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Direct Transformation of Ethylene into Propylene Catalyzed by a Tungsten Hydride Supported on Alumina: Trifunctional Single-Site Catalysis**

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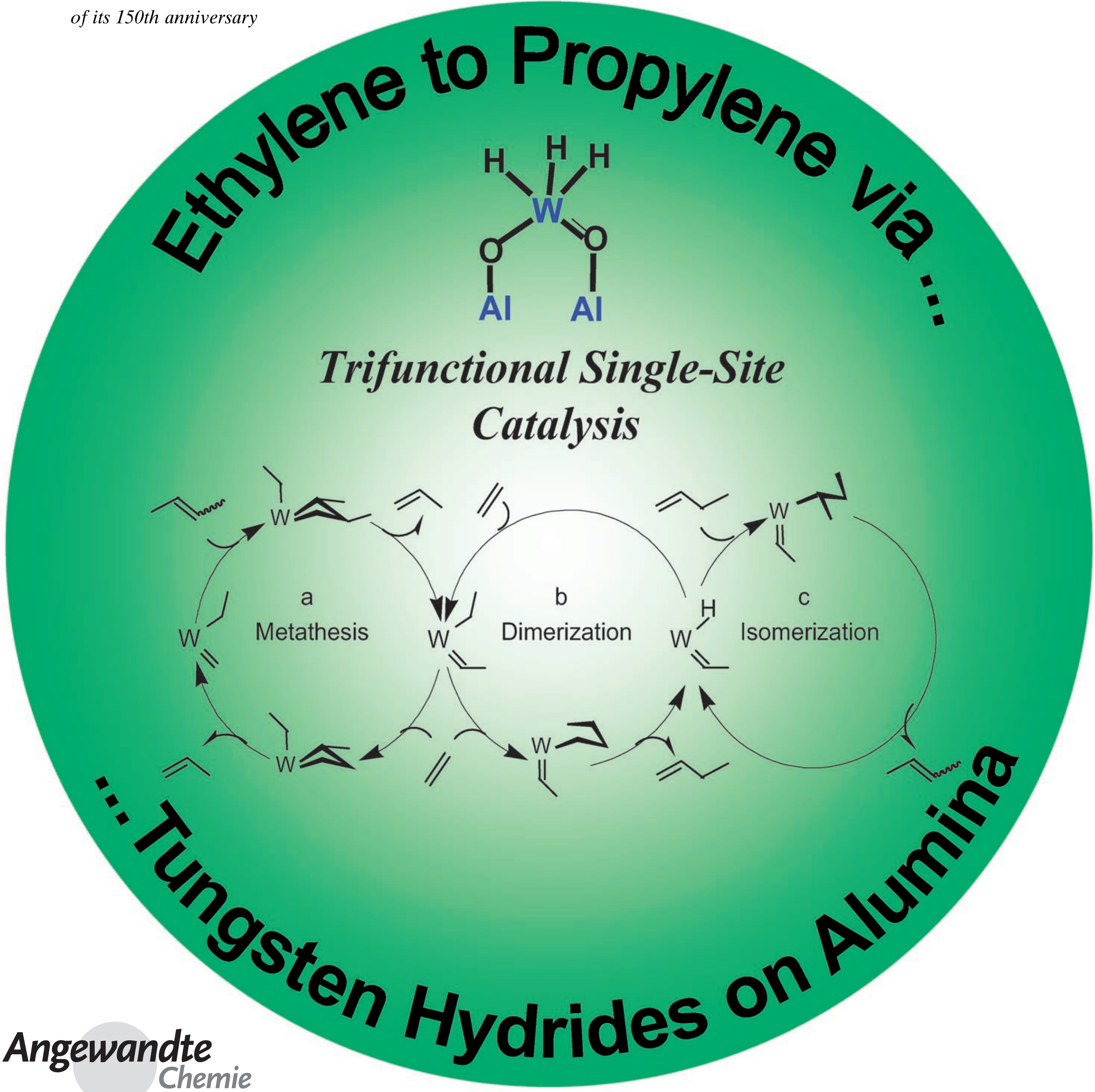
Dedicated to Yves Chauvin and
to Süd-Chemie on the occasion
of its 150th anniversary



There is an increasing worldwide demand for propylene due to a higher demand for polypropylene than polyethylene. Propylene is usually obtained as a co-product of the petroleum industry, either from naphtha steam crackers (about 69%) or from gasoline-making fluidized catalytic crackers.[1,2] Only 2–3% of global propylene production comes from dehydrogenation of propane or Fischer–Tropsch synthesis. The cross-metathesis reaction between ethylene and 2-butenes[3–5] is an alternative route to propylene that is currently undergoing significant industrial development,[2] although it first requires the dimerization of ethylene into 2-butenes. Herein we report a new and efficient catalytic reaction that transforms ethylene directly into propylene with a selectivity higher than 95% [Eq. (1)].


(1)

This reaction is catalyzed by a recently discovered tungsten hydride supported on γ-alumina, namely $W(H)_3/Al_2O_3$ (**3**),[6] which functions as a "trifunctional single-site" catalyst that catalyzes ethylene dimerization into 1-butene, isomerization of 1-butene into 2-butenes, and cross-metathesis between 2-butenes and ethylene to finally form propylene. The tungsten hydride **3**, which has also proved to be an excellent catalyst for alkane metathesis,[7] was obtained by heating the complex $[(Al{-}O)W(\equiv CtBu)(CH_2tBu)_2]$ (**2**), which results from grafting $[W(\equiv CtBu)(CH_2tBu)_3]$[8] (**1**) onto γ-alumina$_{(500)}$ (Johnson Matthey; 200 $m^2 g^{-1}$), at 150 °C under H_2.

Propylene was obtained selectively (95%) by passing ethylene over **3** in a continuous-flow reactor ($P_{C_2H_4} = 1$ bar, $T = 150$ °C, flow rate 4 mL min^{-1} or volume hourly space velocity (VHSV) 260 h^{-1}). The reaction presents an initial steep maximal conversion rate of 0.68 $mol_{C_2H_4} mol_W^{-1} min^{-1}$ before reaching a pseudo-plateau of 0.1 $mol_{C_2H_4} mol_W^{-1} min^{-1}$, with an overall turnover number (TON) of 1120 after 120 h (Figure 1 a). The selectivity for propene increases rapidly up to a plateau at 95%, while that of butenes remains below 4.5%. Higher olefins are present in only trace amounts (less than 0.5%; Figure 1 b).

The initiation and propagation steps were elucidated by identifying the products formed while heating to the reaction temperature of 150 °C (see the Supporting Information). Interestingly, one equivalent of ethane is released per tungsten center after initial contact of **3** with ethylene. This finding suggests the formation of a surface tungsten–ethyl–ethylidene species $\{W\}(CH_2CH_3)(=CHCH_3)$ by the elementary steps displayed in Equation (2).

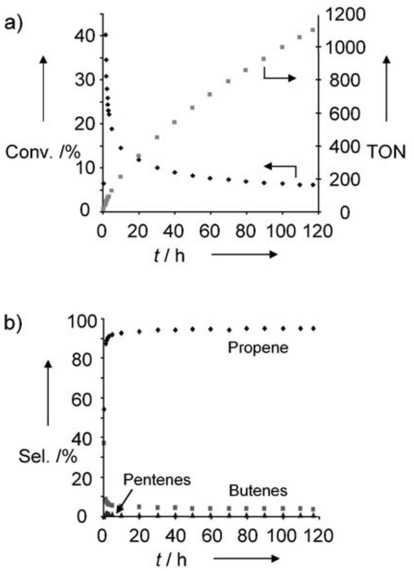
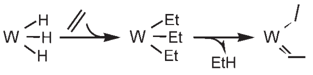
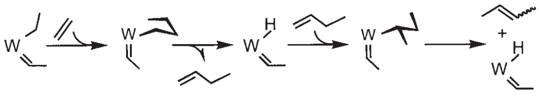


Figure 1. a) Conversion of ethylene (■) and TON (◆). b) Selectivities during the reaction of ethylene to propylene catalyzed by **3** (3.86 wt% W) in a continuous-flow reactor (150 °C, $P_{C_2H_4} = 1$ bar, 4 mL min^{-1}, VHSV = 260 h^{-1}).



(2)

Butene isomers then begin to appear in the gas phase. The initial 1-butene/*trans*-2-butene/*cis*-2-butene/isobutene isomeric distribution of 5.2:1:2:3.1 ($t = 100$ min) changed over time, tending to the ratio 1.7:3.4:1:1.56 (see the Supporting Information). This ratio reveals a deficiency of 2-butenes and isobutene compared to the thermodynamic equilibrium values (1:8:3.84:29.6).[9] In fact, the initial dimerization of ethylene to 1-butene is followed by a fast isomerization of 1-butene to *cis*- and *trans*-2-butenes (see the Supporting Information): the newly formed catalyst $\{W\}(CH_2CH_3)(=CHCH_3)$ can insert ethylene into the ethyl moiety to form an *n*-butyl species, which affords 1-butene and then *cis*- and *trans*-2-butenes after reinsertion of 1-butene and β-H elimination from the *sec*-butyl species [Eq. (3)].



(3)

The high production of all butene isomers during the initial stages of the reaction, combined with the relative deficiency of 2-butenes, suggests that they are primary reaction products. Propene is formed subsequently, which suggests the occurrence of a simple metathesis process involving the newly formed carbene-type complex $\{W\}(CH_2CH_3)(=CHCH_3)$ [Eq. (4)].

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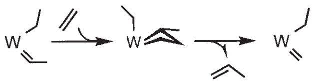
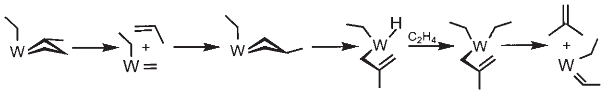


(4)

The formation of isobutene, which also appears in the early stages, requires another process involving free propene. Thus, 2-methyltungstacyclobutane can isomerize into 3-methyl-tungstacyclobutane and then afford isobutenyl-tungsten hydride by β-H abstraction from the β-C atom of the metallacyclobutane;[10] isobutene then forms by ethylene insertion into the W−H bond and α-hydrogen transfer [Eq. (5)].



(5)

Mechanistic information regarding the propagation step was obtained by performing catalytic experiments under steady-state conditions with different ethylene flow rates (2–20 mL min^{-1} (VHSV = 123–1300 h^{-1})) while maintaining chemical regime conditions, as confirmed by the observed linear dependence of the conversion on the inverse space velocity (proportional to contact time; see the Supporting Information). Thus, while the selectivity for propene decreases with decreasing inverse space velocity (or increasing flow rate), the reverse is true for butenes. This relationship indicates that butenes are primary products, since the selectivity intercept with the *y*-axis extrapolates to a nonzero value, and that propene is formed in a reaction that consumes butenes, since their curves are mirror images at any flow rate (Figure 2). Furthermore, the formation of 1-butene also appears to precede that of other butenes since it is the only one for which the selectivity increases with decreasing inverse space velocity (see the Supporting Information).

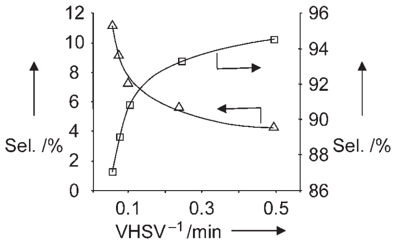
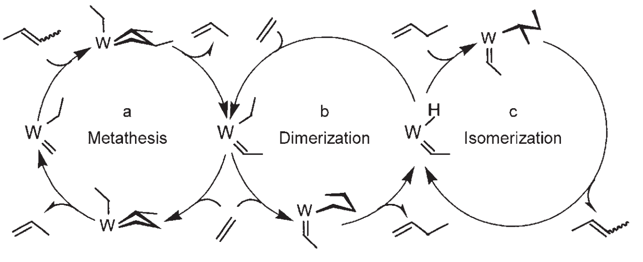


Figure 2. Direct conversion of ethylene into propylene in a continuous-flow reactor (150 °C, $P_{C_2H_4}$ = 1 bar, 520 mg of **3** (3.86 wt % W)). Selectivity versus inverse space velocity expressed in [(min)(volume of catalyst)/(volume of ethylene)]; □: propylene, △: butenes.

Complex **3** was independently shown to be an active catalyst for propene metathesis (batch reactor, $[C_3H_6]/[W] =$ 1470). Thus, propene was converted at 150 °C within 50 minutes to a mixture of ethylene and *n*-butenes with a conversion of 38 % (thermodynamic equilibrium).[11] All the data thus strongly support the proposal that the first catalytic step of the reaction [Eq. (1)] is ethylene dimerization to 1-butene (the alumina support was found not to catalyze this reaction) followed by isomerization to 2-butenes. Propylene is formed in a follow-up cross-metathesis of the resultant ethylene/2-butenes mixture, in agreement with the ability of **3** to catalyze olefin metathesis (Scheme 1).



Scheme 1. Proposed mechanism for the direct conversion of ethylene into propylene.

According to numerous examples,[12] olefin cross-metathesis is expected to be catalyzed by a tungsten–ethyl–ethylidene species following a classical Chauvin mechanism (Scheme 1 a).[13] The same tungsten species is also involved in the observed ethylene dimerization reaction[14] according to the classical Cosse–Arlman mechanism,[15,16] which proceeds by a double ethylene insertion into the W−H bond of the tungsten ethylidene hydride (Scheme 1 b); this latter species also catalyzes the isomerization of 1-butene into 2-butenes (Scheme 1 c).

Thus, $\{W\}(CH_2CH_3)(=CHCH_3)$, which bears both an alkyl and an alkylidene fragment, is able to catalyze the dimerization, isomerization, and metathesis of olefins at the same site. In other words, it behaves as a trifunctional single-site catalyst.

A few examples of the direct transformation of ethylene into propylene have been reported, although none are particularly selective or highly productive. For example, a deficiency of ethylene formation compared to butenes has been observed during the metathesis of propylene catalyzed by $[Mo(CO)_6]/Al_2O_3$ and attributed to the direct transformation of ethylene into propylene.[17] We have also observed this reaction, with a short lifetime, during Fischer–Tropsch synthesis in the presence of small iron nanoclusters formed by the thermal decomposition of $[HFe_3(CO)_{11}]^-/MgO$.[18] This reaction has also been reported to proceed with catalysts based on europium or ytterbium deposited on coal in combination with titanium compounds ($TiCl_4$, $Ti(OiPr)_4$)[19] as well as with MO_x/SiO_2[20] or Ru/SiO_2 catalysts.[21] However, the catalytic performances of all these systems were either not quantified[17] or proved to be very low[19–21] compared to the present $W(H)_3/Al_2O_3$ system.

In summary, the $W(H)_3/Al_2O_3$ system is currently the best single-site catalyst precursor for the direct transformation of ethylene into propylene in terms of both activity and selectivity. It operates as a trifunctional single-site catalyst that catalyzes ethylene dimerization, 1-butene isomerization, and ethylene/2-butenes cross-metathesis. We are currently studying further improvements to this system.

Experimental Section

All experiments were carried out using Schlenk and glovebox techniques for the preparation and handling of organometallic compounds. The alumina-supported tungsten hydride was prepared as reported.[7]

A stainless-steel half-inch cylindrical reactor that can be isolated from the atmosphere was charged with **3** (520 mg, 3.86 wt% W) in a glovebox. After connection to the gas lines and purging of the tubes, a controlled flow of ethylene was passed over the catalyst bed at 150 °C with flow rates varying from 2 to 20 mL min^{-1} (VHSV = 123–1300 h^{-1}). Hydrocarbon products and hydrogen were analyzed online by GC (HP 8890 chromatograph fitted with an Al_2O_3/KCl 50 m × 0.32 mm capillary column, FID detector for hydrocarbons with a 3-m molecular sieve column and a catharometer for hydrogen).

See the Supporting Information for further experimental details and Figures S1–S4.

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