Stability of Bridged and Unbridged η^2-Alkyne−titanocene and −zirconocene Complexes − Influence of Metals, Alkyne Substituents, Cp Substitution and Additional Ligands

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The influence of metals, alkyne substituents, Cp substitution and additional ligands on the stability of bridged and unbridged η^2-alkyne−titanocene and −zirconocene complexes has been investigated. The reduction of the complex $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]TiCl_2$ with magnesium in the presence of tolan (PhC_2Ph) does not give the expected alkyne−titanocene complex $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}PhC_2Ph)$ but by coupling of two tolan molecules the corresponding titanacyclopentadiene $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]TiC_4Ph_4$ (**1**) was obtained. In the analogous reaction with $Me_3SiC_2SiMe_3$ the stable η^2-alkyne complex without additional ligands $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**) was formed, due to the sterical influence of the alkyne substituents. The compounds without additional ligands $(thi)_2Ti(\eta^2\text{-}PhC_2Ph)$ (**3**) and $(thi)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**5**) were isolated from the unbridged titanocene complex $(thi)_2TiCl_2$ (thi = tetrahydroindenyl). Two equivalents of complex **3** reacted with one equivalent of water to yield the dimeric alkylidene-μ-oxo complex $[(thi)_2Ti(CPh{=}CHPh)]_2(\mu\text{-}O)$ (**6**). The reaction of the unbridged zirconocene compound $(thi)_2ZrCl_2$ gave the alkyne complex $(thi)_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**7**) which is stabilized by THF. At higher temperature THF was eliminated from the orange complex **7** forming the green complex $(thi)_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$. This behaviour was investigated in detail using NMR spectroscopy and compared to similar complexes such as $Cp_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (not stable without THF), $(ebthi)_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (ebthi = ethylenebistetrahydroindenyl; stable without THF) and $Cp^*{}_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp* = pentamethyl-Cp, stable without THF). All complexes were characterized by spectroscopic methods. X-ray structural determinations were conducted for the complexes **1**, **3** and **7**. Compound **3** is the first example of a structurally characterized tolan−titanocene complex without additional ligands.

Introduction

Alkyne complexes of group-IV metallocenes can be used synthetically for many purposes.[1] We were the first to produce titanocene complexes of silylalkynes without additional ligands, e.g. $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[2a] and also zirconocene complexes with additional ligands such as $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$[2b][2c] as well as the first example of a zirconocene without additional ligands *rac*-$(ebthi)_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$.[3]

More recently, we reported the synthesis, spectral characteristics and X-ray structural determination of other examples such as Cp-bridged alkyne complexes of the type $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (*ansa* = $Me_2Si-O-SiMe_2$) and $[(\eta^5\text{-}C_5H_4)\text{-}ansa\text{-}(\eta^5\text{-}C_5H_4)]Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (*ansa* = $Me_2Si-O-SiMe_2$, L = py; *ansa* = $SiMe_2$, L = py).[4] The special feature of these reagents when used in conjunction with bis(trimethylsilyl)acetylene is their ability to generate the metallocene $[Cp_2M]$ or *ansa* systems such as $[(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)M]$, $[(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5H_4)M]$ and *rac*-[(ebthi)M], (M = Ti, Zr) under mild conditions. This tendency depends not only on the alkyne substituents but also on the nature of the additional ligands. The factors which determine whether alkyne complexes with or without additional ligands are formed remained unclear, because the stability and reactivity depend strongly on the character of this additional interaction. The use of different additional ligands allows a tuning of the stoichiometric[5a] and catalytic[5b][5c] reactions.

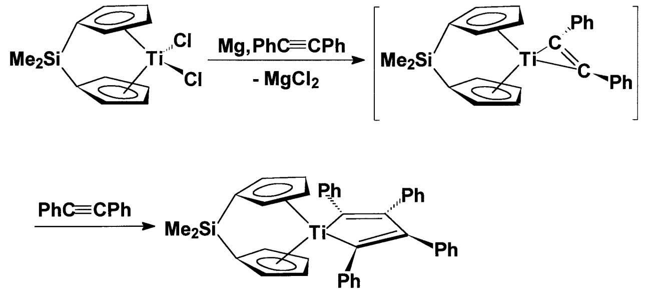
In this paper we report on the influence of metals, alkyne substituents, Cp substitution and additional ligands on the stability of bridged and unbridged η^2-alkyne−titanocene and −zirconocene complexes with and without additional ligands.

Complex Synthesis

The reduction of the complex $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]TiCl_2$[6] with magnesium in the presence of tolan (PhC_2Ph) in THF at room temperature does not give the expected alkyne−titanocene complex $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}PhC_2Ph)$. Instead, the corresponding titanacyclopentadiene $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]TiC_4Ph_4$ (**1**) is obtained in 35% yield by coupling of two tolan molecules (Scheme 1).

This coupling with a second tolan molecule is typical behaviour for coordinatively and electronically unsaturated

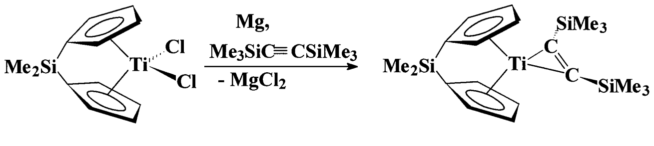
Scheme 1



1

tolan complexes such as $Cp_2Ti(\eta^2\text{-}PhC_2Ph)$[7]; the titanacyclopentadiene with unbridged Cp ligands that is obtained is well-known. By using another alkyne, $Me_3SiC_2SiMe_3$, instead of tolan, the complex $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**) can be isolated (Scheme 2). This is explained by the special character of the silylalkyne which prevents a coupling reaction by sterical hindrance of the large substituents.

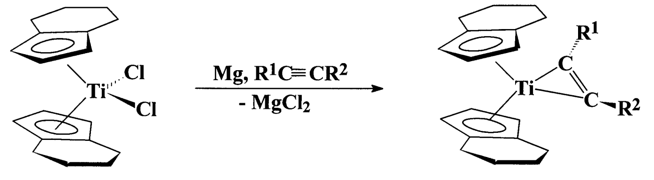
Scheme 2



2

In the reaction of the unbridged complex $(thi)_2TiCl_2$[8] the compound without additional ligands $(thi)_2Ti(\eta^2\text{-}PhC_2Ph)$ (**3**) was isolated. The analogous complexes **4** and **5** were also obtained using other alkynes such as PhC_2SiMe_3 and $Me_3SiC_2SiMe_3$ (Scheme 3).

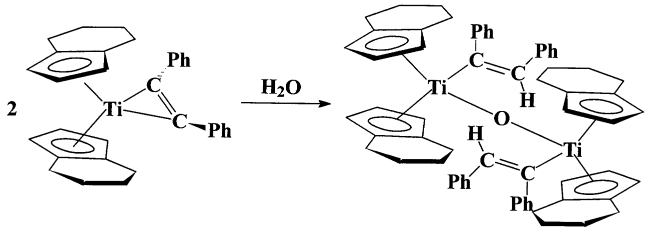
Scheme 3



3 $R^1=R^2=Ph$;
4 $R^1=Ph$, $R^2=SiMe_3$
5 $R^1=R^2=SiMe_3$

Two equivalents of complex **3** react with one equivalent of water to yield the dimeric alkenyl-μ-oxo complex $[(thi)_2Ti(CPh{=}CHPh)]_2(\mu\text{-}O)$ (**6**) (Scheme 4).

Scheme 4

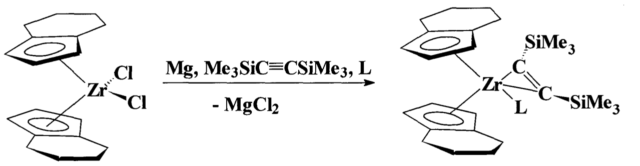


6

This reaction is a typical example of a tolan−titanocene complex, also found in the case of $Cp_2Ti(\eta^2\text{-}PhC_2Ph)$[7], but differs from those of the silylalkyne complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which gave only the elimination of the alkyne[9].

In the reaction of the unbridged zirconocene complex $(thi)_2ZrCl_2$[8] in THF at room temperature, the alkyne complex $(thi)_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**7**), stabilized by THF, was formed (Scheme 5).

Scheme 5



L = thf **7**, L = py **8**

Complex **7** is an analogue of the compound $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$[2b]. Just as for this Cp complex,[2c] coordination by py is also possible for the thi complex **7** which gives $(thi)_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8**).

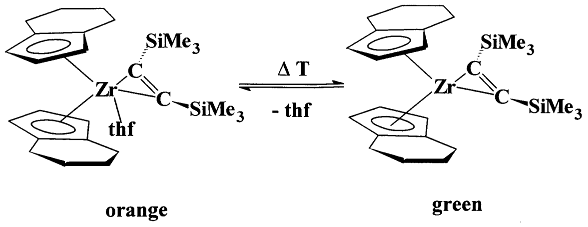
Spectral Characteristics

Complex **1** did not show any IR absorption of a complexed triple bond in the expected region of 1600−1800 cm^{-1}. IR absorptions for other complexes (**2**: 1683 cm^{-1}; **3**: 1671; **4**: 1652; **5**: 1629) and the ^{13}C-NMR-spectroscopic signals of the acetylenic C atoms (**2**: δ = 248.9; **3**: 198.8; **4**: 213.6, 220.0; **5**: 242.3) are typical of values for such alkyne complexes[10] and prove that complexes **2**, **3**, **4** and **5** have a titanacyclopropene structure. These data again show larger spectroscopic shifts (IR, NMR) for the potential π-acceptor groups $SiMe_3$ as alkyne substituents.

Complex **3** is the second example of a tolan−titanocene complex without additional ligands. The other complex $Cp_2Ti(\eta^2\text{-}PhC_2Ph)$[7] is characterized by an IR absorption at 1713 cm^{-1} and ^{13}C-NMR signals at δ = 196.5. Previously, only the complex with a stabilizing ligand, e.g. $Cp_2Ti(CO)(\eta^2\text{-}PhC_2Ph)$, had been reported.[11] In the latter, the alkyne formally acts as a two-electron donor, while it is regarded as contributing four electrons in **3**. This also follows from the frequencies of the C−C stretching vibrations (**3**: 1671 cm^{-1}; CO complex: 1780) in the IR spectra.

The IR and ^{13}C-NMR spectra of complex **7** are typical of those also found for the compound $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$.[2b] The higher shifts of complex **7**, e.g. the absorption in the IR spectra (Cp compound: 1581 cm^{-1}; **7**: 1559) and the ^{13}C-NMR signals of the acetylenic C atoms (Cp compound: 212.9; **7**: δ = 222.0) are typical of values[12] for substituted Cp ligands (Cp* and thi) which are stronger donors than Cp itself. At higher temperatures the orange complex **7** eliminates THF reversibly to give the green complex $(thi)_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Scheme 6), a reaction which is unknown for the Cp complex $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$.

Scheme 6



This reaction was identified using NMR spectroscopy after warming up to 343 K by a low-field shift from δ = 222.0 to 244.0. The same effect has been found for complexes similar to $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ which are not stable without THF, *rac*-$(ebthi)_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ being stable without THF at room temperature and $Cp^*{}_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which did not coordinate with THF at any of the temperatures investigated.[13]

Structural Investigations

The structure of **1** in the crystal is shown in Figure 1. The analogous complex with unsubstituted Cp has already been investigated by X-ray structure analysis.[14] Table 1 lists the relevant data of this complex in comparison with those of complex **1**.

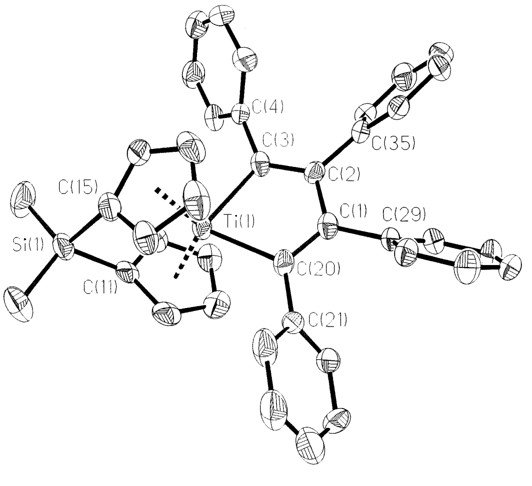


Figure 1. Molecular structure of **1**; shown by an ORTEP plot (50% probability)[a]

[a] Selected distances [Å] and angles [°]: C1−C20 1.364(5), C2−C3 1.362(5), Ti1−C3 2.172(4), Ti−C20 2.160(3); C4−C3−C2 124.5(3), C3−C2−C35 123.1(3), C1−C20−C21 123.0(3), C20−C1−C29 121.0(3), C15−Si−C11 92.7(2).

The bond lenghts and angles of the central five-membered titanacycle are nearly identical and are not influenced by the substitution at the Cp ligands. The structure of **3** in the crystal is shown in Figure 2.

Table 1. Comparision of structural data of $Cp_2TiC_4Ph_4$ and **1**

	$Cp_2TiC_4Ph_4$	**1**
Distances [Å]		
Ti−C3	2.172(5)	2.172(4)
Ti−C20	2.141(5)	2.160(3)
C2−C3	1.369(6)	1.362(5)
C1−C2	1.495(6)	1.493(5)
C1−C20	1.370(6)	1.364(5)
Angles [°]		
C20−Ti−C3	80.3(2)	79.8(1)
Ti−C3−C2	112.5(3)	112.1(3)
Ti−C20−C1	111.0(3)	111.4(2)
C3−C2−C1	117.4(4)	117.2(3)
C20−C1−C2	118.5(4)	119.1(3)
Cp′−Ti−Cp′	134.8(3)	130.7(5)

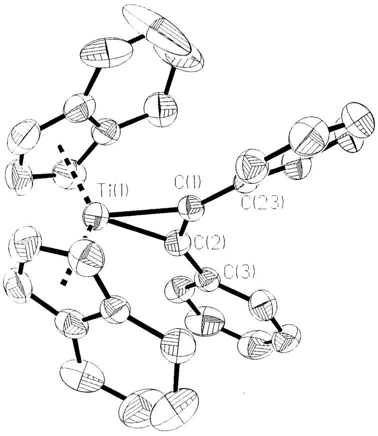


Figure 2. Molecular structure of **3**, shown by an ORTEP plot (50% probability)[a]

[a] Selected distances [Å] and angles [°]: C1−C2 1.287(6), Ti−C1 2.086(4), Ti−C2 2.044(5); C1−Ti−C2 36.3(2), C23−C1−C2 140.7(4), C3−C2−C1 138.7(5), Cp′−Ti−Cp′ 137.5(4).

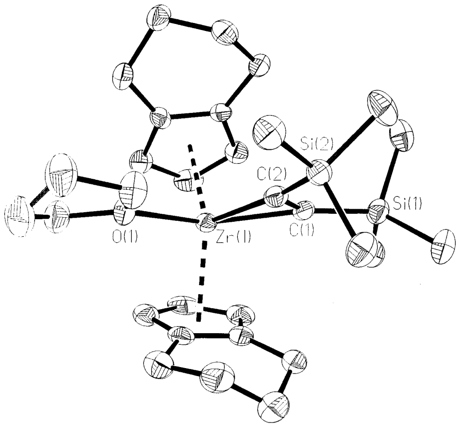
Complex **3** is the first example of a structurally well-characterized tolan−titanocene complex that is stable without additional ligands. Previously, only the structures of complexes with stabilizing ligands, e.g. $Cp_2Ti(CO)(\eta^2\text{-}PhC_2Ph)$, have been described.[11] The comparison is between a complex with one alkyne group acting as a two-electron donor (CO complex) and in the other case as a four-electron donor (**3**). In Table 2 the relevant data of both complexes are listed and compared.

Table 2. Comparison of structural data of $Cp_2Ti(CO)(\eta^2\text{-}PhC_2Ph)$ and **3**

Compound	$Cp_2Ti(CO)(\eta^2\text{-}PhC_2Ph)$	**3**
Distances [Å]		
C1−C2	1.29(1)	1.287(6)
Ti−C1	2.107(7)	2.086(4)
Ti−C2	2.230(7)	2.044(5)
Ti−C(O)	2.050(8)	−
Angles [°]		
C(O)−Ti−C2	71.9(3)	−
C1−Ti−C2	34.3(3)	36.3(2)
C23−C1−C2	138.8(7)	140.7(4)
C3−C2−C1	145.8(7)	138.7(5)
Cp′−Ti−Cp′	133.5(5)	137.5(4)

Both titanocene complexes contain different ligands (Cp and thi) and a detailed comparison and investigation of the influence of the additional CO ligand on the complexation of tolan is therefore not possible. The Ti−C bond lengths are shorter in complex **3**, indicating a stronger complexation of the alkyne as expected. On the other hand, the additional ligand CO alone makes less space available in the coordination sphere at the central atom, reducing the interaction of the alkyne with the titanium atom. The structure of **7** in the crystal is shown in Figure 3.

Figure 3. Molecular structure of **7**, shown by an ORTEP plot (50% probability)[a]



[a] Selected distances [Å] and angles [°]: C1−C2 1.340(7), Zr1−C1 2.218(5), Zr1−C2 2.271(5), Zr1−O1 2.404(4); C1−Zr1−C2 34.7(2), Si1−C1−C2 141.1(4), Si2−C2−C1 124.5(4), C2−Zr1−O1 86.7(1); the structural data of the Cp and the corresponding thi complex **7** are listed and compared in Table 3.

Table 3. Comparison of structural data of $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and **7**

Compound	$Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$	**7**
Distances [Å]		
C1−C2	1.302(9)	1.340(7)
Zr−C1	2.204(7)	2.218(5)
Zr−C2	2.260(7)	2.271(5)
Zr−O1	2.390(5)	2.404(4)
Angles [°]		
C1−Zr−C2	33.9(2)	34.7(2)
C1−C2−Si2	134.4(6)	124.5(4)
C2−C1−Si1	143.5(6)	141.1(4)
C2−Zr−O1	86.8(2)	86.7(1)
Cp′−Zr−Cp′	130.5(3)	131.0(3)

The relatively small differences in the structures of both complexes again demonstrate that the above-mentioned spectroscopical shifts (IR, NMR) are better suited for the characterization of the interaction of the alkyne with the metal atom than the results of an X-ray crystal structural analysis.

Discussion

The influence of metals, alkyne substituents, Cp substitution and additional ligands on the stability of bridged and unbridged η^2-alkyne−titanocene and −zirconocene complexes with and without additional ligands are summarized in Tables 4 and 5 {Cp- and $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]$-ligated complexes are shown as Cp complexes because both show a similar behaviour}. For titanocene the existence of the complex **3** demonstrates clearly the stabilizing effects of the thi ligands compared to Cp {and also $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]$}. The effect of the thi ligands is not found for the zirconocene complexes because zirconium is larger.

Table 4. Existence of complexes $L_2M(\eta^2\text{-}RC_2R)$; influence of metals, alkyne substituents and Cp substitution

	R=SiMe$_3$		R=Ph	
L/L$_2$	Ti	Zr	Ti	Zr
Cp	+	−	+	−
thi	+	−	+	−
rac-ebthi	+	+	unknown	−
Cp*	+	+	+	+

Table 5. Existence of complexes $L_2Zr(L')(\eta^2\text{-}Me_3SiC_2SiMe_3)$; influence of Cp substitution in ligands L and additional ligands L′

L/L$_2$	without L′	L′ = THF	L′ = py
Cp	−	+	+
thi	> 320 K	< 320 K	+
rac-ebthi	+	< 194 K	+
Cp*	+	− until 77 K[13]	−

The complexes of the type $L_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ can coordinate with additional ligands L′ to give the complexes $L_2Zr(L')(\eta^2\text{-}Me_3SiC_2SiMe_3)$. The restriction for this comes mostly from the nature of L/L$_2$. With ligands such as *rac*-ebthi and Cp*, complexes without additional ligands L′ are stable at room temperature. Due to the enhanced flexibility of these ligands at lower temperature in some cases, such as *rac*-ebthi, the coordination of L′ (< 194 K) was observed. With thi as the ligand L the coordination of L′ occurs at room temperature and the complex with an additional THF ligand is stable, but eliminates L′ at higher temperature (< 320 K). With Cp no complex without L′ is stable and with Cp* no complex with L′.

The reason for the stability of the THF complexes toward dissociation of THF seems to come mostly from sterical interactions of alkyne substituents and the ligands L/L$_2$ and L′ and not from electronic effects. Complexes with the flat pyridine ligand are more stable compared to the corresponding THF complexes.

Conclusion

Complexes of the type $L_2M(\eta^2\text{-}RC_2R)$ without stabilizing ligands are sterically and electronically unsaturated. The size of zirconium is larger than that of titanium and as a result, it has a greater tendency to coordinate additional ligands; complexes without additional ligands are very rare and exist only with large alkyne substituents (SiMe$_3$) *and* sterical demanding Cp substitution (*rac*-ebthi[15], Cp*[13]). For the smaller titanium atom, sterically demanding alkyne *or* Cp substituents alone make alkyne complexes without additional ligands possible.

On the basis of these results it seems that it is now possible to understand the stability as well as the reactivity of bridged and unbridged alkyne−titanocene and −zirconocene complexes better. Control of stability is possible only by empirical tailoring of the complexes using different metals, alkyne substituents, Cp substitution and additional ligands.

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Experimental Section

All operations were carried out in argon with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. – The following spectrometers were used: NMR, Bruker ARX 400; IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. – Melting points were measured in sealed capillaries with a Büchi 535 apparatus. – X-ray crystallographic study: Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-86)[16] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[17] The hydrogen atoms were included at calculated positions. All other nonhydrogen atoms were refined anisotropically. Cell constants and other experimental details are compiled in Table 6. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Preparation of $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]TiC_4Ph_4$ (**1**): 1.10 g of $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]TiCl_2$ (3.62 mmol) was dissolved in 20 ml of THF and 0.09 g (3.62 mmol) of magnesium turnings and 0.64 g (3.62 mmol) of tolan were added. The solution was heated to 50°C and the colour changed from red to yellow-brown. The reaction mixture was stirred for 3 h at room temp. and the solvent was removed and replaced by *n*-hexane. After filtration at −30°C, red-brown crystals were formed. The crystals were washed in *n*-hexane and dried in vacuo to give 0.75 g (35%) of **1**, m.p. 203–204°C. – $C_{40}H_{34}SiTi$ (590.68): calcd. C 81.34, H 5.80; found C 81.22, H 5.85. – ^{1}H NMR (C_6D_6): δ = −0.04 $SiMe_2$ (s, 6 H); 4.99, 8.17 CH (d, 4 H each); 6.75–7.10 Ph (m, 20 H). – ^{13}C NMR (C_6D_6): δ = −6.2 $SiMe_2$; 105.0 $C_{q.}$; 117.4, 123.6 CH; 124.8, 125.9, 127.0, 128.1, 128.3, 131.4 Ph; 141.3, 148.7 Ph(q.); 135.3, 201.3 C(alkyne). – MS (70 eV); *m/z*: 590 [M$^+$], 234 [$(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)Ti^+$], 178 [$PhC_2Ph^+$].

Preparation of $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**): Using the same procedure as described for **1**, the title compound was prepared using 0.37 g (1.20 mmol) of $[(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)]TiCl_2$ in 15 ml of THF using 0.029 g of magnesium turnings and 0.27 ml (1.20 mmol) of bis(trimethylsilyl)acetylene. Yield 0.20 g (41.2%) of a yellow-brown oily solid. – ^{1}H NMR (C_6D_6): δ = −0.3 $SiMe_3$ (s, 18 H); 0.27 $SiMe_3$ (s, 6 H); 5.05, 9.33 CH (4 H each). – ^{13}C NMR (C_6D_6): δ = −6.0 $SiMe_2$; 0.6 $SiMe_3$; 114.6 C(C_5H_4); 121.8, 126.9 C_5H_4; 248.9 C(alkyne). – IR (Nujol): ṽ = 1683 cm^{-1}, ν(C=C)$_{\text{coord.}}$ = 1251 cm^{-1} [δ_s (CH_3–Si)]. – MS (70 eV); *m/z*: 234 [M – alkyne$^+$], 234 [$(\eta^5\text{-}C_5H_4)-SiMe_2-(\eta^5\text{-}C_5H_4)Ti^+$], 170 [alkyne$^+$].

Preparation of $(thi)_2Ti(\eta^2\text{-}PhC_2Ph)$ (**3**): To 0.30 g (0.84 mmol) of $(thi)_2TiCl_2$, dissolved in 15ml of THF, were added 0.02 g (0.84 mmol) of Mg turnings and 0.15 g (0.84 mmol) of diphenylacetylene. The colour turned from red to green-brown and the solution was stirred for 3 h at room temp. After removing the solvent and replacing it by *n*-hexane, the brown solution was filtered and allowed to stand at −30°C, to induce precipitation of dark brown crystals (yield 0.25 g, 64%), m.p. 111°C. – $C_{32}H_{32}Ti$ (464.49): calcd. C 82.75, H 6.94; found C 82.32, H 6.99. – ^{1}H NMR (C_6D_6): δ = 1.11–1.22, 1.43–1.58, 1.90–2.02, 2.50–2.62 CH_2 (4 H each); 5.45 CH (2 H); 6.14 CH (4 H); 6.80–6.92 Ph (m, 4 H); 7.10–7.28 Ph (m, 6 H). – ^{13}C NMR (C_6D_6): δ = 22.8, 24.7 CH_2; 126.1 $C_{q.}$; 110.7, 111.4 CH; 142.1 (*ipso*), 125.5, 126.6, 128.6 Ph; 198.8 C(alkyne). – IR (Nujol): ṽ = 1671 cm^{-1} ν(C≡C)$_{\text{coord.}}$ = 1585 cm^{-1} Ph.

Preparation of $(thi)_2Ti(\eta^2\text{-}PhC_2SiMe_3)$ (**4**): 0.30 g (0.84 mmol) of $(thi)_2TiCl_2$ was dissolved in 20 ml of THF and treated with 0.02 g (0.84 mmol) of magnesium turnings and 0.28 ml (1.23 mmol) of phenyl(trimethylsilyl)acetylene. The solution was heated to 50°C until the colour changed to violet. Preparation was the same as described for **2**; violet crystals, yield 0.290 g (75%). m.p. 158–160°C. – $C_{29}H_{36}SiTi$ (460.57): calcd. C 75.63, H 7.88; found C 75.57, H 7.92. – ^{1}H NMR (C_6D_6): δ = 0.03 $SiMe_3$; 2.23–2.70 (10 H), 1.90–1.99 (2 H), 2.51–2.62 (2 H), 2.75–2.83 (2 H) CH_2; 5.66 (2 H), 5.93 (2 H), 6.16 (2 H) CH; 6.45 *o*-Ph (2 H); 6.80 *p*-Ph (1 H); 7.03 *m*-Ph (2 H). – ^{13}C NMR (C_6D_6): δ = 1.4 $SiMe_3$; 23.3, 23.4, 25.4, 25.5 CH_2; 111.2, 111.8, 112.1 CH; 127.8, 127.9 $C_{q.}$; 126.1, 126.8, 129.6, 141.2(q) Ph; 213.6, 220.0 C(alkyne). – IR (Nujol): ṽ = 1652 cm^{-1}, ν(C=C)$_{\text{coord.}}$ = 1589 cm^{-1} Ph, 1242 cm^{-1} [δ_s (CH_3–Si)]. – MS (70 eV) *m/z*: 286 [$(thi)_2Ti^+$], 174 [alkyne$^+$].

Preparation of $(thi)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**5**): To a solution of 0.30 g (0.84mmol) of $(thi)_2TiCl_2$ in 15 ml of THF 0.10 ml of bis(trimethylsilyl)acetylene and 0.20 g of magnesium turnings were added. Reaction and workup according to **4** resulted in the formation of a dark yellow solid. – ^{1}H NMR (C_6D_6): δ = −0.14 $SiMe_3$ (18 H); 1.22–1.39 (4 H), 1.58–1.83 (8 H), 2.68–2.73 (4 H) CH_2; 5.68 CH (2 H); 6.05 CH (4 H). – ^{13}C NMR (C_6D_6): δ = 2.1 $SiMe_3$; 23.6, 25.4 CH_2; 112.2, 113.0 CH; 131.0 $C_{q.}$; 242.3 C(alkyne). – IR (Nujol): ṽ = 1629 cm^{-1}, ν(C=C)$_{\text{coord.}}$ = 1243 cm^{-1} [δ_s (CH_3–Si)]. – MS (70 eV); *m/z*: 286 [$(thi)_2Ti^+$], 170 [alkyne$^+$].

Preparation of $[(thi)_2Ti(CPh{=}CHPh)]_2(\mu\text{-}O)$ (**6**): 0.20 g of **3** were dissolved in 15 ml of wet *n*-hexane. After standing for 3 d, 0.15 g (74.3%) of yellow needles appeared, m.p. 127–128°C. – $C_{64}H_{58}OTi_2$ (938.92): calcd. C 81.87 H 6.23; found C 81.25 H 6.30. – ^{1}H NMR (C_6D_6): δ = 1.39–1.49 (8 H) 1.50–1.59, 1.62–1.73, 2.10–2.18, 2.21–2.30, 2.45–2.54, 2.68–2.78 (4 H) CH_2; 4.84, 5.19, 6.15 (4 H) CH; 6.95–7.20 (20 H) Ph; 7.76 (2 H) CH. – ^{13}C NMR (C_6D_6): δ = 21.4, 21.5, 23.2, 23.4, CH_2; 105.3, 106.7, 115.4 CH; 122.5, 124.8 $C_{q.}$; 123.6, 125.2, 125.9, 126.4, 130.5, 131.0, 139.1 (q), 152.6 (q) Ph; 130.5, 193.5 C(alkene).

Preparation of $(thi)_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**7**): 1.30 g (3.24 mmol) of $(thi)_2ZrCl_2$ was dissolved in 20 ml of THF and treated with 0.08 g magnesium turnings and an equimolar amount of bis(trimethylsilyl)acetylene. The solution was stirred at room temp. until all magnesium had disappeared. The honey-yellow solution was concentrated to dryness, the residue was dissolved in hexane/THF (3:1), filtered, and cooled to −30°C to give 0.65 g (35%) **7** after 3 d, m.p. up to 50°C (elimination of THF). – $C_{30}H_{48}OSi_2Zr$ (572.10): calcd. C 62.98 H 8.46; found C 62.57 H 8.54. – ^{1}H NMR ([D_8]THF): δ = 0.21 $SiMe_3$ (18 H); 1.56 CH_2 (8 H); 2.05, 2.30 CH_2 (4 H each); 1.75, 3.70 THF (4 H each); 5.33 CH (4 H); 5.55 CH (2 H). – ^{13}C NMR ([D_8]THF): δ = 5.1 $SiMe_3$; 24.0, 25.1 CH_2; 100.4, 107.5 CH; 124.3 $C_{q.}$; 222.0 C(alkyne). – IR (Nujol): ṽ = 1559 cm^{-1}, ν(C=C)$_{\text{coord.}}$ = 1241 cm^{-1} [δ_s (CH_3–Si)]. – MS (70 eV); *m/z*: 500 [M – THF$^+$], 329 [$(thi)_2Zr^+$], 170 [alkyne$^+$].

Preparation of $(thi)_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8**): As described for complex **7**, the title compound was formed by adding 0.32 ml (0.40 mmol) of pyridine after all magnesium had disappeared. The red-brown solution was concentrated to dryness and the residue was dissolved in *n*-hexane and filtered. After standing for 2 d at −30°C, 0.98 g (55%) of complex **8** deposited as orange-brown crystals, m.p. 141−142°C. − $C_{31}H_{45}NSi_2Zr$ (579.10): calcd. C 64.30 H 7.83; found C 63.70 H 7.75. − ^{1}H NMR (C_6D_6): δ = 0.45 $SiMe_3$ (18 H); 1.25−1.40 CH_2 (br., 12 H); 2.10−2.20 CH_2 (4 H); 5.15 CH (br., 4 H); 5.80 CH (2 H); 6.53 (2 H), 6.80 (1 H), 9.04 (2 H) pyridine. − ^{13}C NMR (C_6D_6): δ = 3.8 $SiMe_3$; 23.8, 25.0 CH_2; 97.3, 107.2 CH; 112.9 C_q.; 123.3, 136.5, 155.5 pyridine; C(alkyne) not observed at 297 K, broad signal at 216.7 (337 K). − IR (Nujol): $\tilde{\nu}$ = 1548, 1595 cm^{-1}, $\nu(C{=}N)_{py}$ and $\nu(C{=}C)_{coord.}$ = 1240 cm^{-1} [δ_s ($CH_3{-}Si$)]. − MS (70 eV); *m*/*z*: 500 [M − py$^+$], 329 [(THI)$_2$Zr$^+$], 170 [alkyne$^+$].

Table 6. Crystallographic data of **1**, **3**, and **7**[17]

Compound	**1**	**3**	**7**
Formula	$C_{40}H_{34}SiTi$	$C_{32}H_{32}Ti$	$C_{30}H_{48}OSi_2Zr$
Mol. mass	590.66	464.48	572.10
Cryst. colour	yellow-brown	green-brown	orange
Cryst. description	prism	prism	prism
Cryst. size [mm]	0.5 × 0.4 × 0.3	0.3 × 0.2 × 0.1	0.5 × 0.4 × 0.3
Cryst. system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1$
a [Å]	11.344(2)	8.699(1)	8.775(1)
b [Å]	12.6000(2)	19.493(3)	17.004(2)
c [Å]	13.620(2)	14.441(2)	10.318(2)
α [°]	113.60(1)	90.06	90.00
β [°]	90.20(1)	91.63(1)	107.04(1)
γ [°]	115.95(1)	90.00	90.00
Z	2	4	2
T [K]	200(2)	293(2)	200(2)
μ [mm^{-1}]	0.339	0.367	0.475
Abs. cor.	no	no	no
θ range (°)	1.96−24.33	1.76−21.52	2.06−24.30
Largest diff. [e Å^{-3}] peak/hole	0.2/−0.5	0.2/−0.2	0.5/−0.6
No. of reflect. (measd.)	4715	4916	4349
No. of reflect. (indep.)	4715	2519	4261
R (int)	−	0.069	0.023
No. of reflect. (obsvd.)	3086	1430	4038
No. of parameters	379	298	356
[$I > 2\sigma(I)$] $R1$ [$I > 2\sigma(I)$]	0.050	0.047	0.033
wR_2 (all data)	0.134	0.102	0.099

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100666. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. + 44(1223)336033, e-mail: deposit@ccdc.cam.ac.uk].

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