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Author(s):

Pucino, Margherita; Inoue, Mariko; [Gordon, Christopher](#) ; Schowner, Roman; Stöhr, Laura; Sen, Suman; Hegedüs, Csaba; Robé, Emmanuel; Tóth, Flórián; Buchmeiser, Michael R.; [Copéret, Christophe](#)

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Promoting Terminal Olefin Metathesis with Supported Cationic Molybdenum Imido Alkylidene N-Heterocyclic Carbene Catalyst

Margherita Pucino^[a], Mariko Inoue^[a,b], Christopher P. Gordon^[a], Roman Schowner^[c], Laura Stöhr^[c], Suman Sen^[c,d], Csaba Hegedüs^[e], Emmanuel Robé^[e], Flórián Tóth^[e], Michael R. Buchmeiser^{*[c]}, Christophe Copéret^{*[a]}

Abstract: *Silica-supported cationic molybdenum-imido alkylidene N-heterocyclic carbene (NHC) catalysts, prepared via Surface Organometallic Chemistry, display contrasting olefin metathesis activity for terminal and internal olefins. The high metathesis activity towards terminal alkenes is attributed to the strong σ -donating property of the NHC ancillary ligand, which disfavors the formation of the parent square planar metallacyclobutane, an off-cycle reaction intermediate resulting from the reaction with ethylene, one of the metathesis products. This tailored ligand environment also allowed the first trigonal bipyramidal (TBP) metallacyclobutane reaction intermediate for supported Mo metathesis catalysts to be identified.*

Olefin metathesis, a key enabling technology in industry, has received increasing attention due to the development of highly active and selective molecular catalysts.^[1] These developments have been transferred to the preparation of the corresponding immobilized catalysts because they are associated with more efficient processes.^[2] In particular, well-defined silica-supported d^0 metal alkylidenes, prepared via Surface Organometallic Chemistry,^[3] have emerged as highly active, selective and stable catalysts with performances surpassing these of their homogeneous analogues.^[3b] One of the most important criteria for high activity in d^0 metathesis catalysts of the general formula (X)(Y)M(E)(=CHR) resides in balancing the σ -donation ability of the X, Y and the apical E ligands (Scheme 1a).^[4] This design principle has been used to develop more active homogeneous and supported catalysts.^[5] The metathesis activity also depends on the olefin substrates itself, i.e. terminal vs. internal olefins, whose conversion is greatly influenced by both the metal and ligand sets. For instance, in isostructural well-defined silica-supported metathesis catalysts bearing a donating imido and an alkoxide X-ligand, Mo and W display similar activities for internal olefin, where the activity parallels the σ -donating strength of the X-ligand, in that the weaker σ -donating the ligand the faster metathesis is.^[6] In contrast, W-based metathesis catalysts are significantly less active than their Mo analogues for terminal olefins, and their activity increases with increasing σ -donor X ligands. This latter trend has been ascribed to the destabilization of the parent metallacyclobutane, an off-cycle reaction intermediate, which can be formed during the metathesis of terminal olefin due to the generation of ethylene.^[6b, 7]

To date, a large variety of molybdenum and tungsten-based olefin metathesis catalysts have been studied in both homogeneous^[8] and heterogeneous^[9] processes; one of the most active and also robust one is a cationic, silica-supported W oxo alkylidene species with a strong σ -donating N-heterocyclic carbene (NHC) ligand (Scheme 1b), which reaches high turnover frequencies ($> 1000 \text{ min}^{-1}$) and very high turnover numbers (> 1.2 million in the case of propene metathesis).^[7b]

With the emergence of a new family of molecular cationic Mo imido species having stabilizing NHC ligands (Scheme 1c), [8b, 8c, 8e, 10] we decided to investigate the corresponding well-defined silica-supported systems and report their outstanding activity towards terminal olefins in sharp contrast to internal ones. We also disclose the observation of the first supported molybdacyclobutane intermediate, illustrating the specific properties of NHC stabilizing ligands.

Scheme 1. (a) General structure of a d^0 olefin metathesis catalyst and reaction mechanism (b) supported cationic W oxo-alkylidene species bearing an NHC ligand (c) supported cationic Mo imido species bearing an NHC ligand $B(Ar^F)_4 = B(3,5-(CF_3)_2C_6H_3)_4$.

Four representative molecular complexes **1–4**, based on the same NHC, i.e. 1,3-dimesitylimidazol-2-ylidene (Imes), but bearing different imido and ancillary ligands, have been prepared and grafted onto a silica partially dehydroxylated at 700 °C (SiO_{2-700}) yielding the corresponding supported species, **1–4**@ SiO_2 (Scheme 2). Quantification by elemental analysis showed molybdenum loading of 0.45, 0.43, 0.52 and 0.35 Mo/nm² for **1**@ SiO_2 , **2**@ SiO_2 , **3**@ SiO_2 , and **4**@ SiO_2 , respectively, in agreement with solution NMR quantification of the remaining molecular precursor after reaction with silica. In all cases, IR spectroscopy shows that, after grafting, a significant amount of isolated silanols associated with a band at 3747 cm⁻¹ are consumed, consistently with protonolysis reaction, albeit only partially, presumably due to the large size of the molecular precursors, which prevents full coverage.^[8a, 10a-c, 11] In fact, besides the appearance of CH stretching bands between 2800 and 3220 cm⁻¹, a broad feature around 3600 cm⁻¹ indicates the presence of remaining (unreactive) surface silanols in interaction with the aromatic ligand of the grafted complex.^[12] Most important, as can be deduced from the catalytic data (vide infra), these do not negatively interfere with the activity of the supported catalysts. For **1**@ SiO_2 , **3**@ SiO_2 , and **4**@ SiO_2 , two additional bands at 2319 and 2294 cm⁻¹ are also observed and

correspond to coordinated acetonitrile,^[13] which is present in the molecular precursors and remains coordinated after grafting.

Scheme 2 Grafting of **1**, **2**, **3** and **4** on SiO₂₋₇₀₀ to afford **1@SiO₂**, **2@SiO₂**, **3@SiO₂** and **4@SiO₂**.

In order to have full characterization of the supported catalysts, the ¹³C-enriched neopentylidene species **1*** and **2*** and the corresponding silica-supported systems (**1*@SiO₂** and **2*@SiO₂**) were prepared. Magic angle spinning (MAS) ¹H NMR of **1*@SiO₂** and **2*@SiO₂** show the proton alkylidene resonances at δ = 12.8 and 12.3 ppm, respectively, which is similar to what is observed for the corresponding molecular precursors (12.43 and 12.19 ppm). The corresponding ¹³C cross-polarization (CP) MAS spectra show the alkylidene carbon signals at δ = 312.8 and 313.1 ppm, respectively, which is in close correspondence with these observed for **1*** and **2*** (314.0 and 312.9 ppm). For **3@SiO₂** and **4@SiO₂**, the presence of the alkylidene is also confirmed by the observation of the proton resonances at δ = 14.3 and 13.7 ppm vs. 13.90 and 13.53 ppm in the corresponding molecular complexes.

The metathesis activity of the silica-supported Mo-imido alkylidene NHC complexes is then evaluated using 1-nonene and *cis*-4-nonene as prototypical substrates (Table 1). What is notable is that in all cases the activity towards terminal olefins is much higher than what is observed with internal ones.

This observation is in large contrast to what is observed for most silica-supported catalysts.^[6b] Equally important, all catalysts display an induction period with internal olefins for both molecular and supported complexes.

Table 1. Self-metathesis of *cis*-4-nonene and 1-nonene (toluene, 30 °C), 0.014 mol%.

Catalyst	TOF _{ma} / min ⁻¹ (induction period)		Time for maximum conversion (% of conversion)	
	<i>cis</i> -4-nonene	1-nonene	<i>cis</i> -4-nonene	1-nonene
1	<1	119	-	8h (86%)
2	5 ^a (600min)	516	24h (equilibrium)	12h (80%)
3	<1	226	-	8h (86%)
4	24 ^a (120min)	292	22h (equilibrium)	6h (83%)
1@SiO₂	<1	235	-	6h (95%)
2@SiO₂	63 ^a (180min)	165	8h (equilibrium)	12h (78%)
3@SiO₂	25 ^a (60min)	669	~20h (equilibrium)	5h (94%)
4@SiO₂	55 ^a (60min)	86	24h (equilibrium)	6h (97%)

^aTaken after induction period.

This peculiar behavior is most pronounced for **3** and **3@SiO₂**: no activity for internal olefins is observed for the molecular precursor, while 40% of conversion is reached after 5 h with the supported material, albeit with an induction period of 1 h (Figure 2b blue curve). With 1-nonene however, no induction period is observed. Both catalysts **3** and **3@SiO₂** show good activities towards terminal olefin with TOFs reaching ca. 669 min⁻¹ for the latter. Maximum conversion is reached within 5 h at a catalyst loading of 0.014 mol% (Figure 2). The increase activity of the supported catalysts is attributed to the rather small size of surface siloxy ligands.^{[9],[14]} These results largely exceed those previously reported with neutral systems, where the best catalyst shows a TOF of 20 min⁻¹ and a time to full conversion of 8 h at a catalyst loading of 0.1 mol%.^[6b]

Figure 2 Activity of catalyst **3** vs. **3@SiO₂** in the homometathesis of 1-nonene (pink) and *cis*-4-nonene (blue), catalyst loading 0.014 mol%.

The catalyst **3@SiO₂**, the most promising supported species, is also efficient in the metathesis of propene under flow conditions. With a 1:2 mixture of propene:Ar (60 ml/min, 30 °C), the catalyst displays a maximum TOF of 20 min⁻¹ and only 15% of deactivation over 3 days with a selectivity for the metathesis product >99%. The higher activity towards terminal olefins can be explained by the easier initiation with terminal olefins and the presence of strong σ -donor ligands, which reduces the stability of the square planar (SP, unreactive) parent metallacycle.^[6-7] In fact, contacting **3@SiO₂** with carbon-13 di-labeled ethylene (ca. 30 equiv.) provides a material whose carbon-13 solid-state NMR spectrum displays two very sharp peaks at 110 ppm and 0.6 ppm, attributed to the α and β carbon of a trigonal bipyramidal (TBP) metallacycle (Scheme 3a and 3b). No signals associated to SP metallacyclobutane, expected in the 30-50 ppm range, are observed. However, two broad and very intense features at 70 and 62 ppm are additionally observed; they are attributed to ethylene coordinated to a Mo(IV) center.^[15]

Scheme 3. a) Ethylene exposure of $3@SiO_2$, species observed by ss-NMR b) ^{13}C CP MAS NMR spectrum (400 MHz, spinning rate 10 kHz, recycle delay 2s, contact time 2ms) of $3@SiO_2$ contacted with dilabeled ethylene. (* spinning side bands). c) Calculated structures and simulated chemical shifts for the products of ethylene exposure of $3@SiO_2$.

2D NMR and DFT calculations of the chemical shift (Table S1) fully support the attribution of the observed signals to TBP metallacyclobutane and π -ethylene complexes (Scheme 3c). Noteworthy, DFT calculations also indicate that the TBP structure is much more stable than the SP (by at least 7 kcal/mol), in contrast to what is obtained for most other complexes.^[4b, 4c, 16] The observation of a metallacyclobutane is particularly noteworthy since such reaction intermediates have never been observed before in supported Mo-based metathesis catalysts, while there are several examples for the corresponding W-ones;^[17] similar trends are also found for molecular complexes.^[16] Furthermore, the presence of an induction period for internal olefins is also remarkable and shows that initiation with such olefins is particularly difficult with these catalysts. One possible explanation for these observation is the presence of large NHC ligand and $B(Ar^F)_4^-$ counter ion, which can slow down initiation (olefin coordination followed by the exchange of the initial neophylidene for the propagating alkylidenes). In addition, the NHC ligand is likely responsible for the destabilization of the SP-metallacycle, an off-cycle intermediates that does not lead to productive metathesis.^[6a] In fact, adding 14% of 1-nonene into cis-4-nonene drastically shortened the induction period of $3@SiO_2$ from 60 min to 3 min, probably because of faster initiation.

In conclusion, silica-supported cationic molybdenum-imido alkylidene complexes bearing a bulky stabilizing NHC ligand have been developed and fully characterized; they display unusual and contrasting activity between internal vs. terminal olefins in great favor of the latter. In addition, these catalysts show an induction period for internal olefins. These observations are presumably due to a combination of the presence of the large and strong σ -donor NHC ligand as well as the large $B(Ar^F)_4^-$

counter anion. The NHC ligand chosen is also seemingly important in allowing the formation and the observation of the reactive TBP metallacyclobutane intermediate. These results further illustrate how tuning the structure and the electronic properties of supported metal alkylidenes can reshape the catalytic properties.

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Keywords: molybdenum • metallacyclobutane • surface chemistry • olefin metathesis • induction period

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