SOMC-Designed Silica Supported Tungsten Oxo Imidazolin-2iminato Methyl Precatalyst for Olefin Metathesis Reactions

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S Supporting Information

ABSTRACT: Synthesis, structure, and olefin metathesis activity of a surface complex $[(\equiv Si-O-)W(\equiv O)(CH_3)_2$ - $Im^{Dipp}N]$ (4) $(Im^{Dipp} = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-iminato)$ supported on silica by a surface organometallic chemistry (SOMC) approach are reported. The reaction of *N*-silylated 2-iminoimidazoline with tungsten (VI) oxytetrachloride generated the tungsten oxo imidazolin-2-iminato chloride complex $[Im^{Dipp}NW(\equiv O)Cl_3]$ (2). This was grafted on partially dehydroxylated silica pretreated at 700 °C (SiO_{2-700}) to afford a well-defined monopodal surface complex $[(\equiv Si-O-)W(\equiv O)Cl_2-Im^{Dipp}N]$ (3). 3 underwent alkylation



by $ZnMe_2$ to produce $[(\equiv Si-O-)W(=O)(CH_3)_2-Im^{Dipp}N]$ (4). The alkylated surface complex was thoroughly characterized by solid-state NMR, elemental microanalysis, Raman, FT-IR spectroscopies, and XAS analysis. 4 proved to be an active precatalyst for self-metathesis of terminal olefins such as propylene and 1-hexene.

INTRODUCTION

Olefin metathesis has a significant impact on modern petrochemical and polymer industries, and it has been established as a reliable and robust synthetic method in organic synthesis.¹ Several commercial processes rely on this versatile reaction, for instance olefin conversion technology (OCT) from ABB Lummus, or the Shell higher olefin process (SHOP), which operate on a multimillion ton/year scale.² Classical catalytic systems for this reaction involve transition metal (Mo, W, Re) oxides impregnated on inorganic supports (such as silica, alumina, silica-alumina, etc.).³ WO₃/SiO₂, in particular, is prepared by incipient wetness impregnation of ammonium tungstate on silica followed by calcination at ~550 °C. Although it has been shown that olefin metathesis might proceed under very mild conditions,⁴ this industrial catalyst requires high temperatures (350-450 °C).³ This has been attributed to the existence of only a small concentration of the proposed active W-oxo alkylidene sites (Chart 1a) on the illdefined surface of WO₃/SiO₂.⁴ In the current global perspective on improved energy efficiency and reduced greenhouse gas

Chart 1. (a) Proposed Active Site of WO₃/SiO₂ Metathesis Catalyst. (b) The Tungsten Oxo Imidazolin-2-iminato Precatalyst Prepared in This Work



emissions, 5 undefined heterogeneous catalysts are required to evolve to opportunely designed systems where the identity of

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each reactive center is known and tailored to afford high activity and selectivity. Surface organometallic chemistry offers the tools to prepare such catalysts by the reaction of suitable organometallic fragments with the reactive functionalities of the support.⁶ This method has allowed the preparation of highly active heterogeneous catalysts for a broad range of important catalytic reactions including alkane metathesis,⁷ nonoxidative coupling of methane to ethane and hydrogen,⁸ hydroaminoalkylation of olefins,⁹ CO₂ conversion to cyclic carbonates,¹⁰ oxidative dehydrogenation of propane,¹¹ etc.

The SOMC preparation of highly active heterogeneous catalysts for olefin metathesis by the immobilization of tungsten and molybdenum metal alkylidene or metal imido alkylidene precursors has been widely studied.¹² Recently, the main focus has shifted to the development of tungsten oxo alkylidene surface complexes. Such systems have displayed unprecedented catalytic efficiency (cumulative TON > 20000 for propene metathesis in a dynamic reactor) and are relatively more resilient to deactivation when compared to their metal imido analogues.¹³

Moreover, the development of well-defined tungsten oxo alkylidene catalysts that mimic the structure of the active site of WO_3/SiO_2 system can lead to a better understanding of the activity and limitations of the industrial catalysts.^{4,13b}

Two main synthetic strategies have emerged in SOMC for the preparation of silica supported tungsten oxo alkylidene complexes. The classical approach relies on the grafting of organometallic tungsten oxo alkylidene or tungsten oxo alkyl precursors.^{4,13,14} The latter can generate an alkylidene moiety upon thermal treatment. Recently, a new strategy has been introduced that employs easy-to-handle, inorganic tungsten oxo halides that are grafted and subsequently alkylated on the support surface by suitable reagents.¹⁵ The latter pathway is advantageous as the inorganic precursors are much more stable than the organometallic tungsten oxo complexes and their preparation does not require elaborate synthetic procedures. Moreover, we show in this work that these precursors can be easily modified prior to the grafting in order to afford functionalized tungsten oxo derivatives. Such strategy allows the easy introduction of substituents at the tungsten center in an effort to tune the activity and selectivity of the final catalyst. Indeed, strong electron donors (phosphines, thiophenoxides, N-heterocyclic carbenes) have been used as ligands in highly active homogeneous and heterogeneous tungsten oxo olefin metathesis catalysts.^{4,14b,f,16} Moreover, in the case of homogeneous tungsten oxo complexes, the presence of a bulky aryloxy substituent has proved crucial to the preparation of Z-selective catalysts,¹⁷ analogously to what has been observed for the case of the metal imido monoaryloxide monopyrrolide (MAP) complexes.¹⁸

Bearing these observations in mind, we have synthesized a silica supported tungsten oxo complex $[(\equiv Si-O-)W(\equiv O)-(CH_3)_2-L]$, $L = Im^{Dipp}N$ (1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-iminato ligand, Chart 1b). The imidazolin-2-iminato ligand¹⁹ possesses a highly basic nitrogen donor ligand with a high π -electron donation ability.²⁰ This ligand has been used in the past to modulate the electronic properties of the metal centers in ethylene polymerization,²¹ hydroamination,²² and C–H activation.²⁰ The use of the imidazolin-2-iminato ligand in metathesis catalysts has so far been limited to ring opening metathesis²⁰ and alkyne metathesis reactions.²³

RESULTS AND DISCUSSION

Preparation of [Im^{Dipp}NWOCI₃] (2). Silylated iminophosphoranes have been widely used for complexation reactions with various metal halides to yield phosphoraneiminato complexes together with the elimination of trialkylsilyl halides.²⁴Accordingly, treatment of tungsten(VI) oxytetrachloride solution in dichloromethane with 1 equiv of *N*-silylated 2-iminoimidazoline **1** under reflux resulted in the rapid precipitation of complex **2** (Scheme 1) as an orange crystalline



solid in good yield (84%). Desilylation and coordination of the nitrogen site to the metal center resulted in a pronounced downfield shift of the ¹H NMR resonances (Figures S1 and S2) relative to the hydrogen atoms of the imidazoline backbone and, to a minor extent, also of the protons of the aromatic rings as expected for a strong electron release toward the metal center. The ¹H and ¹³C NMR spectra of **2** are in good agreement with those of previously reported complexes bearing the imidazolin-2-iminato ligand such as the (imido)vanadium complexes reported by Nomura et al.^{21c}

The assigned structure of **2** is also supported by the HSQC ¹H, ¹³C correlation NMR spectra (Figure S3; see also the Experimental Section for elemental analysis values). Raman spectroscopic analysis of **2** revealed characteristic stretching bands at 946 cm⁻¹ and at 360 cm⁻¹ (Figure S5) attributable to the W=O²⁵ and to the W-Cl²⁶ bond vibrations, respectively. The signals observed at about 1041 and 1061 cm⁻¹ are expected to originate from the sp³ C-C stretching of the organic ligand (Scheme 1).²⁷

Single crystals of 2 suitable for X-ray crystal structure determination were obtained from a solvent mixture of *n*-hexane–dichloromethane at -30 °C. The single crystal X-ray structure of the molecule is shown in Figure 1 (experimental details are given in section S3 of the Supporting Information) with selected bond distances and angles; the crystal structure confirms the formation of a monomeric tungsten oxo imidazolin-2-iminato chloride compound with a slightly distorted trigonal bipyramidal geometry around W(1) with oxygen and N-ligand in equatorial position. The W–N bond distance is found to be 1.782(5) Å, which is consistent with W–N bond distances observed in other imido tungsten complexes, e.g., W–N = 1.731(6), 1.748(6) Å in $[Me_3CCH=W(N^{dipp})(OCCMe_3)_2]^{28}$ and W–N = 1.708(17) Å in $[PhCH=W(N^{dipp})\{OCCMe_3)_2\}_1^{29}$

The W–Cl bond distance found in 2 of ca. 2.36 Å is comparable to the W–Cl bond distance found in bis(2,4,6tribromophenoxy)tungsten(VI) oxychloride of 2.3104(13)– 2.3302(13) Å.³⁰ Finally, the W=O distance is 1.729(5) Å, comparable to the W=O bond length in W(O)(CH-*t*-Bu)[N(C₆F₅)₂(OHMT)(PMe₂Ph) (1.710(2) Å, HMTO = 2,6-dimesitylphenoxide).³¹ The imidazole ring is in the equatorial plane O(1)–N(1)–Cl(2).

Preparation of $[(\equiv Si-O-)W(=O)Cl_2-Im^{Dipp}N]$ (3). Surface compound 3 was prepared by grafting 2 on silica partially



Figure 1. Single crystal X-ray structure of 2 (ellipsoids at 50% probability level). Selected bond distances (Å) and angles (deg): W(1)-Cl(1) = 2.361(2), W(1)-Cl(2) = 2.364(2), W(1)-Cl(3) = 2.357(2), W(1)-O(1) = 1.729(5), W(1)-N(1) = 1.782(5); O(1)-W(1)-N(1) = 108.7(3), O(1)-W(1)-Cl(3) = 95.2(2), N(1)-W(1)-Cl(3) = 95.5(2), O(1)-W(1)-Cl(1) = 94.0(2), N(1)-W(1)-Cl(1) = 92.9(2), Cl(3)-W(1)-Cl(1) = 165.08(7), O(1)-W(1)-Cl(2) = 123.0(2), N(1)-W(1)-Cl(2) = 128.3(2), Cl(3)-W(1)-Cl(2) = 82.11(7), Cl(1)-W(1)-Cl(2) = 83.02(7).

dehydroxylated at 700 °C (SiO $_{2-700}$, Scheme 2). The reaction was performed in dichloromethane under a mild dynamic



vacuum in order to remove gaseous HCl which evolves during the reaction and to prevent its reaction with the support. Physisorbed molecular complexes were removed by washing with dichloromethane. The resulting light orange solid was dried under dynamic vacuum ($<10^{-5}$ Torr).

The IR spectrum of the grafted complex 3 shows a nearly complete consumption of the surface silanols (\equiv SiOH), as indicated by the nearly complete disappearance of the ν (O–H) peak at 3745 cm⁻¹ corresponding to isolated silanols (Figures 2a, 2b).^{10,11} IR bands associated with the ν (C–H) of the organic ligand appear between 2970 and 2877 cm⁻¹, and those related to ν (C–C) and δ (C–H) in the 1550–1350 cm⁻¹ region. A characteristic ν (C=N) band appears at 1653 cm⁻¹.

The elemental microanalysis of **3** indicates the presence of C, 3.73%, H, 0.51%, N, 0.54%, Cl, 1.13%, and W, 2.17%. Based on these values, a C/W ratio of 26.3 (theoretical value: 27) and a C/N ratio of 3.2 (theoretical value: 3) can be calculated. Within the limit of experimental error of this technique ($\pm 10\%$), these values and the FT-IR analysis are in good agreement with the grafting of **2** on the surface of SiO₂₋₇₀₀ to afford **3** as per the reaction in Scheme 2. The elemental analysis of **3** shows as well a Cl/W ratio of 2.7 (theoretical 2) that is slightly higher than expected. Therefore, an accurate determination of the Cl/W



Figure 2. FT-IR spectra of SiO_{2–700} (a, black), **3** (b, red), and **4** (c, blue) obtained after methylation of **3** with $ZnMe_2$ (*vide infra*).

ratio was performed by suspending 3 (0.4 g) in a NaHCO₃ solution (0.005 M, 100 mL). The resulting chloride ion was titrated with a silver nitrate solution (0.01 M, 90 mL) using potassium chromate as an indicator. A ratio of 2.0 \pm 0.2 chlorine atoms per grafted tungsten was found thus confirming the proposed composition. The tungsten loading on the surface resulted higher than that reported in the literature for $[(\equiv$ SiOW(=O)(=CH-t-Bu)(dAdPO)^{14a}(dAdPO = 2,6-diadamantyl aryloxide) and $[(\equiv SiO)W(\equiv O)(\equiv CH-t-Bu)-$ (HMTO)]^{14c} complexes, which could be attributed to the lower steric hindrance of the imidazolin-2-iminato group when compared to dAdPO and HMTO. Indeed, comparison of the buried volume (% V_{Bur}) of the three ligands dAdPO,^{14a} HTMO,^{14c} and $Im^{Dipp}N$ in the model system [W(=O)-(Cl)₃(X)] (see the Supporting Information for the computational details) shows % V_{Bur} values of 31.2, 25.2, and 21.7 for dAdPO, HTMO, and Im^{Dipp}N, respectively.

Further spectroscopic analysis of **3** was carried out by solidstate NMR. The ¹H magic-angle spinning (MAS) solid-state NMR spectrum of **3** displays broad signals at 1.1, 2.9, 3.6, 5.1, 6.3, and 7.4 ppm analogously to its homogeneous counterpart. The ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectrum of **3** shows distinct signals at $\delta = 22$, 29, 116, 124, 129, and 147 ppm (Figure S4) from the imidazolin-2iminato ligand and the aromatic groups that are in good agreement with the NMR spectrum of **2** in solution (Figure S2).

Preparation of $[(\equiv Si-O-)W(=O)(CH_3)_2-Im^{Dipp}N]$ (4). In order to access the precatalytic complex bearing tungsten methyl functionalities, $ZnMe_2$ was used for the alkylation of 3 (Scheme 3).

A color change from yellow to light gray was observed after treating **3** with an excess of ZnMe₂ (ca. 3 equiv based on the Cl content; molar Zn/W ratio, 3.8; see the Experimental Section for details) in dichloromethane at an initial temperature of -50°C. The FT-IR analysis of **4** (Figure 2c) displays bands in the 3000 cm⁻¹ (ν (C-H)) and 1300–1500 cm⁻¹ (δ (C-H)) regions overlapping those present in parent compound **3**. In addition, a significant shift to 1612 cm⁻¹ for the ν (C=N) band was observed (vs 1653 cm⁻¹ in **3**), which clearly suggests a change in the electronic environment around the tungsten Scheme 3. Synthesis of 4, $[(\equiv Si-O-)W(\equiv O)(CH_3)_2$ -Im^{Dipp}N], by Methylation of 3 with Dimethylzinc



center. The elemental analysis of 4 gave W, 2.09%, C, 4.07%, Zn, 2.56%, and Cl, 1.33%. Upon methylation, the C/W ratio determined by elemental analysis changed from a value of 26.3 in compound 3 to ca. 30 in 4, which is in good agreement with the expected value (theoretical value for 4: 29). To note, a Cl/W molar ratio of ca. 3, comparable to that found by elemental analysis in complex 3, and the presence of Zn (Zn/W molar ratio: 3.5) in an amount close to that added for the methylation step were determined. These values suggest that the ZnCl₂ produced upon methylation and the excess ZnMe₂ (adsorbed or reacted with the surface) could not be effectively removed by washing. A similar behavior was observed in a previous study.^{15b} In order to unequivocally demonstrate the successful methylation of 3, solid-state NMR investigation and EXAFS analysis of 4 were carried out.

The ¹H MAS NMR spectrum of 4 (Figure 3a) displays several broad signals resembling those observed for its parent compound (3) at 1.1, 2.9, 3.6, 5.1, 6.3, and 7.4 ppm along with a new peak at 1.9 ppm. The signal at 1.1 ppm autocorrelates in 2D double-quantum (DQ) and triple-quantum (TQ) ¹H-¹H homonuclear dipolar correlation spectra and is assigned to the

methyl protons of the isopropyl groups of the ligand (Figures 3b and 3c). The new peak at 1.9 ppm autocorrelates as well in the DQ and TQ NMR experiments in agreement with the formation of W-CH₃ moieties upon methylation. As expected, the proton resonances at 2.9, 3.6, 5.1, 6.3, and 7.6 ppm display no autocorrelation in TQ but only in the DQ spectrum which supports their attribution to the protons of the ligand backbone (isopropyl groups CH (2.9 and 3.6 ppm), imidazole CH=CH (5.1 ppm), and phenyl ring protons (6.3 and 7.4 ppm)). The broad signal at -0.1 ppm is presumably due to the formation of \equiv Si-OMe moieties^{7c} by methylation of the residual surface silanols upon the addition of excess ZnMe2; this is supported by autocorrelation in DQ and TQ (Figures 3b and 3c) and by the complete disappearance of the residual silanol stretching at 3745 cm⁻¹ in the FT-IR of 4. In addition, some weak correlations were observed in the DQ spectrum between the aromatic and the alkyl protons of the ligand (Figure 3b).

The ¹³C CP/MAS NMR spectrum (Figure 3d) displays signals at 22, 29, 116, 124, 136, 147, and 153 ppm similarly to parent compound 3 and a new peak at 50 ppm that could be assigned to the newly formed W–CH₃ functionalities.³² This attribution is confirmed by the strong correlation between the proton signal at 1.9 ppm and the carbon signal at 50 ppm in the 2D ¹H–¹³C HETCOR NMR spectrum (Figure 3e) recorded with a short contact time (0.2 ms). Additionally, this spectrum shows a correlation between the methyl protons of the ligand at 1.1 ppm and the corresponding carbon atoms (22, 29 ppm). Similarly, the protons in the aromatics region (6.3–7.4 ppm) correlate in the HETCOR spectrum to the respective carbon atoms in the aromatic region of the spectrum.

The oxidation state and the structure of the grafted tungsten complexes 3 and 4 were further investigated by extended X-ray absorption fine structure spectroscopy (EXAFS). EXAFS investigation was carried out at the W L_{III} -edge (Figure 4,



Figure 3. (a) One-dimensional (1D) ¹H MAS solid-state NMR spectrum of 4 acquired at 600 MHz (14.1 T) with a 22 kHz MAS frequency, a repetition delay of 5 s, and 8 scans. (b) Two-dimensional (2D) ¹H–¹H double-quantum (DQ)/single-quantum (SQ) and (c) ¹H–¹H triple-quantum (TQ)/SQ NMR spectra of 4 (both acquired with 32 scans per t_1 increment, 5 s repetition delay, 32 individual t_1 increments). (d) ¹³C CP/MAS NMR spectrum of 4 acquired at 9.4 T (ν_o (¹H) = 400 MHz) with a 10 kHz MAS frequency, 10000 scans, a 5 s repetition delay, and a 2 ms contact time. An exponential line broadening of 80 Hz was applied prior to Fourier transformation. (e) 2D ¹H–¹³C CP/MAS dipolar HETCOR spectrum of 4 (acquired at 9.4 T with a 10 kHz MAS frequency, 4000 scans per t_1 increment, a 4 s repetition delay, 64 individual t_1 increments, and a 0.2 ms contact time).



Figure 4. Fourier transform of the k^3 -weighted EXAFS (top) at the W L_{III} -edge and its corresponding back Fourier transform in the [0.8, 2.5] Å range (bottom) with comparison to simulated curves for [(\equiv Si-O-)W(\equiv O)Cl₂-Im^{Dipp}N] (3, red) and [(\equiv Si-O-)W(\equiv O)(CH₃)₂-Im^{Dipp}N] (4, blue). Solid lines, experimental; dashed lines, spherical wave theory.

Table 1; see section S5 of the Supporting Information for further details). The previous crystallographic structure of **2** as

Table 1. EXAFS Parameters Obtained for $[(\equiv Si-O-)W(=O)Cl_2-Im^{Dipp}N]$ (3) and $[(\equiv Si-O-)W(=O)(CH_3)_2-Im^{Dipp}N]$ (4)^{*a*}

paths	Ν	d (Å)	$\begin{array}{c} 10^3 imes \sigma^2 \\ (\text{\AA}^2) \end{array}$	ΔE (eV)	R (%)		
$[(\equiv Si-O-)W(=O)Cl_2-Im^{Dipp}N] (3)$							
W→O	1.2 ± 0.2	1.72 ± 0.01	<u>1</u>	5 ± 2	0.2		
$W \rightarrow N/O$	2.4 ± 0.1	1.95 ± 0.02	5 ± 3				
W→Cl	1.6 ± 0.1	2.36 ± 0.01	<u>3.5</u>				
$[(\equiv Si-O-)W(\equiv O) (CH_3)_{1.4}Cl_{0.6}-Im^{Dipp}N]$ (4)							
W→O	1.0 ± 0.2	1.71 ± 0.01	<u>1.5</u>	6 ± 4	0.5		
$W \rightarrow C/O/N$	3.4 ± 0.2	1.95 ± 0.05	11 ± 3				
W→Cl	0.6 ± 0.2	2.28 ± 0.03	<u>3.5</u>				
^a Underlined values denote fixed parameters.							

determined by single crystal X-ray diffraction was used to generate the scattering paths with their related theoretical atomic scattering factors, photoelectron mean free paths, and phase shifts. The initial model for a first shell fitting included a set of two W–O scattering paths with half path lengths of 1.73 and 1.9 Å. These were supplemented by W–N and W–Cl scattering paths with a half path length of 1.79 and 2.35 Å respectively. Attempts to fit the EXAFS data of compound **3**

with the latter model failed because the W–N and W–O paths were found to be merged into one single frequency. A more reasonable model was thus restricted to a single W–N scattering path modeling both the bond to the imidazolin-2iminato ligand and the bond to a siloxide ligand. The total coordination number of the metal center was restrained to 5 in order to decrease the correlation between parameters. The best fit resulted in 1.1 ± 0.1 oxygen atoms at 1.72 ± 0.01 Å, assigned to the shortest W=O bond; 2.4 ± 0.2 nitrogen/oxygen atoms at 1.95 ± 0.02 Å, and 1.6 ± 0.1 chlorine atoms at 2.36 ± 0.01 Å. The coordination calculated for tungsten suggests, on average, a predominantly monopodal grafting of **2**, and it is thus consistent with the formula $[(\equiv Si-O-)W(\equiv O)Cl_2-ImDippN]$ describing the structure of **3** and with a grafting reaction of **2** as in Scheme 2.

Qualitative examination of the Fourier transform of 4, obtained after methylation of 3, shows a large decrease of the peak at 2.0 Å (Figure 4). The latter observation is indeed expected when chlorine atoms are exchanged by carbon atoms which have a much weaker atomic scattering factor. A first model consisting of W–O (W=O), W–N/O (ImDippN, siloxide), and W–C (methyl) scattering paths was used to fit the EXAFS data. The resultant fit, shown in Figure S7 and Table S7, provided an unrealistic total coordination number (\approx 7) and energy shift (>10 eV), together with a lesser statistical agreement with experimental data.

This gave a hint that some chlorine atoms might still be coordinated to the tungsten center. Indeed, the best model used to fit the data included W–O (W=O), W–C (Im^{Dipp}N, siloxide, methyl), and W–Cl scattering paths. The parameters extracted from the fit are consistent with 1.0 ± 0.2 oxo ligands at 1.71 ± 0.01 Å, 3.4 ± 0.2 carbon atoms at 1.95 ± 0.05 modeling siloxide, imidazolin-2-iminato, and methyl ligands, and 0.6 ± 0.2 chlorine atom at 2.28 ± 0.03 Å.

Comparison of the chlorine coordination number of 3 and 4 (1.6 vs 0.6 respectively) shows that the Cl/Me exchange is occurring, but it is not complete, upon reaction with an excess of ZnMe₂. To conclude, EXAFS results (average formula: [(\equiv Si-O-)W(\equiv O)(CH₃)_{1.4}(Cl)_{0.6}-Im^{Dipp}N]) suggest that surface complex 4 could contain [(\equiv Si-O-)W(\equiv O)(CH₃)₂Im^{Dipp}N], [(\equiv Si-O-)W(\equiv O)(CH₃)Cl-Im^{Dipp}N], and, possibly, some residual complex 3. In the likely assumption that upon addition of an excess of ZnMe₂ to 3 the vast majority of the surface complexes undergoes at least partial alkylation, and within the margin of experimental error, 4 should contain nearly equivalent amounts of mono- and dialkylated tungsten oxo complexes (Chart 2).

In order to further investigate the identity of the surface species, the products of the thermal degradation of 4 at 150 °C

Chart 2. Surface Complexes Describing Compound 4 Based on EXAFS Analysis



 $[(\equiv\!\text{Si-O-})W(=\!O)(\text{CH}_3)_2\text{-Im}^{\text{Dipp}}\text{N}] \qquad [(\equiv\!\text{Si-O-})W(=\!O)(\text{CH}_3)\text{CI-Im}^{\text{Dipp}}\text{N}]$

were analyzed by GC and show the evolution of 0.55 mol of methane per tungsten atom (see section S6 of the Supporting Information and Table S8). The evolution of methane is consistent with the formation of the expected catalytically active carbenic species $[(\equiv Si-O-)W(=O)(=CH_2)-Im^{Dipp}N]$ from $[(\equiv Si-O-)W(\equiv O)(CH_3)_2Im^{Dipp}N]$ by α -H-transfer from a methyl ligand to another methyl group on the same tungsten atom. This process, which is supposed to generate methane and the catalytically relevant W-methylidene intermediate,³³ cannot take place on monoalkylated $[(\equiv Si-O-)W(\equiv O) (CH_3)Cl-Im^{Dipp}N$]. As an effect, the latter complex is not expected to be a precatalyst as it is unable to provide the crucial W-methylidene complex. The measured amount of CH₄ released is in good agreement with the nearly stoichiometric (1:1) ratio between mono- and dialkylated tungsten centers as inferred by the analysis of the EXAFS data. Attempts to observe the tungsten carbene moiety by solid-state NMR after thermal treatment of 4 at 150 °C were not successful as no resonances attributable to the metal carbene could be detected. This confirms that the spectroscopic identification of this intermediate is extremely challenging as reported in other studies.^{13a,b,15b}

Catalysis Studies Using 4 in Metathesis Reactions. Material 4 was found to be an active metathesis precatalyst in the presence of an excess (3050 equiv, catalyst loading: 0.03 mol %) of propene in a batch reactor at 150 °C (see the Experimental Section for details). Under these conditions, the formation of an equilibrated mixture of metathesis products (ethene, 2-butenes) was observed within ca. 2 h with a *trans/cis* 2-butene ratio of ca. 1.8 (conversion after 15 h, 38.2%; TON, 1165; TOF (turnover frequency) for the first hour of reaction, 825 h⁻¹; see Figure 5). This ratio is identical to what has been



Figure 5. Product conversion and selectivity vs time plot for the propene metathesis by 4 (3050 equiv of propene/W) (TON = 1165).

observed by Mazoyer et al. using $[(\equiv SiO)(W=O)Np_3]$ (Np: neopentyl) tungsten oxo catalyst under dynamic conditions.^{13a} By allowing the reaction to proceed for a prolonged time, limited quantities of isobutene could also be detected. The catalytic activity of 4 in propene metathesis was compared with that of fully alkylated, tungsten surface complex $[(\equiv SiO-W(CH_3)_5], 5,^{32}$ and of its unfunctionalized tungsten oxo analogue $[(\equiv Si-O-)W(\equiv O)(CH_3)_3], 6,^{15b}$ under the same reaction conditions (see section S7 of the Supporting

Information and Figures S11 and S12). The analysis of these results reveals that the TOF observed for 4 is comparable with that of 5 (TOF after the first hour of reaction: 948 h^{-1}) and it is about 30% lower than that observed for 6 (TOF after the first hour of reaction: 1188 h⁻¹). Both tungsten oxo compounds display similar TON values after an extended reaction time of 15 h (1165 for 4 versus 1180 for 6). In spite of the slower apparent initial reaction rate for 4, it should be considered that whereas 6 is known to display exclusively fully alkylated tungsten oxo moieties,^{15b} only about 50% of the surface complexes of 4 are completely alkylated and therefore potentially active as metathesis precatalysts (according to EXAFS and thermal degradation studies). Based on this observation, a TOF as high as 1650 h^{-1} can be calculated for 4 by taking into account only the active surface sites. Propene being a short terminal olefin for which the steric effects are not expected to play a significant role,³⁴ the comparison of the catalytic activity of 4 and 6 suggests that the presence of the imidazolin-2-iminato ligand does not lead to a deactivation of the tungsten oxo moiety for propene metathesis activity compared to the unfunctionalized complex.

To note, the TON and TOF values obtained for the SOMC precatalysts **4–6** at 150 °C are generally excellent in comparison with those of standard tungsten catalysts for propene metathesis prepared by traditional impregnation of WO₃ on SiO₂. Stair et al. have shown that, unless high temperature (550 °C) preactivation of the catalyst is carried out, a standard WO₃/SiO₂ system (10.4 wt %) is only active above 350 °C and shows a propene conversion lower than 10% under dynamic conditions at 400 °C.³⁵

When 4 was exposed to 150 equiv of propene at 150 °C in a batch reactor, the formation of an equilibrated mixture of metathesis products containing exclusively propene, ethene, and 2-butene (*trans/cis* ratio of 1.93) was observed within 1 h (conversion 38%, Figure S10).

The catalytic activity of 4 toward the self-metathesis of higher terminal olefins was also investigated. The homocoupling of 1-hexene promoted by precatalyst 4 took place slowly at room temperature (2% conversion in 24 h, TON: 70). However, the rate of the reaction could be significantly increased by performing it at 80 °C, leading to the conversion of ca. 19% of the substrate in 24 h with a selectivity toward dec-5-ene of ca. 64% as determined by gas chromatographic analysis (Table 2, see also Table S9 and Figure S18). Once again, we have compared the performance of 4 in the metathesis of 1-hexene with that of tungsten pentamethyl grafted on SiO₂₋₇₀₀ [(\equiv SiO-W(CH₃)₅], **5**,³² and with its oxo analogue [(\equiv Si-O-)W(\equiv O)(CH₃)₃], **6**.^{15b} After 24 h of reaction at 80 °C, we found catalyst 4 to be significantly more selective than **5** and **6** under

Table 2. Catalysis Results for the Metathesis of 1-Hexene Catalyzed by Surface Tungsten Complexes 4–6

2		catalyst 4-6		
		80 °C, 24 h +	//	
catalyst	substrate/ catalyst	$(conversion, \%)/TON/[TOF, h^{-1}]$	selectivity dec-5- ene	
4	3517	(18.6)/654/[27.3]	64	
5	3311	(84.6)/2801/[116.7]	9	
6	1981	(78.5)/1555/[64.8]	34	
6 ^{<i>a</i>}	1981	(19.7/391/[86.9]	48	

^aAt 80 °C for 4.5 h.

the same reaction conditions (see also chromatograms in Figures S19 and S20) but at the cost of a drop in 1-hexene conversion and TOF when compared to the latter catalysts. As the selectivity in olefin metathesis is generally linked to the occurrence of consecutive metathesis processes, we investigated also the selectivity of the reaction catalyzed by 6 at a degree of conversion comparable to that of 4 that was afforded after just 4.5 h of reaction. Even under these conditions the selectivity observed for the unfunctionalized tungsten oxo system (6) was lower than for 4. The reduction in the rate of 1-hexene conversion and the increased selectivity for 4 when compared to 5 and 6 could, in principle, be attributed to steric and/or electronic effects of the imidazolin-2-iminato ligand. As discussed above, the activity data for propene metathesis using 4 and 6 suggests that the presence of the imidazolin-2iminato ligand does not seem to lead to a deactivation of the tungsten oxo center. A closer look at the product distribution obtained after 24 h with catalysts 5 and 6 (Figures S19 and S20) shows the formation of large amounts of alkene byproducts such as C_4-C_9 and $C_{n>10}$ whose presence can be explained by the isomerization of dec-5-ene and/or 1-hexene and by the subsequent metathesis reactions of the resulting internal olefins.³⁶ This effect seems to be very strong in the case of $[(\equiv SiO-W(CH_3)_5] (5)$, whereas the tungsten oxo complex $[(\equiv Si-O-)W(\equiv O)(CH_3)_3]$ (6) appears slightly more selective. The products of metathesis of the isomerized olefins were not observed or were present in minor amounts for the reaction catalyzed by 4 (Figure S18). However, analysis of the C_6 region of the chromatogram shows that isomerization of 1-hexene (initial purity \geq 99%) occurs in the reaction catalyzed by 4. Taken together, these results suggest that the metathesis of the internal olefins produced by isomerization might be suppressed or occurs slowly for 4, when compared to 5 and 6, as an effect of the presence of the bulky imidazolin-2-iminato ligand.

The dec-5-ene formed in the presence of 4 was mostly found as the thermodynamic *E*-isomer product (see Table S9). The preparation of supported *Z*-selective W—oxo catalysts has so far remained elusive in spite of the application of other W—oxo complexes carrying bulky ligands at the metal center such as dAdPO,^{14a} OSi-*t*-Bu₃,⁴ and HMTO.^{14c} Indeed, it appears that the search for the suitable coordination environment leading to *Z*-selectivity in heterogeneous tungsten oxo olefin metathesis catalyst is still open.

CONCLUSION

We have elaborated a straightforward synthetic strategy for the preparation of a functionalized silica-supported W-oxo complex $[(\equiv Si-O-)W(\equiv O)(CH_3)_2 - Im^{Dipp}N]^{-1}(4)$, incorporating a bulky imidazolin-2-iminato ligand. The complex was systematically characterized via elemental microanalysis, FT-IR, solid-state NMR, and EXAFS spectroscopies. Under mild conditions, and without the need of cocatalyst, 4 performed as an active precatalyst in the metathesis of terminal olefins such as propene and 1-hexene. 4 was more selective toward the formation of dec-5-ene than other tungsten-based catalysts applied under the same reaction conditions. This observation highlights the potential of this synthetic approach for the straightforward preparation of metathesis catalysts with enhanced selectivity toward the target olefin. As a future improvement of this approach, a method for the complete alkylation of the surface complex intermediate (such as 3) should be developed in order to limit the formation of inactive surface species and to exploit the full potential of the

functionalized complexes. Further efforts will be directed to the application of this method for the judicious design and preparation of analogues of **4** able to promote the *Z*-selective metathesis of terminal olefins by the choice of the opportune coordination environment around the tungsten oxo moiety.

EXPERIMENTAL SECTION

Materials and General Procedures. All experiments were carried out by using standard Schlenk techniques. Air and moisture sensitive materials were stored and handled in a glovebox. Solvents were purified and dried according to standard procedures. C₆D₆ and CDCl₃ (SDS) were distilled over Na/benzophenone and stored over molecular sieves (3 Å). *N*-Silylated 2-iminoimidazoline was prepared by the Staudinger reaction of 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene with trimethylsilyl azide following the literature procedure (*vide infra*).^{21a} Propene was dried and deoxygenated before use by passing it through a mixture of freshly regenerated molecular sieves (3 Å) and R3-15 catalysts (BASF). SiO_{2−700} was prepared from Degussa Aerosil silica (specific surface area: 200 m² g⁻¹) by partial dehydroxylation at 700 °C under high vacuum (10⁻⁵ Torr) for 15 h. This treatment led to a white solid having a specific surface area of 200 m² g⁻¹ and containing 0.7 ± 0.2 OH nm⁻². 1-Hexene (≥99%) was purchased from Sigma-Aldrich.

Elemental analyses were performed at Mikroanalytisches Labor Pascher (Germany). Gas-phase analyses were performed on a Agilent 6850 gas chromatograph equipped with a flame ionization detector (FID) and an Al_2O_3/KCl on fused silica column (30 m \times 0.53 mm, 20.00 mm, capillary column coated with a stationary phase of aluminum oxide deactivated with KCl was used with helium as a carrier gas at 31.1 kPa).

FT-IR, **Raman**, and Solution NMR Spectroscopies. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF_2 windows. The samples were prepared under Ar within a glovebox. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm⁻¹). Raman spectra were acquired using the 488 nm line of an Ar-ion laser (Melles Griot). The excitation beam was focused on the sample by a 50× long working distance microscope, and the scattered light was analyzed by an air-cooled CCD (Labram HR, Horiba Jobin Yvon). The fluorescence was subtracted from the spectra for clarity. Solution NMR spectra were recorded on an Avance-400 Bruker spectrometer. All chemical shifts were measured relative to residual ¹H or ¹³C undeuterated solvent resonances in the deuterated solvents.

Solid-State NMR Spectroscopy. One-dimensional ¹H MAS and ¹³C CP/MAS solid-state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 600 or 400 MHz resonance frequencies for ¹H. The 400 MHz experiments employed a conventional double-resonance 4 mm CP/MAS probe, whereas experiments at 600 MHz utilized a 3.2 mm HCN triple-resonance probe. In all cases the samples were packed into rotors under inert atmosphere inside gloveboxes. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantane.¹³C CP/MAS NMR experiments used the following sequence: 90° pulse on the proton (pulse length = 4 s), then a crosspolarization step with a contact time of typically 0.2 ms, and finally acquisition of the ¹³C signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ¹H nuclei. The number of scans ranged between 5000 and 10000 for ¹³C and was 32 for ¹H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to the Fourier transformations.

The 2D ¹H–¹³C heteronuclear correlation (HETCOR) solid-state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer operating at 600 MHz using a 3.2 mm MAS probe. These experiments were performed according to the following scheme: 90° proton pulse, t_1 evolution period, CP to ¹³C, and detection of the ¹³C magnetization under TPPM decoupling. During the cross-polarization step, a ramped radio frequency (rf) field

centered at 75 kHz was applied to the protons, whereas the ¹³C channel rf field was matched to obtain an optimal signal. A total of 64 t_1 increments with 4000 scans each were collected; sample spinning frequency was 10 kHz. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment was verified to be selective for the first coordination sphere around tungsten, such that correlations occurred only between pairs of attached ¹H–¹³C spins (C–H directly bonded).

Two-dimensional double-quantum (DQ) and triple-quantum (TQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double-resonance 3.2 mm CP/MAS probe, according to the following general scheme: excitation of DQ coherences, t_1 evolution, z-filter, and detection. The spectra were recorded in a rotor-synchronized fashion in t_1 such that the t_1 increment was set equal to one rotor period (45.45 μ s). One cycle of the standard back-to-back (BABA) recoupling sequences was used for the excitation and reconversion period. Quadrature detection in w_1 was achieved using the States-TPPI method. A spinning frequency of 22 kHz was used. The 90° proton pulse length was 2.5 μ s, whereas a recycle delay of 5 s was used. A total of 128 t_1 increments with 32 scans per increment were recorded. The DQ frequency in the w_1 dimension corresponds to the sum of two single-quantum (SQ) frequencies of the two coupled protons and correlates in the w_2 dimension with the two corresponding proton resonances. The TQ frequency in the w_1 dimension corresponds to the sum of the three SQ frequencies of the three-coupled protons and correlates in the w_2 dimension with the three individual proton resonances. Conversely, groups of fewer than three equivalent spins will not give rise to diagonal signals in the spectrum.

X-ray Crystal Structure Determination. Single crystals were mounted on a glass fiber using perfluoroalkylether (viscosity 1800 cSt, ABCR GmbH & Co. KG Karlsruhe) image plate single crystal diffractometer IPDS2 (STOE) with graphite monochromatized Mo K α (λ = 0.71069 Å) radiation, at 200 K. For data collection, determination, and refinement of the lattice parameters the STOE X-Area software package was used (X-area).³⁷ The intensity data were corrected for absorption numerically using the program X-Shape (X-shape).³⁸ The crystal structure was solved by direct methods and refined using the ShelXT program package.³⁹

X-ray Absorption Spectroscopy (XAS). The experiments were performed on the CRG-FAME beamline (BM30B), at the European Synchrotron Radiation Facility in Grenoble. Spectra were recorded either in fluorescence (grafted materials) or in transmission (tungsten metallic foil) at the W L₃-edge. In the fluorescence mode, spectra of pure samples, also in the pellet form, were collected with the sample positioned at 45° with respect to the beam. The fluorescence yield was measured with a multielement solid-state detector that collected X-rays only in an electronically gated energy interval appropriate for the fluorescence X-rays of the absorbing element (30 elements Ge solid-state detector, Canberra). All measurements with powdered materials were performed using a cell equipped with three beryllium windows including a sample holder for the measurement of five air sensitive compounds (dynamic vacuum, $P < 10^{-5}$ mbar).

Cherokee software was used for the extraction of the EXAFS signal.⁴⁰ The EXAFS spectra were obtained after performing standard procedures for pre-edge subtraction, normalization, polynomial removal, and wave vector conversion. The extracted EXAFS signal was fitted in *R*-space using a Kaiser–Bessel apodization window (dk = 1) with a k-range of about [4.1; 10–11] $Å^{-1}$ for all materials. For each atomic shell, the following structural parameters were adjusted: coordination number (N), bond length distance (R), and the so-called Debye–Waller factor via the mean-square relative displacement (σ^2) of the considered bond length. The amplitude factor (\bar{S}_0^2) was fitted to the EXAFS spectrum obtained for a tungsten metallic foil whose crystal structure $(Im\overline{3}m)$ is well-known;⁴¹ S₀² was then fixed to 0.94 ± 0.09 (see Figure S1 and Table S1). The crystal structure of Im^{Dipp}NWOCl₃ as determined by single crystal X-ray diffraction was used as an input to calculate the theoretical phases, amplitudes, and electron free mean path with the FEFF6 code implemented in IFEFFIT programs suite.42

Synthetic Procedures. *N-Silylated 2-Iminoimidazoline (1).* A solution of 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (10 mmol) in toluene (20 mL) was treated dropwise with trimethylsilyl azide (14 mmol) at ambient temperature, and the resulting reaction mixture was subsequently refluxed for 72 h. Filtration and evaporation of the solvent afforded the imine product as a yellowish solid that could be purified by bulb to bulb distillation at 180 °C/9 mbar. Yield: 94%. ¹H NMR (400 MHz, C₆D₆) δ (ppm): -0.18 (9 H, s, SiCH₃), 1.17–1.19 (12 H, d, CH₃CHCH₃), 1.36–1.38 (12 H, d, CH₃CHCH₃), 3.10–3.21 (4 H, sept, CH₃CHCH₃), 5.93 (2 H, s, NCH), 7.12 (2 H, s, *p-H*), 7.19–7.23 (4 H, m, *m-H*). ¹³C NMR (70 MHz, C₆D₆) δ (ppm): 3.15 (SiCH₃), 23.13 (CH₃CHCH₃), 24.0 (CH₃CHCH₃), 28.5 (CH₃CHCH₃), 113.39 (NCH), 123.54 (*m*-CH), 129.03 (*p*-CH), 134.70 (*ipso*-CH), 140.98 (NCN), 147.61 (*o*-CH). See Figure S3.

 $Im^{Dipp} \hat{N}WOCl_3$ ($Im^{Dipp} = 1,3$ -Bis(2,6-diisopropylphenyl)imidazolin-2-iminato) (2). A solution of 2.0 g (4.2 mmol) of 1 in dichloromethane (10 mL) was added to tungsten(VI) oxytetrachloride 1.44 g (4.20 mmol) in dichloromethane (40 mL) under stirring. The reaction mixture was refluxed overnight. The solvent was evaporated, and the crude material was extracted three times with n-hexane (20 mL) to remove unreacted 1. The crude material was crystallized from an *n*-hexane, dichloromethane mixture at -30 °C to yield 2.5 g of complex 2 [Im^{Dipp}NWOCl₃] (3.54 mmol, 84%). Anal. Calcd for C₂₇H₃₆Cl₃N₃OW: C, 45.75; H, 5.12; Cl, 15.00; N, 5.93; W, 25.94%. Found: C, 44.33; H, 4.97; Cl, 15.20; N, 5.84; W, 25.8%. The C content is slightly lower than expected (the deviation from the expected value is about 3%). This might depend on the presence of residual traces of solvents and grease. Complex 2 was used without further purification for the following step. Raman: 946 cm⁻¹ ν_s (W= O), 360 cm⁻¹ ν_s (W–Cl). ¹H NMR (400 MHz, C₆D₆) δ (ppm): 1.23-1.25 (12 H, d, CH₃CHCH₃), 1.37-1.39 (12 H, d, CH₃CHCH₃), 2.68-2.75 (4 H, sept, CH₃CHCH₃), 7.15 (2 H, s, NCH), 7.36-7.38 (4 H, m, m-H), 7.53-7.56 (2 H, m, p-H). ¹³C NMR (70 MHz, C₆D₆) δ (ppm): (70 MHz, CDCl₃) 22.98 (CH₃CHCH₃), 25.05 (CH₃CHCH₃), 29.34 (CH₃CHCH₃), 121.44 (NCH), 124.70 (m-CH), 129.49 (p-CH), 131.91 (ipso-CH), 145.79 (NCN), 149.44 (o-CH). See Figure S4.

Partially Dehydroxylated Silica at 700 °C (SiO₂₋₇₀₀). The oxide support used in this study is Aerosil 200 silica from Degussa. Aerosil 200 is a nonporous flame silica in the form of regular particles of an average diameter of 150 Å and free of halide impurities. It was dehydroxylated under vacuum (<10⁻⁵ Torr) at 700 °C for a minimum of 15 h leading to SiO₂₋₇₀₀. The specific surface area for SiO₂₋₇₀₀ was 200 ± 2 m²/g. IR (cm⁻¹): 3745 cm⁻¹, ν (SiO–H).

Grafting of 2 on SiO₂₋₇₀₀ To Produce $[(\equiv Si-O-)Im^{Dipp}NWOCl_2]$ (3). In a double Schlenk, a solution of 2 (212 mg, 0.3 mmol, 1.1 equiv with respect to the amount of surface-accessible silanol) in 25 mL of dichloromethane was allowed to react with 1.0 g of SiO₂₋₇₀₀ at 25 °C for 4 h. The reaction was performed under mild dynamic vacuum conditions to remove the HCl produced during the reaction. At the end of the reaction, the solvent was filtered and the resulting yellow solid was washed three times with dichloromethane (20 mL) and dried under a dynamic vacuum (<10⁻⁵ Torr, 2 h). Elemental analysis found C, 3.73; Cl, 1.13; N, 0.5; W, 2.17%. IR (cm⁻¹): 2970–2877 ν (C–H), 1653 cm⁻¹ ν (C=N) and 1550–1350 cm⁻¹ δ (C–H). ¹³C CP-MAS SS NMR (400 MHz, 298 K) δ (ppm): 22 (CH₃CHCH₃), 29 (CH₃CHCH₃), 116 (NCH), 124 (*m*-CH), 129 (*p*-CH), 137 (*ipso*-CH), 147 (NCN) ppm.

Alkylation of 3 To Yield [(\equiv Si-O-)W(\equiv O)(CH₃)₂-Im^{Dipp}N] (4). In a double Schlenk, 3 (0.7 g; based on the elemental analysis values, this amount of material contains Cl, 1.13%, and W, 2.17%, corresponding to 0.22 mmol of Cl and 0.083 mmol of W respectively) was suspended in 20 mL of dichloromethane, and a heptane solution of ZnMe₂ (0.315 mmol, 2.86 equiv with respect to the amount of chlorine in 3, Zn/W = 3.8) was added at -50 °C. The excess of ZnMe₂ employed was set after stoichiometric and, in general, lower amounts of the alkylating reagent had not provided a satisfactory degree of alkylation. The mixture was allowed to warm to room temperature and stirred for a further 2 h. At the end of the reaction, the resulting light gray solid was filtered and thoroughly washed with dichloromethane. The light gray

solid was then dried under dynamic vacuum (<10⁻⁵ Torr) for 4 h. ¹H MAS SS NMR (400 MHz, 298 K) δ (ppm): 1.1 (CH₃CHCH₃), 1.9 (WCH₃), 3.6 (CH₃CHCH₃), 5.1 (NCH), 6.3–7.4 (aromatic CH). ¹³C CP-MAS SS NMR (400 MHz, 298 K) δ (ppm): 22 (CH₃CHCH₃), 29 (CH₃CHCH₃), 50 (WCH₃), 116 (NCH), 124 (*m*-CH), 129 (*p*-CH), 133 (*ipso*-CH, *o*-CH), 147 (NCN). Elemental analysis, found: C, 4.07; Cl, 1.33; N, 0.63; W, 2.09; Zn, 2.56%. Carbon to tungsten ratio (C/W) in complex 4: found, 29.85 \pm 0.2; expected value, 29.

Decomposition of 4 was carried out by placing 100 mg of material in a 270 mL reactor equipped with a septum. It was then heated at 150 °C for 12 h. Gas samples were withdrawn by an airtight 0.5 mL gas syringe and injected into a GC instrument equipped with an FID detector. Methane was the only product detected in the gas phase. Methane calibration was carried out by withdrawing 0.5 mL samples of pure methane at different, known pressure from a high vacuum Schlenk line and by building a graphic correlating the partial pressure of methane with its GC area. The amount of methane liberated by 4 at 150 °C was quantified as 0.028 ± 0.05 mmol of CH₄ g⁻¹ (1.58 ± 0.2 CH₄/W).

Procedure for Catalytic Reactions. Propene Metathesis. In a glovebox, complex 4 [(\equiv Si-O-)W(\equiv O)(CH₃)₂-Im^{Dipp}N] (50 mg, 0.0057 mmol W) was introduced in a batch reactor (160 mL). After evacuation of argon, about 150 (or 3050) equiv (with respect to tungsten) of dry purified propene was added at room temperature and the reactor was heated to 150 °C (heating rate: 4 °C/min). The composition of the gas phase was monitored by GC.

Self-Metathesis of 1-Hexene. In a glovebox, scintillation vials containing a wing shaped magnetic stirrer were charged with the catalyst. 1-hexene (4.0 mmol) was added. The flask was removed from the glovebox and connected to a vacuum line, where it was cooled to -78 °C and evacuated to ca. 300-500 mTorr (usually the onset of bubbling). The flask was sealed under static vacuum and allowed to warm to room temperature. The reaction mixture was stirred at 600 rpm and heated to 80 °C. Aliquots of the reaction mixture were quenched by exposure to air and addition of dichloromethane and subjected to gas chromatography and ¹H NMR analysis to determine the conversion and E/Z selectivity. The resulting solution was analyzed by GC/FID (Agilent 6850) equipped with a fused silica column. The identity of the metathesis products was assessed by the injection of pure standards. The mass recovery ratio was determined by comparison of the total area of all the products in the chromatogram of the reaction mixture (after normalization by the number of carbon atoms in each product and by taking into account the formation of a mole of ethylene for each mole of dec-5-ene) and the area produced by the injection of an identical amount of pure 1hexene as employed for the reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02424.

Spectra, chromatograms, crystallographic data, experimental details, EXAFS, and computational data (PDF)

The crystal structure of complex 2 has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1501262).

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Notes

The authors declare no competing financial interest.

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