



Fused ring systems derived from reactions of half-open titanocenes with diynes: Syntheses, characterization, cage rearrangements, and structural studies

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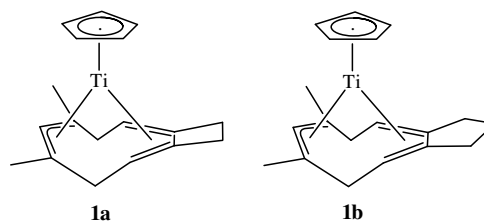
The reactions of several α,ω -diynes with half-open titanocene complexes $[M(C_5H_5)(2,4-C_7H_{11})(PR_3)]$ (C_7H_{11} = dimethylpentadienyl) lead to 5 + 2 + 2 ring constructions, yielding nine-membered rings fused to four-membered and larger rings. These reactions tolerate significant functionalization, even allowing for the presence of heteroatoms such as oxygen and nitrogen. The nine-membered rings provide both allyl and diene coordination to the $Ti(C_5H_5)$ fragments, resulting in 16 electron configurations. On standing, these species undergo cage rearrangements, via C–C bond activation reactions. Structural data have been obtained for a number of the fused ring species, as well as one of the rearrangement products.

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1. Introduction

Half-open metallocenes have been found to be useful in allowing for direct comparisons to be made between cyclopentadienyl and pentadienyl ligands, by removing complications that would otherwise result from comparisons between metallocenes and open metallocenes due to their potential differences in symmetries, steric congestions, and spin configurations [1]. In this regard, the half-open titanocenes, $Ti(C_5H_5)(Pdl)(L)$ (Pdl = various pentadienyl ligands; L = CO, PR_3), have thus far proven particularly interesting, whether structurally, theoretically, or in their reaction chemistry [2]. Thus, it has been clearly established that not only are the pentadienyl ligands more strongly bound than cyclopentadienyl (in large part due to strong δ backbonding interactions [1–3]), they are also more reactive, readily undergoing coupling reactions with unsaturated organic molecules such as ketones, nitriles, isonitriles, imines, alkynes, and diynes. The reactions of $Ti(C_5H_5)(2,4-C_7H_{11})(PET_3)$ (C_7H_{11} = dimethylpentadienyl) with 1,5-hexadiyne and 1,6-heptadiyne have already been shown to lead to interesting products (**1a,b**), containing fused nine- and four- or five-membered rings [4]. As nine-membered rings suffer from significant trans-annular strain, their syntheses are often problematic, so it appeared worth-

while to examine the scope of this coupling reaction. Herein, we report our results on these species.



2. Experimental

Reactions were conducted in oven-dried (120 °C) or flame-dried glassware under a nitrogen atmosphere unless otherwise stated. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes. Solvents were distilled before use: diethyl ether, tetrahydrofuran, pentane, and hexanes from sodium benzophenone ketyl, while benzene- d_6 was bulb to bulb distilled from sodium metal. α,ω -Diynes were either purchased commercially or prepared via standard procedures [5]. $Ti(C_5H_5)(2,4-C_7H_{11})(PR_3)$ complexes were prepared as previously described [6]. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (1H NMR) were recorded at 300 MHz, while carbon nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 75 MHz and are reported

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(ppm) relative to the center line of a triplet at 128.0 ppm for deuterobenzene or 77.0 ppm for deuteriochloroform.

2.1. $Ti(C_5H_5)(2,4-C_7H_{11})(1,5-C_6H_6)$, **1a**

A solution of $Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)$ (0.25 g, 0.77 mmol) in 30 mL THF was cooled to $-30^\circ C$ and 1,5-hexadiyne (120 μL , 0.77 mmol, 50% solution in pentane) was added via syringe. The solution immediately turned dark green. The cold bath was maintained at $-30^\circ C$ for 1 h until the reaction was complete. The solvent was then removed in vacuo to give a green solid. Extraction with 40 mL of pentane gave a dark green solution which was then filtered through a Celite pad on a coarse frit to give a dark green filtrate. The solution was concentrated to ca. 10 mL in vacuo and then cooled to $-80^\circ C$ over 12 h. The supernatant was then removed via syringe and the green crystals were dried under vacuum to give 88 mg (40%) of **1a**. Crystals of suitable quality for single crystal X-ray diffraction studies were obtained by slowly cooling a pentane solution to $-30^\circ C$ over a period of 1 week.

MP (N_2 filled, sealed capillary): $127^\circ C$ (decomp).

1H NMR (C_6D_6): δ 4.75 (s, 5H, Cp), 4.57 (s, 1H, H-5), 3.15 (dd, 2H, $J = 11.9, 2.4$ Hz, H-10,11_{endo}), 2.89 (dd, 2H, $J = 11.5, 8.1$ Hz, H-2,8), 2.75 (dd, 2H, $J = 15.5, 11.6$ Hz, H-3,7_{endo}), 2.11 (dd, 2H, $J = 12.2, 2.4$ Hz, H-10,11_{exo}), 2.05 (s, 6H, 4,6- CH_3), 0.73 (dd, 2H, $J = 15.4, 8.0$ Hz, H-3,7_{exo}).

^{13}C NMR (C_6D_6): δ 117.7 (s, 2C, C-1,9), 102.4 (d quintets, 5C, $J = 165, 6$ Hz, Cp), 100.4 (d, 1C, J obscd., C-5), 44.5 (s, 2C, C-4,6), 31.9 (q, 2C, $J = 122$ Hz, CH_3), 31.0 (t, 2C, $J = 127$ Hz, C-10,11), 28.5 (d, 2C, $J = 127$ Hz, C-2,8), 27.4 (t, 2C, $J = 124$ Hz, C-3,7).

MS (EI, 17 eV, $100^\circ C$) m/z (relative intensity): 287 (26), 286 (100), 284 (34), 282 (21), 206 (42), 172 (23), 159 (20), 157 (36), 129 (21).

HRMS Calc. for $C_{18}H_{22}Ti$: 286.1209. Found: 286.1187.

2.2. $Ti(C_5H_5)(2,4-C_7H_{11})(1,6-C_7H_8)$, **1b**

The title complex may be prepared by the addition of 1 eq. of 1,6-heptadiyne (96 μL , 0.84 mmol) to a magnetically stirred THF solution of $Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)$ (0.27 g, 0.84 mmol) at $-78^\circ C$. The reaction mixture was allowed to warm slowly to ca. $-30^\circ C$ at which point a rapid color change from orange to green occurred. The reaction mixture was allowed to stir for an additional 20 min at $-25^\circ C$ after which time the solvent was pumped off. Diethyl ether, four 40 mL portions, was used to extract the resulting sticky green residue and following filtration through a 1" Celite pad a bright green solution was obtained. The cold filtrate was concentrated in vacuo to ca. 10 mL and then further cooled to $-80^\circ C$ for 6 days. The resulting dark green crystals (mp $95-97^\circ C$) were isolated by removal of the supernatant via syringe.

1H NMR (C_6D_6): δ 4.73 (s, 5H, Cp), 4.62 (s, 1H, H-5), 3.49 (dt, 2H, $J = 14.9, 8.6$ Hz, H-10,12_{endo}), 2.96 (dd, 2H, $J = 13.3, 8.6$ Hz, H-2,8), 2.75 (dd, 2H, $J = 15.5, 14.8$ Hz, H-3,7_{endo}), 2.22 (m, 2H, H-10,12_{exo}), 2.06 (s, 6H, CH_3), 1.82 (m, 1H, H-11_{endo}), 1.50 (m, 1H, H-11_{exo}), 0.98 (dd, 2H, $J = 15.7, 8.3$ Hz, H-3,7_{exo}).

^{13}C NMR (C_6D_6): δ 111.2 (s, 2C, C-1,9), 100.9 (d of quintets, 5C, $J = 172, 7$ Hz, Cp), 99.6 (d, 1C, $J = 146$ Hz, C-5), 45.6 (t, 2C, $J = 129$ Hz, C-3,7), 44.1 (s, 2C, C-4,6), 31.4 (q, 2C, $J = 126$ Hz, CH_3), 29.4 (d, 2C, $J = 168$ Hz, C-2,8), 27.3 (t, 2C, $J = 132$ Hz, C-10,12), 19.7 (t, 1C, $J = 128$ Hz, C-11).

MS (EI, eV, $120^\circ C$) m/z (relative intensity): 302 (45), 285 (41), 239 (12), 99 (13), 85 (61), 71 (77), 57 (100), 44 (11), 43 (14).

2.3. $Ti(C_5H_5)(2,4-C_7H_{11})(1,7-C_8H_{10})$, **1c**

A solution of $Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)$ (0.20 g, 0.61 mmol) in 30 mL THF was cooled to $-30^\circ C$ and 1,7-octadiyne (80 μL ,

0.61 mmol, 1 eq.) was added via syringe. The solution immediately turned dark green. The cold bath was maintained at $-30^\circ C$ for 1 h. The solvent was then removed in vacuo to give a green solid. A portion of the green solid was dissolved in C_7D_8 and a low temperature NMR spectrum was taken. The 1H NMR spectrum was very broad and complicated due to excess diyne and PEt_3 ; however, the ^{13}C NMR spectrum was very clean at $-20^\circ C$, and this allowed characterization of the compound. The complex decomposed even at low temperature within 2 h, and decomposed within minutes in solution at room temperature, yielding intractable solids.

^{13}C NMR (C_7D_8 , $-20^\circ C$): δ 115.5, 102.1, 101.1, 44.4, 38.5, 35.4, 31.6, 28.0, 24.3.

2.4. $Ti(C_5H_5)(2,4-C_7H_{11})[(CH_3CO_2)_2C(CH_2C_2H)_2]$, **1d**

A solution of $Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)$ (0.20 g, 0.61 mmol) in 30 mL THF was cooled to $-30^\circ C$ and the dimethyl-2,2-dipropargyl malonate (0.13 g, 0.61 mmol) was added in a 30 mL THF solution dropwise via a pressure equalizing addition funnel. The solution immediately turned dark green. The cold bath was maintained at $-30^\circ C$ for 1 h. The solvent was then removed in vacuo to give a green solid. Extraction with 40 mL of hexanes gave a dark green solution which was then filtered through a Celite pad on a coarse frit to give a dark green filtrate. The solution was concentrated to ca. 10 mL in vacuo and then cooled to $-80^\circ C$ over 12 h. The supernatant was then removed via syringe and the moderately air stable green crystals were dried under vacuum giving 88 mg (35%) of **1d**. Crystals of suitable quality for X-ray diffraction studies were obtained by slowly cooling a diethyl ether solution to $-30^\circ C$ over a period of 1 week.

MP (N_2 filled, sealed capillary): $123.0-125.0^\circ C$ (decomp).

1H NMR (C_6D_6): δ 4.89 (s, 5H, Cp), 4.58 (s, 1H, H-5), 4.23 (d, 2H, $J = 15.6$ Hz, H-10,12_{endo}), 3.39 (s, 3H, CH_3), 3.30 (3H, CH_3), 3.25 (d, 2H, $J = 15.6$ Hz, H-10,12_{exo}), 2.99 (dd, 2H, $J = 12.9, 8.1$ Hz, H-2,8), 2.70 (dd, 2H, $J = 15.9, 12.9$ Hz, H-3,7_{endo}), 1.99 (s, 6H, CH_3), 0.87 (dd, 2H, $J = 12.0, 8.3$ Hz, H-3,7_{exo}).

^{13}C NMR (C_6D_6): δ 172.7 (s, 1C, C=O), 127.8 (s, 1C, C=O), 109.4 (s, 2C, C-1,9), 102.0 (d quintets, 5C, $J = 172, 7$ Hz, Cp), 101.8 (d, 1C, C-5), 56.8 (s, 1C, C-11), 52.7 (q, 1C, $J = 147$ Hz, CH_3), 52.5 (q, 1C, $J = 148$ Hz, CH_3), 51.3 (t, 2C, $J = 135$ Hz, C-10,12), 45.9 (t, 2C, $J = 5$ Hz, C-4,6), 31.5 (q, 2C, $J = 126$ Hz, CH_3), 30.6 (d, 2C, $J = 131$ Hz, C-2,8), 27.2 (t, 2C, $J = 129$ Hz, C-3,7).

MS (EI, 17 eV, $100^\circ C$) m/z (relative intensity): 416 (57), 304 (30), 302 (60), 292 (35), 290 (37), 244 (36), 242 (32), 242 (53), 229 (41), 227 (62), 225 (66), 221 (25), 189 (27), 183 (50), 175 (38), 144 (32), 94 (100).

Anal. Calc. for $C_{22}H_{28}TiO_4$: C, 66.35; H, 6.78. Found: C, 66.28; H, 6.78%.

2.5. $Ti(C_5H_5)(2,4-C_7H_{11})[(CH_3CH_2CO_2)_2C(CH_2C_2H)_2]$, **1e**

The procedure for the synthesis of **1d** was followed except using 0.15 g (0.61 mmol) of diethyl-2,2-dipropargyl malonate. The green microcrystalline product, 87 mg (32%), was isolated from hexanes.

1H NMR (C_6D_6): δ 4.91 (s, 5H, Cp), 4.58 (s, 1H, H-5), 4.30 (d, 2H, $J = 15.4$ Hz, H-10,12_{endo}), 4.04 (q, 2H, $J = 6.9$ Hz, CH_2), 3.95 (q, 2H, $J = 7.0$ Hz, CH_2), 3.31 (d, 2H, $J = 15.4$ Hz, H-10,12_{exo}), 3.00 (dd, 2H, $J = 12.9, 8.2$ Hz, H-2,8), 2.70 (dd, 2H, $J = 15.9, 12.9$ Hz, H-3,7_{endo}), 1.98 (s, 6H, 4,6- CH_3), 0.95 (t, 3H, $J = 7.2$ Hz, CH_3), 0.90 (t, 3H, $J = 7.1$ Hz, CH_3), 0.87 (dd, $J = 16.0, 8.2$ Hz, H-3,7_{exo}).

^{13}C NMR (C_6D_6): δ 172.0 (s, 1C, C=O), 130.0 (s, 1C, C=O), 110.0 (s, 2C, C-1,9), 102.0 (d quintets, 5C, $J = 173, 7$ Hz, Cp), 101.9 (d, 1C, $J = 140$ Hz, C-5), 62.0 (t, 1C, $J = 147$ Hz, CH_2), 61.9 (t, 1C, $J = 147$ Hz, CH_2), 57.1 (s, 1C, C-11), 51.6 (t, 1C, $J = 134$ Hz, C-10,12), 46.1 (s, 2C, C-4,6), 31.7 (q, 2C, $J = 125$ Hz, 4,6- CH_3), 30.8 (d, 2C, $J = 128$ Hz, C-2,8), 27.4 (t, 2C, $J = 130$ Hz, C-3,7), 14.3 (q, 1C, $J = 127$ Hz, CH_3).

MS (EI, 17 eV, 150 °C) *m/z* (relative intensity): 445 (44), 444 (100), 443 (30), 399 (33), 398 (39), 397 (21), 389 (20), 379 (27), 324 (21), 203 (59), 197 (35), 175 (59), 158 (79).

HRMS Calc. for $C_{25}H_{32}TiO_4$: 444.1780. Found: 444.1775.

2.6. $Ti(C_5H_5)(2,4-C_7H_{11})(C_3H_3)_2O$, **1f**

The synthesis of this compound was similar to those above, using 90 μ L of an 80% solution (0.61 mmol) of diyne. The reaction gave green crystals, 98 mg (35%), from pentane. Crystals suitable for X-ray analysis were obtained by slow recrystallization from THF.

MP (N_2 filled, sealed capillary): 100 °C (decomp).

1H NMR (C_6D_6): δ 5.49 (d, 2H, J = 11.5 Hz, H-10,12_{endo}), 4.84 (s, 5H, Cp), 4.62 (s, 1H, H-5), 4.09 (d, 2H, J = 11.0 Hz, H-10,12_{exo}), 2.67 (m, 4H, H-2,8 and H-3,7_{endo}), 2.02 (s, 6H, 4,6-CH₃), 0.87 (dd, 2H, J = 21.7, 14.0 Hz, H-3,7_{exo}).

^{13}C NMR (C_6D_6): δ 107.7 (s, 2C, C-1,9), 101.5 (d quintets, 5C, J = 173, 7 Hz, Cp), 99.8 (d, 1C, J = 149 Hz, C-5), 83.4 (t, 2C, J = 147 Hz, C-10,12), 44.9 (s, 2C, C-4,6), 31.5 (q, 2C, J = 130 Hz, 4,6-CH₃), 26.9 (d, 2C, J = 128 Hz, C-2,8), 24.7 (t, 2C, J = 125 Hz, C-3,7).

MS (EI, 17 eV, 60 °C) *m/z* (relative intensity): 302 (65), 206 (21), 188 (25), 159 (25), 145 (26), 143 (20), 130 (100), 129 (30), 119 (21), 105 (32).

HRMS Calc. for $C_{18}H_{22}TiO$: 302.1150. Found: 302.1145.

2.7. $Ti(C_5H_5)(2,4-C_7H_{11})(C_3H_3)_2N(CH_2)_3CH_3$, **1g**

The synthesis proceeded as above; 110 μ L (0.61 mmol) of freshly prepared *n*-butyldipropargyl amine were used. However, the product was obtained as an oil and failed to solidify even at –90 °C. The crude air sensitive oil was characterized unambiguously by NMR and no attempts were made to obtain a yield.

1H NMR (C_6D_6): δ 5.05 (s, 5H, Cp), 4.68 (s, 1H, H-5), 4.15 (d, 2H, J = 9.8 Hz, H-10,12_{endo}), 3.33 (d, 2H, J = 10.0 Hz, H-10,12_{exo}), 2.91 (dd, 2H, J = 12.2, 8.1 Hz, H-2,8), 2.75 (dd, 2H, J = 15.5, 12.2 Hz, H-3,7_{endo}), 2.50 (t, 2H, J = 7.0 Hz, CH₂), 2.09 (s, 6H, 4,6-CH₃), 1.35 (m, 4H, 2-CH₂), 0.99 (dd, 2H, J = 15.5, 8.2 Hz, H-3,7_{exo}), 0.89 (t, 3H, J = 7.2 Hz, CH₃).

^{13}C NMR (C_6D_6): δ 108.2 (s, 2C, C-1,9), 101.7 (d quintets, 5C, Cp), 99.7 (d, 1C, C-5), 70.7 (t, 2C, C-10,12), 55.9 (t, 1C, CH₂), 44.2 (s, 2C, C-4,6), 31.8 (t, 1C, CH₂), 31.6 (q, 2C, 4,6-CH₃), 27.2 (t, 1C, C-3,7), 26.7 (d, 2C, C-2,8), 21.0 (t, 2C, CH₂), 14.4 (q, 1C, CH₃).

MS (EI, 70 eV, 60 °C) *m/z* (relative intensity): 326 (31), 325 (100), 324 (19), 323 (35), 322 (16), 321 (46), 319 (17), 307 (16), 306 (40), 282 (16), 268 (17), 212 (24), 197 (15), 175 (27), 171 (21), 137 (18), 119 (20), 82 (31), 61 (15), 60 (21).

HRMS Calc. for $C_{22}H_{31}TiN$: 357.1936. Found: 357.1940.

2.8. $Ti(C_5H_5)(2,4-C_7H_{11})(C_3H_3)_2N(CH_3)$, **1h**

The synthesis proceeded as above; 82 μ L (0.61 mmol) of freshly prepared methylidipropargyl amine were used. The product was recrystallized from pentane giving green crystals in 40% (77 mg) yield. Crystals of the product suitable for X-ray analysis were obtained by slow recrystallization from pentane.

MP (N_2 filled, sealed capillary): 88 °C (decomp).

1H NMR (C_6D_6): δ 5.05 (s, 5H, Cp), 4.67 (s, 1H, H-5), 4.13 (d, 2H, J = 10.0 Hz, H-10,12_{endo}), 3.30 (d, 2H, J = 12.2 Hz, H-10,12_{exo}), 2.87 (dd, 2H, J = 12.3, 8.1 Hz, H-2,8), 2.74 (dd, 2H, J = 15.4, 12.2 Hz, H-3,7_{endo}), 2.31 (s, 3H, CH₃), 2.08 (s, 6H, 4,6-CH₃), 0.98 (dd, 2H, J = 15.4, 8.1 Hz, H-3,7_{exo}).

^{13}C NMR (C_6D_6): δ 108.5 (s, 2C, C-1,9), 101.7 (d quintets, 5C, Cp), 99.8 (d, 1C, C-5), 72.5 (t, 2C, C-10,12), 44.2 (s, 2C, C-4,6), 42.2 (t, 1C, CH₃), 31.6 (q, 2C, 4,6-CH₃), 27.1 (t, 2C, C-3,7), 26.5 (d, 2C, C-2,8).

MS (EI, 25 eV, 80 °C) *m/z* (relative intensity): 316 (28), 315 (100), 313 (30), 311 (35), 295 (37), 206 (21).

HRMS Calc. for $C_{19}H_{25}NTi$: 315.1467. Found: 315.1462.

2.9. $Ti(C_5H_5)(2,4-C_7H_{11})(CH_3CO_2)_2C(CH_2C_2H)_2$, rearrangement product, **2**

Crystals of **1d** were redissolved in toluene, hexanes, or THF in a slightly evacuated Schlenk flask. The resulting green solution was then subjected to photolysis with a mercury lamp for 12 h giving a dark red solution. The solvent was then removed in vacuo and the red solid was dissolved in hexanes. The solution was then filtered through a Celite pad on a coarse frit and allowed to cooled to –90 °C over 15 h, resulting in lumpy orange–red crystals. Crystals of sufficient quality for X-ray diffraction studies were obtained by slow diffusion of solvent away from a hexanes solution of the compound.

MP (N_2 filled, sealed capillary): 147–151 °C.

1H NMR (C_6D_6): δ 5.83 (s, 5H, Cp), 5.02 (s, 1H), 4.55 (s, 1H), 3.50 (d, 1H, J = 17.1 Hz), 3.42 (d, 1H, J = 7.5 Hz), 3.36 (s, 3H), 3.26 (dd, 1H, J = 3.7, 2.7 Hz), 3.11 (s, 3H), 3.00 (d, 1H, J = 17.3 Hz), 2.86 (d, 1H, J = 4.2 Hz), 2.51 (dd, 1H, J = 13.9, 2.7 Hz), 2.48 (d, 1H, J = 14.5 Hz), 2.42 (ddd, 1H, J = 13.9, 4.0, 1.6 Hz), 1.75 (ddd, 1H, J = 11.8, 7.6, 1.6 Hz), 1.73 (d, 1H, J = 4.5 Hz), 1.65 (d, 1H, J = 14.6 Hz), 1.43 (d, 1H, J = 11.8 Hz), 0.86 (s, 3H).

^{13}C NMR (C_6D_6): δ 152.0 (s, 1C), 136.0 (d, 1C), 135.9 (s, 1C), 117.6 (s, 1C), 114.2 (s, 1C), 110.4 (d, 5C, Cp), 106.1 (d, 1C), 76.0 (d, 1C), 60.2 (t, 1C), 57.1 (s, 1C), 54.5 (q, 1C, OCH₃), 52.6 (t, 1C), 51.4 (q, 1C, OCH₃), 49.4 (s, 1C), 48.2 (t, 1C), 47.4 (d, 1C), 45.9 (t, 1C), 39.0 (t, 1C), 27.7 (q, 3C, CH₃).

MS (EI, 17 eV, 150 °C) *m/z* (relative intensity): 416 (100), 384 (37), 272 (69), 244 (46), 243 (78), 242 (32), 213 (39), 212 (28), 183 (46), 175 (28), 94 (82), 59 (49), 58 (42).

Anal. Calc. for $C_{22}H_{28}TiO_4$: C, 66.35; H, 6.78. Found: C, 66.19; H, 6.85%.

2.10. Preparation of 1,7-deuterio-1,6-heptadiyne

To a solution of diisopropylamine (5.8 mL, 44 mmol) in 50 mL of THF was added 2.5 M *n*-BuLi in hexane (17.6 mL, 44 mmol) at 0 °C over 10 min. After cooling to –78 °C, 1,6-heptadiyne (2 mL, 18 mmol) was added. The reaction mixture was stirred for 2 min at –78 °C, followed by addition of an excess of D₂O (6 eq.). The mixture was warmed to ambient temperature and was extracted with ether and the combined organic phases were dried over anhydrous MgSO₄ for 1 h. The crude product distilled between 75 °C and 80 °C at a pressure of ca. 640 mm to give an approximately 50% solution of 1,7-dideuterio-1,6-heptadiyne in THF (1.08 mL, 53%).

1H NMR ($CDCl_3$, ambient): δ 2.34 (t, 4H, J = 7.1 Hz), 1.76 (quin, 2H, J = 7.1 Hz).

2.11. Preparation of “ $Ti(C_5H_5)(C_{14}H_{17}D_2)$ ” (*d*₂-**1b**)

To a solution of $Ti(C_5H_5)(2,4-C_7H_{11})(PMe_3)$ (0.20 g, 0.70 mmol) in 30 mL of THF at –78 °C, an excess of 1,6-dideuterio-1,5-heptadiyne (50% solution in THF, 400 μ L) was added. While being stirred, the reaction mixture was warmed to ambient temperature. The solvent was then removed in vacuo. The resulting residue was redissolved in pentane and filtered through a coarse frit covered by a 1” pad of Celite. After concentration in vacuo until incipient crystallization, the filtrate was cooled to –30 °C to give green crystals of *d*₂-**1b**.

1H NMR (benzene-*d*₆, ambient): δ 4.75 (s, 5H, Cp), 4.65 (s, 1H, H-5), 3.51 (ddd, 2H, J = 14.8, 9.5, 7.7 Hz, H-10,12_{endo}), 2.78 (d, 2H, J = 15.9 Hz, H-3,7_{endo}), 2.22 (ddd, 2H, J = 14.8, 9.8, 4.2 Hz, H-10,12_{exo}), 2.06 (s, 6H, CH₃), 1.79 (m, 1H, H-11_{endo}), 1.48 (m, 1H, H-11_{exo}), 1.03 (d, 2H, J = 15.9 Hz, H-3,7_{exo}).

Table 1
Crystallographic data for diyne coupling products

Compound	1a	1b	1d	1f	1h	2
<i>(a) Crystal parameters</i>						
Formula	C ₁₈ H ₂₂ Ti	C ₁₉ H ₂₄ Ti	C ₂₃ H ₂₈ TiO ₄	C ₁₈ H ₂₂ OTi	C ₁₉ H ₂₇ NTi	C ₂₃ H ₂₈ O ₄ Ti
Space group	P2 ₁ /n	P2 ₁ /c	Pbca	Pna2 ₁	Pnma	P2 ₁ /c
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
a (Å)	7.734(2)	8.288(4)	11.077(2)	13.609(3)	7.760(1)	11.933(2)
b (Å)	13.783(3)	7.969(3)	15.246(3)	8.323(2)	12.582(2)	23.573(5)
c (Å)	13.382(3)	23.700(14)	23.841(5)	26.434(5)	16.368(3)	15.124(3)
β (deg)	92.73(3)	92.46(9)	90	90	90	105.43(3)
V (Å ³)	1424.9(6)	1563.4(14)	4026.3(14)	2994.1(11)	1598.1(4)	4101.0(14)
Z	4	4	8	8	4	8
Crystal dimensions (mm)	0.18 × 0.20 × 0.45	0.45 × 0.40 × 0.06	0.18 × 0.35 × 0.32	0.10 × 0.35 × 0.55	0.20 × 0.24 × 0.46	0.21 × 0.30 × 0.42
Crystal color	Green	Green	Green	Green	Green	Red
D _(calc) (g/cm ³)	1.334	1.276	1.374	1.341	1.319	1.349
μ (Mo Kα) (cm ⁻¹)	5.84	5.48	4.51	5.65	5.29	4.43
Temp (°C)	20	23	20	20	20	20
<i>(b) Data collection</i>						
Diffractometer	Siemens P4	Nicolet R3m	Siemens P4	Siemens P4	Siemens P4	Siemens P4
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ scan range, deg	4–50	4–044	4–48	5–48	4–60	4–45
Data collected	9, +16, +15	9, 9, +25	+12, +17, +27	+13, +9, +30	+10, +17, +23	12, +25, +16
Reflections collected	2656	2180	4247	2692	2680	5587
Independent reflections	2504	1912	3143	2336	2435	5347
Independent reflections observed	1966 (2σ)	1229 (4σ)	1835 (2σ)	1383 (2σ)	1995 (2σ)	2838 (2σ)
Standard reflections	3/197	3/197	3/197	3/197	3/197	3/197
Var. in stds	1%	3%	2%	1%	<1%	2%
<i>(c) Refinement^a</i>						
R(F) (%)	3.89	8.70	6.5	6.8	5.04	7.77
R(wF) (%)	9.14	9.91	13.6	13.9	13.9	18.56
Δ/σ (max)	0.18	0.02	0.12	0.59	3.3	0.00
Δ (ρ) (eÅ ⁻³)	0.28	0.664	0.79	1.01	1.06	0.52
GOF	1.01	1.81	1.01	1.06	1.11	1.01
N _o /N _v	10.5	6.8	12.4	6.5	19.2	10.6

^a Quantity minimized = $\sum w\Delta^2$; $R = \sum \Delta / \sum (F_o)$; $R(w) = \sum \Delta w^{1/2} / \sum (F_o w^{1/2})$; $\Delta = (F_o - F_c)$.

2.12. X-ray structural studies

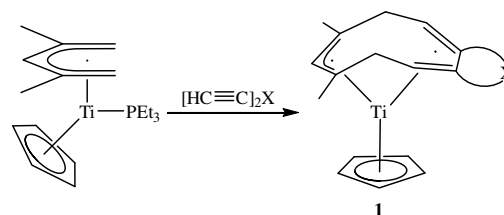
Crystals of the various compounds were of necessity mounted in glass capillaries under a nitrogen atmosphere, using silicone grease to hold them fixed. The structures for **1b** and **2** have previously been communicated [4]. The other structures were solved via direct methods and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included as idealized contributions.

Pertinent data collection and computational parameters are provided in Table 1. The SHELXTL programs library (G. Sheldrick, Siemens XRD, Madison, WI) was used for all calculations.

3. Results and discussion

3.1. Syntheses

The reactions of Ti(C₅H₅)(2,4-C₇H₁₁)(PEt₃) (C₇H₁₁ = dimethylpentadienyl) with a variety of diynes lead to bright green fused ring products derived from the coupling of each diene end to different diyne ends (Scheme 1). That these couplings have occurred is clearly evident from the ¹³C NMR spectra, which display J(¹³C–H) values of ca. 125–135 Hz for the newly coupled CH₂ and CH resonances (see Section 2), and has also been confirmed through diffraction studies (vide infra). The couplings of the diene and alkyne fragments have led to nine-membered rings, to which is fused another ring, constructed from the remainder of the diyne skeleton. Although the ¹H NMR spectra are fairly complicated, assignments of the appropriate resonances and coupling constants



Scheme 1. X = (CH₂)₂ (**1a**), (CH₂)₃ (**1b**), (CH₂)₄ (**1c**), (CH₂)₂C(CO₂CH₃)₂ (**1d**), (CH₂)₂C(CO₂C₂H₅)₂ (**1e**), (CH₂)₂O (**1f**), (CH₂)₂N(*n*-C₄H₉) (**1g**), (CH₂)₂NCH₃ (**1h**).

could be achieved with the help of a selectively deuterated diyne (see Section 2).

A number of pertinent observations can be made relating to the scope of these reactions. First, a significant degree of variability is allowed for both the diyne and diene coupling partners. The reaction tolerates diyne tethers containing heteroatoms such as nitrogen or oxygen (and even sulfur [7]), as well as ester substituents, despite the well recognized electropositive nature of titanium. Furthermore, hexadiynes, heptadiynes, and octadiynes may be employed in these reactions, leading to second ring sizes having 4–6 members. The formation of strained four-membered rings fused to strained nine-membered rings is particularly noteworthy. However, somewhat ironically it is the six-membered fused ring complex that decomposes rapidly at room temperature – perhaps the greater spatial extent of such a ring allows for a closer approach to the electron deficient metal center, and to facile decomposition (intractable products are formed). Low temperature reactions utilizing longer chain diynes also lead to similar green products, per-

haps the analogous fused ring species, but decomposition is even more facile, again leading to intractable products.

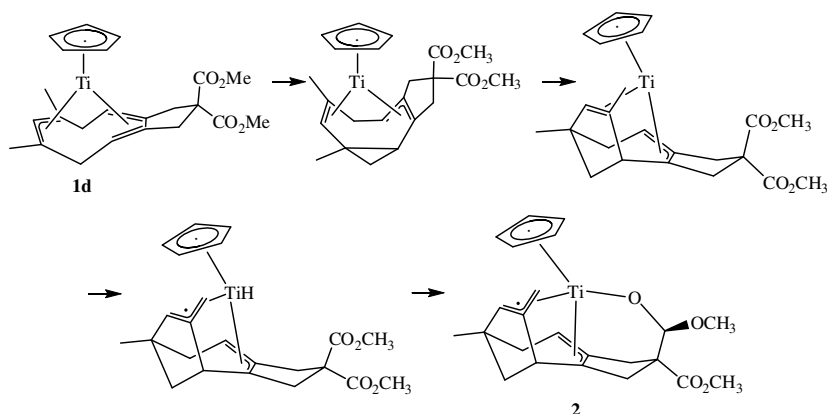
However, even many of the 9,4 and 9,5 fused ring complexes undergo transformations (rearrangement and/or decomposition) at room temperature. The transformations can vary in the time required. Notably, the rearrangement of **1d** does occur reproducibly, especially when promoted by mercury lamp photolysis (see Section 2). One observes an apparently quantitative conversion of the green **1d** to the bright red **2**, whose structure was elucidated through a diffraction study (*vide infra*). Interestingly, the transformation entails not only formation of two new carbon–carbon bonds, but also the selective breakage of a carbon–carbon bond. This can best be explained by invoking the beginnings of a metal-assisted di- π -methane rearrangement, which is interrupted by a vinylcyclopropane–cyclopentene rearrangement (Scheme 2; *vide infra*). Interestingly, other C–C bond cleavage reactions have been discovered in related (bicyclononatrienyl)titanium complexes [8].

Actually one might have expected a rearrangement via hydrogen migration from one of the CH₂ groups bridging the allyl and

diene fragments. Transfer of one of these hydrogen atoms to an appropriate terminal carbon atom of the latter fragments would lead to a fully conjugated cyclononatrienyl ligand, which would likely be subject to less strain (*vide infra*). That this does not occur appears to be a result of the orientations of these bridging CH₂ groups, whose hydrogen atoms have been found to project far away from the titanium center (*vide infra*).

3.2. Solid state structures

The solid state structures of **1a**, **b**, **d**, **f**, and **h** have been determined (see Figs. 1–5), and confirm the fused ring structures that had been suggested by spectroscopic data. An overall description of these species as 16 electron Ti(C₅H₅)(allyl)(diene) complexes is thus appropriate. To facilitate examination of these structures, pertinent averaged parameters, defined by the labeling presented in Scheme 3, are collected in Table 2. As the structure of the fused ring fragment in **1h** is particularly well-determined, it will be used in the following discussions as a representative of the general 9,5 structures.



Scheme 2.

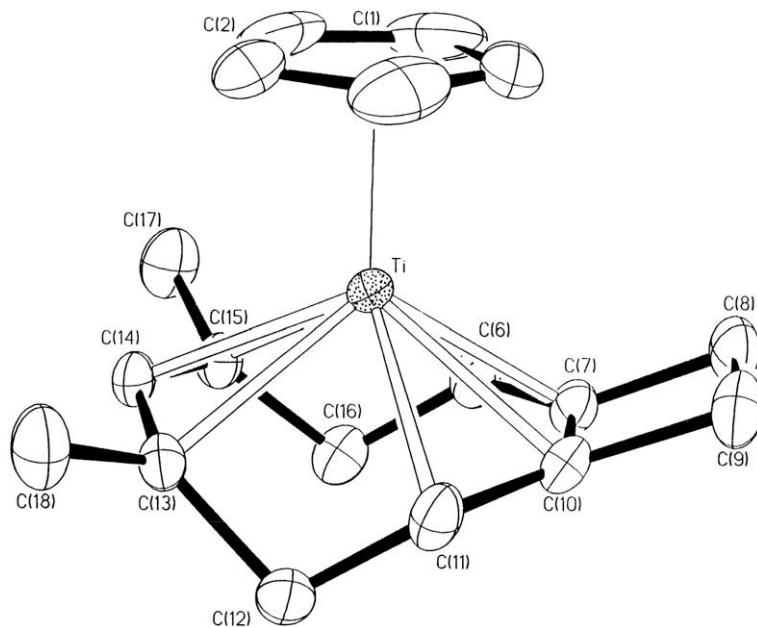


Fig. 1. Perspective view of the Ti(C₅H₅)(2,4-C₇H₁₁)/1,5-hexadiyne coupling product, **1a**.

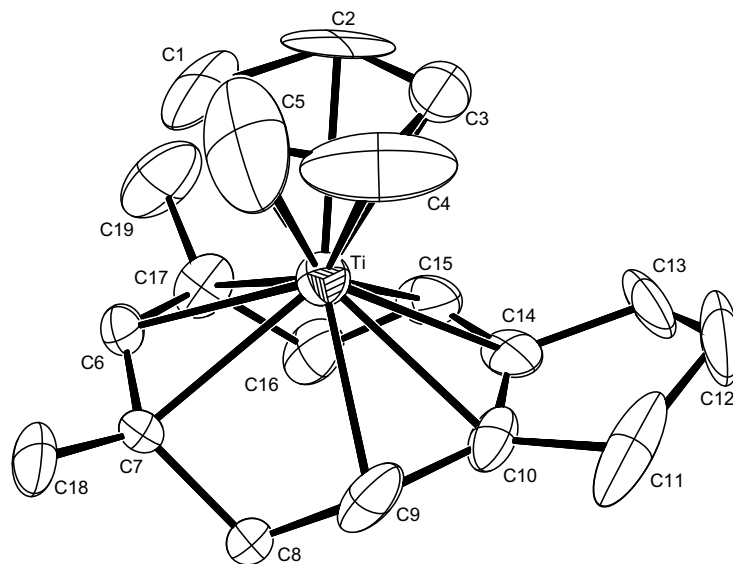


Fig. 2. Solid state structure of the $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})/1,6\text{-heptadiyne}$ coupling product, **1b**.

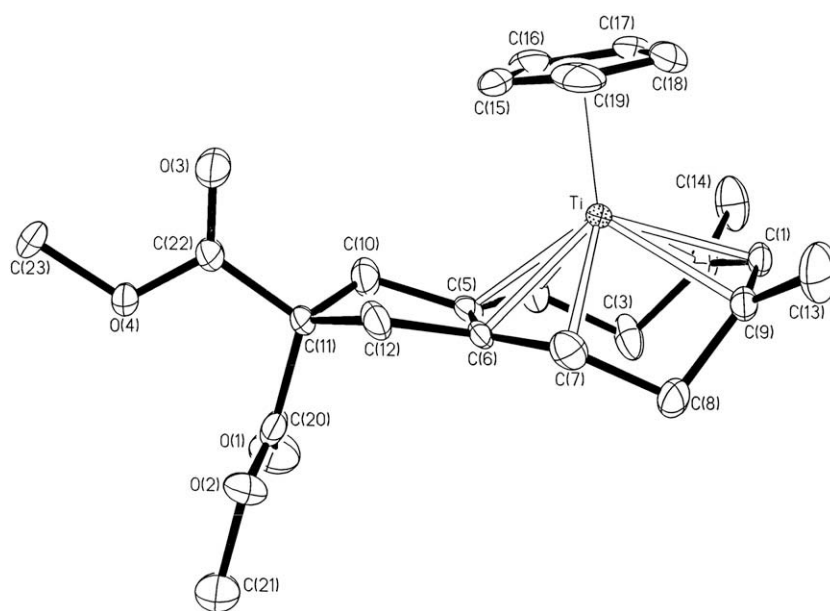


Fig. 3. Structure of the $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})/(\text{HC}_2\text{CH}_2)_2\text{C}(\text{CO}_2\text{Me})_2$ coupling product, **1d**.

First it can be noted that the angles about C(3,7) are rather small (ca. $104\text{--}105^\circ$), while those about C(2,4,6,8) are somewhat large (ca. $126\text{--}129^\circ$). The first distortion may arise from an attempt to bring the allyl and diene fragments closer together, presumably allowing for better overlap with the titanium centers' orbitals. The large angles about C(2,4,6,8) may reflect an attempt to keep the C3 and C7 atoms from engaging in serious repulsive nonbonded contacts. The observed C3–C7 separation of $3.164(3)$ Å in **1h** is indeed significantly less than would be expected based on the van der Waals radius of 1.7 Å for the carbon center [9]. Additionally, intramolecular H–H contacts between the CH_2 groups in the nine-membered rings are also quite short, ranging from 1.73 to 1.84 Å for all but **1a** (2.00 Å). Of course, the interaction of the titanium center with the diene and allyl fragments will also affect the orientations of the substituents present on their terminal carbon atoms (*vide infra*). In fact, in this regard one can note that endo-oriented substituents (such as

C(3,7)) on terminal positions of allyl, diene, or dienyl ligands generally tend to deform substantially out of the ligand plane, away from the metal center [10]. In this case, there is some distortion from the allyl plane (ca. 20.1° based on the torsion angles for **1h**), but somewhat more from the diene plane (ca. 33.2° for **1h**), although not nearly to the extent generally expected. The reason for this difference may be traced to the different separations and orientations of the allyl and diene termini. To a first approximation, the two endo substituents on a planar diene group would be positioned to occupy the remaining ortho sites of a hexagon, and thus would be too close together, while such substituents on an allyl group would occupy *meta* sites of a hexagon, and thereby not generate nearly such significant repulsive interactions. Hence, there is a greater steric incentive, perhaps even necessity, for the endo diene substituents to deform out of the ligand plane, away from the metal center. One final result of the constrained ring geometry is the fact that the satu-

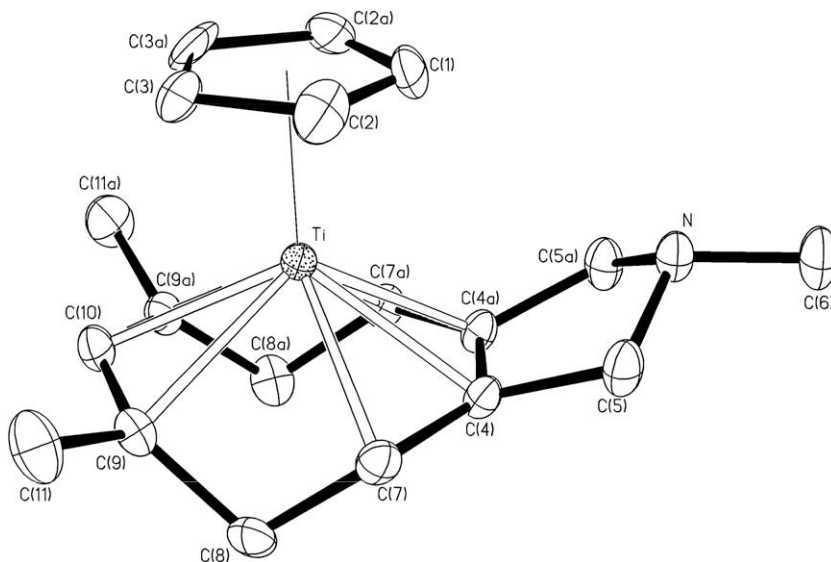


Fig. 4. Solid state structure of the $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})/(\text{HC}_2\text{CH}_2)_2\text{O}$ coupling product, **1f**.

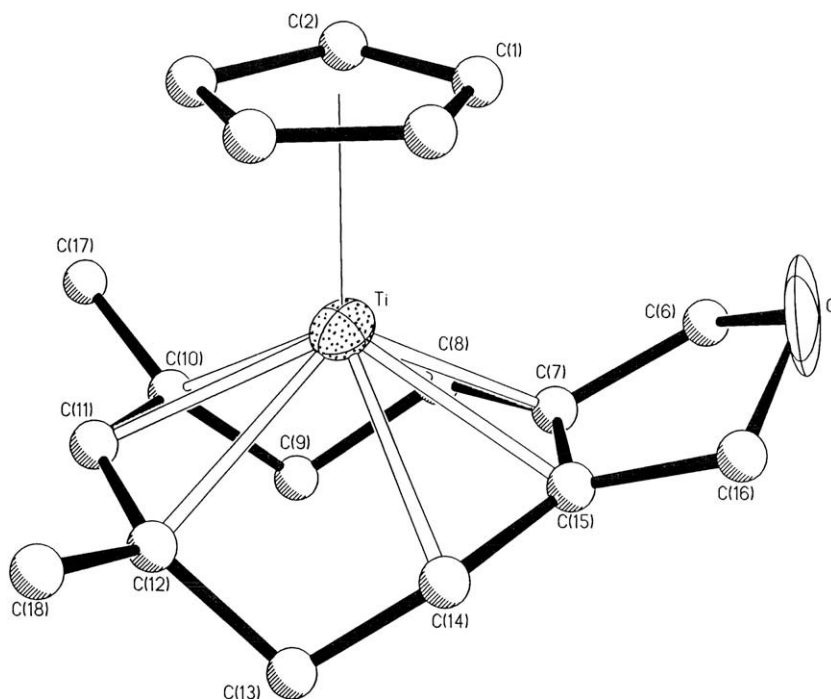
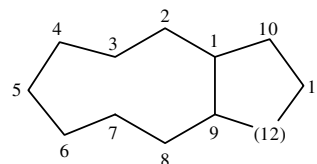


Fig. 5. Perspective view of the $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})/(\text{HC}_2\text{CH}_2)_2\text{NMe}$ coupling product, **1h**.

rated C(3,7) atoms are brought into close proximity to the Ti center, 2.731(1) Å for **1h**. This extremely short separation is closer than those separations in examples of compounds which undergo C–C activation reactions, and hence this readily accounts for the proclivity of these species to undergo skeletal rearrangements, involving C–C bond breakage (*vide infra*). In this regard, these species display some resemblance to carboranes, in which the electron deficient boron (*cf.*, titanium) atom can effect cleavage of C–C bonds.

In fact, a useful comparison may be made with a recently reported zirconium complex (**3**), in which the 6,6-dimethylcyclohexadienyl (6,6-dmch) ligand has undergone a 5+2+2 ring construction with 2 eq. of $\text{PhC}_2\text{SiMe}_3$ [11]. In the formally 16 electron complex, the zirconium center makes even shorter contacts



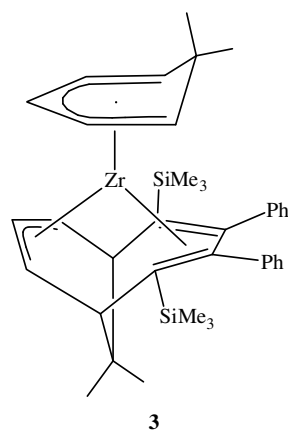
Scheme 3.

with some saturated carbon atoms, attributed to agostic (C–C) \rightarrow Zr interactions by virtue of lengthened C–C bonds (1.567(4), 1.574(4) Å). The fact that zirconium typically forms stronger bonds than titanium [12] is nicely in accord with this

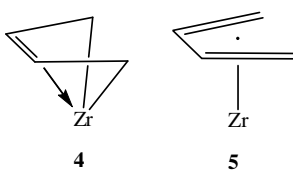
Table 2
Averaged bonding parameters for the fused ring complexes (**1a**, **b**, **d**, **f**, **h**)

Parameter; X =	(CH ₂) ₂ (1a)	(CH ₂) ₃ (1b)	(CH ₂) ₂ C(CO ₂ CH ₃) ₂ (1d)	(CH ₂) ₂ O (1f)	(CH ₂) ₂ NCH ₃ (1h)
Ti–C (Cp)	2.318(8)	2.313(8)	2.319(7)	2.317(8)	2.311(16)
Ti–C(1,9)	2.260(2)	2.264(7)	2.284(4)	2.265(3)	2.273(1)
Ti–C(2,8)	2.290(3)	2.230(8)	2.250(4)	2.280(10)	2.270(1)
Ti–C(4,6)	2.323(2)	2.329(8)	2.325(4)	2.333(3)	2.339(1)
Ti–C(5)	2.286(3)	2.297(10)	2.299(5)	2.283(9)	2.300(2)
C–C (Cp)	1.367(4)	1.329(12)	1.387(4)	1.365(8)	1.361(8)
C1–C2	1.392(3)	1.396(12)	1.402(6)	1.406(9)	1.408(2)
C1–C9	1.438(4)	1.384(15)	1.422(7)	1.436(16)	1.425(2)
C1–C10	1.522(3)	1.512(14)	1.522(5)	1.503(5)	1.517(2)
C2–C3	1.514(3)	1.518(13)	1.522(6)	1.514(13)	1.521(2)
C3–C4	1.520(3)	1.519(11)	1.530(6)	1.518(5)	1.523(2)
C4–C5	1.397(3)	1.358(10)	1.386(6)	1.399(9)	1.400(2)
C10–X	1.547(4)	1.471(19)	1.531(6)	1.434(9)	1.457(2)
C1–C2–C3	126.8(9)	129.1(7)	129.4(4)	129.7(8)	128.9(1)
C1–C10–X	88.0(1)	106.4(10)	104.8(4)	108.2(5)	106.0(1)
C2–C1–C9	134.4(1)	132.1(8)	132.0(4)	132.6(5)	132.6(1)
C2–C1–C10	131.6(2)	117.7(8)	118.0(4)	119.6(2)	118.7(1)
C2–C3–C4	105.2(2)	105.1(6)	105.0(4)	104.0(4)	104.2(1)
C3–C4–C5	125.6(2)	127.4(7)	125.8(4)	126.0(2)	125.7(2)
C4–C5–C6	131.0(2)	128.8(10)	129.9(5)	130.4(5)	130.0(2)
C9–C1–10	92.0(1)	109.1(8)	108.6(4)	106.7(5)	107.6(1)
C10–X–C12	–	107.5(15)	102.6(4)	106.5(4)	106.8(1)

lengthening, though it is not clear if **3** undergoes any subsequent cage rearrangement. Further investigation of these species, particularly via INADEQUATE NMR studies, would be helpful in better assessing the extents of these agostic interactions [11,13].



Concerning comparisons between these fused ring complexes, the only major differences to be noted are found between the 9,4 and 9,5 complexes. The incorporation of C1 and C9 of the diene fragment into the strained four-membered ring can be expected to exert a noticeable effect on the diene. Indeed, while the C1–C2, C1–C9, Ti–C(2,8), and Ti–C(1,9) distances of 1.408(2), 1.425(2), 2.270(1), and 2.273(1) Å in **1h** seem to reflect at least some contribution of an enediyl resonance form (**4**, [14]), the respective distances of 1.393(3), 1.438(4), 2.290(2), and 2.260(2) Å in **1a** reflect a greater contribution of a diene coordination mode (**5**). This is reasonable, given



that it would enhance the contribution from a cyclobutane vs. a more strained cyclobutene ring. Possibly this difference in Ti–diene coordination exerts an effect on the Ti–allyl bonding, as the Ti–C(4,6) distances in **1a** are slightly shorter than those in **1h**.

The structure of the photolytic rearrangement product of **1d** (**2**, Scheme 2), may be seen in Fig. 6. Actually, the product crystallizes as two essentially identical, but crystallographically independent, molecules. In the following discussion, the averaged bonding parameters will be presented, using brackets ({}) instead of parentheses. First the average Ti–C and C–C bond distances for the C₅H₅ ligand are 2.394(7) and 1.382(7) Å. The bond angles in the structure appear unexceptional, as do the bond distances for the saturated carbon–carbon bonds. However, the bonding involving the allylic fragments is quite irregular, most likely due to constraints imposed on their orientations by the tricyclic ring structure. Thus, the Ti–C{9,8,14} distances average 2.330(7), 2.396(6), and 2.620(7) Å, while the Ti–C{19,18,17} distances average 2.268(7), 2.379(7), and 2.585(8) Å, respectively. Along with the asymmetry in Ti–C bond lengths comes a long-short pattern in C–C bond lengths, as expected for a σ-allyl contribution (1.431(9) vs. 1.376(9) Å and 1.434(10) vs. 1.357(10) Å). It can be noted that for both allyl groups, the terminal carbon center being closer to the metal also is less substituted than the other terminus; however, this appears to be coincidental as the difference in each case involves the addition of a single exo-oriented substituent. It seems more likely that the geometry of the tricyclic cage is responsible for the allyl ligands' asymmetries. However, all Ti–C bond distances for the less substituted allyl are shorter than their counterparts for the more substituted allyl (see above). While this could also be ascribed to the tricyclic framework, the fact that the second allyl possesses an endo-oriented substituent on each terminus, while the first allyl has none, strongly suggests that these endo substituents are responsible for this difference.

One may finally consider the Ti–O{1} bonding. As a Ti(C₅H₅)(π-allyl)₂ unit would have a 15 electron configuration, one could expect the alkoxide ligand to function as a three electron donor, as has been observed in other situations [15,16]. In fact, the average Ti–O{1} distance of 1.874(5) Å is similar to those found for related π-alkoxide complexes [17]. However, the average Ti–O{1}–C{22} angle of 146.5(4)° appears closer to the values found for 5 electron alkoxide complexes, although significantly shorter Ti–O bond lengths were often observed (as short as 1.760(10) Å [17a,18]). It is not clear whether it is the large Ti–O–C angle (for a 3 electron alkoxide) or the relatively long Ti–O bond (for a 5 electron alkoxide) in this case which requires explanation. However, a contribution involving an alkoxide ligand serving as a 5 electron donor would necessitate a change from π-allyl to σ-allyl coordination,

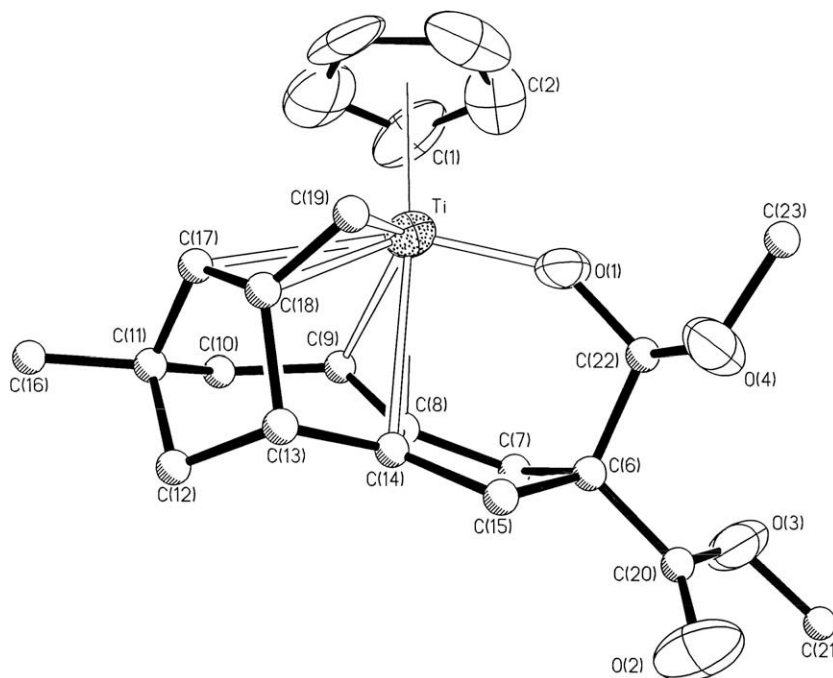


Fig. 6. Structure of the rearranged $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})/(\text{HC}_2\text{CH}_2)_2\text{C}(\text{CO}_2\text{Me})_2$ coupling product, **2**.

which would be in accord with the observed asymmetric allyl bonding, and perhaps with the lengthening of the Ti–C (Cp) bonds relative to the fused ring complexes in Table 2. In all likelihood, there is a competition between the allyl, alkoxide, and cyclopentadienyl ligands for π donation, as has been invoked previously [19].

4. Summary

The reactions of the half-open titanocenes, $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})(\text{PR}_3)_3$, with a variety of substituted α,ω -diynes lead to potentially useful 5 + 2 + 2 coupling processes, resulting in formally 16 electron complexes coordinated by the newly formed fused ring systems. Use of octa- or longer α,ω -diynes appears to lead to such species, though rearrangement and decomposition ensue even below room temperature. Hexadiyne, heptadiyne, and their substituted variants lead to species with enhanced stabilities, though they also undergo rearrangements at room temperature. It is not known if pentadiyne would lead to a similar species. Notably, analogous coupling reactions also take place for other pentadienyl ligands, such as C_5H_7 [20], whose coupling products can undergo multiple rearrangements. In any case, protocols have been developed for the release of these fused ring species, generally as conjugated trienes [20], even for those that are not stable at room temperature.

The rearrangement processes can be attributed to C–C bond activations, brought about via (C–C) \rightarrow Ti agostic interactions, which may be present in the ground state complexes. As noted above, other transformations take place when octadiynes, or longer species, are utilized. In these cases, the presence of a larger ring fused to the nine-membered ring likely results in a close enough approach to the electron deficient metal center to allow decomposition, perhaps via C–H bond activation.

Acknowledgements

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of Utah and the National Science Foundation for partial support of this research.

Appendix A. Supplementary materials

Cif files for the structures of **1a**, **1d**, **1f**, **1h**, and **2**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.008.

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