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Preparation and reactions of monocyclic bis(cyclopentadienyl)titanacyclopentenes and -pentadienes

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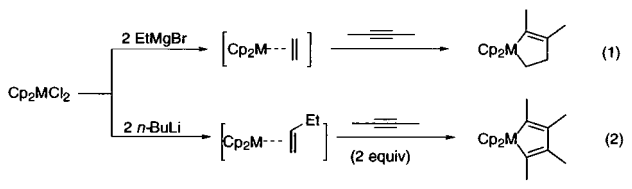
Abstract

A combination of Cp_2TiCl_2–2EtMgBr was found to be very effective for the formation of monocyclic titanacyclopentenes in excellent yields. On the other hand, a combination of Cp_2TiCl_2–2*n*-BuLi was used for intermolecular coupling of two alkynes to form titanacyclopentadienes in good to excellent yields. A reaction temperature range from −10 to −30 °C was critical for the success of the combinations. Reactions of these in situ-prepared titanacycles show interesting similarities to or differences from their zirconacycle analogs. © 2001 Published by Elsevier Science B.V.

Keywords: Titanacyclopentene; Titanacyclopentadiene; Intermolecular coupling; Titanocene–ethylene complex

1. Introduction

Organometallic compounds of the group 4 metals (Ti, Zr, Hf), which are dominated by the use of cyclopentadienyl ligands, have proven very useful as reagents or catalysts in synthetic chemistry [1,2]. In recent years, we have studied the preparation and reactions of bis(cyclopentadienyl)zirconacycles, including zirconacyclopentanes, -pentenes and -pentadienes [3]. Zirconocene dichloride, Cp_2ZrCl_2, reacted with two equivalents of EtMgBr to give a zirconocene–ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ [4], which *inter*molecularly coupled with various unsaturated compounds to give zirconacycles [3]. For example, zirconacyclopentenes can be easily generated in high yields and with high pair-selectivity from the intermolecular coupling of $Cp_2Zr(CH_2{=}CH_2)$ with an acetylene (Scheme 1 (1)) [5].



Scheme 1.

On the other hand, a combination of Cp_2ZrCl_2 with two equivalents of *n*-BuLi has proven very effective for intermolecular coupling of two alkyne molecules or intramolecular coupling of diynes to form mono or bicyclic zirconacyclopentadienes [6]. The reactive species of this combination of Cp_2ZrCl_2–2*n*-BuLi (Negishi reagent) has been proposed to be a zirconocene–butene complex, which has shown a very different reactivity towards various substrates from the aforementioned zirconocene–ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ (Scheme 1 (2)). Although not studied as much, combinations of Cp_2HfCl_2–2EtMgBr [7] and Cp_2HfCl_2–2*n*-BuLi [6b,7] have been successfully applied for the preparation of hafnacyclopentenes and -pentadienes (Scheme 1). However, surprisingly, analogous intermolecular coupling reactions using Cp_2TiCl_2–2EtMgBr and Cp_2TiCl_2–2*n*-BuLi to give titanacyclopentenes and titanacyclopentadienes have not been developed. In this paper, we would like to report the following: (i) titana-

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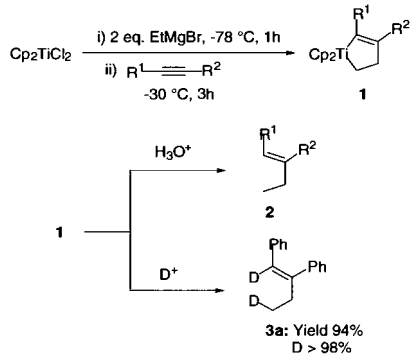


Scheme 2.

cyclopentenes were prepared in high yields and with high pair-selectivity by an intermolecular coupling of Cp_2TiCl_2, EtMgBr and an alkyne; (ii) two molecules of alkynes intermolecularly coupled to form titanacyclopentadienes using a combination of Cp_2TiCl_2–2*n*-BuLi. In addition, reactions of the titanacycles prepared here are presented.

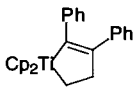
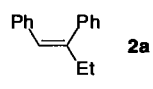
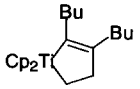
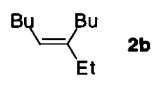
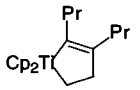
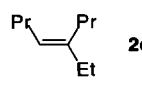
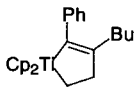
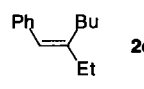
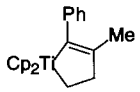
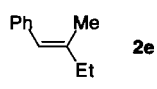
2. Results and discussion

2.1. Preparation of bis(cyclopentadienyl)-titanacyclopentenes by an intermolecular coupling of Cp_2TiCl_2, EtMgBr and an alkyne

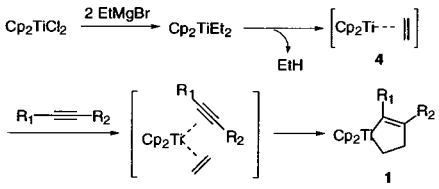
Divalent titanium Ti(II) complexes with ligands other than cyclopentadienyl have been reported and applied for the preparation of titanacyclopentenes and titanacyclopentadienes [8,10]. Among these, an aryloxytitanium compound [8], $(Ar''O)_2Ti$, generated in situ from $(Ar''O)_2TiCl_2$–Na, and an alkoxytitanium–olefin complex [9], (η^2-propene)Ti(O-*i*-Pr)$_2$, generated in situ from Ti(O-*i*-Pr)$_4$–2*i*-PrMgCl have shown interesting reactivity towards a variety of substrates. Combinations of bis(cyclopentadienyl) or bis(pentamethylcyclopentadienyl)titanocene dichloride with various reducing reagents including EtMgBr and *n*-BuLi have been studied [11–15]. However, these combinations have been used almost exclusively as a source of Cp_2TiH for hydrotitanation or hydromagnesation reactions, isomerization reactions or a source of a 'Cp_2Ti' equivalent for *intra*molecular coupling reactions of unsaturated compounds. One major reason for the difficulty of the *inter*molecular coupling is the labile nature of the olefin on titanocene. Binger et al. clearly indicated the difference between a titanocene–butene and a zirconocene–butene complex [16]. In order to realize an *inter*molecular coupling reaction pattern, we used EtMgBr and carried out its coupling reaction at low temperature. Fortunately, we were able to observe the *inter*molecular coupling of ethylene derived from EtMgBr with alkynes using titanocene. Titanacyclopentene derivatives (**1**) were formed in excellent NMR yields, as shown in Scheme 2. Hydrolysis of the reaction mixture with 3 N HCl afforded compounds **2**. Deuterolysis instead of hydrolysis of the reaction mixture gave **3a** in 94% yield with more than 98% of D incorporation. Results are summarized in Table 1.

It is noteworthy that in all cases, coupling products of ethylene derived from EtMgBr with an alkyne were

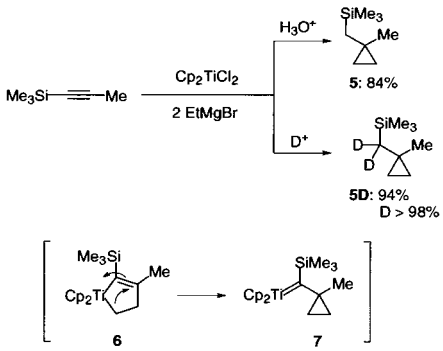
Table 1
Formation of titanacyclopentene compounds by the reaction of Cp_2TiCl_2 with EtMgBr and an alkyne

Entry	Alkyne	Product 1	Yield of 1/%[a]	Product 2	Yield of 2/%[b]
1	Ph—≡—Ph	 **1a**	> 99	 **2a**	95
2	Bu—≡—Bu	 **1b**	> 99	 **2b**	90
3	Pr—≡—Pr	 **1c**	98	 **2c**	97 (68)
4	Ph—≡—Bu	 **1d**	83[c]	 **2d**	95 (73)[c]
5	Ph—≡—Me	 **1e**	88[d]	 **2e**	91 (64)[d]

[a] Yields and ratios were determined by ^{1}H NMR. In all cases, no formation of alkyne dimers was observed. [b] Yields were determined by GC. Isolated yields are given in parentheses. [c] Two regioisomers were obtained in a ratio of 3:1; the major one is shown. [d] Two regioisomers were obtained in a ratio of 10:1; the major one is shown.



Scheme 3.



Scheme 4.

formed in excellent yields. No formation of the alkyne dimer was observed. We have already reported that zirconocene dichloride reacted with two equivalents of EtMgBr to give a zirconocene–ethylene complex, which immediately reacted with one equivalent of an alkyne to afford a zirconacyclopentene [5]. However, in some cases formation of zirconacyclopentadienes was observed in 3–5% yields. In order to completely suppress the formation of zirconacyclopentadienes, introduction of ethylene was required [17]. However, in the case of this titanocene, addition of ethylene was not necessary. Yields and pair-selectivity of the formation of titanacyclopentenes were the same or higher than those in the cases of the corresponding zirconacyclopentenes.

It was necessary to keep the mixture at a low temperature (-30 °C) during the reaction. When the reaction was carried out at 0 °C and at room temperature for 3 h, the yields of **2a** decreased to 86 and 68%, respectively. The use of other Grignard reagents such as *n*-BuMgCl, PrMgCl did not give titanacyclopentene compounds. This is probably because butene or propene formed in situ on titanocene is more labile.

The reaction mechanism for the formation of titanacyclopentenes (**1**) from the combination of Cp_2TiCl_2/2EtMgBr/alkyne is proposed to be analogous with that for zircona- and hafna-cyclopentenes [5]. It involves the formation of a titanocene–ethylene complex (**4**) by β-hydrogen abstraction from Cp_2TiEt_2, followed by intermolecular coupling of the ethylene with an alkyne (Scheme 3).

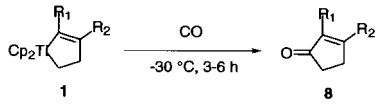
2.2. Unexpected formation of cyclopropane derivatives from reaction of silylated acetylenes with Cp_2TiCl_2–2EtMgBr

When a silylated acetylene such as 1-trimethylsilyl-1-propyne was used to react with Cp_2TiCl_2–2EtMgBr, the expected titanacyclopentene was not formed. Surprisingly, instead, 1-methyl-1-(trimethylsilyl)methyl cyclopropane (**5**) was obtained in 84% yield after hydrolysis of the reaction mixture with 3 N HCl at -30 °C (Scheme 4). This result was different from that obtained in the case of the zirconocenes and hafnocenes, in which a zirconacyclopentene or hafnacyclopentene was formed. Deuterolysis of the reaction mixture instead of hydrolysis afforded a bis-deuterated product (**5D**) in 94% yield with $>98\%$ D incorporation. In comparison with the ^{1}H-NMR spectrum of (**5**), the ^{1}H-NMR spectrum of **5D** indicated that the signal at 0.78 ppm in **5** assignable to two protons of the CH_2 next to the trimethylsilyl group was deuterated in **5D**. The ^{13}C-NMR spectrum of **5D** showed a quintet at 27.16 ppm assignable to the CD_2 moiety. Attempts to isolate the titanium-containing intermediate of this reaction have been so far unsuccessful. α-Silylated titanacyclopentene (**6**) and a titanocene carbene compound (**7**) are proposed to be the key intermediates. Cyclopropane formation by Michael addition-type reaction of the M–C bond (M = Zr or Ti) to the C=C bond with an electron-withdrawing group has been observed in the case of zirconium [18]. In the case of titanium, titanocene carbene complex formation by Michael addition-type reaction in the titanacycle has been reported [19a,b]. A type of complex similar to **7** has been proposed as the key intermediate [19].

2.3. Titanium-mediated intermolecular coupling of an alkyne, EtMgBr (or ethylene) and CO. Formation of cyclopentenone derivatives via CO insertion into titanacyclopentenes

Titanocene and zirconocene-mediated coupling of enynes with CO-forming bicyclic cyclopentenones have been reported via insertion of CO into titana- or zircona-cyclopentenes [3,6,9,20,22]. For the *inter*molecular coupling pattern, we and others have reported zirconocene-mediated reactions [5,21]. However, since there was no titanocene-mediated method for the pair-selective intermolecular coupling of olefins with alkynes, the formation of cyclopentenones by intermolecular coupling of an alkyne, an olefin, and CO mediated by titanocene (Cp_2Ti) has not been developed. Although the reactivity of titanacyclopentenes is quite different in many cases from that of zirconacyclopentenes, insertion of CO into titanacyclopentenes prepared in situ afforded cyclopentenones (Eq. (3)), as already observed for the zirconacyclopentene cases [5]. This

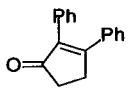
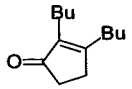
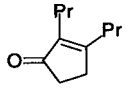
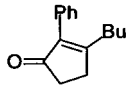
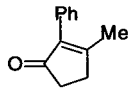
represents the first example of titanocene-mediated intermolecular coupling of an alkyne, an ethylene and CO to form monocyclic useful α,β-disubstituted cyclopentenones [13]. The cyclopentenones were formed in excellent yields when the CO insertion reaction was carried out at −30 °C for 3–6 h. Results are given in Table 2. When the reaction was carried out at room temperature, yields of cyclopentenones decreased.



(3)

It has been pointed out that in order to obtain the desired cyclopentenones from the reaction of zirconacyclopentenes with CO, treatment of the reaction mixture with I_2 is necessary [5,21]. Normal quenching with 3 N HCl gives a mixture of the cyclopentenones and their corresponding alcohols. The use of I_2 and its removal from the extracts are often troublesome. However, interestingly, just normal quenching with 3 N HCl was good enough to obtain cyclopentenones exclusively from the reaction of titanacyclopentenes with CO. No alcohols were obtained. Without I_2, the work-up was simplified and time-saving. In addition, compared with the case of zirconacyclopentenes, the reaction of titanacyclopentenes with CO afforded the corresponding cyclopentenones in remarkably higher isolated yields, since titanacyclopentenes (**1**) were cleanly formed and their further reactions with CO afforded no by-products.

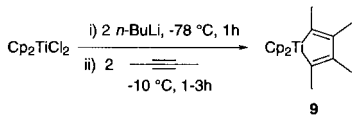
Table 2
Formation of cyclopentenones by insertion of CO into titanacyclopentenes

Entry	Cyclopentanones		Yield/%[a]
1		**8a**	88 (81)
2		**8b**	97 (90)
3		**8c**	99 (83)
4		**8d**	76 (63)[b]
5		**8e**	81 (67)[c]

[a] GC yield. Isolated yields are given in parentheses.
[b] Two regioisomers were obtained in a ratio of 3:1; the major one is shown. [c] Two regio isomers were obtained in a ratio of 10:1; the major one is shown.

2.4. Preparation of bis(cyclopentadienyl)-titanacyclopentadienes by intermolecular coupling of alkynes using Cp_2TiCl_2–2*n*-BuLi

As mentioned previously, monocyclic titanacyclopentadienes with ligation other than cyclopentadienyl [8–11] and bicyclic titanacyclopentadienes with various ligands including cyclopentadienyl [13,14,23,24] have been prepared via intermolecular coupling of two alkynes or via intramolecular coupling of diynes. Although the combination of Cp_2ZrCl_2–2*n*-BuLi (Negishi reagent) has proven to be the most effective and practical for the preparation of mono and bicyclic zirconacyclopentadienes [6], an analogous combination of Cp_2TiCl_2–2*n*-BuLi has not been reported as a reagent for the preparation of titanacyclopentadienes. In the case of Cp_2ZrCl_2–2*n*-BuLi, addition of two equivalents of the same alkynes or one equivalent of a diyne readily affords mono or bicyclic zirconacyclopentadienes at room temperature in quantitative yields normally within 1 h [6]. Hydrolysis of the reaction mixture with 3 N HCl easily gives the corresponding dienes in almost quantitative yields. However, in a simple application of the Cp_2ZrCl_2–2*n*-BuLi–two alkynes system, the same conditions and its work-up procedure for the preparation of titanacyclopentadienes did not work well. The reason is that Cp_2TiBu_2 is not stable at room temperature. As reported, it may be easily converted into Cp_2TiBu or Cp_2TiH. Binger reported the formation of a Cp_2Ti(butene) complex from Cp_2TiBu_2 and the lability of the butene. We carried out the reaction at lower temperature. As we expected, when the reaction temperature was lowered, the yields of titanacyclopentadienes increased. Finally, the range from −10 to −30 °C was found to be the most effective for the formation of titanacyclopentadienes (Eq. (4)). Following these conditions, monocyclic titanacyclopentadienes were prepared intermolecularly in good to excellent NMR yields (Table 3).

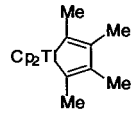
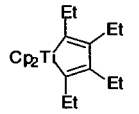
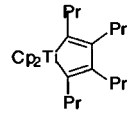
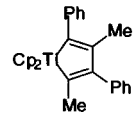
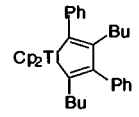


(4)

It is noteworthy that, unlike zirconacyclopentadienes, hydrolysis of titanacyclopentadienes with 3 N HCl gives the corresponding dienes in relatively low yields. Although the reason is not clear yet, isomerization or oligomerization in the process of hydrolysis is assumed to be responsible for the low yields of dienes.

The reaction mechanism for the formation of titanacyclopentadienes from the combination of Cp_2TiCl_2–2*n*-BuLi–two alkynes is proposed to be essentially the same as that for the formation of zirconacyclopentadienes from the combination of Cp_2ZrCl_2–2*n*-BuLi–two alkynes, as shown in Scheme 5.

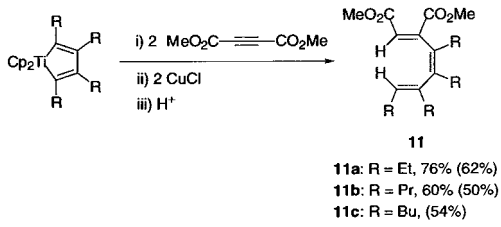
Table 3
Formation of monocyclic titanacyclopentadienes by intermolecular coupling

Entry	Alkyne	Product 9	Yield of 9/%[a]
1	Me—≡—Me	 **9a**	92%
2	Et—≡—Et	 **9b**	93%
3	Pr—≡—Pr	 **9c**	75%
4	Ph—≡—Me	 **9d**[b]	92%
5	Ph—≡—Bu	 **9e**[b]	86%

[a] Yields were determined by ^{1}H NMR. [b] Only one isomer.

2.5. Reaction of titanacyclopentadienes with alkynes in the presence of CuCl

As a demonstration of the different reactivities between zircona- and titana-cyclopentadienes, reactions of titanacyclopentadienes with a third alkyne such as DMAD was carried out, expecting formation of benzene derivatives [25]. We have recently reported that zirconacyclopentadienes react with a third alkyne to form benzene derivatives in the presence of CuCl (Eq. (6)) [26]. However, surprisingly, the reaction of titanacyclopentadienes with DMAD in the presence of CuCl did not give benzene derivatives; instead, linear trienes (**11**) were formed in good yields (Eq. (5)).

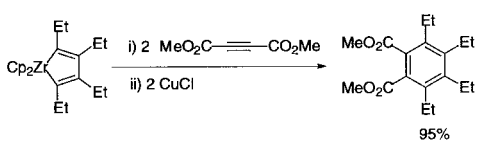


(5)

11

11a: R = Et, 76% (62%)
11b: R = Pr, 60% (50%)
11c: R = Bu, (54%)

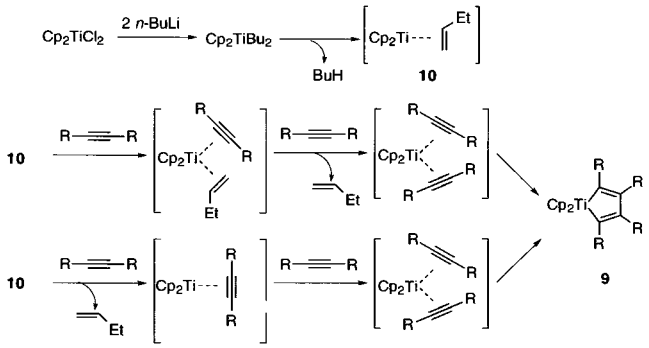
cf.



(6)

3. Conclusions

We have demonstrated in this paper that: (i) Combinations of Cp_2TiCl_2–2EtMgBr and Cp_2TiCl_2–2*n*-BuLi are effective reagents for the intermolecular coupling of ethylene with alkynes to form monocyclic titanacyclopentenes, and for intermolecular coupling of two alkynes to form titanacyclopentadienes. These methods enable easy access to titanacycles and thus will promote studies of their chemistry. (ii) Lower reaction temperature than that in the zirconocene cases is critical for the success of this development. (iii) β-Hydrogen abstraction from Cp_2TiEt_2 and Cp_2TiBu_2 to generate the titanocene–ethylene complex or the titanocene–butene complex is easier than that from their zirconocene analogs. β-Hydrogen abstraction takes place at lower temperature (-30 to -10 °C).



Scheme 5.

4. Experimental

4.1. General methods

All reactions involving organometallic compounds were carried out under nitrogen atmosphere using standard Schlenk tube techniques. Tetrahydrofuran (THF) was distilled and dried with sodium benzophenone ketyl. Titanocene dichloride (Cp_2TiCl_2) was purchased from Aldrich. EtMgBr (0.96 M solution in THF) and *n*-BuLi (1.60 M solution in hexane) were purchased from Kanto Chemical Co. Inc. Unless otherwise noted, chemicals were used without further purification.

^{1}H- and ^{13}C-NMR spectra were recorded with a 400 MHz Bruker NMR spectrometer. The NMR yields were determined using mesitylene as an internal standard. GC analyses were performed on a Shimadzu GC-14B equipped with a flame ionization detector using a Shimadzu capillary column (CBPI-M25-025). The GC yields were determined using suitable hydrocarbon as internal standards.

4.2. Preparation of titanacyclopentenes and isolation of hydrolyzed products

4.2.1. A general procedure

EtMgBr (2.4 mmol, 1.0 M THF solution, 2.4 ml) was added dropwise with a syringe to a THF (5 ml) solution of Cp_2TiCl_2 (1.2 mmol, 299 mg) at −78 °C (dry ice–acetone bath) in a 20 ml Schlenk tube. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. To the reaction mixture, an alkyne (1.0 mmol) was added and stirred for 3 h at −30 °C. Titanacyclopentenes (**1**) were formed and determined by ^{13}C-NMR. Only the Cp signals were determined by ^{1}H-NMR because several peaks overlapped with THF signals. Hydrolysis of the reaction mixture with 3 N HCl followed by normal work-up afforded **2**.

4.2.2. General notes

We have reported the formation and NMR data for compounds **2** (for **2a**,**b**,**d**,**e**, see Ref. [17]; for **2c**, see Ref. [5a]). All these compounds show the same NMR spectra as those reported.

4.2.3. Bis(cyclopentadienyl)-2,3-diphenyl-1-titanacyclopentene (*1a*)

NMR yield 99%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 2.83 (t, 2H, $J = 6.6$ Hz), 6.28 (s, 10H), 6.9–6.4 (m, 10H). ^{13}C-NMR (C_6D_6, Me_4Si): δ 40.7, 60.6, 115.6 (10C), 123.1, 125.3, 127.3, 127.5, 128.0, 129.2, 139.7, 144.4, 150.4, 194.8. HRMS calc. for$C_{26}H_{25}Ti$ [M + H] 385.1436, found 385.1446.

Hydrolysis of the reaction mixture afforded **2a**. GC yield 95%. The NMR data of **2b** are the same as those reported [17].

4.2.4. Isolation of *3a*

Deuterolysis instead of hydrolysis afforded **3a** in 94% GC yield. Isolated yield 90%. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 1.09–1.13 (tt, 2H, $J = 8.1$, 2.2 Hz), 2.55 (t, 2H, $J = 8.0$ Hz), 6.96–6.99 (m, 2H), 7.07–7.13 (m, 3H), 7.19–7.22 (m, 2H), 7.26–7.35 (m, 3H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 12.70 (t, $J = 20.1$ Hz), 33.52, 125.06 (t, $J = 24.2$ Hz), 126.13, 126.90, 127.89, 128.56, 128.63, 129.07, 137.60, 141.63, 144.93. HRMS calc. for $C_{16}D_2H_{14}$ 210.1375, found 210.1379.

4.2.5. Bis(cyclopentadienyl)-2,3-dibutyl-1-titanacyclopentene (*1b*)

NMR yield 99%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 6.18 (s, 10H, Cp). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 14.1, 14.2, 23.4, 24.0, 31.0, 33.0, 35.0, 36.2, 57.9, 114.0, 135.8, 193.8. HRMS calc. for $C_{22}H_{32}Ti$ 344.1983, found 344.1971.

Hydrolysis of the reaction mixture afforded **2b**. GC yield 90%. The NMR data of **2b** are the same as those reported [17].

4.2.6. Bis(cyclopentadienyl)-2,3-dipropyl-1-titanacyclopentene (*1c*)

NMR yield 98%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 5.96 (s, 10H, Cp). ^{13}C-NMR (C_6D_6, Me_4Si): δ 14.7, 15.3, 21.9, 23.8, 35.5, 36.2, 38.0, 58.3, 113.8 (10C), 135.9, 194.2. HRMS calc. for $C_{20}H_{28}Ti$ 316.1670, found 316.1692.

Hydrolysis of the reaction mixture afforded **2c**. GC yield 97%, isolated yield 68%. The NMR data of **2c** are the same as those reported [5a].

4.2.7. Preparation of *1d*

Two regioisomers were obtained in a ratio of 3:1. Combined NMR yield 83%. NMR data for the major: ^{1}H-NMR (C_6D_6, Me_4Si): δ 6.07 (s, 10H, Cp). ^{13}C-NMR (C_6D_6, Me_4Si): δ 14.3, 23.3, 31.4, 34.5, 37.8, 60.2, 115.1, 126.4, 138.5, 150.3, 192.5. HRMS calc. for $C_{24}H_{28}Ti$ 364.1670, found 364.1670.

Hydrolysis of the reaction mixture afforded a mixture of two regioisomers in a ratio of 3:1. Their NMR data are the same as those reported [17].

4.2.8. Preparation of *1e*

Two regioisomers were obtained in a ratio of 10:1. Combined NMR yield 88%. NMR data for the major: ^{1}H-NMR (C_6D_6, Me_4Si): δ 6.16 (s, 10H, Cp). ^{13}C-NMR (C_6D_6, Me_4Si): δ 20.1, 39.9, 59.1, 115.0, 122.6, 125.8, 127.5, 133.6, 150.6, 191.7. HRMS calc. for $C_{21}H_{22}Ti$ 322.1201, found 322.1193.

Hydrolysis of the reaction mixture afforded a mixture of two regioisomers in a ratio of 10:1. Their NMR data are the same as those reported [17].

4.3. Reaction of 1-trimethylsilyl-1-propyne with Cp_2TiCl_2–2EtMgBr. Isolation of cyclopropane derivatives (*5*)

4.3.1. A general procedure

The procedure is essentially the same as described above for the isolation of **2**.

4.3.2. 1-Methyl-1-(trimethylsilyl)methylcyclopropane (*5*)

Colorless liquid, GC yield 84%, isolated yield 51%. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 0.15 (s, 9H), 0.33–0.37 (m, 4H), 0.73 (s, 2H), 1.16 (s, 3H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ −0.06, 13.09, 14.96, 25.87, 28.16. HRMS calc. for $C_8H_{18}Si$ 142.1178, found 142.1178.

4.3.3. 1-Methyl-1-bisdeutero(trimethylsilyl)-methylcyclopropane (*5D*)

Deuterolysis instead of hydrolysis afforded **5D**. Colorless liquid, GC yield 94%, isolated yield 69%. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 0.05 (s, 9H), 0.22–0.26 (m, 4H), 1.05 (s, 3H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ −0.13, 12.94, 14.82, 25.75, 27.16 (quintet, $J = 17.4$ HZ). HRMS calc. for $C_8H_{16}D_2Si$ 144.1301, found 144.1315.

4.4. Insertion of CO into titanacyclopentenes. Preparation of α,β-disubstituted cyclopentenones (8)

4.4.1. A general procedure

Into a THF solution of titanacyclopentenes (1.0 mmol) prepared in situ as described above, was slowly bubbled CO gas at −30 °C for 3 h. The reaction mixture was then quenched with 3 N HCl and extracted with EtOAc. The combination of extracts was washed with water and brine, and dried over $MgSO_4$. Purification by column chromatography (silica gel, hexane–Et_2O = 4:1) afforded pure cyclopentenones.

4.4.2. A general note

We have reported the preparation and characterization of **8a**–**c**,**e** [5b].

4.4.3. 2,3-Dipheylcyclopenten-1-one (8a)

Colorless liquid, GC yield 88%, isolated yield 81%. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 2.62–2.64 (m, 2H), 2.96–2.98 (m, 2H), 7.18–7.31 (m, 10H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 29.18, 34.46, 127.46, 127.73, 128.08, 128.10, 129.12, 129.48, 132.04, 135.34, 139.44, 167.73, 207.10.

4.4.4. 2,3-Dibutylcyclopenten-1-one (8b)

Colorless liquid, GC yield 97%, isolated yield 90%. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, 3H, J = 7.1 Hz), 0.95 (t, 3H, J = 7.2 Hz), 1.27–1.42 (m, 6H), 1.48–1.56 (m, 2H), 2.15 (t, 2H, J = 7.1 Hz), 2.34–2.50 (m, 6H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 13.66, 13.66, 22.55, 22.57, 22.64, 28.71, 29.44, 30.60, 30.67, 34.00, 140.18, 173.63, 209.69.

4.4.5. 2,3-Dipropylcyclopenten-1-one (8c)

Colorless liquid, GC yield 99%, isolated yield 83%. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, 3H, J = 7.3 Hz), 0.98 (t, 3H, J = 7.4 Hz), 1.36–1.44 (m, 2H), 1.52–1.63 (m, 2H), 2.13–2.17 (t, 2H, J = 7.6 Hz), 2.34–2.40 (m, 2H), 2.41–2.44 (t, 2H, J = 7.8 Hz), 2.50–2.52 (m, 2H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 13.85, 13.90, 20.57, 21.60, 24.84, 28.63, 32.90, 33.97, 140.13, 173.63, 209.74.

4.4.6. Isolation of 8d

Cyclopentenone (**8d**) was obtained as mixture of two regioisomers (3:1). Combined GC yield 76%, combined isolated yield 63%. NMR data for the major: *2-Phenyl-3-butylcyclopenten-1-one*. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, 3H, J = 7.3 Hz), 1.29–1.35 (m, 2H), 1.50–1.58 (m, 2H), 2.49–2.54 (m, 4H), 2.65 (t, 2H, J = 4.4 Hz), 7.22–7.41 (m, 5H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 13.61, 22.45, 28.88, 29.60, 31.25, 34.51, 127.33, 128.04, 128.90, 131.87, 140.22, 175.76, 207.73. NMR data for the minor: *2-Butyl-3-phenylcyclopenten-1-one*. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 0.87 (t, 3H, J = 7.4 Hz), 1.26–1.50 (m, 4H), 2.37 (t, 2H, J = 7.5 Hz), 2.50–2.53 (m, 2H), 2.89 (t, 2H, J = 4.6 Hz), 7.26–7.46 (m, 5H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 13.81, 22.95, 23.83, 29.83, 30.45, 34.25, 127.19, 128.86, 129.29, 36.75, 141.32, 167.04, 209.76. HRMS calc. for $C_{15}H_{18}O$ 214.1358, found 214.1348.

4.4.7. Isolation of 8e

Cyclopentenone (**8e**) was obtained as a mixture of two regioisomers (10:1). Combined GC yield 81%, combined isolated yield 67%. NMR data for the major: *2-phenyl-3-methylcyclopenten-1-one*. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 2.14 (s, 3H), 2.48–2.53 (m, 2H), 2.60–2.63 (m, 2H), 7.26–7.43 (m, 5H). ^{13}D-NMR ($CDCl_3$, Me_4Si): δ 18.29, 31.75, 34.81, 127.53, 128.19, 129.09, 131.84, 140.21, 171.96, 207.54. NMR data for the minor: *2-Methyl-3-phenylcyclopenten-1-one*. ^{1}H-NMR ($CDCl_3$, Me_4Si): δ 1.97 (s, 3H), 2.540–2.56 (m, 2H), 2.91–2.94 (m, 2H), 7.42–7.54 (m, 5H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ 9.94, 29.27, 34.02, 127.56, 128.63, 129.48, 136.43, 136.54, 166.60, 209.86.

4.5. Preparation of monocyclic titanacyclopentadienes

4.5.1. A general procedure

n-BuLi (2.4 mmol, 1.6 M hexane solution, 1.5 ml) was added dropwise with a syringe to a THF (5 ml) solution of Cp_2TiCl_2 (1.25 mmol, 299 mg) at −78 °C (dry ice–acetone bath) in a 20 ml Schlenk tube. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. To the reaction mixture, an alkyne (2.0 mmol) was added, then stirred for 3 h at −10 °C (NH_4Cl–ice bath). The formation of titanacyclopentadienes was determined by ^{13}C-NMR. Only the Cp peaks were detected by ^{1}H-NMR, because several peaks overlapped with the THF peaks.

4.5.2. Bis(cyclopentadienyl)-2,3,4,5-tetramethyl-1-titanacyclopentadiene (9a)

NMR yield 92%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 1.30 (s, 6H), 1.65 (s, 6H), 5.83 (s, 10H). ^{13}C-NMR (C_6D_6, Me_4Si): δ 19.5, 92.2, 98.6, 112.2 (5C), 114.7. HRMS calc. for $C_{18}H_{22}Ti$ 286.1201, found 286.1194.

4.5.3. Bis(cyclopentadienyl)-2,3,4,5-tetraethyl-1-titanacyclopentadiene (9b)

NMR yield 93%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 0.99 (t, 6H, J = 7.5 Hz), 1.10 (t, 6H, J = 7.4 Hz), 1.48 (q, 4H, J = 7.3 Hz), 2.07 (q, 4H, J = 7.5 Hz), 5.96 (s, 10H). ^{13}C-NMR (C_6D_6, Me_4Si): δ 14.8, 15.5, 21.0, 27.9, 111.8 (5C), 131.9, 200.7. HRMS calc. for $C_{22}H_{30}Ti$ 342.1827, found 342.1856.

4.5.4. Bis(cyclopentadienyl)-2,3,4,5-tetrapropyl-1-titanacyclopentadiene (9c)

NMR yield 75%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 0.91 (t, 6H, J = 7.2 Hz), 1.03 (t, 6H, J = 7.2 Hz), 1.31–1.42 (m, 8H), 1.67–1.73 (m, 4H), 1.94–1.99 (m, 4H), 5.96 (s,

10H). ^{13}C-NMR (C_6D_6, Me_4Si): δ 15.0, 15.5, 24.0, 24.4, 31.0, 38.8, 112.1 (5C), 131.1, 199.8. HRMS calc. for $C_{26}H_{38}Ti$ 398.2453, found 398.2436.

*4.5.5. Bis(cyclopentadienyl)-1,3-dimethyl-2,4-diphenyl-1-titanacyclopentadiene (**9d**)*

NMR yield 92%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 1.22 (s, 3H), 1.47 (s, 3H), 5.90 (s, 10H), 7.26–6.89 (m, 10H). ^{13}C-NMR (C_6D_6, Me_4Si): δ 18.9, 22.3, 112.8, 113.4 (10C), 114.1, 123.6, 125.6, 126.8 (2C), 128.1 (2C), 129.6 (2C), 130.2, 135.7, 143.2, 148.7, 195.5, 198. HRMS calc. for $C_{28}H_{26}Ti$ 410.1514, found 410.1540.

*4.5.6. Bis(cyclopentadienyl)-1,3-dibutyl-2,4-diphenyl-1-titanacyclopentadiene (**9e**)*

NMR yield 86%. ^{1}H-NMR (C_6D_6, Me_4Si): δ 0.57 (t, 6H, $J = 7.0$ Hz), 0.71 (t, 6H, $J = 6.8$ Hz), 1.23–2.06 (m, 12H), 6.00 (s, 10H), 7.29–6.93 (m, 10H). ^{13}C-NMR (C_6D_6, Me_4Si): δ 13.9, 14.0, 23.0, 23.9, 30.5, 32.9, 33.0, 37.4, 112.4, 113.3 (10C), 114.3, 123.6, 125.5, 126.5 (2H), 128.1 (2C), 130.0 (2C), 132.5, 135.5, 143.3, 149.0, 196.5, 204.3. HRMS calc. for $C_{34}H_{38}Ti$ 494.2453, found 494.2470.

*4.6. Reaction of titanacyclopentadienes with DMAD in the presence of CuCl. Isolation of trienes (**11**)*

4.6.1. A general procedure

To a THF solution of titanacyclopentadienes (1.0 mmol) prepared in situ as described above, were added dimethyl acetylene dicarboxylate (DMAD, 2.0 mmol) and CuCl (2.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. Hydrolysis of the reaction mixture and normal work-up afforded trienes (**11a**–**c**). Purification of the trienes (**11a**–**c**) was achieved using column chromatography on silica gel (hexane–Et_2O = 4:1).

*4.6.2. Isolation of triene (**11a**)*

GC yield 76%, isolated yield 62%. ^{1}H-NMR ($CDCl_3$, $SiMe_4$): δ 0.90–1.03 (m, 12H), 1.96–2.27 (m, 8H), 3.70 (s, 3H), 3.76 (s, 3H), 5.25 (t, 1H, $J = 7.2$ Hz), 5.82 (s, 1H). ^{13}C-NMR ($CDCl_3$, $SiMe_4$): δ 12.96, 13.30, 13.48, 13.78, 21.35, 23.09, 24.24, 24.47, 51.68, 52.13, 121.20, 131.73, 133.91, 139.03, 148.75, 150.01, 165.93, 168.50. We have reported the formation and characterization of this compound [26].

*4.6.3. Isolation of triene (**11b**)*

GC yield 60%, isolated yield 50%. ^{1}H-NMR ($CDCl_3$, $SiMe_4$): δ 0.85–0.95 (m, 12H), 1.30–1.45 (m, 8H), 1.93–2.19 (m, 8H), 3.70 (s, 3H), 3.76 (s, 3H), 5.29 (t, 1H, $J = 7.2$ Hz), 5.78 (s, 1H). ^{13}C-NMR ($CDCl_3$, $SiMe_4$): δ 13.87, 13.98, 14.03, 14.84, 21.53, 21.64, 22.32, 22.55, 30.35, 32.79, 33.10, 33.42, 51.66, 52.15, 121.26, 130.76, 132.45, 138.79, 147.81, 150.42, 165.91, 168.48. HRMS calc. for $C_{22}H_{36}O_4$ 364.2612, found 364.2597.

*4.6.4. Isolation of triene (**11c**)*

Isolated yield 54%. ^{1}H-NMR ($CDCl_3$, $SiMe_4$): δ 0.85–0.93 (m, 12H), 1.27–1.34 (m, 16H), 2.01–2.19 (m, 8H), 3.70 (s, 3H), 3.76 (s, 3H), 5.27 (t, 1H, $J = 7.3$ Hz), 5.77 (s, 1H). ^{13}C-NMR ($CDCl_3$, $SiMe_4$): δ 13.94, 14.02, 22.50, 22.66, 22.75, 23.36, 27.91, 30.22, 30.51, 30.69, 30.87, 31.18, 31.54, 51.64, 52.11, 121.09, 130.71, 132.41, 138.70, 147.81, 150.56, 165.87, 168.48. HRMS calc. for $C_{26}H_{44}O_4$ 420.3237, found 420.3262.

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