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Methane Elimination and Formation of Titanacycles: High Regioselectivity in Intramolecular C–H Activation Reactions of Titanocene Complexes

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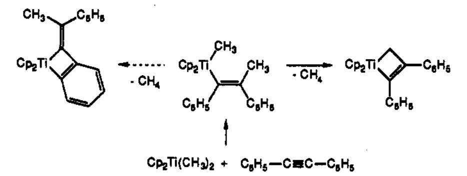
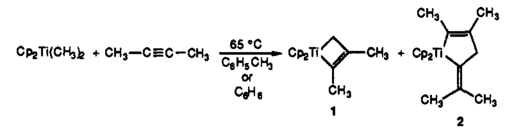
We recently reported the carbometalation of diphenylacetylene by dimethyltitanocene and the subsequent formation of diphenyltitanacyclobutene through an apparent methane elimination reaction of the resulting titanocene methyl vinyl complex.[1,2] The methane elimination reaction appears to be highly regioselective, affording high yields of the titanacyclobutene, even though the intermediate vinyl complex could conceivably have undergone an alternative methane elimination reaction (eq 1).[3] We now report highly regioselective methane elimination reactions from related vinyl titanocene complexes in which titanacyclobutene formation is disfavored relative to the formation of isomeric methane elimination products.



(1)

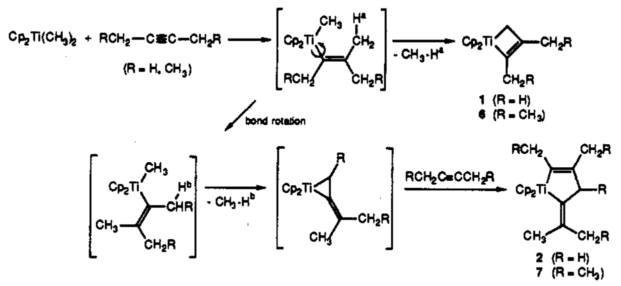
Treatment of a 0.288 mM solution of dimethyltitanocene[4] in perdeuteriobenzene with 1 equiv of 2-butyne at 65 °C affords the known dimethyltitanacyclobutene[5] **1** in ca. 15–20% yield, together with a second product (**2**) which incorporates an additional equivalent of 2-butyne (eq 2). Appreciable polymerization of 2-butyne is also observed. Under these conditions, some dimethyltitanocene remains unreacted. When the reaction is conducted in the presence of 2 equiv of 2-butyne, formation of titanacyclobutene **1** is reduced to less than 2%, and complex **2** may be isolated in near-quantitative yield. Lower reaction temperatures also appear to favor formation of complex **2**.



(2)

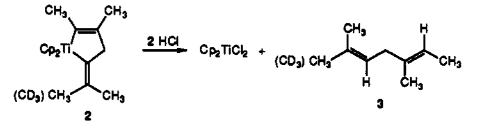
Titanacycle **2** was characterized by ^{1}H and ^{13}C NMR spectroscopy, low- and high-resolution mass spectroscopy, and elemental analysis. Most significantly, the ^{13}C NMR spectrum of **2** displays two resonances in the region of 180–195 ppm, a region which, through extensive studies of titanocene derivatives, we have determined to indicate the presence of vinylic carbons attached to titanium (i.e., of a Ti—*C*=C group).[6] This observation unambiguously identified complex **2** as containing two inequivalent such Ti—C=C groups, thereby immediately ruling out any more symmetrical structures. Other possible alternative structures for **2** were similarly ruled out by ^{1}H and/or ^{13}C NMR spectroscopy.

Scheme 1



The reaction of Cp$_2$Ti(CD$_3$)$_2$ with 2-butyne affords complex **2**-*d*$_3$, which displays only three methyl resonances in its ^{1}H NMR spectrum. All other resonances for **2**-*d*$_3$, in both the ^{1}H and the ^{13}C NMR spectra, are virtually identical to those in undeuterated **2**, with the exception of the carbon resonance for the CD$_3$ group in **2**-*d*$_3$, which is not observed.[7] This result suggests that formation of **2** does not involve a titanocene methylidene intermediate (i.e., Cp$_2$Ti=CD$_2$), as neither a CD$_2$ group nor a CD$_2$H group (which could conceivably arise from a CD$_2$-containing intermediate) is found in **2**-*d*$_3$.

Titanacycle **2** was also characterized by identification of the organic fragment resulting from its protonolysis with dry HCl (eq 3). The so-derived product, **3**, was separated from Cp$_2$TiCl$_2$ by vacuum transfer and identified by ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry. Protonolysis of the deuterated titanacycle, **2**-*d*$_3$, afforded the anticipated diene, displaying ^{1}H and ^{13}C NMR spectral properties completely consistent with the anticipated location of the CD$_3$ group. As in the case of the protio derivative, the protonolysis of **2**-*d*$_3$ was a very clean reaction, with only one volatile product obtained.



(3)

By analogy with the reactivity of diphenylacetylene with dimethyltitanocene,[1] the 2-butyne reaction may be presumed to occur via initial insertion of 2-butyne into a Ti–CH$_3$ bond to yield a methyl 1-propenyltitanocene derivative (Scheme 1, R = H). Methane elimination from this intermediate, which has not proved observable, can occur from either of two allylic sites. While elimination from the methyl group cis to the titanocene fragment (path a) would yield the titanacyclobutene, elimination from the α-methyl group (path b), made accessible by rotation about the Ti–C(vinyl) bond, would yield a titanacyclopropane which, upon insertion of a second equivalent of alkyne, would afford titanacyclopentene **2**. The available data do not rule out the possibility that the titanacyclobutene may also be formed through initial

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(1) Doxsee, K. M.; Juliette, J. J. J.; Mouser, J. K. M.; Zientara, K. *Organometallics* **1993**, *12*, 4682–4686.

(2) Related alkane elimination reactions are well-precedented for the formation of a variety of metallacyclic complexes. For a comprehensive review of alkyne and aryne complexes of zirconocene, together with leading references, see: Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058. Also see: Juliette, J. J. J. Ph.D. Dissertation, University of Oregon, Eugene, OR, 1993.

(3) We have very recently obtained preliminary evidence that, at higher temperatures, the diphenylacetylene reaction may in fact provide a low yield of the benzotitanacyclobutene (eq 1) in addition to the titanacyclobutene: Wood, N.; Doxsee, K. M., unpublished results.

(4) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104–124. Clauss, K.; Bestian, H. *Liebigs Ann. Chem.* **1962**, *654*, 8–19.

(5) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149–6151. Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.

(6) Mouser, J. K. M. Ph.D. Dissertation, University of Southern California, Los Angeles, CA, 1991.

(7) The absence of resonances for perdeuterated methyl groups is well-precedented and is attributed to spin–spin splitting, quadrupolar broadening, and a diminished nuclear Overhauser effect from deuterium, all leading to a significant reduction in signal intensity: Reich, H. J.; Jautelat, M.; Messe, M. T.; Weigert, J. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 7445–7454. Bhacca, N. S.; Giannini, D. D.; Jankowski, W. S.; Wolff, M. E. *J. Am. Chem. Soc.* **1973**, *95*, 8421–8426. Eggert, H.; Djerassi, C. *J. Org. Chem.* **1973**, *38*, 3788–3792.

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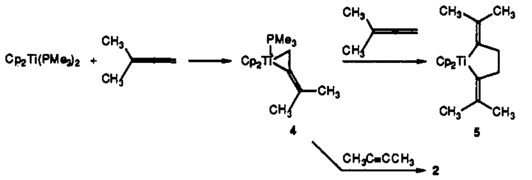
formation of $Cp_2Ti{=}CH_2$ via the thermal decomposition of dimethyltitanocene,[8] followed by addition of alkyne to this reactive intermediate.[9]

The transient titanacyclopropane represents an allene complex of titanocene.[10] Consistent with this, as the reaction progresses (>80% consumption of dimethyltitanocene, 0.29 mM in C_6D_6 at 63 °C) a singlet is observed in the ^1H NMR spectrum at 4.71 ppm. This appears to correspond to a low-valent titanocene species on the basis of its similarity to the chemical shifts of the cyclopentadienyl resonances in other low-valent titanocene complexes, including $Cp_2Ti(CO)_2$ (4.58 ppm/C_6D_6)[11] and $Cp_2Ti(PMe_3)_2$ (4.51 ppm/C_7D_8).[12] This resonance disappears upon completion of the reaction and may correspond to the intermediate titanocene allene complex.

Although our attempts to trap the allene complex from the reaction mixture as its trimethylphosphine adduct were unsuccessful, we have independently prepared this trimethylphosphine adduct (**4**) through the addition of 1 equiv of 3-methyl-1,2-butadiene to $Cp_2Ti(PMe_3)_2$ in dry benzene (eq 4). Complex **4**, which appears to be the first reported allene complex of titanium,[13] may be isolated in analytically pure form by removal of solvent in vacuo at 0 °C.[14] Removal of solvent in vacuo at room temperature results in partial formation of a complex incorporating 2 equiv of the allene; use of an excess of the allene permits the synthesis of this coupling product (**5**) in pure form. Significantly, allene complex **4** reacts readily with 2-butyne to afford complex **2**, lending credence for the proposed mechanism of formation of **2**.



(4)

The reaction of dimethyltitanocene with 3-hexyne again appears to proceed via an intermediate vinyl complex formed through carbometalation of the alkyne, followed by competitive methane elimination reactions, affording either the titanacyclobutene **6** or the allene complex. The latter reacts with a second equivalent of 3-hexyne to afford a titanacyclopentene (**7**, Scheme 1, R = CH_3) analogous to complex **2**. Higher reaction temperatures favor formation of the titanacyclobutene **6**, with formation of **7** essentially completely suppressed at 100 °C, and we have previously reported isolation of titanacyclobutene **6** in good yield from reactions conducted at higher temperatures.[1] (Again, an alternative mechanism for the formation of the titanacyclobutene involving initial formation of $Cp_2Ti{=}CH_2$ via the thermal decomposition of dimethyltitanocene, followed by addition of alkyne to this reactive intermediate, cannot be ruled out.) The temperature dependence of the reaction appears rather profound, and complex **7** is favored over **6** by a factor of ca. 1.4 when the reaction is conducted at 60 °C.

We are continuing to examine the preparation and methane elimination reactions of titanocene vinyl complexes presenting the possibility of formation of regioisomeric products and will report the results of synthetic and kinetic studies in due course.

Acknowledgment. This work was supported by the National Institutes of Health, Institute of General Medical Sciences (GM39494). Support from the U.S. Department of Education Graduate Assistance in Areas of National Need program for J.J. and G.N. is gratefully acknowledged.

Supplementary Material Available: Experimental details, compound characterizations, and ^1H and ^{13}C NMR spectra of allene complex **4** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(8) Erskine, G. J.; Hartgerink, J.; Weinberg, E. L.; McCowan, J. D. *J. Organomet. Chem.* **1979**, *170*, 51–61. Razuvaev, G. A.; Mar'in, V. P.; Andrianov, Yu. A. *J. Organomet. Chem.* **1979**, *174*, 67–75 and references therein.

(9) Kinetic evidence recently reported in support of this mechanism for the reaction of dimethyltitanocene with diphenylacetylene (Petasis, N. A.; Fu, D.-K. *Organometallics* **1993**, *12*, 3776–3780) is also in accord with a mechanism involving alkyne carbometalation followed by rate-determining methane elimination.

(10) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71-C79. Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939–2947.

(11) Sikora, D. J.; Macomber, D. W.; Rausch, M. D. *Adv. Organomet. Chem.* **1986**, *25*, 317–379.

(12) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 694–696.

(13) Jones very recently reported formation of cyclic allene complexes of zirconocene, apparently the first group 4 allene complexes to appear in the literature, via related alkane elimination reactions of vinyl complexes: Yin, J.; Abboud, K. A.; Jones, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 3810–3811.

(14) To a stirred solution of $Cp_2Ti(PMe_3)_2$ (0.100 g, 0.303 mmol) in 2 mL of C_6D_6 were added 30 μL of 3-methyl-1,2-butadiene (1.0 equiv) and 100 μL of PMe_3. The mixture was stirred at room temperature for 1 h and then frozen in a −5 °C bath. Volatiles were removed from the frozen sample in vacuo, yielding complex **4** in analytically pure form as a greenish-brown solid (0.079 g, 81%), mp 120 °C. ^1H NMR (C_6D_6): δ 4.82 (s, 10H, Cp), 2.41 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 0.83 (br s, 9H, PMe_3), 0.29 (br s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 172.0 ($={C}{=}CH_2$), 118.5 [$(CH_3)_2{C}{=}C$], 113.7 ($C{=}{C}H_2$), 99.6 (Cp), 29.7 (CH_3), 24.2 (CH_3), 7.2 (PMe_3). ^{13}C NMR (C_6D_6): δ 172.0 (s), 118.5 (s), 113.7 (m), 99.6 (d, $^1J_{CH}$ = 174 Hz), 29.7 (q, $^1J_{CH}$ = 127 Hz), 24.2 (q, $^1J_{CH}$ = 123 Hz), 7.2 (m, J_{app} = 150 Hz). Anal. Calcd for $C_{18}H_{27}PTi$: C, 67.08; H, 8.44; P, 9.61. Found: C, 67.12; H, 8.33; P, 9.50.