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Well Defined Silica Supported bipodal Molybdenum Oxo Alkyl Complexes: Model of the Active Sites of Industrial Olefin Metathesis Catalyst

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Well-defined, silica-supported molybdenum oxo alkyl species, $(\equiv\text{SiO})_2\text{Mo}(\text{=O})(\text{CH}_2^t\text{Bu})_2$, was prepared by the selective grafting of $\text{Mo}(\text{=O})(\text{CH}_2^t\text{Bu})_3\text{Cl}$ onto a silica partially dehydroxylated at 200 °C using rigorous surface organometallic chemistry approach. The immobilized bipodal surface species, partly resembling to the active species of industrial $\text{MoO}_3/\text{SiO}_2$ olefin metathesis catalysts, exhibited excellent functional group tolerance in conjunction to its high activity in homocoupling, self and ring closing olefins metathesis.

Olefin metathesis holds an important role in the synthesis of C=C bond containing molecules. Large scale industrial processes employ olefin metathesis in the on-propose propylene production and fabrication of α -olefins.¹ Moreover, the versatility of this reaction offers a clean and easy access to polymers,²⁻⁴ natural products and fine chemicals.^{5,6}

Typical olefin metathesis catalysts are based on Mo, W, Re and Ru. Homogeneous catalysts based on the aforementioned metal complexes have been extensively exploited (except the Re system).⁷⁻⁹ Highly active, as well as stereo-selective homogeneous catalysts have already been reported.^{10,11} However, current challenge in the search of novel olefin metathesis catalyst lies on the development of cheap, highly active, stable and selective heterogeneous catalysts with high tolerance towards functional substrates. Although homogeneous catalysis remains central in certain applications, in particular for the Ru-based catalysts,¹² an heterogeneous system presents several advantages: facile separation of the products from the catalyst, working under continuous flow (gas and liquid substrates), regeneration of the catalyst and finally

easy avoiding contamination of the corresponding transition metal in the products.

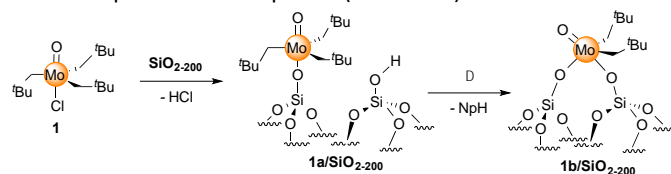
Supported Re based catalysts are generally highly active, even at low temperature, but suffer from rapid deactivation.¹³⁻¹⁵ Even though the active Re center can be dramatically stabilized after chlorination of the support,¹⁶ the cost of this element is still high. The remaining options (Mo and W) have been widely exploited over the decades to produce propylene and α -olefins,¹ mainly due to their low cost, robustness and their ability to be regenerated. Generally, Mo is more active than W and can operate at lower temperature.¹⁷ These catalysts are simply MoO_3 or WO_3 supported on conventional supports, such as silica or alumina. The main drawback of the industrial catalysts is a low concentration of the active metal sites (postulated to be bipodal Mo/W oxo carbene species)^{18,19} after in-situ activation by the olefinic substrate.^{17, 20-22} An evident strategy to increase the concentration of active center is to use alternative synthesis techniques by entering the catalytic center directly from a reaction intermediate namely a carbene or its immediate precursor. The best way to do so is to use surface organometallic chemistry (SOMC), which has shown to be a powerful tool to prepare well-defined organometallic fragment on conventional oxide supports, like silica,^{23,24} silica-alumina,²⁵ alumina¹⁹, silicated alumina²⁶ and zeolite.²⁷ Bearing in mind that the ancillary oxo ligand has a striking effect in the stability compared to the imido counterpart,²⁸⁻³⁰ we have studied olefin metathesis catalysts based on supported group VI neutral oxo species for several years.²⁹⁻³⁷ Previous investigations on the silica-supported W-oxo system have evidenced that the bipodal $[(\equiv\text{SiO})_2\text{WO}(\text{CH}_2\text{SiMe}_3)_2]$ ³³ pre-catalyst can exhibit superior activity in propylene self-metathesis than the monopodal $[(\equiv\text{SiO})\text{W}(\text{=O})(\text{CH}_2\text{SiMe}_3)_3]$ counterpart,³⁴ as well as the iso-electronic monopodal $[(\equiv\text{SiO})\text{W}(\text{=O})(\text{CH}_2\text{SiMe}_3)_2\text{OAr}]$ species.³¹ Herein, we present the preparation and characterization of silica-supported bipodal Mo-oxo alkyl species that can be in-situ transformed into highly active olefin metathesis catalyst after contacting with olefinic substrates. The strategy used to access a bipodal molybdenum surface species rely on the grafting of

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Mo(=O)(CH₂^tBu)₃Cl³⁸ on a silica partially dehydroxylated at 200 °C. This mildly heat treated silica bearing ~2.5 OH groups per nm², has proven to selectively lead to bipodal surface species upon reaction with organometallics precursors.^{33,39-42} The novel material disclosed here was fully characterised and investigated in olefin metathesis. Moreover, a substantial attention has been paid to substrates, especially those containing functional groups and known to be challenging towards this catalysis endeavour. A comparison in catalytic activity to the monopodal Mo-oxo analogue and the W-oxo analogue are provided. Following SOMC strategy, the complex **1** was grafted on silica partially dehydroxylated at 200 °C, with the anticipation^{33, 35} that the resulting tris alkyl molybdenum surface species obtained after the Mo-Cl bond cleavage would react with a proximate silanol at an elevated temperature to give the desired bipodal surface species (Scheme 1).



Scheme 1. Reaction of **1** with SiO₂₋₂₀₀

The grafting was performed under a similar set of reaction condition that was followed for preparation of monopodal analogue,³⁰ **1/SiO₂₋₇₀₀**. Following grafting of **1** on SiO₂₋₂₀₀ at room temperature, the DRIFT spectrum (Fig. 1) shows the disappearance of free surface silanol groups, although a significant amount of interacting silanols could be observed in addition of the presence of CH stretching bands in the range of 2850 to 3000 cm⁻¹. Elemental analysis of **1a/SiO₂₋₂₀₀** (Scheme 1) reveals the presence of 2.26 and 3.88 wt% of molybdenum and carbon respectively, which correspond to a C/Mo ratio of 13.7. This ratio is closer to the expected value of 15 for a monopodal species, especially if we take into account the high propensity of molybdenum alkyl species to give lower C/Mo ratio by this characterization technique.³⁰ Gas phase analysis of the volatile shows that in addition of HCl, only a traces of neopentane are released during the grafting of Mo(=O)(CH₂^tBu)₃Cl at room temperature.

Furthermore, the ¹H MAS spectrum of **1a/SiO₂₋₂₀₀** (Fig. 2a) shows the presence of neopentyl ligands as evidenced by the resonances at 2.7 and 1.2 ppm assigned to methylene and methyl group respectively. The ¹³C CPMAS spectrum (Fig. 2b) shows only three peaks at 86.4 (CH₂^tBu), 34.9 (CH₂CMe₃) and 30.6 ppm (CH₂CMe₃) as expected for a neopentyl ligand. These data are comparable to those of **1/SiO₂₋₇₀₀**.³⁰

All the spectroscopic data are in line with the formation of monopodal surface species at room temperature. This behaviour is reminiscent of the reactivity observed with tungsten oxo alkyls, where only monopodal species are formed at room temperature.³³ Therefore the resulting surface species was heated at 80 °C overnight under dynamic vacuum in order to trigger a second silanolysis with an adjacent silanol group. The DRIFT spectrum of **1b/SiO₂₋₂₀₀** obtained after heat treatment shows that the interacting silanols have partially

been consumed and the C-H stretching bands intensity have significantly been reduced in comparison to **1a/SiO₂₋₂₀₀**. Elemental analysis of **1b/SiO₂₋₂₀₀** reveals a similar molybdenum loading, as expected along with a much lower carbon content, thus giving a C/Mo ratio of 7.

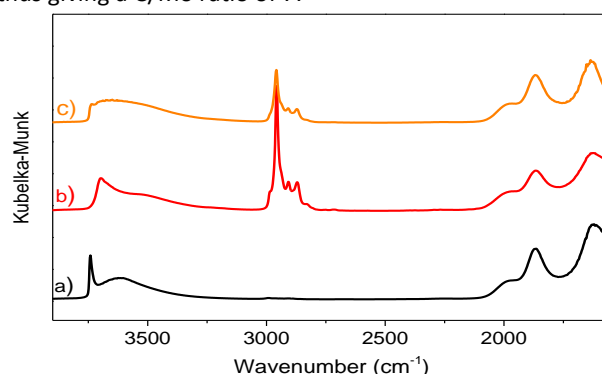


Fig. 1. DRIFT spectra of SiO₂₋₂₀₀ (a), grafted Mo(=O)(CH₂^tBu)₃Cl (b) and heat treated (80 °C) (c).

The ¹H MAS spectrum of **1b/SiO₂₋₂₀₀** (Fig. 2c) has been altered significantly in comparison to that was observed for **1a/SiO₂₋₂₀₀**. The intensity of the neopentyl resonances at 2.7 and 1.2 ppm have been reduced. Free and interacting silanols are now observed at 1.8 ppm and as a shoulder from 2.8 to 4.5 ppm. The ¹³C CPMAS spectrum (Fig. 2d) also showed a substantial decrease of ¹³C signal intensities which has been attributed to the loss of a neopentyl ligand and also to the diminished mobility of the bipodal complex compared to the monopodal complex. In addition, the potential development of paramagnetic Mo(V) species (~ 25% as evidenced by the EPR study, Fig. S1, ESI) also contributes to the fairly low C/Mo ratio determined by elemental analysis). It is worth noting at this point that the reduced species have neither been observed in monopodal species nor in bipodal tungsten oxo alkyl surface species. This difference with the tungsten analogue can be emphasized by the enhanced reducibility of the molybdenum center. We tentatively explain the reduction occurring from the monopodal to the bipodal surface species, by donor ligand

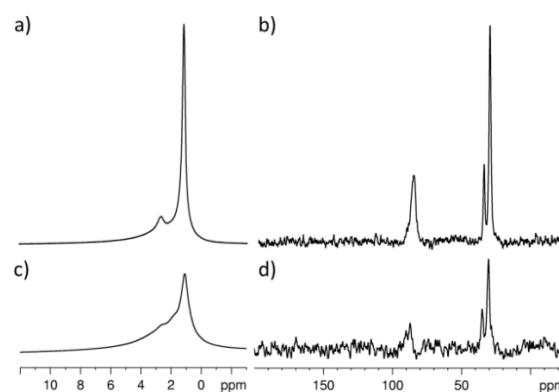


Fig. 2. (a) ¹H MAS, (b) ¹³C CP MAS of **1a/SiO₂₋₂₀₀** before heating and (c) ¹H MAS, (d) ¹³C CP MAS of **1b/SiO₂₋₂₀₀** after heating (11.75 T, spinning speed 10 kHz).

triggered reduction as, i) addition of donor ligand has been reported to initiate one electron reduction in some cases,⁴³ and ii) previous studies on bipodal species have shown that neighbouring siloxane bridge can interact with the metal center.^{44, 45}

The structure of the supported complex **1b/SiO₂₋₂₀₀** was also studied by EXAFS (Fig. 3 and Table 1). The results are consistent with the following coordination sphere around Mo: (i) one oxo ligand at 1.675(8) Å, (ii) ca. two oxygen at 1.937(11) Å, which can be assigned to the siloxide ligands and (iii) ca. two carbon atoms at 2.13(2) Å, attributed the neopentyl ligands. The lengths found for Mo-O and Mo-C single-bonds are in the usual range observed for molecular complexes as in [(*c*-C₅H₉)₇Si₇O₁₂SiO-Mo(=NH)(CH₂CMe₃)₃] (1.984(2) Å for Mo-O and 2.116 to 2.126 Å for Mo-C),⁴⁶ [Mo(CH₂CMe₂Ph)₃(N=NPh₂)(OC₆F₅)] (2.011(2) Å for Mo-O and 2.123 to 2.155 Å for Mo-C),⁴⁷ as well as the length found for the Mo=O bond, which is for instance 1.699(3) Å for [Cp*Mo(=O)(CH₂CMe₃)(2,2-dimethylpropyl nitrosyl)] (2.204(4) Å for Mo-C).⁴⁸ Similar parameters were obtained when fitting the $k^2 \cdot \chi(k)$ spectrum. The fit could be improved by adding a layer of further back-scatterers, three carbon and one silicon atoms at 3.16(7) and 3.25(12) Å respectively, attributed to the quaternary carbon of the neopentyl and to the silicon of the surface siloxide ligand and one oxygen at 2.75(3) Å which can be attributed to a surface oxygen from a siloxane bridge of the silica support. This EXAFS study then agrees with the structure (\equiv SiO)₂Mo(=O)(CH₂^tBu)₂ for the silica supported complex **1b/SiO₂₋₂₀₀**.

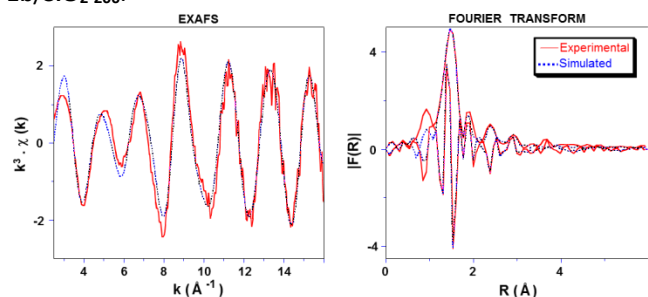


Fig. 3. Molybdenum K-edge k^3 -weighted EXAFS (left), for the sample resulting from the grafting reaction of Mo(=O)(CH₂^tBu)₃Cl onto SiO₂₋₂₀₀ and corresponding Fourier transform (right; modulus and imaginary part). Solid lines: experimental; dashed lines: fit using the spherical wave theory.

Table 1. EXAFS parameters for the supported complex **1b/SiO₂₋₂₀₀**.^a

Type of neighbour	Number of neighbours	Distance (Å)	σ^2 (Å ²)
Mo=O	1.0	1.675(8)	0.0014(9)
Mo-OSi	1.9(4)	1.937(11)	0.0015(12)
Mo-CH ₂ CMe ₃	1.8(6)	2.13(2)	0.0027(21)
Mo-O(Si) ₂	1.0	2.75(3)	0.002(2)
Mo-CH ₂ -CMe ₃	1.8 ^b	3.16(7)	0.0062(53)
Mo-O-Si	1.9 ^b	3.25(12)	0.018(17)

The errors generated by the EXAFS fitting program “RoundMidnight” are indicated in parentheses.^a Δk : [2.4-16.0 Å⁻¹] - ΔR : [0.5-3.5 Å] ([0.4-2.1 Å], when considering only the first coordination sphere); $S_0^2 = 0.65$; $\Delta E_0 = 8.3 \pm 1.9$ eV (the same for all shells); Fit residue: $\rho = 6.9$ %; Quality factor: $(\Delta\chi)^2/\nu = 2.58$, with $\nu = 13 / 28$ ($[(\Delta\chi)^2/\nu]_1 = 3.80$ with $\nu = 7 / 16$, considering only the first coordination sphere: =O, -O and -C.^b Shell constrained to parameters above.

The successful preparation of a bipodal molybdenum oxo bis alkyl as major surface species using Mo(=O)(CH₂^tBu)₃Cl, shows the increased reactivity of the Mo-C bond in comparison to the W-C bond, as W(=O)(CH₂^tBu)₃Cl only leads to a monopodal surface species by W-Cl bond cleavage. In fact, the tungsten oxo dialkyl bipodal species could only be obtained using W(=O)(CH₂SiMe₃)₃Cl thanks to the ability of the silicon atom to stabilise a negative charge on the α carbon.³³

1b/SiO₂₋₂₀₀ was tested in Homo Metathesis (HM), Self Metathesis (SM) and Ring Closing Metathesis (RCM) of different substrates. Results are compiled in Table 2. Noteworthy, the bipodal surface species is globally more active than the monopodal counterpart. For example, a TON of 1220 is reached with 4-nonene when only around a 130 TON is achieved with the monopodal molybdenum species. Molybdenum catalyst have been reported to be more tolerant toward functional groups.⁴⁹ Thus polar substrates were also tested and **1b/SiO₂₋₂₀₀** displays a high activity in both diethyl diallylmalonate RCM and ethyl oleate SM. When 2000 equivalent of ethyl oleate are allowed to react with **1/SiO₂₋₂₀₀** at 60 °C the thermodynamic equilibrium (ca. 50%) is reached in less than 30 minutes (Fig. S2, ESI) with an initial TOF at 5 minutes of 126 min⁻¹. On the other hand, applying the tungsten analogue (\equiv SiO)₂W(=O)(CH₂SiMe₃)₂ under the same reaction (4 h, 60 °C) conditions afforded only 13.5% conversion of ethyl oleate. In agreement with previously reported results^{17,49} these results also show that the Mo-based metathesis catalysts are more active than the tungsten analogue and seem to be more tolerant to functional groups.

Table 2. Conversion and TON obtained in olefin metathesis reactions with **1/SiO₂₋₇₀₀** and **1b/SiO₂₋₂₀₀**^a

Substrate	1/SiO₂₋₇₀₀		1b/SiO₂₋₂₀₀	
	Conversion	TON	Conversion	TON
HM				
Allyl trimethyl silane	0.3	7	11.7	234
Allylbenzene	78	1560	87	1740
RCM				
Diethyl diallyl malonate	1.1	22	61	1220
SM				
4-nonene	6,7	134	50 ^b	1000
Ethyl oleate	-	-	50 ^b	1000

^a Catalyst:substrate = 1:2000, 60 °C in toluene for 4 h. ^b Time to reach thermodynamic equilibrium <25 min.

In conclusion, in this work we have prepared the first example of bipodal molybdenum surface species that only combines oxo and alkyl ligands. We have shown that the single site approach by using surface organometallic chemistry, leads to a bipodal precatalyst, $(\equiv\text{SiO})_2\text{Mo}(\text{=O})(\text{CH}_2^t\text{Bu})_2$, characterised by mass balanced analysis, DRIFT, Solid State NMR, ESR and EXAFS. This surface species can be a direct precursor of bipodal highly active catalyst in olefin metathesis, $(\equiv\text{SiO})_2\text{Mo}(\text{=O})(\text{=CH}^t\text{Bu})$, with functional group tolerance. This represents a significant step toward the understanding of $\text{MoO}_3/\text{SiO}_2$ industrial catalyst.

Note

The authors declare no competing financial interests.

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Notes and references

- J. C. Mol, *J. Mol. Catal. A*, 2004, **213**, 39-45.
- C. W. Bielawski and R. H. Grubbs, *Prog. Polym. Sci.*, 2007, **32**, 1-29.
- C. Larabi, K. C. Szeto, Y. Bouhoute, M. O. Charlin, N. Merle, A. De Mallmann, R. M. Gauvin, L. Delevoye and M. Taoufik, *Macromol. Rapid Commun.*, 2016, **37**, 1832-1836.
- R. R. Schrock, *Acc. Chem. Res.*, 2014, **47**, 2457-2466.
- C. B. Wang, M. Yu, A. F. Kyle, P. Jakubec, D. J. Dixon, R. R. Schrock and A. H. Hoveyda, *Chem. Eur. J.*, 2013, **19**, 2726-2740.
- D. E. White, I. C. Stewart, B. A. Seashore-Ludlow, R. H. Grubbs and B. M. Stoltz, *Tetrahedron*, 2010, **66**, 4668-4686.
- G. Doledec and D. Commereuc, *J. Mol. Catal. A*, 2000, **161**, 125-140.
- R. R. Schrock, *Chem. Rev.*, 2009, **109**, 3211-3226.
- G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746-1787.
- M. B. Herbert and R. H. Grubbs, *Angew. Chem.Int. Ed.*, 2015, **54**, 5018-5024.
- M. Yu, R. R. Schrock and A. H. Hoveyda, *Angew. Chem.Int. Ed.*, 2015, **54**, 215-220.
- S. Hubner, J. G. de Vries and V. Farina, *Adv. Synth. Catal.*, 2016, **358**, 3-25.
- S. Lwin and I. E. Wachs, *ACS Catal.*, 2016, **6**, 272-278.
- A. M. J. Rost, H. Schneider, J. P. Zoller, W. A. Herrmann and F. E. Kuhn, *J. Organomet. Chem.*, 2005, **690**, 4712-4718.
- A. Salameh, A. Baudouin, D. Souilivong, V. Boehm, M. Roeper, J. M. Basset and C. Coperet, *J. Catal.*, 2008, **253**, 180-190.
- A. Gallo, A. Fong, K. C. Szeto, J. Rieb, L. Delevoye, R. M. Gauvin, M. Taoufik, B. Peters and S. L. Scott, *J. Am. Chem. Soc.*, 2016, **138**, 12935-12947.
- K. L. Ding, A. Gulec, A. M. Johnson, T. L. Drake, W. Q. Wu, Y. Y. Lin, E. Weitz, L. D. Marks and P. C. Stair, *ACS Catal.*, 2016, **6**, 5740-5746.
- W. Grunert, R. Feldhaus, K. Anders, E. S. Shpiro and K. M. Minachev, *J. Catal.*, 1989, **120**, 444-456.
- N. Popoff, E. Mazoyer, J. Pelletier, R. M. Gauvin and M. Taoufik, *Chem. Soc. Rev.*, 2013, **42**, 9035-9054.
- K. Amakawa, S. Wrabetz, J. Krohnert, G. Tzolova-Muller, R. Schlogl and A. Trunschke, *J. Am. Chem. Soc.*, 2012, **134**, 11462-11473.
- J. G. Howell, Y. P. Li and A. T. Bell, *ACS Catal.*, 2016, **6**, 7728-7738.
- S. Lwin and I. E. Wachs, *ACS Catal.*, 2017, **7**, 573-580.
- N. Riache, E. Callens, J. Espinas, A. Dery, M. K. Samantaray, R. Dey and J. M. Basset, *Catal. Sci. Technol.*, 2015, **5**, 280-285.
- R. Dey, M. K. Samantaray, A. Poater, A. Hamieh, S. Kavitate, E. Abou-Hamad, E. Callens, A. H. Emwas, L. Cavallo and J. M. Basset, *Chem. Commun.*, 2016, **52**, 11270-11273.
- S. Norsic, C. Larabi, M. Delgado, A. Garron, A. de Mallmann, C. Santini, K. C. Szeto, J. M. Basset and M. Taoufik, *Catal. Sci. Technol.*, 2012, **2**, 215-219.
- C. Larabi, A. Garron, P. Rouge, K. C. Szeto, S. Norsic, A. De Mallmann, N. Merle and M. Taoufik, *ChemCatChem*, 2017, **9**, 2160-2166.
- K. C. Szeto, A. Gallo, S. Hernandez-Morejudo, U. Olsbye, A. De Mallmann, F. Lefebvre, R. M. Gauvin, L. Delevoye, S. L. Scott and M. Taoufik, *J. Phys. Chem. C*, 2015, **119**, 26611-26619.
- X. Solans-Monfort, C. Coperet and O. Eisenstein, *Organometallics*, 2012, **31**, 6812-6822.
- E. Mazoyer, N. Merle, A. de Mallmann, J. M. Basset, E. Berrier, L. Delevoye, J. F. Paul, C. P. Nicholas, R. M. Gauvin and M. Taoufik, *Chem. Commun.*, 2010, **46**, 8944-8946.
- N. Merle, F. Le Quemener, Y. Bouhoute, K. C. Szeto, A. De Mallmann, S. Barman, M. K. Samantaray, L. Delevoye, R. M. Gauvin, M. Taoufik and J. M. Basset, *J. Am. Chem. Soc.*, 2017, **139**, 2144-2147.
- Y. Bouhoute, I. Del Rosal, K. C. Szeto, N. Merle, D. Grekov, A. De Mallmann, E. Le Roux, L. Delevoye, R. M. Gauvin, L. Maron and M. Taoufik, *Catal. Sci. Technol.*, 2016, **6**, 8532-8539.
- Y. Bouhoute, A. Garron, D. Grekov, N. Merle, K. C. Szeto, A. De Mallmann, I. Del Rosal, L. Maron, G. Girard, R. M. Gauvin, L. Delevoye and M. Taoufik, *ACS Catal.*, 2014, **4**, 4232-4241.
- Y. Bouhoute, D. Grekov, K. C. Szeto, N. Merle, A. De Mallmann, F. Lefebvre, G. Raffa, I. Del Rosal, L. Maron, R. M. Gauvin, L. Delevoye and M. Taoufik, *ACS Catal.*, 2016, **6**, 1-18.
- D. Grekov, Y. Bouhoute, K. C. Szeto, N. Merle, A. De Mallmann, F. Lefebvre, C. Lucas, I. Del Rosa, L. Maron, R. M. Gauvin, L. Delevoye and M. Taoufik, *Organometallics*, 2016, **35**, 2188-2196.
- N. Merle, G. Girard, N. Popoff, A. De Mallmann, Y. Bouhoute, J. Trebosc, E. Berrier, J. F. Paul, C. P. Nicholas, I. Del Rosal, L. Maron, R. M. Gauvin, L. Delevoye and M. Taoufik, *Inorg. Chem.*, 2013, **52**, 10119-10130.
- Z. S. Qureshi, A. Hamieh, S. Barman, N. Maity, M. K. Samantaray, S. Ould-Chikh, E. Abou-hamad, L. Falivene, V. D'Elia, A. Rothenberger, I. Llorens, J. L. Hazemann and J. M. Basset, *Inorg. Chem.*, 2017, **56**, 861-871.
- A. Hamieh, Y. Chen, S. Abdel-Azeim, E. Abou-hamad, S. Goh, M. Samantaray, R. Dey, L. Cavallo and J. M. Basset, *ACS Catal.*, 2015, **5**, 2164-2171.
- J. R. M. Kress, M. J. M. Russell, M. G. Wesolek and J. A. Osborn, *J. Chem. Soc. Chem. Commun.*, 1980, 431-432.
- S. Barman, N. Merle, Y. Minenkov, A. De Mallmann, M. K. Samantaray, F. Le Quemener, K. C. Szeto, E. Abou-Hamad, L. Cavallo, M. Taoufik and J. M. Basset, *Organometallics*, 2017, **36**, 1550-1556.
- K. C. Szeto, B. Loges, N. Merle, N. Popoff, A. Quadrelli, H. P. Jia, E. Berrier, A. De Mallmann, L. Delevoye, R. M. Gauvin and M. Taoufik, *Organometallics*, 2013, **32**, 6452-6460.
- S. L. Scott, A. Q. Fu and L. A. MacAdams, *Inorg. Chim. Acta*, 2008, **361**, 3315-3321.
- P. Mania, S. Conrad, R. Verel, C. Hammond and I. Hermans, *Dalton Trans.*, 2013, **42**, 12725-12732.
- E. A. Maatta, Y. H. Du and A. L. Rheingold, *J. Chem. Soc. Chem. Commun.*, 1990, 756-757.
- N. Merle, J. Trebosc, A. Baudouin, I. Del Rosal, L. Maron, K. Szeto, M. Genelot, A. Mortreux, M. Taoufik, L. Delevoye and R. M. Gauvin, *J. Am. Chem. Soc.*, 2012, **134**, 9263-9275.
- L. Zhong, M. Y. Lee, Z. Liu, Y. J. Wanglee, B. P. Liu and S. L. Scott, *J. Catal.*, 2012, **293**, 1-12.
- F. Blanc, M. Chabanas, C. Coperet, B. Fenet and E. Herdweck, *J. Organomet. Chem.*, 2005, **690**, 5014-5026.
- J. R. Dilworth, V. C. Gibson, C. Redshaw, A. J. P. White and D. J. Williams, *J. Chem. Soc. Dalton Trans.*, 1999, 2701-2704.
- P. M. Graham, M. S. A. Buschhaus, R. A. Baillie, S. P. Semproni and P. Legzdins, *Organometallics*, 2010, **29**, 5068-5072.
- G. C. Bazan, R. R. Schrock, H. N. Cho and V. C. Gibson, *Macromolecules*, 1991, **24**, 4495-4502.