Metallacyclobutene–Metallabutadiene (Vinylcarbene Complex) Interconversions: Ring Opening of Titanacyclobutenes

Kenneth M. Doxsee,* Jerrick J. J. Juliette, John K. M. Mouser, and Kenneth Zientara

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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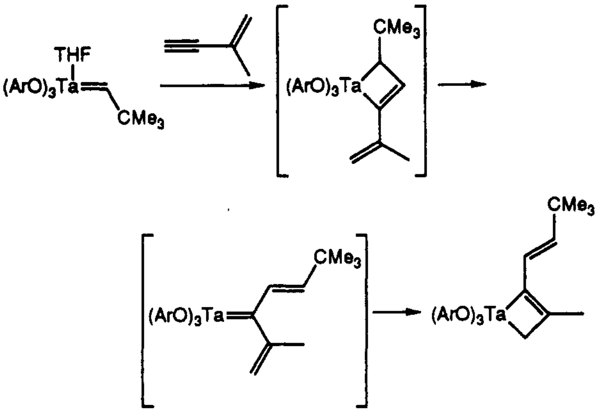
Summary: Preparation of titanacyclobutenes bearing vinyl substituents on the α-position of the metallacyclobutene ring is reported. Ring opening of such titanacyclobutenes is anticipated to afford divinylcarbene complexes (or their biradical analogs); reclosure of the titanacyclobutene ring then can result in either regeneration of the starting complex or in the formation of an isomeric titanacyclobutene. Experimentally, the instantaneous isomerization observed is consistent with rapid, reversible ring opening.

Interconversion of metallacyclobutenes and vinylcarbene complexes (1-metallabutadienes, eq 1) has been proposed as a key mechanistic step in a number of important transition metal complex mediated transformations, including the polymerization of alkynes[1] and the synthesis of complex organic molecules via the coupling of alkynes with Fischer-type carbene complexes (the so-called Dötz reaction).[2]

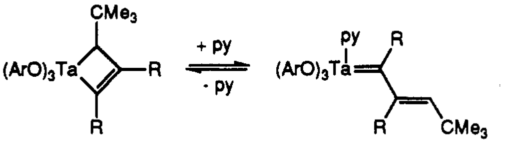
(1)

Despite the perhaps pivotal role played by this interconversion, comparatively little experimental information is available to address it. Schrock has rationalized the formation of a tantalum metallacyclobutene of unexpected structure on the basis of such an interconversion (eq 2)[3,4] and has additionally reported isolation of a metallacyclobutene and its corresponding vinylcarbene complex (eq 3).[4]

Even in these cases, however, some ambiguity remains; theoretical studies suggest that these may in fact be η^3-vinylcarbene–η^1-vinylcarbene rather than metallacyclobutene–η^1-vinylcarbene rearrangements.[5] Analogous theoretical studies have also suggested that the Dötz reaction does not proceed via metallacyclobutene intermediates but rather through η^3-vinylcarbene complexes.[6]



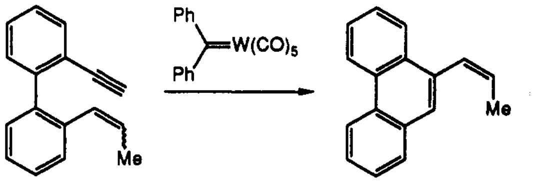
(2)



(3)

R = Me, Ph; py = pyridine; ArO = 2,6-i-Pr_2-C_6H_3-O

Perhaps the most convincing example of metallacyclobutene–vinylcarbene interconversion is that provided by Katz (eq 4),[7] although as in the case of the Dötz reaction there would appear to be some uncertainty about whether a true metallacyclobutene serves as an intermediate here as well.



(4)

We have focused our attention on the potential ring opening of titanocene-based metallacyclobutenes,[8] complexes which are demonstrated both by theory[9] and by X-ray diffraction crystallography[10] to be discrete metallacyclobutenes, rather than η^3-vinylcarbene complexes. Binger has reported the synthesis of vinylcarbene complexes of titanocene (eq 5), compounds which could formally result from the ring opening of the corresponding metallacyclobutene, from the reaction of the titanocene

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[1] See, e.g.: Han, C.-C.; Katz, T. J. *Organometallics* 1985, *4,* 2186–2195.

[2] See, e.g.: Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* 1987, *334,* 9–56. Dötz, K. H. *Pure Appl. Chem.* 1983, *55,* 1689–1706 and references therein. Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* 1984, *106,* 5363–5364.

[3] Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* 1979, *101,* 3210–3220. See also: Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* 1979, *101,* 7282–7292.

[4] Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* 1989, *8,* 644–654.

[5] Hofmann, P.; Hämmerle, M.; Unfried, G. *New J. Chem.* 1991, *15,* 769–789.

[6] Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* 1989, *27,* 908–910.

[7] Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* 1985, *107,* 737–738.

[8] Doxsee, K. M.; Farahi, J. B.; Mouser, J. K. M. *Synlett* 1992, 13–21.

[9] Eisenstein, O.; Hoffmann, R.; Rossi, A. *J. Am. Chem. Soc.* 1981, *103,* 5582–5584. McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* 1981, *103,* 5584–5586. Erker, G. *Acc. Chem. Res.* 1984, *17,* 103–109.

[10] Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* 1980, *102,* 6151–6153.

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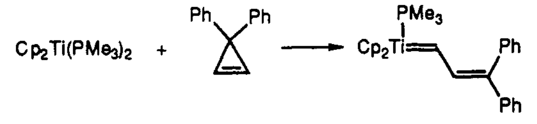
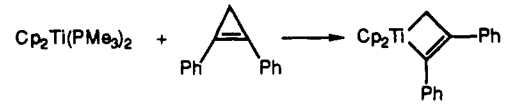
bis(trimethylphosphine) complex with 3,3-disubstituted cyclopropenes.[11] A titanacyclobutene was formed in an analogous reaction with 1,2-diphenylcyclopropene (eq 6),[12] lending credence to the intermediacy of titanacyclobutenes in eq 5.

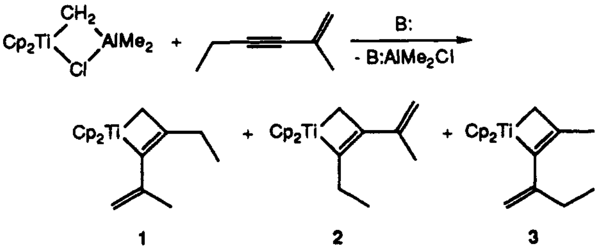


(5)



(6)

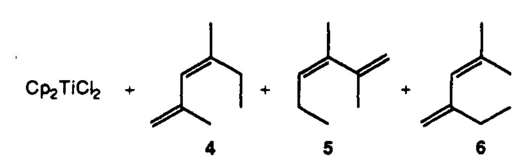
Schrock's isomerization reaction (eq 2) suggested the use of an α-vinyl substituent as a probe for the ring opening of titanacyclobutenes. Ring opening of such a titanacyclobutene would afford a divinylcarbene complex, which could then either re-form the starting metallacyclobutene or close to form the isomeric metallacyclobutene. Treatment of $Cp_2Ti{=}CH_2{\cdot}AlMe_2Cl$ ("Tebbe's reagent")[13] or 3-*tert*-butyl-1-titanacyclobutane[14] with 1 equiv of 2-methyl-1-hexen-3-yne and 1 equiv of triethylamine, pyridine, or 4-(dimethylamino)pyridine (to sequester the Me_2AlCl byproduct) produced an inseparable mixture of three titanacyclobutenes (eq 7).[15] Careful analysis of both ^1H and ^{13}C NMR spectra, aided by relative integrals and by 2D COSY studies, permitted unambiguous structural assignments for the three isomeric metallacycles.[16]



(7)

B = Et$_3$N, pyridine, 4-(dimethylamino)pyridine

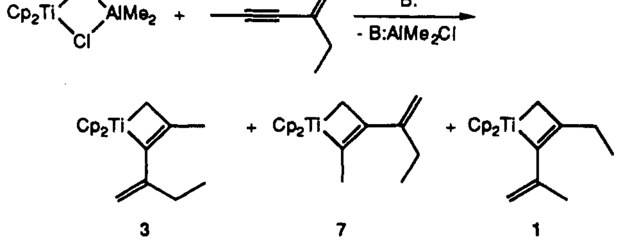
The generally poor regioselectivity[17] in the addition of unsymmetrical alkynes to sources of $[Cp_2Ti{=}CH_2]$ is mirrored in the formation of regioisomeric products 1 and 2. Complex 3 represents the anticipated rearrangement product (vide infra). Confirmation of these structures was obtained through protonolysis of the mixture of metallacycles, using either dry HCl or CH_3CO_2H, yielding a mixture of substituted butadienes (eq 8). GC analysis



(8)

revealed three major components. Diene 6, resulting from protonolysis of rearranged metallacycle 3, was independently synthesized and displays gas chromatographic retention times on two different packed columns, high-resolution mass spectral fragmentation data, and ^1H and ^{13}C NMR spectral properties identical with those of one of the dienes obtained from the acidolysis of the mixture of 1, 2, and 3.

Additional verification of the structure of 3 was obtained through its independent generation from the appropriate isomeric enyne (eq 9). Again, a mixture of three isomeric



(9)

B = Et$_3$N, pyridine, 4-(dimethylamino)pyridine

metallacyclic products was obtained, containing the anticipated regioisomeric metallacycles 3 and 7 together with the rearranged metallacycle 1.[18] Importantly, as in eq 7, the three isomers were obtained essentially upon time of mixing at room temperature. Thus, isomerization appears to be an exceptionally facile process. The roughly equivalent ratios of 1 and 3 obtained from both isomeric enynes suggests that equilibrium between the two isomers is readily established.

Formation of the rearranged metallacycles can be rationalized on the basis of metallacyclobutene–vinylcar-

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(11) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *27*, 610–611.

(12) Binger, P.; Müller, P.; Herrmann, A. T.; Philipps, P.; Gabor, B.; Langhauser, F.; Kruger, C. *Chem. Ber.* **1991**, *124*, 2165–2170. Binger, P.; Müller, P.; Langhauser, F.; Sandmeyer, F.; Philipps, P.; Gabor, B.; Mynott, R. *Chem. Ber.* **1993**, *126*, 1541–1550.

(13) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.

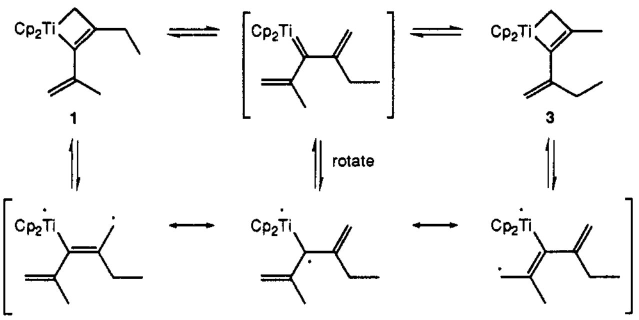
(14) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358–7361.

(15) Under an atmosphere of dry nitrogen, a side-arm round-bottom flask was charged with β-*tert*-butyltitanacyclobutane (169 mg, 0.612 mmol) and benzene (10 mL). To this solution was added 2-methyl-1-hexen-3-yne (76 μL, 1 equiv) via syringe. The mixture was stirred at ambient temperature (ca. 15 °C) for 12 h and then brought to dryness *in vacuo*, affording an inseparable mixture of isomeric metallacycles 1, 2, and 3 as a red solid in quantitative yield. Anal. Calcd for $C_{18}H_{22}Ti$: C, 75.52; H, 7.75. Found: C, 75.49; H, 7.78. HRMS: calcd. for $C_{18}H_{22}Ti$ 286.1201, found 286.1199. Titanacycle 1: ^1H NMR (C_6D_6) δ 5.56 (s, 10H, Cp), 4.99 (s, 1H, $=CH$), 4.34 (s, 1H, $=CH$), 3.28 (s, 2H, $Ti{-}CH_2$), 2.26 (q, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3), 1.81 (s, 3H, $=CCH_3$), 1.04 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 213.4 ($Ti{-}C{=}C$), 149.7 ($C{=}CH_2$), 111.0 (Cp), 104.6 ($C{=}CH_2$), 94.4 ($Ti{-}C{=}C$), 76.9 ($Ti{-}CH_2$), 24.3 ($=CCH_3$), 23.8 (CH_2CH_3), 13.4 (CH_2CH_3). Titanacycle 2: ^1H NMR (C_6D_6) δ 5.55 (s, 10H, Cp), 4.67 (s, 1H, $=CH$), 4.61 (s, 1H, $=CH$), 3.34 (s, 2H, $Ti{-}CH_2$), 2.68 (q, 2H, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3), 1.78 (s, 3H, $=CCH_3$), 0.69 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 221.6 ($Ti{-}C{=}C$), 156.6 ($C{=}CH_2$), 110.6 (Cp), 109.2 ($C{=}CH_2$), 94.5 ($Ti{-}C{=}C$), 77.2 ($Ti{-}CH_2$), 30.8 (CH_2CH_3), 22.7 ($=CCH_3$), 16.1 (CH_2CH_3). Titanacycle 3: ^1H NMR (C_6D_6) δ 5.56 (s, 10H, Cp), 4.70 (s, 1H, $=CH$), 4.67 (s, 1H, $=CH$), 3.28 (s, 2H, $Ti{-}CH_2$), 2.10 (q, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3), 1.64 (s, 3H, $=CCH_3$), 0.86 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 213.2 ($Ti{-}C{=}C$), 150.6 ($C{=}CH_2$), 111.1 (Cp), 102.6 ($C{=}CH_2$), 91.2 ($Ti{-}C{=}C$), 81.2 ($Ti{-}CH_2$), 30.2 (CH_2CH_3), 16.7 ($=CCH_3$), 13.3 (CH_2CH_3).

(16) A discussion of key spectral features aiding in these structural assignments is provided in the supplementary material.

(17) Meinhart, J. D. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1987.

bene rearrangement, followed by formation of the isomeric metallacyclobutene through ring closure involving the alternate vinyl group in the divinyl intermediate (eq 10). Alternately, the rearrangement may occur via a biradical intermediate, which essentially represents a divinylcarbene complex in which the Ti═C bond is twisted 90° from the angle required for formation of the π bond (eq 10).[19] We are continuing to study the generality and energetics of this rearrangement.[20]



(10)

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Supplementary Material Available: Text giving experimental details and compound characterization data (7 pages). Ordering information is given on any current masthead page.

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(18) Under an atmosphere of dry nitrogen, a side-arm round-bottom flask was charged with β-*tert*-butyltitanacyclobutane (180 mg, 0.65 mmol) and benzene (10 mL). To this solution was added 2-ethyl-1-penten-3-yne (1.7 mL of a 0.4 mM solution in C_6D_6, 1 equiv) via syringe. The mixture was stirred at ambient temperature (ca. 15 °C) for 36 h and then brought to dryness *in vacuo*, affording an inseparable mixture of isomeric metallacycles **1**, **3**, and **7** as a red solid in quantitative yield. Anal. Calcd for $C_{18}H_{22}Ti$: C, 75.52; H, 7.75. Found: C, 75.42; H, 7.86. HRMS: calcd for $C_{18}H_{22}Ti$ 286.1201, found 286.1213. The characterization of metallacycles **1** and **3** is reported above. Titanacycle **7**: ^{1}H NMR (C_6D_6) δ 5.52 (s, 10H, Cp), 4.84 (s, 1H, ═CH), 4.55 (s, 1H, ═CH), 3.24 (q, 2H, $^5J_{HH}$ = 1.2 Hz, Ti—CH_2), 2.23 (br s, 3H, CH_3), 2.1 (m, 2H, CH_2CH_3), 1.0 (m, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 215.2 (Ti—*C*═C), 156.6 (*C*═CH_2), 110.4 (Cp), 109.2 (C═CH_2), 94.2 (Ti—C═*C*), 75.2 (Ti—CH_2), 29.2 (CH_2CH_3), 23.1 (═CCH_3), 13.2 (CH_2CH_3).

(19) A concerted mechanism may also be considered, although the placement of the α-vinyl substituent would not appear to be optimal for such a concerted process.

(20) Preliminary NOESY and magnetization transfer studies of the titanacyclobutene derived from 2-methyl-1-penten-3-yne confirm that it rapidly undergoes the anticipated degenerate rearrangement.