Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct observation of supported W bis-methylidene from supported W-methyl/methylidyne species

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General considerations. All experiments were conducted under argon atmosphere using glove box techniques. The syntheses and the treatments of the surface species were carried out using high vacuum lines ($< 10^{-5}$ mbar) and glove box techniques. Pentane and dichloromethane were distilled respectively from Na and CaH_2. Elemental analyses were performed at the London Metropolitan University in London and Mikroanalytisches Labor Pascher in Remagen. Cyclooctane was purchased from Aldrich, distilled from sodium/potassium alloy under nitrogen, degassed *via* several freeze-pump-thaw cycles, filtered over activated alumina and stored under nitrogen. Supported pre-catalyst [(≡SiO)W(Me)$_5$] **1** and W-methylidyne/methylidene **2** were prepared according to literature.[1]

GC measurements were performed with an Agilent 7890A Series (FID detection). Method for GC analyses: Column HP-5; 30m length x 0.32mm ID x 0.25 µm film thickness; Flow rate: 1 mL/min (N_2); split ratio: 50/1; Inlet temperature: 250 °C, Detector temperature: 250 °C; Temperature program: 40°C (1 min), 40-250 °C (15 °C/min), 250 °C (1 min), 250-300 °C (10 °C/min), 300 °C (30 min); Cyclic alkanes retention time: t_R (cyclooctane): 6.51 min, t_R (cyclohexadecane, dimer): 13.56 min, t_R (cyclotetraeicosane, trimer): 19.30 min. GC-MS measurements were performed with an Agilent 7890A Series coupled with Agilent 5975C Series. GC/MS equipped with capillary column coated with none polar stationary phase HP-5MS was used for molecular weight determination and identification that allowed the separation of hydrocarbons according to their boiling points differences. GC response factors of available cC_5-cC_{12} standards were calculated as an average of three independent runs. The plots of response factor *versus* cyclic alkanes carbon number were determined and a linear correlation was found. Then, we extrapolated the response factors of this plot for the other cyclic alkanes.[2]

General Procedure for cyclooctane metathesis catalytic runs. All the reactions were carried out following the same way: an ampoule is filled with the catalyst (50 mg, 6.5 µmol, W loading: 2.4 %wt, 0.2% equivalent) in a glove box and the cyclic alkane (0.5 mL, 3.7 mmol) is then added. The ampoule is sealed under vacuum, immersed in an oil bath and heated at 150 °C. At the end of the reaction, the ampoule is allowed to cool to -78 °C. Then, the mixture is diluted by addition of external standard *n*-pentane and after filtration the resulting solution is analysed by GC and GC/MS.

Preparation of species 3 and 4 on SiO_{2-700}. Enriched ^{13}C supported species **2** (50 mg, 3.49% wt) was added in a batch reactor. A vapor pressure of PMe_3 was added trap to trap to the reactor. The wet powder was allowed to react at room temperature for 5 minutes. Next, the excess of PMe_3 was removed under dynamic high vaccum ($< 10^{-5}$ mbar) for 30 min. Elemental analysis: W: 1.56 %wt, C: 1.08 %wt, P: 0.51%. P/W ratio: 2.

The same procedure was repeating using cyclohexene instead of PMe_3.

Solid-State Nuclear Magnetic Resonance Spectroscopy

One dimensional ^{1}H MAS, ^{13}C CP/MAS and ^{31}P CP/MAS solid state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 MHz resonance frequencies for ^{1}H with a conventional double resonance 4 mm CP/MAS probe at a spinning frequency of 10 kHz. The samples were packed into rotors under inert atmosphere inside glove boxes. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references tetramethylsilane (TMS) and adamantane for ^{1}H and ^{13}C and from Na_2HPO_4, $2H_2O$ for ^{31}P spectra. For ^{13}C and ^{31}P CP/MAS NMR experiments, the following sequence was used: 90^0 pulse on the proton (pulse length 2.4 s), followed by a cross-polarization using a linear ramp of radio frequency (RF) field amplitude on the ^{1}H channel with a contact time of 2 ms then for ^{1}H RF field strength ^{31}P channel, the RF field strength was chosen for optimum transfer efficiency. Finally, acquisition of the ^{13}C and ^{31}P NMR signal was performed under SPINAL-64 proton decoupling[3] at a RF field of 100 kHz. The delay between the scans was set to 4 s to allow the complete relaxation of the ^{1}H nuclei and the number of scans ranged: between 3000-10000 for ^{13}C, 500-5000 for ^{31}P and 32 for ^{1}H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

The 2D ^{1}H-^{13}C and ^{1}H-^{31}P heteronuclear correlation (HETCOR) solid state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer operating at 400 MHz using a 4 mm MAS probe. The experiments were performed according to the following scheme: 90^0 proton pulse, t_1 evolution period, CP to ^{13}C and ^{31}P and detection of the magnetization under TPPM decoupling. For the cross-polarization step, a ramped RF field[4] centered at 75 kHz was applied to the protons, while the ^{13}C and ^{31}P channel RF field were matched to obtain optimal signal. A total of 32 t_1 increments with 4000 scans per increments were collected for ^{13}C. For ^{31}P, a total of 32 t_1 increments with 400 scans per increment were collected. The sample spinning frequency was 8.5 kHz for ^{13}C and 10 kHz for ^{31}P. Using a short contact time (0.2 ms) for the CP step for ^{13}C and for ^{31}P (1 ms), the polarization transfer in the dipolar correlation experiment was selective for the first coordination sphere on the tungsten, that is to lead to correlations only between pairs of attached ^{1}H-^{13}C spins and ^{1}H-^{31}P.

1D refocused zfr-INADEQUATE (^{31}P-^{1}H)[5] spectrum were obtained using a 4 mm MAS double resonance probe at a spinning frequency of 12.5 kHz (the length of the echo period τ-π-τ was experimentally optimized). The 90^0 pulse was 2.5 μs. Ramped cross-polarization with a contact time of 5 ms was used to transfer the magnetization from protons to phosphorous. SPINAL-64 proton decoupling was applied during evolution and acquisition periods at a RF field of 100 kHz. 90^0 and 180^0 pulse length of 2.5 and 5 μs were respectively used. Unless stated, the τ delay was set to 3 ms. The time of double quantum coherence evolution was 3 μs and the recycle delay was 2 s.

2D ^{31}P-^{31}P spin-diffusion with DARR (dipolar-assisted rotational resonance)[6, 7] spectrum was obtained using a 4 mm MAS double resonance probe at a spinning frequency of 10 kHz with a mixing time τ_{mix}= 40 ms. The 90^0 pulse was 3.5 μs. Sequence begins with VACP using a ramped pulse on ^{31}P channel. After the evolution period, magnetization is placed along the z-axis with a 90^0. Pulse and mixing occurs longitudinally with a low power ^{1}H recoupling pulse in DARR. During the DARR mixing period, the ^{1}H RF field strength is set to the n = 1 rotational resonance condition. Two-pulse phase modulated decoupling is used during acquisition and evolution. 400 scans per t_1 increment, a 4 s repetition delay, 128 individual increments and 4 ms contact time was used.

2D ^{13}C-^{13}C double-quantum (DQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 400 MHz with a conventional double resonance 4 mm CP/MAS probe.[8] We use back-to-back (BABA) recoupling sequences with cross polarization for weak dipole-dipole couplings, to compensate pulse imperfection.[9] SPINAL-64 proton decoupling was applied during evolution and acquisition periods at a RF field of 100 kHz. During the MQ excitation and reconversion periods the rotor-synchronized pulse sequences are applied. The excitation part is phase-cycled in 900 steps to provide a double-quantum filter, whereas the reconversion period is 900 phase, shifted from the excitation sequence but with no phase cycling. The delay after the reconversion part is included for the dephasing of spurious transverse magnetization. Typical variants of the broadband BABA pulse sequence, acting on multiple rotor periods ($2\tau_R$) were employed. Quadrature detection in w_1 was achieved using the States-TPPI method. A MAS frequency of 10 kHz was used. The 90° proton pulse length was 2.5 μs with a recycle delay of 5 s. A total of 256 t_1 increments with 1000 scans per increment with a contact time of 3 ms were recorded. The DQ frequency in the w_1 dimension corresponds to the sum of two single quantum (SQ) frequencies of the two coupled Carbon and correlates in the w_2 dimension with the two corresponding Carbons resonances. Conversely, groups of less than two equivalent spins will not give rise to diagonal signals in this spectrum.

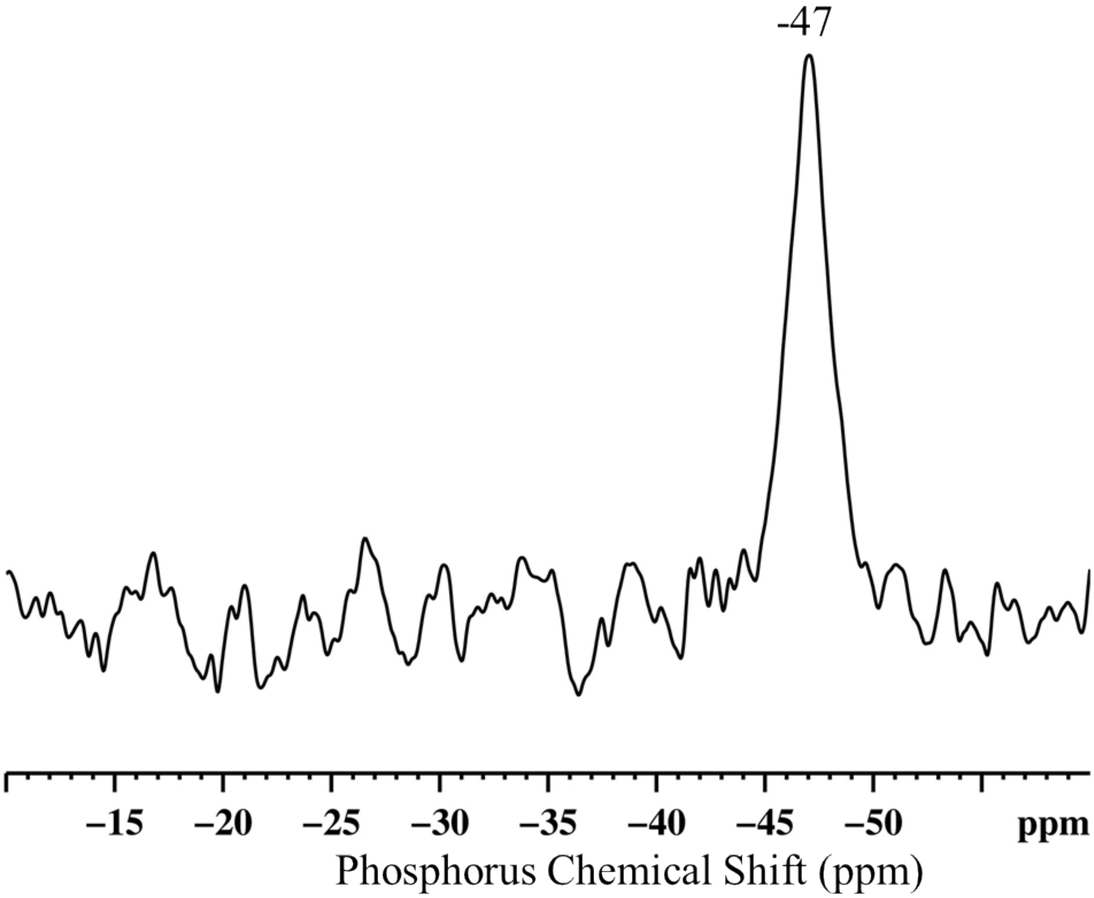

Figure S1: ^{31}P CP/MAS spectrum of PMe_3 physisorbed on silica (acquired at 9.4 T (v0 (1H) = 400 MHz) with a 10 kHz MAS frequency, 5000 scans, 4 s repetition delay and a 2 ms contact time. Exponential line broadening of 80 Hz was applied prior to Fourier transformation.

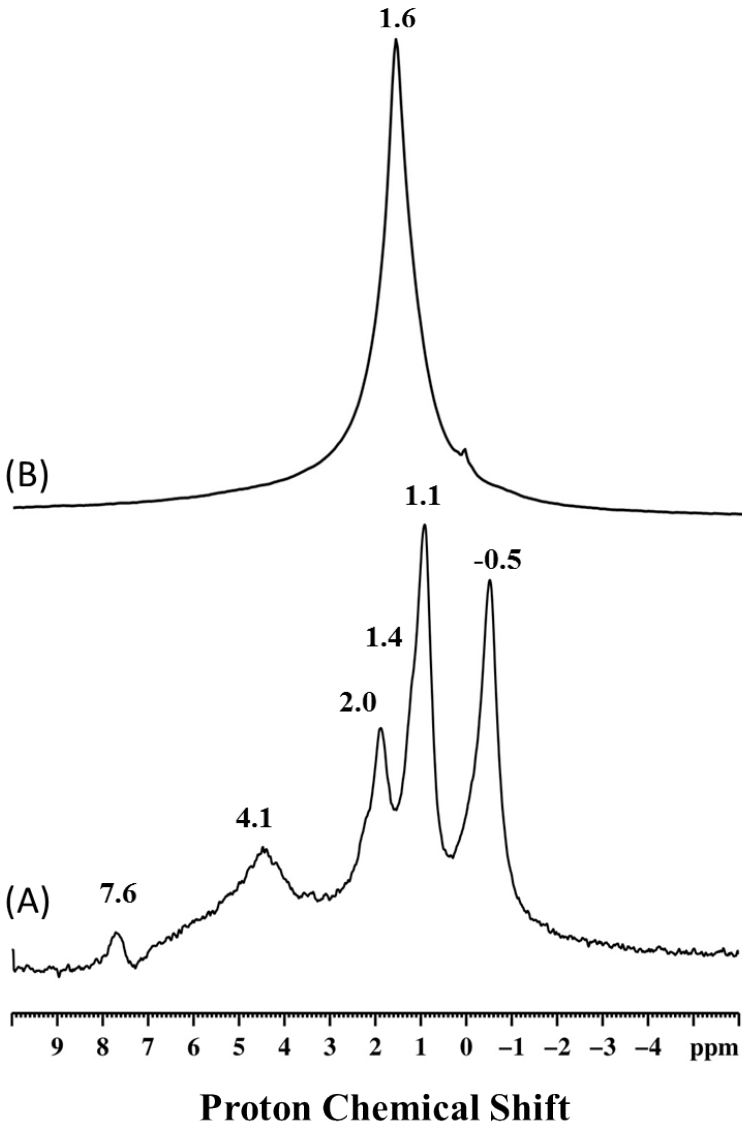

Figure S2: (A) ^{1}H spin-echo MAS solid-state NMR spectrum of (A) W-methylidyne **2**, (B) W-methylidyne and W bis-methylidene PMe_3 adducts (both acquired at 9.4 T (v0 (1H) = 400 MHz) with a 15 kHz MAS frequency, 8 scans and 5 s repetition delay.

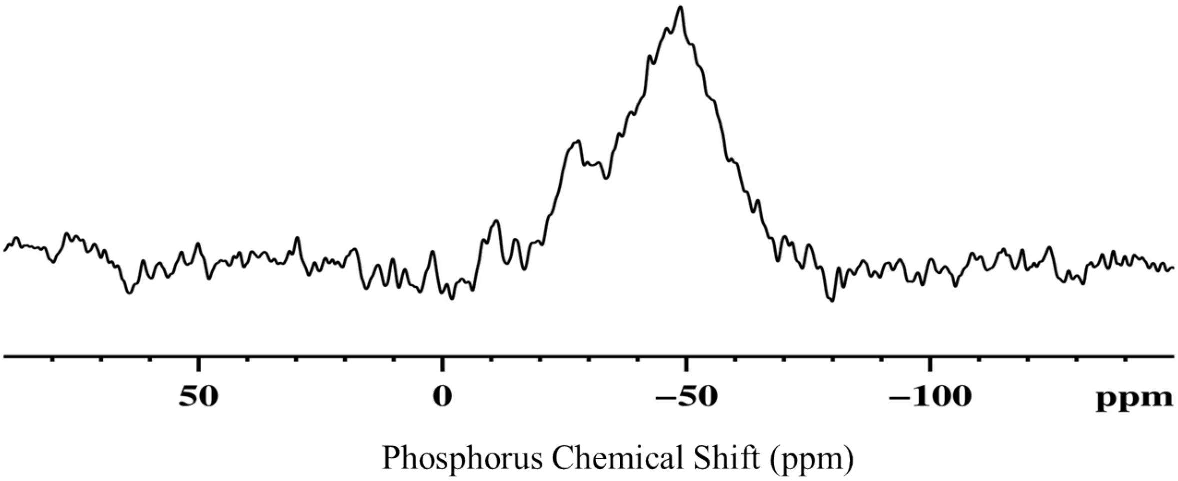

Figure S3: One-dimensional ^{31}P refocused INADEQUATE spectrum of species **3** and **4**, (acquired at 9.4 T (v0 (1H) = 400 MHz) with a 12.5 kHz MAS frequency. A total 10240 scans were accumulated with a recycle delay of 2s. The delay τ was set to 3 ms for the two echo periods and z-filter delay of 3 ms was used before acquisition.

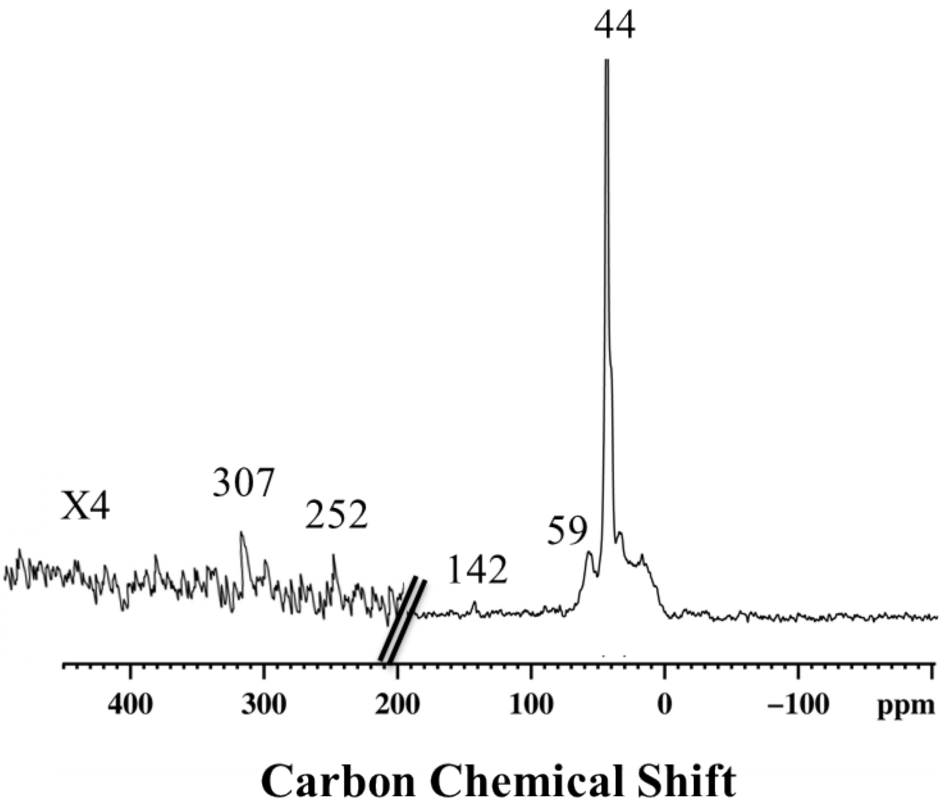

Figure S4: ^{13}C CP/MAS spectrum of gratifyingly, contacting cyclohexene to the supported W-methylidyne (acquired at 9.4 T (v0 (1H) = 400 MHz) with a 10 kHz MAS frequency, 20000 scans. A 4 s repetition delay and a 2 ms contact time. Exponential line broadening of 80 Hz was applied prior to Fourier transformation.

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