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Characterization of Surface Organometallic Complexes Using High Resolution 2D Solid-State NMR Spectroscopy. Application to the Full Characterization of a Silica Supported Metal Carbyne: $\equiv$SiO$-$Mo($\equiv$C$-$Bu-*t*)(CH$_2$$-$Bu-*t*)$_2$

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We report herein the characterization of a well-defined alkylidyne complex of Mo supported on silica, namely $\equiv$SiO$-$Mo($\equiv$C$-$Bu-*t*)(CH$_2$$-$Bu-*t*)$_2$, **1**, using two-dimensional (2D) heteronuclear solid-state NMR correlation spectroscopy.

One of the principal handicaps of classical heterogeneous catalysis is the difficulty in developing a clear understanding of the structure of the "active site" which, despite extensive studies, often remains unknown.[1] This difficulty arises from the low concentration of the so-called active sites and their short lifetime. Surface OrganoMetallic Chemistry (SOMC) provides a new approach to the design, construction, and understanding at a molecular level of the coordination sphere of supported metals, through the generation in the ideal case of "well-defined single-site" catalysts. Using this approach, we and other groups have reported a series of alkyl- or alkylidene-based heterogeneous catalysts for the polymerization or the metathesis of olefins.[2] It is noteworthy that the activity of these supported complexes increases when they are directly attached to the oxygen of a surface siloxy group compared to the activity (in solution) of their molecular perhydrocarbyl precursors.[3] We have shown that tetrakis(neopentyl)group IV metal (M = Ti, Zr, Hf) and tris(neopentyl)neopentylidene tantalum complexes selectively generate the corresponding monosiloxy surface complexes $\equiv$SiO$-$M(CH$_2$$-$Bu-*t*)$_3$ and $\equiv$SiO$-$Ta(=CH$-$Bu-*t*)(CH$_2$$-$Bu-*t*)$_2$, respectively, when contacted with silica partially dehydroxylated at the proper temperatures.[4] The characterization of these complexes was performed using IR spectroscopy, EXAFS and their chemical reactivity, for example, hydrolysis, hydrogenolysis, pseudo-Wittig reactions, and microanalysis as well as solid-state NMR (however, the observation of carbon directly attached to the metal has been elusive).[5] The characterization lacked important information routinely available in molecular organometallic chemistry, that is, high-resolution 2D NMR spectra. In our continuing effort to understand the reactivity of organometallics on oxide surfaces, we have studied the grafting of **2**, Mo($\equiv$C$-$Bu-*t*)(CH$_2$$-$Bu-*t*)$_3$, on silica, and unequivocally determined the structure of corresponding surface complex **1**, $\equiv$SiO$-$Mo($\equiv$C$-$Bu-*t*)(CH$_2$$-$Bu-*t*)$_2$ using high-resolution solid state 2D NMR spectroscopy.

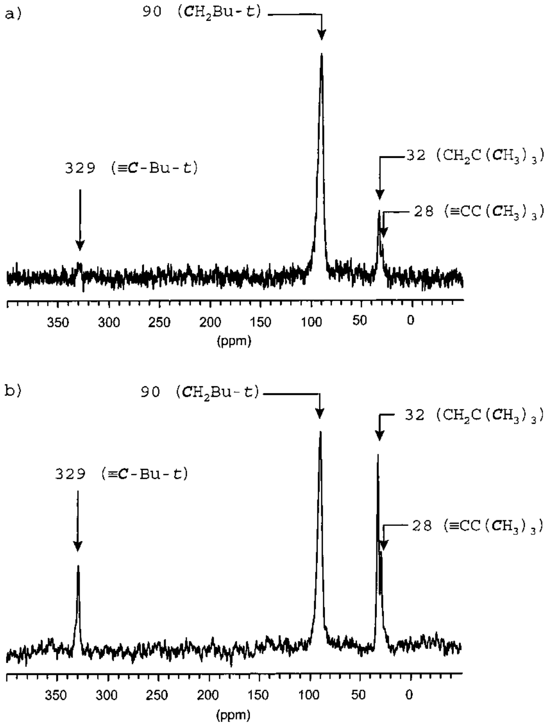

Figure 1. (a) Solid-state CP/MAS ^{13}C NMR spectrum of **1***. **(**b) Solid-state directly excited (HPDEC) MAS ^{13}C NMR spectrum of **1***.

The grafting procedure was the following: a mixture of 1.16 g of SiO$_{2-(700)}$ and a solution of 125 mg (0.33 mmol) of **2**[6] in pentane (10 mL) was stirred for 5 h at 20 °C. After filtration, three washing cycles followed by drying under vacuum (10^{-5} Torr) yielded 1.21 g of a yellow powder containing 2.04 wt % of Mo.

During the grafting step, 1.0 $\pm$ 0.1 equiv of neopentane evolves per equiv of grafted Mo. The treatment of **1** with H$_2$ at 250 °C for 4 h gave reproducibly 15 $\pm$ 1 CH$_4$/Mo, which corresponds to an average of 3.0 $\pm$ 0.2 neopentyl or neopentyl-like ligands around the metal center. This observation is consistent with the structure of **1** (Scheme 1). NMR spectroscopy under magic angle

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(1) For example, see what has been reported in the development of classical heterogeneous catalysts in the area olefin metathesis: Ivin, K. J.; Mol, J. C. *In Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.

(2) (a) For a review on the early stage of SOMC and its application to catalysis, see: Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, V. A. In *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1981; Vol. 8. (b) For references of group VI olefin metathesis catalysts prepared via SOMC, see: Weiss, K.; Loessel, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 62; Buffon, R.; Leconte, M.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 361; Buffon, R.; Leconte, M.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 1723. Herrmann, W. A.; Stumpf, A. W.; Priermeier, T.; Bogdanovic, S.; Dufaud, V.; Basset, J.-M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2803. (b) For reviews on olefin polymerization supported metallocene catalysts prepared by SOMC, see: Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57 as well as a special issue of *Chemical Reviews*: *Chem. Rev.* **2000**, *100*, 1167−1682. (c) For single-site Phillips catalysts prepared by SOMC, see: Amor Nait Ajjou, J.; Scott, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 8968.

(3) This was in fact recognized very early by Ballard et al.: Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263.

(4) (a) For the characterization of silica-supported group IV metals, see: Quignard, F.; Lecuyer, C.; Bougault, C.; Lefebvre, F.; Choplin, A.; Olivier, D.; Basset, J.-M. *Inorg. Chem.* **1992**, *31*, 928; Quignard, F.; Lécuyer, C.; Choplin, A.; Olivier, D.; Basset, J.-M. *J. Mol. Catal.* **1992**, *74*, 353; Corker, J.; Lefebvre, F.; Lécuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966. (b) For the characterization of silica supported group V metals, see: Dufaud, V.; Niccolai, G. P.; Thivolle-Cazat, J.; Basset, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 4288; Lefort, L.; Chabanas, M.; Maury, O.; Meunier, D.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M. *J. Organomet. Chem.* **2000**, *593−594*, 96.

(5) In most cases, the only chemical shifts reported for surface organometallics is, for example, those of the methyls of a neopentyl ligand (M$-$CH$_2$C(**C**H$_3$)$_3$). There is no report of the chemical shift for M$\equiv$**C**R and M=**C**HR (R = Bu-*t*) type surface organometallic complexes or even M$-$**C**H$_2$R with good signal-to-noise ratio (>5).

(6) For the synthesis of **2**, see: (a) Clark, D. N.; Schrock, R. R.; *J. Am. Chem. Soc.* **1978**, *100*, 6774. (b) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987.

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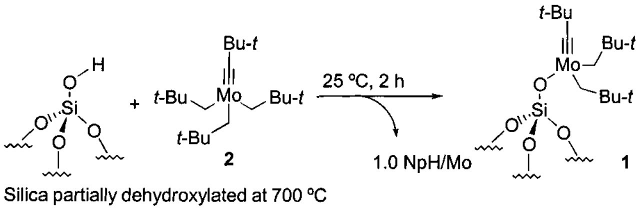
Scheme 1



spinning (MAS) was used to further characterize the structure of **1**. The ^{1}H NMR spectrum of this compound shows one broad peak centered at 1.1 ppm and a shoulder at 1.3 ppm (See Supporting Information). The natural abundance ^{13}C NMR spectrum shows four peaks at 28 ($\equiv CC(\boldsymbol{C}H_3)_3$), 32($CH_2C(\boldsymbol{C}H_3)_3$), 54($\equiv C\boldsymbol{C}(CH_3)_3$)[7] and 90 ppm ($\boldsymbol{C}H_2C(CH_3)_3$). The proposed assignment is made by analogy with the ^{13}C spectrum of the parent complex **2** in solution, which has the following ^{13}C NMR signals: 30.2 ($\equiv CC(\boldsymbol{C}H_3)_3$), 33.5($CH_2\boldsymbol{C}(CH_3)_3$), 34.0 ($CH_2C(\boldsymbol{C}H_3)_3$), 53.5-($\equiv C\boldsymbol{C}(CH_3)_3$), 88.1($\boldsymbol{C}H_2C(CH_3)_3$) and 323.8 ppm($\equiv \boldsymbol{C}C(CH_3)_3$). Thus, the resonances of the quaternary carbon of the neopentyl ligand and the molybdenum−carbyne carbons are not observed in the solid under these conditions. To confirm the assignment of the ^{13}C NMR spectrum, the partially ^{13}C-enriched, **2***, in which the enrichment was on the α-position to the metal, was prepared and reacted with $SiO_{2-(700)}$ to give $\equiv SiO-Mo(\equiv C^{*}Bu\text{-}t)(C^{*}H_2Bu\text{-}t)_2$, **1***. In this case, the ^{13}C solid-state NMR of **1*** unequivocally shows a signal at 329 ppm in the cross-polarization (CP/MAS) spectrum (Figure 1a), and more strongly in the directly excited ^{13}C (HP-DEC) NMR spectrum (Figure 1b), as well as the enhanced CH_2 signal at 90 ppm. In the characterization of molecular structures in solution, the use of 2D NMR spectra is often an essential step in order to make unequivocal assignments. The application of 2D heteronuclear correlation spectroscopy (HETCOR) shows the power of this technique to characterize **1**.[8] The pulse sequence used for this 2D experiment consists first in a 90° proton pulse which rotates the proton magnetization into the *xy* plane. Then it evolves during t_1 and is subsequently transferred to the ^{13}C spin via a cross-polarization step. The ^{13}C magnetization is then detected during t_2 under continuous wave proton decoupling. A 2D Fourier transformation gives through space correlation between pairs of neighboring carbon (in F2) and proton (in F1) nuclei.[9] Note that due to large proton line width, polarization transfers through scalar J_{CH} couplings would be difficult in such compounds. However, using a short contact time for the CP step, the polarization transfer in the dipolar correlation experiment is expected to be quite selective, that is to lead to correlation only between pairs of attached $^{1}H-^{13}C$ spins. The 2D NMR spectrum, recorded with a contact time of 2 ms, shows clear correlations between methyl protons at 1.1 and 1.3 ppm and the carbons at 32 and 28 ppm, respectively (Figure 2a).[10] From the relative intensities and the chemical shifts, the two ^{13}C resonances at high field can be assigned to the two different *tert*-butyl fragments of the neopentyl and the neopentylidyne ligands (at 32 and 28 ppm, respectively). Moreover, in the 2D spectrum, the ^{13}C resonance of methylene groups of the equivalent neopentyl ligands (90 ppm) gives two correlations with protons at 1.1 and 2.8 ppm as shown in Figure 2a and b. These two proton resonances correspond to the two diastereotopic protons. Note that the proton signal at 2.8 ppm is hardly visible in the 1D spectrum. It is worth pointing out that the choice of contact time is important in this type of experiment, since a longer contact time gives rise to long-range correlation peaks. In this particular case a correlation between the carbynic carbon and the adjacent *tert*-butyl of the neopentyl is visible for a 10 ms contact time (see Supporting Information for the observed spectra).

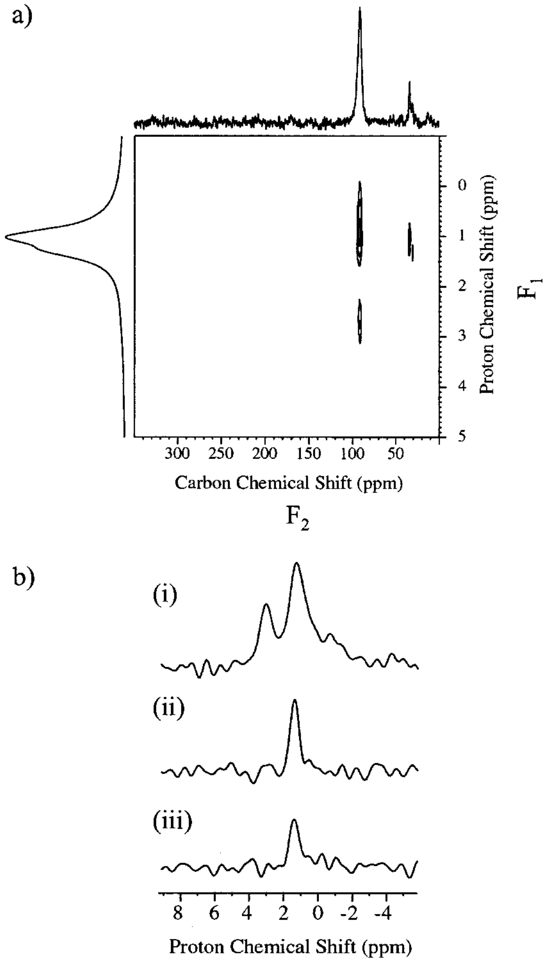


Figure 2. (a) $^{1}H-^{13}C$ HETCOR of 1*. (b) Traces perpendicular to F_2 at (i) 90 ppm, (ii) 32 ppm and (iii) 28 ppm.

In conclusion, the combination of 2D solid-state NMR spectroscopy techniques with other readily available spectroscopic and chemical methods applied to surface organometallic complexes can be used much like it is in molecular organometallic chemistry. Two-dimensional solid-state NMR spectroscopy has allowed the characterization of the structure of a well-defined surface alkylidyne complex. We are currently investigating the reactivity of this well-defined “heterogeneous” surface complex.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[7] This carbon is usually difficult to detect under standard conditions.

[8] For a recent review on these techniques, see: Burum, D. P. *Encyclopedia of NMR*, 1997; p 2323.

[9] During t_1, no proton−proton decoupling sequence was applied since it did not improve the proton resolution.

[10] These experiments were conducted on a Bruker DSX 500 sprectrometer using 4-mm MAS probe. For the cross-polarization step, a ramped rf field centered at 77 kHz was applied on protons while the carbon rf field was matched to obtain optimal signal. During acquisition, the proton decoupling field strength was also set to 77 kHz. A total of 64 t_1 increments with 256 scans each were collected. The spinning frequency was 10 kHz and the contact time for the cross-polarization step set to 2 ms. Quadrature detection in ω_1 was achieved using the TPPI method (Marion, D.; Wütrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967).