

A well-defined silica-supported dinuclear tungsten(III) amido species: synthesis, characterization and reactivity†‡

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Grafting of $[\text{W}_2(\text{NMe}_2)_6]$ onto dehydroxylated silica affords the well-defined surface species $[(\equiv\text{Si}-\text{O})\text{W}_2(\text{NMe}_2)_5]$, characterized by elemental analysis, and infrared, Raman and NMR spectroscopies, and the catalytic reactivity of this supported tungsten(III) $\text{d}^3\text{-d}^3$ dimer and of its alkoxide derivatives towards alkynes has been probed.

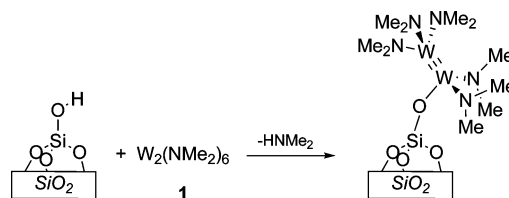
Compounds containing metal–metal multiple bonds have emerged as an important category in modern inorganic and organometallic chemistry.¹ More particularly, Group 6 dimeric derivatives of the $\text{d}^3\text{-d}^3$ type, involved in metal-to-metal triple bonding, have found applications in numerous fields, such as in materials² and organometallic synthesis,³ and in catalysis.⁴ One of the most versatile entries into this class of compounds relies on the substitution of amido ligands of the $\text{M}_2(\text{NR}_2)_6$ species through protonolysis or halogenation.⁵ Controlled grafting of these compounds onto an inorganic support to afford single-site grafted species is a most desirable goal, considering the importance of designing efficient and well-defined supported catalysts.⁶ The immobilization of such key compounds onto an inorganic support to generate heterogeneous dinuclear amido derivatives is therefore of great interest.

We report here the selective synthesis of a silica-supported well-defined ditungsten pentaamide,⁷ which has been characterized by elemental analysis, infrared, Raman and multidimensional solid-state NMR spectroscopies, as well as preliminary results on the catalytic reactivity toward alkynes of this supported amido species and of an alkoxide derivative.

Tungsten amides are known to react with alcohols to afford the corresponding alkoxides.⁵ Bearing in mind the analogy between the silanol groups present on silica surfaces and molecular alcoholic functions, efficient grafting of tungsten amides onto such a support is expected to take place.⁸ The choice of a support bearing only isolated silanol groups, such as silica dehydroxylated at 700 °C ($\text{SiO}_2\text{-700}$),⁹ is expected, after reaction with the molecular precursor, to lead to the formation of a surface species containing a single metal–oxygen bond.

Reaction between the hexakis(dimethylamide)ditungsten complex (**1**)¹⁰ and $\text{SiO}_2\text{-700}$ suspended in pentane at room temperature

followed by treatment under high vacuum (40 °C, 10^{-4} Pa) affords a yellow material (**2**, Scheme 1).[‡] Release of HNMe_2 is shown by NMR follow-up of the reaction in an NMR tube. Elemental analysis indicates a tungsten loading of 10.15 wt%, corresponding to 0.55 mmol g^{-1} . The respective nitrogen to tungsten and carbon to tungsten molar ratio of 2.57 and 5.01 are consistent with a formulation of $\equiv\text{Si}-\text{O}-\text{W}_2(\text{NMe}_2)_5$ (theoretical values: 2.50 and 5.00, respectively).



Scheme 1 Formation of **2** from reaction of **1** with $\text{SiO}_2\text{-(700)}$.

Diffuse reflectance infrared studies carried out on **2** (Fig. 1c) show complete consumption of the isolated silanols (sharp peak at 3747 cm^{-1} on the starting $\text{SiO}_2\text{-700}$ material, Fig. 1b) upon reaction of the dehydroxylated-silica support with the molecular precursor **1** (Fig. 1a). New bands appear on the W-modified silica, in the $2980\text{--}2700\text{ cm}^{-1}$ ($\nu_{\text{C-H}}$) and in the $1465\text{--}1398\text{ cm}^{-1}$ ($\delta_{\text{C-H}}$) ranges, as observed in the molecular precursor spectrum. Moreover, no N–H bands were observed in the expected range ($3000\text{--}3500\text{ cm}^{-1}$), revealing an absence of chemi- or physisorbed dimethylamine.¹¹

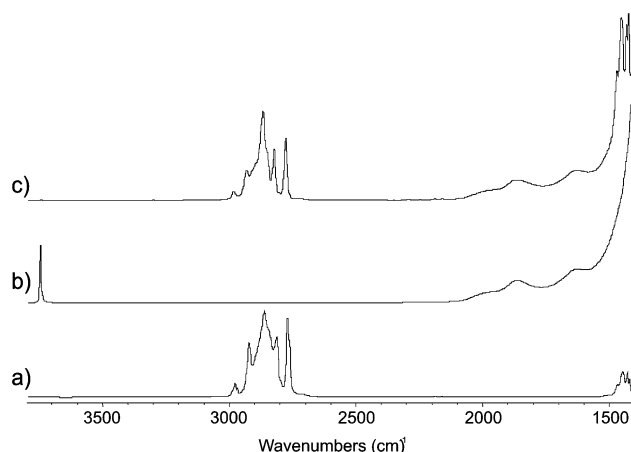


Fig. 1 DRIFT spectra of a) $\text{W}_2(\text{NMe}_2)_6$ (**1**), b) $\text{SiO}_2\text{-700}$, c) **2**.

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‡ Electronic supplementary information (ESI) available: Experimental details on synthetic and catalytic procedures, additional spectroscopic data and DFT calculations. See DOI: 10.1039/b708356b

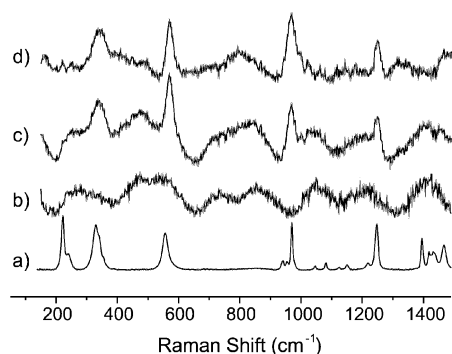


Fig. 2 Raman spectra of a) **1**, b) SiO₂-700, c) **2**, and d) subtraction of SiO₂-700 from the spectrum of **2**.

The Raman spectrum of material **2** (Fig. 2c) exhibits lines roughly similar to those of molecular precursor **1** (Fig. 2a). The subtraction of the SiO₂-700 spectrum provides a clearer view of the spectral modifications following the grafting of **1** (Fig. 2d) and the comparison with the spectrum of **1** (Fig. 2a) reveals significant modifications. DFT early calculations on **1** and on model compounds [(MeO)₃SiO]W₂(NMe₂)₅, W₂(NH₂)₆ and W₂(OMe)₆ have been used to assign the lines and understand the observed changes.[‡] The main modifications come out in the low frequency region (200–600 cm^{−1}) in which lines result from vibration modes involving tungsten centers, essentially combined with other modes. The line at 558 cm^{−1} in **1** assigned to a W–N stretching vibration is shifted to 571 cm^{−1} in **2** and the low frequency vibration (around 220 cm^{−1}) has entirely vanished in the spectrum of **2** (Fig. 2d). Moreover, the line at 328 cm^{−1} is asymmetrically enlarged towards higher wavenumbers. Regarding the low frequency lines, the above-mentioned shifts are consistent with the lowering of the symmetry when going from **1** to **2** and with the substitution of one amido functionality by a surface siloxide group, in accordance with the elemental analysis results. Because of the high degree of coupling over these vibrations, straightforward assignment remains hazardous. W≡W stretching vibrations clearly contribute to the 233 and 328 cm^{−1} lines in **1**. The triple bond stretching mode heavily contributes to the latter, though the observed frequency is influenced by strong coupling with vibrations involving CH₃ and/or W–W–N moieties, as previously discussed by Cotton^{10b} and Gilbert.¹² Assignment of the line at 233 cm^{−1} in **1** is more controversial: Indeed, though no additional triple bond stretching mode is expected, DFT calculations reveal that it clearly involves W≡W stretching motions. This may originate from the effective coupling of symmetric W–W–N bending modes, the impediment of which by steric effects may lead to significant W≡W stretching. The extinction of this low frequency mode in **2** is possibly due to a loss of symmetry, rendering the coupling ineffective for geometrical reasons. Conversely, the 328 cm^{−1} line is still observed in **2**, which confirms the important weight of the W≡W stretching mode contribution in this case. The new broad features observed around 400 and 780 cm^{−1} (Fig. 2d) might be due to structural modifications, *i.e.* changes in the Si–O–Si equilibrium angle induced by the grafting or contribution of Si–O–W bending modes, rather than to the presence of minor species.¹³

Solid-state NMR spectroscopy affords a deeper insight into the grafted species structure. The room-temperature ¹H MAS

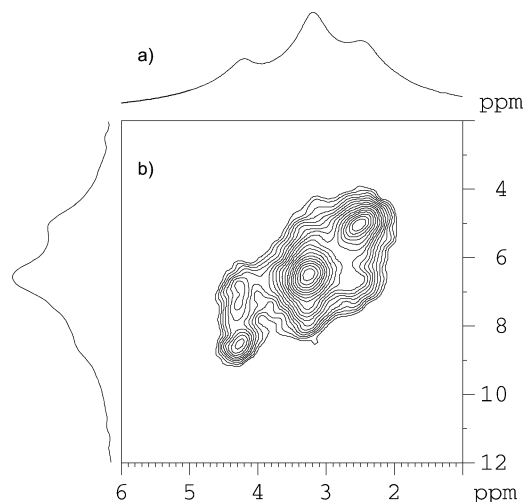


Fig. 3 Solid-state NMR spectra of **2** at 9.4 T: a) ¹H at a MAS speed of 13 MHz, obtained with 32 transients and a recycle delay of 5 s; b) ¹H-¹H DQ-MAS at a spinning speed of 20 kHz and a recycle delay of 10 s.[‡]

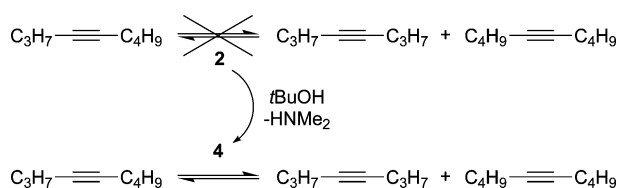
spectrum displays three peaks at 4.2, 3.2 and 2.5 ppm, with the central one being the most intense (Fig. 3a). These spectral features are reminiscent of those reported by Chisholm and co-workers for a series of rare examples of W₂(NMe₂)₅(X) compounds.¹⁴ In the benzyl derivative (X = CH₂Ph), the amido methyl groups of the W(NMe₂)₃ moiety are rapidly rotating (fast exchange regime) and give rise to a single peak (3.38 ppm, 18H). On the other hand, the distal and proximal methyl groups of the W(CH₂Ph)(NMe₂)₂ moiety are not equivalent, due to the hindered rotation of the dimethylamido ligands along the W–N bond (slow on the NMR time scale), and, therefore, the protons of the proximal and distal NMe groups resonate at 4.21 (6H) and 2.12 ppm (6H), respectively. The striking similarity of these spectral features to those of **2** does not only confirm the (≡Si–O)(Me₂N)₂W≡W(NMe₂)₃ formulation, but also indicates that, in the grafted amido species, as in the model benzyl complex, the 3 WNMe₂ groups vicinal to the siloxide group rotate freely along the metal–nitrogen bond on the NMR time scale. On the contrary, the rotation of the WNMe₂ groups geminal to the siloxide group is hindered, most probably due to the silica surface acting as a bulky ligand. It is therefore acceptable to assign the most intense signal at 3.2 ppm to the methyl groups of the W(NMe₂)₃ moiety, and the two other signals at 4.2 and 2.5 ppm to the methyl groups of the (≡Si–O)W(NMe₂)₂ moiety.

In order to confirm and refine these assignments, bidimensional solid-state NMR spectroscopy studies were performed. ¹H-¹H double-quantum (DQ-MAS) correlation spectroscopy provides the mean to determine the spatial arrangement of protons in the solid-state.¹⁵ The DQ excitation and reconversion blocks have been set to two rotor periods to ensure that long distance correlations appear on the spectrum. As shown in Fig. 3b, in the spectrum recorded using the BABA2rot sequence, interactions are observed between the signals at 4.2 and 2.5 ppm on one hand, and between peaks centered at 4.2 and 3.2 ppm on the other hand.[‡] Bearing in mind the assignments of the central peak to the rapidly rotating equivalent NMe₂ on the tungsten vicinal to the siloxide ligand, and of the two other signals to frozen N(Me)(Me) groups of (≡Si–O)W(NMe₂)₂, this allows full

assignment of the ^1H signals: proximal (geminal to ($\equiv\text{Si-O}$)) methyl groups resonate at 4.2 ppm, and are close to both the vicinal methyl (3.20 ppm) and to distal (geminal to ($\equiv\text{Si-O}$)) methyl groups (2.50 ppm). These assignments are analogous to those made for $\text{W}_2(\text{NMe}_2)_3(\text{CH}_2\text{Ph})$ by Chisholm *et al.*¹⁴ The deshielding of the proximal NCH_3 and the shielding of the distal NCH_3 are in line with the trends observed in similar molecular compounds.⁵ Moreover, under the experimental conditions (2 rotor periods for double quantum evolution), no significant interaction can be detected for distal geminal $\text{W}(\text{NMeMe})_2$ and vicinal $\text{W}(\text{NMe}_2)_3$ methyl groups, as expected from the proposed assignments.

The ^{13}C CP-MAS NMR spectrum consists of three peaks, at 58.2, 47.8 and 37.6 ppm.[‡] Again, this is in good agreement with the data reported for the NMe_2 signals of the benzyl derivative (59.53, 49.54 and 40.60 ppm). ^1H - ^{13}C HETCOR spectroscopy allows us to determine the correlations between the proton and carbon signals, and thus to fully assign them: vicinal $\text{W}(\text{NMe}_2)_3$ methyl groups resonate at 49.54 ppm, and $\text{W}(\text{NMe}_2)_3$ proximal and distal methyl groups, at 58.2 and 37.6 ppm, respectively.

Preliminary studies on the reactivity of **2** toward alkynes have been carried out.^{‡16} Material **2** proved to be unreactive toward the internal alkyne 4-nonyne. However, in the presence of 92 equivalents of 1-heptyne per W_2 unit, this material slowly catalyzes the formation of conjugated poly(heptyne)-coated silica. The modest conversion (3%) tends to indicate slow initiation. Even if no metathesis products were observed, this contrasts with the reactivity of **1**, which does not afford any oligomer or polymer under similar conditions. Bearing in mind that the alcoholysis of dimethylamido ligands in **1** by *tert*-butanol leads to $\text{W}_2(\text{OtBu})_6$ (**3**), a precursor for metathesis catalysts of the $(t\text{BuO})_3\text{W}\equiv\text{C-R}$ type,⁴ we attempted to generate *in situ* a supported version of **3** by following a similar reaction scheme. Addition of 5 equivalents of *t*BuOH per W_2 to **2** affords a deep-orange material (**4**). Analyses reveal that under these reaction conditions, alcoholysis of the amido functions is not complete.¹⁷ However, in the presence of 50 equivalents of 4-nonyne per W_2 , **4** affords the metathesis products 4-octyne and 5-decyne (equilibrium reached at room temperature within 30 min, as shown by GC analysis, Scheme 2). Under similar reaction conditions using $(t\text{BuO})_3\text{W}\equiv\text{CtBu}$ as catalyst, equilibrium is reached within 20 min.



Scheme 2 Alkyne metathesis mediated by **4**.

With the more challenging terminal alkyne 1-heptyne as a substrate (50 equivalents), a conversion of 80% is reached within 15 h, with modest selectivity towards metathesis (4%), as polymerization takes place.¹⁶ Based on the reactivity of the hexakis(*tert*-butoxide) ditungsten species, the most probable reaction scheme is the splitting of the $\text{W}\equiv\text{W}$ triple bond which generates two types of carbyne: soluble and surface-supported species. The question regarding the nature of the metathesis active species (homogeneous

and/or heterogeneous) has been addressed: after the metathesis run and subsequent washing of the material, addition of a fresh solution of 4-nonyne leads to no detectable metathesis activity. However, the orange modified silica vigorously polymerized 1-heptyne (300 equivalent per initial W). Further work is targeted at the understanding of the nature of the involved supported species and on the tuning of their reactivity.

In summary, synthesis and full characterization of a well-defined supported ditungsten amide has been achieved. Moreover, we have shown that as simple *in situ* modification of the ligand sphere of this surface species is possible: the derivatization into *tert*-butoxide surface species triggers the reactivity toward alkyne metathesis. The catalytic applications opened by this approach are not restricted to the design of supported metathesis tungsten-based catalysts, since further oxidation can give access to highly dispersed metal oxides. Moreover, the versatility of the protonolysis approach implies that a broad range of ligands can be introduced around the $[(\equiv\text{Si-O})(\text{M}\equiv\text{M})]^{2+}$ core, not only for tungsten, but also for molybdenum. This could afford access to immobilized versions of species which cannot be isolated in solution due to oligomerization pathways,¹⁸ for instance, and may thus pave the way to small ligand chemistry of supported $\text{d}^3\text{---d}^3$ dimers of tungsten and molybdenum.

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