## Supporting information

## <sup>17</sup>O MAS NMR Studies of oxo-based Olefin Metathesis Catalysts: a Critical Assessment of Signal Enhancement Methods.

D. Grekov\*,a Y. Bouhoute, b I. Del Rosal, c L. Maron, M. Taoufik, B R. M. Gauvina and L. Delevoye\*,a

*a-* Unité de Catalyse et de Chimie du Solide, CNRS UMR 8181, Université de Lille, F-59655 Villeneuve d'Ascq, France

*b-* Laboratoire de Chimie, Catalyse, Polymères et Procédés, UMR 5265 CNRS, UCBL, ESCPE Lyon, 43 Boulevard du 11 Novembre 1918, F-69616 Villeurbanne Cedex, France.

*c*- *Laboratoire de Physico-Chimie des Nano-Objets, CNRS UMR 5215, Université de Toulouse, INSA, UPS, 135* Avenue de Rangueil, F-31077 Toulouse, France.

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Site	ð, ppm	C <sub>Q</sub> , MHz	$\eta_{Q}$
P-O-Na	88	4.5	0.5
P-O-P	124	7.7	0.4

Table S1. <sup>17</sup>O NMR parameters of NaPO<sub>3</sub> glass extracted from best fit simulation



**Figure S1.** <sup>17</sup>O central transition signal intensity of NBO site (P-O-Na) in a sodium phosphate glass, NaPO<sub>3</sub>, as a function of the DFS pulse duration, at different RF field amplitudes (6, 12, 20 and 30 kHz) for final sweep frequency of (a) 600, (b) 400, (c) 200 and (d) 100 kHz. The DFS pulse was set prior to central transition 90° excitation pulse. The start sweep frequency was set to 800 kHz for all experiments. The signal intensity is calculated with respect to spectrum obtained without DFS.



**Figure S2.** <sup>17</sup>O central transition signal intensity of NBO site (P-O-Na) in a sodium phosphate glass, NaPO<sub>3</sub>, as a function of the HS pulse duration, at different RF field amplitudes (6, 12, 20 and 30 kHz) for HS offsets of (a) 600, (b) 400, (c) 200 and (d) 100 kHz. The HS pulse was set prior to central transition 90° excitation pulse similarly to DFS. The signal intensity is calculated with respect to spectrum obtained without HS.



**Figure S3.** <sup>17</sup>O central transition signal intensity of NBO site (P-O-Na) in NaPO<sub>3</sub> glass, as a function of HS offset, at different RF field amplitudes (6, 12, 20 and 30 kHz). The signal intensity is calculated with respect to spectrum obtained without HS. For an RF field amplitude of 6 kHz (empty diamonds), the time needed to achieve maximal signal enhancement is longer than 4 ms.



**Figure S4**. <sup>17</sup>O MAS NMR spectra of NaPO<sub>3</sub> glass acquired at 9.4 T under 20 kHz of spinning frequency without (red line) and with (black line) DFS with final sweep frequencies of 200, 400 and 600 kHz and DFS pulse RF field strengths of (a) 20 and (b) 12 kHz.

Site	б, ррт	CSA, ppm	η <sub>csa</sub>	C <sub>Q</sub> , MHz	$\eta_Q$	
Oxo 1 exp	747.6	-758	0.27	5.61	0.03	
Oxo 1 DFT*	724.3	-741.9	0.01	5.92	0.0	
Oxo 2 exp	757.3	-758	0.27	5.42	0.03	
Oxo 2 DFT*	761.1	-721	0.01	6.05	0.01	
Bridging exp	441.9	-195	0.01	0.7	0.3	
Bridging DFT*	418.1	-221.2	0.01	0.9	0.03	

Table S2. Experimental and theoretical <sup>17</sup>O NMR parameters of oxygen sites in [(WONp<sub>3</sub>)<sub>2</sub>O]

\* N. Merle, G. Girard, N. Popoff, A. De Mallmann, Y. Bouhoute, J. Trébosc, E. Berrier, J.-F. Paul, C. P. Nicholas, I. Del Rosal, L. Maron, R. M. Gauvin, L. Delevoye, M. Taoufik, *Inorg. Chem.*, 2013, **52**, 10119



Figure S5. <sup>17</sup>O MAS NMR spectra of  $[(WONp_3)_2O]$  acquired at 18.8 T (a) with and (b) without DFS showing C<sub>Q</sub>-dependent signal enhancement.



**Figure S6.** (a) <sup>17</sup>O MAS NMR spectrum of  $[(WONp_3)_2O]$  acquired w/o signal enhancement pulse, (b), (c), (d) – differential <sup>17</sup>O MAS spectra of  $[(WONp_3)_2O]$  obtained subtracting referential spectrum from the spectra recorded with DFS characterized by end sweep frequency of (b) 600, (c) 300 and (c) 100 kHz and pulse durations of 0.1 ms – black, 1.0 ms – red and 3.7 ms – blue lines. DFS pulse amplitude was set to 12 kHz. The spectra were normalized at left end side of isotropic chemical shift resonance before subtraction.

System	Site/Data	δ, ppm	CSA, ppm	η <sub>CSA</sub>	C <sub>Q</sub> , MHz	η <sub>Q</sub>
[WO(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>3</sub> Cl] on silica-700	W=O/Exp	775±2	-740±20	0.2±0.2	5.2	0.6±0.2
	W=O/DFT <sup>a</sup>	760	-758	0.07	5.7	0.17

**Table S3.** Experimental and theoretical <sup>17</sup>O NMR parameters of [WO(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>Cl] grafted on the surface of silica-700.

<sup>a</sup>DFT calculation from D. Grekov, Y. Bouhoute, K. C. Szeto, N. Merle, A. De Mallmann, F. Lefebvre, I. Del Rosal, L. Maron, R. M. Gauvin, L. Delevoye and M. Taoufik, *Organometallics*, 16, **35**, 2188.

## **Details on DFT Calculations**

All DFT calculations were performed with Gaussian 03.<sup>i</sup> Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.<sup>ii</sup> Geometry optimizations were achieved without any symmetry restriction. Calculations of vibrational frequencies were systematically done in order to characterize the nature of stationary points. Stuttgart effective core potentials and their associated basis set were used for silicon and tungsten.<sup>iii</sup> The basis sets were augmented by a set of polarization functions ( $\zeta_d = 0.284$  for Si and  $\zeta_f = 0.823$  for W). Hydrogen, carbon, chlorine, and oxygen atoms were treated with 6-31G(d,p) double- $\zeta$ basis sets.<sup>iv</sup> The optimized structures were used for <sup>17</sup>O NMR calculations. These calculations were also performed using a higher Dunning's correlation consistent basis set cc-PVTZ for the oxygen atoms.<sup>v</sup> In all cases, among the various theories available to compute chemical shielding tensors, the Gauge Including Atomic Orbital (GIAO) method has been adopted for the numerous advantages it presents.vi Typically, in order to compare our calculations with experimental values, <sup>17</sup>O chemical shielding has been converted to chemical shift using the usual equation:  $\delta_{iso} = \sigma_{iso ref} - \sigma_{iso sample}$ , where  $\sigma_{iso ref}$  is the isotropic <sup>17</sup>O chemical shielding of the liquid water. However, because of the arbitrariness in the choice of the isotropic chemical shift of the reference - the value of  $\sigma_{iso ref}$  depends on the level of theory and the used basis sets<sup>vii</sup> an internal reference is used for the calibration of the  $\sigma_{iso}$  ref value. As a consequence, we have calibrated the  $\sigma_{iso ref}$  value with respect to the <sup>17</sup>O  $\delta$  of isolated silanol groups without interaction with organometallic fragments, i.e., the calculated  $\sigma_{iso sample}$  of 287.6 ppm is attributed to an experimental  $\delta$  of 4.6 ppm:  $\sigma_{iso ref} = 292.2$  ppm. The <sup>17</sup>O quadrupolar coupling constant  $C_Q$  and the asymmetry parameter  $\eta_Q$ , which describes the interaction between nuclear quadrupolar moment of the oxygen nuclei with the electric field gradient (EFG) arisen at these sites, are calculated from the EFG tensor eigenvalues V<sub>11</sub>, V<sub>22</sub>, and V<sub>33</sub>, according to:

$$C_{Q} = \frac{e^{2}qQ}{h} = \frac{e^{2}V_{33}Q}{h}, |V_{33}| > |V_{22}| > |V_{11}|, (1)$$
$$\eta_{Q} = \frac{V_{11} - V_{22}}{V_{33}}, (1 \ge \eta_{Q} \ge 0), (2)$$

<sup>ii</sup> J. P. Perdew, In Electronic Structure of Solids; P. Ziesche, H. Eschrig, Eds.; Akademie: Berlin, 1991; Chapter Unified Theory of Exchange and Correlation Beyond the Local Density Approximation.; J. P.Perdew, K. Burke, Y. Wang, *Phys. Rev. B*, 1996, **54**, 16533; K. Burke, J. P. Perdew, Y. Wang, In Electronic Density

<sup>III</sup> W. Küechle, W. M. Dolg, H. Stoll, H. Preuss, *Mol. Phys.*, 1991, **74**, 1245.

<sup>iv</sup> P. C. Harihara, J. A. Pople, *Theo. Chim. Acta*, 1973, **28**, 213; W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

<sup>v</sup> E. R. Davidson, Chem. Phys., 1996, 260, 514; D. E. Woon, T. H. Dunning, J. Chem. Phys., 1993, 98, 1358.

<sup>vi</sup> K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251; R. McWeeny, *Phys. Rev.*, 1962, **126**, 1028; J. L. Dodds, R. McWeeny, A. J. Sadlej, *J. Mol. Phys.*, 1980, **41**, 1419; R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789; P. C. Junk, J. W. Steed, *J. Organomet. Chem.*, 1999, **587**, 191.

<sup>vii</sup> R. E. Walishen, S. Mooibroek, J. B. Macdonald, *J. Chem. Phys.*, 1984, **81**, 1057; J. Kongsted, C. B. Nielsen, K. V. Mikkelsen, O. Christiansen, K. J. Ruud, *Chem. Phys.*, 2007, **126**, 034510.

<sup>&</sup>lt;sup>1</sup> M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Jr. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. I. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision B.05; Gaussian Inc.: Wallingford, CT, 2003.