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The Transient Titanocene(II): Direct Synthesis from Solvated Titanium(II) Chloride and Cyclopentadienylsodium and Ensuing Interception with Diphenylacetylene as 1,1-Bis(cyclopentadienyl)-2,3,4,5-tetraphenyltitanacyclopentadiene[‡]

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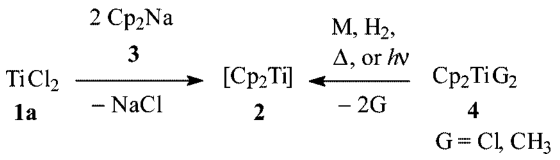
For the first time the unstable titanocene(II) has been directly synthesized by the Wilkinson metallocene approach, namely the interaction of a THF-soluble form of titanium(II) chloride with two equivalents of cyclopentadienylsodium in THF solution at 0°–25 °C. Because of the transient existence of the titanocene(II) thereby obtained, it could only be chemically trapped in high yield as 1,1-bis(cyclopentadienyl)-2,3,4,5-tetraphenyltitanacyclopentadiene by two equivalents of diphenylacetylene, if the acetylene was added at 25 °C, *without* removal of the by-product LiCl and NaCl. If the addition of the acetylene was delayed, in order to filter off the LiCl and NaCl from the reaction mixture, then no trace of the titanacyclopentadiene derivative was found upon hydrolytic workup. Instead, a significant portion of the acetylene was found to have undergone hydrotitanation. This finding is clear evidence that the titanocene(II) had undergone a precedented rearrangement to a known dimer having the structure of a titanocene(III) hydride with a fulvalene bridge between the titanium centers. We suggest that the LiCl and NaCl present in the unfiltered reaction mixture form a dichloro complex with titanocene(II) and thereby retard its dimerizing rearrangement to the titanocene(III) hydride.

Introduction

Shortly after the serendipitous synthesis and discovery of ferrocene through the independent routes of Pauson and Kealy[2] and of Miller and co-workers[3] the systematic synthesis of analogous cyclopentadienyl derivatives of transition metals was undertaken with great success by both the Wilkinson and the Fischer research groups.[4] From group 4 tetrahalides the bis(cyclopentadienyl)metal(IV) dihalides were the most readily formed and isolated. Although the preparation of bis(cyclopentadienyl)titanium(III) halides was achieved by the activated metal reduction of Cp_2TiX_2 in donor, nonprotic solvents,[5,6] the preparation of bis(cyclopentadienyl)titanium(II) or titanocene(II) (**2**) has received the attention of many researchers during the period of 1956–1976 with an overall indecisive outcome.[7]

The attempted preparations of titanocene(II) (**2**) have involved either the direct reaction of polymeric $TiCl_2$ (**1a**) in ethereal suspension with two equiv. of bis(cyclopentadienyl)sodium (**3**)[8a,8b] or the α-elimination of the two groups G from Cp_2TiG_2 (**4**) (G = Cl, or CH_3) by an active metal for G = Cl,[9] dihydrogen,[10] heat,[11] or light[12] for G = CH_3 (Scheme 1). None of the socalled "titanocene" products thus generated could be isolated in a crystalline form suitable for single-crystal X-ray structure analysis.



Scheme 1.

A range of different "titanocene" products have been accordingly isolated, varying in color (green, brown, violet or black) and in spectroscopic as well as magnetic properties. It is generally agreed that none of these products is titanocene (**2**) itself, which should be very reactive due to its carbenoid nature.[13,14] Therefore, in order to take into account the anticipated high reactivity of authentic titanocene (**2**), provision was made to capture **2** as it was purportedly formed by the reduction of Cp_2TiCl_2 with the sodium–naphthalene adduct in THF.[9a] When diphenylacetylene (**5**) was included as the trapping agent in the reaction, the titanacyclopentadiene **6** was isolated in low yield. This finding was taken as convincing evidence that titanocene (**2**) had

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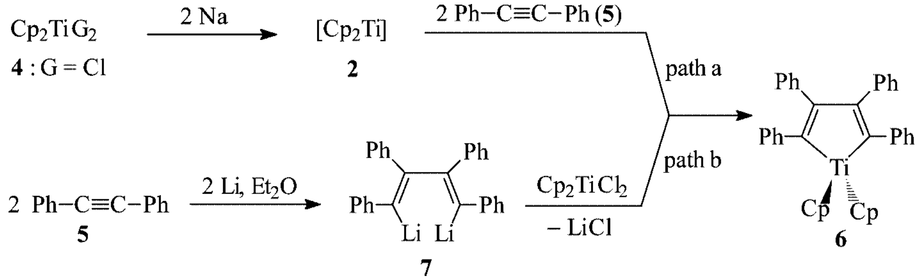


Scheme 2.

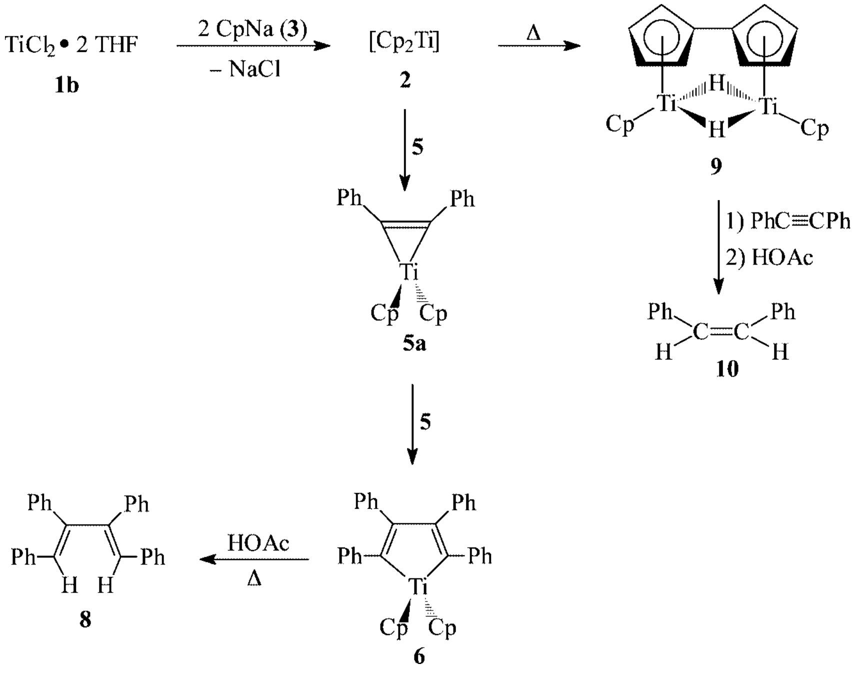
been generated [**4** (G = Cl)→**2**] and had been captured by diphenylacetylene (**5**) (path a, Scheme 1, **2**→**6**).[15] However, the conclusion that titanocene (**2**) has been captured in this experiment is ambiguous and thus inconclusive. It has long been recognized that alkali metals in general and lithium metal in particular can effect the reductive dimerization of diphenylacetylene in ethers (**5**→**7**, Scheme 2).[16,17] The 1,4-dilithiobutadiene of proven (*E*,*E*)-configuration has been successfully employed for the synthesis of **6** and several other metallacyclopentadienes.[18,19] Thus the titanocycle **6** isolated from the reaction of Cp_2TiCl_2 and diphenylacetylene with sodium could equally as well have been formed from path b in Scheme 2 (**5**→**7**→**6**) and would *not* have required the presence of free titanocene (**2**), as in path a.

Results and Discussion

In the present research the direct reaction of titanium(II) chloride with bis(cyclopentadienyl)sodium (**3**) was again investigated but with one significant difference. Instead of employing the insoluble, polymeric form, $[TiCl_2]_x$ (**1a**), obtainable by the high-temperature disproportionation of titanium(III) chloride, a newly discovered, THF-soluble form of titanium(II) chloride (**1b**), $[TiCl_2{\cdot}THF]_n$, generated by the alkylative reduction of titanium(IV) chloride,[20] has been used to great advantage [Equations (1) and (2)]. The degree of aggregation (*n*) of **1b** is not yet known with certainty but the existence of the paramagnetic open-chain, trimeric biradical, $[Ti(O\mathit{i}Pr)_2]_3$, supports the proposal that the diamagnetic **1b** may form a cyclic trimer in which a core of 3 titanium atoms is bonded as a triangular structure.[1]

$$TiCl_3 \xrightarrow{\Delta} \underset{\mathbf{1a}}{[TiCl_2]_x} + TiCl_4\uparrow \qquad (1)$$

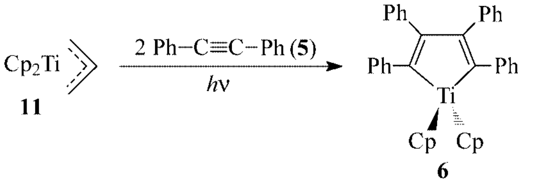
$$TiCl_4 \xrightarrow[-\,78^{\circ}C,\ THF]{2\ BuLi} [Bu_2TiCl_2] \xrightarrow[r.t.,\ -2\ Bu\bullet]{THF} \underset{\mathbf{1b}}{[TiCl_2\bullet 2\ THF]_n} \qquad (2)$$



Scheme 3.

A THF solution of 0.10 mmol of freshly prepared **1b**, still containing the LiCl by-product, was treated at 0 °C with 0.22 mmol of bis(cyclopentadienyl)sodium (**3**). The black reaction mixture, presumably containing titanocene(II) (**2**), was brought to 25 °C and the LiCl and NaCl solids filtered off. Treating the filtrate with diphenylacetylene (**5**), however, produced no trace of 1,1-bis(cyclopentadieny)-l-2,3,4,5-tetraphenyltitanacyclopentadiene (**6**). This conclusion was reached after protolysis of the reaction mixture with acetic acid was shown to produce no (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**8**) (Scheme 3), the expected protolysis product that would have arisen from **6**, which would have formed by the trapping of **2** by diphenylacetylene (**5**) (path a, Scheme 2). That on the other hand *cis*-stilbene (**10**) was isolated as the sole protolysis product is consistent with the view that any **2** formed from **1b** and **3** had undergone the known rearrangement to **9** before it could be intercepted by **5**.[7b] The resultant **9** could then have hydrotitanated acetylene **5** and hence have generated *cis*-olefin **10**, upon protolysis.

In our further attempt to intercept any titanocene(II) (**2**) formed from **1b** and **2**, we repeated the reaction between **1b** and **2** at 0 °C, brought the reaction mixture to 25 °C, but this time immediately added the diphenylacetylene (**5**) *without attempting to filter off the suspended LiCl and NaCl.* A nonhydrolytic workup involving removal of any solids from the hexane extracts of the final reaction mixture led, via epititanation to titanacyclopropene **5a**,[14] to the isolation of **6** in 83% yield. Its identity was confirmed by ^{1}H NMR and IR spectral comparisons with an authentic sample of **6** prepared according to a previously outlined method,[21] whose details are published here for the first time [Equation (3)]. Furthermore, the sample of **6** isolated from **1b** and **2** was smoothly protolyzed to yield solely **8** in high yield (Scheme 3).



(3)

The success of this present procedure for generating **2** from **1b** and **3** and in trapping titanocene(II) (**2**) before it could rearrange to **9** we ascribe to two factors: 1) the shorter time the THF solution of **2** stood at 25 °C before acetylene **5** was introduced; and 2) the presence of LiCl and NaCl, which furnish an ample source of Lewis basic chloride ions, capable of coordinating with monomeric Cp_2Ti and thereby retarding its rearrangement to **7** [Equation (4)]. A relevant precedent is the complex **12** formed from **1a** and NaCl as shown in Equation (5).[22]

$$Cp_2Ti + 2\,NaCl \rightleftarrows 2\,Na^+\ [TiCp_2Cl_2]^{2-} \qquad (4)$$

$$\underset{\textbf{1a}}{TiCl_2} + 2\,NaCl \rightleftarrows \underset{\textbf{12}}{2\,Na^+\ [TiCl_4]^{2-}} \qquad (5)$$

Conclusions

From the foregoing experiments we have now shown that the transient titanocene(II) can also be prepared by the classic method introduced by the Wilkinson group some 50 years ago. Its existence, although short, has been firmly established by its chemical trapping with diphenylacetylene as the titanacyclopentadiene **6**.[23]

Experimental Section

Starting Materials, Reaction Conditions and Instrumentation: The starting $TiCl_4$ employed was of at least 98% purity as commercially available and the *n*-butyllithium used was as a 1.60 M solution in hexane. The cyclopentadiene was obtained from the thermolysis of commercial dicyclopentadiene under argon and collected in an ice bath. The sample for the preparation of cyclopentadienylsodium resulted from a redistillation of the monomer just before use.[24] The titanium(II) chloride in THF, containing 2 equiv. of the by-product, LiCl, was obtained from the treatment of $TiCl_4$ in THF with 2 equiv. of *n*-butyllithium at low temperatures according to the published procedure.[20] In the same reference are given experimental details for removing LiCl from the product and obtaining analytically pure $TiCl_2$·THF.[20] However, for its reaction here with cyclopentadienylsodium, the titanium(II) chloride/lithium chloride mixture was used directly. Finally, the diphenylacetylene used in trapping reactions was 99% pure and was shown by TLC and ^{1}H NMR spectroscopy to be free of *cis*- or *trans*-stilbene. All reactions, transfers and separations were carried out under a positive pressure of anhydrous, oxygen-free argon.[25] All solvents employed, mainly tetrahydrofuran, heptane and toluene, with these air- and moisture-sensitive reagents were dried and distilled from a sodium metal benzophenone ketyl mixture prior to use.[25]

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker spectrometer, model AM-360, with tetramethylsilane (Me_4Si) as the internal standard. The chemical shifts reported are expressed on the δ-scale in parts per million (ppm) from the Me_4Si reference signal.

1,1-Bis(cyclopentadienyl)-2,3,4,5-tetraphenyltitanacyclopentadiene (6): Although an authentic sample of this known compound can be prepared by a number of previous published methods,[12,15] a method developed in our laboratory proved most convenient,[21] because its starting material, **11** is available through a verified experimental procedure.[26,27] A 100-mL quartz phototube, having ground-glass joints at the upper end for attachment to the argon source and for a rubber septum, respectively, was repeatedly evacuated and filled with argon gas. Then a solution of η^3-allylbis(cyclopentadienyl)titanium(III) (365 mg, 1.67 mmol) prepared under argon in anhydrous, deoxygenated cyclohexane (25 mL) was introduced into the tube through the septum, after which a similarly prepared solution of diphenylacetylene (594 mg, 3.34 mmol) in 10 mL of purified cyclohexane was introduced. The reaction solution was irradiated for 48 h in a Rayonet photochemical reactor, model 100, equipped with a cylindrical array of phototubes emitting radiation at 254 nm. The cylindrical cavity of the lamp bank had a diameter of 24 cm. During this time the initial purple color of the reaction mixture became greenish-yellow. The cyclohexane was removed from the photolysate under reduced pressure and the dark green residue was extracted under argon with 3 × 10-mL portions of hexane. Such combined extracts were filtered and then concentrated. Storage of the hexane solution at 0 °C led to the deposition of between 339 mg to 491 mg of dark green **6** (38–55%) in two different runs; m.p. (capillary under argon) 148.5–150 °C [lit. 150 °C];[17] ^{1}H NMR (C_6D_6): δ = 6.06(s, 10 H), 6.4–6.9 (m, 20 H) ppm. IR (KBr): $\tilde{\nu}$ = 697 cm^{-1} (vs), 725 (m), 750 (m), 770 (s), 780 (m), 800 (vs), 807 (vs), 830 (sh), 840 (w), 905 (vw), 945 (vw), 1015 (s), 1075 (s), 1095 (sh), 1145 (sh), 1155 (w), 1180 (w), 1245 (w), 1260 (w), 1362 (w), 1370 (sh), 1440 (s), 1480 (s), 1590 (s), 3040 (w), 3060 (w), 3080 (w) cm^{-1}.

Interaction of Bis(cyclopentadienyl)sodium (3) with Titanium(II) Chloride–Bis(tetrahydrofuran) (1b) in Tetrahydrofuran

1) Reaction at 0 °C, Removal of Alkali Metal Salts by Filtration and Reaction of the Titanocene Filtrate with Diphenylacetylene (5): A solution of titanium(IV) chloride (1.90 g, 10 mmol) in toluene (10 mL) was added to dry THF (60 mL) and the mixture cooled to –78 °C to yield a yellow suspension. Then *n*-butyllithium (20 mmol) in hexane (2.50 M) was introduced into the yellow slurry dropwise. Allowing this reaction mixture to come to 25 °C over 1 h produced a black slurry of $TiCl_2$·THF (**1b**) in solution with suspended LiCl by-product, as has been established by a published procedure.[22] Then an orange solution of the cyclopentadienylsodium **3** (22 mmol), previously prepared from sodium metal dispersion (0.51 g, 22 mmol) and freshly distilled cyclopentadiene (1.50 g, 23 mmol) in THF (50 mL) was added rapidly to the solution of **1b** maintained at 0 °C. The resulting reaction mixture was allowed to stand at 25 °C for 2 h before the suspended salts (LiCl and NaCl) were filtered off on a glass frit under argon. The filtration step required about 90 min. The green-black filtrate was then treated with a solution of diphenylacetylene (**5**) (3.56 g, 20 mmol) in THF (40 mL). This final mixture was allowed to stand at room temp. for 10 h and then heated at reflux for 6 h. Treatment of an aliquot of the reaction mixture with glacial acetic acid and usual hydrolytic workup of the dried organic extract showed that 35% of the diphenylacetylene initially introduced had been converted into *cis*-stilbene (**10**) (7.0 mmol.). Equally noteworthy was the absence of any (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**8**), the protolysis product expected to arise if any **6** had been formed from the reaction of the titanocene(II) **2** with the added diphenylacetylene.

2) Reaction at 25 °C, Followed by the Immediate Addition of Diphenylacetylene (5) without the Removal of Alkali Metal Salts: Parallel to the foregoing procedure, a freshly prepared black slurry of $TiCl_2$·THF (**1b**, 10 mmol) and LiCl (20 mmol) in THF (60 mL) was treated dropwise at 0 °C with **3** (22 mmol) in THF (50 mL). The resulting mixture was allowed to stand for 2 h at 20–25 °C, after which time a solution of diphenylacetylene (**5**) (3.56 g, 20 mmol) in THF (40 mL) was added rapidly. The final reaction mixture was kept at room temp. for 10 h and then heated at reflux for 6 h. After removal of all volatiles under reduced pressure the residue was extracted with 4 × 15-mL portions of warm hexane, the combined extracts filtered and the filtrate concentrated to about half its volume. Storage of the hexane solution at 0 °C deposited 4.27 g (83%) of dark green crystals of **6**, m.p. 148–150 °C, whose ^{1}H NMR (C_6D_6) and IR (KBr) spectra were identical with those of the authentic sample. Treatment of a sample of such a product with hot glacial acetic acid, followed by the usual hydrolytic workup, afforded pure (*E*,*E*)-1,2,34-tetraphenyl-1,3-butadiene (**8**), m.p. 181–183 °C, as the only nonvolatile organic product. ^{1}H NMR ($CDCl_3$): δ = 6.40 (s, 2 H), 6.98–7.38 (m, 20). When the protolysis of **6** was repeated with glacial *O*-deuterioacetic acid (99%), the resulting **8** lacked the ^{1}H NMR singlet at δ = 6.40 ppm, showing that this sample of **8** was deuteriated at the C^1 and C^4 sites.

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