Radical Reactions of Titanium(III) Propargyl Complexes. Titanacyclobutene Formation by Dimerization and by Regioselective Addition of Organic Free Radicals

Sensuke Ogoshi*,† and Jeffrey M. Stryker*

Department of Chemistry, University of Alberta
Edmonton, Alberta T6G 2G2 Canada

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Although many fundamental aspects of propargyl and allenyl transition-metal chemistry remain poorly understood, the synthetic potential and unique reactivity of η^3-propargyl complexes have been the subject of considerable recent attention.[1−3] In view of the recently reported regioselective radical alkylation of titanium(III) η^3-allyl complexes,[4] we considered that the corresponding η^3-propargyl system might be an even more effective radical trap based on the greater overlap of the singly occupied metal $1a_1$-orbital and the Ψ^3-orbital of the propargyl fragment (Figure 1).[5] Here we report the generation of paramagnetic titanium(III) propargyl complexes and a general, convenient, and highly regioselective synthesis of substituted titanacyclobutene complexes[6] by the addition of organic free radicals. In addition, the dimerization of η^3-propargyl titanium complexes has been observed, leading to the formation of structurally interesting 3,3′-bi(titanacyclobutene) complexes linked by a carbon−carbon bond between titanacyclobutene β-carbon atoms.

Initially, the synthesis of the unknown propargyltitanium(III) structural class was attempted by treatment of Cp^*_2TiCl ($Cp^* = \eta^5$-C_5Me_5) with allenyllithium, analogous to previous preparations of alkyltitanium(III) complexes.[7] This reaction, however, provides neither propargyl nor allenyl products, but proceeds instead to give the novel dimeric 3,3′-bi(titanacyclobutene) complex **1** in modest isolated yield (36%).[8−10] Dimeric complex **1** is obtained more conveniently and in higher yield from the reaction of Cp^*_2-TiCl and propargyl bromide in the presence of 2 equiv of SmI_2 (Scheme 1). The compound shows a characteristic titanacyclobutene signal at δ 7.86 for the methine proton[11] and displays a narrow $^4J_{HH}$ coupling to the methylene protons. The complex is too sparingly soluble in compatible solvents to analyze by ^{13}C NMR spectroscopy. In contrast, under identical conditions, the reaction of 1-phenyl-3-bromopropyne provides the titanium(III) η^3-phenylpropargyl complex **2**[8] in quantitative yield (Scheme 1), with no trace of the diamagnetic dimer. The propargyl coordination is assigned on the basis of the strong IR absorption at 1902 cm^{-1}, characteristic of η^3-hapticity.[3d] The corresponding η^3-butynyl complex decomposes at room temperature to uncharacterized paramagnetic material(s).

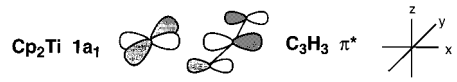
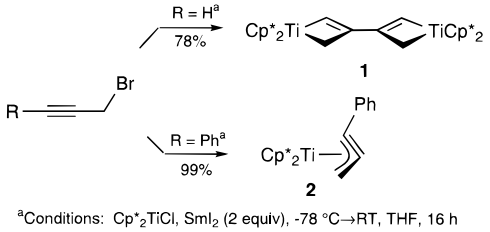


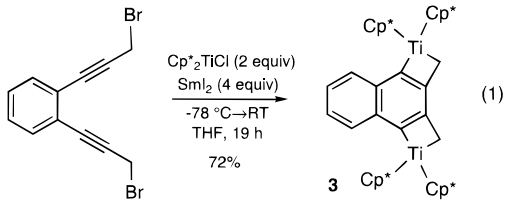
Figure 1.

Scheme 1



[a]Conditions: Cp^*_2TiCl, SmI_2 (2 equiv), -78 °C→RT, THF, 16 h

In part to evaluate this difference in reactivity, 1,2-bis-(3-bromopropynyl)benzene[12] was prepared and subjected to similar conditions, leading to the isolation of the intramolecular coupling product, the structurally intriguing tetracyclic [1,2:3,4-bis(2,2′-titanacyclobuteno)]naphthalene (**3**) (eq 1),[8,13] spectroscopically consistent with simpler metallabenzocyclobutene complexes of titanium and hafnium.[14] Whether this result is attributable to favorable entropic considerations or to the aromaticity of the naphthalene core remains under investigation.



Titanium(III) η^3-propargyl complexes efficiently trap organic free radicals, even in cases where the complexes dimerize or decompose. By adopting SmI_2-mediated radical generation,[4,15] a convenient and general one-pot synthesis of substituted titanacyclobutene complexes has been developed (Table 1).[16] In these reactions, the η^3-propargyl complex is prepared *in situ* by using

† Permanent address: Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan.

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(8) Experimental, spectroscopic, and analytical data are provided as Supporting Information.

(9) Selected spectroscopic data: ^1H NMR (C_6D_6) δ 1.79 (s, 60H), 2.12 (d, J = 1.5 Hz, 4H), 7.86 (t, J = 1.5 Hz, 2H).

(10) Beckhaus has noted a related 3, 3′-bis(α-methylenetitanacyclobutene) structure formed by a complex reaction between $Cp^*_2Ti(CH{=}CH_2)CH_3$ and $(OC)_5Cr{=}C(NR_2)CH_3$. Beckhaus, R.; Oster, J. *J. Organomet. Chem.* In press.

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(13) Selected spectroscopic data: ^1H NMR (C_6D_6) δ 1.69 (s, 60H), 2.79 (s, 4H), 7.36 (m, 4H); ^{13}C NMR (C_6D_6) δ 12.50 (q, J_{CH} = 126.4 Hz), 73.78 (t, J_{CH} = 135.2 Hz), 105.95(s), 118.90 (s), 122.28 (dd, J_{CH} = 156.5, 8.0 Hz), 133.31 (d, J_{CH} = 153.8 Hz), 137.22 (s), 210.20 (s); HRMS calcd for $C_{52}H_{68}Ti_2$ 788.4280, found *m/e* 788.4306.

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Table 1

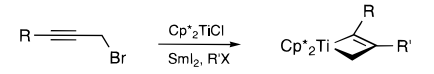
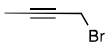
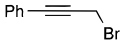


Table I[a] **4-10**

R	R'X	product	yield[b]
H	$PhCH_2Cl$	**4**	94%
CH_3		**5**	99%[c]
CH_3	$PhCH_2Cl$	**6**	99%
CH_3		**7**	99%
Ph		**8**	93%[c]
Ph	$PhCH_2Cl$	**9**	87%[d]
Ph		**10**	99%

[a]Conditions: (i) Cp^*_2TiCl (1 equiv), SmI_2 (3 equiv), THF, -78 °C, 10 m, then (ii) R'X (1 equiv), -78°C→RT, THF, overnight. [b]Isolated yield. [c]Both equivs of the propargyl bromide added at once. [d]Prior to addition of $PhCH_2Cl$, the reaction mixture was warmed to room temperature, then recooled to -78 °C.

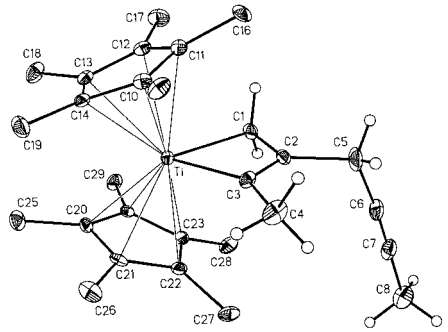
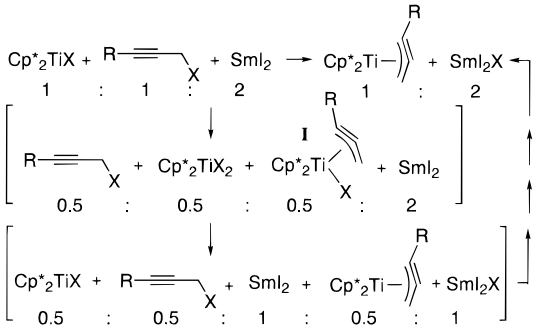
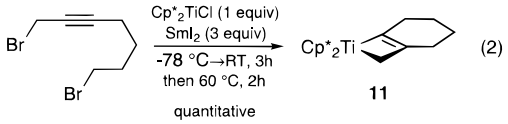


Figure 2.

an excess of SmI_2, followed by the addition of the alkyl halide and warming the reaction mixture. Titanacyclobutene complexes **4**−**10** are formed with complete regioselectivity in near quantitative yields. For the unsubstituted propargyl complex, this procedure is limited to relatively stabilized organic radicals that can be generated at low temperature, below that at which the η^3-propargyl complex undergoes competitive dimerization (ca. ≤−30 °C). For the formation of 3-benzyl-2-phenyltitanacyclobutene (**9**), the reaction mixture was warmed to room temperature and recooled prior to the addition of benzyl chloride, avoiding the formation of a green paramagnetic byproduct (presumably $Cp^*_2TiCH_2Ph$). For confirmation of the spectroscopic assignments, the structure of complex **5** has been determined by X-ray crystallography (Figure 2).[17] Intramolecular alkylation leads to the formation of a bicyclic titanacyclobutene[8] (eq 2), a reaction that suggests the potential for further development of synthetic organic methodology. This cyclization requires a higher temperature to generate the primary radical center, but nonetheless proceeds quantitatively.

Scheme 2





Mechanistically, this reaction can be divided into two stages: (i) generation of the propargyltitanium(III) intermediate and (ii) alkyl radical formation and addition. Preliminary observations suggest that the mechanism of propargyl complex formation proceeds by initial interaction of the propargyl halide with Cp^*_2-TiCl rather than with SmI_2 (Scheme 2). Thus, despite control experiments that demonstrate that SmI_2 reacts with neither propargyl bromide nor Cp^*_2TiCl at low temperature, the addition of propargyl bromide to a solution of Cp^*_2TiCl and SmI_2 at −78 °C leads to a color change from blue to violet, indicating that Cp^*_2TiCl and propargyl bromide react first to form a mixture of the Ti(IV) complexes $Cp^*_2TiX_2$ (X = Cl and/or Br) and **I** (0.5 equiv each). Reduction of both intermediates by SmI_2 must then occur at a slower rate, producing the propargyltitanium(III) complex and regenerating Cp_2*TiX, which then continues to react with the remaining propargyl bromide. In the alkylation stage, the alkyl radical may be generated by direct reaction with SmI_2 or by a cascade similar to the first stage, but mediated by the propargyltitanium(III) intermediate. Both pathways may proceed at competitive rates, with the partitioning dependent on the nature of the alkyl halide.

The generality and complete regioselectivity inherent in this process contrasts with titanium alkylidene/alkyne [2 + 2] cycloaddition,[6] the only alternative methodology for titanacyclobutene synthesis, which fails for terminal alkynes and leads to regioisomeric mixtures for unsymmetrical alkynes.[19] Further investigation of the radical alkylation, the propargyl complex dimerization, and the conversion of the titanacyclobutenes into organic products is in progress.

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Supporting Information Available: Experimental procedures and spectroscopic and analytical data for all new products; details of the X-ray structure determination, tables of atomic coordinates and anisotropic thermal parameters, bond distances, and bond angles for complex **5** (15 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(16) All manipulations were carried out under nitrogen using anhydrous THF. Typical procedure: To a solution of 35.4 mg of Cp^*_2TiCl (0.1 mmol) and 141.5 mg of SmI_2 (0.35 mmol, 3.5 mL of 0.1 M solution in THF) in THF (5 mL) was added 19.5 mg of 3-phenylpropargyl bromide (0.1 mmol) in THF (1 mL) at −78 °C. After 30 min, 17.0 mg of isopropyl iodide (0.1 mmol) in THF (1 mL) was added at −78 °C. The mixture was allowed to warm very slowly to room temperature and stirred for 14 h. The reaction mixture was concentrated *in vacuo*, and the residue was extracted with pentane, filtered through Celite, and concentrated to give titanacyclobutene **10** as a spectroscopically homogeneous dark red oil (47.7 mg, 99%). An analytical sample was prepared by recrystallization from pentane at −30 °C. Partial spectroscopic data:[8] ^{1}H NMR (C_6D_6) δ 1.18 (d, J = 6.7 Hz, 6H), 1.70 (s, 30H), 2.18 (s, 2H), 3.40 (hep, J = 6.7 Hz, 1H), 6.98 (m, 3H), 7.26 (t, J = 7.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 12.26, 23.56, 28.34, 68.54, 116.50, 119.34, 123.47, 128.97, 145.18, 202.30.

(17) The structure is very similar to other crystallographically determined titanacyclobutene complexes.[6,18] Crystal data for **5**:[8] $C_{28}H_{40}Ti$, monoclinic, $P2_1/n$, a = 9.7994(10) Å, b = 19.221(2) Å, c = 12.7802(12) Å, β = 93.581 (6)°, V = 2402.5(4) Å^3, Z = 4 (D_{calc} = 1.174 g/cm^3); $R_1(F)$ = 0.0918 ($F_o^2 \geq 2\sigma(F_o^2)$), $wR_2(F^2)$ = 0.1728 (all data).

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