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

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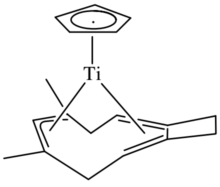
ABSTRACT

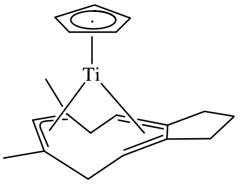
The reactions of several α,ω-diynes with half-open titanocene complexes $[M(C_5H_5)(2,4\text{-}C_7H_{11})(PR_3)]$ (C_7H_{11} = dimethylpentadienyl) lead to 5 + 2 + 2 ring constructions, yielding nine-membered rings fused to four-membered and larger rings. These reactions tolerate significant functionalization, 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.

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 $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ (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 worthwhile to examine the scope of this coupling reaction. Herein, we report our results on these species.



1a



1b

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]. $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PR_3)$ 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 deuterochloroform.

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 °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 °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 °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 °C over a period of 1 week.

MP (N_2 filled, sealed capillary): 127 °C (decomp).

^{1}H 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 °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 °C. The reaction mixture was allowed to warm slowly to ca. −30 °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 °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 °C for 6 days. The resulting dark green crystals (mp 95–97 °C) were isolated by removal of the supernatant via syringe.

^{1}H 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 °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 °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 °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 ^{1}H 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 °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 °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)$_2$C(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 °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 °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 °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 °C over a period of 1 week.

MP (N_2 filled, sealed capillary): 123.0–125.0 °C (decomp).

^{1}H 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 °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})[($CH_3CH_2CO_2$)$_2$C(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.

^{1}H 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).