

Silica-Supported Cationic Tungsten Imido Alkylidene Stabilized by an *N*-Heterocyclic Carbene Ligand Boosts Activity and Selectivity in the Metathesis of α -Olefins

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Dedicated to Prof. *Antonio Togni* for his contribution to coordination and fluorine chemistry

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A well-defined silica-supported cationic W imido alkylidene was prepared through surface organometallic chemistry. This catalyst shows preferential activity towards α - over internal olefins, which is atypical for W-based catalysts, but consistent with the strong σ -donating ability of the NHC ancillary ligand. Complementing the studies on tungsten-based d⁰ metathesis catalysts, the silica-supported cationic W imido alkylidene displays the highest activity among W imido catalysts for α -olefins and shows improved selectivity for this class of olefins compared to Mo-based catalysts.

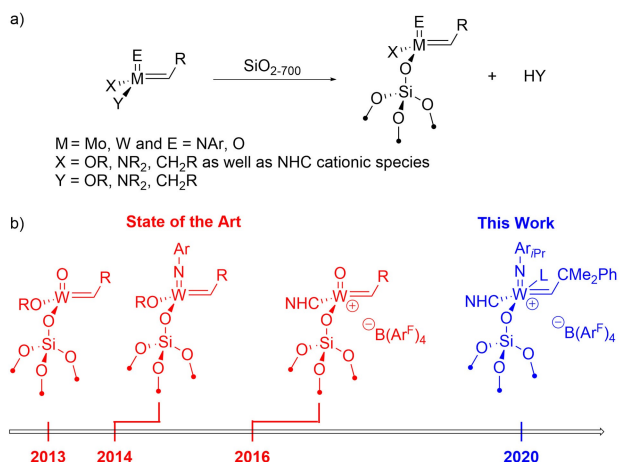
Keywords: olefin metathesis, surface organometallic chemistry, surface chemistry, tungsten, tungsten *N*-heterocyclic carbene.

Introduction

Alkene metathesis is a robust and atom-economic synthetic method for the creation of carbon-carbon double bonds; it has thus found ample use in both academia and industry.^[1–3] Over the last decades, substantial efforts have been put in developing efficient molecular catalysts,^[4–15] but immobilized analogs have received increasing attention because of their benefits for process intensification^[16,17] and their improved performance with the development of well-defined supported systems, mostly prepared through surface organometallic chemistry (SOMC).^[18–23] SOMC, a molecular approach to generate well-defined heterogeneous catalysts, in which the surface is exploited as a ligand to covalently anchor molecular complexes,

has been particularly successfully employed for the preparation of silica-supported Schrock-type metathesis catalysts of the general formula [(\equiv SiO)M(E)(=CHR)(X)] (M = Mo or W, E = NR or O), that display high activity, selectivity and stability with performances often surpassing those of their homogeneous counterparts (*Scheme 1*).^[24–33] Yet, these metathesis catalysts display pronounced reactivity differences between terminal versus internal olefins, that depend on the metal and the σ -donation ability of the X and E ligands. For example, increased activity in the metathesis of internal olefins is observed for weaker σ -donating X-ligands in supported metathesis catalysts bearing a donating imido ligand.^[26,28,31] In contrast, the metathesis of α -olefins proceeds more efficiently with increasing σ -donor properties of the X-ligands;^[30,31] the latter has been associated with the destabilization of the parent off-cycle metallacyclobutane, which can be formed during the metathesis of α -olefins as a consequence of the formation of

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Scheme 1. a) General route describing the grafting of alkylidenes. b) Development of well-defined silica-supported tungsten alkylidenes since 2013 (state of the art) and this work.

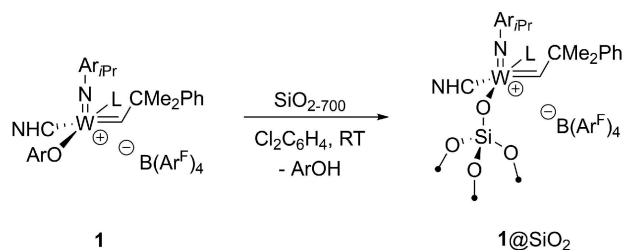
ethylene.^[27,34] In this regard, W-based metathesis catalysts are significantly less active than their Mo analogs for the metathesis of α -olefins owing to their generally more stable metallacyclobutanes.^[35] The incorporation of a strong, neutral, σ -donating *N*-heterocyclic carbene (NHC) ligand in a tetracoordinated cationic species has emerged as a solution to boost the activity in the metathesis of α -olefins.^[34,36,37] Noteworthy, the supported cationic W oxo alkylidene NHC complex (X=NHC)-[(=SiO)W(=O)(NHC)(=CHR)]⁺[B(3,5-(CF₃)₂C₆H₃)₄]⁻ not only showed very high activity, but also appeared to be remarkably stable, reaching TONs >1 million in the metathesis of propene under flow conditions.

With the emergence of cationic W imido alkylidene species with stabilizing NHC ligands,^[12] we decided to evaluate whether or not it would be possible to boost the activity of W imido catalysts towards α -olefins, which have so far shown comparably poor catalytic activity towards these substrates.

Results and Discussion

The representative complex **1** was grafted on silica partially dehydroxylated at 700 °C (SiO₂₋₇₀₀), yielding the corresponding supported species **1**@SiO₂ (Scheme 2).

Elemental analysis showed a tungsten loading of 1.34 wt% that corresponds to 0.07 mmol [W]/g, in agreement with solution NMR quantification of the remaining molecular precursor in solution after reac-



Scheme 2. Immobilization of **1** on silica-700 (NHC = 1,3-diisopropylimidazol-2-ylidene; OAr = OC₆F₅; L = *t*BuCN).

tion with silica. Both data show that grafting takes place on *ca.* 30% of the surface silanols, consistent with the IR data: IR spectroscopy shows that, while a large amount of isolated silanols associated with the band at 3747 cm⁻¹ are consumed upon grafting (Figure S11), a broad absorption band around 3500 cm⁻¹ appears along with CH stretching bands observed between 2800 and 3200 cm⁻¹. These bands are consistent with the presence of unreacted OH groups interacting with the ligands of the grafted tungsten site. An additional band is observed at 2276 cm⁻¹, indicating the coordination of pivalonitrile to the grafted tungsten sites as observed in the molecular precursor. ¹H magic angle spinning NMR spectra of **1**@SiO₂ show a proton resonance at 12.4 ppm, associated with the alkylidene proton (Figure S9).^[12] Additional resonances at 1.7 ppm can be attributed to methyl protons of pivalonitrile, the neophylidene, NHC and imido moieties, while the resonance at 4.5 ppm corresponds to the protons on the tertiary carbon of the isopropyl moieties. In order to fully characterize the supported catalyst, the ¹³C-enriched silica-supported neopentylidene compound **1***@SiO₂ was prepared. The ¹³C cross-polarization MAS spectrum shows a signal at δ = 299.2 ppm, further confirming the presence of the alkylidene ligand (Figure S13). An extra signal at 78 ppm is also observed, consistent with the formation of small amounts of [(=SiO)W(NAr_{*i*Pr})(NHC)(CH₂*t*Bu)(OAr)(L)]⁺[B(3,5-(CF₃)₂C₆H₃)₄]⁻, likely due to the partial protonation of the alkylidene.^[26,38,39]

The catalytic activity (turnover frequency recorded after 3 min – TOF_{3min}) of both molecular and immobilized complexes was evaluated in the homometathesis of two prototypical substrates, namely *cis*-4-nonene, yielding *cis/trans* 4-octenes and 5-decenes and 1-nonene, yielding *cis/trans*-8-hexadecenes and ethylene, respectively (Table 1, see Supporting Information for more details). It is noteworthy that the activity of **1**@SiO₂ towards α -olefins is higher than for internal

Table 1. Homocoupling of *cis*-4-nonene and 1-nonene (0.1 mol%, 30 °C).

Catalyst ^[a]	TOF _{3min} ^[a]	Time to equilibrium conversion
Metathesis of <i>cis</i> -4-Nonene ^[b]		
1	28 (8%)	1 h
1 @SiO ₂	5 (1%)	44% after 2 h
Metathesis of 1-Nonene ^[c]		
1	52 (15%)	97% after 4 h
1 @SiO ₂	16 (4%)	97% after 6 h

^[a] TOF at 3 min, given in min⁻¹ with the corresponding conversions given in brackets. ^[b] Equilibrium conversion is 50%.

^[c] Equilibrium conversion is 100%.

ones (16 min⁻¹ vs. 5 min⁻¹), while the molecular catalyst **1** performs slightly better than the grafted counterpart with the same trend (52 min⁻¹ vs. 28 min⁻¹). In contrast to their molybdenum analogs,^[37] where induction periods of up to 10 h could be observed with *cis*-4-nonene, the tungsten-based catalysts are readily active. Furthermore, no isomerization products, commonly found with molybdenum-based catalysts, could be observed during the metathesis of 1-nonene.^[31]

Note that, in sharp contrast, these catalysts are less active towards internal olefins than the corresponding neutral silica-supported W imido alkylidenes (Figure 1). This is in line with the reactivity trend built over the years, namely stronger σ -donating X ligand decrease metathesis activity towards internal olefins, possibly because of the over destabilization of the corresponding substituted metallacyclobutane intermediates.

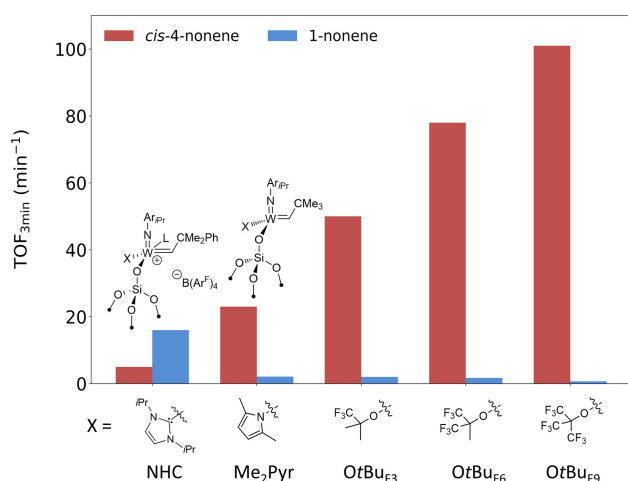


Figure 1. Comparison of the activity of the neutral silica-supported W imido alkylidenes vs. **1**@SiO₂ in the metathesis of internal and α -olefins.^[31]

Conclusions

Overall, introducing an NHC-ligand in cationic tungsten imido alkylidene catalysts significantly boosts their activity towards α -olefins, thus opening new possibilities for W-based imido catalysts due to their significantly higher selectivity (no olefin isomerization) than their molybdenum analogs. We are currently exploring such systems, in view of the tunability of the imido and NHC ligands.

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Author Contribution Statement

J. D. J. S. and M. P. designed and performed the heterogeneous catalyst synthesis and catalytic tests. D. M. performed the characterization through ssNMR. M. J. B. and I. E. synthesized the homogeneous catalysts. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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