VIP Metathesis Catalysts Very Important Paper

Deutsche Ausgabe: DOI: 10.1002/ange.201509390
Internationale Ausgabe: DOI: 10.1002/anie.201509390

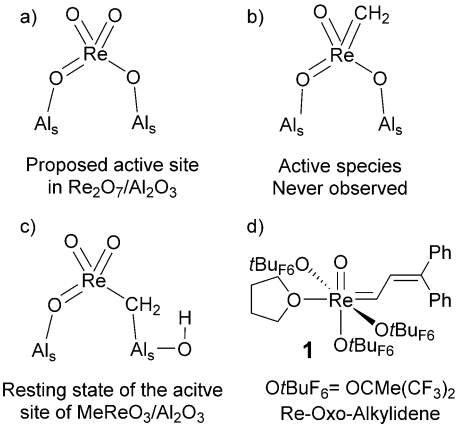
Switching on the Metathesis Activity of Re Oxo Alkylidene Surface Sites through a Tailor-Made Silica–Alumina Support

*Maxence Valla, David Stadler, Victor Mougel, and Christophe Copéret**

Abstract: *Re oxo alkylidene surface species are putative active sites in classical heterogeneous Re-based alkene-metathesis catalysts. However, the lack of evidence for such species questions their existence and/or relevance as reaction intermediates. Using Re(O)(=CH-CH=CPh$_2$)(OtBu$_{F6}$)$_3$(THF), the corresponding well-defined Re oxo alkylidene surface species can be generated on both silica and silica–alumina supports. While inactive on the silica support, it displays very good activity, even for functionalized olefins, on the silica–alumina support.*

With its high atom economy, metathesis has become one of the pillars of the petrochemical and fine-chemical industry, and a key reaction for the development of more sustainable processes.[1] In heterogeneous catalysis, metathesis mainly relies on supported Mo, W, and Re oxides. Of these, Re_2O_7/Al_2O_3 and Re_2O_7/SiO_2-Al_2O_3 are unique, because of their room-temperature activity and their tolerance of functional groups upon activation with R_4Sn.[1b,2] A perrhenate (that is, ReO_4^-) surface species coordinated to Al Lewis sites is proposed as the precursor of the active species (Scheme 1 a)[1] but the alkylidene propagating species have never been detected experimentally (Scheme 1 b).

Most recent studies have focused on using supported CH_3ReO_3/Al_2O_3 as a possible model for Re_2O_7/Al_2O_3 and related systems.[3] However, while highly active in alkene metathesis, the expected alkylidene intermediates have never been detected in these systems. Instead, μ-methylene species, a resting state for the catalyst, have been identified (Scheme 1 c). To date, (≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH$_2$*t*Bu) is the only reported well-defined supported rhenium alkylidene metathesis catalyst.[4] Nonetheless, the absence of oxo ligands makes it difficult to relate this system to the classical heterogeneous catalysts. Although recent reports have shown that molecular and silica-supported W oxo alkylidene complexes are highly efficient alkene-metathesis catalysts,[5] analogous Re oxo alkylidene surface species have remained elusive. Only a few molecular rhenium oxo alkylidene molecular complexes are known,[6] and Re(O)(=CH-CH=CPh$_2$)(OtBu$_{F6}$)$_3$(THF) (OtBu$_{F6}$=OCMe(CF$_3$)$_2$) (**1**, Scheme 1 d) is the only reported active alkene metathesis catalyst, but requires activation by $GaBr_3$ or $AlCl_3$.[6b]



Scheme 1. a) Proposed active sites in the heterogeneous catalysts Re_2O_7/Al_2O_3. Al_s = surface Al. b) Putative Re oxo alkylidene active species of Re-based heterogeneous catalysts. c) Resting state of the active site (μ-methylene) in $MeReO_3/Al2O_3$ and d) Re(O)(=CH-CH=CPh$_2$)(OtBu$_{F6}$)$_3$(THF).

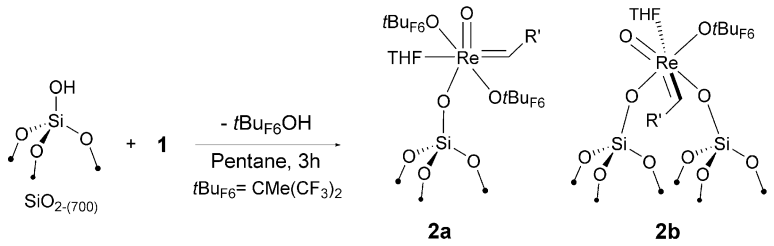
Herein, we explore the formation of well-defined, active supported Re oxo alkylidene species through surface organometallic chemistry,[7] and show that the incorporation of Al Lewis acid sites on silica is essential for metathesis activity.

Grafting **1** (1.05 equiv) on silica partially dehydroxylated at 700 °C ($SiO_{2-(700)}$) yields a dark red material along with 0.8–0.9 equivalents of tBu$_{F6}$OH per initial surface OH. The decrease of the isolated silanol IR band at 3747 cm^{-1} (Figure S8 in the Supporting Information) is consistent with the consumption of surface silanol sites and the formation of (≡SiO)Re(O)(=CH-CH=CPh$_2$)(OtBu$_{F6}$)$_2$(THF) (**2a**), as the main surface species (Scheme 2). The Re loading of 3.03 wt% is consistent with the grafting on 72% of the surface silanol moieties, consistent with the observation of residual silanol by IR. Elemental analyses (4.5 wt% C, 0.41 wt% H, and 3.12 wt% F) are consistent with **2a** being present as a major surface species (C/Re: 23 (27 exp.); H/Re: 26 (26 exp.) and F/Re: 10 (12 exp.) along with a minor amount of bis-grafted species **2b** (expected: C/Re: 19, H/Re: 23, and F/Re: 6).

The surface species was further characterized by solid-state NMR spectroscopy. The ^{1}H MAS NMR spectrum displays two peaks at δ = 12.4 and 9.5 ppm assigned to the α- and β-C–H of the alkylidene ligand, respectively, along with the other resonances associated with phenyl (δ = 7.4 ppm), THF (δ = 4.4 and 1.8 ppm) and tBu$_{F6}$O (δ = 1.8 ppm) moieties (Figure S3). The presence of the alkylidene ligand was confirmed by the presence of the two signals at δ = 280 and 167 ppm associated to the α- and β-carbons in the ^{13}C

[*] M. Valla, D. Stadler, Dr. V. Mougel, Prof. Dr. C. Copéret
Department of Chemistry and Applied Biosciences
Vladimir Prelog Weg 1–5
8093 Zürich (Switzerland)
E-mail: ccoperet@inog.chem.ethz.ch

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201509390.



Scheme 2. Grafting of **1** on $SiO_{2\text{-}(700)}$ yielding $(\equiv SiO)Re(O)(=CH\text{-}CH=CPh_2)(OtBu_{F6})_2$-(THF) (**2**). $R' = CH\text{-}CH=CPh_2$.

cross-polarization (CP) MAS NMR spectrum of the corresponding carbon-13 labeled complex, **2***. The signals observed at $\delta = 69$ and 24 ppm correspond to THF (Figure S4). However, in contrast to $(\equiv SiO)Re(\equiv CtBu)(=CHtBu)(CH_2tBu)$, **2** does not present any significant metathesis activity.[4a,c] By analogy with the molecular W oxo alkylidene complexes,[5a,b] activation of **2** (0.1 mol %) with 1 equiv of $B(C_6F_5)_3$ allows metathesis of *cis*-4-nonene, reaching only 19 % conversion.

We thus reasoned that tailoring a support containing an anchoring OH site and a Lewis acid site could be ideal to activate rhenium oxo alkylidene complexes.[3g] Using a thermolytic precursor approach,[8] the formation of isolated metal silicate with adjacent OH groups is possible through the grafting of molecular tris(*tert*-butoxy)silanolate complexes followed by a thermolysis step under vacuum.[5d,8,9] We thus explored the formation of Al silicates exploiting a similar strategy.

$Al(OSi(OtBu)_3)_3$ was obtained in 87 % yield by reaction of $Al(iBu)_3$ with 3 equiv of $(tBuO)_3SiOH$. The temperature-sensitive complex was characterized by solid-state NMR spectroscopy and single-crystal X-ray diffraction (Figure S5, Figure S12, and Table S1–S3). This compound, $Al(OSi(OtBu)_3)_3$, displays a distorted tetrahedral coordination with one bidentate κ^2-siloxy ligand (Figure S12). Low-temperature high-field solid-state NMR spectroscopy (−30 °C, 850 MHz) allowed the single fitting of the aluminum quadrupolar pattern with a δ_{iso} of 53.7 ppm and a C_Q value of 19.5 MHz (Figure S5), consistent with a four-coordinate ^{27}Al center. However, in contrast to the Cr^{III} analogue,[9] $Al(OSi(OtBu)_3)_3$ does not readily graft on silica. Alternatively, impregnation of this complex on $SiO_{2\text{-}(700)}$ at room temperature followed by a thermolysis step at 400 °C under high vacuum (10^{-5} mBar) affords a high-surface area material $Al@SiO_2$ (Figure 1 a). The absence of C–H containing groups was confirmed by IR spectroscopy. The signals arising from the surface silanols appear slightly red-shifted at 3743 cm^{-1} by comparison to isolated silanol sites, consistent with interaction with nearby Lewis acid sites (Figure S9).[9,10] The presence of Lewis acid sites was confirmed by pyridine adsorption experiments, with the presence of three bands at 1626, 1497, and 1458 cm^{-1}, characteristic of surface Lewis acid sites (Figure S10).[11] Al elemental analysis (0.6 %) and titration of surface hydroxy groups by CH_3MgBr (0.54 mmol of CH_4 released per gram of support) show the presence of 0.75 Al nm^{-2} and 1.6 OH per nm^{-2}. This density corresponds to roughly to 2.1 OH functionalities per Al site. The ^{27}Al spin echo NMR spectrum, measured on a 1 GHz spectrometer at 60 kHz, shows a highly resolved spectrum (Figure 1 b), which can be deconvolved into two components with one major peak (93 %) with a chemical shift and a quadrupolar constant (C_Q) of 65.7 ppm and 17.5 MHz, respectively. These values are very close to the values found for the molecular complex (see above) and a tetra-coordinated Al surface site. The minor peak (7 %) has a chemical shift of $\delta = 21.8$ ppm and a C_Q of 12 MHz, consistent with the presence of a more symmetric

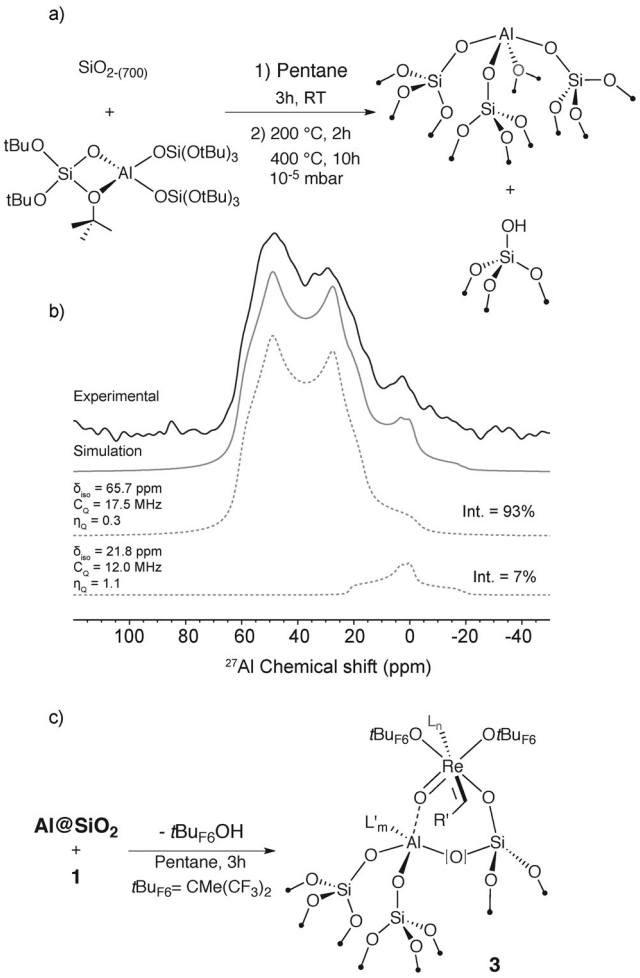


Figure 1. a) Synthetic route to the $Al@SiO_2$ material. b) ^{27}Al spin-echo MAS with full echo acquisition of $Al@SiO_2$, 1 GHz, 60 kHz spinning speed. 15 k scans with a recycling delay of 1 s. The radio-frequency field was calculated to be at 25 kHz according to Al nitrate reference sample. c) Grafting of **1** on $Al@SiO_2$ yields **3**. $L = C_4H_8O$, $n = 0$ or 1, $L' = C_4H_8O$ or siloxane bridge (Si-*O*-Si), $m = 0,1$. The $|O|$ indicates that the Al and Si are not necessarily directly bounded to each other through an oxygen bridge but can be separated by additional SiO_3 units. $R' = CH\text{-}CH=CPh_2$.

environment, such as a five-coordinate surface Al site resulting from the coordination of an additional siloxane bridge.[12]

Grafting of 1 equiv of **1** (with respect to Al) on $Al@SiO_2$ yielded a dark purple solid containing 3.51 wt % Re along

with 0.8–0.9 equiv of $tBu_{F6}OH$. No THF was detected in solution. Elemental analyses (5.80 wt% C, 0.44 wt% H, and 3.65 wt% F) are consistent with the expected values for **3** (Figure 1c), $(\equiv SiO)Re(O)(=CH\text{-}CH=CPh_2)(OtBu_{F6})_2(THF)/Al$ (C/Re: 27 (exp 26); H/Re: 23 (exp 26), F/Re: 10.3 (exp 12). This corresponds to the grafting of 0.86 equiv of the alkylidene on the $Al@SiO_2$ surface with respect to the Al sites.

IR spectroscopy revealed a sharp decrease in the intensity of the isolated silanol signal at 3743 cm^{-1} upon grafting of **1** along with the concomitant appearance of a broad band centered at 3640 cm^{-1} assigned to silanols in interaction with the surface complex (Figure S11).[13] ^1H NMR spectroscopy indicates the presence of an alkylidene species after grafting, as shown by with the signals at $\delta = 12.3$ and 9.6 ppm corresponding to the α- and β-C–H of the alkylidene ligand and the resonances associated with phenyl ($\delta = 7.6$ ppm), THF ($\delta = 4.5$ and 1.9 ppm) and $tBu_{F6}O$ ($\delta = 1.9$ ppm) groups (Figure S6). The corresponding 20% carbon-13 labeled surface species exhibits very similar NMR signals to **2** (Figure 2a), but with a much larger chemical shift anisotropy (CSA) for the alkylidene carbon; the broad spinning side band manifold ($\delta_{iso} = 281$ ppm, $\Omega = 467$ ppm, $k = 0.3$, Figure S7) is consistent with a restricted dynamic of the Re alkylidene surface sites in **3**.

In addition, ^{27}Al NMR spectroscopy shows signals of approximately equivalent intensities for the presence of two Al sites, with lower C_Q than the original Al sites, at $\delta/C_q =$ 58.9 ppm/10.8 MHz and 42.6 ppm/12.6 MHz, consistent with a more symmetric environment, associated with coordination of Re=O and/or THF on Al (Figures 1c and 2b). The ^{27}Al signal can be attributed to four- and five-coordinate aluminum, consistent with the coordination of THF, Re=O, or a siloxane bridge to Al. Taken together, these data are consistent with a more rigid oxo alkylidene species grafted to the surface via a surface siloxy ligand and further interacting with adjacent Al sites, as shown in Figure 1c.

Unlike **1** and **2**, **3** shows good metathesis activity. With a catalyst loading of 0.05 mol%, a TOF at 3 min (TOF_{3min}) of 22 min^{-1} and equilibrium conversion of 240 min were observed in *cis*-4-nonene metathesis (Table 1). Catalytic activity was maintained with a catalyst loading of 100 ppm, reaching thermodynamic conversion in five days. The catalyst is also active in 1-nonene metathesis with a TOF_{3min} of 3 min^{-1} at 0.1 mol% catalyst loading, but quantitative conversion requires about 100 h, indicating the deleterious effect of ethylene. The surface complex **3** also catalyzes the metathesis of ethyl oleate at 0.2 mol% catalyst loading, reaching 28% conversion with an initial TOF of 0.3 min^{-1} without the need of a co-catalyst, in contrast to Re_2O_7/Al_2O_3.[2h]

This study shows that well-defined alkylidene oxo Re complexes are metathesis active when the support contains Lewis acid sites. Such species catalyze the metathesis of olefins, including oleate esters without any activator, in contrast to Re_2O_7/Al_2O_3. With this information in hand, we are now further exploring Re_2O_7/Al_2O_3 and hope to track the active sites and reaction intermediates.

Table 1: Catalytic activity of **3** in toluene at 30°C.

Substrates	mol %	TOF_{3min}[a]	Time to equilibrium
cis-4-nonene	0.1	19	< 120 min
cis-4-nonene	0.05	22	< 240 min
cis-4-nonene	0.01	16	130 h
1-nonene	0.1	3	106 h
Ethyl oleate	0.2	0.3	28% after 6 h

[a] TOF at 3 min in min^{-1}.

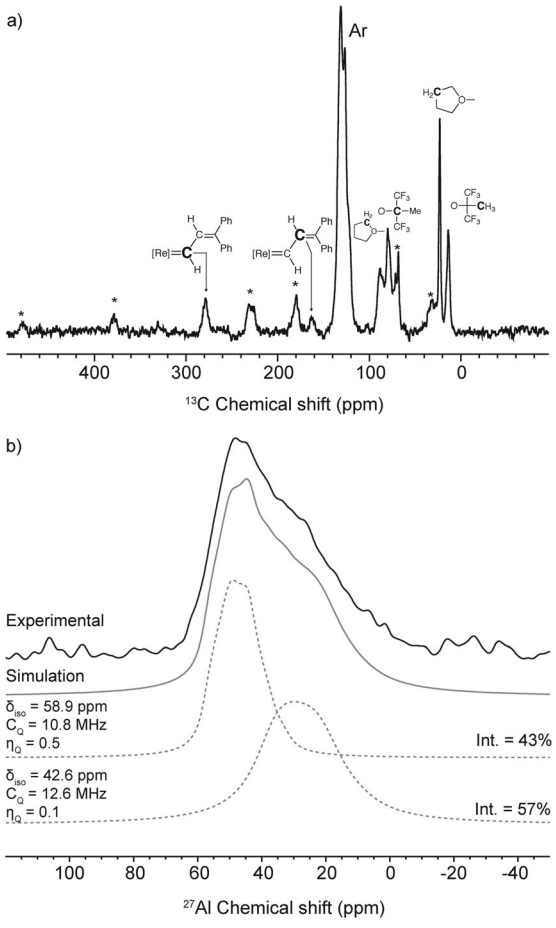


Figure 2. a) ^1H-^{13}C CPMAS signature of $Re(O)(=CH\text{-}CH=CPh_2)(OtBu_{F6})_3(THF)$ supported on $Al@SiO_2$ 400 MHz, d1 = 1 s, 10 KHz spinning speed. Asterisks indicate the spinning side bands. b) ^{27}Al Spin-echo MAS with full-echo acquisition, 1 GHz, 60 kHz spinning speed. 15 k scans with a recycling delay of 1 s. The radio-frequency field was calculated to be at 25 kHz according to Al nitrate reference sample. .

Acknowledgements

M.V. thanks the Swiss National Foundation (SNF) for financial support (grant no. 200021_143600). D. Gajan, A. Lesage and P. Florian are acknowledged for the assistance with ^{27}Al NMR and fruitful discussions. Financial support from the TGIR-RMN-THC Fr3050 CNRS for conducting the research is gratefully acknowledged. Georges Siddiqui is acknowledged for helping with the editing of the paper.

Keywords: alumina · metathesis · oxo alkylidene · rhenium · supported catalysts

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 1124 – 1127
Angew. Chem. **2016**, *128*, 1136 – 1139

[1] a) J. C. M. Kenneth, J. Ivin, *Olefin Metathesis and Metathesis Polymerization*, **1997**, Academic Press, Waltham; b) S. Lwin, I. E. Wachs, *ACS Catal.* **2014**, *4*, 2505 – 2520.

[2] a) R. L. Banks, G. C. Bailey, *Ind. Eng. Chem. Prod. Rd.* **1964**, *3*, 170; b) F. K. Evert Verkuijlen, J. C. Mol, C. Boelhouwer, *J. Chem. Soc. Chem. Commun.* **1977**, 198 – 199; c) J. C. Mol, *J. Mol. Catal. A* **2004**, *213*, 39 – 45; d) N. Popoff, E. Mazoyer, J. Pelletier, R. M. Gauvin, M. Taoufik, *Chem. Soc. Rev.* **2013**, *42*, 9035 – 9054; e) M. J. Lawrenson, (Ed.: U. A), M. J. Lawrenson, US Patent US3974233A, **1976**; f) J. C. Mol, *Catal. Today* **1999**, *51*, 289 – 299; g) Y. Imamoğlu, *Metathesis Polymerization of Olefins and Polymerization of Alkynes*, Kluwer, Dordrecht, **1998**; h) M. Valla, M. P. Conley, C. Copéret, *Catal. Sci. Technol.* **2015**, *5*, 1438 – 1442; i) S. Lwin, C. Keturakis, J. Handzlik, P. Sautet, Y. Li, A. I. Frenkel, I. E. Wachs, *ACS Catal.* **2015**, *5*, 1432 – 1444.

[3] a) W. A. Herrmann, W. Wagner, U. Flessner, U. Volkhardt, H. Komber, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1636 – 1638; *Angew. Chem.* **1991**, *103*, 1704 – 1706; b) A. M. J. Rost, H. Schneider, J. P. Zoller, W. A. Herrmann, F. E. Kuhn, *J. Organomet. Chem.* **2005**, *690*, 4712 – 4718; c) J. R. McCoy, M. F. Farona, *J. Mol. Catal.* **1991**, *66*, 51 – 58; d) R. Buffon, A. Auroux, F. Lefebvre, M. Leconte, A. Choplin, J. M. Basset, W. A. Herrmann, *J. Mol. Catal.* **1992**, *76*, 287 – 295; e) A. Salameh, J. Joubert, A. Baudouin, W. Lukens, F. Delbecq, P. Sautet, J. M. Basset, C. Copéret, *Angew. Chem. Int. Ed.* **2007**, *46*, 3870 – 3873; *Angew. Chem.* **2007**, *119*, 3944 – 3947; f) A. Salameh, A. Baudouin, D. Soulivong, V. Boehm, M. Roeper, J.-M. Basset, C. Copéret, *J. Catal.* **2008**, *253*, 180 – 190; g) A. Salameh, A. Baudouin, J. M. Basset, C. Copéret, *Angew. Chem. Int. Ed.* **2008**, *47*, 2117 – 2120; *Angew. Chem.* **2008**, *120*, 2147 – 2150; h) A. W. Moses, C. Raab, R. C. Nelson, H. D. Leifeste, N. A. Ramsahye, S. Chattopadhyay, J. Eckert, B. F. Chmelka, S. L. Scott, *J. Am. Chem. Soc.* **2007**, *129*, 8912 – 8920; i) Y.-Y. Lai, M. Bornand, P. Chen, *Organometallics* **2012**, *31*, 7558 – 7565.

[4] a) M. Chabanas, A. Baudouin, C. Copéret, J.-M. Basset, *J. Am. Chem. Soc.* **2001**, *123*, 2062 – 2063; b) A. Lesage, L. Emsley, M. Chabanas, C. Copéret, J.-M. Basset, *Angew. Chem. Int. Ed.* **2002**, *41*, 4535 – 4538; *Angew. Chem.* **2002**, *114*, 4717 – 4720; c) M. Chabanas, C. Copéret, J.-M. Basset, *Chem. Eur. J.* **2003**, *9*, 971 – 975; d) M. Chabanas, A. Baudouin, C. Copéret, J.-M. Basset, W. Lukens, A. Lesage, S. Hediger, L. Emsley, *J. Am. Chem. Soc.* **2003**, *125*, 492 – 504.

[5] a) D. V. Peryshkov, R. R. Schrock, M. K. Takase, P. Müller, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 20754 – 20757; b) D. V. Peryshkov, W. P. Forrest, R. R. Schrock, S. J. Smith, P. Müller, *Organometallics* **2013**, *32*, 5256 – 5259; c) M. P. Conley, V. Mougel, D. V. Peryshkov, W. P. Forrest, D. Gajan, A. Lesage, L. Emsley, C. Copéret, R. R. Schrock, *J. Am. Chem. Soc.* **2013**, *135*, 19068 – 19070; d) M. P. Conley, M. F. Delley, G. Siddiqi, G. Lapadula, S. Norsic, V. Monteil, O. V. Safonova, C. Copéret, *Angew. Chem. Int. Ed.* **2014**, *53*, 1872 – 1876; *Angew. Chem.* **2014**, *126*, 1903 – 1907; e) M. P. Conley, W. P. Forrest, V. Mougel, C. Copéret, R. R. Schrock, *Angew. Chem. Int. Ed.* **2014**, *53*, 14221 – 14224; *Angew. Chem.* **2014**, *126*, 14445 – 14448; f) V. Mougel, M. Pucino, C. Copéret, *Organometallics* **2015**, *34*, 551 – 554; g) R. Schowner, W. Frey, M. R. Buchmeiser, *J. Am. Chem. Soc.* **2015**, *137*, 6188 – 6191.

[6] a) S. Cai, D. M. Hoffman, D. A. Wierda, *J. Chem. Soc. Chem. Commun.* **1988**, 1489 – 1490; b) B. T. Flatt, R. H. Grubbs, R. L. Blanski, J. C. Calabrese, J. Feldman, *Organometallics* **1994**, *13*, 2728 – 2732.

[7] a) C. Copéret, M. Chabanas, R. Petroff Saint-Arroman, J.-M. Basset, *Angew. Chem. Int. Ed.* **2003**, *42*, 156 – 181; *Angew. Chem.* **2003**, *115*, 164 – 191; b) M. Tada, Y. Iwasawa, *Coord. Chem. Rev.* **2007**, *251*, 2702 – 2716; c) S. L. Wegener, T. J. Marks, P. C. Stair, *Acc. Chem. Res.* **2012**, *45*, 206 – 214.

[8] C. G. Lugmair, K. L. Fujdala, T. D. Tilley, *Chem. Mater.* **2002**, *14*, 888 – 898.

[9] M. F. Delley, F. Núñez-Zarur, M. P. Conley, A. Comas-Vives, G. Siddiqi, S. Norsic, V. Monteil, O. V. Safonova, C. Copéret, *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 11624 – 11629.

[10] a) F. Héroguel, G. Siddiqi, M. D. Detwiler, D. Y. Zemlyanov, O. V. Safonova, C. Copéret, *J. Catal.* **2015**, *321*, 81 – 89; b) M. Valla, A. J. Rossini, M. Caillot, C. Chizallet, P. Raybaud, M. Digne, A. Chaumonnot, A. Lesage, L. Emsley, J. A. van Bokhoven, C. Copéret, *J. Am. Chem. Soc.* **2015**, *137*, 10710 – 10719.

[11] E. P. Parry, *J. Catal.* **1963**, *2*, 371 – 379.

[12] R. Wischert, P. Florian, C. Copéret, D. Massiot, P. Sautet, *J. Phys. Chem. C* **2014**, *118*, 15292 – 15299.

[13] B. Rhers, A. Salameh, A. Baudouin, E. A. Quadrelli, M. Taoufik, C. Copéret, F. Lefebvre, J.-M. Basset, X. Solans-Monfort, O. Eisenstein, W. W. Lukens, L. P. H. Lopez, A. Sinha, R. R. Schrock, *Organometallics* **2006**, *25*, 3554 – 3557.

Received: October 7, 2015
Published online: December 3, 2015

