Synthesis of Allenylketenimines *via* Titanocene Vinylidene Complexes

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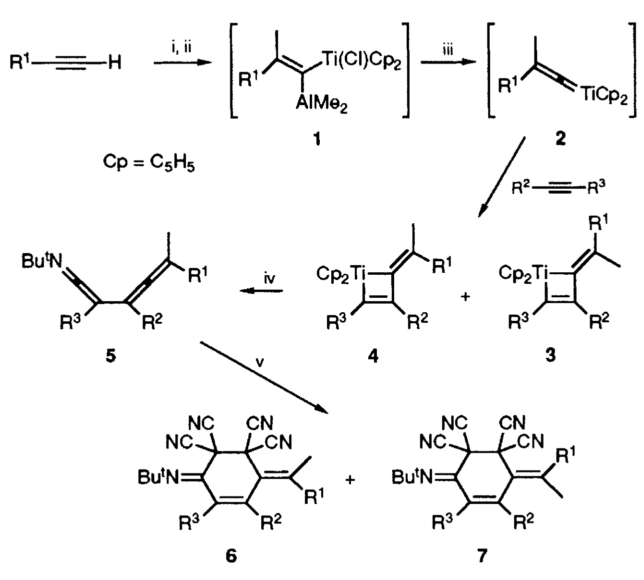
The intermolecular addition of *in situ* generated titanocene vinylidene complexes to alkynes gives titanacyclobutenes which undergo an insertion–rearrangement with *tert*-butyl isocyanide to afford allenylketenimines in high yield.

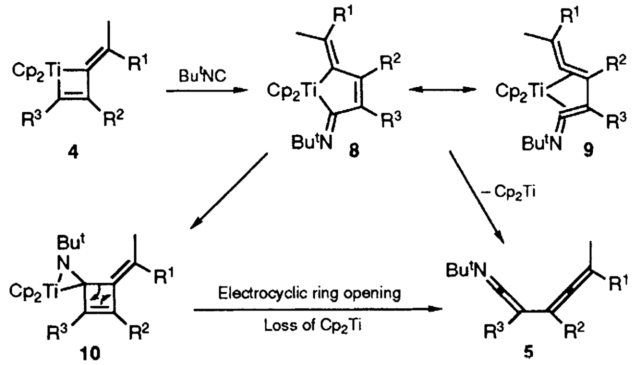
We recently reported[1] that titanocene vinylidene complexes could be generated *in situ* by dechloroalumination of 1-dimethylalumino-1-bis(η^5-cyclopentadienyl)chlorotitanoalkenes and trapped in an intramolecular fashion by unactivated alkenes and alkynes to afford bicyclic titanacyclobutanes or titanacyclobutenes. This novel carbometallation would be of greater versatility if the intermolecular version could be developed. Initial studies were discouraging, intermolecular trapping of *in situ* generated vinylidene complexes by alkenes, even activated examples such as norbornene, failed. However, alkynes seemed to react well although protonolysis of the supposed intermediate titanacyclobutenes afforded only low yields of mixtures of isomeric dienes. Further investigation has shown that much of the problem lay with the demetallation procedure and we report here an efficient elaboration of unactivated alkynes to the previously unknown allenylketenimine functionality.

A 1 : 1 mixture of Me_2AlCl and $Cp_2TiMeCl$ ($Cp = C_5H_5$) in toluene was formed *in situ* from Cp_2TiCl_2 and Me_3Al (room temperature, 1 h) and added to a solution of PhC≡CLi in toluene. The lithioacetylene reacts selectively with the dimethylaluminium chloride to form an acetylenic alane which is then regiospecifically carbometallated by the $Cp_2TiMeCl$ to form the *gem*-dimetallic reagent **1a**.[2] After 2 h at room temperature oct-4-yne (1.2 equiv.) was added followed by hexamethylphosphoramide (HMPA) (1 equiv.). The latter strongly complexes to dimethylaluminium chloride driving the conversion of **1a** into the vinylidene complex **2a** which is trapped *in situ* by the oct-4-yne to form a 2 : 1 mixture of the isomeric titanacyclobutenes **3a** and **4a** (vinylic methyl groups at δ_H 2.52 and 2.18, respectively). After 15 min the solvent was removed *in vacuo*, the residue extracted into hexane and washed through a small amount of neutral alumina on a sinter. Evaporation of solvent afforded a pure mixture of **3a** and **4a** as a very dark-purple (black in bulk) gum. The stereochemistry shown is that expected on the basis of the incoming alkyne avoiding the large phenyl group which lies in the same plane as the π-system being attacked, and is according to limited precedent,[1] but was not proven. The good yield of metallacycle was encouraging since previous attempts to assay this reaction by protonolysis gave poor recovery of the expected diene.



Scheme 1 *Reagents and conditions*: i, BuLi, 20 °C, 15 min; ii, $Cp_2TiMeCl$, Me_2AlCl, toluene, 20 °C, 2 h; iii, HMPA, 20 °C, 15 min; iv, Bu^tNC, hexane, 16 h, room temp.; v, TCNE, $CHCl_3$, 0 °C, 30 min

Addition of Bu^tNC (2 equiv.) to a solution of titanacyclobutenes **3a** and **4a** in hexane gave an immediate reaction with a colour change to brown–orange and slow precipitation of a black solid (probably 'titanocene'[3]). Much to our surprise the NMR spectrum of the supernatant showed an absence of cyclopentadienyl peaks and only a single product! This was identified as the allenylketenimine **5a**† and isolated as a light-brown oil, pure by the NMR spectrum, in 92% yield by filtration of the hexane solution through celite and removal of solvent. It could be chromatographed on neutral alumina to afford an 83% yield of a colourless oil. The key observation which led to the structure assignment was a strong IR absorption at 2008 cm^{-1}. In the transformation from the metallacycles to **5a** the geometrical isomerism of the alkene is converted to optical isomers of the allene, hence the formation



Scheme 2 Mechanism of insertion–rearrangement

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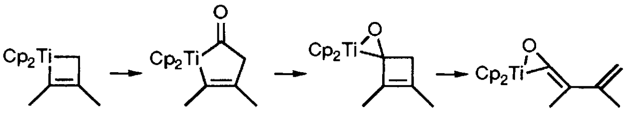
† All compounds gave satisfactory ^1H and ^{13}C NMR, mass spectra and IR data. Compounds **6a–f**, **7a** and **d** gave satisfactory combustion analyses.

Spectroscopic data for **5a** and **6a**: **5a** ν_{max}/cm^{-1} (CCl_4) 2965s, 2007.7s, 1922.5s, 1596s; λ_{max} (Et_2O) 259 nm; δ_H (270 MHz, C_6D_6) 7.8–7.2 (5H, m), 2.49 (2H, t, *J* 7.5 Hz), 2.37 (2H, t, *J* 7.5 Hz), 2.30 (3H, s), 1.88 (2H, q, *J* 7.5 Hz), 1.76 (2H, q, *J* 7.5 Hz), 1.25 (9H, s), 1.16 (3H, t, *J* 7.4 Hz), 1.10 (3H, t, *J* 7.4 Hz); δ_C (67.5 MHz, C_6D_6) 203.23 (s), 186.41 (s), 139.17 (s), 129.28 (d), 127.45 (d), 126.78 (d), 106.43 (s), 105.22 (s), 71.25 (s), 59.26 (s), 35.27 (t), 31.61 (t), 30.96 (q), 23.00 (t), 22.73 (t) 18.45 (q), 14.98 (q), 14.92 (q); MS *m/z* (EI) 309 (M^+, 27%), 253 (95), 238 (4), 196 (7), 181 (5), 168 (13).

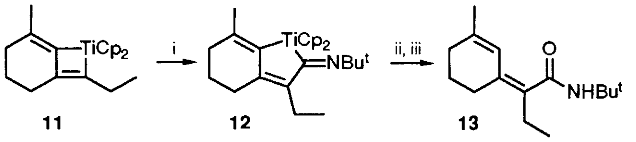
6a White crystals m.p. 161 °C (decomp.) from hexane: ν_{max}/cm^{-1} (CCl_4) 2966s, 2932s, 2874m, 1668m, 1466m; ν_{max}/cm^{-1} (raman) 2253; λ_{max} (Et_2O) 228 nm (ε = 70 000), 275 (37 000), 282 sh (36 000); δ_H (270 MHz, $CDCl_3$) 7.4 (3H, m), 7.1 (2H, m), 2.6 (3H, s), 2.38 (2H, m), 1.55 (4H, m), 1.40 (9H, s), 1.27 (2H, tq, *J* 8.1, 7.1 Hz), 0.98 (3H, t, *J* 7.1 Hz), 0.66 (3H, t, *J* 7.1 Hz); δ_C (90 MHz, $CDCl_3$) 148.01 (s), 147.82 (s), 142.75 (s), 141.80 (s), 138.13 (s), 129.48 (d), 129.12 (d), 127.00 (d), 120.65 (s), 110.26 (s), 59.53 (s), 54.03 (s), 44.79 (s), 34.57 (t), 32.45 (t), 29.77 (q), 25.03 (q), 21.35 (t), 21.19 (t), 14.62 (q), 14.16 (q); MS *m/z* (EI) 437 (M^+, 2%), 422 (4), 381 (18), 354 (11), 352 (9), 338 (11), 327 (6), 325 (6), 316 (21), 311 (8), 303 (7), 289 (6), 274 (5), 269 (13), 253 (11), 224 (8), 57 (100).

Table 1 Percentage yields and isomer ratios for compounds **3**–**7**

	R^1	R^2	R^3	Yield (%) 3 + 4	Ratio 3 : 4	Yield (%) 5	Yield (%) 6 + 7	Ratio 6 : 7
a	Ph	C_3H_7	C_3H_7	74	2 : 1	83	48	6 : 1
b	Ph	H	$SiMe_3$	63	2 : 3	97	46	**6** only
c	Ph	C_5H_{11}	$SiMe_3$	85	2 : 1	85	72	**6** only
d	C_5H_{11}	H	Ph	86	1 : 1	94	60	1.4 : 1
e	C_5H_{11}	Ph	Ph	88	1 : 1	84	43	3 : 1
f	C_3H_7	H	C_3H_7	69	1 : 1	80	33	3 : 1



Scheme 3 Insertion of CO into a titanacyclobutene



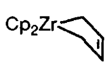
Scheme 4 *Reagents and conditions*: i, Bu^tNC, room temp., 0.5 h; ii, anhydrous Bu^tOH in CH_2Cl_2; iii, HCl, −30 °C

of a single isomer (neglecting the rapidly inverting nitrogen centre). As far as we are aware this is the first report of allenylketenimines, though vinylketenimines have found some use in organic synthesis.[4] Since **5a** was too unstable for successful combustion analysis, and conclusive structural assignment was made difficult by the array of contiguous quaternary centres it was reacted with tetracyanoethylene (TCNE) to form the crystalline Diels–Alder adducts **6a** and **7a** in a 6 : 1 ratio (48% combined yield). The stereochemistry of cycloaddition is that expected on the basis of the incoming dienophile avoiding the face of the diene on which the bulky phenyl group lies. In the ^1H NMR spectrum of the minor isomer **7a** a 4% NOE (nuclear Overhauser effect) was observed between the vinylic methyl group and the adjacent vinylic methylene, absent in the major isomer **6a**.

Optimisation studies showed that only a slight excess of the alkyne trap needed to be used, and that the insertion–rearrangement worked best with 2 equiv. of Bu^tNC; with only 1 equiv. the yield of the allenylketenamine dropped to 66%.

In a similar fashion the metallacycles **3b–f** and **4b–f**, allenylketenimines **5b–f**, and TCNE adducts **6b–f** and **7d–f** were formed in the yields and ratios given in Table 1. One point worthy of note is that the addition of the titanocene vinylidenes to both trimethylsilyl substituted, and terminal acetylenes is completely regioselective (entries **b**, **c**, **d** and **f**), the larger of the substituents on the acetylene ending up close to the metal. This is expected because the substituents on the titanocene vinylidene lie in the same plane as the incoming alkyne and hence have a very pronounced steric effect.

The assignment of regiochemistry of addition to the alkynes, and the stereochemistry of the TCNE adducts rests on NOE experiments. Key observations are that the vinylic hydrogens in **7d**, and **7f** show a large NOE (12–16%) to the vinylic methyl group whereas in **6d** and **f** similar values are observed to the corresponding vinylic methylene. In **6b** a 6% NOE is observed between the vinyl proton and the phenyl protons, and in **6c** weak NOE's are seen between the Me_3Si and Bu^t groups. The structure of compound **6b** was confirmed by X-ray crystallography.[5]



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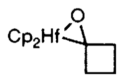

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Plausible mechanisms for the insertion–rearrangement reaction are given in Scheme 2. A precedent for this unusual rearrangement comes from the formation of a titanocene ketene complex in the carbonylation of a titanocene cyclobutene reported by Grubbs[6] (Scheme 3). He considers several similar pathways and favours that which occurs *via* a cyclobutene as shown, strong evidence being presented for the indicated regiochemistry of CO insertion. In our case we expect the regiochemistry of isocyanide insertion to be the opposite of this leading to **8**, evidence being the insertion of Bu^tNC into the bicyclic complex **11** to give **12** and hence the amide **13** on work-up (Scheme 4). At first sight the direct decomplexation of Cp_2Ti from **8** (analogous to chelotropic reactions such as the extrusion of SO_2 from 3-sulfolenes) appears unlikely since the Ti–C bonds, which are to break, should be orthogonal to the π-orbital of the alkene that must also be involved. However, **8** can also be viewed as an η^4-diene complex **9** which would be expected to easily lose Cp_2Ti. Group IV metallocene–diene complexes such as **14** are well known and though they are best described as titanacyclopent-3-enes (the ligand being σ^2, π-bonded) and adopt an envelope conformation, decomplexation of the diene is a facile process.[7] The alternative mechanism shown in Scheme 2 *via* the cyclobutene **10** has precedent in the formation of the η^2-hafnium-cyclobutanone complex **15** by carbonylation of a hafnacyclobutane[8] but we would not expect the electrocyclic opening of **10** to the diene system to occur under such mild conditions.

Overall we have developed an efficient transformation of unactivated alkynes into the previously unknown allenylketenimine functionality, a conversion in which new carbon–carbon bonds are formed at both ends of the substrate alkyne.

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