Supplementary Information

Synthesis and Reactivity of Molybdenium Imido Alkylidene bis-Pyrazolide Complexes.

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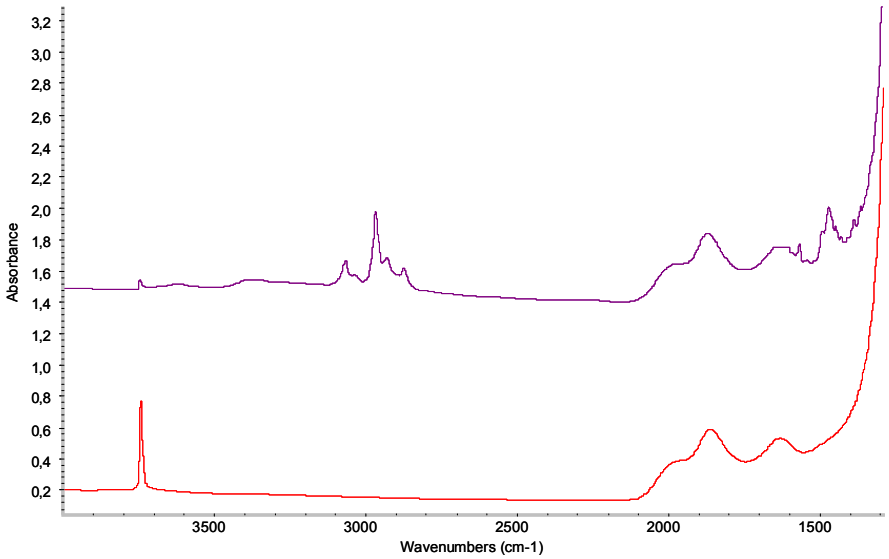
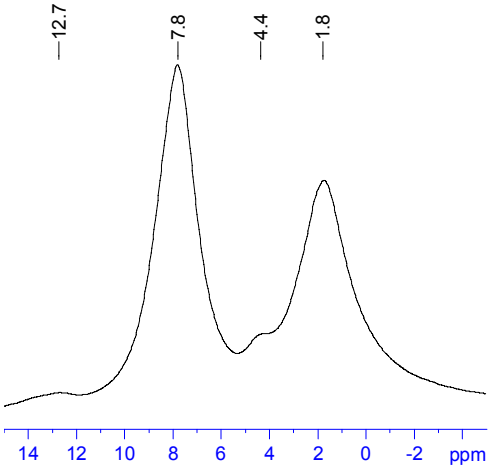


Figure S1. Grafting of [Mo(≡NAr)(=CHCMe$_2$Ph)(dppz)$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) **1-dppz-Ph** on a silica partially dehydroxylated at 700 ºC, SiO$_{2-(700)}$, monitored by IR spectroscopy. SiO$_{2-(700)}$ pellet (30 mg) (bottom spectrum) After impregnation of [Mo(≡NAr)(=CHCMe$_2$Ph)(dppz)$_2$] (7 mg) in benzene (10 mL) (3 h, 25 ºC), followed by three washings (30 min, 25 ºC) in benzene and a drying step under vacuum (1.34 Pa, 1 h, 25 ºC) (top spectrum).

a)



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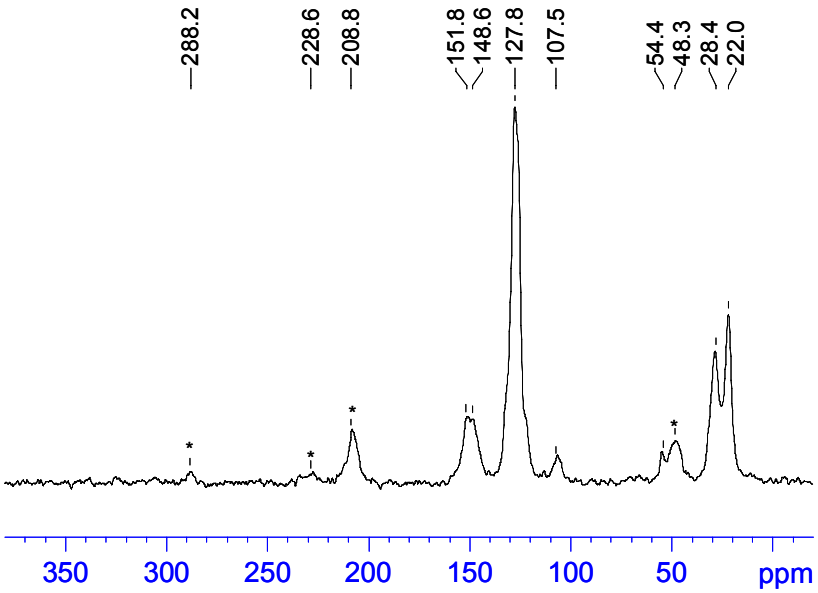
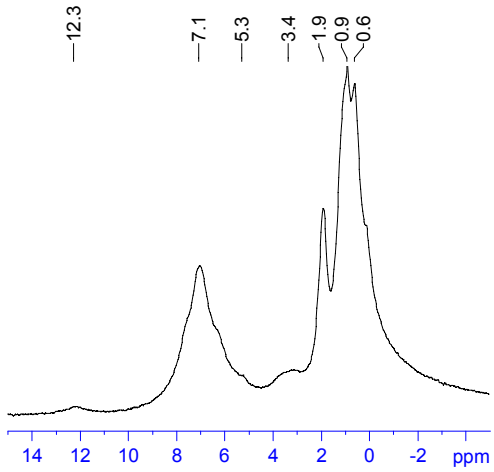


Figure S2. a) One-dimensional solid state proton single pulse spectrum of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(dppz)] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (**1-dppz-Ph**/SiO$_2$) recorded under MAS frequency of 10 kHz. 8 scans were coadded at a recycle rate of 64 s. b) ^{13}C CP solid state NMR spectrum of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(dppz)] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (**1-dppz-Ph**/SiO$_2$) recorded under MAS frequency of 10 kHz. 38193 scans were coaded at a recycle rate of 2 s.

a)



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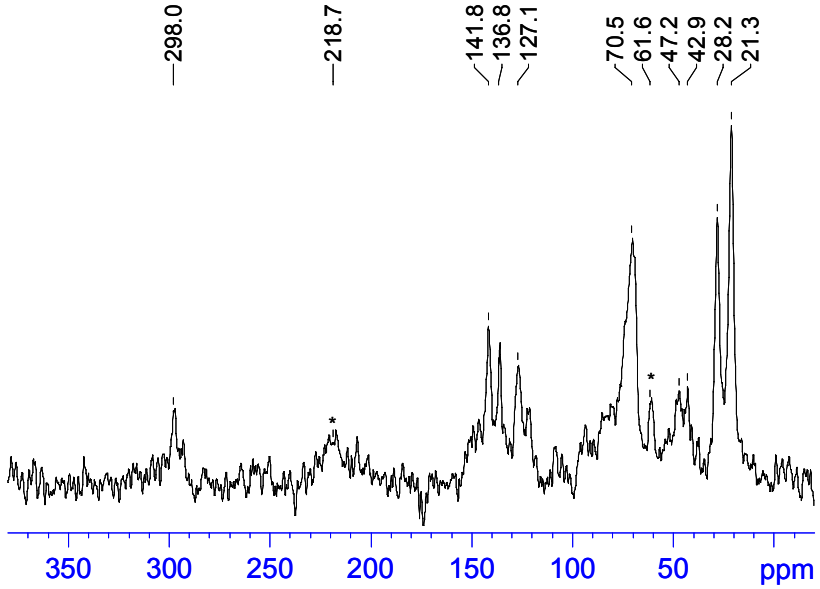


Figure S3. a) One-dimensional solid state proton single pulse spectrum of [(≡SiO)Mo(≡NAr)(=CHCMe$_3$)(dtpz)] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (**1*-dppz-Me**/SiO$_2$) recorded under MAS frequency of 10 kHz. 8 scans were coadded at a recycle rate of 4 s. b) ^{13}C CP solid state NMR spectrum of [(≡SiO)Mo(≡NAr)(=CHCMe$_3$)(dtpz)] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (**1*-dppz-Me**/SiO$_2$) recorded under MAS frequency of 10 kHz. 30720 scans were coaded at a recycle rate of 2 s.

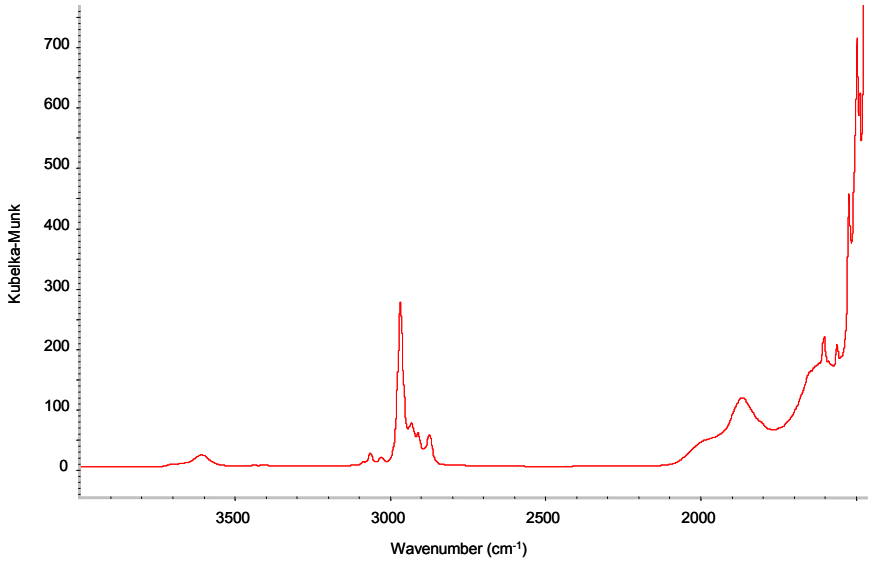
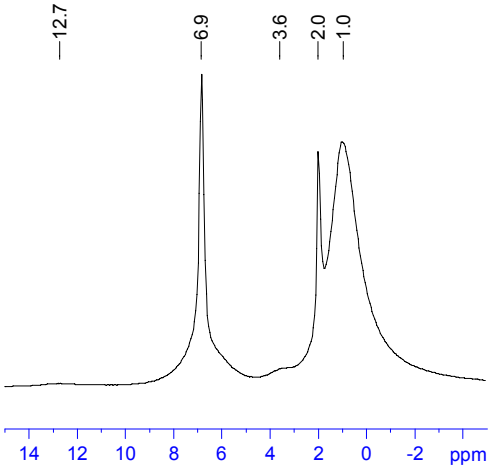


Figure S4. DRIFT spectroscopy of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(dtpz)$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (**1-dtpz-Ph**/SiO$_2$).

a)



b)

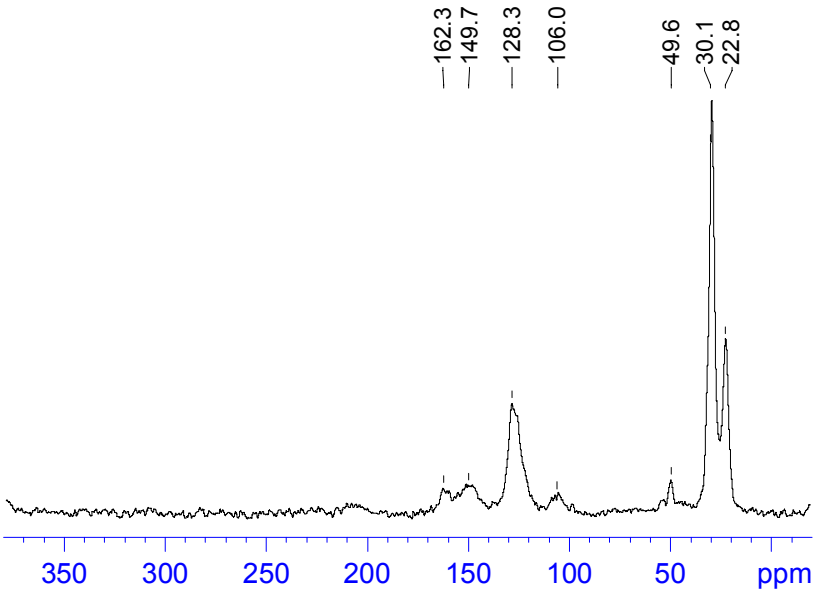


Figure S5. a) One-dimensional solid state proton single pulse spectrum of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(dtpz)] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (**1-dtpz-Ph**/SiO$_2$) recorded under MAS frequency of 10 kHz. 8 scans were coadded at a recycle rate of 4 s. b) ^{13}C CP solid state NMR spectrum of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(dtpz)] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (**1-dtpz-Ph**/SiO$_2$) recorded under MAS frequency of 10 kHz. 30720 scans were coaded at a recycle rate of 2 s.

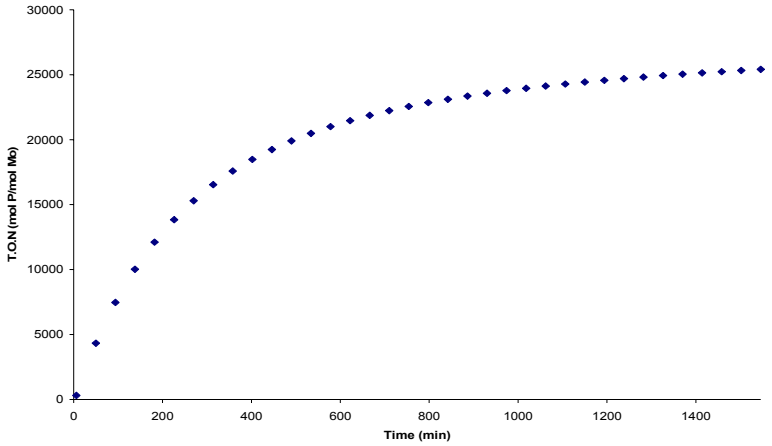


Figure S6. Activity in propene metathesis catalysed by **1-dppz-Ph/SiO_2** cumulative TON as a function of time. 17.4 μmol Mo was used, propene was flowed at 16 mol × mol(Mo)$^{-1}$ × s^{-1} at a temperature of 30 °C. A initial $TOF_{(6min)}$ 1.73 s^{-1} and a cumulative $TON_{(1550min)}$ of 25400 were obtained. $TOF_{(1550\ min)}$ 0.03 s^{-1}.

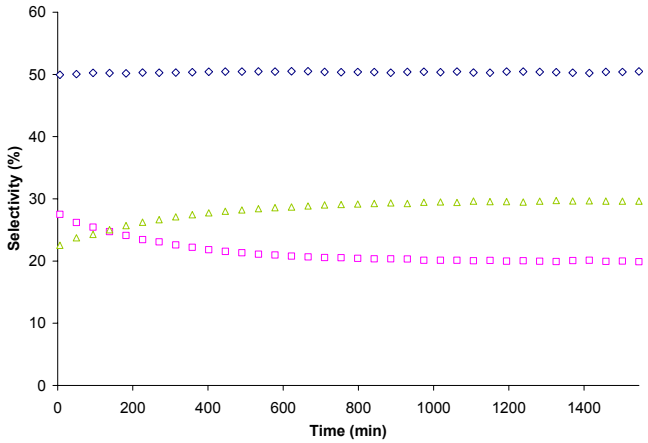


Figure S7. Selectivity in propene metathesis catalysed by **1-dppz-h/SiO_2**. Product selectivity as a function of time. Ethylene (◊), E-2-butene (□), Z-2-butene (Δ). Selectivity in ethene and 2-butenes > 99.9%.

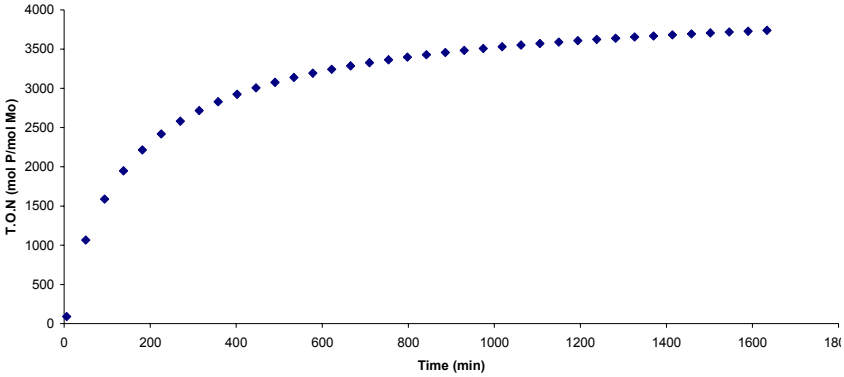


Figure S8. Activity in propene metathesis catalysed by **1-dtpz-Ph/SiO_2** cumulative TON as a function of time. 17.5 μmol Mo was used, propene was flowed at 16 mol × mol(Mo)$^{-1}$ × s^{-1} at a temperature of 30 °C. A initial $TOF_{(6min)}$ 1.72 s^{-1} and a cumulative $TON_{(1550min)}$ of 25300 were obtained. $TOF_{(1550\ min)}$ 0.03 s^{-1}.

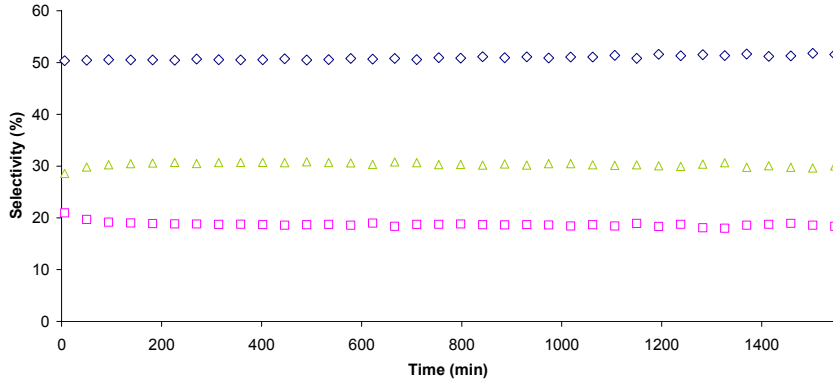


Figure S9. Selectivity in propene metathesis catalysed by **1-dtpz-Ph**/SiO_2**.** Product selectivity as a function of time. Ethylene (◊), E-2-butene (□), Z-2-butene (Δ). Selectivity in ethene and 2-butenes > 99.9%.