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Note

Revisiting the Metathesis of ^{13}C-Monolabeled Ethane

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Summary: The metathesis of ^{13}C-monolabeled ethane leads to the parallel occurrence of degenerate and productive reactions, affording the statistical distribution of the various product isotopomers, which can be rationalized in terms of a mechanistic reaction scheme combining both processes.

The catalytic transformation of alkanes remains one of the most important challenges in chemistry, considering the inertness of their C−H and C−C bonds but also their considerable application potential.[1−4] Using a "single-site approach", we reported in 1997 the discovery of a new reaction: alkane metathesis where a highly electrophilic tantalum hydride supported on silica, [(≡SiO)$_2$Ta−H] (**1**),[5] could catalytically transform at moderate temperatures any light alkane into its lower and higher homologues by both cleavage and formation of C−H and C−C bonds (eq 1).[6,7]

$$2C_nH_{2n+2} \rightleftharpoons C_{n-i}H_{2(n-i)+2} + C_{n+i}H_{2(n+i)+2} \qquad (1)$$

$$n \geq 2 \quad i = 1, 2, \ldots n-1$$

Kinetic studies in the case of propane metathesis, carried out at extremely low contact time in a continuous flow reactor, revealed the primary products of the reaction: namely, alkenes and H$_2$.[8] This observation as well as elementary steps known in tantalum organometallic chemistry led us to propose a mechanism based on the following key steps: (i) alkane dehydrogenation via C−H bond activation leading to a metal alkyl with subsequent formation of an alkene and a metal hydride, (ii) alkene metathesis on a metallocarbene formed in parallel via α-H abstraction from the metal alkyl, and (iii) hydrogenation of the new alkenes on the metal hydride.[8]

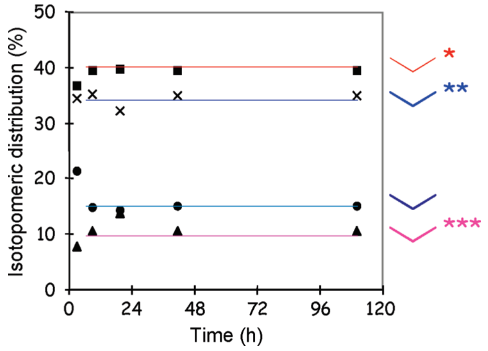

Figure 1. Isotopomeric distribution of nonlabeled and mono-, di-, and trilabeled propane obtained during the metathesis of 100% ^{13}C-monolabeled ethane catalyzed by [(≡SiO)$_2$Ta−H] (**1**) in a batch reactor (150 °C, 16 kPa, $^*CH_3-CH_3$:Ta = 120).

In the case of 100% ^{13}C-monolabeled ethane, a previous study performed in a batch reactor has evidenced that, in addition to the productive process leading mainly to a mixture of methane (70%) and propane (27%) along with a small amount of butanes (2.8%), a degenerate process also takes place by which ^{13}C-monolabeled ethane is transformed into an equimolar mixture of unlabeled ethane and ^{13}C-dilabeled ethane (Figure S1 in the Supporting Information).[9] This detectable degenerate metathesis was expected to be accompanied by a fully degenerate metathesis at the same rate, by which two ^{13}C-monolabeled ethane molecules exchange their methyl groups to form two new ^{13}C-monolabeled ethane molecules (Scheme S1 in the Supporting Information). Under these conditions, the total degenerate process (eq 2) gave after about 100 h a calculated turnover number (TON) of 65, 5 times higher than that of the productive process (Figure S2 in the Supporting Information). Further investigation by GC/MS analysis of the products, particularly methane and propane, is reported now, indicating that whatever the conversion of ethane or the reaction time, constant isotopomeric distributions of methane and propane were respectively obtained; typically a 1:1 distribution of nonlabeled (CH$_4$) and labeled ($^*CH_4$) methane was observed, whereas in the case of propane, a 15:39:34:11 distribution of nonlabeled and mono-, di-, and trilabeled propane was obtained, which is close to

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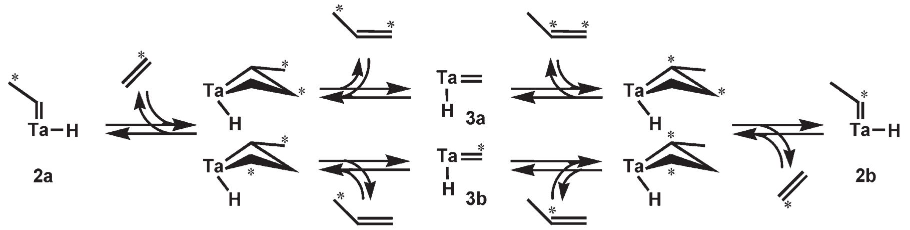
Scheme 1



the expected statistical distribution (12.5:37.5:37.5:12.5 or 1:3:3:1) (Figure 1).

$$4{}^*CH_3-CH_3 \rightarrow CH_3-CH_3 + 2{}^*CH_3-CH_3 + {}^*CH_3-{}^*CH_3 \qquad (2)$$

Therefore, it is worth emphasizing that if ^{13}C-monolabeled ethane is progressively scrambled into unlabeled ethane and ^{13}C-dilabeled ethane (Figure S1), methane and propane are liberated totally scrambled in the gas phase and their isotopomeric distributions remain constant during the entire reaction time. If the previously reported alkane metathesis mechanism[8] is applied directly to the initially pure ^{13}C-monolabeled ethane, a 1:1 distribution of CH_4 and $^*CH_4$ would be effectively obtained but for propane only a mixture of mono- and dilabeled compounds would be generated: that is, a 0:1:1:0 distribution instead of the observed 1:3:3:1 (Scheme 1 and Scheme S2 (Supporting Information)).

This mechanistic scheme indicates in fact that the propane formation involves an interaction between the Ta=C_2 carbene species **2a**,**b** (tantalum ethylidene) and the C_2 alkene ethylene, leading to a tantalacyclobutane species,[10-13] as it is known in alkene metathesis;[14] the tantalum ethylidene species **2a**,**b** ensue from the C−H bond activation of ethane on the tantalum hydride **1**, followed by α-H abstraction, whereas a β-H elimination affords the liberation of ethylene (Scheme S2).[8] The combinatorial examination of all the possible interactions between the Ta=C_2 carbene species and the C_2 alkene shows that the observed 1:3:3:1 propane distribution can be reached only if the Ta=C_2 carbene species has undergone a total scrambling, that is, if it contains a 1:2:1 distribution of nonlabeled and mono- and dilabeled C_2 fragments, whatever the isotopomeric distribution of ethylene (Table 1).

Therefore, a mechanistic scheme has to be considered combining the scrambling process of ethane and the productive formation of methane and propane. The scrambling process can be explained, when starting from the two labeled and nonlabeled tantalum methylidene hydride intermediates **3a**,**b**; these latter species result from the liberation of propylene molecules from the tantalacyclobutane species formed by the interaction of the tantalum ethylidenes **2a,b** with ethylene (Scheme 1 and Scheme S2). This corresponds to the first initiating cycle during which the 0:1:1:0 distribution of propane would be produced (Scheme 1 and Scheme S2). Afterward, the tantalum methylidene hydrides **3a**,**b** could also interact with ^{13}C-monolabeled ethylene to form the new tantalacyclobutane species **4a**,**b**, from which nonlabeled and dilabeled ethane can be formed through various known elementary steps depicted in Scheme 2b; note that in addition to the formation of the productive species **4a**,**b**, the unmentioned unproductive species **4a′**,**b′** can be considered (Scheme S3 in the Supporting Information).

Table 1. Theoretically Expected Isotopomeric Distribution of Methane and Propane According to the Isotopomeric Compositions of the Ta=C_2 Carbene Species and the C_2 Alkene

starting		ending	
Ta=C_2 carbene	ethylene	methane	propane
0:1:0	0:1:0	1:1	0;1:1:0
0:1:0	1:2:1	1:1	0:1:1:0
1:2:1	0:1:0	1:1	1;3:3:1
1:2:1	1;2:1	1:1	1:3:3:1

In particular, the tantalacyclobutanes **4a**,**b** can be formed from or evolve to the tantalum methylidene (ethylene) hydrides **5a**−**d**. These latter species can undergo ethylene insertion into the Ta−H bond to form the four tantalum methylidene ethyl species **6a**−**d** variously labeled on carbons. From complexes **6a**,**c**, non- and dilabeled ethane can be liberated via σ-bond metathesis by the ^{13}C-monolabeled ethane reagent,[15,16] leading to the progressive scrambling of the gas phase. It is worth noting that the population of species **6a**−**d** responds to the 1:2:1 distribution of a total scrambling of C_2-alkyl fragments or the stoichiometry of eq 2. Otherwise, the same complexes **6a**,**c** can enter into a productive but slower metathesis cycle as shown in Scheme 2a,c (clockwise mode), ensuring the formation of nonlabeled and ^{13}C-trilabeled propane. This productive cycle involves in particular the C−H bond activation of the ^{13}C-monolabeled ethane reagent on the tantalum−methylidene double bond, as previously reported by Rothwell,[15,16] to form the tantalum trialkyl species **7a**−**d**. The activation of a C−H bond by a carbene is also consistent with the observation of initiation products during the metathesis of propane with tantalum neopentyl neopentylidene supported on silica.[17,18] Complexes **6b**,**d** can behave in the same way as **6a**,**c**, leading to mono- and dilabeled propane (not represented in Scheme 2).

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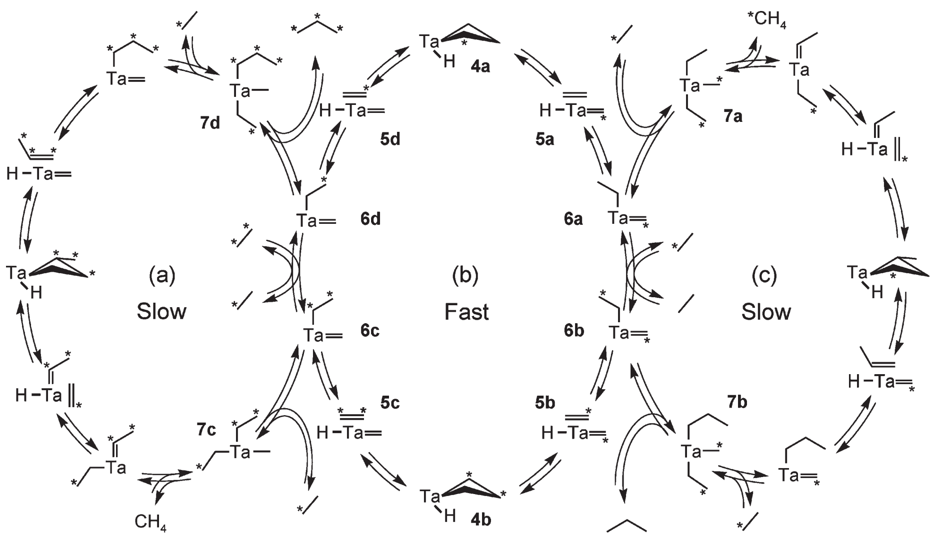
Scheme 2. Proposed Mechanistic Cycles for the Scrambling of ^{13}C-Monolabeled Ethane (b) and the Productive Formation of Nonlabeled (c) and ^{13}C-Trilabeled Propane (a)



In conclusion, degenerate and productive reactions take place concomitantly during the metathesis of ^{13}C-monolabeled ethane, leading to the formation of all the isotopomers of either ethane or the metathesis products, i.e. methane and propane, in a statistical distribution. The previously reported alkane metathesis mechanism, applied to the pure reagent, the ^{13}C-monolabeled ethane, only explains the formation of mono- and dilabeled propane. The presence of all the propane isotopomers in a statistical distribution (1:3:3:1) necessarily involves the total scrambling of the C_2-hydrocarbyl fragment in a tantalum ethylidene intermediate. The combination of two mechanistic reaction schemes involving the scrambling process of ^{13}C-monolabeled ethane as well as its productive metathesis enables us to rationalize the formation of all the various product isotopomers.

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Supporting Information Available: Text giving experimental procedures, Figures S1 and S2, giving details of the conversion of ^{13}C-monolabeled ethane and distribution of labeled ethane versus time, and Schemes S1−S3, giving details of the degenerate metathesis, application of the classical alkane metathesis mechanism, and formation of productive (**4a**,**b**) and nonproductive (**4a′**,**b′**) tantalacyclobutane intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.