A Novel Intramolecular Cyclisation of Titanocene Vinylidene Complexes: Formation of Bicyclic Titanacyclo-butanes and -butenes

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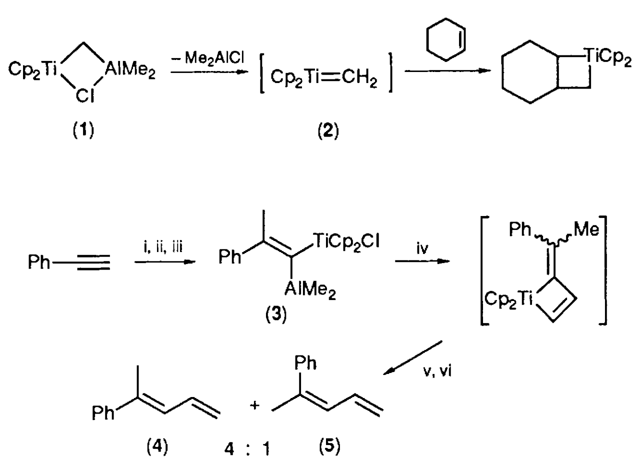
The intramolecular addition of a titanocene vinylidene complex formed by dechlorodimethylalumination of a 1-dimethylalumino-1-bis(η^5-cyclopentadienyl)chlorotitano-alkene to an unactivated alkene or alkyne affords bicyclic titanacyclobutanes or titanacyclobutenes.

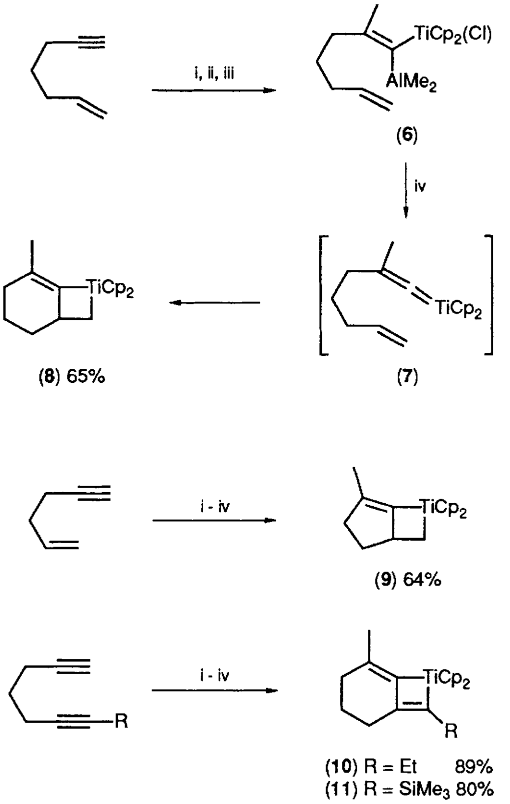
As part of our studies on the use of early transition metal complexes for the carbometallation of unactivated alkenes and alkynes we were interested in the formation and elaboration of titanacyclo-butanes and -butenes. These may be formed by the [2 + 2] addition of titanocene methylene (**2**), generated from the Tebbe reagent (**1**),[1] to unactivated alkenes or alkynes.[1,2] For application to organic synthesis however this reaction suffers from the limitation that only the parent carbene species can be used owing to problems with β-hydrogen elimination, so we decided to investigate the use of the analogous vinylidene complexes. These have been previously generated *via* a metathesis reaction between titanocene methylene and allenes and used to convert ketones into allenes.[3] We required a more direct route and noted a report by Negishi that 1-dimethylalumino-1-bis(η^5-cyclopentadienyl)chlorotitano-alkenes could be readily formed by methyltitanation of an alkynylalane, and converted cyclohexanone to the corresponding allene.[4] Indeed treatment of the titano-dimethylalumino alkene (**3**) derived from phenylacetylene with hexamethylphosphoramide (HMPA) (to complex the dimethylaluminium chloride), in the presence of acetylene followed by acidic work-up gave a 4 : 1 mixture of the dienes (**4**) and (**5**) which would be expected from titanacyclobutene intermediates. Unfortunately the use of substituted alkynes as traps gave complex mixtures of isomeric diene products and the yields were generally poor.



Cp = η^5-cyclopentadienyl

Scheme 1. *Reagents and conditions*: i, BuLi, 0 °C, hexane; ii, $AlMe_2Cl$; iii, $Cp_2Ti(Me)Cl$, 1,2-dichloroethane, 25 °C, 0.5 h; iv, HMPA, THF, C_2H_2, −20 °C; v, HCl gas, −78 °C; vi, aq. $NaHCO_3$.

We then turned our attention to the intramolecular variant of this reaction hoping for higher yields and imposed regiocontrol (Scheme 2). Treatment of hept-6-en-1-yne with BuLi followed by dimethylaluminium chloride to form an alkynylalane, then carbometallation with titanocene methyl chloride gave the gem-dimetallic alkene (**6**). Much to our delight addition of HMPA gave the bicyclic titanacyclobutane (**8**)† in near quantitative yield, presumably *via* the vinylidene complex (**7**). This was purified by extraction into hexane, filtration through Celite, and recrystallisation from ether to afford the air- and moisture-sensitive dark red microcrystalline product in 65% yield. The high field ^1H and ^{13}C NMR spectra together with ^1H–^1H and ^1H–^{13}C COSY 2D-spectra were in accordance with the shown structure and allowed full assignment of all resonances (Figure 1). Reaction with HCl gas at −78 °C followed by aqueous work-up gave 1,3-dimethylcyclohex-1-ene. For large-scale work the preparation could be simplified by forming both dimethylaluminium chloride and titanocene methyl chloride *in situ* by reaction between titanocene dichloride and trimethylaluminium.



Scheme 2. *Reagents and conditions*: i, BuLi, 0 °C, toluene; ii, $AlMe_2Cl$, 20 °C, 30 min; iii, $Cp_2Ti(Me)Cl$, 20 °C, 30 min; iv, HMPA or pyridine, THF.

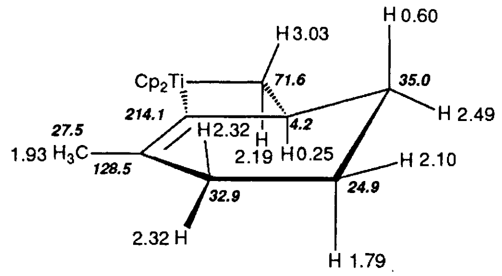
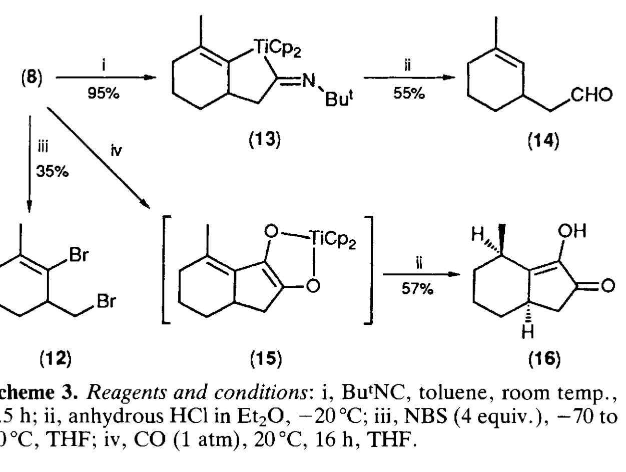


Figure 1. NMR assignments for titanacycle (**8**). ***Bold italics***: ^{13}C chemical shifts, 90 MHz, C_6D_6; plain: ^1H chemical shifts, 360 MHz, C_6D_6.



Scheme 3. *Reagents and conditions*: i, Bu^tNC, toluene, room temp., 0.5 h; ii, anhydrous HCl in Et_2O, −20 °C; iii, NBS (4 equiv.), −70 to 20 °C, THF; iv, CO (1 atm), 20 °C, 16 h, THF.

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† NMR data for the titanacycles, ^1H at 360 MHz, ^{13}C at 90 MHz, both in C_6D_6: (**8**), ^1H: δ 5.73 (5H, s), 5.63 (5H, s), 3.03 (1H, dd, *J* 11.3, 8.4 Hz), 2.49 (1H, dq, *J* 12.1, 3.3 Hz), 2.32 (2H, m), 2.19 (1H, t, *J* 8.1 Hz), 2.10 (1H, ddt, *J* 10.2, 3.1, 1.8 Hz), 1.93 (3H, dt, *J* 2.2, 1.2 Hz), 1.79 (1H, dddt, *J* 14, 10.2, 8.2, 3.8 Hz), 0.60 (1H, ddt, *J* 12.7, 11.0, 3.2 Hz), and 0.25 (1H, m); ^{13}C δ 214.09 (s), 128.48 (s), 109.19 (d, Cp), 108.34 (d, Cp), 71.64 (t), 34.99 (t), 32.91 (t), 27.47 (q), 24.87 (t), and 4.19 (d).

(**9**), ^1H (270 MHz): δ 5.65 (5H, s), 5.55 (5H, s), 3.11 (1H, ddddq, *J* 14.7, 11.4, 6.0, 3.1, 1.5 Hz), 2.73 (1H, ddd, *J* 11.1, 6, 4.3 Hz), 2.67 (1H, ddd, *J* 15, 7.7, 0.8 Hz), 2.57 (1H, dd, *J* 10.6, 7.4 Hz), 2.15 (3H, ddd, *J* 2.3, 1.6, 0.7 Hz), 1.56 (1H, dd, *J* 8.8, 7.3 Hz), 0.97 (1H, m), and 0.79 (1H, td, *J* 11.1, 7.8 Hz); ^{13}C (67.5 MHz): δ 240.35 (s), 140.74 (s), 108.40 (d, Cp), 107.39 (d, Cp), 58.72 (t), 45.64 (t), 38.37 (t), 19.91 (q), and 18.63 (d).

(**10**), ^1H: δ 5.80 (10H, s), 2.81 (2H, q, *J* 7.6 Hz), 2.30 (2H, t, *J* 6.0 Hz), 2.16 (2H, t, *J* 6.2 Hz), 2.08 (3H, s), 1.82 (2H, tt, *J* 6.2, 6.0 Hz), and 1.37 (3H, t, *J* 7.5 Hz); ^{13}C: δ 216.9 (s), 198.4 (s), 113.92 (s), 110.05 (d, Cp), 85.08 (s), 33.95 (t), 30.15 (t), 27.26 (q), 24.04 (t), 22.72 (t), and 16.65 (q).

(**11**), ^1H: δ 5.80 (10H, s), 2.3 (4H, m), 2.0 (3H, s), 1.8 (2H, quintet, *J* 5.8 Hz), and 0.50 (9H, s); ^{13}C: δ 216.02 (s), 200.19 (s), 132.76 (s), 110.46 (d, Cp), 104.73 (s), 34.13 (t), 28.43 (t), 27.38 (q), 24.15 (t), and 2.33 (q).

The titanacycles also gave satisfactory IR and mass spectral data.

Addition of the lithiated alkyne then gave the *gem*-dimetallic alkene (**6**) directly. Investigation of less hazardous Lewis bases than HMPA showed that pyridine and tetrahydrofuran (THF) worked as well, the former being most convenient for isolation of the pure metallacycles.

This cyclisation has proven to be quite general (Scheme 2) extending to the formation of a 5-membered ring in (**9**), and to the use of alkynes as traps to give (**10**) and (**11**). The higher yields of pure material in these latter cases reflect the greater crystallinity of the titanacycles. Although moisture-sensitive these metallacycles are quite thermally stable, even in solution, surviving for several days in $[^2H_6]$benzene at 4 °C and for months in the solid state at -20 °C.

The remaining carbon–metal bonds in the metallacycles offer great potential for further elaboration to organic products. This was illustrated for the complex (**8**) (Scheme 3); reaction with *N*-bromosuccinimide (NBS) gave the dibromide (**12**); insertion of t-butyl isocyanide occurred regiospecifically to afford the imino complex (**13**) which gave the aldehyde (**14**) on acidic work-up; and reaction with carbon monoxide followed by an acidic work-up gave the ketone (**16**), presumably *via* the ene-diolate complex (**15**).[2] The yields given are not optimised.

This novel cyclisation to produce titanacycles with a great potential for further elaboration should be useful in organic synthesis.

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