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Mechanism of Rearrangement of Titanacyclobutanes[†]

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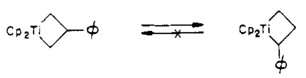
Summary: The rearrangement of β-phenyltitanacyclobutane (I) to α-phenyltitanacyclobutane (II) is shown through labeling experiments to proceed by a stepwise mechanism. Ring opening of I to the metal–methylidene species followed by readdition of styrene affords both complexes I and II.

It is now generally accepted that the olefin metathesis reaction proceeds by a stepwise mechanism with alternating metallacarbene and metallacyclobutane intermediates.[1,2] Earlier studies of the rearrangement of platinum metallacyclobutanes suggested concerted isomerization of α- to β-substituted complexes.[3-5] We previously have reported the isolations of stable titanacyclobutanes from an olefin metathesis system.[6,7] In this paper, we wish to address the mechanism of the isomerization reaction of β-phenyltitanacyclobutane (I) to α-phenyltitanacyclobutane (II) for comparison to the corresponding platinum reactions.

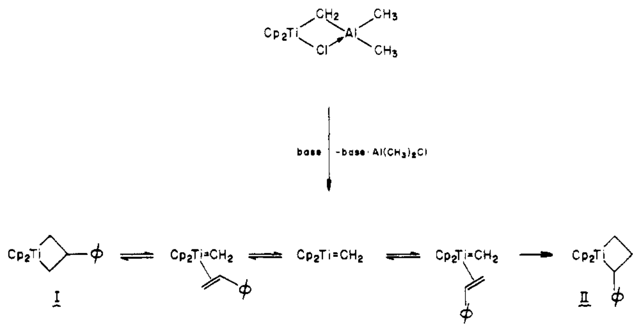
As reported before, the reaction of the "Tebbe" reagent with styrene in toluene solution containing (dimethylamino)pyridine (DMAP) gives a 1:2.5 mixture of the β-isomer I and the α-isomer II,[8] which are easily separated due to their widely different solubilities in toluene[9] (eq 1).

(1)

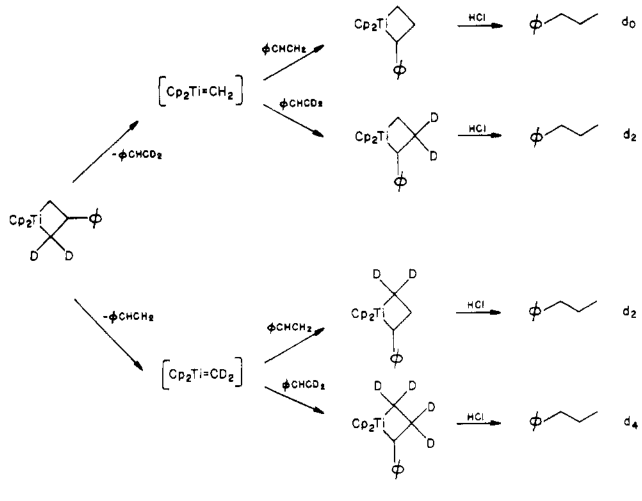


(2)

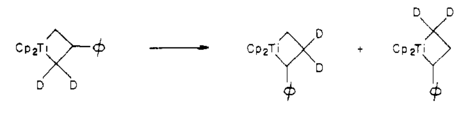
Scheme I



Scheme II



Solutions of complex I in toluene readily isomerize to the α-isomer II at room temperature (eq 2). The α-isomer is unreactive under the isomerization conditions, even with added styrene. The isomerization is characterized by first-order kinetics.[10] By comparison with the results of other titanacyclobutane reactions, the rate-determining step in the isomerization of I is considered to be the ring opening of the titanacyclobutane to the titanium methylidene–olefin complex or the free titanium–carbene species.[6c] The detailed mechanism of the isomerization is further probed by using isotopically labeled I and ^{2}H NMR.[11] I-*2,2*-d_2 isomerizes in toluene at room temperature to give II-*3,3*-d_2 and II-*4,4*-d_2 in a 1.6:1 ratio which is consistent with a secondary deuterium isotope effect[12] (eq 3). Isomerization reaction of I in the presence of



I-2,2-d_2 II-3,3-d_2 II-4,4-d_2 (3)

PhCHCD$_2$ gives II-*3,3*-d_2 as the major product (75%). II-*4,4*-d_2 and I-*2,2*-d_2 are also detected in 9 and 15% yields, respectively (eq 4). Since II-*4,4*-d_2 can only be formed from reactions of I-*2,2*-d_2, the above result indicates that olefin exchange reaction has occurred to give both the α- and β-isomer in a 3:1 ratio. In the absence of free olefins,

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[†] Contribution No. 7092.

[1] Grubbs, R. H. *Prog. Inorg. Chem.* **1979**, *24*, 1. Grubbs, R. H. "Comprehensive Organometallic Chemistry"; 1982; Chapter 54.

[2] Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.

[3] Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Organomet. Chem.* **1976**, *113*, 91.

[4] Al-Essa, R. J.; Puddephatt, R. J.; Thompson, P. J.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1980**, *102*, 7549.

[5] Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

[6] (a) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (b) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358. (c) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *Ibid.* **1982**, *104*, 7491.

[7] Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074.

[8] The ratio of α- to β-isomer is probably a factor of steric rather than electronic, since reactions of methyl- and methoxy-substituted styrenes give similar isomer ratios as styrene.

[9] A 1 M toluene solution of "Tebbe" reagent with 2 equiv of styrene and 2.2 equiv of DMAP was stirred at −10 °C for 1 h. The β-isomer I precipitated as an orange solid and was collected by filtration and washed with cold toluene and pentane. Recrystallization from THF–pentane with slow cooling to −50 °C yielded long needles in 35% yield: ^{1}H NMR (90 MHz, C_6D_6) δ 6.99–7.40 (m, 5 H), 5.52 (s, 5 H), 5.40 (s, 5 H), 2.84 (dd, J = 11, 9 Hz, 2 H), 2.39 (dd, J = 9, 9 Hz, 2 H), 0.33 (m, 1 H). The α-isomer II was obtained from extraction of the reaction residue with *n*-hexane. Concentration of the extract gave the α-isomer as a deep red solid: ^{1}H NMR (90 MHz, C_6D_6) δ 6.71–7.35 (m, 5 H), 5.31 (s, 5 H), 5.08 (s, 5 H), 4.74 (t, J = 9 Hz, 1 H), 3.12 (m, 2 H), 0.24 (m, 2 H).

[10] $k = 3.0 \times 10^{-4}$ s^{-1} at 25 °C. E_a = 25.5 kcal/mol. First-order reaction was observed for at least 2.5 half-lives. Addition of styrene (2–10 equiv) does not affect the rate of isomerization. Other trapping agents such as acetylenes and olefins react more rapidly. For example, cyclopentene yields the corresponding metallacyclobutane with $k = 4.4 \times 10^{-4}$ s^{-1}.

[11] Deuterium-labeled styrenes prepared by known methods were used in the synthesis of labeled I. Labinger, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

[12] The unusual large secondary isotope effect has been addressed in the previous paper.[6c]

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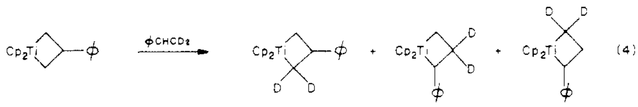
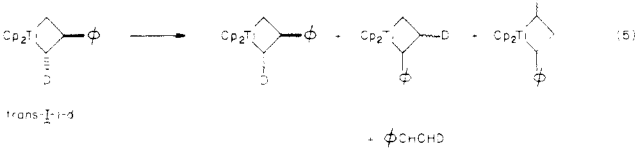


isomerization can occur via carbene or olefin rotation in the metal carbene–olefin complex. High rotation barrier of the carbene rule out the first.[13] To address the olefin rotation possibility, we employed stereospecifically labeled I, since rotation of olefin should define the relative stereochemistry of the α-isomer to be either *trans*-II-*3*-d_1 or *cis*-II-*4*-d_1. Isomerization of *trans*-I-*2*-d_1 in toluene without added styrene, however, gives all possible stereoisomers of II (eq 5). Equal amounts of *cis*- and *trans*-II-*4*-d_1 are present as are the scrambled β-isomers I-*2*-d_1 and styrene-d_1. We therefore rule out olefin rotation as a major isomerization pathway. From the labeling experiments, we conclude that isomerization of I is due to readdition of olefin to the titanium methylene species (Scheme I).



The intermolecular process is further supported by the following observations. A solution of I-*2,2*-d_2 is allowed to equilibrate at room temperature for 1 h before hydrolysis with anhydrous hydrogen chloride. The organic products are analyzed by GC/MS. Isopropylbenzene is mostly d_2 as expected from unreacted I-*2,2*-d_2. The *n*-propylbenzene, from hydrolysis of II, contained molecules containing from d_0 to d_5 deuteria. The ratio of d_0:d_2:d_4 *n*-propylbenzene is approximately 1:2.5:1.1, or that approaching a statistical olefin exchange[14] (Scheme II). The presence of odd-numbered deuterium atoms in the *n*-propylbenzenes is rationalized in terms of reactions involving titanium hydrides or deuterides that are generated from the decomposition of I.[15]

In contrast to the rearrangement of platinacyclobutanes where a concerted mechanism is suggested, titanacyclobutane isomerizations proceed through a metal–carbene intermediate. This result provides an important step for olefin metathesis in the form of olefin exchange reaction. If the α-isomer could then ring-open to give a substituted metal alkyidene[16] such as Cp$_2$Ti═CHPh, a complete metathesis system would then be generated.

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(13) Schrock has estimated the ΔG^* for the rotation of tantalum alkylidene to be 25 kcal mol^{-1}. Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. The calculated torsional barrier for Cp$_2$Ti═CH$_2$ is 52 kcal mol^{-1}. Frand, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1983**, *2*, 815.

(14) In the presence of a large excess of a 1:1 mixture of styrene-d_0 and -d_2, the kinetic ratio of *n*-propylbenzene d_4:d_2:d_0 should be 1:2.6:1.6. However, under the reaction conditions with no added styrene, both the styrene-d_2/d_0 and the carbene-d_2/d_0 are controlled by the isotope effect and result in a predicted kinetic ratio of 1.6:(1 + 2.56):1.6 or 1:2.2:1. Since multiple exchanges occur, neither of these situations apply directly.

(15) Other decomposition products, ethylbenzene, styrene, and α-methylstyrene, were also detected in significat amounts and showed deuterium scrambling.

(16) Substituted titanium alkylidene species have been observed and isolated. Gilliom, L. R.; Grubbs, R. H., manuscript in preparation.

$5f^3$ vs. $4f^3$. Routes to and Properties of Highly Reactive Neodymium(III) Hydrocarbyl and Hydride Complexes[†]

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Summary: The reaction of Cp'$_2$NdCl$_2^-$Li(ether)$_2^+$ (Cp' = η^5-(CH$_3$)$_5$C$_5$) with LiCH[Si(CH$_3$)$_3$]$_2$ yields the early lanthanide alkyl Cp'$_2$NdCH[Si(CH$_3$)$_3$]$_2$ (**1**). The molecular structure of this complex features an unusually short Nd–methyl contact. Reaction of **1** with hydrogen yields the highly reactive hydride (Cp'$_2$NdH)$_2$ (**3**). At 25 °C, 1-atm gas pressure, **3** polymerizes ethylene with $N_t > 80\,000$ min^{-1} and hydrogenates 1-hexene with $N_t = 77\,000$ h^{-1}. Cyclohexene is hydrogenated with $N_t = 8300$ h^{-1}. Kinetic measurements indicate that Nd–C hydrogenolysis is rate limiting for 1-hexene and that hydride + olefin addition is rate limiting for cyclohexene.

Despite the recent burgeoning of organoactinide[1] and organolanthanide[1a,2] chemistries, few meaningful comparisons exist between isoelectronic, isoleptic 4f^n and 5f^n systems. A potentially informative comparison to known Cp'$_2$UR/(Cp'$_2$UH)$_n$ chemistry[3] (Cp' = η^5-(CH$_3$)$_5$C$_5$) would require the corresponding, unknown Nd(III) analogues. Approaches to *ether- and halide-free* compounds of this type are circuitous for later lanthanides[1a,2b,4] and undeveloped for early (La–Nd) lanthanides.[2] We report here that bulky[3,5] hydrocarbyl groups offer a facile *entrêe* into such systems, the unusual molecular structure of a Cp$_2$'Nd^{III} alkyl, and preliminary chemical/mechanistic observations portending very high catalytic activity.

The reaction of Cp'$_2$NdCl$_2^-$Li(ether)$_2^{+\,6}$ with [bis(trimethylsilyl)methyl]lithium proceeds according to eq 1 to give hydrocarbyl 1 in 81% isolated yield after recrystallization from pentane (−30 °C).

$$\mathrm{Cp'_2NdCl_2^-Li(ether)_2^+ + LiCH[Si(CH_3)_3]_2 \xrightarrow[15\ h]{toluene,\ 0\ ^\circ C} Cp'_2NdCH[Si(CH_3)_3]_2 + 2LiCl + 2\,ether} \quad (1)$$

1, blue-green crystals

Complex 1 was characterized by elemental analysis,[7a] infrared spectra,[7b] iso-

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[†] This contribution is dedicated to Earl Muetterties, an outstanding scientist and a friend.

(1) (a) Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21. (b) Marks, T. J. *Science* (*Washington, D.C.*) **1982**, *217*, 989–997. (c) Marks, T. J.; Fischer, R. D., Eds. "organometallics of the f-Elements"; D. Reidel: Dordrecht, 1979. (d) Marks, T. J. *Prog. Inorg. Chem.* **1979**, *25*, 224–333.

(2) (a) Schumann, H. *Angew. Chem.*, in press. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.*, in press. (c) Evans, W. J. In "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Ed.; Wiley: New York, 1982; Chapter 12. (d) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 52–107.

(3) (a) Fagan, P. J.; Mariquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170–180. (b) Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 865–867. (c) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075–5078. (d) Duttera, M. R.; Mauermann, H.; Suzuki, H.; Marks, T. J., manuscript in preparation.

(4) Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, No. *212*, 459–479 and references therein.

(5) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140–141.

(6) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267–3270.

0276-7333/85/2304-0200$01.50/0