Surface Organometallic Chemistry

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Alkane Metathesis Catalyzed by a Well-Defined Silica-Supported Mo Imido Alkylidene Complex: [(≡SiO)Mo(=NAr)(=CH*t*Bu)(CH$_2$*t*Bu)]**

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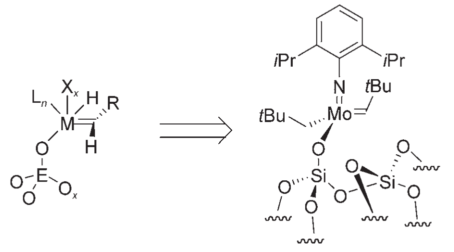
The conversion of alkanes at low temperatures has gained interest over the past few years because more efficient routes to chemicals are necessary to optimize oil resources.[1,2] Within this context, we reported in 1997, the reaction of alkane metathesis, which catalytically transforms a given alkane into its lower and higher homologues using a silica-supported tantalum hydride[3] prepared by surface organometallic chemistry (SOMC). Based on kinetic and structure–reactivity relationship studies, we have shown that π-bond metathesis (interaction of an olefin and a carbene) was the key carbon–carbon bond-cleavage and formation process and that alkylidene hydrides are critical intermediates (Scheme 1).[4–7] Other systems have been reported[8,9] that are based on a combination of dehydrogenation/hydrogenation and olefin metathesis catalysts, with the most recent example[9] using a mixture of homogenous catalysts.[10–13] The best catalysts prepared by SOMC[14] are based on very simple monoatomic systems: hydrides, alkyl alkylidenes, or alkyl alkylidynes of Group 5 or 6 metals supported on oxides. Although introducing ligands that play a key role in controlling the reactivity and the selectivity of catalysts has been a long-term goal, all ancillary ligands introduced so far (alkylidyne, pentamethylcyclopentadiene (Cp*), Cl) have been detrimental to catalyst performances.[5] Herein, we report that a well-defined silica-supported alkyl alkylidene/Mo complex containing an imido ligand (**1a**)[15] is a good catalyst precursor for alkane metathesis (Scheme 1).[5,6]



Active site **1a**

Scheme 1. Proposed active sites in alkane metathesis and possible catalyst precursor **1a**.

When propane (540 equiv) is brought into contact with **1a** at 150 °C in a batch reactor, it is converted into mainly ethane (56.1 %), butane (35.3 %), and small quantities of methane (0.1 %), isobutane (2.7 %), and pentanes (5.9 %). These selectivities are constant over time (see the Supporting Information), and noteworthy the selectivity in methane, probably produced by hydrogenolysis,[16] is low as already observed for other Group 6 supported systems.[7,17] Moreover, the turnover frequency is constant for 40 h (ca. 1 TON h^{-1}; TON = turnover number), and then there is a reproducible decrease of conversion (Table 1 and Figure 1). Note that this well-defined catalyst precursor achieves about the same TON (55) in 120 h as the original tantalum hydride catalyst supported on silica (TON = 60) despite the presence of ancillary ligands.

Besides propane metathesis products, 2,2-dimethylpropane (*t*BuCH$_2$–H; 0.82 equiv), 2,2-dimethylbutane (*t*BuCH$_2$–Me; 0.34 equiv), and 2,2-dimethylpentane (*t*BuCH$_2$–Et; 0.10 equiv) are formed within 120 h (Table 2), whereas no *t*BuCH$_2$–Pr is detected (< 0.01 % if any). Firstly, 2,2-dimethylpropane is probably formed by exchange of the neopentyl by a propyl ligand, either directly through σ-bond metathesis or in two steps through C–H activation on the neopentylidene unit followed by a decomposition of the penta-coordinated complex through an α-H abstraction to regenerate an alkylidene alkyl/Mo center (**1b**, R = Et, R′ = *t*Bu;

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Table 1: TONs and selectivities in the metathesis of various alkanes catalyzed by **1a** in a batch reactor after 120 h.

Alkane	TON[a]	Alkane selectivity[b]						
		C_1	C_2	C_3	C_4[c]	C_5[c]	C_6[d]	C_7[d]
ethane	2 (0.4)	35.9	n.a.[e]	62.0	1.5/0.8	n.o.[f]	n.o.	n.o.
propane	55 (9.9)	0.1	56.1	n.a.	35.3/2.7	5.2/0.7	0.6	<0.1
butane	90 (17.7)	<0.1	11.1	56.5	n.a./0.5	21.7/0.4	7.7	2.0
isobutane	3 (0.7)	1.0	35.9	17.1	7.0/n.a.	16.4/n.o	22.8	n.o.

[a] TON is expressed in mol of alkane transformed per mol of Mo. The values in parentheses are conversions. [b] The selectivities are defined as the amount of product *i* over the total amount of products (they do not significantly change with time and conversion). [c] Linear/branched alkanes. [d] Selectivity for the sum of all isomers. [e] n.a. = not applicable. [f] n.o. = not observed (<0.01 % if any).

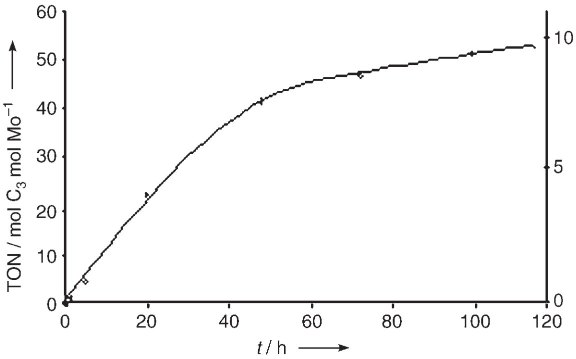


Figure 1. Turnovers obtained (expressed in mol of propane converted per mol of Mo) during the metathesis of propane catalyzed by **1a** in a batch reactor.

Scheme 2). Secondly, 2,2-dimethylbutane and 2,2-dimethylpentane are probably obtained through cross-metathesis of the neopentylidene ligand attached to the Mo center and a propene moiety, which results from β-H transfer on the propyl chain in **1b**, followed by metathesis and subsequent similar reverse steps (insertion of the olefin into a metal hydride and exchange of the ligand by successive C–H activation on the carbene ligand and α-H abstraction). Note that the alkane cross-metathesis products are obtained in a 3.4:1 ratio, which is very close to the ratio of olefin cross-metathesis products 3,3-dimethylbutene and (*E*)-4,4-dimethyl-2-pentene, obtained during the metathesis of propene on **1a** (that is, 2.7:1), and this is consistent with the proposed elementary steps, and especially with olefin metathesis being the key carbon–carbon bond-formation step.[15]

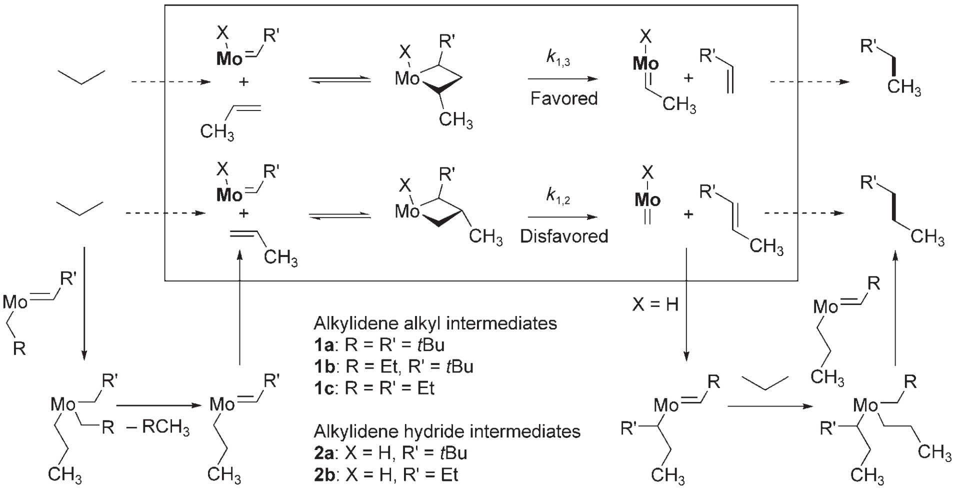
Table 2: Cross-metathesis products in the metathesis of various alkanes catalyzed by **1** in a batch reactor after 120 h.[a]

Alkane	$t\mathrm{BuCH_2H}$	$t\mathrm{BuCH_2Me}$	$t\mathrm{BuCH_2Et}$	$t\mathrm{BuCH_2Pr}$	$t\mathrm{BuCH_2}i\mathrm{Pr}$
ethane	1.01	0.35	n.o.[b]	n.o.	n.o.
propane	0.82	0.34	0.10	n.o.	n.o.
butane	0.88	0.10	0.14	0.05	n.o.
isobutane	0.83	0.20	0.04	n.o.	n.o.

[a] The values given are equivalents of alkanes per Mo. [b] n.o. = not observed (<0.01 % if any).

The selectivity of initiation products can therefore be understood on the basis of the model developed for olefin metathesis, which is based on the minimization of steric interactions in the metalla-cyclobutane intermediates (or in their formation);[18] that is, by the relative position of the substituents: typically substituents in the [1,3]-positions of the metalla-cyclobutane intermediate generate less steric hindrance than in the [1,2]-positions (Scheme 2). This model is also consistent with the observed product selectivity and explains the greater selectivity of butane relative to that of pentane when starting from **1c** (R = R′ = Et) and when the cross-metathesis of the resulting propagating alkylidene hydride intermediate **2b** (X = H, R = Et) and propene is involved. Lower alkane homologues are formed using the same elementary steps, that is, by exchanging ligands through C–H activation on carbene intermediates and extrusion processes (α-H abstraction). Although this mechanism is based on a single-site mechanism, it is also possible to involve two sites, one that generates the olefin and the other that carries out the metathesis.

Butane is also converted efficiently into its lower and higher homologues (TON = 90 in 120 h) and its cross-meta-



Scheme 2. Metathesis of propane catalyzed by **1**.

thesis products (Table 1 and Table 2), whereas ethane is not. This finding is in contrast to that observed for Ta-based catalysts, for which an equimolar mixture of methane and propane is obtained from ethane; however, it consistent with the absence of methane in the metathesis of other alkanes (propane and butane). Finally, **1a** does not catalyze the metathesis of 2-methylpropane, a branched alkane, under the same reaction conditions, despite the presence of a reasonable amount of one of the initiation products. Therefore, the propagation step is probably hindered by the olefin-metathesis step, which would require a disfavored [2+2] cycloaddition between a disubstituted carbene and a disubstituted olefin.

In conclusion, the well-defined Mo/imido surface complex **1a** belongs to a new type of silica-supported catalyst precursor for the metathesis of linear alkanes at moderate temperatures (150 °C). The product selectivity clearly shows that the products are formed by π-bond metathesis as a key carbon–carbon bond-breaking and -forming step. Nonetheless, this system involves a single metal with dual properties in contrast to the Goldman–Brookhart system, which relies on mixing two catalysts. More importantly, this result shows for the first time that ancillary ligands, an imido group in this case, can be used. Further development of alkane metathesis catalysts through the investigation of structure–reactivity relationships are currently underway.

Experimental Section

General procedure: All experiments were carried out under dry oxygen-free Ar using either high-vacuum lines (1.34 Pa) or glovebox techniques. $[(\equiv\text{SiO})\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$ (**1a**) was obtained according to a previously reported procedure:[15] $[\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$[19] (Ar = 2,6-diisopropylphenyl) was impregnated on silica that had been partially dehydroxylated at 700 °C. The alkanes were dried and deoxygenated before use by passing them through a mixture of freshly regenerated molecular sieves (3 Å) and R-3-15 catalysts (BASF).

Procedure for the metathesis reaction of alkanes in a batch reactor: A mixture of catalyst precursor **1a** (13.5 μmol) and dry alkane (540–580 Torr, 500–540 equiv) were heated at 150 °C in batch reactor of known volume (220 mL). Aliquots were drawn and analyzed by gas chromatography over time (HP5890 apparatus, $\text{KCl/Al}_2\text{O}_3$ on a fused-silica column, 50 m × 0.32 mm) and the products identified by GC–mass-spectrometric analysis. The selectivities S_i are defined as the amount of product *i* over the total amount of products.

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