ACCOUNTS
of chemical research

Metathesis of Alkanes and Related Reactions

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RECEIVED ON AUGUST 3, 2009

CONSPECTUS

The transformation of alkanes remains a difficult challenge because of the relative inertness of the C—H and C—C bonds. The rewards for asserting synthetic control over unfunctionalized, saturated hydrocarbons are considerable, however, because converting short alkanes into longer chain analogues is usually a value-adding process. Alkane metathesis is a novel catalytic and direct transformation of two molecules of a given alkane into its lower and higher homologues; moreover, the process proceeds at rela-

Alkane Metathesis on Single Site Catalyst

tively low temperature (ambient conditions or higher). It was discovered through the use of a silica-supported tantalum hydride, (≡SiO)$_2$TaH, a multifunctional catalyst with a single site of action. This reaction completes the story of the metathesis reactions discovered over the past 40 years: olefin metathesis, alkyne metathesis, and ene—yne cyclizations. In this Account, we examine the fundamental mechanistic aspects of alkane metathesis as well as the novel reactions that have been derived from its study.
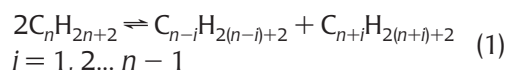
The silica-supported tantalum hydride catalyst was developed as the result of systematic and meticulous studies of the interaction between oxide supports and organometallic complexes, a field of study denoted surface organometallic chemistry (SOMC). A careful examination of this surface-supported tantalum hydride led to the later discovery of alumina-supported tungsten hydride, W(H)$_3$/Al$_2$O$_3$, which proved to be an even better catalyst for alkane metathesis. Supported tantalum and tungsten hydrides are highly unsaturated, electron-deficient species that are very reactive toward the C—H and C—C bonds of alkanes. They show a great versatility in various other reactions, such as cross-metathesis between methane and alkanes, cross-metathesis between toluene and ethane, or even methane nonoxidative coupling. Moreover, tungsten hydride exhibits a specific ability in the transformation of isobutane into 2,3-dimethylbutane as well as in the metathesis of olefins or the selective transformation of ethylene into propylene.

Alkane metathesis represents a powerful tool for making progress in a variety of areas, perhaps most notably in the petroleum and petrochemical fields. Modern civilization is currently confronting a host of problems that relate to energy production and its effects on the environment, and judicious application of alkane metathesis to the processing of fuels such as crude oil and natural gas may well afford solutions to these difficulties.
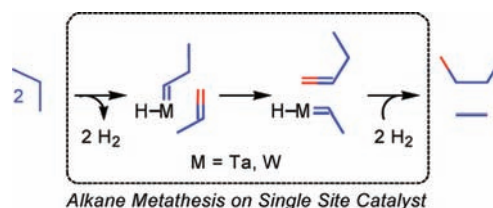
Introduction

The catalytic activation of alkanes remains one of the most important challenges in chemistry in view of their inertness and considerable application potential.[1,2] Alkane metathesis is a catalytic reaction which directly transforms a given paraffin into its lower and higher homologues at low temperatures of 25 °C or above (eq 1):

$$2C_nH_{2n+2} \rightleftharpoons C_{n-i}H_{2(n-i)+2} + C_{n+i}H_{2(n+i)+2}$$
$$i = 1, 2... n - 1 \tag{1}$$

It was discovered by the group of Basset using a tantalum hydride supported on silica, (≡SiO)$_2$TaH, **1a**, that is a single-site system.[3] This silica supported tantalum hydride catalyst has resulted from a systematic and broad investigation of the reactions between organometallic complexes and oxide surfaces which is usually called surface organometallic
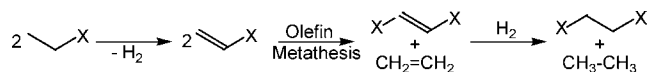
chemistry on oxides.[4] In subsequent studies, an alumina-supported tungsten hydride W(H)$_3$/Al$_2$O$_3$, **1b**, was elaborated giving better activity.

The catalytic reaction of alkane metathesis completes the story of the various metathesis reactions discovered over the last 40 years: metathesis of olefins,[5,6] alkynes,[7−9] or ene−yne cyclizations.[10,11] However, as an intrinsic difference, whereas in paraffin metathesis one or several sp^{3}C−sp^{3}C bonds can be cleaved and recombined, in olefin metathesis, usually only the one sp^{2}C=sp^{2}C double bond is cleaved and recombined. This explains the "apparent" lack of selectivity observed in the metathesis of acyclic alkanes illustrated in eq 1, by the variation of i between 1, 2,... and $(n − 1)$. In fact, the product selectivity obeys the following order with a few exceptions:

$$C_{n+1} > C_{n+2} > C_{n+3} \dots \; ; \quad C_{n-1} > C_{n-2} > C_{n-3} \dots$$
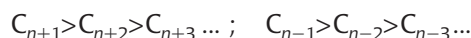
This selectivity order is directly related to mechanistic aspects of the reaction, involving the stability of key intermediates. Based on kinetic studies, the primary products of the reaction have been identified as olefins and H$_2$; according to elementary steps known in tantalum organometallic chemistry, this observation led to the proposition of a mechanism based on the following key steps: (i) paraffin dehydrogenation via C−H bond activation leading to a metal-alkyl with subsequent formation of an olefin and a metal-hydride; (ii) olefin metathesis on a metallocarbene formed in parallel via α-H elimination from the metal-alkyl; and (iii) hydrogenation of the new olefin on the metal-hydride.[12]

Therefore "alkane metathesis" with a single-site system totally differs from the so-called "tandem metathesis of paraffins" based on a dual-catalyst system, combining a heterogeneous catalyst for dehydrogenation/hydrogenation and a catalyst for olefin metathesis (Scheme 1).[13−16]

In the past, this approach was used as an alkane conversion process by Chevron.[16] This global dual system reaction is thermoneutral, but the thermodynamically disfavored formation of olefins from alkanes requires high temperatures as in the Chevron process, using a mixture of Pt/Al$_2$O$_3$ (dehydrogenation/hydrogenation) and WO$_3$/SiO$_2$ (metathesis), which proceeds typically at 400 °C under 60 bar.[15] Homogeneous systems based on pincer-iridium dehydrogenation/hydrogenation catalysts and "Schrock-type" Mo-based olefin metathesis catalysts have been reported more recently.[13] These systems can afford some good selectivity for higher products such as in the conversion of *n*-hexane to ethane

and *n*-decane as the major products. They are also able to carry out ring-opening metathesis of cycloalkanes.[17]

Starting from these fundamental mechanistic aspects, various unprecedented reactions derived from alkane metathesis will be discussed in the following.

Alkane Metathesis: A Discovery Resulting from the Surface Organometallic Chemistry of Zirconium, Tantalum, and Tungsten

The discovery of the reaction on single-site systems arose from the development of surface organometallic chemistry of zirconium,[18] tantalum,[19,20] and tungsten.[21−23] Using this approach, it is possible to create, at the surfaces of oxides, relatively well-defined metallic entities which have both molecular-like and surface-like characters. Most of this chemistry originated from the reaction of ZrNp$_4$ with the surface of partially dehydroxylated silica which gave rise to well-defined (≡Si−O)ZrNp$_3$.[18] This single-site species was further transformed by treatment under hydrogen at 150 °C into a mixture of highly electrophilic (≡Si−O)$_3$Zr$^{(IV)}$H and (≡Si−O)$_2$Zr$^{(IV)}$(H)$_2$.[24] During this treatment, Zr−C bonds are cleaved, leading to intermediate surface zirconium polyhydrides; simultaneously, a surface rearrangement around the metallic centers takes place involving the opening of surface siloxane bridges ≡Si−O−Si≡, the migration of one or two hydrides onto silicon atoms, and the formation of one or two Zr−O bonds (Scheme 2). The resulting zirconium hydrides are able to hydrogenolyze paraffins (with the exception of ethane)[25] and polyolefins at very moderate temperature.[26]

In the case of tantalum, the formation of silica supported tantalum hydride (≡Si−O)$_2$Ta(H)$_x$[20] resulted from the treatment under hydrogen of the surface complex (≡Si−O)Ta(=CH-CMe$_3$)(CH$_2$CMe$_3$)$_2$.[19] Again, this treatment cleaves the Ta−C bonds and leads to intermediate surface tantalum polyhydrides. Similarly to the case of zirconium (*vide supra*), the silica surface also rearranges, leading to the formation of another Ta−O bond and surface silane species (Scheme 3).

Note that there is, under hydrogen, an equilibrium between (≡Si−O)$_2$Ta$^{(V)}$(H)$_3$ and (≡Si−O)$_2$Ta$^{(III)}$H.[27] As in the case of zirconium, tantalum hydrides are extremely electron deficient, since they can be considered as 10- or 8-electron complexes or possibly 14- or 12-electron complexes if the (p$_\pi$)−(d$_\pi$) back-donation is taken into account. Although this tantalum hydride is considered as a single-site system, EXAFS data obtained on mesoporous MCM-41 silica indicate that, on this support at least, some interactions with surface atoms take place (Scheme 4).[27]

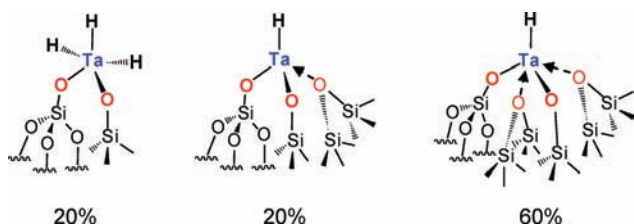Roughly 20% of the tantalum would be linked only with two σ-bonded siloxy oxygens (≡Si−O−), whereas in other cases
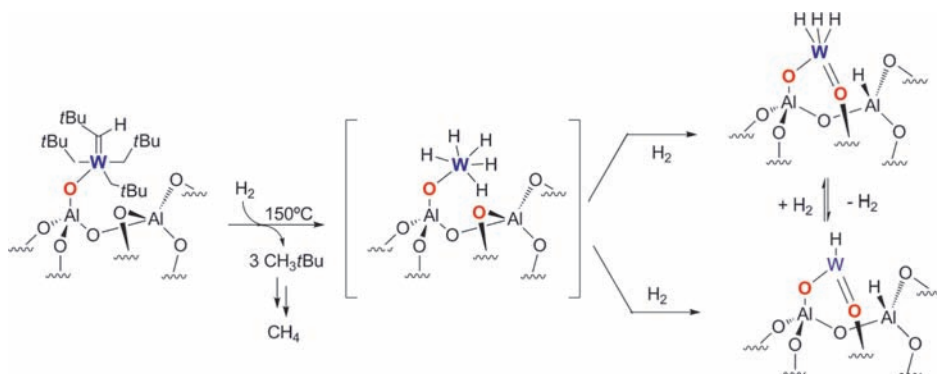
SCHEME 2
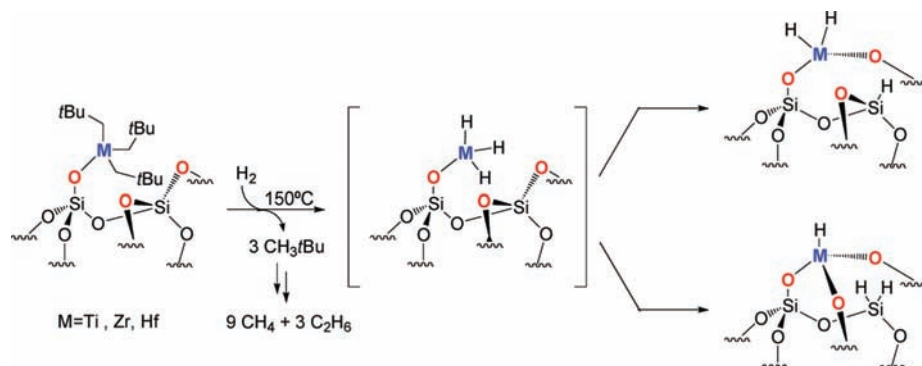
SCHEME 3
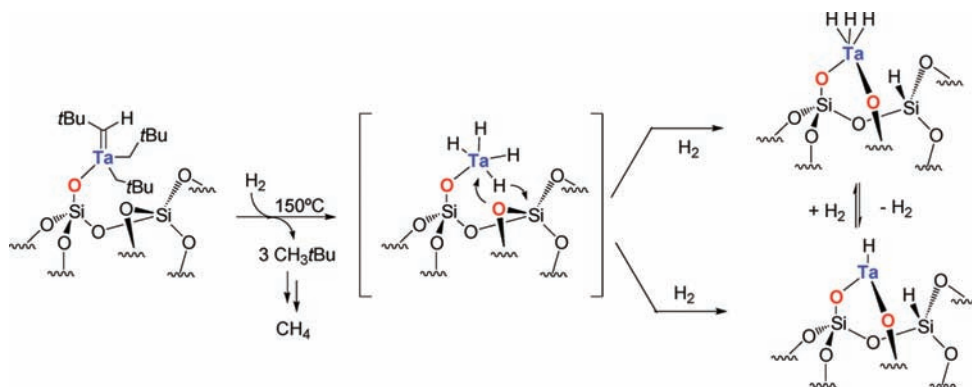
SCHEME 4

there would be up to 80% of one or two π-bonded oxygens (from ≡Si−O−Si≡), at a distance ranging between 2.6 and 2.9 Å.[27] It is clear that these oxygen atoms close to the tantalum occupy a coordination site. However it is not known if there is a

dynamic process in which these oxygens can move easily to or from the tantalum to give a higher percentage of the highly coordinatively and electronically unsaturated 8- or 10-electron species (≡Si−O)$_2$Ta$^{(III)}$H, and (≡Si−O)$_2$Ta$^{(V)}$(H)$_3$.

Tungsten-hydride catalysts have been obtained on silica with partial sintering of the metal;[22] they were efficiently formed on silica−alumina[21] and alumina[23] from hydrogen treatment at 150 °C of the supported species [(≡M−O)W(≡CtBu)(CH$_2t$Bu)$_2$] (M = Si, Al). In the latter case, the characterization of the surface tungsten-hydrido species is still under way, but recent theoretical calculations tend to indicate that a W$^{(VI)}$-oxo trishydride

SCHEME 5

[(≡Al−O)W(=O)(H)₃], was formed, with the oxo ligand being π-bonded to an adjacent Lewis acid aluminum atom (Scheme 5).

The Catalytic Performances

Alkane metathesis, as defined by eq 1, is almost thermoneutral with a $\Delta G°_{273}$ value close to zero (Figure 1) which prevents quantitative conversions just like olefin metathesis.

In a continuous flow reactor for propane metathesis, (≡Si−O)₂TaH proves to be active during several days. The results are comparable to those obtained in a batch reactor, in terms of turnover number (TON) and selectivity (Figure 2).[3]

Under these conditions, the reaction selectivity is better at the steady state, because an equilibrated ratio is observed between the resulting higher and lower alkanes. The apparent TON remains modest but corresponds to the productive reaction, whereas degenerate processes also take place as illustrated in the case of ethane. Besides the classical transformation of ethane
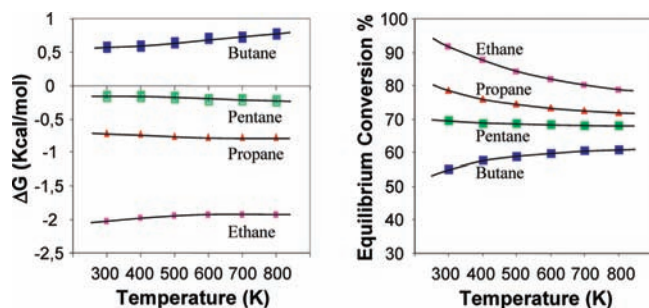
into methane and propane, ¹³C-monolabeled ethane can be transformed into an equimolar mixture of unlabeled ethane and ¹³C-dilabeled ethane (eq 2) (Figure 3).[28]

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

Comparison between Supported Tantalum- and Tungsten-Hydrides

Various tungsten-hydrido compounds prepared on silica,[22] silica−alumina,[21] or alumina[23] supports have been tested in propane metathesis in batch conditions in order to compare their properties with those of the silica or alumina-supported tantalum-hydrides.[29]

Results in terms of turnover number (TON) indicate that silica−alumina or alumina-supported tungsten-hydrides give very similar results but are ca. twice as active as (≡Si−O)₂TaH and even more active than tantalum-hydride on alumina or tungsten-hydride on silica (Figure 4). Regarding selectivity, tungsten-hydrides on various supports give a narrower product distribution than the tantalum ones (Figure 5). Indeed, methane and heavier homologues (pentanes) are formed in lower amounts. In addition, tungsten catalysts give higher linear/branched ratios of the higher homologues (from 10 to 12

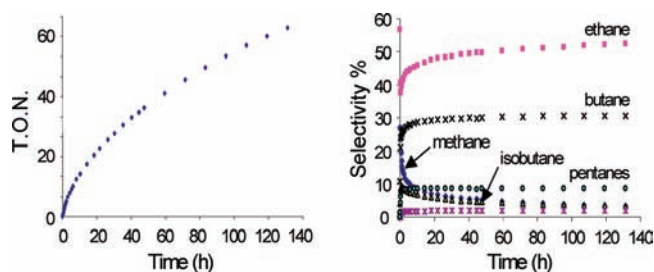**FIGURE 1.** Gibbs energy for the metathesis of alkanes and corresponding equilibrium conversion.

FIGURE 2. Propane metathesis catalyzed by (≡SiO)₂TaH, in a continuous flow reactor (520 mg of 5.3% Ta/SiO₂; 1 atm, 150 °C, 1 mL/min or VHSV = 38 h⁻¹): TON and selectivity.

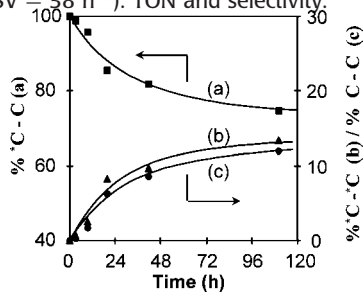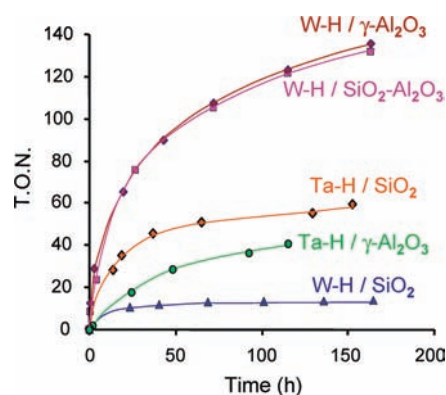**FIGURE 3.** Degenerate metathesis of ethane in the presence of (≡Si−O)₂TaH: evolution of the distribution of ¹³C-labeled and unlabeled ethane over time.

FIGURE 4. Propane metathesis in a batch reactor (150 °C, 1 atm, C₃H₈/M = 750): comparison of the activity of various supported tantalum and tungsten hydrides.
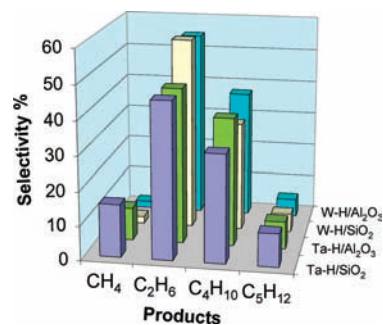

FIGURE 5. Selectivity of products obtained during the metathesis of propane (150 °C, 1 atm, C₃H₈/M = 750) after 120 h with the various supported tantalum and tungsten hydrides.

for butanes and from 4 to 8 for pentanes) than the tantalum-hydride ones (of 3 and 2 respectively).

The Mechanism of Alkane Metathesis

The mechanism of alkane metathesis has been approached by means of several experimental kinetic studies leading to the elucidation of some elementary steps of the process following identification of the primary products. Regarding the elementary steps, it has been shown that methane reacts with the tantalum hydride to give a tantalum methyl plus one mole of hydrogen.[20,27,30] It has also been shown that, with Ta/silica and W/silica−alumina, reaction with methane above 150 °C leads to the formation of the M-methyl, M-methylene, and M-methylidyne species (M = Ta, W). These observations demonstrate that the first step of alkane metathesis involves the cleavage of the C−H bond of the alkane to form a metal-alkyl derivative. This could occur via either an oxidative addition if the active site is the $(\equiv Si-O)_2Ta^{(III)}H$ or a σ-bond metathesis if the active site is the d^0 $(\equiv Si-O)_2Ta^{(V)}(H)_3$, according to the fact that the two species are in equilibrium.

Primary products were identified by kinetic studies under dynamic conditions. Propane metathesis conversion increases linearly with contact time, showing that the reaction is under dynamic control with no intergranular diffusion limitation. The selectivity for olefins and hydrogen increases with decreasing contact time, whereas that of alkanes decreases. The alkane/olefin ratio tends simultaneously to zero when the con-

tact time approaches zero. Thus, olefins and hydrogen appear as primary products of the alkane metathesis reaction (Figure 6).[12]

These results as well as the known properties of tantalum-alkyl complexes developed by Bercaw and Schrock in the 1980s allowed us to propose a reasonable mechanism for this reaction (Scheme 6). This mechanism begins by the alkane C−H bond activation in the same way as observed in the case of methane or cyclic alkanes.[20,30] In the case of propane, this leads to the formation of *n*- and isopropyl-Ta with hydrogen evolution. These alkyl-Ta species can then be transformed into two carbene-hydride complexes $Ta(H)(=CH(CH_3)_2)$ and $Ta(H)(=CH-CH_2-CH_3)$ by transfer of a hydrogen in the α-position[31,32] or into an olefin-hydride complex $Ta(H)(\eta^2-CH_2=CH-CH_3)$ by transfer of a hydrogen in the β-position;[32−34] indeed, tantalum is known to perform these two types of hydrogen transfer. The resulting propene can then leave the coordination sphere of the $Ta(H)(\eta^2-CH_2=CH-CH_3)$ complex to interact with the carbenic species and form four different metallacyclobutanes with methyl or ethyl groups in [1,2] or [1,3] positions (Scheme 6).[35−38]

These metallacyclobutanes can decompose into new olefins and new carbene-hydrides after an interconversion of the hydride ligand around the tantalum (Scheme 7).[39]

The catalytic cycle then continues via hydride reinsertion into the carbene as well as olefin insertion into the hydrides. The final alkane liberation proceeds via a cleavage of metal-alkyl compounds by hydrogen, a process already observed in
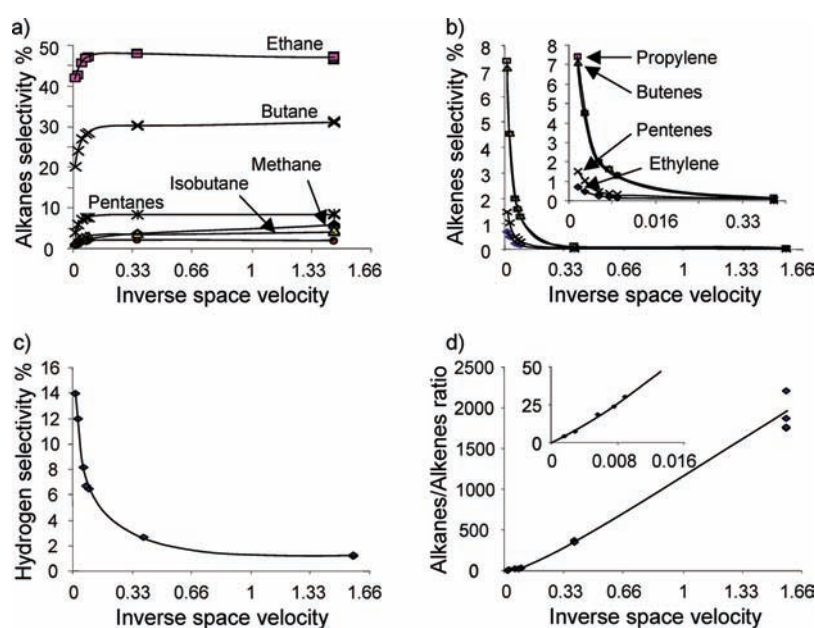

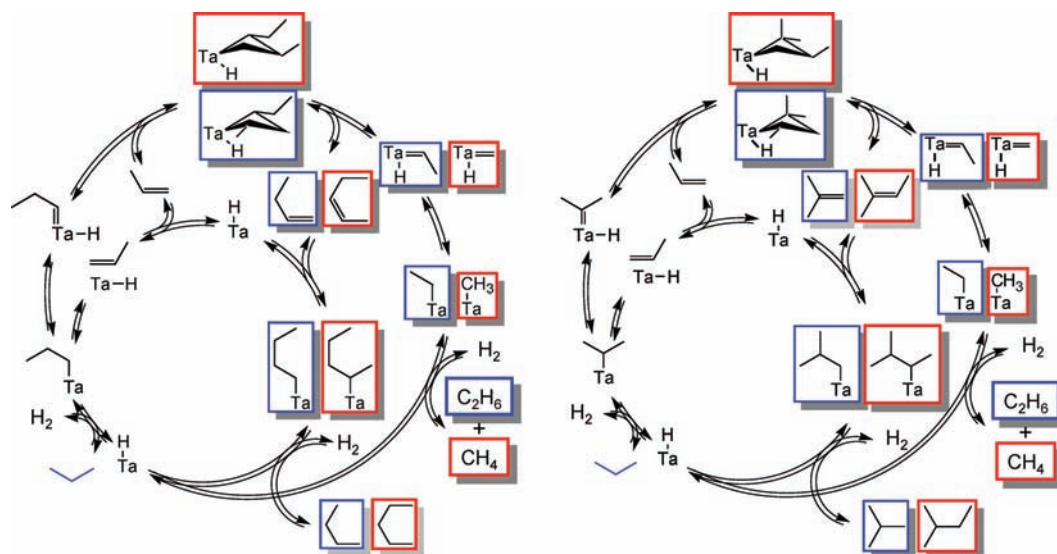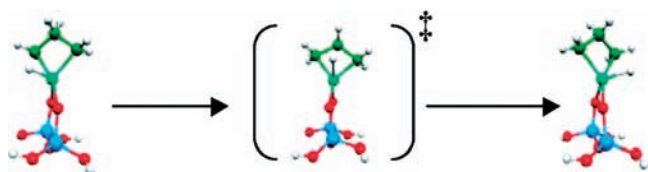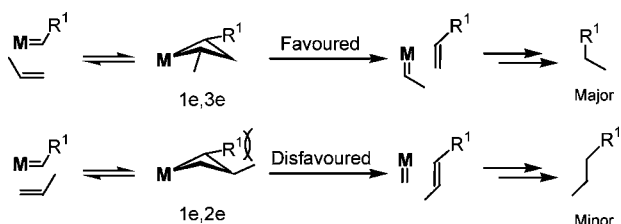**FIGURE 6.** Propane metathesis catalyzed by $(\equiv SiO)_2TaH$ in a continuous flow reactor (520 mg of 5.3% Ta/SiO$_2$; 1 atm, 150 °C, 1 to 100 mL/min or VHSV = 38 to 3800 h^{-1}); effect of contact time on product selectivity and alkane/olefin ratio.

SCHEME 6. Proposed Mechanism for the Metathesis of Propane: Formation of Linear Products (Left) and Branched Products (Right)


SCHEME 7

SCHEME 8

alkane hydrogenolysis,[40] or possibly via a displacement by the entering alkane by σ-bond metathesis.[41] Interestingly, the catalyst has a multiple functionality: (i) C–H bond activation to produce a primary or seconday metal-alkyl, (ii) α- or β-H elimination to produce carbene-hydride or olefin-hydride, (iii) olefin metathesis, and (iv) hydrogenolysis of metal-alkyl. The product selectivity for C_{n+1}, C_{n+2}, C_{n-1}, and C_{n-2} can be explained in terms of steric interactions between substituents in [1,2] or [1,3] positions in tantallacyclobutane intermediates or during their formation.[42] Indeed, butane, a C_{n+1} product coming from a 1,3-substituted metallacycle, is formed in higher amount than pentane, a C_{n+2} product coming from a 1,2-substituted metallacycle in which the substituents are more constrained (Scheme 8).

The same is true for branched homologues: isobutane and isopentane. Similarly, *n*-butane is favored by comparison with isobutane coming from a 1,1,3-trisubstituted metallacycle

which is more constrained than a 1,3-substituted metallacycle. Generally speaking, this mechanistic scheme agrees well with the observation that $C_{n+1} > C_{n+2}$ in the homologue products as well as with the favored formation of linear rather than branched products, starting from a linear alkane.[12]

Metathesis of 2-Methylpropane

Whereas the silica-supported tantalum hydride $(\equiv SiO)_2Ta(H)_x$ transforms classically 2-methylpropane into propane and 2-methylbutane,[3] the tungsten hydride $W(H)_3/Al_2O_{3-500}$, leads to an unusual selectivity with the main formation of 2,3-dimethylbutane (41.7%) and ethane (41.3%) (Figure 7) (eq 3).[43]

$$2 \quad \diagup\!\!\diagdown \quad \longrightarrow \quad \diagup\!\!\diagdown\!\!\diagup + \quad — \qquad (3)$$
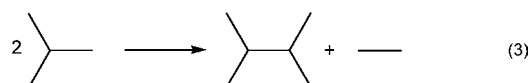
The higher homologues can be ordered as $C_{n+2} \gg C_{n+1} > C_{n+3}$ which is different from the metathesis of linear alkanes, where the order is $C_{n+1} > C_{n+2} > C_{n+3}$.[21,23,29]

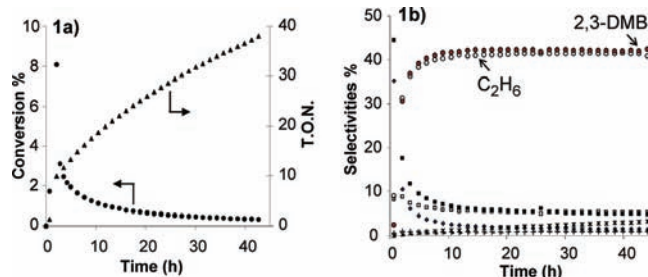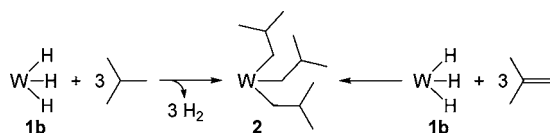**FIGURE 7.** Metathesis of 2-methylpropane catalyzed by $(W(H)_3/Al_2O_3$ (3.86 wt % W). (a) Conversion of 2-methylpropane (●) and TON (▲). (b) Selectivities: (◆) methane, (○) ethane, (■) propane; (∗) 2-methylpropene; (□) 2-methylbutane; (●) 2,3-dimethylbutane (2,3-DMB); (+) 2,4-dimethylpentane; (−) octanes.

SCHEME 9

2-Methylpropene was observed (up to 3.1%) among the products, and therefore, its metathesis was also checked over W(H)$_3$/Al$_2$O$_3$ in a continuous flow reactor (eq 4) (Figure S1 in the Supporting Information).

$$2 \quad \rightarrow \quad + \quad \qquad (4)$$
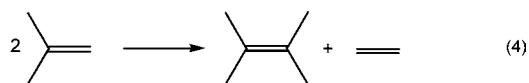
At steady state, the product selectivities were 2,3-dimethylbutenes 50%, ethylene 30%, 2,4,4-trimethylpentenes 12%, neohexene 9%, isopentene 3%, and propene 1%. The 2,4,4-trimethylpentenes (TIP-1 and TIP-2) were likely formed by dimerization of isobutene on the acidic sites of alumina dehydroxylated at 500 °C,[44,45] while the presence of neohexene is explained by a cross metathesis between 2,4,4-trimethylpentenes and ethylene. Metathesis of 2-methylpropene is usually known as a degenerate process with classical olefin metathesis catalysts.[5,6] W(H)$_3$/Al$_2$O$_{3-500}$ **1b** is the first compound able to catalyze the productive self-metathesis of 2-methylpropene into 2,3-dimethylbutene.

The initiation steps of both isobutane and isobutene metathesis occur, respectively, on the tungsten tris-hydride by C−H bond activation or C=C double bond insertion. Both elementary steps lead to the same tris(isobutyl)tungsten intermediate **2** (Scheme 9).

The tris(isobutyl)tungsten complex **2** leads via α-H transfer and β-H elimination to the initiating hydrido-tungsta-carbene **4** (Scheme 10). 2-Methylpropene used as a reactant (2-methylpropene metathesis) or released from any isobutyl tungsten species by β-H elimination (2-methylpropane metathesis) can react with this hydrido-tungsta-carbene **4**. Depending on the two different modes of coordination and reaction of 2-methylpropene toward **4**, two possible tungstacyclobutanes, **5a** and **5b**, are obtained, which have *gem*-methyl and isopropyl substituents in either [1,2] or [1,3]-positions (Scheme 10). These two tungstacycles will further undergo metathetical cleavages: (i) **5a** giving 3-methyl-1-butene and the new hydrido-tungsta-carbene **6a**, [W(H)(=C(CH$_3$)$_2$)]/Al$_2$O$_{3-500}$ and (ii) **5b** giving 2,4-dimethyl-2-pentene and the hydrido-tungsta-methylene **6b**, [W(H)(=CH$_2$)]/Al$_2$O$_{3-500}$ (Scheme 10), thus initiating the catalytic cycles of metathesis of 2-methylpropene (Scheme 11b) or 2-methylpropane (Scheme 11a−c).

The hydrido-tungsta-carbenes **6a** and **6b** can then react further with isobutene, giving the corresponding tungstacyclobutane intermediates **7a** and **7b** (Scheme 11b). Again, these two tungstacycles can undergo metathetical cleavage, with **7a** giving 2,3-dimethyl-2-butene and the hydrido-tungsta-carbene **6b**, and **7b** giving ethylene and the hydrido-tungsta-carbene **6a**, thus ensuring the metathesis of 2-methylpropene (Scheme 11b).

Regarding the 2-methylpropane metathesis, this process proceeds with the insertion of all the olefins released in cycle b (Scheme 11) into tungsten-hydride species such as **6a** or **6b**. The resulting tungsten alkyl groups can be further displaced via σ-bond metathesis, by the incoming 2-methylpropane present in excess, affording the liberation of ethane, 2-methylbutane, 2,3-DMB, and 2,4-dimethylpentane.
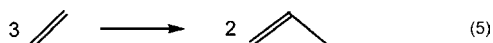
SCHEME 10
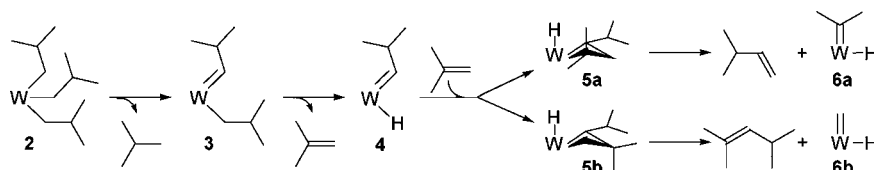
SCHEME 11. Mechanistic Pathways in the Metathesis of 2-Methylpropane (a−c) or 2-Methylpropene (b) (M = W)
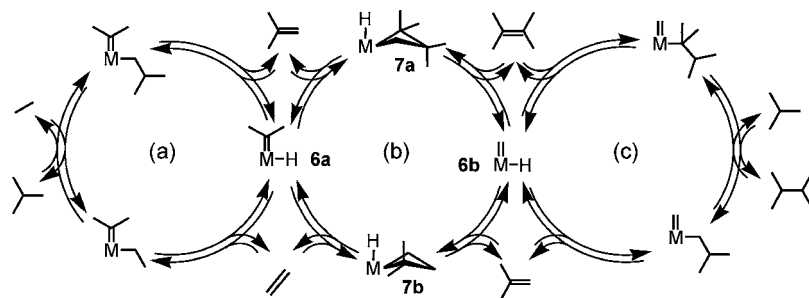
Direct Conversion of Ethylene to Propylene

W(H)$_3$/Al$_2$O$_{3-500}$ **1b** was also found to be a very efficient catalyst for the direct transformation of ethylene to propylene with a selectivity higher than 95% (eq 5) (Figure 8).[46]

$$3 \; /\!/ \longrightarrow 2 \; \bigwedge \qquad (5)$$

It was demonstrated that this reaction proceeds via a "trifunctional single-site" catalyst affording: ethylene dimerization to 1-butene, isomerization of 1-butene to 2-butenes followed by cross metathesis between 2-butenes and ethylene leading to propylene.

The initiation and propagation steps could be determined by identification of the products formed during the early stages (formation of ethane) or by varying contact time at steady state (formation of 1-butene then 2-butene then propylene):

One equivalent of ethane per W was released after immediate contact of the tungsten hydride with ethylene, suggesting the formation of a surface tungsten-ethyl-ethylidene species, [W](CH$_2$CH$_3$)(=CHCH$_3$), by the following elementary steps (Scheme 12).

Note that the coordination sphere of W is very similar to the one obtained in the metathesis of 2-methylpropane and 2-methylpropene. It is also very close to the precursor species obtained in most alkane metathesis reactions.

Contact time experiments clearly show that 1-butene is isomerized to 2-butene (Figure S2 in the Supporting Information), which undergoes cross metathesis with ethylene to form propylene. The newly formed catalyst [W](CH$_2$CH$_3$)(=CHCH$_3$) can insert ethylene into the ethyl moiety to form a *n*-butyl species affording 1-butene and then *cis*- and *trans*-2-butenes after
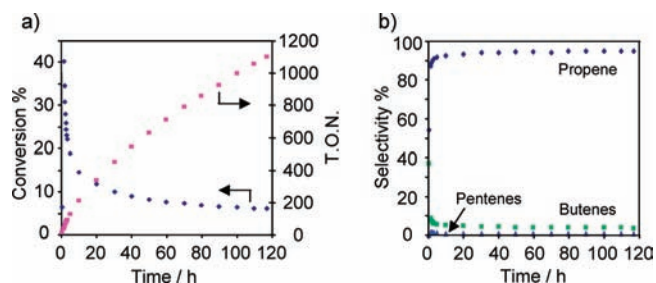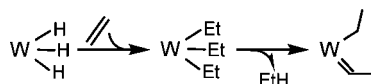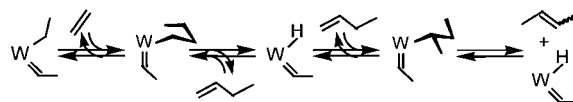
FIGURE 8. (a) Conversion and TON of ethylene. (b) Selectivities obtained during the homologation of ethylene to propylene catalyzed by W(H)$_3$/Al$_2$O$_{3-500}$ **1b** (3.86 wt % W) in a continuous flow reactor (150 °C, $P_{C_2H_4}$ = 1 bar, 4 mL/min, VHSV = 260 h^{-1}).
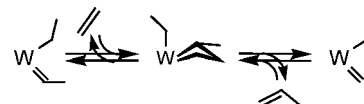
SCHEME 12

SCHEME 13

SCHEME 14

reinsertion of 1-butene and β-H elimination on the *sec*-butyl species (Scheme 13).

The high production of all the butene isomers during initiation combined with the relative deficiency of 2-butenes hint that they are primary products of the reaction. In fact, propene was formed afterward, which suggests the occurrence of a simple metathesis process with the newly formed carbenic complex [W](CH$_2$CH$_3$)(=CHCH$_3$) (Scheme 14).

While the selectivity in propene dropped with decreasing inverse space velocity, the reverse was true for butenes, indicating that (i) the latter were primary products, since the selectivity intercept with the *y*-axis extrapolated to a nonzero value, and (ii) propene was formed in a reaction consuming butenes, since their curvatures are the opposite at any flow rate (Figure 9). Furthermore, 1-butene also appears to precede other butenes, since it is the only one for which the selectivity increases when decreasing inverse space velocity (see Figure S2 in the Supporting Information).
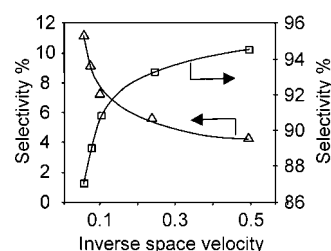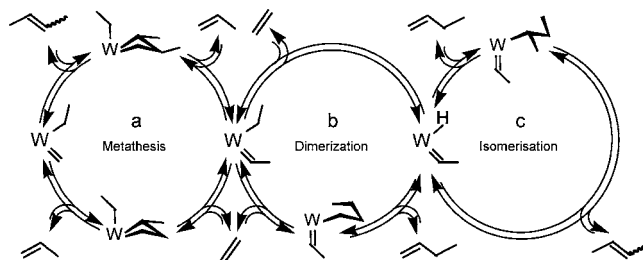
FIGURE 9. Direct conversion of ethylene to propylene in a continuous flow reactor (150 °C, $P_{C_2H_4}$ = 1 bar, 520 mg of W(H)$_3$/Al$_2$O$_{3-500}$ **1b**, 3.86 wt % W); selectivity versus inverse space velocity expressed in [(min)(volume of catalyst)/(volume of ethylene)]; (□) propylene, (△) butenes.

SCHEME 15. Proposed Mechanism for the Direct Conversion of Ethylene to Propylene

Thus, $[W](CH_2CH_3)(=CHCH_3)$ which bears both an alkyl and an alkylidene fragment is able to carry out, on the same single-site, dimerization, isomerization, and metathesis of olefins, that is, to behave as a "trifunctional single-site" catalyst (Scheme 15).

Methane−Propane Cross Metathesis: The Reverse of Ethane Metathesis

The reaction between methane and propane leading to ethane has a positive Gibbs free energy $\Delta G° = +2$ kcal/mol at 150 °C for a methane/propane ratio of 1, which limits the conversion, but this can be overcome by increasing this ratio to 1250, allowing 98% propane conversion to ethane at 250 °C (eq 6) (Figure 10).[47]

$$CH_4 + C_3H_8 \rightleftharpoons 2C_2H_6 \qquad (6)$$
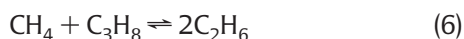
This reaction can also be considered between methane and any other alkane to form a hydrocarbon mixture and constitutes a valorization of methane. It involves the breaking and the formation of a CH and a C−C bond.

In order to avoid competing reactions of propane hydrogenolysis or propane metathesis, it was necessary to work at complete conversion of propane in order to form 2 equiv of ethane per mol of propane introduced and to determine carefully the mass balance. After an initiation step (evacuation of the hydrogen evolved due to C−H activation), the methane/propane (1250/1) mixture leads to the major formation of ethane; indeed, 1.88 mol of ethane are formed per mol of propane introduced, that is to say 94% of propane is transformed by the cross metathesis reaction with methane.

Methane incorporation into one C−C bond of propane has also been confirmed by repeating the previous experiment in a dynamic reactor and by using $^{13}CH_4$ labeled methane. At steady state, the resulting ethane is mainly doubly labeled (>85%), which confirms that ethane comes from a reaction with methane. The high degree of labeling is related to the quite long contact time allowing carbon exchange with $^{13}CH_4$ methane following a degenerate process which has also been highlighted (eq 7).
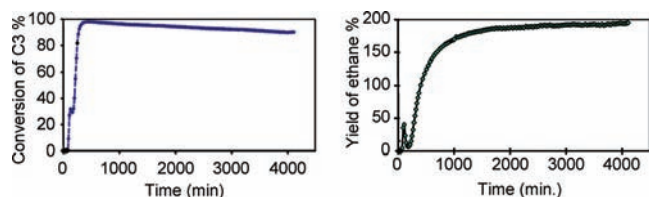
FIGURE 10. Cleavage of propane by methane (continuous flow reactor, 1.5 mL/min, $CH_4/C_3H_8 = 1250$, 50 bar, 250 °C, catalyst ($\equiv$SiO)$_2$TaH **1a**).

$$*CH_4 + CH_3 - CH_3 \rightarrow CH_4 + *CH_3 - CH_3 \qquad (7)$$

Nonoxidative Coupling of Methane to Ethane and Hydrogen: The Reverse of Ethane Hydrogenolysis

Tungsten hydride supported on alumina or silica−alumina and tantalum hydride supported on silica catalyze the coupling of methane to ethane and hydrogen above 250 °C.[48] Interestingly, this reaction is just the reverse of the hydrogenolysis of ethane which does not proceed by β-methyl transfer (impossible in the case of ethane) but by deinsertion of a methylene fragment from a Ta-ethyl fragment (Scheme 16).[40]

SCHEME 16
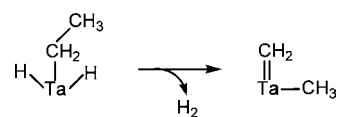
After an induction period due to modification of the coordination sphere of the metal under methane, the coupling reaction occurs with selectivity close to 100% (eq 8).

$$2CH_4 \rightarrow C_2H_6 + H_2 \qquad (8)$$
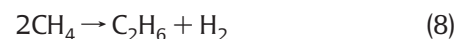
The reaction is quite slow at 250 °C with TON of about 10/M (M: Ta, W) after 100 h (Figure 11), and its mechanism has been rationalized due to the simultaneous observation by ^{13}C NMR of tungsten-methylidyne, -methylidene, and -methyl under methane at 250 °C (Figure 12).

The presence of hydride ligands was not observable above 200 °C, which suggests that these hydrides are transformed into methyl groups under high pressure of methane. In the case of W/silica−alumina and Ta/silica, one can also observe the presence of surface Si-Me, indicating some methyl transfer from tungsten or tantalum to silicon. Besides, the reaction occurs up to 450 °C with a much higher TON but also higher rates of deactivation. Two types of deactivation are observed: a reversible and an irreversible one since the catalyst can be regenerated under hydrogen but incompletely.
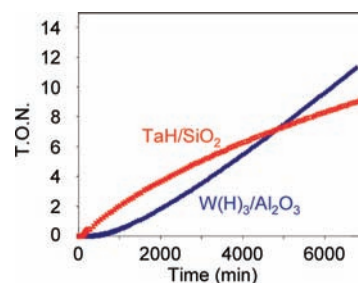
FIGURE 11. Coupling of methane to ethane and hydrogen catalyzed by supported tantalum or tungsten hydrides **1a** and **1b** (3 mL/min, 50 bar, 350 °C, 110 μmol MH/Supp).
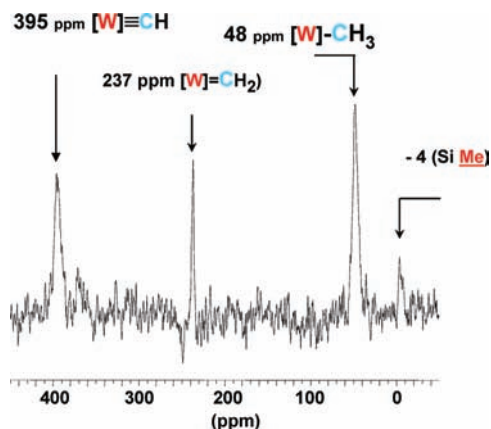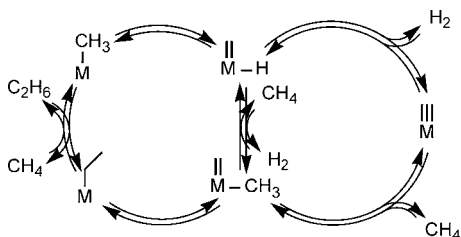
FIGURE 12. Formation of W-methylidyne, -methylidene, and -methyl as well as silicon-methyl upon reaction of methane with tungsten hydride supported on silica−alumina at 250 °C.

SCHEME 17. Proposed Mechanism for the Nonoxidative Coupling of Methane (M = Ta, W)

The postulated mechanism involves the formation of tungsten-methylene-hydride as the key intermediate as in most of the reactions observed in the area of alkane metathesis (Scheme 17). However, in the particular case of methane, the following step is C−H bond activation on the hydride via σ-bond metathesis with the formation of a tungsten-methyl-methylidene. A *cis* migration of the methyl to the methylidene occurs, affording the formation of the C−C bond as already observed on a corresponding model tantalum complex.[32] Then the cleavage of the resulting tungsten-ethyl by methane would take place. Considering this whole process, it is difficult to know which is the rate determining step. Regarding reversible deactivation, one can assume that it is related to the formation of a carbyne. Irreversible deactivation is likely to involve methyl transfer to the support.

Cross Metathesis between Toluene and Ethane

Ethylbenzene can be prepared by cross metathesis between toluene and ethane, catalyzed by (≡SiO)$_2$TaH, according to (eq 9):[49]

$$C_6H_5 - CH_3 + CH_3 - CH_3 \rightarrow C_6H_5 - C_2H_5 + CH_4 \quad (9)$$
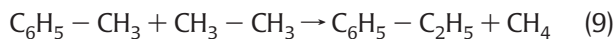
Ethylbenzene formation is indeed observed (batch reactor at 150 °C and then 200 °C), but also xylenes are produced.
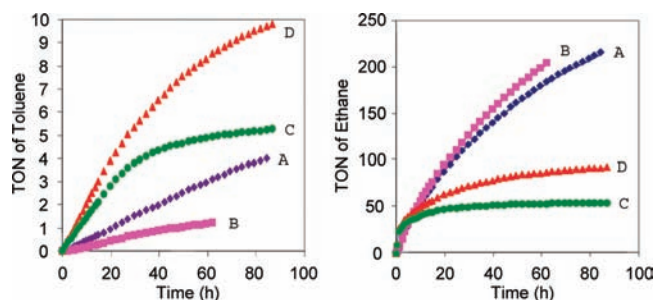

FIGURE 13. Toluene and ethane pressure effect on their TON during their crossed metathesis reaction at 250 °C; (≡SiO)$_2$TaH **1a** (400 mg); ethane/toluene (bar/Torr): (A) 10/28, (B) 25/28, (C) 10/310, (D) 25/540.

Formation of ethylbenzene and xylene implies initial activations of sp^{3}C−H bonds on the methyl group or sp^{2}C−H bonds of the aromatic ring, respectively. Then a methyl group should be transferred from an ethane molecule to a resulting Ta-benzyl or Ta-methylphenyl to produce accordingly ethylbenzene or xylenes. GC/MS analysis confirmed the occurrence of such a process when starting with ^{13}C monolabeled toluene (eq 10):
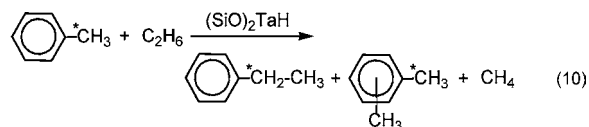
In a continuous flow reactor, formation of ethylbenzene is catalytic, but the reaction competes with conventional ethane metathesis which produces methane, propane, and butanes. Best results have been obtained under the following conditions: 25 bar of ethane and 540 Torr of toluene at 250 °C, ensuring a turnover number (TON) of 10 in toluene (Figure 13).

The mechanism of ethylbenzene formation is simply deduced from the alkane metathesis one. In contrast, formation of xylenes very likely involves the insertion of a methylene fragment into a σ-aryl bond in the same way as the insertion of a methylene unit into a tantalum methyl bond in the nonoxidative coupling of methane to ethane and hydrogen:
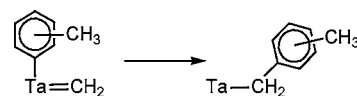
Concluding Remarks

Alkane metathesis opens up an almost unexplored area of chemistry which is crucial for the best utilization of alkanes and natural gas. This is an important domain not only for energy but also for the environment. The fact that methane can be coupled to form ethane and hydrogen is also essential, since it indicates that, *in fine*, methane can be transformed into higher homologues. We

are just at the beginning of a fascinating domain where chemists from various horizons are trying to develop this unexplored area. Numerous applications for alkane metathesis involving petrochemicals and fuels can be envisaged.

Supporting Information Available. Figures S1 and S2 related, respectively, to metathesis of 2-methylpropene and homologation of ethylene. This material is available free of charge via the Internet at http://pubs.acs.org.

BIOGRAPHICAL INFORMATION

Jean Marie Basset currently serves as scientific director of the school of Chemistry, Physics and Electronics at the University of Lyon in France. He was appointed research Director at the Centre National de la Recherche Scientifique (CNRS) in 1987, and funded his laboratory of Surface Organometallic Chemistry that he has directed since 1994. Dr. Basset also founded the consortium, "Actane," on alkane activation as well as the European Network of Excellence: Integrated Design of Catalytic Nanomaterials for a Sustainable Production (IDECAT) which includes 40 laboratories and 20 companies. Distinguished author of over 450 journal and conference papers, Dr. Basset's research interests include the relationship between homogeneous and heterogeneous catalysis, and the synthesis of single-site catalysts in various fields of chemistry, petroleum, and polymers. He is the recipient of several international and national awards, and is Doctor *Honoris Causa* of several universities.

Christophe Copéret got his Ph.D. degree in 1996 at Purdue University under the supervision of Prof. Ei-ichi Negishi, with the main focus on Pd-catalyzed carbonylative cyclizations. Then he went to the *Scripps Research Institute* to work with Prof. K. Barry Sharpless on the development of selective oxidation methods. He then accepted a full-time position at CNRS in the Laboratory of Surface Organometallic Chemistry at ESCPE Lyon (France) where he now teaches several courses on organometallic chemistry and catalysis, and leads a research group of several students. Their current research interest is focused on finding new reactivities through site isolation (development of materials and single-site heterogeneous catalysts).

Daravong Soulivong worked under the supervision of Dr. Dominique Matt and got his Ph.D. at the University of Strasbourg (France) in 1996. Then he joined the group of Frank J. Feher at the University of California Irvine. He came back to France and joined the Laboratory of Surface Organometallic Chemistry at ESCPE Lyon (France).

Mostafa Taoufik worked in the Institut de Recherches sur la Catalyse and the Laboratory of Surface Organometallic Chemistry at ESCPE Lyon (France) where he got his Ph.D., in 1996, under the supervision of Dr Catherine Santini. Then he got a position as Senior Research Associate at CNRS (Centre National de la Recherche Scientifique) where he initiated and developed several scientific themes; among his scientific interests are the activation of nitrogen, alkanes, and olefins.

Jean Thivolle Cazat worked in the Institut de Recherches sur la Catalyse and got his Ph.D. in 1980 at the University of Lyon (France). He spent 1 year as a postdoc fellow in the group of Yves Chauvin of Institut Français du Pétrole (IFP - Rueil-Malmaison) in 1986. Then he joined the Laboratory of Surface Organometallic Chemistry and discovered the alkane metathesis reaction; he keeps a scientific interest in alkane activation with single-site heterogeneous catalysts.

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