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

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I. General considerations.

All experiments were carried out under an argon atmosphere in a M-Braun glove-box or by using Schlenk techniques. Toluene, pentane and decane (Aldrich) were dried over sodium, distilled under nitrogen and degassed by three freeze-pump-thaws prior to use. Alkynes (Aldrich) were dried over CaH_2 , distilled under argon and degassed by three freeze-pump-thaws prior to use. $\text{W}_2(\text{NMe}_2)_6$ ¹ and $(t\text{BuO})_3\text{W}\equiv\text{CtBu}^2$ were synthesized as described in the literature. Aerosil 380 silica (Degussa, specific area $380\text{ m}^2\text{ g}^{-1}$ prior heat-treatment) was subjected to heating under secondary vacuum (10^{-6} mmHg) at $500\text{ }^\circ\text{C}$ over 15 hours followed by 4 hours of heating at $700\text{ }^\circ\text{C}$, and stored in a glove-box. Solid-state MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer (^1H : 400.1 MHz, ^{13}C : 100.6 MHz). For ^1H experiments, the spinning frequency was 13 kHz, the recycle delay was 5 s and 32 scans were collected using a 90° pulse excitation of 3 μs . For the two-dimensional homonuclear experiment (DQ-MAS), the DQ excitation and reconversion blocks were set to two rotor periods (100 μsec) with back-to-back pulse lengths of 3 μsec . The recycling delay was 10 s. The 2D spectrum resulted from 16 transients for each of the 200 increments in the t_1 domain. The STATES acquisition mode was used. The ^{13}C CP MAS experiment was obtained at a spinning frequency of 10 kHz, with a recycle delay of 5 s and 1024 scans were collected. For the CP step, a ramped radio frequency (RF) field centered at 50 kHz was applied on protons, while the carbon RF field was matched to obtain optimal signal. The contact time was set to 1.5 ms. The ^{13}C - ^1H CP-HETCOR MAS spectrum was obtained at 100.62 MHz (9.4T) at a spinning speed of 10 kHz with a recycle delay of 4 s. The Hartmann-Hahn condition was experimentally optimized with a constant RF field amplitude of 55 kHz on the ^{13}C channel and a ramped pulse on the ^1H channel center on 55 kHz. The contact time was set to 3 msec. A ^1H decoupling pulse of 80 kHz (TPPM) was used during the ^{13}C acquisition. The 2D spectrum was obtained with 128 scans for each of the 64 increments, using STATES acquisition mode. Chemical shifts were given in ppm with respect to TMS as external reference for ^1H and ^{13}C NMR. Diffuse reflectance infrared spectra were collected using a Harrick cell on a Nicolet Avatar spectrometer fitted with a MCT detector. Micro-Raman spectra were recorded under Ar atmosphere at room temperature using the 531.95 nm second harmonic line of a Nd:YAG laser. A 50X microscope objective was used to focus the excitation beam (13.6 mm spot) and collect the scattered light at the same time. The scattered light was collected through a confocal hole (150 μm) by a nitrogen-cooled CCD (Labram Infinity, Jobin-Yvon). Before experiment, the gratings were thoroughly calibrated with the 524 cm^{-1} Raman line of a pure Si plate and the accuracy of the measured shift was successfully checked after measurements. Elemental analyses were carried out at the Service Central d'Analyse du CNRS (tungsten), and in the Service d'Analyse Élémentaire, LSEO, Université de Bourgogne (C, H, N). Gas chromatography analyses were performed on a Chrompack CP9001 gas chromatograph under N_2 flow with a CPSil 8 CB column (15 m length, 0.32 mm diameter, 0.25 μm film thickness). DFT calculations have been performed using the g03 program,³ at the B3PW91⁴ level with the sddall⁵ basis set as provided by the program package.

¹ M. H. Chisholm, J. D. Martin, J. E. Hill, I. P. Rothwell *Inorganic Syntheses*, **1992**, 29, 137-140.

² J. H. Wengrovius, J. Sancho, R. R. Schrock, *J. Am. Chem. Soc.* **1981**, 103, 3932.

³ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. 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. J. 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, and J. A. Pople, *Gaussian 03*, Revision D.01, Gaussian, Inc., Wallingford CT, 2004.

⁴ A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, 45, 13244.

⁵ M. Dolg, H. Stoll, H. Preuss, R.M. Pitzer, *J. Phys. Chem.* **1993**, 97, 5852; A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, 80, 1431; T. H. Dunning, Jr. *J. Chem. Phys.* **1970**, 53, 2823.

II. Materials synthesis

• *Synthesis of 2.*

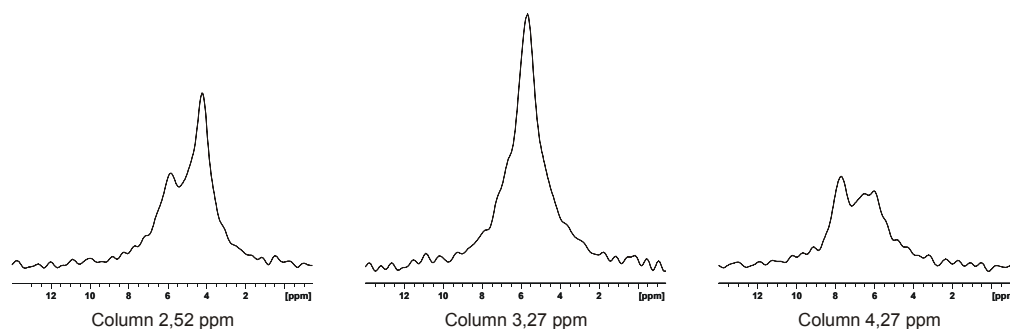
Impregnation was carried out in a double-Schlenk flask loaded in a glove-box. To 730 mg of dehydroxylated SiO₂ (Degussa Aerosil 380, heated under vacuum for 15 hours at 500°C then 4 hours at 700°C) suspended in 20 mL of pentane was added a 10 mL pentane solution of 170 mg ($2.7 \cdot 10^{-4}$ mol) of W₂(NMe₂)₆. Instantaneous colour change of the silica was observed with concomitant fading of the supernatant yellow colour. After 3 hours of stirring at room temperature, the modified silica was separated by filtration and washed thrice with 30 mL of pentane. Pre-drying under primary vacuum followed by drying under secondary vacuum (40°C) afforded 830 mg of **2** as a yellow powder. Elemental analysis (%): W: 10.15, C: 3.32, H: 0.86, N: 1.99.

• *Synthesis of 4.*

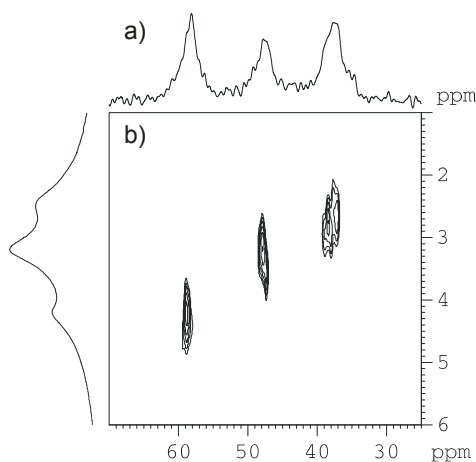
In the glove-box, to a suspension of **2** (203 mg, $2.88 \cdot 10^{-4}$ mol W) in 5 mL pentane was added dropwise a solution of *t*BuOH (53 mg, $7.2 \cdot 10^{-4}$ mol) in pentane (2 mL). The silica material darkened quickly, turning to brown-orange. After 2h30 stirring at room temperature, the solid was separated by decantation and washed with pentane (4×4 mL). The brown-orange powderous material was then dried under dynamic secondary vacuum (10^{-6} mmHg, 20 hours, RT), affording an orange solid (195 mg). Elemental analyses show the presence of residual NMe₂ ligands, but no X-H (X= NMe₂, *Ot*Bu) is detected in the material by DRIFTS.

III. Solid-state NMR spectra of **2**.

• *Slices from DQ-MAS spectrum*



• ¹³C CP MAS and ¹H-¹³C HETCOR MAS



- a) ¹³C CP-MAS (100.62 MHz, NS= 10000, spinning speed of 13 kHz, recycle delay of 4 s)
b) ¹H-¹³C HETCOR MAS (100.62 MHz, spinning speed of 10 kHz, recycle delay of 4 s)

IV. DFT calculations

- Optimised geometry of the $W_2(N(CH_3)_2)_6$ molecule

C	3.0974	-2.1855	-0.5887
N	1.6629	-1.8568	-0.5166
C	0.8584	-3.0349	-0.8494
W	1.1627	0.0077	-0.0090
W	-1.1625	-0.0087	0.0077
N	-1.6121	-1.3842	1.3771
C	-0.7690	-2.2421	2.2116
N	1.6152	1.3909	-1.3691
C	0.7754	2.2618	-2.1936
C	3.0407	1.6421	-1.6446
N	-1.6580	-0.5123	-1.8581
C	-0.8490	-0.8353	-3.0343
N	-1.6619	1.8571	0.5087
C	-0.8579	3.0391	0.8268
C	-3.0912	-0.6067	-2.1854
C	-3.0965	2.1839	0.5887
C	-3.0366	-1.6416	1.6520
H	3.7172	-1.3169	-0.3430
H	3.3797	-2.5209	-1.5985
H	3.3555	-2.9894	0.1175
H	1.0587	-3.8611	-0.1484
H	-0.2023	-2.7911	-0.8038
H	1.0925	-3.3996	-1.8625
H	3.3110	2.6863	-1.4254
H	3.2811	1.4457	-2.7006
H	3.6822	0.9979	-1.0341
H	-0.2766	2.0708	-1.9837
H	0.9595	2.0895	-3.2661
H	0.9881	3.3234	-1.9888
H	-3.7131	-0.3667	-1.3171
H	-3.3583	-1.6223	-2.5158
H	-3.3608	0.0920	-2.9923
H	-1.0563	-1.8580	-3.3879
H	-1.0706	-0.1482	-3.8667
H	0.2096	-0.7600	-2.7912
H	-3.7166	1.3105	0.3625
H	-3.3698	2.5333	1.5962
H	-3.3632	2.9768	-0.1266
H	-1.0632	3.8586	0.1197
H	0.2031	2.7970	0.7797
H	-1.0883	3.4120	1.8380
H	-3.2979	-2.6913	1.4480
H	-3.2825	-1.4310	2.7039
H	-3.6812	-1.0126	1.0292
H	0.2823	-2.0477	2.0015
H	-0.9549	-2.0590	3.2820
H	-0.9766	-3.3069	2.0182
N	1.6543	0.5066	1.8594
C	3.0863	0.6090	2.1893
H	3.3439	1.6228	2.5322
H	3.3616	-0.0970	2.9877
H	3.7108	0.3859	1.3183
C	0.8402	0.8167	3.0362
H	1.0615	0.1240	3.8639
H	1.0421	1.8376	3.3982
H	-0.2174	0.7388	2.7882

Calculated frequencies (wave-numbers, cm^{-1}) between 200 and 500 cm^{-1} .

The mode active in Raman spectroscopy with an important weight of the W-W stretching bond are labeled by *:

209; 212; 221; 222; 227*; 228*; 230; 241; 246; 253; 301; 331; 314; 319; 322; 331; 332; 333; 339; 364; 365; 366; 372; 379*.

- Optimised geometry of the $W_2(N(CH_3)_2)_5[OSi(OCH_3)_3]$ molecule.

C	-0.4116	-3.2494	-1.9566
N	0.3916	-2.0488	-1.6523
C	1.4396	-1.8597	-2.6559
W	-0.0923	-1.0656	-0.0100
W	1.4130	0.7104	0.0110
N	0.9992	1.6687	-1.6856
C	0.0360	1.3932	-2.7530
O	-1.9005	-0.3472	-0.0348
N	0.3416	-2.0412	1.6489
C	1.3433	-1.8297	2.6943
C	-0.4537	-3.2537	1.9239
N	3.2181	-0.1342	0.0616
C	3.6442	-1.5319	0.0656
N	0.9164	1.6967	1.6689
C	-0.0791	1.4233	2.7072
C	4.3845	0.7625	0.1146
C	1.6268	2.9526	1.9600
C	1.7631	2.8899	-1.9883
Si	-3.2924	0.5768	0.0075
O	-4.5345	-0.1748	-0.8591
C	-4.7589	-0.2739	-2.2779
O	-3.0593	2.0983	-0.6824
C	-2.3098	3.2512	-0.2511
O	-3.8443	0.7568	1.5930
C	-4.7664	-0.0355	2.3659
H	-1.2235	-3.3743	-1.2330
H	0.2067	-4.1590	-1.9397
H	-0.8683	-3.1667	-2.9536
H	1.0008	-1.7510	-3.6596
H	2.0173	-0.9650	-2.4274
H	2.1203	-2.7247	-2.6826
H	-0.9552	-3.1746	2.8993
H	0.1807	-4.1522	1.9383
H	-1.2298	-3.3962	1.1652
H	1.9120	-0.9244	2.4854
H	2.0383	-2.6815	2.7530
H	0.8606	-1.7254	3.6780
H	4.0759	1.8135	0.1123
H	5.0465	0.6079	-0.7512
H	4.9765	0.5922	1.0270
H	4.2870	-1.7537	-0.8017
H	4.2236	-1.7685	0.9729
H	2.7706	-2.1817	0.0292
H	2.3675	3.1787	1.1854
H	0.9283	3.8020	2.0107
H	2.1571	2.8958	2.9230
H	0.3949	1.3688	3.7008
H	-0.5838	0.4781	2.5130
H	-0.8414	2.2163	2.7463
H	2.3198	2.7867	-2.9325
H	1.0989	3.7625	-2.0834
H	2.4894	3.1097	-1.1985
H	-0.5046	0.4707	-2.5446
H	-0.6972	2.2084	-2.8460
H	0.5458	1.2882	-3.7246
H	-5.0257	0.5518	3.2471
H	-5.6684	-0.2559	1.7879
H	-4.2962	-0.9736	2.6797
H	-5.7326	-0.7452	-2.4123
H	-4.7634	0.7182	-2.7392
H	-3.9882	-0.8936	-2.7496
H	-2.4954	4.0378	-0.9830
H	-2.6502	3.5836	0.7344
H	-1.2402	3.0209	-0.2170

Calculated frequencies (wave-numbers, cm^{-1}) between 200 and 500 cm^{-1} .

The mode active in Raman spectroscopy with an important weight of the W-W stretching bond are labeled by *:

203; 206; 207; 216; 218; 228; 234; 238; 241; 246; 249; 255; 273; 290; 304; 319; 322; 331; 336; 341; 343; 358*; 370**; 371; 373; 375; 391* (coupling with Si-OCH₃); 393* (coupling with Si-OCH₃); 427.
The two Si-OCH₃-coupled active modes may change depending on the surface model.

• *Optimised geometry of the $W_2(NH_2)_6$ molecule.*

N	1.5525	1.9341	-0.0027
W	1.1520	0.0000	-0.0005
W	-1.1519	0.0004	0.0002
N	-1.5516	1.7490	-0.8254
N	1.5480	-0.9645	1.6761
N	-1.5457	-0.1583	1.9288
N	-1.5506	-1.5896	-1.1004
N	1.5466	-0.9717	-1.6740
H	2.5021	2.2902	-0.0834
H	-2.4935	-0.2707	2.2810
H	-0.8699	-0.1021	2.6831
H	0.8808	2.6848	0.1166
H	-2.5018	2.1035	-0.9055
H	-0.8817	2.3748	-1.2595
H	-0.8783	-2.2769	-1.4240
H	-2.5002	-1.8404	-1.3659
H	0.8735	-1.4461	2.2609
H	2.4970	-1.0827	2.0229
H	2.4950	-1.2174	-1.9477
H	0.8704	-1.2454	-2.3788

Calculated frequencies (wave-numbers, cm^{-1}) between 200 and 500 cm^{-1} .

The mode active in Raman spectroscopy with an important weight of the W-W stretching bond are labeled by *:

191; 192; 194; 196; 198; 200; 211; 282; 313*; 368; 427; 430; 491; 494.

• *Optimised geometry of the $W_2(OCH_3)_6$ molecule.*

C	0.9525	-3.2160	-0.4465
W	1.1747	-0.0790	-0.0138
W	-1.1739	0.0794	0.0139
C	1.2870	1.8998	-2.4971
C	-0.9493	3.2164	0.4446
C	-1.2991	-1.8991	2.4975
C	-1.3008	-1.1349	-2.9199
H	-0.1406	-3.1367	-0.4101
H	1.3029	-3.8776	0.3505
H	1.2609	-3.6244	-1.4129
H	1.6076	1.5023	-3.4641
H	1.7400	2.8840	-2.3480
H	0.1946	1.9891	-2.4785
H	0.1436	3.1364	0.4025
H	-1.2534	3.6204	1.4142
H	-1.3026	3.8817	-0.3479
H	-0.2074	-1.9962	2.4790
H	-1.6173	-1.4994	3.4644
H	-1.7589	-2.8800	2.3481
H	-1.7807	-2.1077	-3.0583
H	-1.5953	-0.4702	-3.7367
H	-0.2115	-1.2573	-2.9155
C	1.3037	1.1264	2.9246
H	1.6134	0.4636	3.7373
H	1.7717	2.1051	3.0623
H	0.2128	1.2338	2.9301
O	-1.5580	1.9276	0.2697
O	-1.7527	-1.0143	1.4619
O	-1.7525	-0.5709	-1.6795
O	1.7539	0.5715	1.6795
O	1.7478	1.0185	-1.4615
O	1.5604	-1.9263	-0.2754

Calculated frequencies (wave-numbers, cm^{-1}) between 200 and 500 cm^{-1} .

The mode active in Raman spectroscopy with an important weight of the W-W stretching bond are labeled by *:

201; 216; 231; 245; 248; 253; 273*; 290; 315; 332; 333; 351; 369**.

V. Catalytic reactions procedures

• Hept-1-yne metathesis with 2.

A Schlenk tube was charged with **2** (5 mg, $2.72 \cdot 10^{-6}$ mol W), toluene (2 mL), and a magnetic stir bar. The solution was stirred at room temperature and hept-1-yne (500 μL , $3.812 \cdot 10^{-3}$ mol) was added to the suspension. The reaction mixture turned yellow after a few minutes and was stopped after 24 hours. All volatile compounds were removed under vacuum and the solid yellow residue dried for 2 hours under vacuum affording 17 mg of silica-coated polymer (12 mg of polymer, corresponding to a conversion of 3%).

• Hept-1-yne metathesis with 4 and $(t\text{BuO})_3\text{W}\equiv\text{CtBu}$

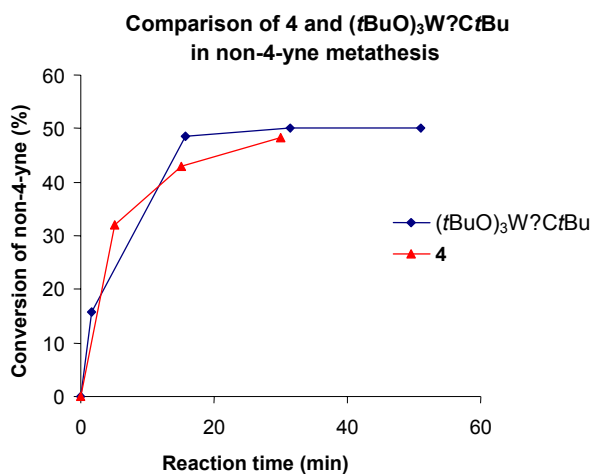
A Schlenk tube was charged with toluene (5 mL), decane (100 μL) and hept-1-yne (190 μL) affording solution A. A Schlenk tube was charged with $(t\text{BuO})_3\text{W}\equiv\text{CtBu}$ (13 mg, $2.75 \cdot 10^{-5}$ mol) and 2.87 mL of solution A. A second Schlenk tube was charged with **4** (15 mg, $0.82 \cdot 10^{-5}$ mol) and 857 μL of solution A. Both reactions have $[\text{hept-1-yne}]/[\text{W}]=25$, and $[\text{hept-1-yne}]=0,2896 \text{ mol}\cdot\text{L}^{-1}$. Reactions are stopped after 15 hours and analyzed by GC. Results are summarized in the following table.

Catalyst	Conversion (%)	Metathesis (%)	Polymerization (%)
$(t\text{BuO})_3\text{W}\equiv\text{CtBu}$	100	20	80
4	80	4	76

• Non-4-yne metathesis with 4 and $(t\text{BuO})_3\text{W}\equiv\text{CtBu}$

a) A Schlenk tube was charged with **4** (17.3 mg, $W = 7.99 \cdot 10^{-6}$ mol), toluene (2 mL), and a magnetic stir bar. Non-4-yne (35 μL , $2.1 \cdot 10^{-4}$ mol) was then added to the suspension and the reaction was stirred at room temperature. Aliquot were withdrawn from the reaction mixture and analyzed by GC to follow the conversion of non-4-yne into oct-4-yne and dec-5-yne.

b) A Schlenk tube was charged with $(t\text{BuO})_3\text{W}\equiv\text{CtBu}$ (1.9 mg, $W = 1.99 \cdot 10^{-6}$ mol), toluene (4 mL), and a magnetic stir bar. Non-4-yne ($3.98 \cdot 10^{-4}$ mol) was then added to the catalytic solution and the reaction was stirred at room temperature. The results are gathered on the following graph.



• *Attempt of formation of a grafted carbyne and reactivity toward non-4-yne and hept-1-yne*

A Schlenk tube was charged with **4** (90 mg, $W = 41.42 \cdot 10^{-6}$ mol), pentane (3 mL), and a magnetic stir bar. Non-4-yne (35 μ L, $2.1 \cdot 10^{-4}$ mol) was then added to the suspension and the reaction was stirred at room temperature for 2 hours and decanted for 1 hour. GC analysis of the supernatant confirmed the metathesis equilibrium was obtained after these 3 hours. The orange solid was washed three times with pentane and dried under vacuum. To the obtained material, pentane (3 mL) and non-4-yne (70 μ L, $4.2 \cdot 10^{-4}$ mol) were added and stirred at room temperature for 24 hours. No metathesis products were observed after this time. Volatile compounds were then removed under vacuum and hept-1-yne (1.63 mL, 0.012 mol) was added to the orange solid at room temperature. A vigorous exothermic polymerization started as soon as hept-1-yne was introduced. The deep orange insoluble polymer-coated silica was not characterized.