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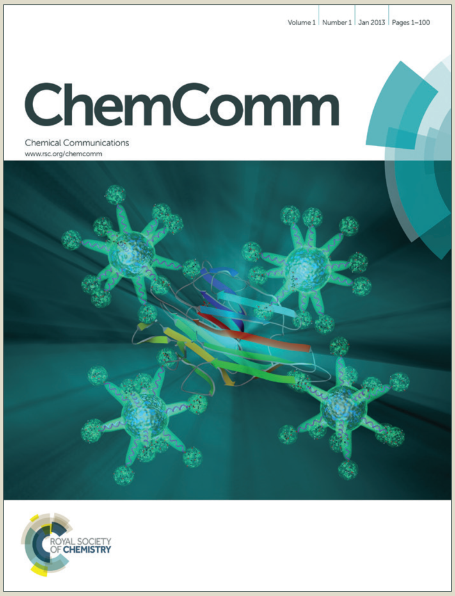

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Simple addition of silica to an alkane solution of Wilkinson WMe_6 or Schrock W alkylidyne complex give active complex for saturated and unsaturated hydrocarbons metathesis

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Addition of partially dehydroxylated silica (PDS) to a solution of the Wilkinson WMe_6 as well as the Schrock W neopentilidyne tris neopentyl complex catalyzes linear or cyclic alkanes to produce respectively a distribution of linear alkanes from methane up to triacontane or a mixture of cyclic and macrocyclic hydrocarbons. This single catalytic system transforms also linear α-olefins into higher and lower homologues *via* isomerization/metathesis mechanism (ISOMET). This complex is also efficient towards functionalized olefins. Unsaturated fatty acid esters (FAEs) are converted into diesters corresponding to self-metathesis products.

Introduction

Conversion of linear or cyclic alkanes to higher and lower homologues, namely alkane metathesis, is a promising valuable transformation in petrochemical industry.[1] Disproportionation of hydrocarbons was initially discovered by Burnett and Hughes employing two supported heterogeneous catalytic systems operating at high temperature.[2] Later, it was found that silica supported tantalum polyhydrides and silica supported group VI polyhydrides, prepared by surface organometallic chemistry are efficient multifunctional single metal pre-catalysts for propane metathesis.[3] Inspired by the early work in the dual catalyst system, Goldman and Brookhart reported a total homogeneous tandem catalytic system for this transformation.[4] This catalytic process employs typically an iridium ligated pincer complex, for hydrogenation/dehydrogenation reactions, associated with a molybdenum Schrock-type catalyst for olefin metathesis.[4] They found that either linear alkanes[4] or cyclic alkanes[5] are catalyzed into the corresponding lower and higher homologues. Following our surface organometallic strategy, the preparation and characterization of homoleptic complex WMe_6 supported on silica, $[(\equiv Si\text{-}O\text{-})WMe_5]$ **1** was recently disclosed in our group.[6] **1** was found to be an active efficient pre-catalyst for propane metathesis,[6] higher molecular weight linear alkanes[7] and cycloalkane metathesis.[8] Herein we describe that it is not necessary to graft the organometallic complex and modify its coordination sphere by an appropriate treatment (thermal and/or under hydrogen) before doing catalysis: a simple addition of the precursor in the reaction medium containing the alkane and the addition of silica by a simple impregnation protocol is enough to observe alkane and cycloalkane metathesis (**Chart 1**). This catalytic procedure is easier to implement than the existing well defined single supported catalytic or dual catalytic systems in an industrial perspective. In this work, we report a straightforward procedure for cyclic and linear alkane metathesis transformation employing solely a fully alkylated complex, for instance Wilkinson d^0 WMe_6 or Schrock type d^0 W metal alkylidyne complex impregnated initially on PDS. The catalytic activity of such heterogeneous systems with unfunctionalized and functionalized olefins is also reported.

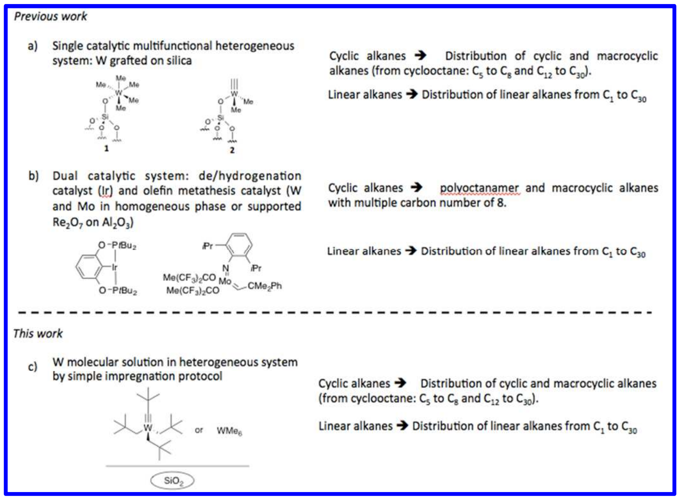

Chart 1: Conversion of cyclic or linear alkanes towards the corresponding higher and lower homologues by (a) single multifunctional heterogeneous catalytic system (grafted initially on oxide); (b) dual homogeneous or heterogeneous catalytic system; (c) single multifunctional heterogeneous catalytic system (initial adsorption on the support).

We started our study by synthesizing a solution of WMe_6 in *n*-decane, (0.00197 mmol/mL) following literature procedure.[6] Running the catalytic reaction with exclusively this molecular organometallic solution at 150°C for 2 days period of time showed no apparent alkane metathesis products. However, an initial addition of partially dehydroxylated silica (pretreated at 700°C) (PDS_{700}) into this organometallic solution under the same reaction conditions led to a mixture of lower and higher alkanes (**Figure 1**). Moreover, employing a molecular solution of WMe_6 in cyclooctane (0.046 mmol/mL) in the presence of an initial amount of PDS_{700} produced also a distribution of higher molecular weight macrocyclic alkanes along with lower molecular weight cyclic alkanes resulting from ring contraction. In both cases (linear and cyclic alkanes metathesis), the alkane products distribution is similar to the one observed while starting with pre-catalyst **1** (see **Figure 1**, for *n*-decane metathesis, see Figure S1 for cyclooctane metathesis). These results emphasize the crucial role of the oxide support towards an active alkane metathesis system. In fact, it is well-known in homogeneous system that these electron-deficient W complexes decompose into inactive species through a dimerization processes.[9] Thus, addition of silica would prevent such processes.

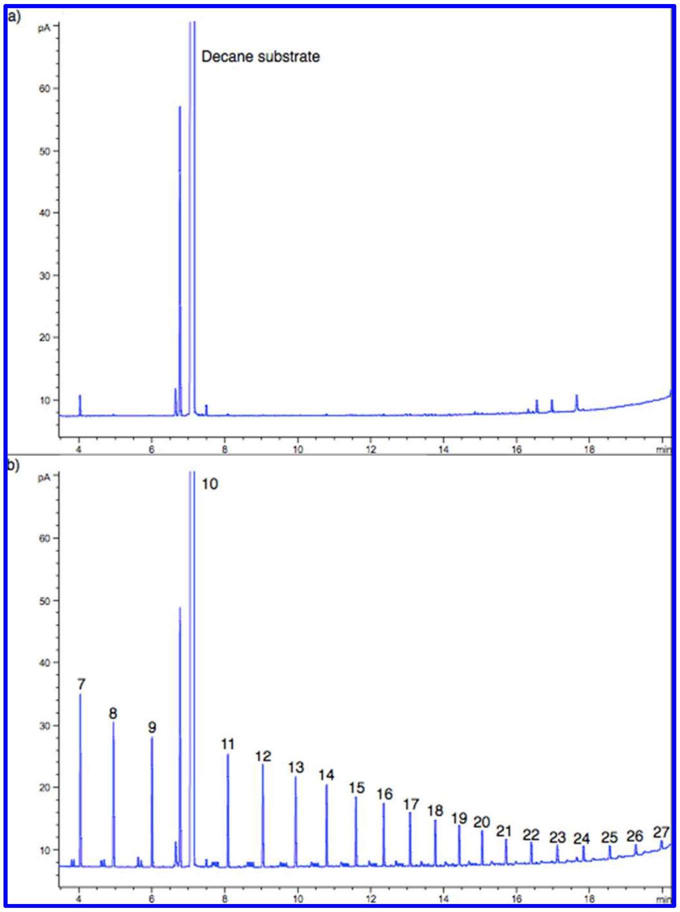

Figure 1: GC chromatogram of a) *n*-decane before reaction and b) *n*-decane metathesis products, reaction catalyzed by a molecular solution of $[WMe_6]$ in decane (0.98 µmol, 1.97 µmol/mL), *n*-decane (0.5 mL, 2.57 mmol), PDS_{700} (50 mg), 500 rpm, 150°C, 2 days.

We earlier found that **1** is thermally transformed into its corresponding W(methyl)methylidyne species **2** at 150°C by extensive solid state NMR studies (see Scheme S2).[6] Moreover, **2** was found to be an active catalyst precursor for the propane[6] and cyclooctane metathesis[8] as well as for alkyne cyclotrimerization.[10] These previous works highlighted that a silica supported W-carbyne moiety associated with σ-ligand is crucial for the transformation of alkane metathesis to occur. Thus, we envisage that employing commercial available Schrock type d^0 W $(tBuCH_2)_3W{\equiv}CCMe_3$[11] would be a better alternative organometallic precursor instead of highly volatile unstable homoleptic WMe_6.[12] The former possess neopentyl/neopentylidyne groups, which could form a W bis-alkylidene through α-proton migration observed in homogeneous systems.[13,14] Such transformation has also been experimentally observed for supported W(methyl)methylidyne **2** in the presence of either an olefin or PMe_3.[15] Thus, to validate this hypothesis we initially prepared silica supported W Schrock complex by stirring $(tBuCH_2)_3W{\equiv}CCMe_3$ with PDS_{700}.[16] The metathesis activity of this silica supported complex $\equiv Si\text{-}O\text{-}W(\equiv CCMe_3)(CH_2tBu)_2$ (**3**) was tested with cyclooctane and *n*-decane at 150°C, over 3 days. Surprisingly, the results showed even better activity than pre-catalyst **1** (see Figure S3). After 72 h, an overall turnover number (TON) of 225 is obtained for cyclooctane metathesis catalyzed with **3** compared to 44 for **1**. The product distribution showed shorter cyclic alkanes (cyclopentane, cyclohexane and cycloheptane) for pre-catalyst **3**. *n*-Decane is also transformed into metathesis products by **3** with TONs of 136 (see Figure S4). This value is closed to the one observed with catalyst **1**. Replacement of the tris(neopentyl)neopentylidyne W complex by the tris(*tert*-butoxy) $(tBuO)_3W{\equiv}CCMe_3$[17] derivative gave no apparent activity in the *n*-decane metathesis. These bulky alkoxides ligands are known to prevent the bimolecular decomposition of the catalyst but nevertheless they are ineffective for the alkane metathesis.[18] Encouraged by the activity observed with **3**, we envisaged employing a one-pot protocol for this catalytic procedure. A molecular solution of the Schrock complex $(tBuCH_2)_3W{\equiv}CCMe_3$ (19.8 µmol) in cyclooctane solution (3.72 mmol, 0.5 mL) (W:alkane ratio of 1:188) and silica pretreated at 700°C (50 mg) gave gratifyingly a distribution of cyclic alkanes; see **Figures 2** and **S5** ("@" denotes that W complex was not initially grafted on metal oxide but added in a one pot procedure).

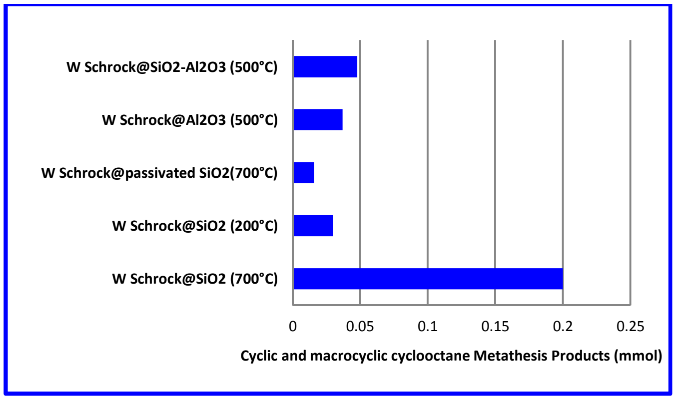

Figure 2: Cyclooctane metathesis catalyzed by a one-pot procedure with different supports. Reaction conditions: batch reactor, $(tBuCH_2)_3W{\equiv}CCMe_3$ (8.9 mg, 19.8 µmol), cyclooctane (0.5 mL, 3.72 mmol) and surface oxide (50 mg), 500 rpm, 150°C, 72 h.

Substituting PDS_{700} with other oxides (50 mg) that were partially deshydroxylated under high vacuum (< 10^{-5} mbar) at different temperatures (such as silica pretreated at 200°C, silica-alumina and γ-alumina pretreated at 500°C) produce similarly a distribution of cyclic alkanes (**Figure 2**). In all these catalytic runs regardless to the nature of the oxide material, cyclooctane was transformed into a mixture of cyclic and macrocyclic alkanes albeit in lower activity than the initial PDS$_{700}$. (It should be noted that the reaction conditions were not optimized for different oxide materials). The observed activity for γ-alumina oxide is not surprising because it has been previously shown that γ-alumina supported (tBuCH$_2$)$_3$W≡CCMe$_3$ could catalyze the propane metathesis.[19] To account for this activity, it was postulated that γ-alumina is responsible for the propane dehydrogenation step towards propene.[20] However, these findings are not consistent with our experimental studies because **3** is also active for cyclooctane metathesis. Rather, olefin intermediates should be formed through the classical *β*-H elimination.[21] The use of passivated silica support in which all proton silanols groups have been transformed into their corresponding methylated supported species showed the lowest catalytic activity for the cyclooctane metathesis. This result strongly supports that a W Schrock complex physisorbed on the surface is not sufficient to provide comparable catalytic activity but rather the organometallic precursor should be chemisorbed or grafted *in situ*. This implies that forming isolated Si-O-W linkages is necessary to achieve catalytic performance because it would lead to a supported organometallic species spaced apart from another W metal center.[22] Comparing the catalytic activity between **3** and the one pot procedure under similar W:cyclooctane molar ratio at 150°C showed better activity for **3**. Obviously with species **3**, bimolecular decomposition of the W neopentylidene complex is virtually non-existent on the oxide surface.[23] Additionally, an improved catalytic activity of cyclooctane metathesis was observed while the reaction mixture was stirred at elevated temperatures (200°C) producing a higher amount of cyclic alkane products (1.96 mmol compared to 0.2 mmol) under equal W:alkane molar ratio (see Figure S6).

Next, this catalytic procedure was extended to linear alkanes. *n*-decane was converted into lower and higher homologues giving a similar distribution than the tandem dual catalytic system using (POCOP)Ir (POCOP= resorcinolbisphosphinite) and Mo(NAr)(=CHCMe$_2$Ph)(ORF$_6$)$_2$ complex (Ar = (2,4,6)-*i*-PrC$_6$H$_2$, R$_{F6}$ =O(CF$_3$)$_2$CH$_3$).[4]

These observations are in contrast with the cyclooctane metathesis products in which the two different catalytic systems (single multifunctional and dual catalytic system) differ dramatically (see Figure S7). Enhanced activity with this one pot protocol was also observed when the catalytic run is carried out at 200°C for 3 days (**Figure 3**).

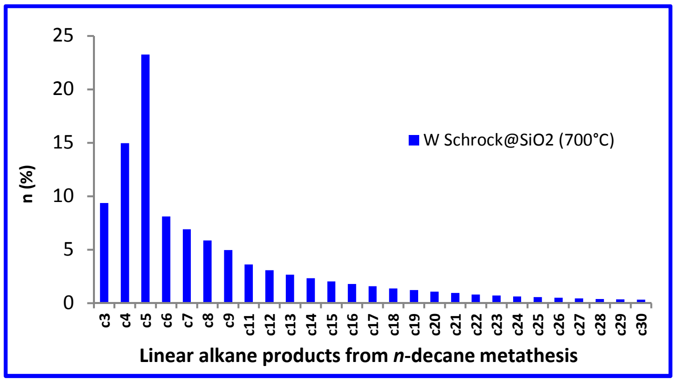

Figure 3: *n*-decane metathesis products catalyzed by W Schrock@SiO$_2$ Reaction conditions: batch reactor, (tBuCH$_2$)$_3$W≡CCMe$_3$ (8.9 mg, 19.8 μmol), *n*-decane (0.5 mL, 2.57 mmol) and SiO$_2$ (50 mg), 500 rpm, 200°C, 72 h.

To demonstrate the industrial potential of this catalytic procedure, we scaled up the reaction by a factor of 40. A solution of (tBuCH$_2$)$_3$W≡CCMe$_3$ (300 mg) in cyclooctane (20 mL) in the presence of partially dehydroxylated silica pre-treated at 700°C (2 g) was stirred and heated at 150°C for a five days period of time. A high selectivity in the formation of the C$_{16}$ cyclohexadecane was observed (> 76% of total macrocyclic alkane products). To verify the reproducibility of these results, this catalytic run was repeated twice and gave similar results. This observed high selectivity for cyclohexadecane was attributed to an initial low conversion of cyclooctane. Indeed, previous work on kinetic studies of cyclooctane metathesis revealed that during the initial phase of the process (at low conversion), the dimer and the trimer macrocyclic alkane products are the predominant products (see **Figure 4**).[8] Such high selectivity of the dimer (C$_{16}$) was observed at 12 hours when running a catalytic run of cyclooctane (0.5 mL) catalyzed by [(≡Si-O-)WMe$_5$] **1**. We envisage that the mechanism of such molecular species adsorbed on solid supports should be similar to the one with defined catalyst **3.** Thus, the alkane products formation should involve a bis-carbene intermediate in an elementary step as previously described.[7]

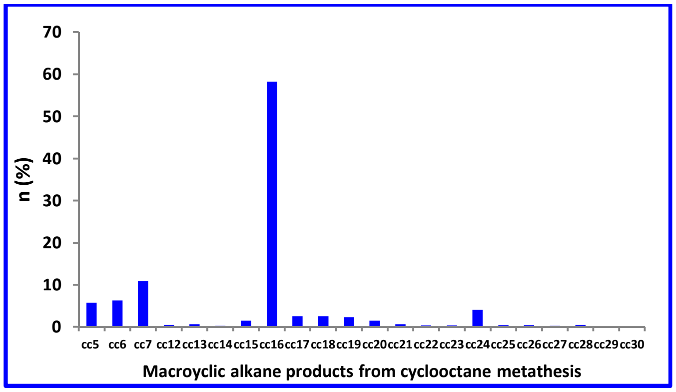

Figure 4: Cyclooctane metathesis products catalyzed by W Schrock@SiO$_{2(700)}$. Reaction conditions: batch reactor, (tBuCH$_2$)$_3$W≡CCMe$_3$ (300 mg, 667 μmol), cyclooctane (20 mL, 148.8 mmol) and SiO$_2$ (2 g), 500 rpm, 150°C, 5 days. Formation of cyclic (C$_5$-C$_7$) and macrocyclic C$_{12}$-C$_{30}$ alkanes.

Finally, we found that this one pot protocol with Schrock type d^0 W metal alkylidyne complex is also active for the olefin metathesis. Indeed, 1-decene was converted into an equilibrium mixture of C$_2$-C$_{30}$ terminal and internal olefins by successive isomerization and olefin metathesis (ISOMET), previously described for **1** (see Figure S8). **3** catalyzes also the ISOMET reaction of 1-decene, **Figure 5** and Figure S9. This would suggest that metal alkylidyne solution in the presence of PDS$_{700}$ reacts with olefins through likely a W bis-carbene intermediate.[16, 24, 25] As it is generally assumed that high oxidation state W alkylidyne without pendent alkyl groups catalyze alkyne metathesis and not olefin metathesis,[26-28] our result demonstrates thus the importance of the alkyl groups in the W coordination sphere. Besides, replacing 1-decene with 1-decyne led predominantly to substituted tri-alkyl benzene products with tetra substituted benzene from a cylotrimerization reaction.[10] The formation of the latter would suggest the formation of 5-octadecyne resulting from the metathesis of 1-decyne as previously described (see **scheme S10**).

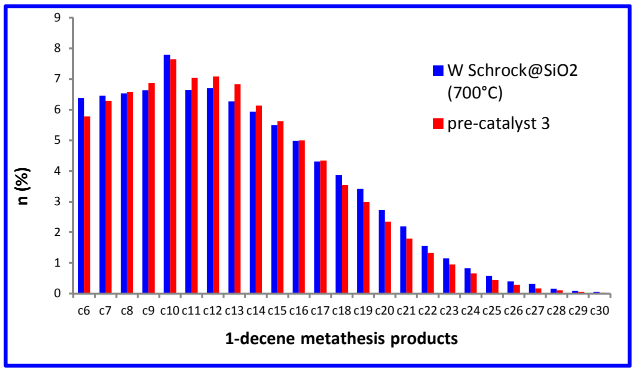

Figure 5: 1-decene metathesis products catalyzed by W Schrock@SiO$_2$ or **3**. Reaction conditions: batch reactor, (tBuCH$_2$)$_3$W≡CCMe$_3$ (8.9 mg, 19.8 µmol) and SiO$_2$ (50 mg) or **3** (50 mg, 3.6 µmol, W loading: 3.36%), 1-decene (0.5 mL, 2.64 mmol), 500 rpm, 150°C, 72 h.

This one pot protocol was also efficient in converting fatty acid esters (FAE) into the corresponding diesters. For instance, ethyl undecylenate and ethyl oleate produced the corresponding self-metathesis products. Interestingly, for ethyl oleate, the initial products of the cross metathesis between the neopentylidene W ligands and FAE, neopentyl olefins were observed (in green, see Figure S11). These results are in agreement with the tertiary alkane products observed from the metathesis of propane in the presence of silica supported Ta, Re and Mo neopentylidene precatalysts.[29] The formation of these olefins strongly supports a W bis-carbene intermediate from a silica supported W alkyl/alkylidyne species.

This work emphasizes the W single multifunctional character on metal oxide of this system and paves the way to the development of novel family of catalysts for the alkane and olefin metathesis reaction. Future studies would aim to modify the W coordination sphere (direct alkylation from WCl$_6$ for example) to enhance the catalytic activity of such system. Following the successful work demonstrated by the silica immobilization of second generation Hoveyda-Grubbs Ru catalyst,[30-33] we also intend to study the feasibility of such catalytic protocol in a continuous reactor.

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Notes and references

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Detailed experimental procedures, alkane products distribution diagrams can be found in this supplementary information.

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