

Electronic supplementary information

GRAFTING OF GROUP 6 IMIDO–ALKYL COMPLEXES ON SILICA: Mo vs. W

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General

Unless otherwise stated all manipulations were carried out under argon atmosphere using standard Schlenk techniques or MBraun UniLab glovebox. All glassware was dried in an oven at 130 °C for at least 2 h prior to use. Solvents were distilled from Na/Ph₂CO (THF, Et₂O, C₆H₆, C₆D₆, toluene, heptane) or CaH₂ (CH₂Cl₂, CDCl₃), degassed by 3 freeze-pump-thaw cycles and stored over activated 3 Å MS. Complexes Mo(=NMes)₂(CH₂CMe₂Ph)₂ (**1**)¹ and W(=NMes)₂Cl₂(dme)² were prepared as previously reported.

Silica (Degussa Aerosil, 200 m² g⁻¹) was compacted with distilled water, calcined at 500 °C under air overnight, and then treated at 700 °C under high vacuum (*ca.* 10⁻⁵ mbar) for no less than 10 h (support referred to as SiO₂₋₇₀₀). The reported value of 0.26 mmol ≡SiOH per g was used in calculations.³

NMR spectra were recorded using Bruker Avance 300 and 400 spectrometers. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. ¹H chemical shifts were referenced relative to the residual solvent peak: 7.16 (C₆D₆). ¹³C chemical shifts were referenced relative to the solvent peak: 128.06 (C₆D₆). Quantitative ¹H NMR measurements were performed using ferrocene as internal standard (recycle delay in these experiments was set to 60 sec).

Solid-state NMR spectra were recorded on Bruker Avance III 400 WB spectrometer equipped with a 4 mm DVT MAS BB/HF probe (15 kHz). The samples were loaded in 4 mm zirconia rotors inside a glovebox and tightly closed. ¹H MAS spectra were recorded using single-pulse sequence with 30–45° pulse at 14 kHz MAS with a recycle delay of 5 sec. ¹³C cross-polarization magic angle spinning (CP MAS) spectra were recorded with a recycle delay of 2 sec and CP contact time of 4 msec at 12 kHz MAS. ¹³C spectra were recorded under high-power proton decoupling conditions using SPINAL64 sequence. Chemical shifts were externally referenced relative to the CH₂ resonance of solid adamantane (38.5 ppm).

The samples for IR measurements were pressed into pellets inside a glovebox. The spectra of SiO₂₋₇₀₀ and the material **1s** were recorded using a Bruker spectrometer operated inside glovebox (measurements performed at ETH Zürich). The spectrum of **2s** was recorded using Shimadzu IRPrestige-21 instrument operated under ambient conditions using a home-made air-tight cell that was packed inside glovebox.

Elemental analyses were performed in Microanalysis laboratory of INEOS RAS. Metal content was determined by X-Ray fluorescence analysis using Spectroscan MAKC-GVM WDXRF spectrometer (Spectron Ltd.) with external standard method and 100- to 200-fold dilution of microsamples (5–10 mg) with emulsion polystyrene.⁴

Catalytic tests were performed as described previously.^{5, 6} GC/FID was performed using Chromatec Crystal 5000.2 gas chromatograph equipped with a Restek RTX-35 column.

Preparation of the materials

W(=NMe)₂(CH₂CMe₂Ph)₂ (2). To a stirred solution of W(=NMe)₂Cl₂(dme) (208 mg, 0.34 mmol) in toluene (2 mL) was added solid Mg(CH₂CMe₂Ph)₂ (99 mg, 0.34 mmol) at -35 °C. The reaction was warmed to room temperature and stirred overnight, then the solvent was evaporated under vacuum, and the residue was extracted with toluene and filtered to give an orange solution. The solvent was evaporated and the resulting yellow-orange solid was triturated in heptane and washed several times with heptane, until the washings became yellow, and dried to give yellow powder. Yield: 177 mg (73%).

¹H NMR (400 MHz, C₆D₆): δ 7.40 (d, ³J = 7.5, 4H, *o*-CH), 7.19 (t, ³J = 7.5, 4H, *m*-CH), 7.08 (t, ³J = 7.3, 2H, *p*-CH), 6.76 (s, 4H, CH_{Mes}), 2.20 (s, 12H, *o*-Me_{Mes}), 2.15 (s, 6H, *p*-Me_{Mes}), 1.63 (s, 4H, CH₂CMe₂Ph), 1.44 (s, 12H, CH₂CMe₂Ph).

¹³C NMR (100 MHz, C₆D₆): δ 153.25 (quat), 151.08 (quat), 133.59 (quat, *p*-C_{Mes}), 132.58 (quat, *o*-C_{Mes}), 128.71 (CH), 128.53 (CH), 126.70 (CH), 126.33 (*p*-CH_{Ph}), 87.16 (CH₂), 39.91 (quat CH₂CMe₂Ph), 33.03 (CH₂CMe₂Ph), 21.02 (*p*-Me_{Mes}), 18.81 (*o*-Me_{Mes}).

Elem. Anal. Found (Calcd, C₃₈H₄₈N₂W), %: C, 63.74 (63.69); H, 6.60 (6.75); N, 4.08 (3.91).

Grafting of Mo(=NMe)₂(CH₂CMe₂Ph)₂ (1s). A solution of Mo(=NMe)₂(CH₂CMe₂Ph)₂ (1) (96 mg, 153 μmol) in benzene was added to a suspension of SiO₂₋₇₀₀ (590 mg) in benzene at RT. The suspension was slowly stirred overnight. The solid was separated by decantation and washed several times with benzene. The resulting solid was dried in high vacuum (*ca.* 10⁻⁵ mbar) for 2 h to afford **1s** as orange powder. Washings were collected and analyzed with ¹H NMR using ferrocene as internal standard indicating the release of 106 μmol PhCMe₃ (0.69 equiv/Mo) together with 17 μmol (11%) of unreacted complex. Volatiles after drying were also collected and analyzed with GC to confirm no additional PhCMe₃. Elemental analysis (wt%): Mo 1.4% (0.15 mmol Mo g⁻¹), C 5.23%, N 0.53%; Mo/N/C: 1/2.6/29.8 (expected: 1/2/28).

Grafting of W(=NMe)₂(CH₂CMe₂Ph)₂ (2s). A solution of W(=NMe)₂(CH₂CMe₂Ph)₂ (2) (27 mg, 37.7 μmol) in benzene was added to a suspension of SiO₂₋₇₀₀ (150 mg) in benzene at RT. The suspension was slowly stirred overnight. The solid was separated by decantation and washed several times with benzene. The resulting solid was dried in high vacuum (*ca.* 10⁻⁵ mbar) for 1 h to afford **2s** as yellow-orange powder. Washings were collected and analyzed with ¹H NMR using ferrocene as internal standard indicating the release of ~4.7 μmol PhCMe₃ (0.12 equiv/W) together with ~8.4 μmol (22%) of unreacted complex. Volatiles after drying were also collected and analyzed with GC to give additional ~0.01 equiv/W PhCMe₃. Elemental analysis (wt%): (#1) W 3.0% (0.16 mmol W g⁻¹), C 6.27%, N 0.44%; W/N/C: 1/1.9/32.0; (#2) C 7.35%, N 0.43%; N/C: 2/39.9 (expected: intermediate between 1/2/28 and 1/2/38).

NMR spectroscopy

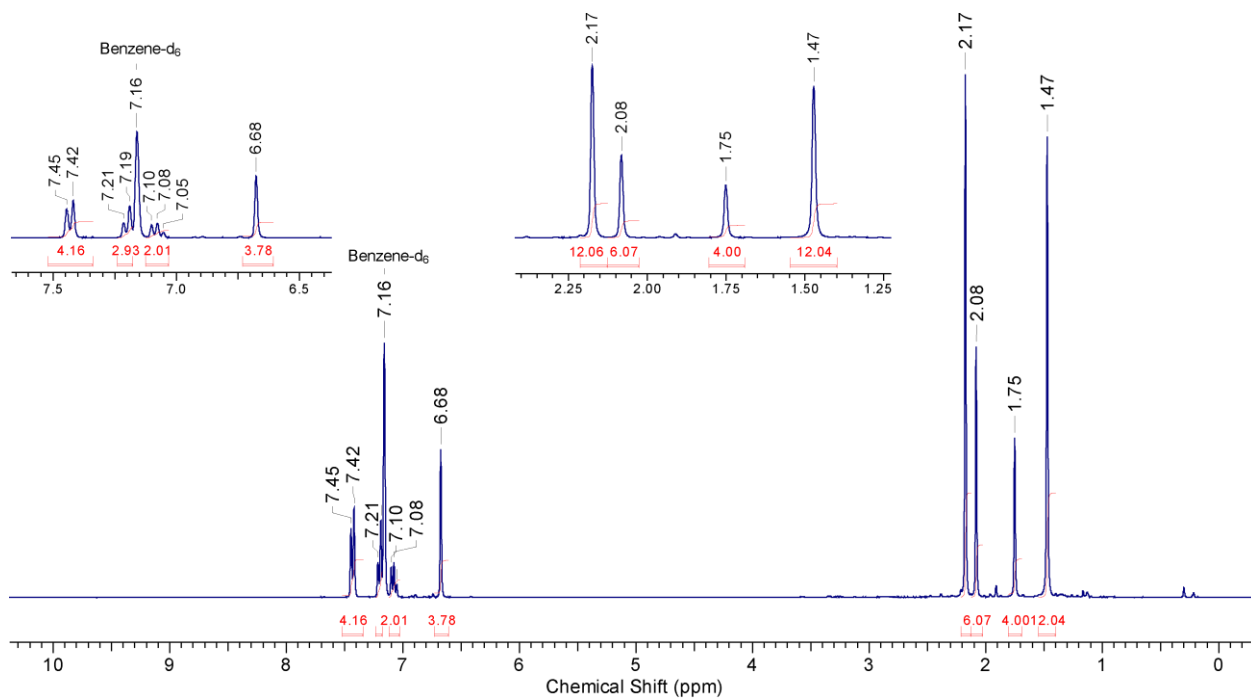


Fig. S1. ^1H NMR spectrum of $\text{Mo}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (**1**).

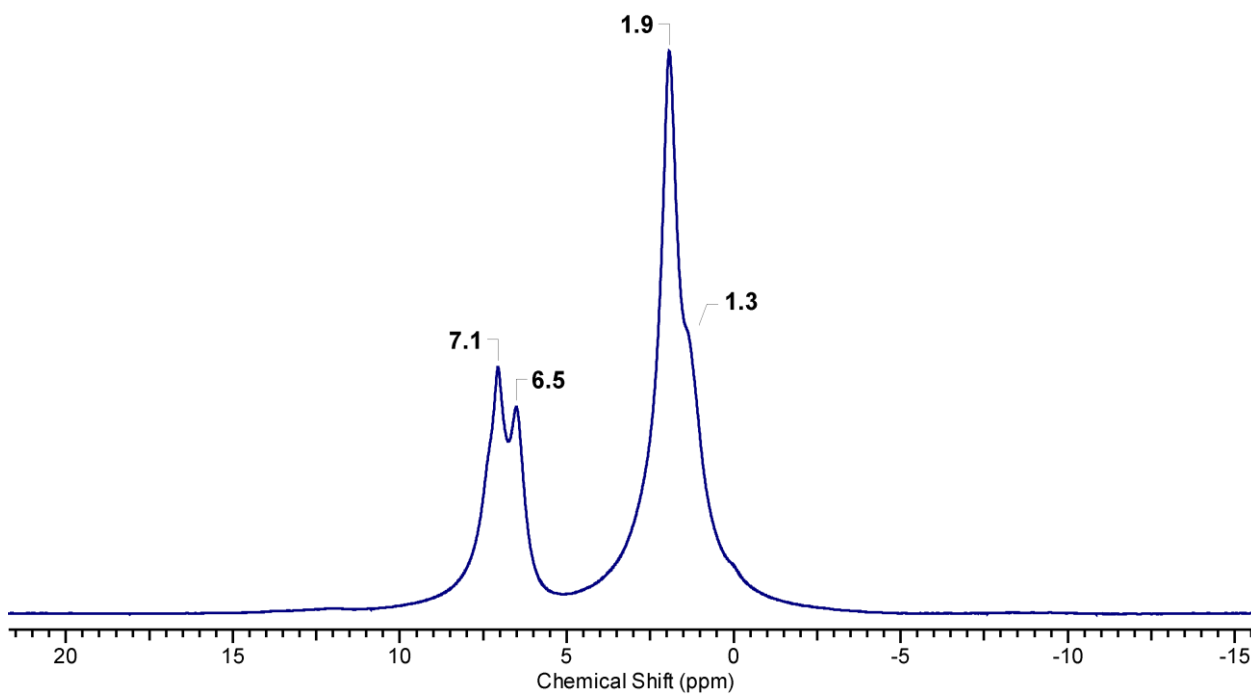


Fig. S2. ^1H MAS SSNMR spectrum of $\text{Mo}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2/\text{SiO}_2\text{-700}$ (**1s**) (400 MHz; 4 mm; 14 kHz MAS; d1 5 s; ns 32; 20 $^\circ\text{C}$).

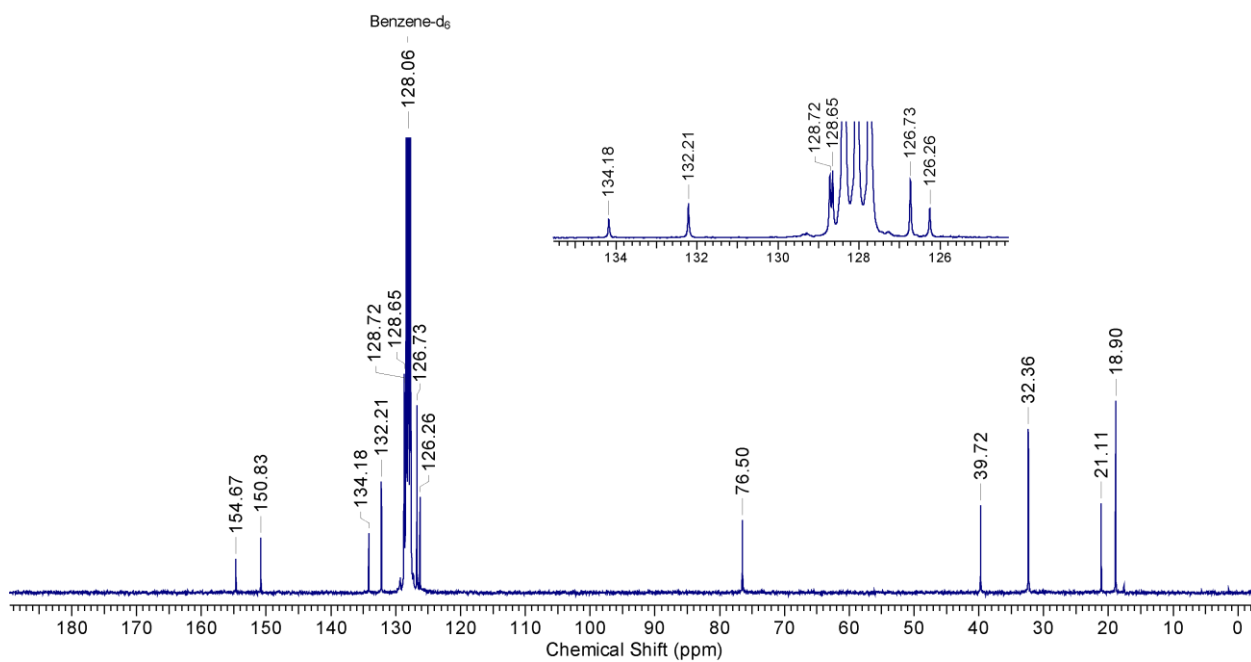


Fig. S3. ^{13}C NMR spectrum of $\text{Mo}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (**1**).

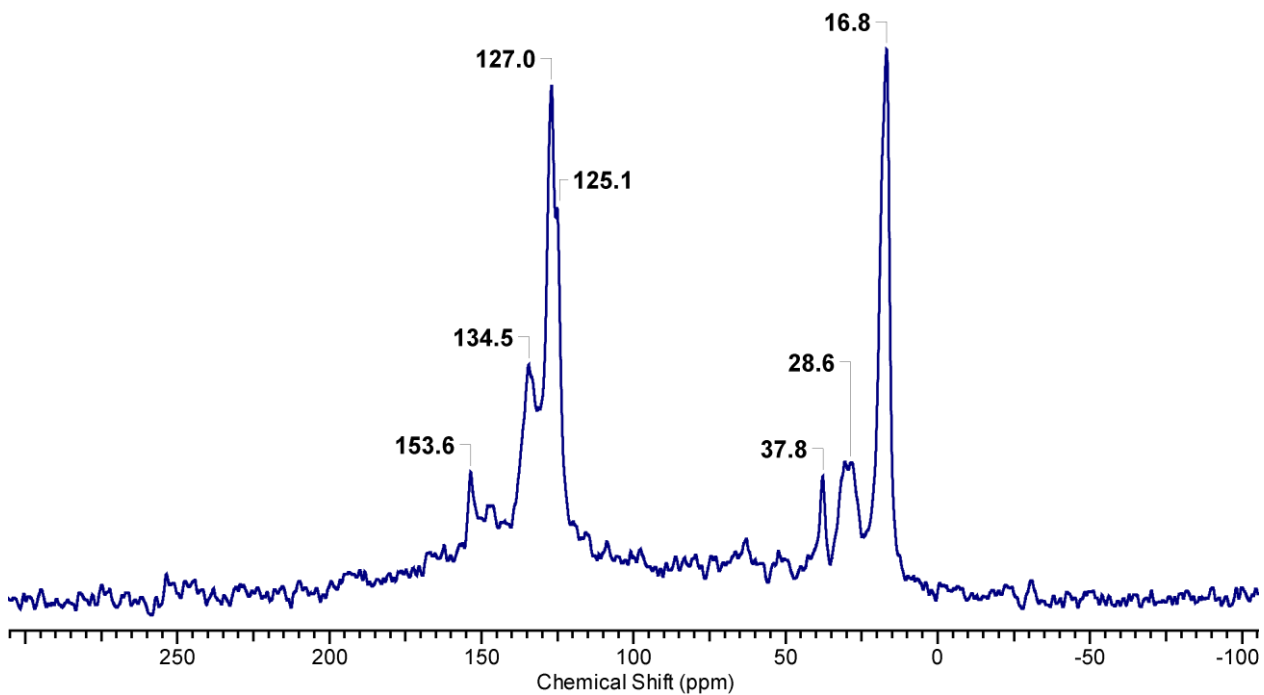


Fig. S4. ^{13}C CP/MAS SSNMR spectrum of $\text{Mo}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2/\text{SiO}_2\text{-700}$ (**1s**) (100 MHz; 4 mm; 12 kHz MAS; CP contact time 4 ms; d1 2 s; ns 37,000; 20 °C).

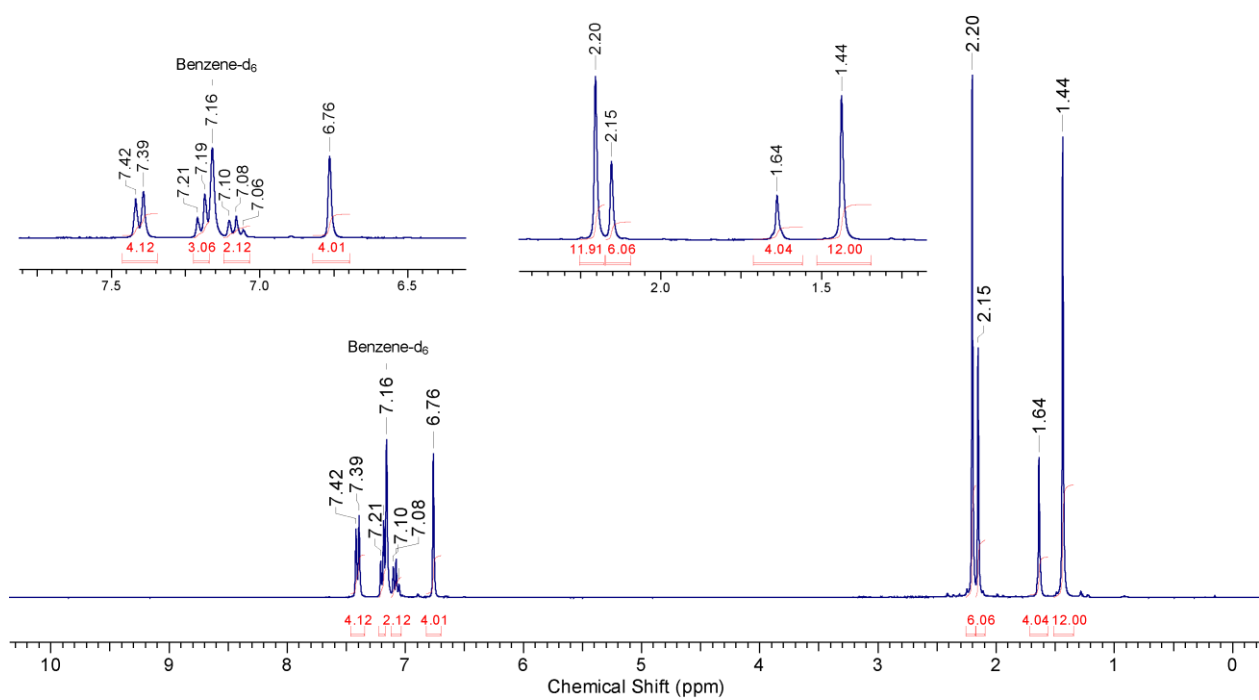


Fig. S5. ^1H NMR spectrum of $\text{W}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (**2**).

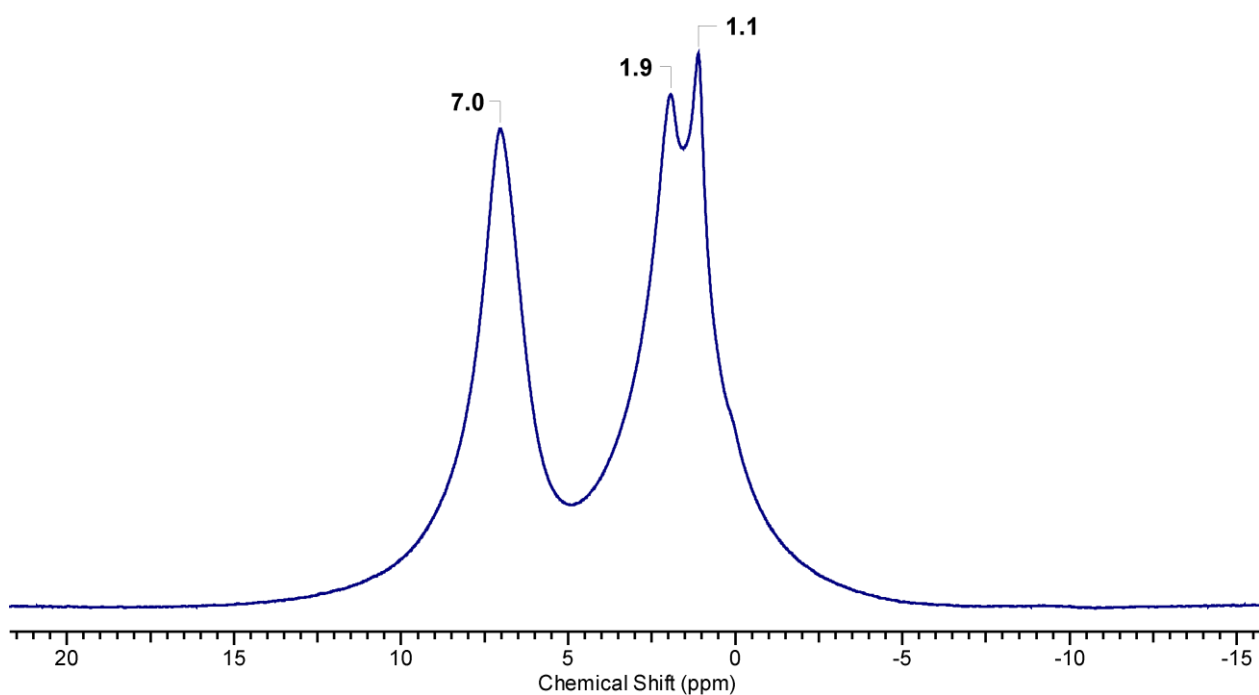


Fig. S6. ^1H MAS SSNMR spectrum of $\text{W}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2/\text{SiO}_{2-700}$ (**2s**) (400 MHz; 4 mm; 14 kHz MAS; d1 5 s; ns 32; 20 °C).

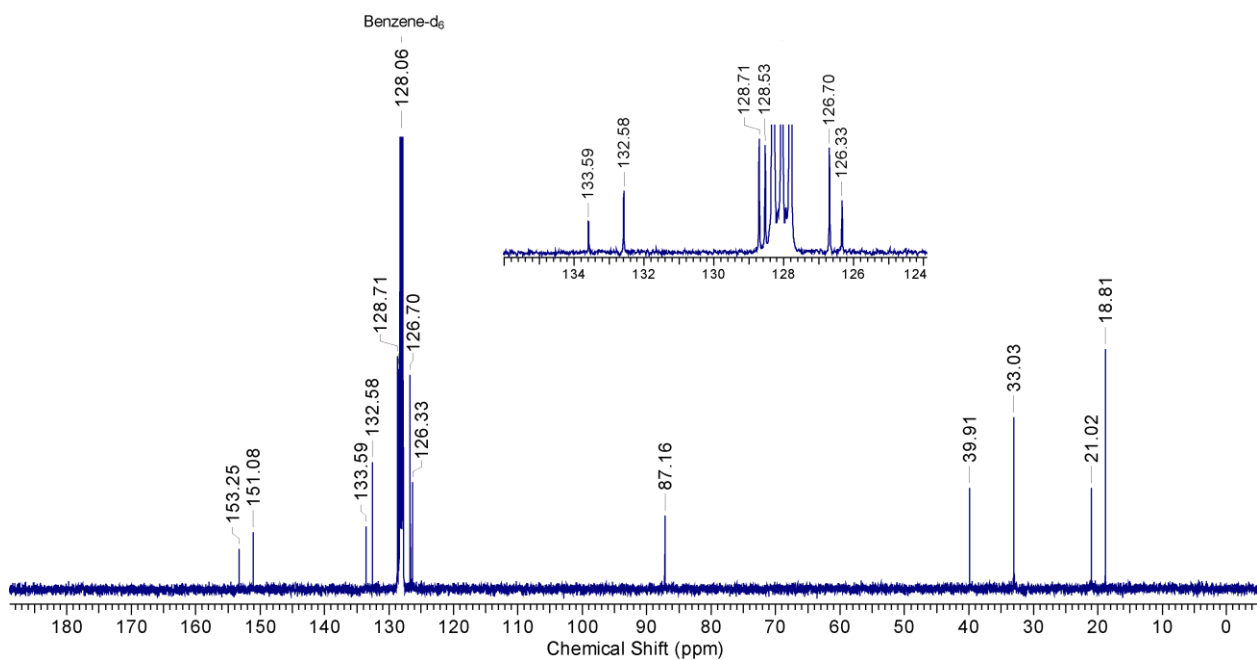


Fig. S7. ^{13}C NMR spectrum of $\text{W}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (**2**).

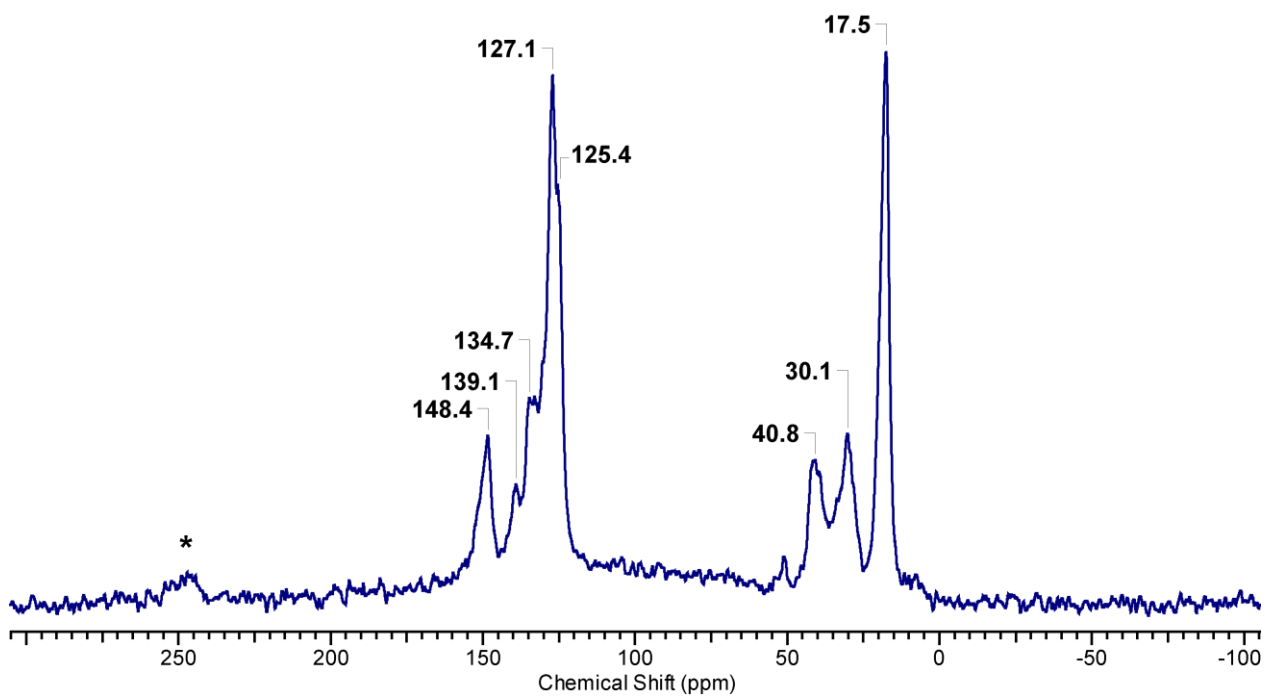


Fig. S8. ^{13}C CP/MAS SSNMR spectrum of $\text{W}(=\text{NMe})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2/\text{SiO}_2\text{-700}$ (**2s**) (100 MHz; 4 mm; 12 kHz MAS; CP contact time 4 ms; d1 2 s; ns 25,000; 20 °C). Asterisk indicate spinning side-band.

Catalysis

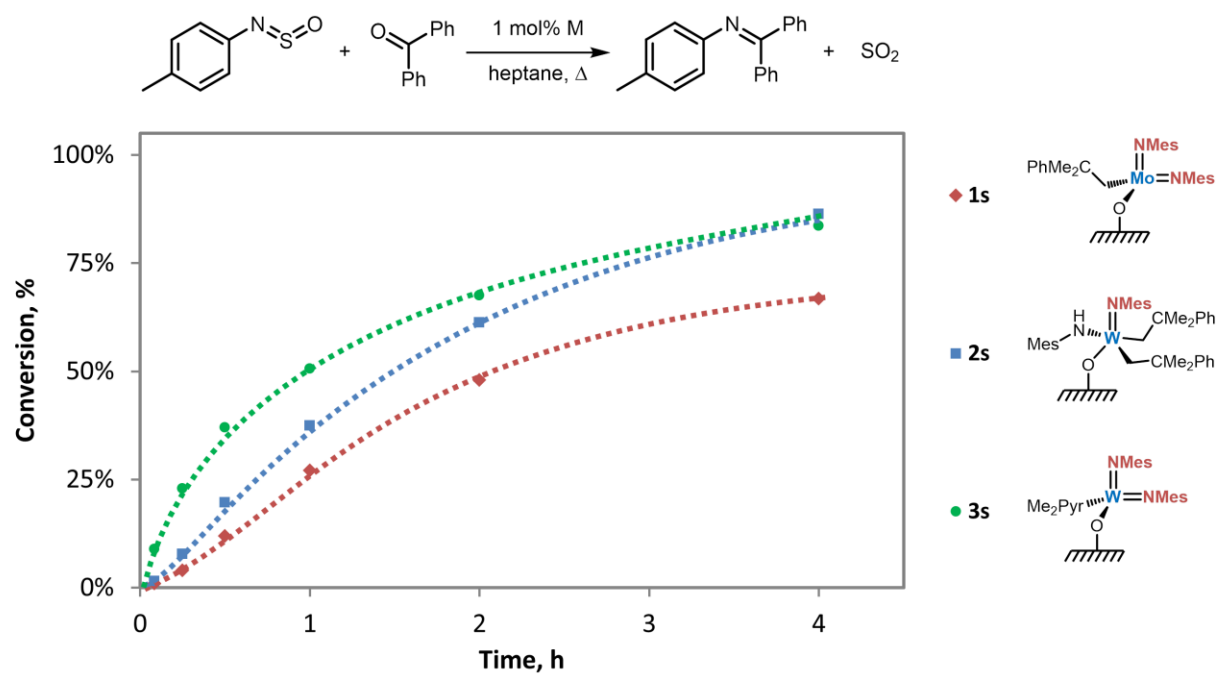


Fig. S9. Comparison of the catalytic performance of the materials **1s–3s** in oxo/imido heterometathesis.

References

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