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'Tucked-in' titanocene alkyls and alkylidenes

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Dedicated in honor of Professor Richard R. Schrock

Abstract

Titanocene neopentyl complexes with one cyclometallated *tert*-butylcyclopentadienyl group, $(\eta^5\text{-}C_5H_4R)(\eta^5,\eta^1\text{-}C_5H_4CMe_2CH_2)Ti(CHCMe_3)$, are readily obtained from the corresponding titanocene dichlorides and bis(neopentyl)magnesium. These compounds lose neopentane by α-H abstraction from the cyclometallated ligand to generate alkylidene species in which the alkylidene moiety is connected to one of the cyclopentadienyl ligands. The alkylidene $(C_5H_4Me)(C_5H_4CMe_2CH)Ti(PMe_3)$ reacts with benzene-d_6 by stereoselective addition of a C–D bond across the Ti=C bond. These 'tucked-in' alkylidene species also exhibit a wide range of reactivity towards unsaturated substrates (alkynes, ethene, benzonitrile), initiated by cycloaddition to the Ti=C bond.

Keywords: Alkylidene; C–H bond activation; Titanium; Alkyne; Ethene

1. Introduction

The α-H elimination process in transition-metal dialkyl species is the classical route for the formation of metal alkylidenes [1,2]. The principle of microscopic reversibility requires the reverse reaction, addition of C–H bonds to alkylidenes, to be feasible as well. Several examples of *intra*molecular addition of C–H bonds to (either proposed or actually observed) metal alkylidene intermediates were reported from the 1980s onward [3], but the *inter*molecular C–H addition to metal alkylidenes was only established after reports of the same reaction for metal nitrenes (M=NR) [4]. The titanocene neopentylidene, generated by an α-H elimination process from $Cp_2Ti(CH_2CMe_3)_2$, was found to add aromatic and benzylic C–H bonds to give mixed aryl/benzyl-neopentyl titanocenes [5]. This reaction should be quite general, provided that the alkylidene generated is electronically unsaturated, does not readily give stable dimers, and the overall reaction is thermodynamically favoured. Indeed, subsequent reports revealed intermolecular C–H activation reactions for a range of alkylidene species of various metals (e.g. Ti [6], Cr [7], W [8]).

In this contribution we describe the *intra*molecular addition of C–H bonds of *tert*-butyl-cyclopentadienyl ancillary ligands to titanocene alkylidenes. The resulting alkyl complexes with cyclometallated *tert*-butyl-cyclopentadienyl ligands provide a route to highly reactive intramolecularly chelating ('tucked-in') alkylidene species. For example, the 'tucked-in' alkylidene complex $(C_5H_4Me)(C_5H_4CMe_2CH)Ti(PMe_3)$ is a rare example of a stable, isolable alkylidene compound that is able to effect benzene C–H activation. The reactivity of this and related alkylidenes with reagents such as alkynes, ethene and benzonitrile has been evaluated using reactions on NMR-tube scale.

2. Results and discussion

2.1. Synthesis and thermolysis of $(C_5H_4R)(C_5H_4CMe_2CH_2)Ti(CHCMe_3)$

The reaction of the titanocene dichlorides $(\eta^5\text{-}C_5H_4R)(\eta^5\text{-}C_5H_4tBu)TiCl_2$ (R = Bu^t, **1a**; Me, **1b**; H,

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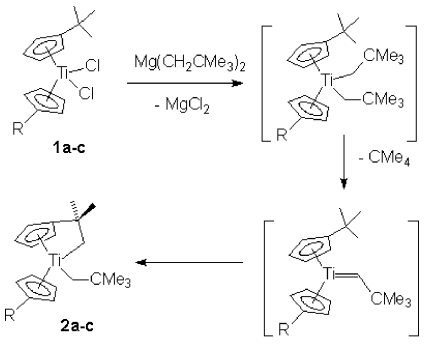
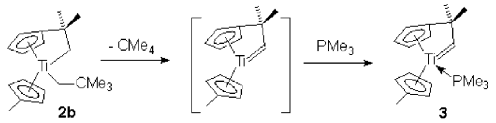
1c) with $(Me_3CCH_2)_2Mg\cdot$dioxane in diethyl ether, followed by extraction with pentane at ambient temperature, yielded the cyclometallated complexes (η^5-C_5H_4R)(η^5,η^1-$C_5H_4CMe_2CH_2$)Ti(CH_2CMe_3) (R = Bu^t, **2a**; Me, **2b**; H, **2c**) as red–brown crystalline solids (Scheme 1). The NMR spectra of these cyclometallation products are distinguished by the upfield resonances of the methylene protons of the $C_5H_4CMe_2CH_2$-group, found e.g. for **2b** at δ −2.57 (*endo*-H) and −0.02 ppm (*exo*-H) with a $^2J_{HH}$ of 9.5 Hz. These features are similar to those observed by Erker et al. in (C_5H_4R)($C_5H_4CMe_2CH_2$)TiPh, obtained by thermolysis of the related titanocene diphenyl complexes [9]. These resonances are readily distinguished from the methylene resonances of the neopentyl group (**2b**: δ 0.07 and 1.29 ppm, $^2J_{HH}$ = 9.9 Hz). The ^{13}C NMR resonances of the methylene carbons in **2b** are found at δ 45.3 ppm ($^1J_{CH}$ = 132 Hz) for the cyclometallated ligand and δ 76.6 ppm ($^1J_{CH}$ = 113 Hz) for the neopentyl group. In none of the reactions could the intermediate bis(neopentyl) titanocene compound be observed, indicating that the α-H abstraction processes in these substituted titanocene bis(neopentyl) species are fast. It was observed previously that α-H abstraction in (C_5H_4R)$_2$Ti(CH_2CMe_3)$_2$ is significantly faster for R = Me than for R = H [5]. This α-H abstraction is then followed by a rapid intramolecular addition of a C–H bond of the cyclopentadienyl Bu^t substituent to yield the cyclometallated compounds **2**. This reactivity is comparable with that observed upon thermolysis of (C_5H_4R)($C_5H_4CMe_3$)TiPh_2, in which case the C–H activation is performed by an η^2-benzyne intermediate [9].

Warming solutions of (C_5H_4Me)($C_5H_4CMe_2CH_2$)-Ti(CH_2CMe_3) (**2b**) to 80 °C in toluene in the presence of an excess of PMe_3 in a closed reaction vessel, followed by extraction with and crystallisation from pentane, yielded the unusual 'tucked-in' alkylidene complex (C_5H_4Me)($C_5H_4CMe_2CH$)Ti(PMe_3) (**3**, Scheme 2) as a yellow–brown solid. Although crystals of **3** suitable for single crystal X-ray diffraction could not be obtained, the nature of the compound is evident from NMR spectroscopy. It shows characteristic ^{1}H and ^{13}C NMR



Scheme 1.



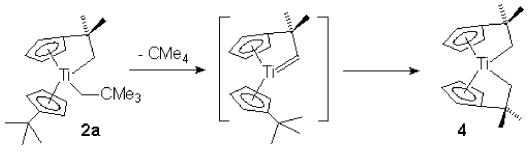
Scheme 2.

resonances for the alkylidene Ti=CH group at δ 11.92 ($^3J_{PH}$ = 4.3 Hz) and 312.0 ppm ($^1J_{CH}$ = 133 Hz, $^2J_{PC}$ = 25 Hz), respectively. Comparison with the spectral data of the titanocene neopentylidene Cp_2Ti($CHCMe_3$)PMe_3 [5] (δ 12.32 ppm, $^3J_{PH}$ = 7.2 Hz; δ 312.9 ppm, $^1J_{CH}$ = 110 Hz, $^2J_{PC}$ = 27 Hz) shows that the C–H coupling constant on the alkylidene fragment in **3** is significantly larger, probably in response to the smaller Ti–C–C angle enforced by the bridge to the C_5H_4-moiety. The ^{31}P NMR resonance of the coordinated phosphine in **3**, at δ 1.4 ppm, is considerably upfield from that in Cp_2Ti($CHCMe_3$)PMe_3 (δ 12.9 ppm), which may suggest a more weakly bound phosphine ligand in **3**.

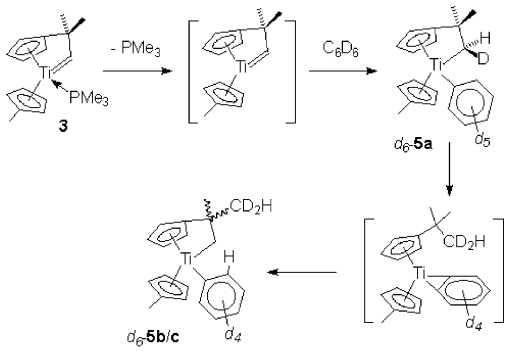
The chelating alkylidene moiety, generated by α-H abstraction in the complexes (C_5H_4R)($C_5H_4CMe_2$-CH_2)Ti(CH_2CMe_3), can also undergo intramolecular C–H addition. Warming ($C_5H_4Bu^t$)($C_5H_4CMe_2CH_2$)-Ti(CH_2CMe_3) (**2a**) in toluene solvent at 80 °C for 2 h (or prolonged standing of **2a** at ambient temperature in pentane) leads to liberation of neopentane and the formation of a red compound that, on the basis of its NMR spectra, was characterised as the doubly cyclometallated compound (η^5,η^1-$C_5H_4CMe_2CH_2$)$_2$Ti (**4**, Scheme 3). The ^{1}H NMR spectrum of **4** simply shows four multiplets for the non-equivalent protons on the Cp-ring, two singlets for the diastereotopic methyl groups and the two doublets characteristic for the methylene protons of the cyclometallated ligand, in accordance with the expected C_2-symmetry of **4**.

2.2. Reactivity of (C_5H_4Me)($C_5H_4CMe_2CH$)Ti(PMe_3) (3)

Warming a solution of the 'tucked-in' alkylidene **3** in C_6D_6 at 80 °C and monitoring the sample by NMR spectroscopy shows that under these conditions **3** will gradually react with C_6D_6 under liberation of PMe_3 to give the addition product (η^5-C_5H_4Me)(η^5,η^1-$C_5H_4CMe_2CHD$)Ti(C_6D_5) (d$_6$-**5a**). This can be distinguished by a broadened ^{1}H NMR resonance at δ −0.10 ppm for the *exo*-proton of the CHD-group in d$_6$-**5a**, indicating that the addition across the Ti=C bond in **3**



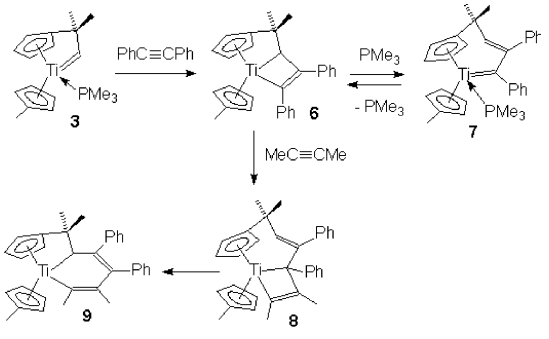
Scheme 3.



Scheme 4.

has taken place in a stereoselective manner (Scheme 4). In the course of the reaction, two sets of doublet resonances emerge gradually in the upfield region of the ^{1}H NMR spectrum, at δ −2.26/−2.28 ppm (*endo*-H) and −0.03/−0.06 ppm (*exo*-H) with $^2J_{HH} = 9.8$ Hz, and accompanied by a *o*-Ph resonance at δ 6.42 ppm. These resonances are attributed to the two isomers of $(C_5H_4Me)[C_5H_4C(CH_3)(CD_2H)CH_2]Ti(C_6D_4H)$ (d_6-**5b/c**) that are the product of *o*-metallation of the C_6D_5-group, followed by intramolecular addition of a C–H bond of one of the methyl groups in the $C(CH_3)_2(CD_2H)$ substituent to the benzyne intermediate generated by the *o*-metallation (Scheme 4). A continuation of this process eventually leads to extensive H/D-scrambling between the aryl and metallated tBu groups. These results indicate that, at 80 °C, the phosphine-stabilised 'tucked-in' alkylidene **3** is able to add arene C–H bonds to the Ti=C bond. Compound **3** thus appears to be much more reactive than the titanocene neopentylidene $Cp_2Ti(CHCMe_3)PMe_3$, which under the same conditions shows no reactivity.

The reactivity of the 'tucked-in' alkylidene **3** with unsaturated organic substrates was probed by reactions on NMR tube scale. With 1 equiv. of diphenylacetylene, **3** reacts at ambient temperature in toluene-d_8 to give a mixture of two compounds in a 3:1 ratio. These are the titanacyclobutene complex $(C_5H_4Me)(C_5H_4CMe_2CHCPh{=}CPh)Ti$ (**6**), the product that may be expected from the [2+2] cycloaddition of the alkyne to the Ti=C bond in **3**, and the vinylalkylidene complex



Scheme 5.

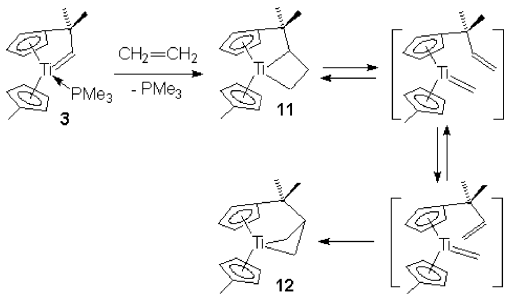
$(C_5H_4Me)(C_5H_4CMe_2CH{=}CPhCPh)Ti(PMe_3)$ (**7**), the product of ring-opening of **6** upon coordination of PMe_3 (Scheme 5). Characteristic for the titanacyclobutene species **6** are the NMR resonances of the Ti–*C*(Ph)= (δ 217.8 ppm) and Ti–*CH* (^{1}H NMR: δ 2.19 ppm; ^{13}C NMR δ 80.2 ppm) moieties, with the resonances for the CPh groups very similar to those reported for $Cp_2Ti(CH_2CPh{=}CPh)$ [10]. For the vinylalkylidene compound **7**, the Ti=*C*Ph resonance is found at δ 305.7 ppm ($^2J_{PC} = 22$ Hz), the –*C*Ph= resonance at 163.0 ppm ($^2J_{PC} = 4$ Hz), and the =*CH*– resonances at 113.9 (^{13}C) and 5.22 ppm (^{1}H, $^5J_{PH} = 1.8$ Hz). The two species can be shown to be in equilibrium by evaporating the volatiles from the above solution, followed by the redissolution of the brown solid in C_6D_6. The NMR spectrum of this solution shows exclusively the titanacyclobutene **6**, whereas the subsequent addition of a fourfold excess of PMe_3 results in a mixture of **6** and **7** in a 1:3 ratio, i.e. with the vinylalkylidene as the dominant species. Although ring-opening of metallacyclobutenes to give vinylalkylidenes has been studied before (as a reaction step in the catalysed polymerisation of alkynes by metal alkylidenes) [11], the observation of both species in equilibrium is quite rare. Such an equilibrium was observed in the reaction of the tantalacyclobutene $(DIPP)_3Ta(CR{=}CRCHCMe_3)$ (DIPP = 2,6-diisopropylphenoxide) with pyridine, but rapid interconversion of the two species precluded their simultaneous observation as separate species [11b].

Addition of an excess of 2-butyne to a solution of the titanacyclobutane **6** in toluene-d_8, prepared as described above, and subsequent cooling to −20 °C, reveals the formation of a new product that is tentatively identified as the cycloaddition product of the intermediate vinylalkylidene with 2-butyne (**8**, Scheme 5). Although the compound appears to be sterically very crowded, the ^{1}H and ^{13}C NMR characteristics of the species are consistent with the proposed structure, e.g. Ti–*C*(Me)= δ 245.6 ppm, and =C*H*– δ 5.46 ppm (singlet). At ambient temperature, **8** rearranges in 1–2 h to a new compound that is inert to further added alkyne. Its NMR spectroscopic features are consistent with its formulation as the titanacyclohexadiene $(C_5H_4Me)(C_5H_4CMe_2CHCPh{=}CPhCMe{=}CMe)Ti$ (**9**, Scheme 5). Characteristic NMR spectral features include the Ti–*C*(Me)= (δ 206.2 ppm) and Ti–*CH* (^{13}C: δ 75.8 ppm, $^1J_{CH} = 135$ Hz; ^{1}H: δ −1.28 ppm) resonances. The related tetramethyl-titanacyclohexadiene $(C_5H_4Me)(C_5H_4CMe_2CHCMe{=}CMeCMe{=}CMe)Ti$ (**10**) is obtained from the reaction of the alkylidene **3** with an excess of 2-butyne at ambient temperature. The formation of **9** from **8** may be considered to proceed through intramolecular attack on the Ti-centre by the vinyl =CH– group in the vinyl-substituted titanacyclobutene **8**. In this way, the link to the cyclopentadienyl ligand causes the system to deviate from the metallacyclobutene-vinylalkylidene sequence

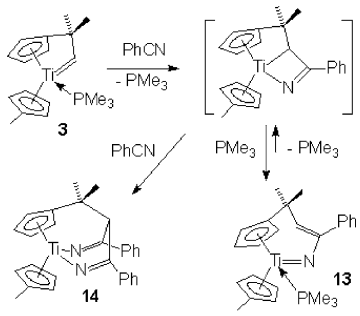
(leading to alkyne polymerisation) to form a species that is no longer reactive towards alkynes.

Reaction of the alkylidene complex **3** with 1 equiv. of ethene proceeds smoothly at ambient temperature with liberation of PMe_3 and formation of the asymmetric titanacyclobutane cycloaddition product (C_5H_4Me)-$(C_5H_4CMe_2CHCH_2CH_2)Ti$ (**11**, Scheme 6). A full assignment of the ^1H NMR resonances and couplings of the 2-substituted titanacyclobutane ring in **11** could be made from a $^1H,^1H$ COSY NMR spectrum and decoupling experiments. Typical spectral features of this compound are the upfield shift (δ −0.54 ppm) of the β-H atom *trans* to the substituent on the ring, and the upfield ^{13}C NMR chemical shift (δ −5.3 ppm) of the β-carbon. At ambient temperature, compound **11** gradually isomerises to a C_s-symmetric species, the 3-substituted titanacyclobutane complex $(C_5H_4Me)[C_5H_4$-$CMe_2CH(CH_2)_2]Ti$ (**12**). This compound is related to the $(C_5Me_5)[C_5Me_4CH_2CH(CH_2)_2]Ti$ complex reported by Luinstra et al. from the reaction of $(C_5Me_5)(C_5$-$Me_4CH_2)TiCl$ with $CH_2{=}CMeCH_2MgBr$ [12]. The isomerisation from **11** to **12** is likely to occur through a cleavage of the titanacyclobutane to give a methylidene intermediate, followed by rotation of the pendant vinylic substituent and subsequent readdition (Scheme 6).

The alkylidene **3** also reacts readily with nitriles. Upon reaction with 1 equiv. of benzonitrile, **3** is converted to the vinylimido complex $(C_5H_4Me)(C_5H_4$-$CMe_2CH{=}CPhN)Ti(PMe_3)$ (**13**, Scheme 7). Characteristic spectral features of this species include the resonances of the $=CH-$ (^1H NMR: δ 4.70 ppm, ^{13}C NMR: δ 110.2 ppm, $^4J_{CP} = 2.4$ Hz) and $C{=}N$ (δ 158.3 ppm, $^3J_{CP} = 2.7$ Hz) moieties. Titanocene vinylimido species are typical products from the reaction of titanocene alkylidenes with nitriles, via an initial cycloaddition reaction followed by ring-opening and base coordination [11a,13,14]. Warming solutions of **13** in the presence of excess benzonitrile leads to phosphine loss and the formation of a C_s-symmetric product, the 2,6-diaza-titanacyclohexa-2,5-diene complex (C_5H_4Me)-$[C_5H_4CMe_2CH(PhCN)_2]Ti(PMe_3)$ (**14**, Scheme 7). This product formation is similar to that observed for other titanocene vinylimido complexes with excess nitrile, with the main difference that in **14** the H-atom on the 4-carbon of the ring cannot migrate to one of the nitrogen atoms (leading to 2,6-diaza-titanacyclohexa-2,4-diene compounds [13,14]), due to the constraint applied by the anchoring of this carbon atom to the cyclopentadienyl ligand system.



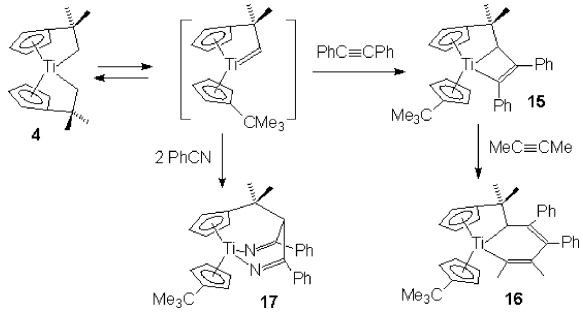
Scheme 6.



Scheme 7.

2.3. Reactivity of $(C_5H_4CMe_2CH_2)_2Ti$ (4)

The doubly cyclometallated complex $(C_5H_4CMe_2$-$CH_2)_2Ti$ (**4**) is itself a titanocene dialkyl compound containing α-hydrogen atoms. As it orginated from intramolecular addition of a Bu^t C–H bond to a 'tucked-in' alkylidene, it should in principle be capable of reactivity characteristic both of that of a dialkyl and those of an alkylidene. Indeed, the reactivity of **4** towards alkynes and nitriles leads to the same type of products as those of the reactions of the 'tucked-in' alkylidene **3** with these reagents. The main difference is that, in order to display alkylidene-like reactivity, compound **4** needs to be warmed to 80–90 °C or higher temperatures to give significant reaction rates. Under these conditions, **4** reacts with 1 equiv. of diphenylacetylene to give the titanacyclobutene $(C_5H_4Bu^t)(C_5H_4$-$CMe_2CHCPh{=}CPh)Ti$ (**15**) which, in similar fashion to **6**, can be converted with 2-butyne to the titanacyclohexadiene $(C_5H_4Bu^t)(C_5H_4CMe_2CHCPh{=}CPhCMe{=}$-$CMe)Ti$ (**16**, Scheme 8). With an excess of benzonitrile, **4** is converted to the 2,6-diaza-titanacyclohexa-2.5-diene complex $(C_5H_4Bu^t)[C_5H_4CMe_2(PhCN)_2]Ti$ (**17**, Scheme 8). Because of the lack of PMe_3 in these reactions, and the higher reaction temperatures required, intermediates

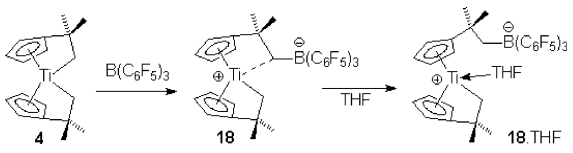


Scheme 8.

like the vinylalkylidene and vinylimido species cannot be observed. To form the products **15** and **17** it is not required to isolate the compound **4**: the same results can be obtained by the reaction of the cyclometallated mono(neopentyl) complex $(C_5H_4Bu^t)(C_5H_4CMe_2CH_2)$-$Ti(CH_2CMe_3)$ (**2a**) with the appropriate reagents under these conditions, with the concomitant formation of 1 equiv. of neopentane.

The dialkyl character of **4** is expressed e.g. in its reaction towards the Lewis acid $B(C_6F_5)_3$. In C_6D_6 solvent, this leads to the rapid formation of the zwitterionic compound $(C_5H_4CMe_2CH_2)[C_5H_4CMe_2$-$CH_2B(C_6F_5)_3]Ti$ (**18**, Scheme 9) by electrophilic attack of the Lewis acid on one of the alkyl α-carbons. We previously reported such an attack on a cyclometallated *tert*-butylcyclopentadienyl ligand in the zirconium compound $(C_5Me_5)(C_5H_4CMe_2CH_2)Zr(CH_2CMe_3)$, turning it into a highly selective catalyst for the dimerisation of 1-alkenes [15]. As with this Zr-compound, the low temperature ^{19}F NMR spectrum of **18** indicates hindered rotation of the borate C_6F_5 groups (showing 15 separate resonances), but no evidence for C–F···Ti interactions. This shows that the anionic alkyl(triaryl)borate fragment primarily interacts with the metal through the methylene group, the ^1H NMR resonances of which are observed as broad signals in the upfield region of the spectrum at δ −1.60 and −1.08 ppm. The resonance of the *endo* proton of the cyclometallated Bu^tCp ligand is found at very high field, δ −3.60 ppm, although not as extreme as that observed for the cationic niobium species $[(C_5H_4Bu^t)(C_5H_4CMe_2CH_2)Nb$-$(CH_2Ph)]^+$ (δ −5.58 ppm) [3e].

Upon standing for an hour or more at ambient temperature, benzene-d_6 solutions of **18** deposit a crystalline solid that is insoluble in weakly coordinating polar solvents like bromobenzene. This material (which unfortunately is of insufficient crystal quality to allow an X-ray structure determination) is probably a kind of coordination polymer of the zwitterionic compound. It dissolves in THF-d_8 to give a product that is identical to that formed by addition of a stoichiometric amount of THF to a C_6D_6 solution of **18** or dissolution of **18** in THF-d_8, $(C_5H_4CMe_2CH_2)[C_5H_4CMe_2CH_2B(C_6F_5)_3]$-$Ti(THF)$ (**18**·THF, Scheme 9). In this adduct, the coordinated THF has displaced the borate methylene group from the coordination sphere of the metal, as can be seen from the downfield shift of the BCH_2 ^1H NMR resonances to δ 1.91 and 2.19 ppm.



Scheme 9.

3. Conclusions

The methylene group of cyclometallated *tert*-butylcyclopentadienyl ligands in titanocene alkyls can itself undergo α-H abstraction to yield alkylidene species in which the alkylidene is linked to the cyclopentadienyl group. This link applies a geometrical constraint to the alkylidene that is expressed e.g. in an increased $^1J_{CH}$ coupling constant relative to titanocene neopentylidene species. It also increases the reactivity of the PMe_3-stabilised titanocene alkylidene, and allowed us to establish that the addition of a C_6D_6 C–D bond over the Ti=C double bond in $(C_5H_4Me)(C_5H_4C$-$Me_2CH)Ti(PMe_3)$ (**3**) proceeds in a stereoselective manner, initially yielding the addition product $(\eta^5$-$C_5H_4Me)(\eta^5,\eta^1$-$C_5H_4CMe_2CHD)Ti(C_6D_5)$ (d_6-**5a**) with the deuterium on the methylene group exclusively in the *endo* position. These 'tucked-in' alkylidenes exhibit normal $[2\pi+2\pi]$ cycloaddition chemistry with unsaturated substrates and allowed the observation of many intermediate species, e.g. in the reactivity towards alkynes. All the reaction steps required for alkyne polymerisation were observed (titanacyclobutene, vinylalkylidene, titanacyclobutene derived from cycloaddition to vinylalkylidene), but actual polymerisation was aborted by an intramolecular cyclisation induced by the link to the cyclopentadienyl ligand. The chemistry of these intramolecularly chelating alkylidenes thus provides interesting mechanistic information on the behaviour of titanocene alkylidenes and derived compounds.

4. Experimental

4.1. General

All experiments were performed under nitrogen atmosphere using standard glove-box and Schlenk techniques. Deuterated solvents (Aldrich, Acros) were flushed with nitrogen, dried over molecular sieves and stored and used in a glove-box. Other solvents were distilled under Ar atmosphere from sodium or sodium benzophenone ketyl. Compounds $(C_5H_4R)(C_5H_4Bu^t)TiCl_2$ ($R = Bu^t$, **1a**; Me, **1b**; H, **1c**) [16] and $Mg(CH_2CMe_3)_2$-(dioxane) [17] were prepared following published procedures. Commercially available diphenylacetylene, PMe_3 and ethene were used as received. Benzonitrile was stored on molecular sieves under nitrogen. $B(C_6F_5)_3$ was obtained in hydrocarbon solution (AKZO Nobel) and recovered as a solid after removal of the solvent in vacuo. NMR spectra were run on Varian XL-200, Gemini 300 and Inova 400 spectrometers.

4.2. Synthesis of $(C_5H_4R)(C_5H_4CMe_2CH_2)Ti(CH_2CMe_3)$

4.2.1. $(C_5H_4Bu^t)(C_5H_4CMe_2CH_2)Ti(CH_2CMe_3)$ (**2a**)

A solution of $(C_5H_4Bu^t)_2TiCl_2$ (**1a**, 0.523 g, 1.45 mmol) in 60 ml of Et_2O was cooled to −10 °C. A solution of $(Me_3CCH_2)_2Mg\cdot$dioxane (0.370 g, 1.45 mmol) in 20 ml of Et_2O was added, after which the mixture was allowed to warm to room temperature over 15 min. The mixture was centrifuged to remove salts, and the solvent was removed in vacuo from the supernatant after decantation. The residue was taken up into C_5H_{12} and the solution was centrifuged again. Concentration of the supernatant and cooling to −40 °C produced 0.444 g (1.23 mmol, 85%) of red–brown solid **2a**. ^{1}H NMR (C_6D_6): δ −2.60 (d, $J = 9.3$ Hz, 1H, *endo*-C*H*H), −0.02 (d, $J = 9.3$ Hz, 1H, *exo*-CH*H*), 0.03 (d, $J = 10.4$ Hz, 1H, TiC*H*HCMe$_3$), 0.98 (12 H, Me+CMe$_3$), 1.28 (s, 9H, CMe$_3$), 1.49 (s, 3H, Me), 1.55 (d, $J = 10.4$ Hz, 1H, TiCH*H*CMe$_3$), 4.48, 4.82, 5.14, 5.33, 6.07, 6.24 (2 ×), 7.29 (m, 1H each, Cp CH). ^{13}C{^{1}H} NMR (C_6D_6): δ 29.0, 29.3 (Me), 32.1, 34.9 (C*Me*$_3$), 33.6, 38.7 (C), 46.8 (Ti–CH$_2$), 75.5 (Ti–*C*H$_2$CMe$_3$), 105.8, 106.3, 109.8, 110.8, 113.0, 113.8, 114.5 (Cp CH), 117.4, 139.0 (Cp C).

4.2.2. $(C_5H_4Me)(C_5H_4CMe_2CH_2)Ti(CH_2CMe_3)$ (**2b**)

This compound was prepared following the same procedure as described for **2a**, starting from $(C_5H_4Me)(C_5H_4Bu^t)TiCl_2$ (**1b**). ^{1}H NMR (C_6D_6): δ −2.57 (d, $J = 9.5$ Hz, 1H, *endo*-C*H*H), −0.52 (d, $J = 9.5$ Hz, 1H, *exo*-CH*H*), 0.07 (d, $J = 9.9$ Hz, 1H, TiC*H*HCMe$_3$), 0.95 (s, 9H, CMe$_3$), 0.98 (s, 3H, Me), 1.29 (d, $J = 9.9$ Hz, 1H, TiCH*H*CMe$_3$), 1.47 (s, 3H, Me), 1.99 (s, 3H, Cp Me), 4.36, 4.64, 5.05, 5.10, 5.78, 6.25, 6.51, 7.31 (m, 1H each, Cp H). ^{13}C NMR (C_6D_6): δ 15.4 (q, $J = 127$ Hz, Cp Me), 29.1, 29.2 (q, $J = 124$ Hz, Me), 33.6 (s, C), 35.2 (q, $J = 124$ Hz, C*Me*$_3$), 38.8 (s, C), 45.3 (t, $J = 132$ Hz, Ti–CH$_2$), 76.6 (t, $J = 113$ Hz, Ti–*C*H$_2$CMe$_3$), 106.8, 109.0, 109.4, 112.1, 113.9, 114.1, 117.1 (d, $J = 165$–170 Hz, Cp CH), 118.7, 123.2 (s, Cp C). *Anal*. Calc. for $C_{20}H_{30}Ti$ (318.34): C, 75.46; H, 9.50; Ti, 15.04. Found: C, 75.22; H, 9.44; Ti, 15.20%.

4.2.3. $(C_5H_5)(C_5H_4CMe_2CH_2)Ti(CH_2CMe_3)$ (**2c**)

This compound was prepared following the same procedure as described for **2a**, starting from $(C_5H_5)(C_5H_4Bu^t)TiCl_2$ (**1c**). ^{1}H NMR (C_6D_6): δ −2.57 (d, $J = 9.3$ Hz, 1H, *endo*-C*H*H), −0.30 (d, $J = 9.3$ Hz, 1H, *exo*-CH*H*), 0.15 (d, $J = 10.0$ Hz, 1H, TiC*H*HCMe$_3$), 0.94 (12H, Me+CMe$_3$), 1.22 (d, $J = 10.0$ Hz, 1H, TiCH*H*CMe$_3$), 1.45 (s, 3H, Me), 4.37, 4.60, 6.27, 7.24 (m, 1H each, Cp H), 5.81 (s, 5H, Cp).

4.3. Synthesis of $(C_5H_4Me)(C_5H_4CMe_2CH)Ti(PMe_3)$ (**3**)

A solution of **2b** (0.49 g, 1.54 mmol) and an excess of PMe_3 (0.66 ml, 6.33 mmol) in 15 ml of $C_6H_5CH_3$ was stirred at 80 °C for 4 h in a closed thick-walled glass reaction vessel with a Teflon stopcock. The solvent and remaining phosphine was subsequently removed in vacuo, and the residue was recrystallised from a small volume of C_5H_{12} at −40 °C. This yielded **3** as a yellow–brown solid (0.15 g, 0.46 mmol, 30%). The material appears to be pure by NMR spectroscopy, but some paramagnetic impurities may still be present. The material is difficult to purify further by crystallisation. ^{1}H NMR (C_6D_6): δ 0.71 (d, $^2J_{PH} = 5.7$ Hz, 9H, PMe$_3$), 1.32, 1.49 (s, 3H each, Me), 1.92 (s, 3H, Cp Me), 4.84, 4.87, 4.95, 5.15, 5.30, 5.33, 5.50, 5.82 (m, 1H each, Cp H), 11.92 (d, $^3J_{PH} = 4.3$ Hz, Ti=CH). ^{13}C NMR (C_6D_6): δ 16.2 (q, $J = 125$ Hz, Cp Me), 20.5 (d, $^1J_{CP} = 15.3$ Hz, q, $J = 127$ Hz, PMe$_3$), 25.4 (d, $^4J_{CP} = 5.9$ Hz, q, $J = 124$ Hz, Me), 26.6 (d, $^4J_{CP} = 5.7$ Hz, q, $J = 125$ Hz, Me), 43.9 (s, C), 95.7, 98.4, 98.8, 100.0, 101.4, 102.0, 102.7, 104.6 (d, $J = 165$–167 Hz, Cp CH), 114.0, 114.6 (s, Cp C), 312.0 (d, $^2J_{CP} = 25$ Hz, d, $J = 133$ Hz, Ti=CH). ^{31}P{^{1}H} NMR (C_6D_6): δ 1.4.

4.4. Conversion of **2a** to $(C_5H_4CMe_2CH_2)_2Ti$ (**4**)

Warming a solution of **2a** in C_6D_6 to 80 °C for 2 h results in liberation of CMe_4 and formation of **4**. Thermolysis of **2a** at this temperature is accompanied by formation of a small amount of a paramagnetic impurity. Red crystalline **5** that is free of this impurity was obtained by allowing a solution of **2a** (0.20 g, 0.55 mmol) in C_5H_{12} to stand at ambient temperature for 3 weeks, follwed by cooling the solution to −20 °C, yielding 0.10 g (0.35 mmol, 63%) of **4**.

^{1}H NMR (C_6D_6): δ −3.05 (d, $J = 9.3$ Hz, 2H, *endo*-TiC*H*H), −0.38 (d, $J = 9.3$ Hz, 2H, *exo*-TiCH*H*),1.03, 1.38 (s, 6H each, Me), 4.75, 4.96, 5.93, 6.65 (m, 2H each, Cp CH). ^{13}C{^{1}H} NMR (C_6D_6): δ 28.9, 29.9 (Me), 34.2 (C), 47.9 (TiCH$_2$), 104.2, 109.0, 113.0, 114.9 (all Cp CH), 120.2 (Cp C).

4.5. Reaction of **3** with C_6D_6 and C_6H_6

A solution of **3** (10.0 mg, 0.03 mmol) in C_6D_6 was placed in an NMR-tube equipped with a Teflon valve, and warmed to 80 °C in the probe of a Varian VXR-300 spectrometer. The progress of the reaction was monitored by ^{1}H NMR at regular intervals. After 30 min a broadened singlet resonance at δ −0.10 was observed for the *exo*-proton in d$_6$-**5a**. After 1.5 h, two sets of doublets can be observed in addition, at δ −2.26, −2.28, −0.06 and −0.03 ($J = 9.8$ Hz) for *exo*- and *endo*-TiC*H*H, respectively of d$_6$-**5b/c**, together with a

resonance at δ 6.42 ppm for the Ti–C_6HD_4 *o*-H. Over longer periods of time, extensive H/D scrambling occurs between the phenyl group and the cyclometallated Bu^t group.

A sample of non-deuterated **5** was obtained by warming **3** in C_6H_6 at 80 °C for 6 h, after which the solvent was removed in vacuo and the residue was dissolved in C_6D_6. ^{1}H NMR (C_6D_6): δ −2.25 (d, $J = 9.7$ Hz, 1H, *endo*-TiC*H*H), −0.04 (d, $J = 9.7$ Hz, 1H, *exo*-TiCH*H*), 1.00, 1.35 (s, 3H each, Me), 1.80 (s, 3H Cp Me), 4.56, 4.96, 5.32, 5.46, 5.48, 5.85 (2 ×), 6.79 (m, 1H each, CH CH), 6.40 (m, 2H, Ph *o*-H), 6.96 (t, 1H, Ph *p*-H), 7.06 (m, 2H, Ph *m*-H).

4.6. Reaction of *3* with diphenylacetylene

Diphenylacetylene (11 mg, 0.06 mmol) and **3** (20 mg, 0.06 mmol) were dissolved in 0.6 ml of $C_6H_5CH_3$-d_8 at ambient temperature. By NMR, formation of a 3:1 mixture of the titanacyclobutene **6** and the vinylalkylidene **7** was observed. Evaporation of the volatiles and redissolution of the residue in $C_6H_5CH_3$-d_8 resulted in exclusive formation of the titanacyclobutene **6**. Addition by microsyringe of a fourfold excess of PMe_3 to this solution resulted in a 1:3 mixture of **6** and **7**.

4.6.1. (C_5H_4Me)($C_5H_4CMe_2CHCPh{=}CPh$)Ti (*6*)

^{1}H NMR ($C_6H_5CH_3$-d_8): δ 1.20, 1.33, 1.58 (s, 3H each, Me), 2.19 (s, 1H, Ti–CH), 4.94, 5.17, 5.40, 5.42, 5.64, 6.07, 6.18 (m, 1H each, Cp CH), 6.6–7.2 (Ph and 1H Cp CH). ^{13}C{^{1}H} NMR ($C_6H_5CH_3$-d_8): δ 15.5 (Cp Me), 26.2, 27.7 (Me), 39.9 (C), 80.2 (Ti–CH), 103.2, 107.2, 107.8, 109.1, 109.8, 110.1, 112.8, 113.5, 116.7 (Cp CH and =*C*Ph), 117.4 (Cp C), 124.6 (MeCp C) 126.2, 126.8, 128.3, 130.4 (Ph CH, others overlapped by solvent), 139.8, 146.1 (Ph C), 217.8 (Ti–C=).

4.6.2. (C_5H_4Me)($C_5H_4CMe_2CH{=}CPhCPh$)Ti(PMe_3) (*7*)

^{1}H NMR ($C_6H_5CH_3$-d_8): δ 0.84 (d, $^2J_{PH} = 5.7$ Hz, 9H, PMe_3), 1.32, 1.55, 1.61 (s, 3H each, Me), 4.45, 4.59, 4.80 (m, 1H each, Cp CH), 4.9–5.1 (3H, Cp CH), 5.22 (d, $^5J_{PH} = 1.5$ Hz, 1H, =CH–), 5.48, 6.53 (m, 1H each, Cp CH), 6.8–7.2 (Ph CH). ^{13}C{^{1}H} NMR ($C_6H_5CH_3$-d_8): δ 16.1 (Cp Me), 19.2 (d, $^1J_{PC} = 15.8$ Hz, PMe_3), 27.9, 34.3 (Me), 35.2 (C), 99.0, 101.6, 102.3, 102.6, 104.0, 104.6, 105.1, 107.0, 113.9 (Cp CH and =CH–), 121.9 (Cp C), 124.9 (MeCp C), 126.8 (Ph CH, others overlapped by solvent), 147.4, 158.6 (Ph C), 163.0 (d, $^3J_{PC} =$ 4.0 Hz, *C*(Ph)=), 305.7 (d, $^2J_{PC} = 22.2$ Hz, Ti=C).

4.7. Reaction of *6* with 2-butyne

In a refrigerator inside a drybox, a twofold excess of 2-butyne was added by microsyringe to a solution of titanacyclobutene **6** in $C_6H_5CH_3$-d_8, prepared as described above. After addition the solution was transferred in an NMR tube to the probe of an NMR spectrometer (−20 °C) and monitored by NMR spectroscopy, revealing formation of a new titanacyclobutene species, **8**. Upon standing at ambient temperature in $C_6H_5CH_3$-d_8 solution, **8** rearranges within a few hours to the green titanacyclohexadiene complex **9**.

4.7.1. (C_5H_4Me)($C_5H_4CMe_2CH{=}CPhCPhCMe{=}CMe$)Ti (*8*)

^{1}H NMR ($C_6H_5CH_3$-d_8, −20 °C): δ 1.14, 1.24, 1.27,1.60, 1.91 (s, 3H each, Me), 4.69, 4.89 (m, 1H each, Cp CH), 5.20–5.25 (m, 3H, Cp CH), 5.30, 5.47 (m, 1H each, Cp CH), 5.64 (s, 1H, =CH–), 5.79 (m, 1H, Cp CH), 6.8–7.2 (Ph CH). ^{13}C(APT) NMR ($C_6H_5CH_3$-d_8, −20 °C): δ 12.0, 14.4, 15.2, 20.6, 22.1 (Me), 35.5 (C), 95.3, 96.9 (Ti–C and β =*C*Me–), region between 100 and 130 too complicated for careful analysis, 140.8 (Cp C), 149.7, 150.7, 155.4 (Ph C and =*C*Ph–), 245.6 (Ti–*C*Me=).

4.7.2. (C_5H_4Me)($C_5H_4CMe_2CHCPh{=}CPhCMe{=}CMe$)Ti (*9*)

^{1}H NMR ($C_6H_5CH_3$-d_8): δ −1.28 (s, 1H, Ti–CH), 1.00, 1.31, 1.39, 1.46 (s, 3H each, Me), 1.62 (s, 3H, Cp Me), 4.53, 5.04, 5.32, 5.39, 5.74, 5.96, 6.04, 6.66 (m, 1H each, Cp CH), 6.7–7.1 (Ph CH). ^{13}C NMR ($C_6H_5CH_3$-d_8): δ 15.7 (Cp Me), 18.8, 21.2, 22.0, 34.7 (Me), 37.8 (C), 75.8 (d, $J = 135$ Hz, Ti–CH), 108.8, 109.2, 110.1, 110.6, 111.0, 111.8, 112.6, 113.1 (Cp CH), 117.7 (Cp C), 123.1 (MeCp C), 124.8, 125.3, 127.5, 130.7 (Ph CH, others overlapped by solvent), 133.0 (=*C*Me–), 142.9, 143.5, 145.8, 149.0 (Ph C and –*C*Ph–), 206.2 (Ti–*C*Me=).

4.8. Reaction of *3* with excess 2-butyne

Addition of a threefold excess of 2-butyne (using a cooled microsyringe) to a solution of **3** (16 mg, 0.05 mmol) in C_6D_6 and allowing this to stand at ambient temperature leads to full conversion to the titanahexadiene complex **10** in 24 h. ^{1}H NMR (C_6D_6): δ −2.07 (s, 1H, TiCH), 0.84, 1.19, 1.32, 1.63, 1.74, 1.75, 1.83 (s, 3H each, Me), 4.62, 5.13, 5.36, 5.47, 5.60, 5.81, 6.71 (m, 1H each, Cp CH). ^{13}C NMR (C_6D_6): δ 15.83 (q, $J = 126$ Hz, Cp Me), 15.97 (q, $J = 124$ Hz, Me), 19.14, 19.25, 21.70, 26.86 (q, $J = 125$ Hz, Me), 34.23 (q, $J = 126$ Hz, Me), 36.81 (s, C), 77.18 (d, $J = 131$, Ti–CH), 108.36, 108.76, 109.62, 110.06, 110.60, 111.23, 112.54, 112.60 (d, $J = 164$–168, Cp CH), 119.07 (Cp C), 122.65 (MeCp C), 132.48, 133.75, 135.60 (s, –*C*Me=), 198.77 (s, Ti–*C*Me=).

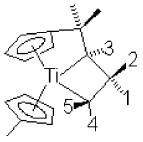
4.9. Reaction of *3* with ethene

A solution of **3** (20 mg, 62 μmol) in C_6D_6 was transferred to a NMR tube which was sealed by a

septum. Ethene (1.4 ml, 63 μmol) was added by gas-tight syringe at ambient temperature. By NMR, clean liberation of PMe_3 and formation of titanacyclobutane **11** was observed. Upon standing at ambient temperature, **11** gradually isomerises to the 3-substituted titanacyclobutane **12** (after 15 h approximately 75% conversion). Subsequently warming the solution to 40 °C for 1 h drives this reaction to completion.

*4.9.1. (MeCp)($C_5H_4CMe_2CHCH_2CH_2$)Ti (**11**)*

^{1}H NMR (C_6D_6): δ (for H-atom numbering, see illustration) −0.54 (m, 1H, H^1), 0.05 (m, 1H, H^2), 1.07, 1.16 (s, 3H each, Me), 1.73 (s, 3H, Cp Me), 2.14 (m, 1H, H^3), 2.82 (m, 1H, H^4), 3.26 (m, 1H, H^5), 4.85, 4.96, 4.99, 5.10, 5.14, 5.22, 5.30, 5.88 (m, 1H each, Cp CH). $J(1,2) = 12$ Hz, $J(1,3) = 10$ Hz, $J(1,4) = 12$ Hz, $J(1,5) = 5$ Hz, $J(2,3) = 3$ Hz, $J(2,4) = 4$ Hz, $J(2,5) = 13$ Hz, $J(3,4) = 0$ Hz, $J(4,5) = 8$ Hz. ^{13}C{^{1}H} NMR (C_6D_6): δ −5.3 (β-CH_2), 15.1 (Cp Me), 24.9, 27.0 (Me), 38.5 (C), 77.6 (Ti–CH_2), Ti–CH not observed, 101.1, 105.4, 105.6, 107.5, 108.1, 109.5, 115.7 (Cp CH), 118.5 (Cp C), 112.9 (MeCp C).



*4.9.2. (MeCp)[$C_5H_4CMe_2CH(CH_2)_2$]Ti (**12**)*

^{1}H NMR (C_6D_6): δ 1.07 (M, 2H, TiC*H*H), 1.43 (s, 6H, Me), 1.75 (m, 2H, TiCH*H*), 1.88 (s, 3H, Cp Me), 2.01 (m, 1H, β-CH), 5.04, 5.49, 5.54, 5.83 (m, 2H each, Cp CH). ^{13}C NMR (C_6D_6): δ 16.0 (q, $J = 127$ Hz, Cp Me), 25.5 (d, $J = 135$ Hz, β-CH), 26.1 (q, $J = 125$ Hz, Me), 39.0 (s, C), 64.3 (t, $J = 138$ Hz, Ti–CH_2), 104.0, 106.0, 107.3, 111.4 (d, 164–167 Hz, Cp CH), 123.1, 124.9 (Cp C).

*4.10. Reaction of **3** with PhCN*

A solution was made of **3** (16 mg, 0.05 mmol) in 0.6 ml of C_6D_6. Subsequent addition by microsyringe of 1 equiv. of PhCN to the solution at ambient temperature led to the formation of the vinylimido complex **13**. Subsequent addition of a twofold excess of PhCN, followed by warming the solution to 50 °C, led to phosphine loss and formation of the 2,6-diaza-titanacyclohexa-2,5-diene complex **14**.

*4.10.1. (MeCp)($C_5H_4CMe_2CH$=CPhN)Ti(PMe_3) (**13**)*

^{1}H NMR (C_6D_6): δ 0.68 (d, $J_{PH} = 7.0$ Hz, 9H, PMe_3), 1.46, 1.74 (s, 3H each, Me), 2.24 (s, 3H, Cp Me), 4.59 (m, 1H, Cp CH), 4.70 (s, 1H, =CH–), 4.77, 5.01 (m, 1H each, Cp CH), 5.4 (m, 2H, Cp CH), 5.66 (m, 1H, Cp CH), 5.8 (m, 2H, Cp CH), 6.8–7.2 (m, 5H, Ph). ^{13}C(APT) NMR (C_6D_6): δ 16.1 (MeCp Me), 17.4 (d, $J_{PC} = 17.9$ Hz, PMe_3), 27.2, 43.1 (Me), 35.3 (C), 100.2, 101.4, 102.9, 104.0, 104.6, 106.7, 107.7, 108.4 (all Cp CH), 110.2 (d, $J_{CP} = 2.4$ Hz, =CH–), 123.4 (MeCp C), 126.4 (Ph *m*-CH), 127.9 (Ph *o*-CH), Ph *p*-H not observed, 129.8 (Cp C), 141.2 (d, $J_{CP} = 2.4$ Hz, Ph C), 158.3 (d, $J_{CP} = 2.7$ Hz, N*C*=). ^{31}P NMR (C_6D_6): δ −0.51.

*4.10.2. (MeCp)[$C_5H_4CMe_2CH(PhCN)_2$]Ti (**14**)*

^{1}H NMR (C_6D_6): δ 1.20 (s, 6H, CMe_2), 2.22 (s, 3H, Cp Me), 5.45, 5.57 (m, 1H each, Cp CH), 5.68 (s, 1H, CH), 5.9 (br m, 4H, MeCp CH), 7.1–7.3 (m, 6H, Ph *p*-H and *m*-H), 7.89 (d, $J = 7.8$ Hz, 4H, Ph *o*-H). ^{13}C(APT) NMR (C_6D_6): δ 15.8 (MeCp Me), 28.6 (C*Me*$_2$), 45.4 (C), 78.6 (CH), 104.9, 109.7, 113.4, 117.3 (all Cp CH), 127.4 (Ph *m*-CH), 128.4 (Ph *p*-CH), 128.6 (Ph *o*-CH), 128.5 (MeCp C), 130.6 (Cp C), 140.9 (Ph C), 159.5 (N=*C*).

*4.11. Sequential reaction of **4** with diphenylacetylene and 2-butyne*

A solution of **4** (15 mg, 0.05 mmol) and diphenylacetylene (9 mg, 0.05 mmol) in 0.6 ml $C_6H_5CH_3$-d_8 in an NMR tube sealed with a Teflon stopcock was warmed at 115 °C for 3 h. This resuled in complete conversion to the titanacyclobutene complex **15**. The same compound can be obtained (with concomitant formation of neopentane) by warming a solution of equimolar amounts of **2a** and diphenylacetylene in C_6D_6 at 60 °C overnight. Addition (by cooled microsyringe) of a threefold excess of 2-butyne to the solution of **15** in $C_6H_5CH_3$-d_8 described above, and allowing the tube to stand at ambient temperature overnight, resulted in full conversion to the titanacyclohexadiene complex **16**.

*4.11.1. (Bu^tCp)($C_5H_4CMe_2CHCPh$=CPh)Ti (**15**)*

^{1}H NMR ($C_6H_5CH_3$-d_8): δ 0.77 (s, 9H, Bu^t), 1.15, 1.41 (s, 3H each, Me), 2.46 (s, 1H, TiCH), 5.25, 5.34, 5.39, 5.47, 5.57, 5.79, 6.17, 6.43 (m, 1H each, Cp CH), 6.8–7.1 (Ph H), 7.25 (d, $J = 7.3$ Hz, 2H, Ph *o*-H).

*4.11.2. (Bu^tCp)($C_5H_4CMe_2CH$=CPhCPhCMe=CMe)Ti (**16**)*

^{1}H NMR ($C_6H_5CH_3$-d_8): δ −1.15 (s, 1H, TiCH), 0.73 (s, 9H, Bu^t), 1.12, 1.32, 1.37, 1.48 (s, 3H each, Me), 4.66, 5.24, 5.41, 5.69, 5.73, 6.08, 6.28, 6.70 (m, 1H each, Cp CH), 6.8–7.2 (Ph H).

*4.12. Reaction of **4** with PhCN*

A solution of **4** (12 mg, 0.04 mmol) in 0.6 ml of $C_6H_5CH_3$-d_8 was placed in an NMR tube equipped with

a Teflon stopcock, and a fourfold excess of PhCN was added by microsyringe. The tube was closed and warmed at 95 °C overnight, after which conversion to **17** was complete. To facilitate the analysis of the ^{13}C NMR spectra, the volatiles were removed from the solution, and the orange solid product was redissolved in C_6D_6. ^1H NMR (C_6D_6): δ 1.14 (s, 6H, CMe_2), 1.30 (s, 9H, Bu^t), 5.42, 5.62 (m, 2H each, Cp CH), 5.63 (s, 1H, CH), 6.02, 6.14 (M, 2H each, Cp CH), Ph *o*-H obscured by solvent, 7.25 (t, $J = 7.6$ Hz, 4H, Ph *m*-H), 7.81 (d, $J = 7.6$ Hz, 4H, Ph *o*-H). ^{13}C NMR (C_6D_6): δ 28.61 (q, $J = 126$ Hz, CMe_2), 31.32 (q, $J = 125$ Hz, CMe_3), 32.91 (s, CMe_3), 45.68 (s, CMe_2), 78.81 (d, $J = 130$ Hz, CH), 105.27, 109.33, 111.62, 117.35 (all d, $J = 170$–175 Hz, Cp CH), 127.42, 128.65, 128.77 (all d, $J = 165$–170 Hz, Ph CH), 130.49 (s, Cp C), 140.29 (s, Bu^tCp C), 141.03 (s, Ph C), 159.55 (s, N=*C*).

4.13. Reaction of **4** with $B(C_6F_5)_3$

A mixture of solid **4** (22 mg, 0.076 mmol) and $B(C_6F_5)_3$ (39 mg, 0.076 mmol) was dissolved in 0.6 ml of C_6D_6, resulting in a brown solution. Clean formation of the zwitterionic compound **18** was observed by NMR spectroscopy. Allowing this solution to stand at ambient temperatures for more than 1 h results in the gradual formation of a brown crystalline solid that does not dissolve in C_6D_5Br. Addition of THF redissolved this material as the THF-adduct of **18** (vide infra). The rate of precipitation appears to decrease with decreasing concentation and temperature.

4.13.1. $(C_5H_4CMe_2CH_2)[C_5H_4CMe_2CH_2B(C_6F_5)_3]Ti$ (**18**)

^1H NMR (C_6D_6): δ −3.60 (d, $J = 10.0$ Hz, 1H, TiC*H*H), −1.60, −1.08 (br, 1H each, BCH_2), 0.26, 0.37, 1.42, 1.58 (s, 3H each, Me), 2.35 (d, $J = 10.0$ Hz, 1H, TiCH*H*), 3.78, 4.25, 4.93, 5.16, 5.58, 6.12, 6.40, 6.95 (m, 1H each, Cp CH). ^{19}F NMR ($C_6H_5CH_3$-d_8, 25 °C): δ −130.3 (br, *o*-F), −159.6 (br, *p*-F), −164.3 (br, *m*-F). ^{19}F NMR ($C_6H_5CH_3$-d_8, −60 °C): δ −126.8, −127.8, −129.0, −132.2, −132.7, −133.6 (m, all *o*-F), −157.9, −158.8, −159.2 (m, all *p*-F), −160.7, −162.5, 163.6, −164.0, −164.4, −166.3 (m, all *m*-F).

4.14. Reaction of **18** with THF

To a solution of 0.014 mmol of **18** in C_6D_6, prepared as described above, THF (2.1 μl, 0.026 mmol) was added by microsyringe to give a clear yellow–green solution of **18**.THF. No exchange of free and coordinated THF was observed on NMR timescale at ambient temperature. Dissolution of **18** in neat THF-d_8 gives the same species. ^1H NMR (C_6D_6): δ −3.24 (d, $J = 9.0$ Hz, 1H, TiC*H*H), 0.53 (s, 3H, Me), 0.64 (d, $J = 9.0$ Hz, 1H, TiCH*H*), 0.95 (m, 4H, THF β-H), 0.98, 1.07, 1.18 (s, 3H each, Me), 1.91, 2.19 (br d, $J = 12$ Hz, 1H each, BCH_2), 2.50, 2.63 (m, 2H each, THF α-H), 3.78, 3.83, 4.30, 5.22, 5.72, 5.77, 5.93, 6.30, 6.74 (m, 1H each, Cp CH). ^{19}F NMR (C_6D_6): δ −131.1 (*o*-F), −164.4 (*p*-F), −167.6 (*m*-F). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 26.38, 28.03, 29.91, 32.41 (all Me), 35.51, 37.62 (both CMe_2), 38 (br, BCH_2), 59.48 ($TiCH_2$), 110.33, 111.70, 111.83, 114.56, 116.44 (all Cp CH), 120.56 (Cp C), 121.13, 122.69, 123.30 (all Cp CH), 128.1 (br B–Ar C), 137.2 (d, $^1J_{CF} = 247$ Hz, *m*-CF), 138.4 (d, $^1J_{CF} = 245$ Hz, *p*-CF), 149.2 (d, $^1J_{CF} = 240$ Hz, *o*-CF), 151.13 (Cp C).

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