

Coupling reactions of alkynes with half-open titanocenes: Agostic (C–C) → Ti interactions in a tetra(alkyne) coupling product with the Ti(C₅H₅)(*c*-C₈H₁₁) fragment

Benjamin G. Harvey, Atta M. Arif, Richard D. Ernst *

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, UT 84112-0850, United States

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Abstract

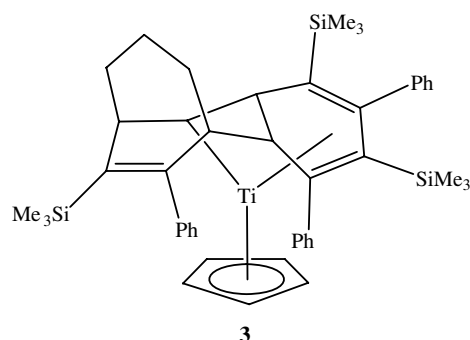
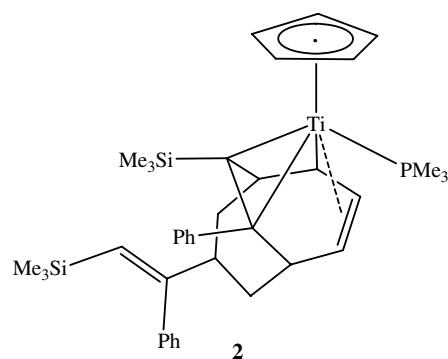
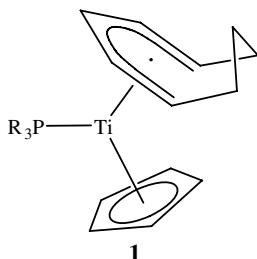
The reaction of the half-open titanocene Ti(C₅H₅)(*c*-C₈H₁₁)(PMe₃) (*c*-C₈H₁₁ = cyclooctadienyl) with four equivalents of PhC₂SiMe₃ has been found to lead to an unusual, very electron deficient coupling product, containing both metallacyclobutane and metallacyclobutene fragments. Structural studies of both complexes have been carried out, and for the latter reveal apparent (C–C) → Ti agostic interactions in both the metallacyclobutane and metallacyclobutene fragments.

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1. Introduction

The 16 electron half-open titanocene complexes, Ti(C₅H₅)(*c*-C₈H₁₁)(PR₃) (**1a**, R = Me; **1b**, R = Et), have been found to react with PhC₂SiMe₃, leading, respectively, to the incorporation of two and three equivalents of the alkyne, yielding **2** [1] and **3** [2].



In each case, formally electron deficient (14 electron) titanium complexes resulted,¹ in which the metal centers were

* Corresponding author. Tel.: +1 801 581 8639.

E-mail address: ernst@chem.utah.edu (R.D. Ernst).

¹ In the case of **2**, the extent of olefin coordination was assessed as being unimportant to a first approximation.

surrounded by cage-like arrangements of C–C bonds, reminiscent of the electron deficient boron centers in carboranes. In fact, related 16 electron “cage-like” complexes formed from similar reactions involving diynes had been observed to undergo C–C bond activation reactions [3]. While C–C bond activations were not readily observed for **2** and **3** (though **2** does seem to undergo a slow transformation to another, yet unidentified species), **2** and **3** have been the first species to be characterized as having (C–C) → M agostic interactions, involving formal donation of C–C sigma bonding electron density, on the basis of structural, spectroscopic, and theoretical studies [2]. Subsequently, several other such species have been proposed to exist [4–6], based primarily on structural data [1], although spectroscopic data, particularly $J(^{13}\text{C}-^{13}\text{C})$ values, and theoretical studies [8], have revealed that electron deficient metallacyclobutanes also possess such agostic interactions. Notably, these interactions appear to play some part in the olefin metathesis process [7], specifically in the conversion of the metallacyclobutane structure to olefin and a metal carbene complex [1,8]. The presence of the agostic interactions could readily facilitate the activation of the C–C bond that is required for the formal cycloreversion step.

It has more recently been observed that a third coupling product of $\text{PhC}_2\text{SiMe}_3$ with the $\text{Ti}(\text{C}_5\text{H}_5)(\text{c}-\text{C}_8\text{H}_{11})$ fragment may be isolated. This product has been found to incorporate four equivalents of alkyne, and its formation actually appears to be related straightforwardly to a reaction of the fourth alkyne with **3**. Once again, a cage-like structure of carbon atoms was observed to surround an electron deficient (formally 14 electron) metal center, which then made close approaches to C–C bonds. An interesting aspect of the present case is the occurrence of a titanacyclobutene fragment, which provides the metal center with competitive opportunities to interact with C–C and C=C bonds. Herein we provide spectroscopic and structural data for this new compound in an effort to understand its bonding.

2. Experimental

All reactions were carried out under a nitrogen atmosphere in Schlenk apparatus. Hydrocarbon and aromatic solvents were dried by passage through activated alumina columns under a nitrogen atmosphere, while THF was dried by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. $\text{Ti}(\text{C}_5\text{H}_5)(\text{c}-\text{C}_8\text{H}_{11})(\text{PMe}_3)$, $\text{Ti}(\text{C}_5\text{H}_5)(\text{c}-\text{C}_8\text{H}_{11})(\text{PET}_3)$, and the latter's tris(alkyne) coupling product were prepared as previously described [1,2]. Elemental analyses were obtained from Desert Analytics. NMR assignments were aided using HETCOR and COSY spectra.

2.1. Tetra($\text{PhC}_2\text{SiMe}_3$) coupling product with the $\text{Ti}(\text{C}_5\text{H}_5)(\text{c}-\text{C}_8\text{H}_{11})$ fragment, **4**

To a slurry of 0.50 g (1.5 mmol) $\text{Ti}(\text{C}_5\text{H}_5)(\text{c}-\text{C}_8\text{H}_{11})\text{PET}_3$ at -78° in 50 mL of pentane was added 1.03 g (5.9 mmol) of 1-phenyl-2-(trimethylsilyl)acetylene via a syringe. A slow

transition from an orange-brown slurry to a dark red solution occurred. The cold bath was removed and the flask was allowed to warm to room temperature and was stirred for at least 2 h to bring about conversion of the initially formed **3–4**. The solution was then filtered through Celite on a coarse Schlenk frit. The Celite was washed with several 10 mL aliquots of pentane until the washings were colorless. The deep red filtrate was concentrated to ca. 50 ml and left to sit under nitrogen at room temperature overnight. On some occasions, deep red crystalline cubes deposited on the sides of the flask and were isolated by syringing off the supernatant and drying in vacuo. When this was not the case, concentration to ca. 30 mL followed by placement in a -30° freezer for two days yielded the crystalline product. Further solid can be isolated by concentration of the supernatant and cooling of the solution to -60° , although the solid from later crystallizations is waxy and less pure. Overall yields were ca. 30%. After crystallization, the solid is only slightly soluble in pentane but moderately soluble in benzene. Pentane was always observed in the NMR spectra for this molecule and was also present in the crystal lattice. This observation was even made for samples that had been dried for 2 h under dynamic high vacuum (10^{-3} Torr). The presence of pentane in the solid is also suggested by the elemental analysis results which revealed higher values than expected for both hydrogen and carbon. These data support a formulation of **4**- C_5H_{12} for the initially isolated material.

^1H NMR (benzene- d_6 , ambient): δ 7.8–6.6 (m, 18H, Ph), 6.42 (s, 5H, Cp), 6.20 (q, 1H, $J = 6$ Hz, Ph), 6.11 (d, 1H, $J = 7.2$ Hz, Ph), 3.94–3.82 (m, 2H, H13, H15), 3.73 (d, 1H, $J = 10$ Hz, H9), 2.73 (s, 1H, H18), 2.01–1.92 (m, 1H, H14), 1.62–1.24 (m, 4H, H19a,b, H20a,b), 1.13–0.90 (m, 2H, H21a,b), 0.24 (s, 9H, SiMe_3), 0.21 (s, 9H, SiMe_3), 0.15 (s, 9H, SiMe_3), 0.02 (s, 9H, SiMe_3).

^{13}C NMR (benzene- d_6 , ambient): δ 157.9 (s, 1C), 151.5 (s, 1C), 150.0 (s, 1C), 149.5 (s, 1C), 148.2 (s, 1C), 144.4 (s, 1C), 142.8 (s, 1C), 141.3 (s, 1C), 133–126 (21C, Ph), 121.6 (s, 1C), 117.3 (s, 1C), 111.2 (s, 1C), 109.2 (d, 5C, $J = 171$ Hz, Cp), 54.8 (d, 1C, $J = 119$ Hz, C14), 51.8 (d, 1C, $J = 131$ Hz, C18), 47.4 (d, 1C, $J = 121$ Hz, C9), 47.0 (d, 1C, $J = 122$ Hz, C13), 33.0 (t, 1C, $J = 125$ Hz, C19), 31.4 (d, 1C, $J = 138$ Hz, C15), 28.3 (t, 1C, $J = 123$ Hz, C21), 25.1 (t, 1C, $J = 129$ Hz, C20), 3.2 (q, 3C), 2.7 (q, 3C), 2.5 (q, 3C), 0.5 (q, 3C).

Anal. Calc. for $\text{C}_{57}\text{H}_{72}\text{Si}_4\text{Ti}$: C, 74.63; H, 7.91. Found: C, 74.91; H, 8.28%.

2.2. X-ray diffraction studies

Single crystals of **1a** were obtained by slowly cooling its concentrated solutions in ether to -60° , while suitable single crystals of **4** could be isolated directly, as described above. In each case, these crystals were handled under Paratone oil, and transferred to a Nonius Kappa CCD diffractometer for study. The structures were solved using direct methods and difference Fourier maps. Subsequent least squares refinements employed anisotropic thermal parame-

Table 1
Crystallographic parameters for $\text{Ti}(\text{C}_5\text{H}_5)(c\text{-C}_8\text{H}_{11})(\text{PMe}_3)$ (**1a**) and its tetra(alkyne) coupling product (**4**)

Formula	$\text{C}_{16}\text{H}_{25}\text{PTi}$	$\text{C}_{62}\text{H}_{84}\text{Si}_4\text{Ti}$
Formula weight	296.23	989.55
Temperature (K)	200(1)	200(1)
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	10.6805(4)	13.4292(3)
<i>b</i> (Å)	13.2338(4)	14.5628(4)
<i>c</i> (Å)	21.9151(4)	15.0506(4)
α (°)	90	100.6560(11)
β (°)	90	100.6274(16)
γ (°)	90	93.3357(15)
Volume (Å ³)	3097.56(16)	2830.01(13)
<i>Z</i>	8	2
<i>D</i> _{calc}	1.270	1.161
Absorption coefficient (cm ⁻¹)	6.38	2.73
θ Range (°)	3.2–32.6	3.1–27.5
Limiting indices	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-25 \leq l \leq 26$	$-17 \leq h \leq 15$, $-14 \leq k \leq 18$, $-19 \leq l \leq 16$
Reflections collected	8713	18433
Independent reflections; <i>n</i> : $I > n\sigma(I)$	4811; 2	12496; 2
<i>R</i> (<i>F</i>)	0.0408	0.0483
<i>R</i> _w (<i>F</i> ²)	0.0926	0.1039
Maximum/minimum difference Fourier peak (e Å ⁻³)	0.30/–0.29	0.38/–0.38

Table 2
Selected bond distances (Å) and angles (°) for $\text{Ti}(\text{C}_5\text{H}_5)(c\text{-C}_8\text{H}_{11})(\text{PMe}_3)$

<i>Bond distances</i> (Å)			
Ti–C1	2.163(2)	Ti–C9	2.394(2)
Ti–C2	2.282(2)	Ti–C10	2.389(2)
Ti–C3	2.337(2)	Ti–C11	2.367(2)
Ti–C4	2.275(2)	Ti–C12	2.370(2)
Ti–C5	2.168(2)	Ti–C13	2.395(2)
Ti–P	2.6394(5)	C9–C10	1.398(5)
C1–C2	1.439(3)	C9–C13	1.389(4)
C2–C3	1.404(3)	C10–C11	1.382(4)
C3–C4	1.415(3)	C11–C12	1.398(3)
C4–C5	1.440(3)	C12–C13	1.372(3)
<i>Bond angles</i> (°)			
C1–C2–C3	125.2(2)	Ti–P–C14	116.07(8)
C2–C3–C4	130.1(2)	Ti–P–C15	117.04(7)
C3–C4–C5	125.4(2)	Ti–P–C16	120.44(8)

ters for all nonhydrogen atoms. The hydrogen atoms in **1a** were refined isotropically, as were the hydrogen atoms on framework carbon atoms (C1–C21) of **4**, while methyl and phenyl hydrogen atoms of **4** were assigned idealized positional and thermal parameters. Crystal, data collection, and refinement parameters are provided in Table 1, while pertinent bonding parameters are given in Tables 2 and 3.

3. Results and discussion

The structure of $\text{Ti}(\text{C}_5\text{H}_5)(c\text{-C}_8\text{H}_{11})(\text{PMe}_3)$ (**1a**) reveals an arrangement rather similar to that of the 6,6-dimethylcyclohexadienyl analogue, $\text{Ti}(\text{C}_5\text{H}_5)(6,6\text{-dmch})(\text{PMe}_3)$ [9], in that the PMe_3 ligand is situated opposite to the electronically

Table 3
Selected bond distances (Å) and angles (°) for **4**

<i>Bond distances</i> (Å)			
Ti–C1	2.425(2)	Ti–C7	2.316(2)
Ti–C2	2.409(2)	Ti–C8	2.042(2)
Ti–C3	2.399(2)	Ti–C9	2.457(2)
Ti–C4	2.384(2)	Ti–C10	2.236(2)
Ti–C5	2.390(2)	Ti–C11	2.412(2)
Ti–C6	2.074(2)	Ti–C12	2.707(2)
C6–C7	1.364(3)	C9–C10	1.562(2)
C7–C8	1.534(3)	C10–C11	1.430(3)
C8–C9	1.570(3)	C11–C12	1.402(3)
<i>Bond angles</i> (°)			
Ti–C6–C7	81.90(13)	Ti–C8–C9	84.64(10)
Ti–C6–Si1	144.47(11)	Ti–C8–C18	142.58(14)
Ti–C8–C7	79.35(11)	Ti–C10–C9	78.40(10)
C6–Ti–C8	75.33(8)	C8–Ti–C10	75.10(7)
C7–C6–Si1	128.91(16)	C7–C8–C9	111.23(15)
C6–C7–C8	120.34(17)	C7–C8–C18	114.12(15)
C6–C7–C25	119.56(17)	C9–C8–C18	118.20(16)
C8–C7–C25	118.96(16)	C8–C9–C10	112.98(15)
C9–C10–C11	116.41(16)	C10–C11–C12	123.79(17)

open dienyl edge (Fig. 1). This can be attributed directly to a steric influence of the bridge, given that in the 2,4-dimethylpentadienyl analogue, $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})(\text{PEt}_3)$, the phosphine ligand is positioned by the open edge [10]. Nonetheless, in either case the average Ti–C distance for the electronically open dienyl ligand is shorter than that for the C_5H_5 ligand, the values for **1a** being 2.245 vs. 2.383 Å, reflecting notably stronger bonding for the cyclooctadienyl ligand. The location of the phosphine ligand, with $d(\text{Ti–P}) = 2.6394(5)$ Å, close to C3 rather than the C1–C5 edge, also leads to a reversal in the relative tilts of the Ti–P vector relative to the dienyl ligands. Whereas $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})(\text{PEt}_3)$ displays a greater tilt for the C_5H_5 ligand (108.2° vs. 95.7°), for the $c\text{-C}_8\text{H}_{11}$ complex, the values are 105.3° and 123.5°. It can be seen that the value for the C_5H_5 ligand is relatively unchanged, so that the change in the phosphine tilt relative to the $c\text{-C}_8\text{H}_{11}$ ligand must be compensated for by a change in the tilt between the dienyl ligands. In both complexes, the dienyl ligands are oriented relative to each other in such a way as to avoid intramolecular interactions. The positioning of the phosphine by C3 also leads to a trend in which C3 is furthest from the metal center at 2.337(2) Å, with the C(2,4) atoms closer (average, 2.279(2) Å), and the C(1,5) atoms closest (average, 2.166(2) Å). A very similar trend was found for $\text{Ti}(\text{C}_5\text{H}_5)(6,6\text{-dmch})(\text{PMe}_3)$. In comparison, $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})(\text{PEt}_3)$, which lacks an edge-bridge, also has a long Ti–C3 bond, but does not show a clear pattern for the other Ti–C bonds.

The hydrogen atom substituents on the $c\text{-C}_8\text{H}_{11}$ ligand display the expected tilts out of the dienyl plane, toward the metal center, by respective averages of 23.0°, 15.0°, and 4.6° for H(1,5), H(2,4), and H(3). For the C_5H_5 ligand, there is a smaller average deviation of 2.3° toward the metal, reflecting the smaller girth of this ligand.

Although the 6,6-dmch and $c\text{-C}_8\text{H}_{11}$ ligands may seem nearly identical structurally from the above discussion,

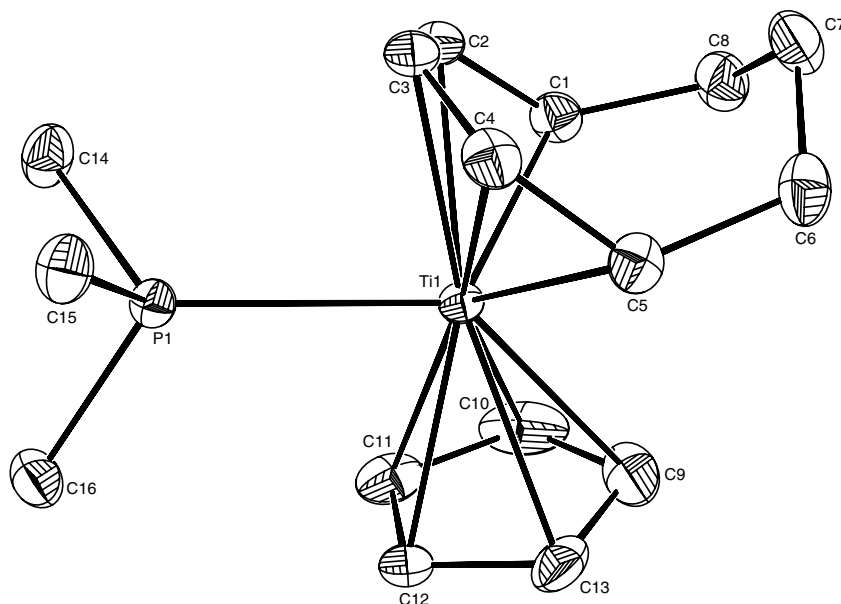
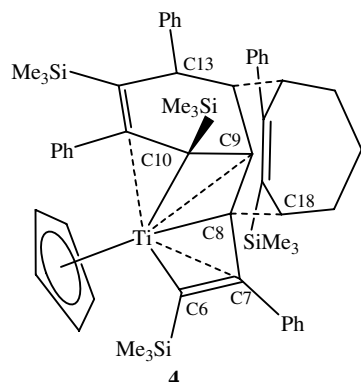


Fig. 1. Solid state structure of $\text{Ti}(\text{C}_5\text{H}_5)(c\text{-C}_8\text{H}_{11})(\text{PMe}_3)$ (**1a**).

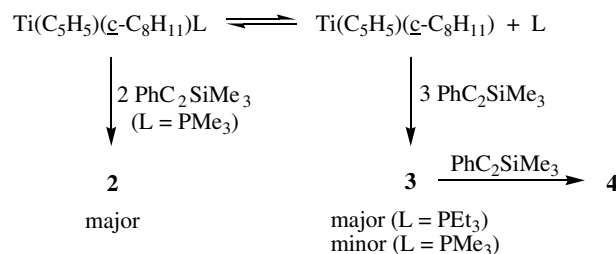
the fact that zirconium also forms 16 electron $\text{M}(\text{C}_5\text{H}_5)(c\text{-C}_8\text{H}_{11})(\text{PR}_3)$ complexes [11], but 18 electron $\text{Zr}(\text{C}_5\text{H}_5)(6,6\text{-dmch})(\text{PMe}_3)_2$ and $\text{Zr}(\text{C}_5\text{H}_5)(2,6,6\text{-tmch})(\text{PMe}_3)_2$ complexes [12] (tmch = trimethylcyclohexadienyl), reveals that there must be a significant difference; in particular, $c\text{-C}_8\text{H}_{11}$ must be sterically more demanding than 6,6-dmch or 2,6,6-tmch. In looking more closely at the edge-bridged half-open titanocenes cited above, one observes only fairly slight differences in bond distances and angles. However, one does see a significant difference in the distance from the titanium center to the 6,6-dmch (1.723 Å) and $c\text{-C}_8\text{H}_{11}$ (1.497 Å) planes, each defined by the five metal-bound atoms, which results from the respective difference in C1–C5 separations (2.43 vs. 3.08 Å). The greater girth of the $c\text{-C}_8\text{H}_{11}$ ligand, together with its closer approach to the metal center, readily accounts for its greater steric influence.

The new tetra(alkyne) coupling product **4** was first isolated as a minor byproduct of the reaction used to prepare **2**. The fact that **4**'s framework actually resembled **3** rather than **2** suggested that at least minor amounts of **3** were actually formed during the preparation of **2**, and some of that **3** could subsequently react with another equivalent of alkyne to yield **4**.



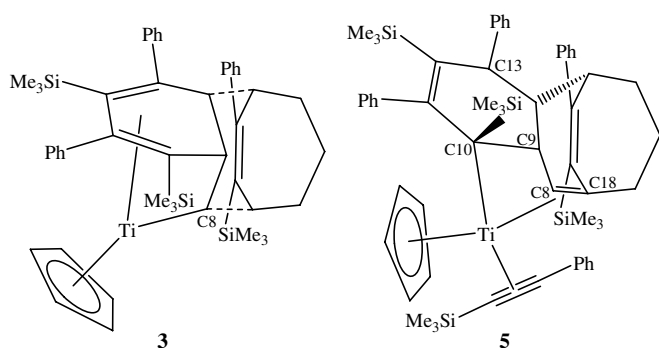
The preferred formation of **2** rather than **3** from the reaction of $\text{PhC}_2\text{SiMe}_3$ with $\text{Ti}(\text{C}_5\text{H}_5)(c\text{-C}_8\text{H}_{11})(\text{PMe}_3)$ could be explained by the stronger binding of PMe_3 vs. PEt_3 to the half-open titanocene fragment, which might thereby inhibit coordination by alkyne, and lead to an alternative reaction pathway. The occurrence of a somewhat competitive dissociation of PMe_3 , then, would allow for the formation of some **3** as a minor product from the PMe_3 complex, just as **3** is the major product from the PEt_3 complex (Scheme 1). That **4** can be prepared either from the reaction of **3** with a fourth equivalent of alkyne, or by the direct reaction of **1b** with four equivalents of alkyne, supports the general features of the scheme. The incorporation of the fourth equivalent of alkyne occurs significantly more slowly than for the first three equivalents.

In the structure of **4**, one can recognize that the fourth alkyne has added to C8 (also labeled C8 in **3**), while the hydrogen atom on C8 appears to have been transferred to C13. For this to happen directly, the alkyne could couple to C8 without first coordinating to the metal center, thus leading to H8 being positioned close to the metal, allowing for its subsequent transfer to C13. Although most indications are that alkyne coordination usually



Scheme 1.

takes place prior to coupling [12,13], the steric crowding in **3** as well as the fact that direct (exo) oxidation of di-nyl ligands has been observed [9,14], seems to leave this possibility open. Alternatively, activation of the C8–H bond could occur prior to coordination and coupling of the fourth alkyne, although this would require formation of a Ti=C8 bond. A less direct process in which alkyne coordination took place prior to coupling would be possible, requiring that the hydrogen atom originally on C18 be transferred to C13, leading to a metal-stabilized bridgehead double bond (C8=C18, e.g., **5**). Activation of the C8–H bond would potentially lead to a π -vinyl complex, which could lead to **4** after coupling of the fourth alkyne to C8 and transfer of the activated hydrogen atom to C18.



The structure of **4** may be seen in Figs. 2 and 3, while pertinent bonding parameters are presented in Table 3. The key features in **4** include binding by a cyclopentadienyl ligand, asymmetric allyl coordination through C(10–12), and a metallacyclobutene fragment, involving C(6–8). The metallacyclobutene unit is close to being planar, as can be seen

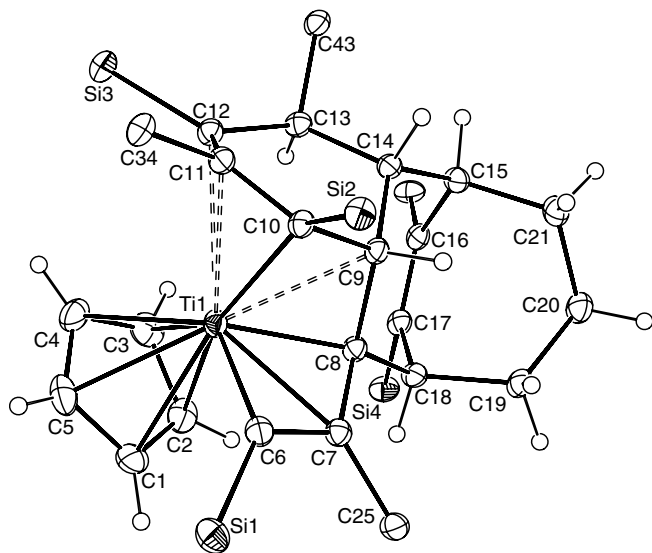


Fig. 2. Structure of the tetra(alkyne) coupling product, **4**. The silyl methyl groups and all but the ipso carbon atom of each phenyl group have been removed for clarity.

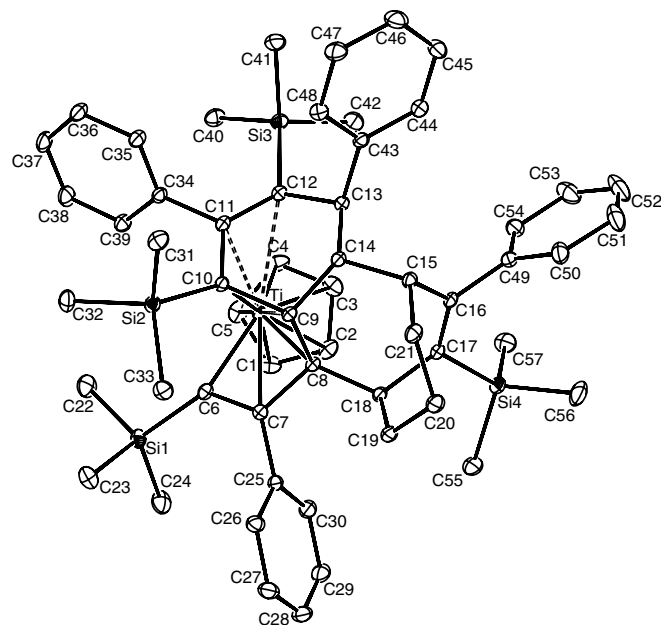
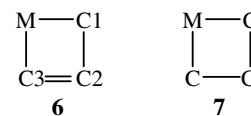
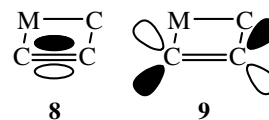


Fig. 3. Structure of the tetra(alkyne) coupling product, **4**.

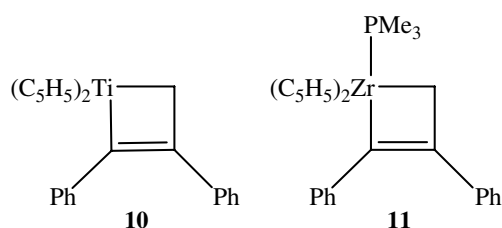
from the value of the Ti–C6–C7–C8 torsion angle, 16.7° . Concerning a formal electron count based upon classical bonding interactions, the only ambiguity rests with the allyl ligand. Although the bonding is quite asymmetric, with Ti–C(10–12) distances of 2.236(2), 2.412(2), and 2.707(2) Å, the similarity of the C10–C11 and C11–C12 distances, at 1.430(3) and 1.402(3) Å, and the significant deviation of the four bonds to C10 relative to an ideal tetrahedral disposition, favor a π allyl formulation. Considering then the titanacyclobutene coordination in a classic sense, as in **6**, would lead to a 14 electron count for **4**. However, given that the presence of (C–C) \rightarrow M agostic interactions has been established for electron deficient metallacyclobutenes [1], one can also expect to find additional interactions in electron deficient metallacyclobutenes.



These could include an agostic interaction with the C1–C2 bond (and perhaps to a lesser extent, with the sigma bonding density in the C=C bond), and/or coordination by the π C=C bond. As a result of the metallacyclobutene geometry, any olefin donation would be of π symmetry (**8**), analogous to the situation arising when an alkyne serves as a 4 electron donor [15].



As any backbonding for the second π system in an alkyne would entail a δ interaction, such might also be proposed for any olefin coordination in a metallacyclobutene. While that cannot be entirely ruled out, the asymmetry in the M–C (olefin) distances (vide infra) leads to the π orbital component of one carbon atom being much closer to the metal center than that of the other carbon atom, as in **9**. Thus, it could be that any backbonding interaction could actually be of π symmetry, somewhat akin to that for a carbonyl ligand. In such a circumstance, the olefin would actually serve as a π donor and a π acceptor. Of course, for a d^0 complex such as **4**, **10**, or **11**, there would formally be no electron density available for a backbonding interaction.



While the effectiveness of the olefin coordination would be reduced by the fact that the central carbon atom will be positioned further from the metal atom than the other unsaturated carbon atom, one could still expect in general to observe a competition between a (C–C) \rightarrow M agostic interaction and olefin coordination in electron deficient metallacyclobutenes.

Complex **4**, however, also has the makings of a metallacyclobutane complex (**7**), by virtue of a Ti–C8 σ bond, and a Ti–C10 interaction with significant σ bond character to C10. This would allow for potential (C–C) \rightarrow Ti agostic interactions involving the C8–C9 and C9–C10 bonds, in addition to one from at least the C7–C8 bond component of the titanacyclobutene fragment. Considering first the pseudo-titanacyclobutane fragment, C9 is relatively close to the metal center, 2.457(2) Å, which can be compared to values of ca. 2.60 Å in 16 electron titanacyclobutenes for which agostic interactions have been established [1]. Further, the C8–C9 and C9–C10 bonds are significantly lengthened, at 1.570(3) and 1.562(3) Å, respectively, which are also similar to values in the established agostic titanacyclobutane compounds.

In order to assess the extent of any (C–C) \rightarrow Ti agostic interaction or olefin coordination in the titanacyclobutene fragment, it is necessary to have a reasonable basis for evaluation. This can be provided through a structural comparison of similar 16 and 18 electron metallacyclobutenes, incorporating the Ti(C₅H₅)₂ and Zr(C₅H₅)₂(PMe₃) fragments, as in **10** [16,17] and **11** [18]. Particularly telling are the relative C1–C2, C2–C3, and \angle C1–M–C3 values, as defined in **6**. For the 18 electron zirconium complex, the values are 1.483(8) Å, 1.344(8) Å, and 59.6(2) $^\circ$, while for

the 16 electron titanium complex, the values are 1.537(6) Å, 1.344(6) Å, and 69.3(2) $^\circ$. One thus sees a trend analogous to that in 16 vs. 18 electron metallacyclobutenes, in which geometric distortions occur for the electron deficient complexes, leading to a closer approach of the C–C bonds to a given metal center. To make a valid comparison between **10** and **11**, one must naturally take the differing metal sizes into account. One indeed observes that the respective Ti–C(1–3) distances are shorter than their Zr counterparts (2.122(5), 2.533(5), 2.104(4) vs. 2.386(6), 2.793(6), 2.306(5) Å) by more than the 0.13 Å difference in metal size, or the 0.14 Å difference in M–C (C₅H₅) distances. That there is greater shortening for the Ti–C1 rather than the Ti–C3 bond could suggest a lesser degree of involvement of olefin coordination, although the presence of the phosphine ligand in **11** could also play a role. In fact, the C=C distances also do not provide any evidence in support of olefin coordination. For complex **4**, the corresponding C1–C2, C2–C3, and \angle C–Ti–C values are 1.534(3) Å, 1.364(3) Å, and 75.33(8) $^\circ$, being more in accord with the pattern displayed by the electron deficient **10** rather than **11**. Hence, it would appear that a (C–C) \rightarrow Ti agostic interaction also occurs for the titanacyclobutene fragment in **4**. It is nonetheless interesting to note that the metallacyclobutane C–C bonds in **4** are longer than the metallacyclobutene C–C bond, given that the latter's greater expected strain should enhance the favorability of an agostic interaction. Comparable differences are, however, found between 18 electron metallacyclobutenes [1] and metallacyclobutenes [18], indicating that both types of C–C bond are experiencing similar degrees of lengthening. Although there could be some lengthening of the C=C bond in **4** relative to **10**, which could be a result of the greater electron deficiency of **4**, the increase is on the order of the statistical uncertainties, and hence a conclusion can not be reached regarding the possibility of olefin coordination in **4** based on the structural data. **4** does then join **2** in providing an example in which a (C–C) \rightarrow Ti agostic interaction appears to be at least competitive with olefin coordination.

Notably, support for the presence of agostic (C–C) \rightarrow M interactions in electron deficient metallacyclobutenes can be observed through a comparison of reported ¹³C NMR data. Thus, in going from the 18 electron Zr(C₅H₅)₂(C₃Ph₂H₂)(PMe₃) complex (**11**) to the 16 electron Zr(C₅H₅)₂(C₃Ph₂H₂) [17], one observes respective significant downfield and upfield shifts for the C _{α} (45 ppm) and C _{β} (26 ppm) resonances. Analogous shifts were indeed observed between 18 vs. 16 electron metallacyclobutane complexes [1]. A downfield shift (27 ppm) for the unsaturated C _{α'} resonance also occurs in passing from **11** to Zr(C₅H₅)₂(C₃Ph₂H₂). Based on the earlier INADEQUATE NMR spectral studies, it can be expected that the ¹³C–¹³C coupling constants for the C7–C8 (and also C8–C9, C9–C10) bond in **4**, and the C1–C2 bond in **10** (as defined in **6**), would all be anomalously low, whereas that for the C1–C2 bond in **11** would be higher.

4. Conclusions

Complex **4** provides at least the third example of an alkyne-pentadienyl coupling product to have (C–C) → Ti agostic interactions. Conceivably, related diyne coupling products [3], which do undergo C–C bond activations, may also possess these agostic interactions. Notably, analogous Ph₂C₂ and PhC₂SiMe₃ coupling products prepared from Zr(C₅H₅)(*c*-C₈H₁₁)(PR₃) complexes have been isolated in which C–C or C–Si bond activations have taken place [19]. Also of note is the demonstration of the presence of these (C–C) → M agostic interactions in electron deficient metallacyclobutenes, and especially the indication that these interactions could be more important than the potentially competitive donation from the C=C bond. Additional spectroscopic investigations are underway to provide a better understanding of the bonding in such species.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, Nos. 610561–610562. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [fax: +44 1223 336 033] or e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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