Selective and unexpected transformations of 2-methylpropane to 2,3-dimethylbutane and 2-methylpropene to 2,3-dimethylbutene catalyzed by an alumina-supported tungsten hydride†

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Received (in Cambridge, UK) 24th December 2008, Accepted 30th January 2009
First published as an Advance Article on the web 16th March 2009
DOI: 10.1039/b823226a

2-Methylpropane and 2-methylpropene, in the presence of the $W(H)_3/Al_2O_3$ catalyst, are unexpectedly transformed to 2,3-dimethylbutane and 2,3-dimethylbutenes, respectively, with high selectivity; in case of 2-methylpropane, this reaction represents the first example of the transfer of two carbons in alkane metathesis.

The transformation of lower alkanes into higher homologues remains a great challenge in chemistry, in particular for branched alkanes in view of fuel needs.[1–3] Using a "single site approach", we reported in 1997 the discovery of a new reaction, the alkane metathesis where a highly electrophilic tantalum hydride supported on silica, $[(\equiv SiO)_2Ta–H]$ **1a**, could catalytically transform at moderate temperatures any light alkane into its lower and higher homologues.[2] This reaction consists mainly in the transfer of a single carbon from one chain to another, by both cleavage and formation of C–H and C–C bonds (Scheme 1).

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

Scheme 1

Typically propane gives mainly ethane (45–50%) and butanes (30–35%) along with methane and higher C_5+ alkanes. Ethylbenzene and methane can also be obtained by cross-metathesis between toluene and ethane.[4] In all experiments carried out so far, the selectivity for the formation of the C_{n+1} product proved to be higher than that of the C_{n+2} one, in agreement with the previously proposed mechanism.[5] In fact, kinetic studies on propane metathesis, carried out at extremely low contact time in a continuous flow reactor, revealed the primary products of the reaction, namely olefins and H_2. 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) 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 olefins on the metal-hydride.[5]

Recently, we have developed a $W(H)_3/Al_2O_{3-500}$ catalyst, **1b**, giving higher turnover numbers (TON) and having a much greater stability than Ta hydrides.[6–9] The peculiarity of both systems lies in the fact that Ta or W hydrides are "multifunctional–single site" catalysts (alkane dehydrogenation, olefin metathesis and olefin hydrogenation). Herein, we report that 2-methylpropane, in the presence of the $W(H)_3/Al_2O_{3-500}$ catalyst, **1b**, is unexpectedly transformed to 2,3-dimethylbutane (2,3-DMB) with a high selectivity.[10] This metathesis reaction of an iso-C_n paraffin leading to an iso-C_{n+2} product instead of an iso-C_{n+1}, involves formally the selective transfer of two carbons, which is unexpected in view of the classical mechanism previously proposed for this reaction (see ESI Scheme S1†).[5] Interestingly, 2,3-DMB exhibits the highest octane number (RON = 104) among the hexane isomers.[11] Similarly, the $W(H)_3/Al_2O_{3-500}$ catalyst, **1b**, also unexpectedly transforms 2-methylpropene to 2,3-dimethylbutenes (2,3-$DMB^=$) with a good selectivity which is the first case of productive metathesis of 2-methylpropene[12,13] and again fits with the role of 2-methylpropene as a primary product for the metathesis of 2-methylpropane.

Typically, when 2-methylpropane was passed over the alumina-supported tungsten hydride, $W(H)_3/Al_2O_{3-500}$, **1b**, ($P_{i\text{-}C4H10}$ = 1 bar, T = 150 °C, flow rate 4 mL min^{-1} or volume hourly space velocity (VHSV) 260 h^{-1}) its conversion reached a maximum at 8% and approximately 37 TON were achieved over 43 h (Fig. 1(a)). At the pseudo-steady state, the observed selectivities in 2-methylpropane metathesis are 2,3-DMB (41.7%), ethane (41.3%), 2-methylbutane (5.3%), propane (5.2%), methane (1.5%), heptanes (1.0%) and 2-methylpropene (3.1%) (Fig. 1(b)). The higher homologues can be ordered as follows: $C_{n+2} \gg C_{n+1} > C_{n+3}$. These results are quite different from those obtained with $W(H)_3/Al_2O_{3-500}$ in metathesis of linear alkanes, where the selectivities always follow the order: $C_{n+1} > C_{n+2} \gg C_{n+3}$.[6–8] Interestingly the ratio of selectivities of 2,3-DMB/ethane and 2-methylbutane/propane are close to unity.

2-Methylpropene was observed (up to 3.1%) among the products of 2-methylpropane metathesis and therefore, its metathesis was also checked over **1b** in a continuous flow reactor ($P_{i\text{-}C4H8}$ = 1 bar, T = 150 °C, flow rate 4 mL min^{-1} or volume hourly space velocity (VHSV) 260 h^{-1}) (Fig. 2). The reaction presented an initial maximal conversion rate of 0.61 $mol_{i\text{-}C4H8}\ mol_W^{-1}\ min^{-1}$ before reaching a pseudo-plateau

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† Electronic supplementary information (ESI) available: Experimental details, Schemes S1 and S2. See DOI: 10.1039/b823226a

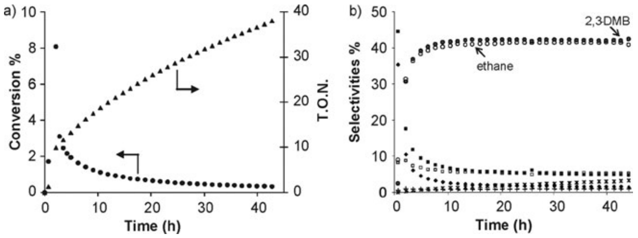


Fig. 1 Metathesis of 2-methylpropane catalyzed by $(W(H)_3/Al_2O_3$, **1b** (3.86 wt% W): (a) conversion of 2-methylpropane (●) and TON (▲); (b) selectivities: (◆) methane, (○) ethane, (■) propane; (*) 2-methylpropene; (□) 2-methylbutane; (●) 2,3-dimethylbutane (2,3-DMB); (+) 2,4-dimethylpentane; (–) octanes.

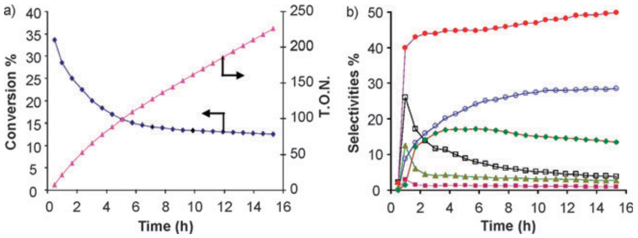
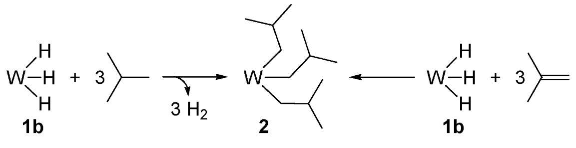


Fig. 2 Metathesis of 2-methylpropene catalyzed by $(W(H)_3/Al_2O_3$, **1b** (3.86 wt% W): (a) conversion of 2-methylpropene (◆) and TON (▲); (b) selectivities: (○) ethylene, (■) propene; (▲) 2-methylbutene; (□) neohexene, (●) 2,3-dimethylbutene (2,3-DMB$^{=}$); (◆) 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.

of 0.22 $mol_{i\text{-}C4H8}$ mol_W^{-1} min^{-1}, with an overall turnover number (TON) of 235 after 16 h (Fig. 2(a)). At the pseudo-steady state, the product selectivities were 2,3-dimethylbutenes 50%, ethylene 30%; 2,4,4-trimethylpentenes 12%, neohexene 9%, isopentene 3% and propene 1% (Fig. 2(b)).

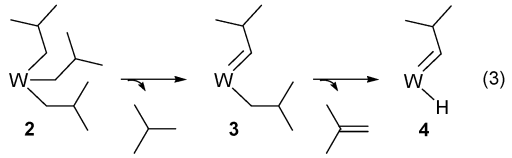
2,4,4-Trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene are likely formed by dimerisation of 2-methylpropene on the acidic sites of alumina dehydroxylated at 500 °C[13,14] while the presence of neohexene can be explained by a cross-metathesis between 2,4,4-trimethylpentenes and ethylene. In summary, whereas the metathesis of 2-methylpropene is usually known as a degenerate process with the classical olefin metathesis catalysts,[12,13] $W(H)_3/Al_2O_{3\text{–}500}$ also proves to be the first compound capable of catalyzing the productive self-metathesis of 2-methylpropene into 2,3-dimethylbutene. Interestingly, 2,3-dimethylbutene has the same carbon skeleton as the major product formed during the metathesis of 2-methylpropane *i.e.* 2,3-DMB. These observations confirm that 2-methylpropene is a primary product which leads to a specific mechanistic pathway for 2-methylpropane metathesis as explicated hereafter.

The initiation steps of both 2-methylpropane and 2-methylpropene, respectively by C–H bond activation or C═C double bond insertion in **1b** are expected to lead to the same tris(isobutyl)tungsten intermediate **2** (Scheme 2); in the first case hydrogen is also evolved which is likely consumed *via* hydrogenolysis of 2-methylpropane leading to the sharp initial peaks of methane and propane (Fig. 1(b)), as **1b** is known to catalyze such a reaction.[6–8]



Scheme 2

The trisisobutyl tungsten complex **2**, $[W(CH_2CH(CH_3)_2)_3]/Al_2O_{3\text{–}500}$, resulting from the initiation steps, can undergo an α-H transfer to form **3**, $[W(CH_2CH(CH_3)_2)({=}CHCH(CH_3)_2)]/Al_2O_{3\text{–}500}$, which further leads to the carbene-hydride **4**, $[W(H)({=}CHCH(CH_3)_2)]/Al_2O_{3\text{–}500}$ by β-H elimination (Scheme 3).[9]

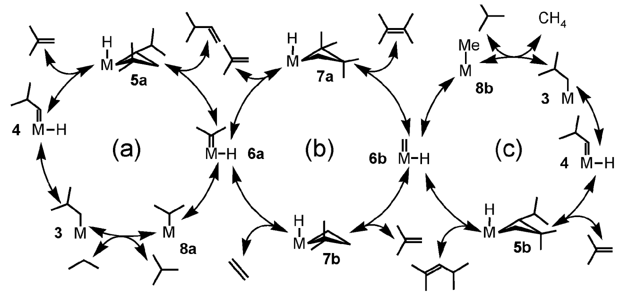


Scheme 3

As known in the classical olefin metathesis mechanism[15] and also proposed for alkane metathesis,[5] the 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 the hydrido-tungsta-carbene **4**. Depending on the two coordinative approaches of 2-methylpropene, two possible tungstacyclobutanes **5a** and **5b**, are obtained, which have *gem*-methyl and -isopropyl substituents in either the [1,2] or [1,3]-positions (Scheme 4a and c). These two tungstacycles will further undergo metathetical cleavages: (i) **5a** giving 3-methyl-1-butene and the new hydrido-tungsta-carbene **6a**, $[W(H)({=}C(CH_3)_2)]/Al_2O_{3\text{–}500}$, (ii) **5b** giving 2,4-dimethyl-2-pentene and the hydrido-tungsta-carbene **6b**, $[W(H)({=}CH_2)]/Al_2O_{3\text{–}500}$.

The hydrido-tungsta-carbenes **6a** and **6b** can also react further with 2-methylpropene giving the corresponding tungstacyclobutanes intermediates **7a** and **7b** (Scheme 4b). Again, these two tungstacycles can undergo metathetical cleavage, **7a** giving 2,3-dimethyl-2-butene and the hydrido-tungsta-carbene **6b**, **7b** giving ethylene and the hydrido-tungsta-carbene **6a** (Scheme 4b).

Paradoxically, **7a** is *a priori* the less thermodynamically favored intermediate, compared to **5b** and particularly **5a**, since it has *gem*-methyl substituents in the [1,2]-positions generating a sterically encumbered tungstacyclobutane intermediate.[5,16] Two other intermediates **7a′** and **7b′** could be formed from the reverse favored approach of 2-methylpropene on **6a** and **6b** but they lead to degenerate metathesis (Scheme S2†). Productive metathesis of 2-methylpropene involving **7a** is thus disfavored for steric reasons which accounts for the fact that it was not reported previously[12,13] and a moderate activity is observed with $W(H)_3/Al_2O_{3\text{–}500}$ by comparison with metathesis of linear alkenes, such as propylene.[17] From the various catalytic cycles (**a**), (**b**), (**c**), the 2-methylpropane metathesis process proceeds with the insertion of all the released olefins into tungsten-hydride species such as **4**, **6a** or **6b**. The resulting tungsten alkyl groups can be further cleaved by H_2 (Scheme S1†), affording the liberation of ethane, 2-methylbutane, 2,3-DMB and 2,4-dimethylpentane.[5] The alkyl groups could



Scheme 4 (a) and (c) classical and (b) unusual mechanistic pathways in the metathesis of 2-methylpropane and 2-methylpropene (M = W).

also be displaced *via* σ-bond metathesis, by the incoming 2-methylpropane present in excess. The excess of 2-methylbutane (5%) over 2,4-dimethylpentane (0.5%) can be understood on the basis of the stability of the key metallacyclobutanes or of the facility of their formation (**5a** > **5b**), which both depends on the interaction between the substituents in the [1,2] or [1,3]-positions as proposed for olefin metathesis.[16]

Alternatively, although unfavorably, the hydrido-tungsta-carbenes **6a** and **6b** could undergo the migration of the hydride onto the carbene ligands involving the formation of $W^{IV}(–CH(CH_3)_2)$ **8a** and $W^{IV}(–CH_3)$ **8b** but also a concomitant disfavored reduction of W^{VI} to W^{IV}.[18] The resulting alkyl groups could again be displaced by H_2 or the incoming alkane reactant *via* σ-bond metathesis giving propane and methane in minor amounts (Scheme 4a and 1c). Finally, it should be mentioned here that 2,3-DMB, which is of interest for its high octane number (RON = 104),[11] is currently obtained by paraffin isomerisation with the use of two major commercial bifunctional catalysts: Pt on highly chlorinated alumina, and Pt on mordenite; however, the selectivity remains low around 8% and both catalysts are deactivated by coke formation.[19]

In conclusion, tungsten hydride supported on alumina $W(H)_3/Al_2O_{3-500}$ catalyzes both 2-methylpropene and 2-methylpropane metathesis with a common core mechanistic scheme affording the main formation of 2,3-DMB$^{=}$ and 2,3-DMB. A new mechanistic pathway is proposed based on two key hydrido-tungsta-carbenes **4** and **6a** which accounts for the formation and the selectivities of all the products observed.

Notes and references

1 A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski and M. Brookhart, *Science*, 2006, **312**, 257–261.
2 V. Vidal, A. Theolier, J. Thivolle-Cazat and J. M. Basset, *Science*, 1997, **276**, 99–102.
3 C.-Y. Chen, D. J. O'Rear and S. R. Brundage, Chevron USA Inc, USA, *WO* 2002000578, 2002.
4 M. Taoufik, E. Schwab, M. Schultz, D. Vanoppen, M. Walter, J. Thivolle-Cazat and J. M. Basset, *Chem. Commun.*, 2004, 1434–1435.
5 J. M. Basset, C. Coperet, L. Lefort, B. M. Maunders, O. Maury, E. Le Roux, G. Saggio, S. Soignier, D. Soulivong, G. J. Sunley, M. Taoufik and J. Thivolle-Cazat, *J. Am. Chem. Soc.*, 2005, **127**, 8604–8605.
6 E. Le Roux, M. Taoufik, C. Coperet, A. de Mallmann, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders and G. J. Sunley, *Angew. Chem., Int. Ed.*, 2005, **44**, 6755–6758.
7 E. Le Roux, M. Taoufik, A. Baudouin, C. Coperet, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders and G. J. Sunley, *Adv. Synth. Catal.*, 2007, **349**, 231–237.
8 M. Taoufik, E. Le Roux, J. Thivolle-Cazat, C. Coperet, J.-M. Basset, B. Maunders and G. J. Sunley, *Top. Catal.*, 2006, **40**, 65–70.
9 M. Taoufik, E. Le Roux, J. Thivolle-Cazat and J. M. Basset, *Angew. Chem., Int. Ed.*, 2007, **46**, 7202–7205.
10 J.-M. Basset, F. Stoffelbach, M. Taoufik and J. Thivolle-Cazat, BP Oil International Limited, UK, *WO* 2008001040, 2008.
11 N. Nikolaou, C. E. Papadopoulos, I. A. Gaglias and K. G. Pitarakis, *Fuel*, 2004, **83**, 517–523.
12 K. J. Ivin and I. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, 1996.
13 T. Kawai, H. Kudo, T. Suzuki and T. Iyoda, *J. Mol. Catal. A.*, 2000, **158**, 533–540.
14 T. Yamamura and S. Nakatomi, *J. Catal.*, 1975, **37**, 142–147.
15 J. L. Hérisson and Y. Chauvin, *Markromol. Chem.*, 1970, **141**, 161.
16 J. L. Bilhou, J. M. Basset, R. Mutin and W. F. Graydon, *J. Am. Chem. Soc.*, 1977, **99**, 4083–4090.
17 J. M. Basset, J. Thivolle-Cazat, M. Taoufik, E. Le Roux and C. Coperet, CPE Lyon FCR, France, *WO* 2006013263, 2006.
18 S. Y. S. Wang, D. D. VanderLende, K. A. Abboud and J. M. Boncella, *Organometallics*, 1998, **17**, 2628–2635.
19 M. Stoecker, *Microporous Mesoporous Mater.*, 2005, **82**, 257–292.