.3; 0.8 (2 SiMe$_3$); 12.1 (C$_5$*Me$_5$); 108.8; 121.6 (C≡C); 126.5 (*C$_5$*Me$_5$); 163.2; 167.1 (C−CO); 221.9 (*C*Ti).

Preparation of Cp*$_2$Ti(O$_2$CC≡C-t-Bu) (7). (a) From Complex 2. A 267 mg amount (0.48 mmol) of **2** was dissolved in 10 mL of THF. The green solution was stirred for 3 h at room temperature under an atmosphere of CO$_2$. The THF was evaporated under vacuum, and the residue was extracted three times with 3 mL portions of n-hexane. Cooling for 48 h at −40 °C afforded 90 mg (42.5%) of green crystals of **7**: mp 196−197 °C.

(b) From Complex 5. A 176 mg amount (0.44 mmol) of **5** was dissolved in 10 mL of n-hexane under argon, and the resulting brown solution was filtered. Argon was then carefully removed in vacuo, and the flask with the solution was filled with CO$_2$ at room temperature. The color of the solution

rapidly changed to green. After 1 day greenish blue crystals had formed which were separated, washed with cold *n*-hexane, and dried in vacuo to give 64 mg of complex **7**. Subsequent cooling of the mother liquor to −78 °C gave an additional 110 mg of **7**. The total yield is 174 mg (89%): mp 204−205 °C. Anal. Calcd for $C_{27}H_{39}O_2Ti$ (443.49): C, 73.12; H, 8.86. Found: C, 72.61; H, 8.82. IR (Nujol; ν (cm^{-1})): 2720 w, 2267 w, 2218 vs, 1520 s, 1416 vs, 852 s. MS (70 eV; CI, m/z (u)): 443 [M]$^+$, 317 [Cp*$_2$Ti − H]$^+$.

Preparation of Cp*$_2$Ti(C≡CPh)$_2$ (8). (a) From Complex 3. A 140 mg (0.21 mmol) amount of **3** was dissolved in 10 mL of THF. The green solution was stirred for 3 h at room temperature under an atmosphere of CO_2. The THF was evaporated under vacuum, and the residue was extracted three times with 3 mL portions of *n*-hexane. Cooling for 48 h at −40 °C afforded 35 mg (32%) of red crystals of **8**.

(b) By Salt Elimination. A 0.59 mL (5.6 mmol) solution of phenylacetylene in 5 mL of THF was cooled to −78 °C and treated with 2.24 mL (5.6 mmol) of *n*-butyllithium (2.5 M/*n*-hexane). After 10 min the solution was warmed to room temperature and stirred for 1 h. A 1.09 g amount (2.8 mmol) of Cp*$_2$TiCl$_2$ was added, the solution was stirred for 12 h, the solvent was removed in vacuo, and the residue was extracted with 10 mL of *n*-hexane at 60 °C. After filtration and crystallization at −78 °C, 0.685 g (47%) of red crystals was formed, which was filtered and dried in vacuo: mp 173−177 °C. Anal. Calcd for $C_{36}H_{40}Ti$ (520.59): C, 83.06; H, 7.74. Found: C, 82.88; H, 7.92. IR (Nujol; ν (cm^{-1})): 2068 m, 1592 m, 1482 vs, 1261 vs, 1202 m, 758 vs. ^{1}H NMR (THF-d_8, 297 K): δ 2.09 (s, 30 H, Cp*), 7.08 (2 H, *p*-Ph), 7.18 (4 H; *m*-Ph), 7.26 (4 H, *o*-Ph). ^{13}C NMR (THF-d_8, 297 K): δ 13.3 (C$_5$*Me*$_5$), 122.1 (*i*-Ph), 123.9 (*C*$_5$Me$_5$), 126.4 (*p*-Ph), 127.9 (*C*Ph), 128.6 (*m*-Ph), 131.1 (*o*-Ph), 162.3 (*C*Ti). MS: (70 eV; CI, m/z (u)): 520 [M]$^+$, 505 [M − Me]$^+$, 317 [Cp*$_2$Ti − H]$^+$.

Preparation of Cp*$_2$Ti(O$_2$CC≡CPh) (9). A solution of 0.12 mL of phenylacetylene (1.07 mmol) in 20 mL of THF was cooled to −78 °C and treated with 0.43 mL (1.07 mmol) of *n*-butyllithium (2.5 M/*n*-hexane). After 10 min the solution was warmed to room temperature and stirred for 1 h. Carbon dioxide was bubbled into the solution for 30 min, and 0.346 g

(0.98 mmol) of Cp*$_2$TiCl was added. The solution was stirred for 12 h, the solvent was removed in vacuo, and the residue was extracted with 10 mL of *n*-hexane at 60 °C. After filtration and crystallization at −78 °C, 0.150 g (33%) of dark blue crystals was formed, which were filtered and dried in vacuo: mp 128 °C. Anal. Calcd for $C_{29}H_{35}O_2Ti$ (463.48): C, 75.15; H, 7.61. Found: C, 74.80; H, 7.44. IR (Nujol; ν (cm^{-1})): 2721 w, 2213 vs, 1520 s, 1412 vs, 947 m, 691 m, 616 m. MS (70 eV; EI, m/z (u)): 463 [M]$^+$, 317 [Cp*$_2$Ti − H]$^+$.

Reaction of [Cp$_2$Ti(C≡C-*t*-Bu)$_2$Li(THF)$_2$] with Carbon Dioxide. A 150 mg amount (0.31 mmol) of [Cp$_2$Ti(C≡C-*t*-Bu)$_2$]-[Li(THF)$_2$] was dissolved in 6 mL of THF. The solution was stirred for 3 h under an atmosphere of CO_2 at room temperature. The solvent was removed, and the residue was extracted three times with 3 mL portions of diethyl ether. Cooling of the concentrated green solution for 48 h at −78 °C afforded 65 mg (82.0%) of green [Cp$_2$Ti]$_2$[μ-η^2(1,3):η^2(2,4)-*t*-BuC$_2$C$_2$*t*-Bu], which was separated from the mother liquor by filtration and dried in vacuo. The analytical and spectroscopic data of the sample are identical with those described in ref 16a.

X-ray Crystallographic Study of Complexes 5 and 7. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[21] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[22] The hydrogen atoms were included at calculated positions. All other non-hydrogen atoms, except the atoms of the disordered groups, were refined anisotropically. Cell constants and other experimental details were collected and recorded in Table 1. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Supporting Information Available: Tables giving X-ray crystallographic data for **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010404F

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