Reactivity of a *trans*-[H-Mo≣Mo-H] Unit Towards Alkenes and Alkynes. Bimetallic Migratory Insertion, H-Elimination and Other Reactions

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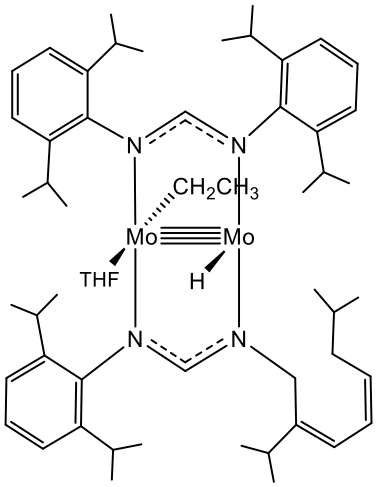
SUPPORTING INFORMATION

Experimental details for compounds A, 2, 3, B and 4

General considerations**:** All manipulations were carried out using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried and degassed prior to use. Toluene (C_7H_8) and n-pentane (C_5H_{12}) were distilled under nitrogen over sodium. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen over sodium/benzophenone. Benzene-d6, thf-d8 and toluene-d8 were distilled under argon over sodium and stored over 4 Å molecular sieves. Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external $SiMe_4$ (δ: 0 ppm) using the residual proton solvent peaks as internal standards (^{1}H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by routine one- and two-dimensional NMR experiments (^{1}H, ^{13}C, ^{13}C {^{1}H}, COSY, NOESY, HSQC and HMBC) where appropriate. For elemental analyses a LECO TruSpec CHN elementary analyzer, was utilized. Infrared spectra were recorded on a Bruker Vector 22 spectrometer and sampling preparation was made in Nujol. Gas chromatography coupled to a mass spectrometer was performed in a Shimadzu GCMS-QP2010plus.

Compound **1·THF** was synthesized as described previously (M. Carrasco, N. Curado, C. Maya, R. Peloso, A. Rodríguez, E. Ruiz, S. Álvarez, E. Carmona, *Angew. Chem. Int. Ed.* 2013, **52**, 3227; M. Carrasco, N. Curado, E. Álvarez, C. Maya, R. Peloso, A. Rodríguez, E. Ruiz, S. Álvarez, E. Carmona, *Chem. Eur. J*., 2014, **20**, 6092)

[Mo_2(H) CH_2CH_3)(μ-Ad^{Dipp_2})$_2$(THF)] (A)

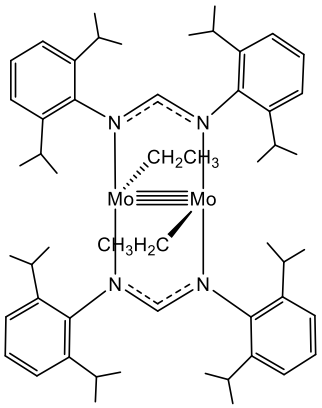


Compound **1·THF** (30 mg, 0.028 mmol) was dissolved in toluene-d_8 (C_7D_8) in a J. Young NMR tube. The solution was frozen, the headspace was evacuated and ethylene (C_2H_4, 1 bar) was introduced at room temperature. The tube was shaken for some seconds to facilitate the solution of ethylene at room temperature until the solution turned green. The solution was then cooled to -30 degrees and complex **A** was characterized by NMR at low temperature to avoid further evolution to complex **2**.

^{1}H NMR (400 MHz, tol-d_8, -30 °C) δ (ppm): 0.53, 0.57, 1.08, 1.39, 1.42 (d, 30H, 6H each, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.25-1.36 (m, 18 H, CH*Me*$_2$), 0.70 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_2-C*H*$_3$), 1.33 (m, OCH_2CH_2), 1.92 (m, 2H, C*H*$_2$-CH_3), 3.47 (m, OCH_2CH_2), 3.70, 3.78, 3.99, 4.27 (sept, 8H, 2H each, $^3J_{HH}$ = 6.6 Hz, C*H*Me_2), 5.25 (C_2H_4), 6.9-7.15 (m, 12 H, *m, p*-Dipp), 8.48 (s, 2H, NC(H)N).

^{13}C {H} NMR (100 MHz, tol-d_8, -30 °C) δ (ppm): 11.8 (br, CH_2-*C*H_3), 23.2, 23.4, 24.0, 24.3, 25.9, 26.1, 26.8, 27.3 (CH*Me*$_2$), 25.1 (br, *C*H_2-CH_3), 25.5 (OCH_2CH_2), 27.6, 27.8, 28.1, 28.3 (*C*HMe_2), 68.4 (OCH_2CH_2),122.92 (C_2H_4), 123.3, 123.6, 123.9, 124.5, 125.7, 125.8, 142.5, 143.7, 143.8, 144.5, 145.2, 145.6 (4 *m*-Dipp, 2 *p*-Dipp 2 *ipso*-Dipp, 4 *o*-Dipp), 161.7 (NC(H)N).

$[Mo_2(CH_2CH_3)_2(\mu\text{-}Ad^{Dipp_2})_2]$ (2)



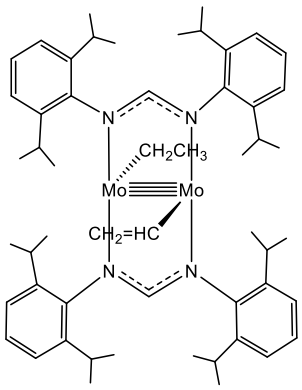
Compound **1·THF** (30 mg, 0.028 mmol) was dissolved in benzene-d_6 (C_6D_6) in a J. Young NMR tube. The solution was frozen, the headspace was evacuated, ethylene (C_2H_4, 1 bar) was introduced at room temperature and the tube was shaken to facilitate the solution of ethylene at room temperature. After six hours the solution became red, indicating complete conversion to complex **2**. Removal of ethylene atmosphere caused the decomposition of complex **2**. Isolation of this complex was achieved by crystallization. Complex **1·THF** (80 mg, 0.075 mmol) was dissolved in an ampoule in toluene under argon and the atmosphere substituted by ethylene. The solution was stirred for 6 hours at room temperature, then the solution was cooled down to 0° during 12 hours to achieve bright red crystals of **2** in *ca.* 55 % isolated yield. Crystals were also obtained from a still saturated solution of compound **1·THF** under ethylene atmosphere after 12 h at room temperature.

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 0.84, 1.25, 1.32, 1.37 (d, 48H, $^3J_{HH}$ = 6.9 Hz, 12 H each CH*Me*$_2$), 2.25 (t, 6H, CH_3(Et), $^3J_{HH}$ = 7.3 Hz), 2.61 (q, 4H, CH_2(Et), $^3J_{HH}$ = 7.3 Hz), 3.14, 4.14 (sept, 8H, 2H each, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$), 5.25 (C_2H_4), 6.9-7.14 (m, 12 H, *m*, *p*-Dipp*)*, 8.50 (s, 2H, NC(*H*)N).

^{13}C {H} NMR (100 MHz, C_6D_6, 25 °C) δ (ppm): 17.4 (*C*H_3(Et)), 24.1, 24.5, 25.6, 27.5 (CH*Me*$_2$), 28.5, 30.2 (*C*HMe$_2$), 31.0 (*C*H_2(Et)), 122.96 (C_2H_4), 123.2, 125.3, 125.8 (2 *m*-Dipp, 1 *p*-Dipp), 143.2, 144.1 (2 *o*-Dipp) 145.8 (*ipso*-Dipp), 162.9 (N*C*(H)N).

Elemental Analysis (%) for $C_{54}H_{80}Mo_2N_4$: Calc. C, 66.4; H, 8.3; N, 5.7. Exp. C, 66.7; H, 8.3; N, 5.4.

$[Mo_2(CH_2CH_3)(CH{=}CH_2)(\mu\text{-}Ad^{Dipp_2})_2]$ (3)



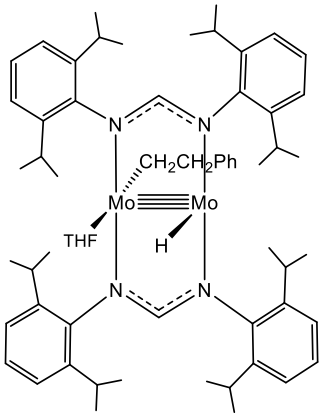
Complex **1·THF** (30 mg, 0.028 mmol) was dissolved in benzene-d_6 (C_6D_6) in a J. Young NMR tube. The solution was frozen, ethylene (C_2H_4, 1 bar) was introduced at room temperature and the tube was shaken to facilitate dissolution of ethylene. Complete conversion to **3** occurred after five days at room temperature under ethylene atmosphere. Suitable crystals for X-ray diffraction studies were grown by stirring a concentrated solution of **1·THF** (80 mg in 1 mL of toluene) for a few hours and then allowing it to stand for one week at room temperature, producing red crystals of **3** in *ca.* 84 % of isolated yield.

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 0.75, 0.78, 1.15, 1.32, 1.34, 1.49 (d, 36 H, 6 H each, CH*Me*$_2$, $^3J_{HH}$ = 6.8 Hz), 1.20-1.31 (m, 12 H, CH*Me*$_2$), 1.33 (m, 2H, CH_2), 1.95 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3), 3.49, 3.71, 4.01, 4.43 (sept. 8H, 2H each, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 5.25 (C_2H_4), 6.26 (dd, 1H, $^3J_{HH}$ = 15.7 y 1.8 Hz, C*H*$_2$=CH), 6.97 (m, 1H, C*H*$_2$=CH), 6.9-07.3 (m, 12 H, *m*, *p*-Dipp), 8.54 (s, 2H, NC(H)N), 11.20 (dd, 1 H, H_2C=C*H*, $^3J_{HH}$ = 15.7 Hz, $^3J_{HH}$ = 9.8 Hz).

^{13}C {H} NMR (100 MHz, C_6D_6, 25 °C) δ (ppm): 17.6 (CH_2-*C*H_3), 22.7, 24.2, 24.7, 25.2, 25.8, 26.2, 27.8, 28.1 (CH*Me*$_2$), 28.2, 28.6, 29.1, 29.5 (*C*HMe$_2$), 32.3 (*C*H_2-CH_3), 113.4 (*C*H_2=CH, $^1J_{CH}$= 150 Hz), 122.94 (C_2H_4), 122.9, 123.2, 124.8, 125.4, 126.0, 126.3 (4 *m*-Dipp, 2 *p*-Dipp), 143.1, 143.9, 144.1, 144.9, 145.6, 146.5 (2 *ipso*-Dipp, 4 *o*-Dipp), 163.0 (NC(H)N), 207.4 (Mo-*C*H=CH_2, $^1J_{CH}$=145 Hz).

Elemental Analysis (%) for $C_{54}H_{78}Mo_2N_4$: Calc. C, 66.5; H, 8.1; N, 5.8. Exp. C, 66.5; H, 8.0; N, 6.5.

[$Mo_2(C_2H_4Ph)(H)(\mu\text{-}Ad^{Dipp2})_2(THF)$] (B)

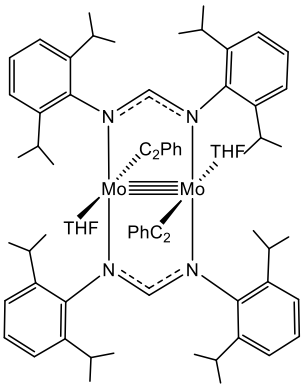


Complex **1·THF** (80 mg, 0.075 mmol) was dissolved in toluene, then dry styrene (1.1 equiv.) was added under argon atmosphere and the solution stirred for one hour to yield compound **B** in 90% spectroscopic yield. When a toluene solution in the presence of some THF was exposed to visible light, the solution turned red, showing dichroic properties. Compound **B** without coordinated THF molecules exhibits a red color in solution and eliminates ethylbenzene upon exposure to vacuum. As **B** decomposes when it is exposed to low pressure it was not possible to obtain a solid suitable for elemental analysis. Unfortunately, no crystals were obtained despite numerous tries.

^{1}H NMR (400 MHz, C_6D_6, 25°C): δ (ppm) 0.62, 0.66, 1.08, 1.13, 1.41 (d, 30 H, 6H each,$^3J_{HH}$ = 6.4 Hz, CH*Me*$_2$),1.30-1.37 (m, 18 H, CH*Me*$_2$), 1.40 (m, OCH_2CH_2), 2.14 (m, 2H, Mo-CH_2-CH_2-Ph), 2.99 (m, 2H, Mo-CH_2-CH_2-Ph), 2.90 (s, 1 H, Mo-*H*), 3.50 (m, OCH_2CH_2), 3.54, 3.83, 4.09, 4.21 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, C*H*Me_2), 6.96-7.14 (m, 17 H, *p*-Ph*, m, p*- Dipp), 7.28 (t, 2H, *m*-Ph*,* ,$^3J_{HH}$ = 7.5 Hz), 7.47 (d, 2H, o-Ph*,* $^3J_{HH}$ = 7.5 Hz), 8.48 (s, 2H, NC(H)N).

^{13}C {H} NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 23.6, 24.1, 24.4, 24.5, 26.0, 26.1, 26.8, 27.1 (CH*Me*$_2$), 25.7 (OCH_2CH_2), 27.9, 28.1, 28.2, 28.7 (*C*HMe_2), 33.1 (Mo-*C*H_2-CH_2-Ph, $^1J_{C\text{-}H}$= 240 Hz), 38.5 (Mo-CH_2-*C*H_2-Ph, $^1J_{C\text{-}H}$= 250 Hz), 68.8 (OCH_2CH_2), 123.4, 124.0, 124.2, 124.5, 125.1, 125.8, 125.9 (4 *m*-Dipp, 2 *p*-Dipp, *p*-Ph), 127.9, 128.2 (*o*-Ph, *m*-Ph), 143.2, 144.1, 144.2, 144.8, 145.6, 146.3 (4 *o*-Dipp, 2 *ipso*-Dipp), 149.5 (*ipso*-Ph), 162.2 (NC(H)N, $^1J_{C\text{-}H}$= 173 Hz).

[Mo_2(C≡CPh)$_2$ (μ-Ad^{Dipp_2})$_2$(THF)$_2$] (4)



Compound **1·THF** (80 mg, 0.075 mmol) was dissolved in toluene (5mL) in an ampoule under argon atmosphere. To this solution was added 2.1 equivalents of phenylacetylene and the solution was stirred at room temperature for about 10 minutes. The reaction proceeded rapidly at 25 °C with complete conversion to complex **4**, as observed by ^{1}H NMR with 92% spectroscopic yield. The solution was concentrated and the resulting solid precipitated in crystalline form, in 76 % isolated yield. When all the solvent was removed under vacuum and the resulting solid was washed with pentane a brown solid precipitated with polymeric appearance.

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 0.99, 1.24, 1.43, 1.58 (d, 48 H, 12 H each $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 1.23 (m, 8H, OCH$_2$C*H*$_2$), 3.38 (m, 8H, OC*H*$_2$CH$_2$), 4.35, 4.54 (sept, 8H, $^3J_{HH}$ = 6.7 Hz, C*H*Me$_2$), 6.9-7.1 (m, 12 H *m*, *p*-Dipp + 2 *p*-H-Ph), 7.31 (t, 4H, $^3J_{HH}$ = 7.52 Hz, *m*-*H* (Ph)), 7.78 (d, 4H, *o*-*H* (Ph), $^3J_{HH}$ = 7.52 Hz), 8.69 (s, 2H, NC(*H*)N).

^{13}C {H} NMR (100 MHz, C_6D_6, 25 °C) δ (ppm): 24.9, 25.1, 26.6, 28.4 (CH*Me*$_2$), 25.6 (OCH$_2$*C*H$_2$), 28.8, 29.2 (*C*HMe$_2$), 68.3 (O*C*H$_2$CH$_2$), 113.7 (Mo-*C*≡*C*-), 123.9, 124.4, 125.9, 126.6 (*p*-Dipp, 2 *m*-Dipp, *p*-Ph), 128.4, 130.5 (*o*, *m*-Ph), 134.2 (Mo-*C*≡*C*-), 144.7, 145.8 (2 *o*-Dipp), 146.9 (*ipso*-Dipp), 157.3 (*ipso*-Ph), 165.9 (N*C*(H)N).

Elemental analysis (%) for $C_{74}H_{96}Mo_2N_4O_2$: Calc. C, 69.9; H, 7.9, N, 4.8; Exp. C, 70.2, H, 7.7, N, 4.4.

IR (nujol): 2057 cm^{-1} (C≡C)

^{1}H NMR Monitoring of the reaction of 1·THF with C_2H_4 by (Figure S1)

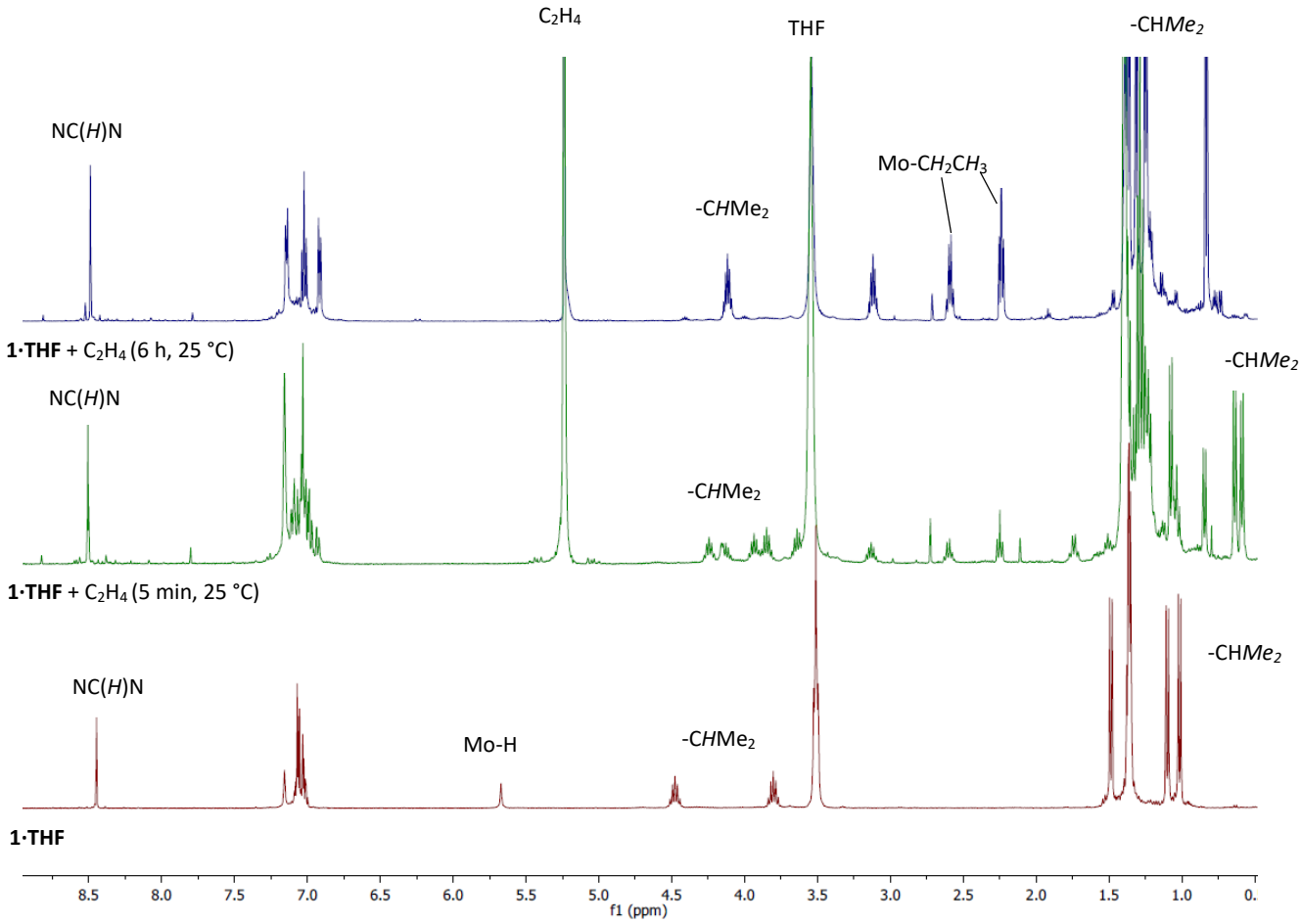
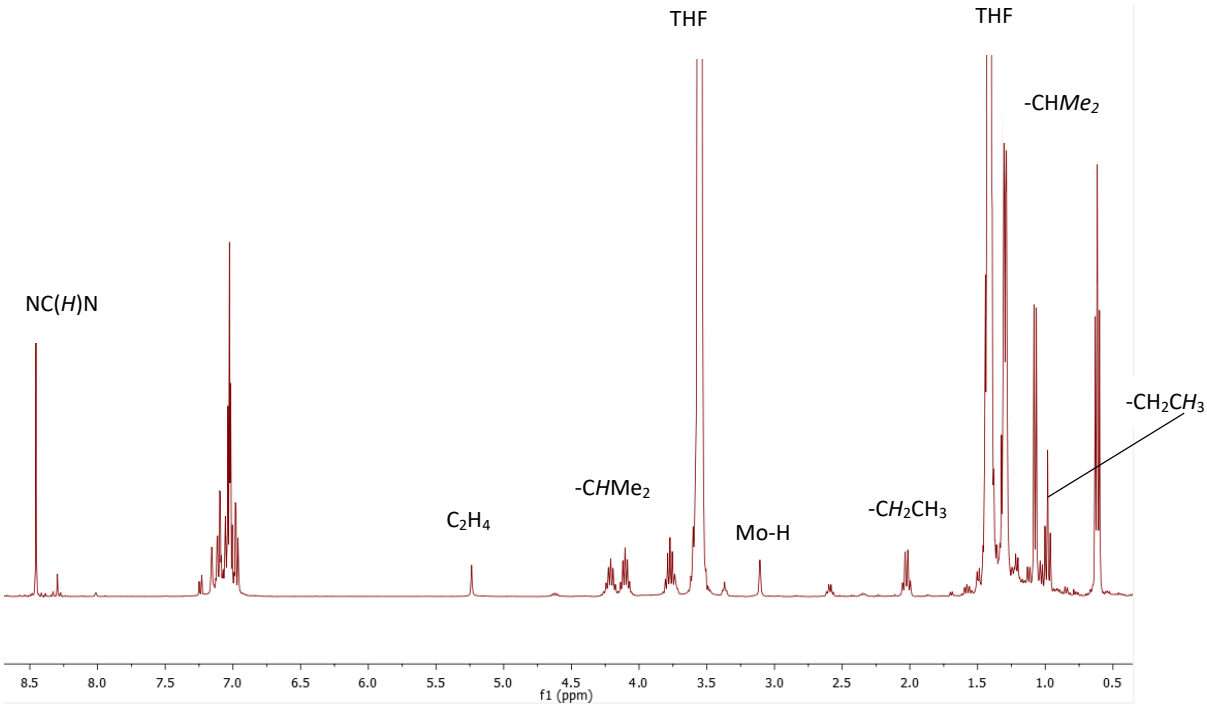


Figure S1: Reaction of complex **1·THF** with C_2H_4

Room temperature generation of intermediate A

10 mg (0.01 mmol) of the bis(hydride) complex **1** were dissolved in 0.5 mL of C_6D_6, after freezing the solution and evacuating the N_2 atmosphere, the tube was charged with 0.04 mmol of ethylene employing the system described in page S16. The reaction proceeds slower than with excess of ethylene (1bar) and it was possible to measure the ^{1}H NMR spectrum at room temperature showing a characteristic signal for the hydride Mo-H at 3.10 ppm.

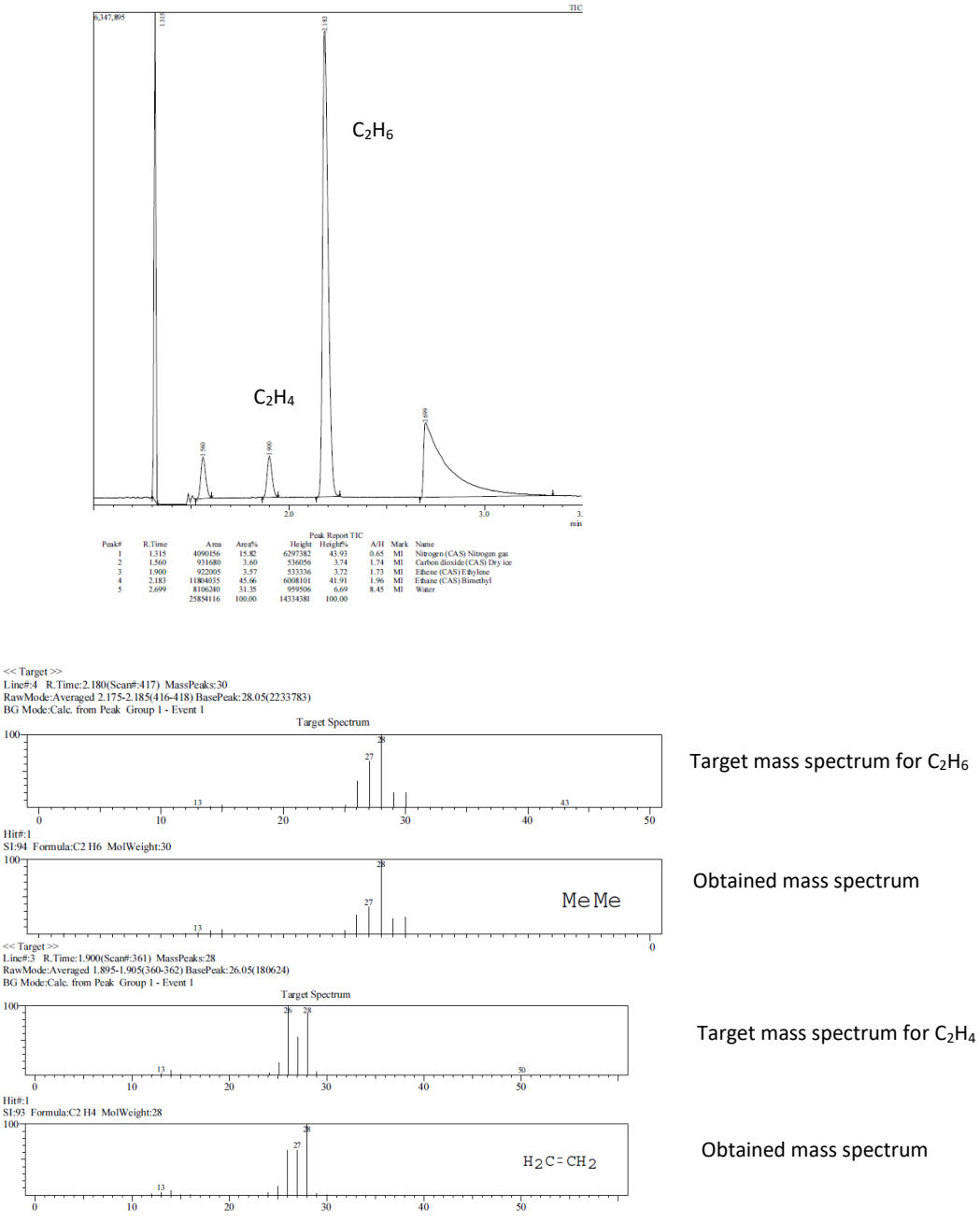


^{1}H NMR (400 MHz, C_6D_6, 25 °C)

Figure S2. ^{1}H NMR spectrum of intermediate **A**.

GC-MS analysis of decomposition of complex A in the absence C_2H_4

GC-MS analysis of the headspace after the decomposition of complex **A** in the absence of C_2H_4, liberating C_2H_4 and C_2H_6. Both gases, ethylene and ethane, were detected at 1.90 and 2.18 min (retention times) respectively. Nitrogen, carbon dioxide and water were also detected due to the sample injection. Complex **A** was prepared as described previously in a J. Young NMR tube at -30 ^{o}C. Then, the ethylene atmosphere was evacuated by doing several Ar/vacuum cycles. The headspace of the tube was analyzed by GC-MS. The gas cromatograph and the mass spectrum of both gases are shown in the figures below.



Target mass spectrum for C_2H_6

Obtained mass spectrum

Target mass spectrum for C_2H_4

Obtained mass spectrum

Figure S3

^{1}H NMR and ^{13}C {^{1}H} NMR of intermediate B

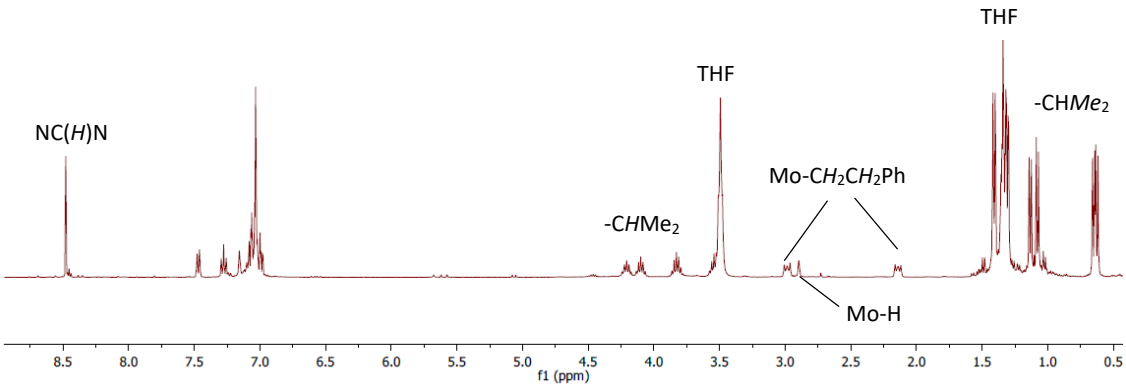


Figure S4. ^{1}H NMR of intermediate **B**, (400 MHz, C_6D_6, 25 °C)

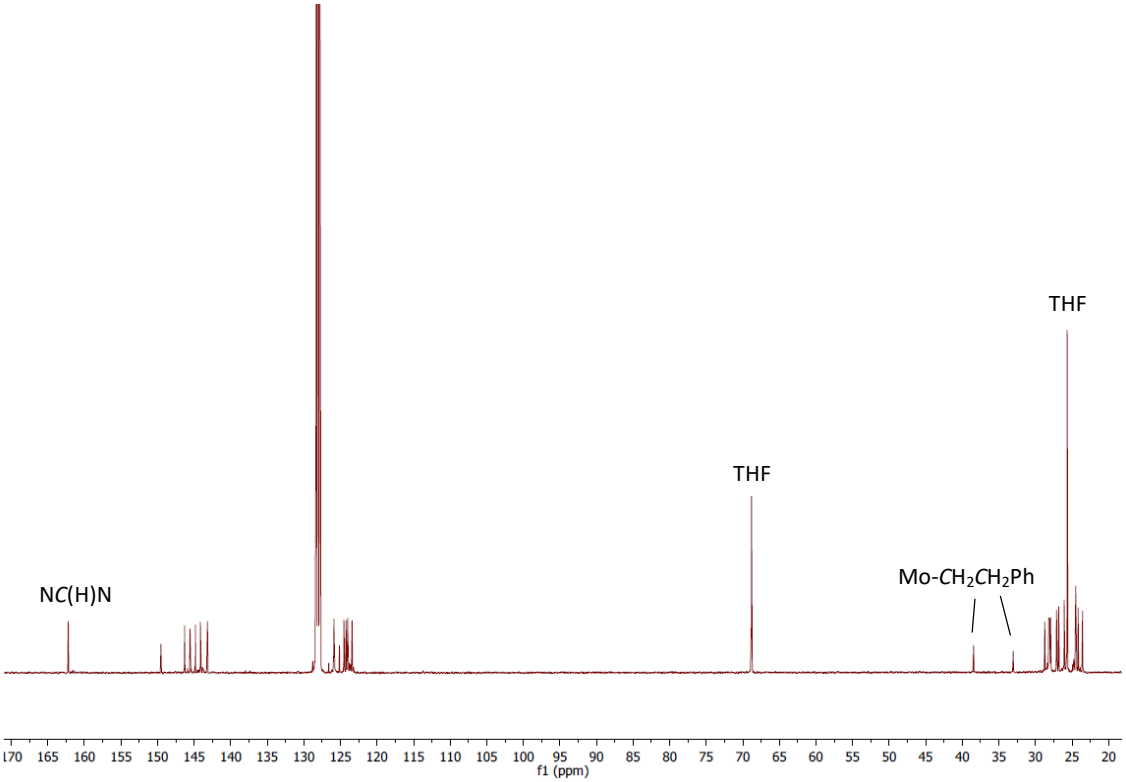
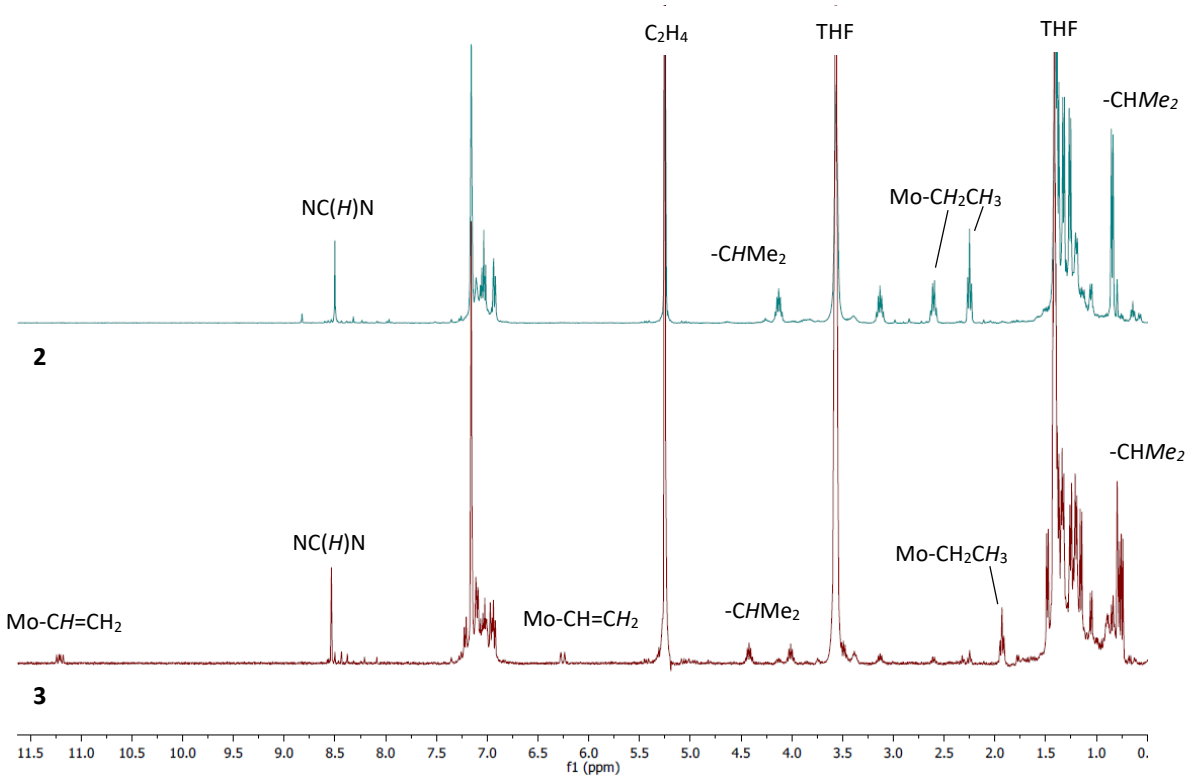


Figure S5. ^{13}C {^{1}H} NMR of intermediate **B** (400 MHz, C_6D_6, 25 °C)

^{1}H NMR Monitoring of the conversion 2 to 3 under C_2H_4

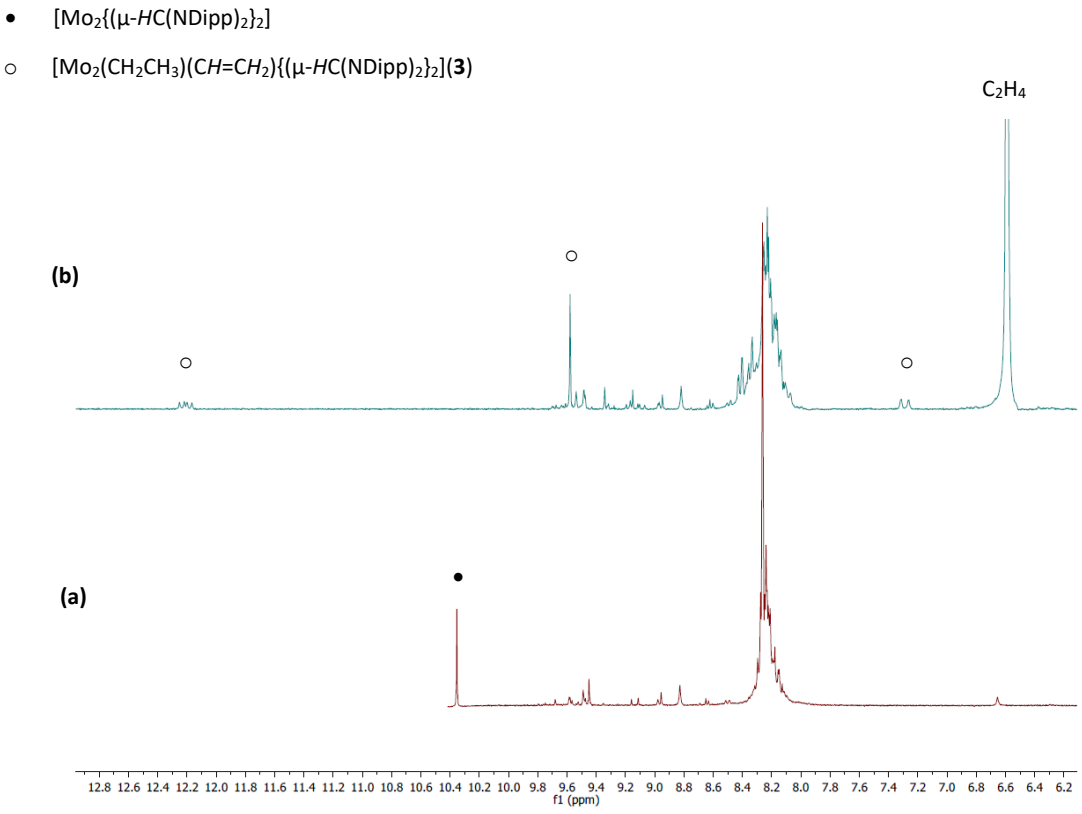


^{1}H NMR (400 MHz, C_6D_6, 25 °C)

Figure S6. Conversion of complex **2** into **3** under C_2H_4 atmosphere after 4 days at room temperature.

Reaction of $[Mo_2\{(\mu\text{-}HC(NDipp)_2\}_2]$ with C_2H_4

Complex $[Mo_2\{(\mu\text{-}HC(NDipp)_2\}_2]$ with a quintuple Mo-Mo bond was prepared by UV irradiation (365 nm) of complex **1·THF** in cyclohexane. A J. Young NMR tube with 10 mg of sample was prepared in C_6D_{12} and was charged with 1 bar of C_2H_4. The reaction occurred in 15 minutes and yielded complex **3**.



^1H NMR (300 MHz, C_6D_{12}, 25 °C)

Figure S7. (a) High-frequency region of the ^1H NMR spectrum of complex $[Mo_2\{(\mu\text{-}HC(NDipp)_2\}_2]$ (b) Spectrum recorded under C_2H_4 as explained above.

^{2}H NMR spectra of the reaction of 1-d_2 and 2 equivalents of PhC≡CH

10 mg of complex **1·THF** were dissolved in 0.5 mL of benzene (C_6H_6) in a J. Young NMR tube. After the N_2 was evacuated, the tube was charged with 1 bar of D_2 to access the deuterated hydride **1-d_2**. Once the H/D exchange reached completion, the D_2 atmosphere was substituted by argon and 2 equivalents of phenylacetylene were added. The transformation was followed by ^{2}H NMR experiments (500 MHz, C_6H_6, 25 °C).

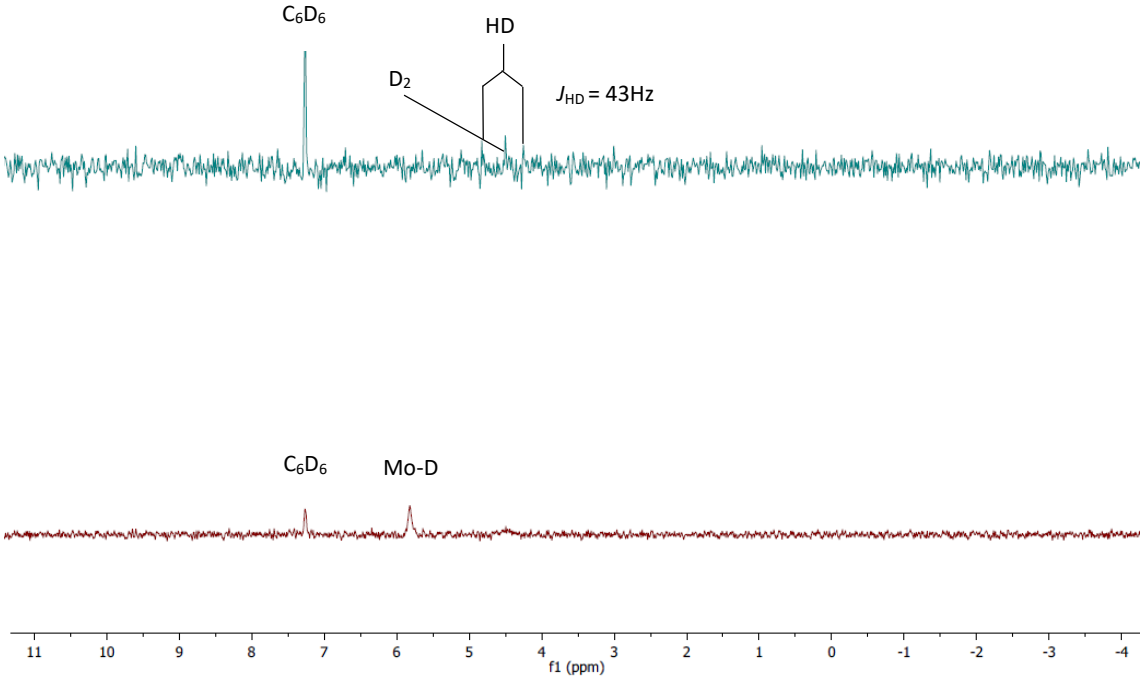


Figure S8. ^{2}H NMR spectra of **1-d_2** (below) and its reaction with PhC≡CH (above)

System for controlled ethylene loading

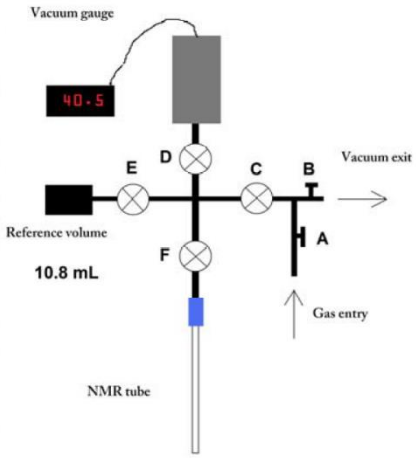


Figure S9. Schematic diagram of the system used for controlled loading of gases

The system for adding a precise number of mmol of a gas[1] (ethylene in this work) in a NMR tube is shown in the picture above. The system contains a gas entry and a vacuum exit, controlled by stopcocks A and B respectively, both connected to the manifold through C. A vacuum gauge is connected through D which is kept open. The system features in addition a cylindrical deposit of a known volume (10.8 mL) which is employed as reference connected through E. Stopcock F allows the incorporation of the NMR tube to the manifold.

The volume of the system (V_s; with *system* we mean the region defined by stopcocks C, E, the NMR tube cap and the vacuum gauge) can be determined by pressure differences. A known pressure of the gas, P_1, is introduced and then the gas is allowed to expand by opening E. The resulting pressure, P_0, is measured and V_s determined by means of the equation $P_1 \cdot V_s = P_0 \cdot V_0$, where $V_0 = V_s + 10.8$ mL).

The volume of the NMR tube can be determined in a similar way: the system is charged with gas pressure (V_s with a known pressure P_1) with the NMR tube cap closed. Then, the NMR tube is opened causing a decrease in the pressure (P_2) for the new volumen, $V_2 = V_s + V_{tube}$. Through the ideal gas equation, $P \cdot V = n \cdot R \cdot T$, the pressure needed to introduce the desired quantity (moles) of the gas into the tube is calculated.

X-Ray Structural Characterization of compounds 2, 3 and 4

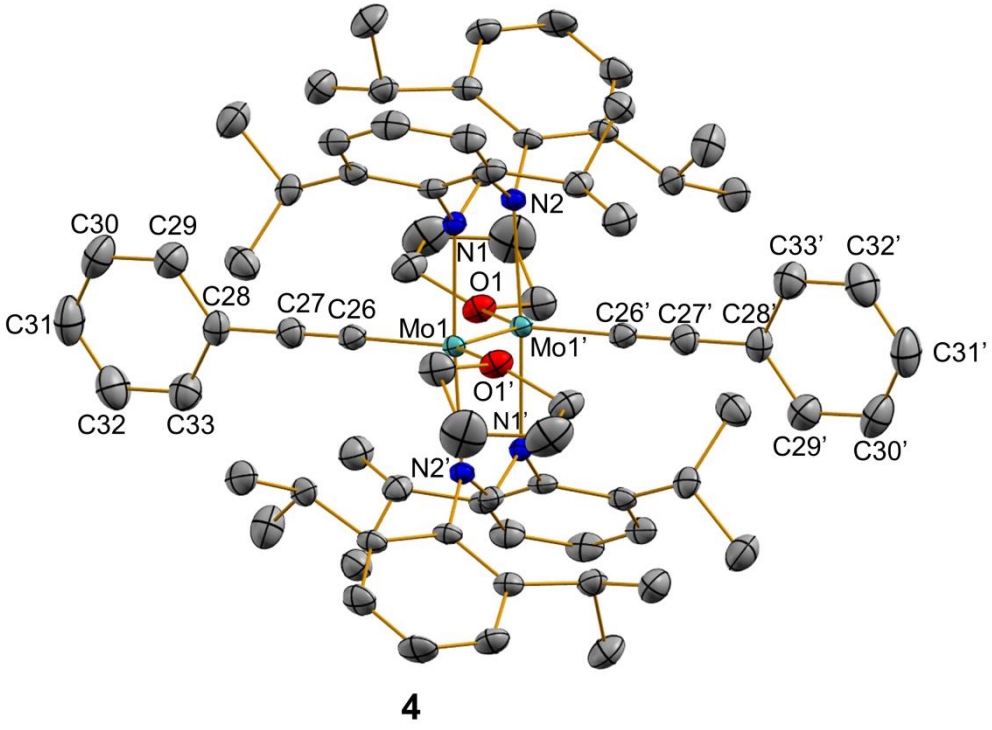


Figure S10. ORTEP diagram of compound **4** represented at 50% ellipsoids probability. Hydrogen atoms were omitted for clarity. Selected X-Ray Diffraction distances: 2.1223(4) Å (Mo-Mo), 2.113(4) Å (Mo-C), 1.217(4) Å (C≡C), 1.435(4) Å (C-*ipso*-C(Ph)).

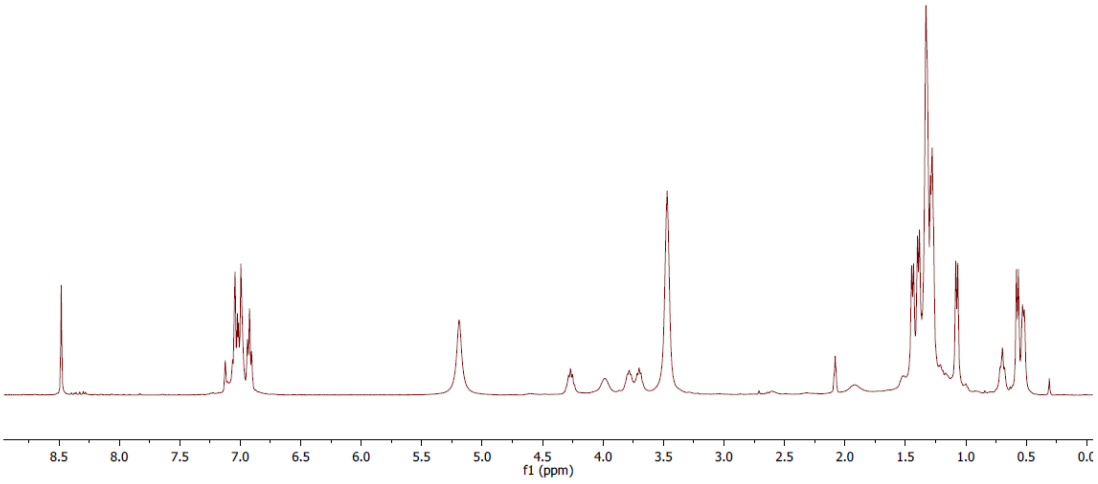
Crystallographic details. A single crystal of suitable size, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 193 K] to the goniometer head. Data collection was performed on a Bruker APEX-II CCD diffractometer using monochromatic radiation λ(Mo $K_{\alpha 1}$) = 0.71073 Å generated by a fine-focus sealed tube by means of ω and ϕ scans at the Instituto de Investigaciones Químicas (IIQ, Sevilla). The data were reduced (SAINT) [2] and corrected for Lorentz polarization effects and absorption by multiscan method applied by SADABS.[3]The structure was solved by direct methods and refined against all F^2 data by full-matrix least-squares techniques using the SHELXTL package (v. 6.14).[4] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions, except for those directly bonded to the vinyl fragment in compound **3** that were located in the difference electron density Fourier map and their C-H bond distances restrained using DFIX instruction. Hydrogens were refined riding on their respective carbon atoms with C-H = 0.95 Å or C-H = 0.98 Å for methyl H atoms, and U_{iso}(H) = 1.2 U_{eq} (C) or U_{iso}(H) = 1.5 U_{eq} (C) for methyl H atoms. CCDC 1850351-1850353 contain the supplementary crystallographic data for the three crystal structures included in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for compounds **2**, **3** and **4**.

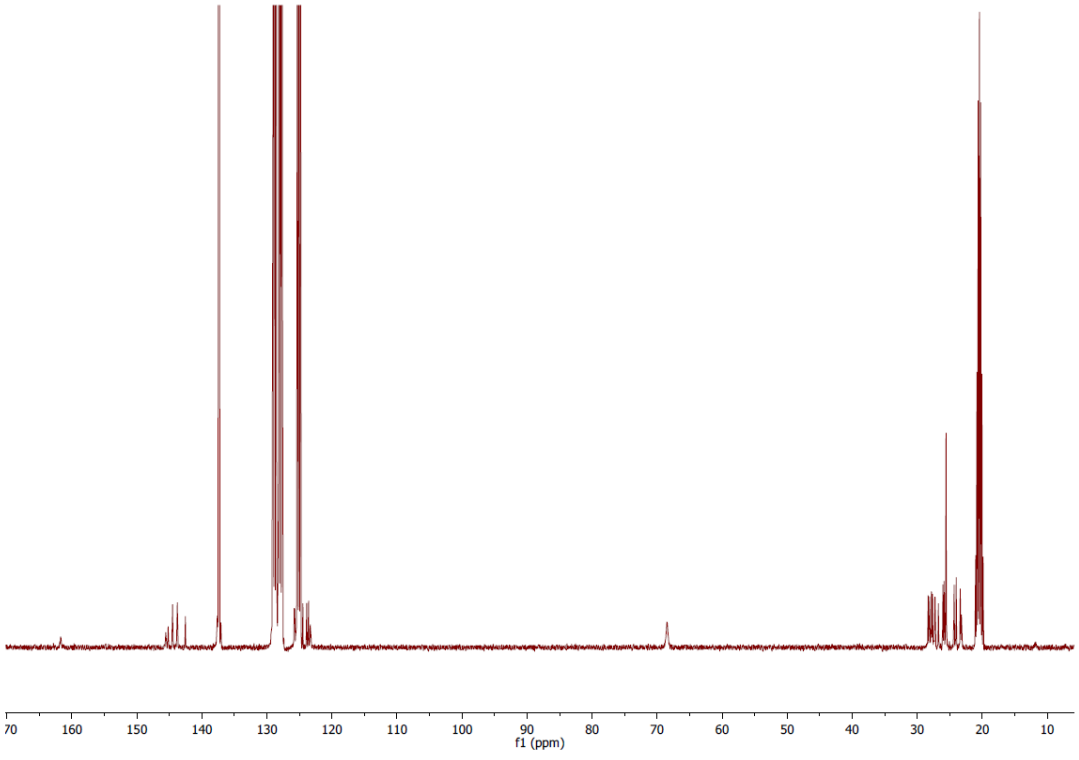
	2	**3**	**4**
formula	$C_{54}H_{80}Mo_2N_4$	$C_{60}H_{84}Mo_2N_4$	$C_{122}H_{144}Mo_2N_4O_2$
fw	977.10	1053.19	1890.28
cryst.size, mm	0.12 × 0.10 × 0.06	0.16 × 0.10 × 0.04	0.20 × 0.14 × 0.12
crystal system	Monoclinic	Monoclinic	Triclinic
space group	*C*2/*c*	$P2_1/c$	*P-1*
a, Å	23.4539 (6)	12.1639 (6)	12.1566 (3)
b, Å	11.5987 (3)	19.6377 (9)	12.4253 (3)
c, Å	18.4225 (4)	23.5597 (11)	17.8335 (5)
α, deg	90	90	99.015 (1)
β, deg	91.682 (1)	101.505 (2)	93.299 (1)
γ, deg	90	90	101.706 (1)
V, Å^3	5009.4 (2)	5514.7 (5)	2593.99 (12)
T, K	193	193	193
Z	4	4	1
ρ_{calc}, g cm^{-3}	1.296	1.269	1.210
μ, mm^{-1} (MoKα)	0.54	0.50	0.29
F(000)	2064	2224	1004
absorption corrections	Multi-scan, 0.58-0.75	Multi-scan, 0.62-0.75	Multi-scan, 0.76-0.85
θ range, deg	2.2 – 28.3	2.0 – 30.5	2-3 – 27.9
no. of rflns measd	57044	118441	61801
R_{int}	0.054	0.047	0.041
no. of rflns unique	6234	16789	12855
no. of params / restraints	288 / 3	612 / 0	594 / 0
R_1 ($I > 2\sigma(I)$) [a]	0.033	0.038	0.036
R_1 (all data)	0.052	0.056	0.050
wR_2 ($I > 2\sigma(I)$)	0.080	0.089	0.077
wR_2 (all data)	0.090	0.098	0.083
Diff.Fourier.peaks min/max, eÅ^{-3}	-0.46 / 0.50	-1.01 / 1.31	-0.49 / 0.98

Other NMR spectra for new complexes

Intermediate A: $[Mo_2(H)(THF)(CH_2CH_3)\{(\mu\text{-}HC(NDipp)_2\}_2]$

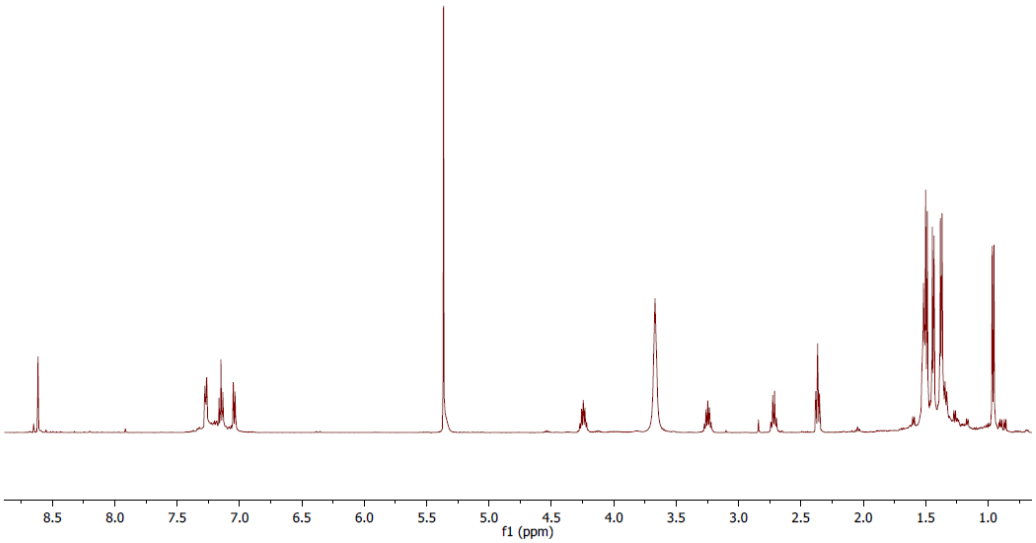


^{1}H NMR (400 MHz, tol-d_8, -30 °C)

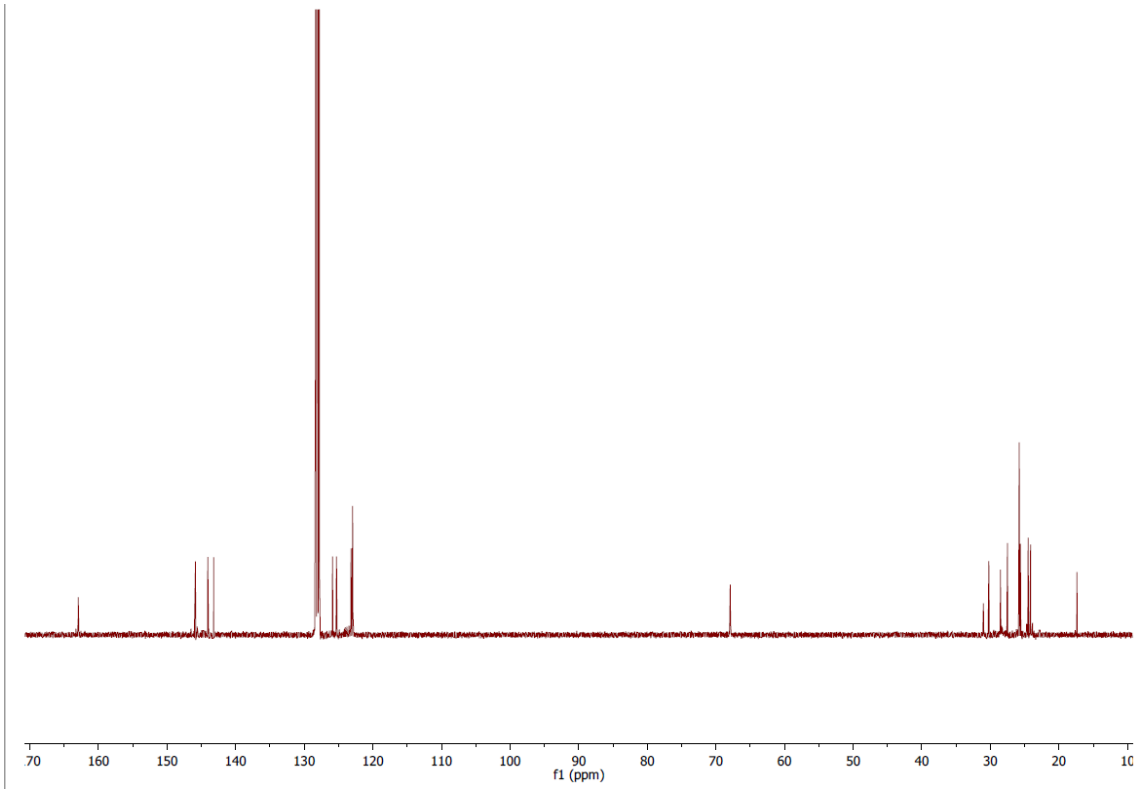


^{13}C {^{1}H} NMR (400 MHz, tol-d_8, -30 °C)

Compound 2: $[Mo_2(CH_2CH_3)_2\{(\mu\text{-}HC(NDipp)_2\}_2]$

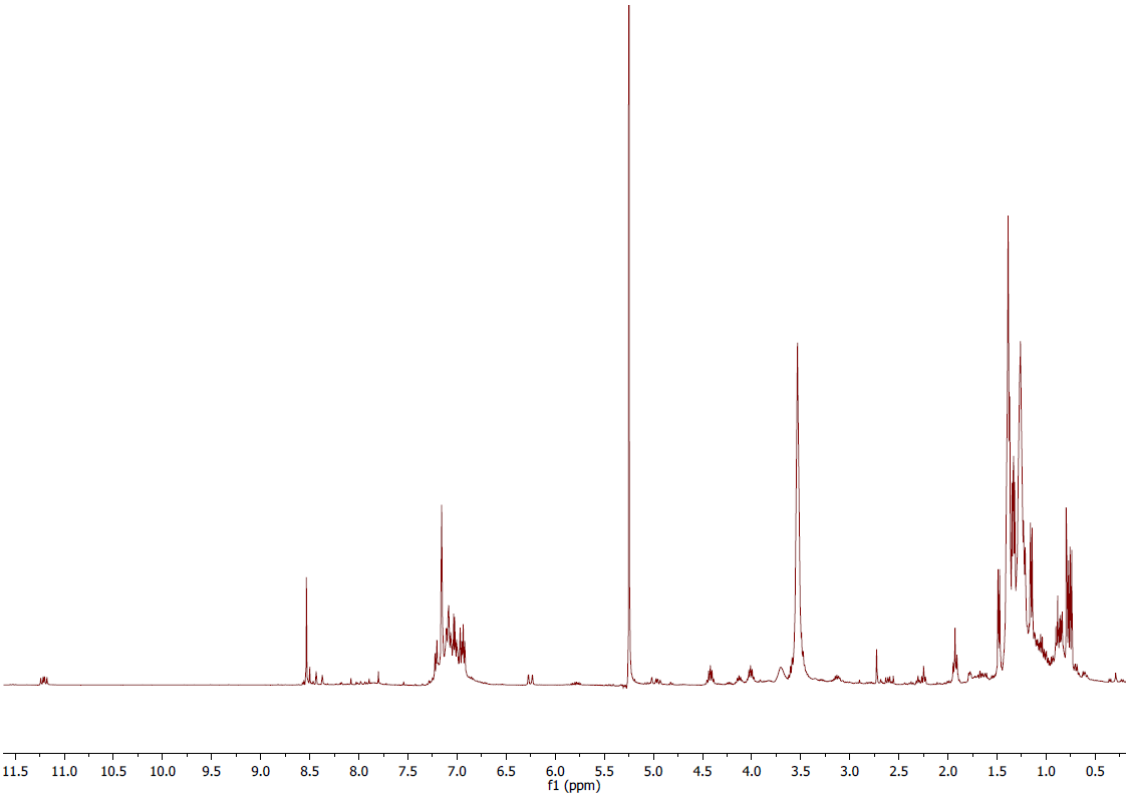


^{1}H NMR (400 MHz, C_6D_6, 25 °C)

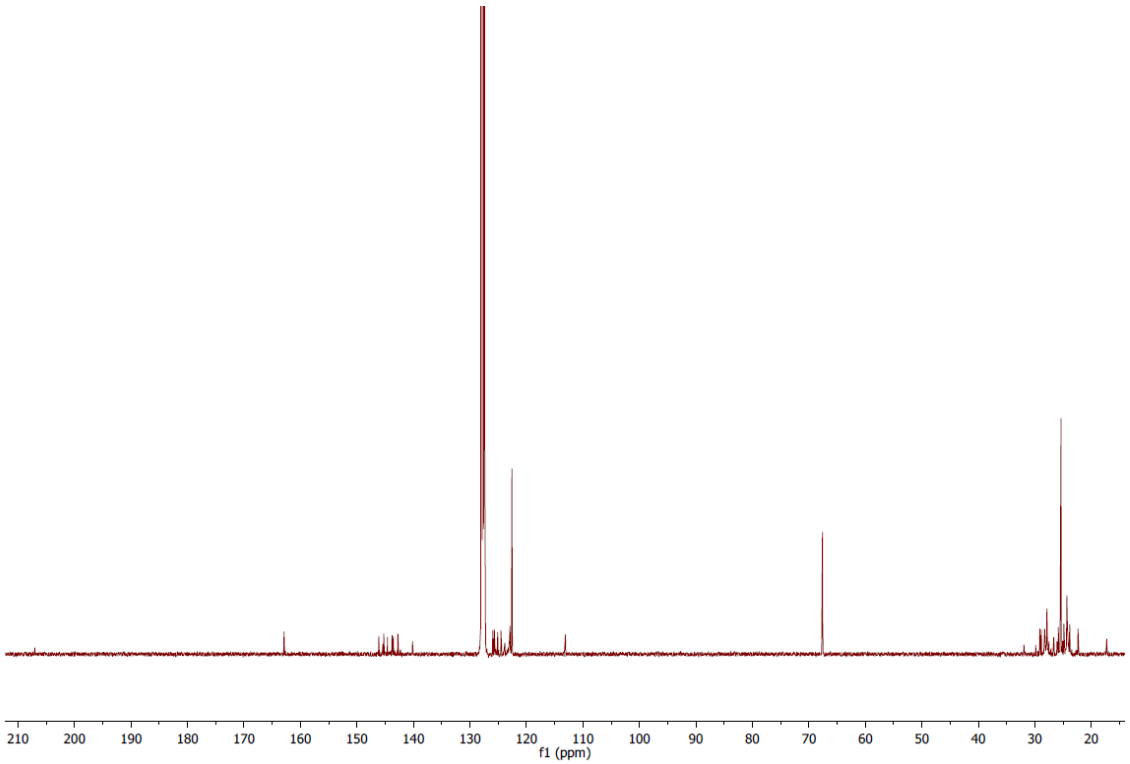


^{13}C $\{^{1}H\}$ NMR (400 MHz, C_6D_6, 25 °C)

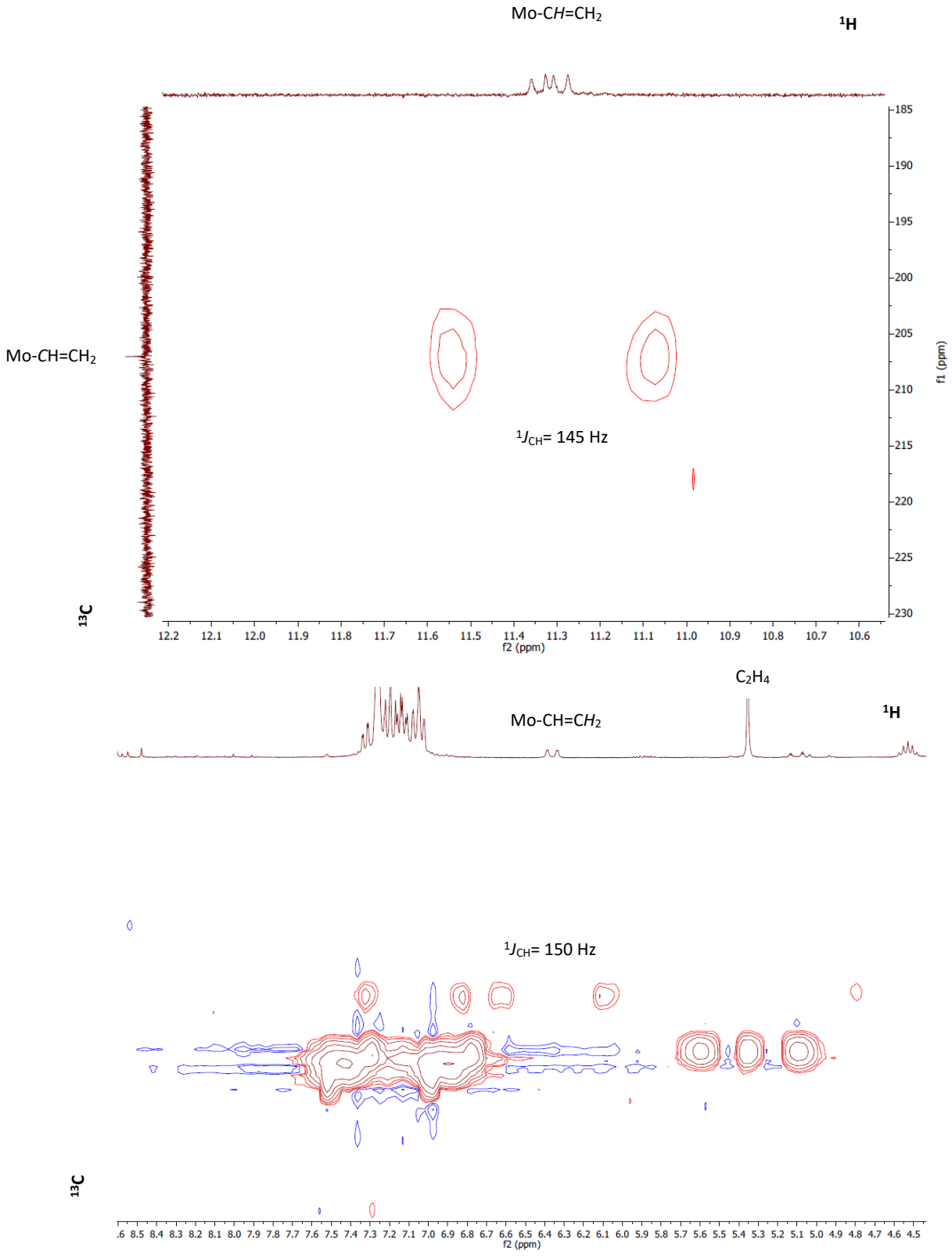
Compound 3: [$Mo_2(CH{=}CH_2)(CH_2CH_3)\{(\mu\text{-}HC(NDipp)_2\}_2]$



^{1}H NMR (400 MHz, C_6D_6, 25 °C)

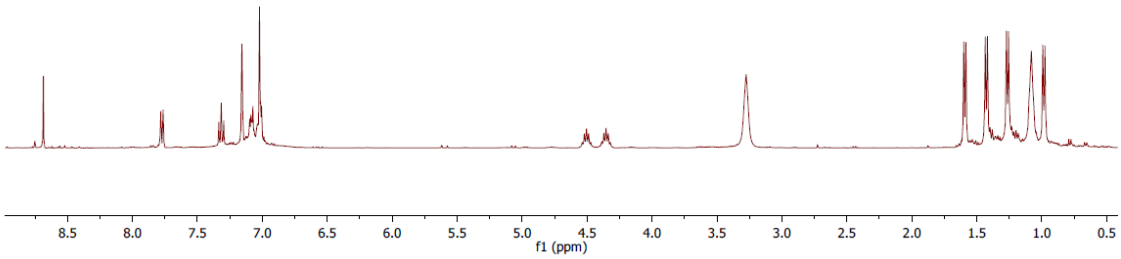


^{13}C {^{1}H} NMR (400 MHz, C_6D_6, 25 °C)

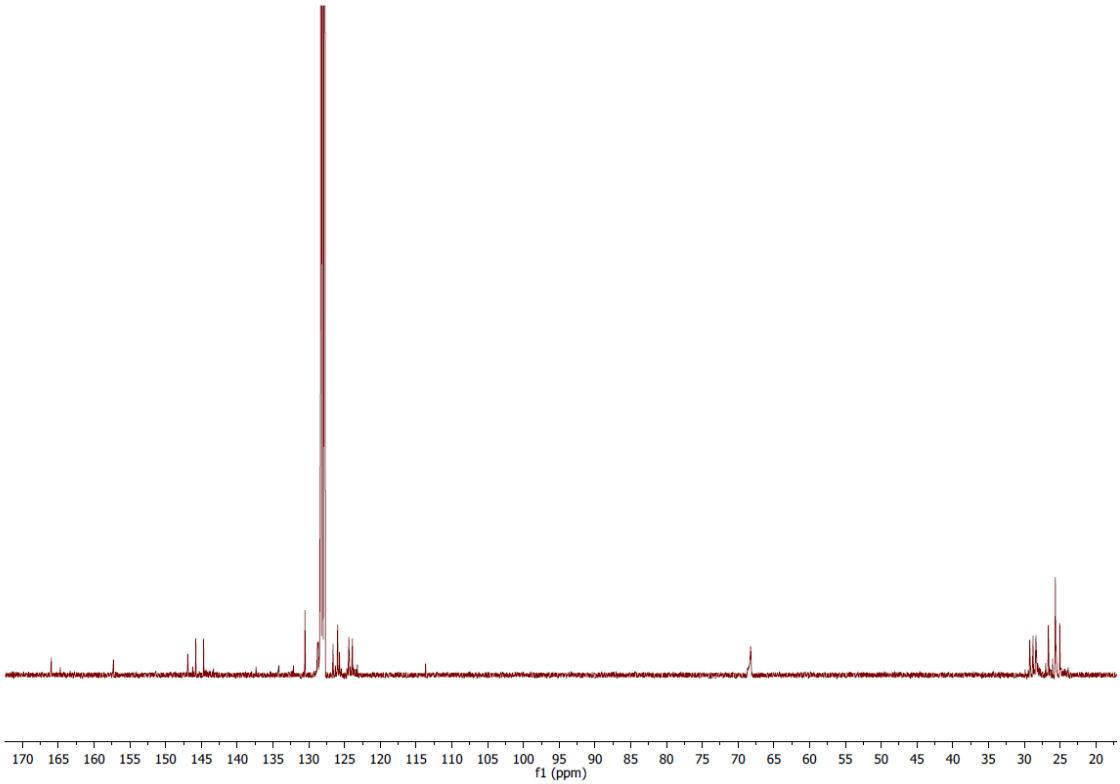


HSQC experiments of compound **3** (300 MHz, C_6D_6, 25 °C)

Compound 4: $[Mo_2(C_2Ph)_2(THF)_2\{(\mu\text{-}HC(NDipp)_2\}_2]$



^{1}H NMR (400 MHz, C_6D_6, 25 °C)



^{13}C $\{^{1}H\}$ NMR (400 MHz, C_6D_6, 25 °C)

IR spectra of complex 4

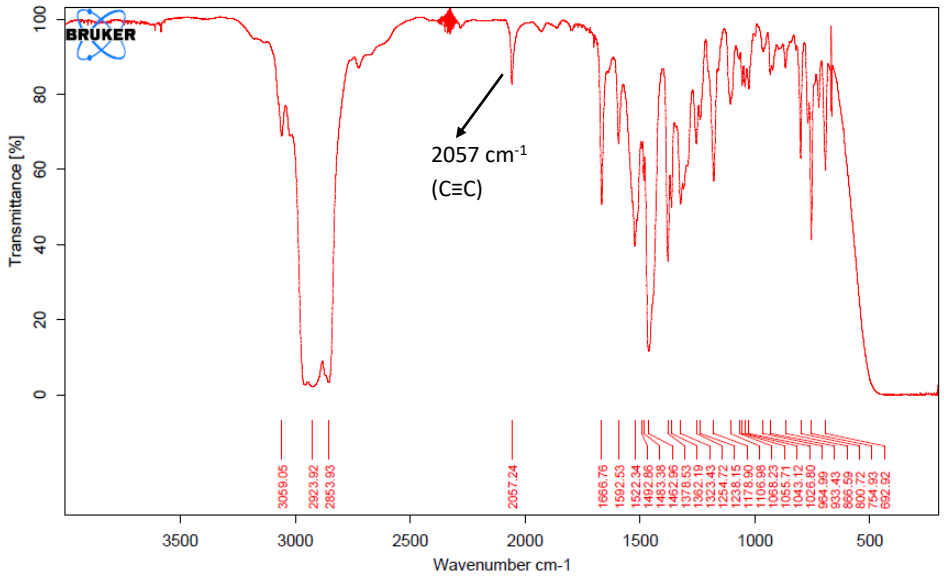


Figure S11: IR spectra of complex **4** (Nujol)

Computational studies

Calculations were performed with Gaussian 09[5] at the DFT level, using the separate range functional of Head-Gordon wB97XD with empirical dispersion corrections.[6] H, C, N and O atoms were represented with the 6-31G(d,p) basis set[7] whereas Mo atoms were described by the Stuttgart/Dresden Effective Core Potential and the associated basis set as implemented in Gaussian 09.[8] All molecular geometries were optimized within the SMD continuum solvent (benzene) model[9] without any geometry constrains. Frequency calculations were performed at the same level of theory to characterize the stationary points as minima (no imaginary frequencies) or saddle points (transition states, one imaginary frequency), as well as to calculate the Zero-point energy, enthalpy (H) and free energy (G) corrections. The two minima connected by a given transition state were confirmed from vibrational analysis. Natural Bonding Orbital (NBO) analysis was carried out with the NBO 6.0[10] software from electron density calculated at the same level of theory.

Ethylene migratory insertion.

Removal of one molecule of THF from **1·THF** (Figure 2) to generate a vacant site (**1'**) takes place with almost no change in free energy and allows ethylene coordination (**1'·C_2H_4**) and migratory insertion into one Mo-H bond. This step has a barrier of 17.1 kcal·mol^{-1} whereas its microscopic reverse *β*-H elimination from **A** requires overcoming 20.1 kcal·mol^{-1}. Extrusion of THF from the mixed valence Mo(+1)Mo(+3) species $\mathbf{A_{isom}}$, initiates barrierless hydride transfer to the adjacent Mo atom to afford the isomeric species **A'**, which yields the observed species **A** upon THF re-coordination. **A** is more stable than **1·THF** by -3.0 kcal·mol^{-1}, in agreement with the experimental observations. THF extrusion from $\mathbf{A_{isom}}$, not studied here, would account for the upper kinetic barrier to isomerization (isomerization process must compete with *β*-H elimination).

Alternatively, elimination of the two THF molecules of **1·THF** to afford **1''** is also accessible (Figure S21) and coordination of ethylene (**1''·C_2H_4**) leads to migratory insertion through an energy barrier ($\Delta G^{\ddagger}$ = 21.8 kcal·mol^{-1}), which is higher than in the previous case with one THF coordinated. Interestingly, no mixed valence species was located, as the corresponding transition state connects directly to **A'**.

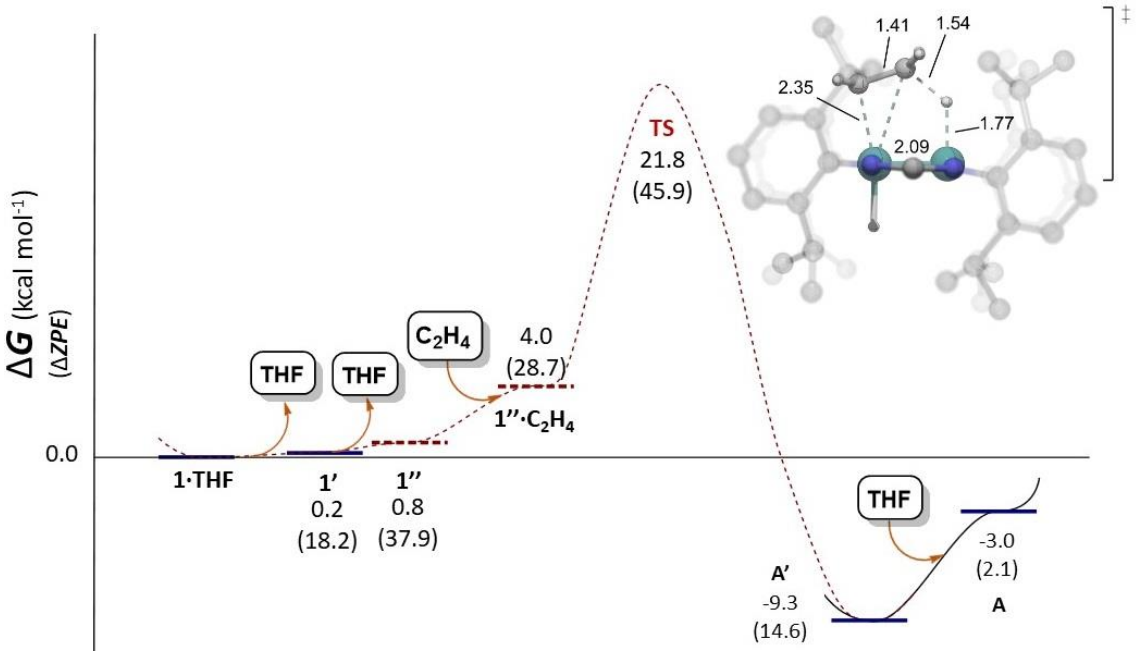


Figure S12. Free energy profile for the first migratory insertion of ethylene into one of the Mo-H bonds of **1''**. Free energies and zero-point (in parentheses) energies are given in kcal·mol^{-1}. The inset corresponds to the DFT-optimized geometry for the transition state of the insertion step.

Inspection of the optimized geometries of the transition states for ethylene migratory insertion suggest an *early* nature. Indeed, localized orbital (NBO) analysis of the electronic structure of TS(**1'·C_2H_4->A_{isom}**) and TS(**1''·C_2H_4->A'**) shows that their H-[Mo≡Mo]-H core remains almost intact, with quadruple Mo-Mo bonds. Interactions between the metal and ethylene fragments are described in terms of electron density donation-back donation, with the π orbital of ethylene donating electron density to a σ* combination of one Mo-H bond and the remaining Mo-H populating the π* orbital of ethylene with electron density from its σ orbital (Figure S13).

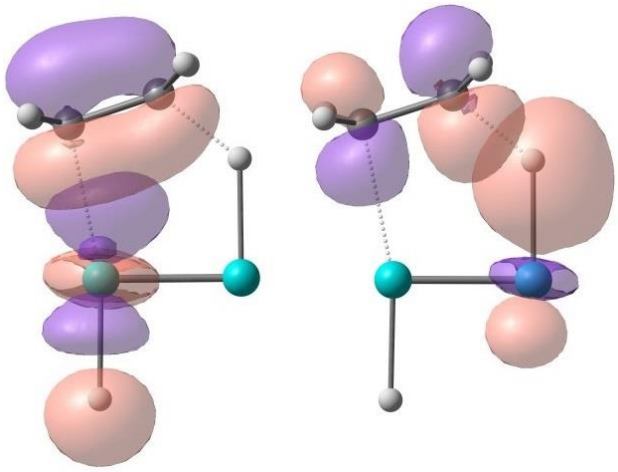


Figure S13. Relevant localized orbitals (NBO) interactions between the H-[Mo≡Mo]-H and ethylene fragments of TS(**1''·C_2H_4->A'**).

NBO analysis of $\mathbf{A_{isom}}$ reveals four MOs localized between the Mo atoms, but the orbital of δ symmetry appears polarized towards the, formally, Mo(+1) atom. This result can be interpreted as the Mo(+1) atom donating electron density to the Mo(+3) atom. In addition, one *β*-CH agostic interaction is established between the ethyl ligand and the neighboring Mo, via electron density donation from the corresponding C-H σ orbital, to an empty *d* orbital localized on the Mo atom (Figure S14 and scheme S1). The Mo-Mo distance in $\mathbf{A_{isom}}$ is within the expected for Mo≡Mo quadruple bonds, as well as the Wiberg bond order (WBOs for the Mo-Mo bonds of $\mathbf{A_{isom}}$ and **A** are 2.94 and 3.14 Å respectively).

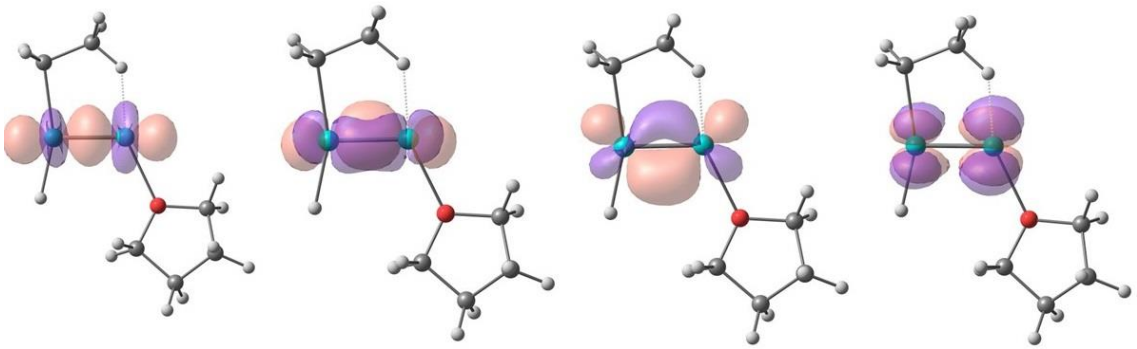
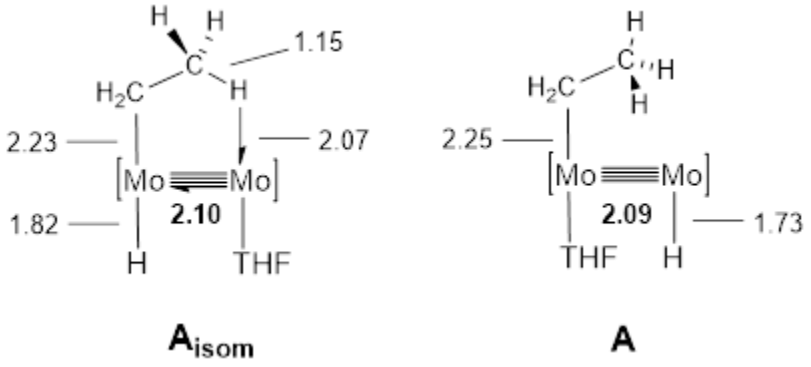


Figure S14. The four localized NBOs between the Mo atoms of $\mathbf{A_{isom}}$. Notice the δ MO is polarized towards the Mo(+1) atom supporting the THF ligand.



Scheme S1. Bonding scheme of $\mathbf{A_{isom}}$ and **A** excluding the amidinate ligands. Notice the similarity of the calculated Mo-Mo bond lengths for both species, within the expected for Mo≡Mo quadruple bonds.

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