

Supporting Information

for

A molecular  $\text{Mo}_4\text{Bi}_4$  framework composed exclusively of  
unsupported metal-metal bonds

*Christina Knispel and Christian Limberg\**

Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin,  
Germany

\* To whom correspondence should be addressed: [christian.limberg@chemie.hu-berlin.de](mailto:christian.limberg@chemie.hu-berlin.de)

**Contents**

Experimental Section – Synthetic and Spectroscopic Details	S2
References	S4

## Experimental Section – Synthetic and Spectral Details

**General Procedure.** All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry and oxygen-free argon atmosphere. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AV 400 NMR spectrometer ( $^1\text{H}$ , 400.1 MHz;  $^{13}\text{C}\{^1\text{H}\}$ , 100.6 MHz) in dry deoxygenated benzene- $d_6$  as solvent. The spectra were calibrated against the internal residual proton and natural abundance  $^{13}\text{C}$  resonances of the deuterated solvent (benzene- $d_6$   $\delta_{\text{H}}$  7.15 ppm,  $\delta_{\text{C}}$  128.0 ppm). Microanalyses were performed on a HEKAtech Euro EA 3000 elemental analyser. Infrared (IR) spectra were recorded in the region 4000 – 400  $\text{cm}^{-1}$  using solid samples prepared as KBr pellets with a Shimadzu FTIR 8400s spectrometer. The thermal behaviour was studied by simultaneously coupled TA-MS measurements for a sample protected against air (for the transfer from the glovebox into the apparatus) by a alumina layer. A NETZSCH thermoanalyzer STA 409 C *Skimmer*<sup>®</sup> system, equipped with a BALZERS QMG 421, was used to record the thermoanalytical curves (T, DTA, TG, DTG) together with the ionic current (IC) curves in the multiple ion detection (MID) mode.<sup>S1,S1</sup> Further experimental details were as follows: DTA-TG sample carrier system; Pt/PtRh10 thermocouples; platinum crucibles (beaker, 0.8 ml); sample mass 25 mg (measured versus empty reference crucible); constant purge gas flow of 70 ml/min nitrogen 5.0 (AIRLIQUIDE); constant heating rate 10 K/min; raw data evaluation with manufacturer's software PROTEUS<sup>®</sup> (v. 4.3) and QUADSTAR<sup>®</sup> 422 (v. 6.02) without further data treatment, e.g. such as smoothing.

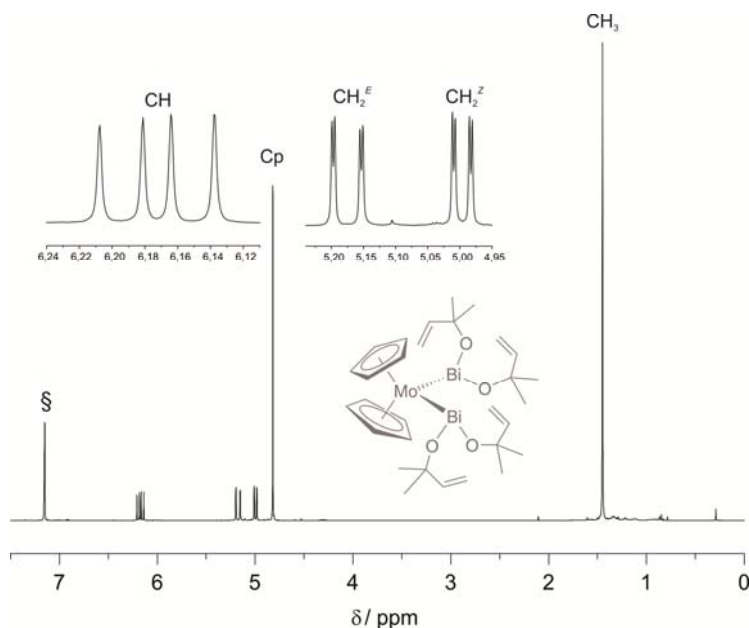
The determination of the initial ( $T_i$ ), extrapolated onset ( $T_{\text{on}}^{\text{ex}}$ ) and peak ( $T_p$ ) temperatures was performed following international recommendations.<sup>S3</sup>

**Materials.** All solvents were dried by an MBraun SPS solvent purification system prior to use. The starting materials  $[\text{Bi}\{\text{OCH}_2\text{CH}=\text{CH}_2\}_3]$ ,<sup>S4</sup>  $[\text{Bi}\{\text{OCH}(\text{CH}_3)\text{CH}=\text{CH}_2\}_3]$ ,<sup>S5</sup>

$[\text{Bi}\{\text{OC}(\text{CH}_3)_2\text{CH}=\text{CH}_2\}_3]^{\text{S1}}$  and  $[\text{Cp}_2\text{MoH}_2]^{\text{S2}}$  were prepared according to literature procedures.

**Synthesis of  $[\text{Cp}_2\text{Mo}\{\text{Bi}(\text{OCH}_2\text{CH}=\text{CH}_2)_2\}_2]$ , **1**:** A colourless solution of  $[\text{Bi}\{\text{OCH}_2\text{CH}=\text{CH}_2\}_3]$  (133 mg, 0.35 mmol) in 5 mL of toluene was added to a stirred yellow solution of  $[\text{Cp}_2\text{MoH}_2]$  (40 mg, 0.18 mmol) in 10 mL of the same solvent at ambient temperature. During the addition the colour changed from yellow to bright orange, and darkened to red while stirring the solution at ambient temperature for 3 h. Removal of all volatile components and drying of the residue in vacuo yielded **1** (71 mg, 0.08 mmol, 46 %) as a dark-red oil.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ [ppm] = 6.15 (m, 4H, CH), 5.41 (dd, 4H,  $^3J_{\text{HH}}^{\text{E}} = 17.1$  Hz,  $^1J_{\text{H}^{\text{E}}\text{H}^{\text{Z}}} = 1.7$  Hz,  $^{\text{CH}_2}\text{H}^{\text{E}}$ ), 5.35 (s br, 8H,  $\text{CH}_2$ ), 5.17 (dd, 4H,  $^3J_{\text{HH}}^{\text{Z}} = 10.0$  Hz,  $^1J_{\text{H}^{\text{E}}\text{H}^{\text{Z}}} = 1.7$  Hz,  $^{\text{CH}_2}\text{H}^{\text{Z}}$ ), 4.82 (s, 10H,  $^{\text{Cp}}\text{H}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ [ppm] = 135.0 (CH), 112.5 ( $=\text{CH}_2$ ), 82.2 ( $^{\text{Cp}}\text{C}$ ), 72.5 ( $\text{CH}_2$ ).

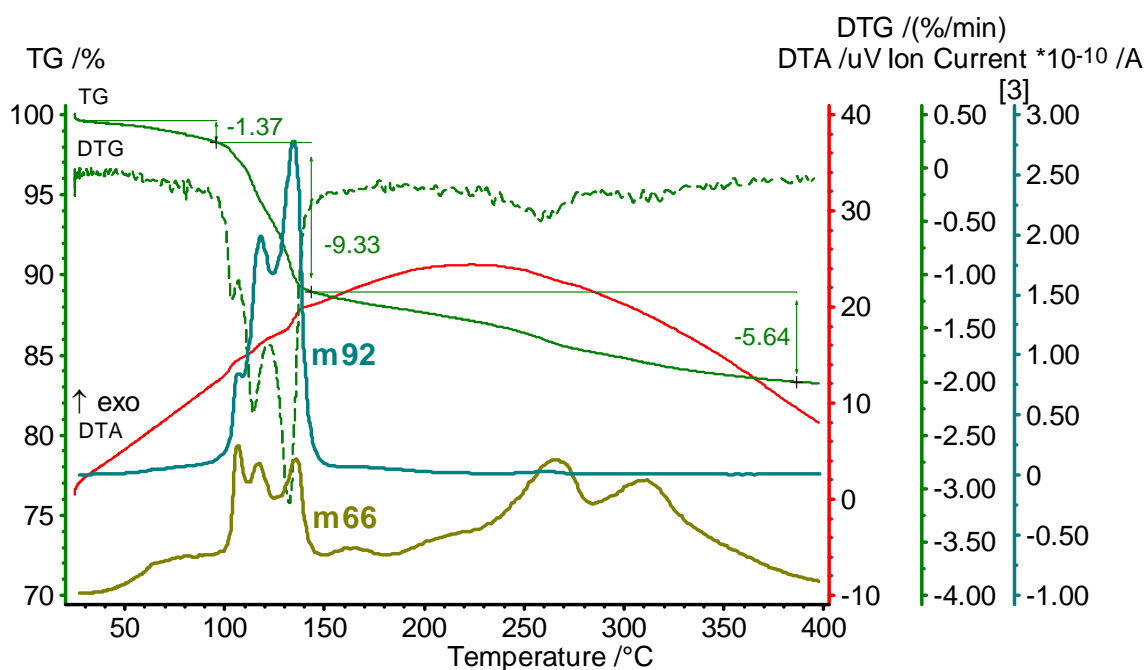
**Synthesis of  $[\text{Cp}_2\text{Mo}\{\text{Bi}(\text{OC}(\text{CH}_3)_2\text{CH}=\text{CH}_2)_2\}_2]$ , **2**:** To a stirred, yellow solution of  $[\text{Cp}_2\text{MoH}_2]$  (40 mg, 0.18 mmol) in 10 mL toluene a colourless solution of  $[\text{Bi}\{\text{OC}(\text{CH}_3)_2\text{CH}=\text{CH}_2\}_3]$  (162 mg, 0.35 mmol) in the same solvent (5 mL) was added at ambient temperature. A bright orange solution was initially formed, that darkened to red while stirring the solution at ambient temperature for 3 h. Removal of all volatile components and drying of the residue in vacuo yielded **2** (123 mg, 0.12 mmol, 71 %) as a dark-red highly viscous oil.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ [ppm] = 6.17 (dd, 4H,  $^3J_{\text{HH}} = 17.5, 10.6$  Hz, CH), 5.18 (dd, 4H,  $^3J_{\text{HH}}^E = 17.5$  Hz,  $^2J_{\text{H}^E\text{H}^Z} = 1.7$  Hz  $\text{CH}_2^E$ ), 5.00 (dd, 4H,  $^3J_{\text{HH}}^Z = 10.6$  Hz,  $^2J_{\text{H}^E\text{H}^Z} = 1.7$  Hz  $\text{CH}_2^Z$ ), 4.82 (s, 10H,  $\text{CpCH}$ ), 1.45 (s, 24H,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ [ppm] = 151.8 (CH), 109.3 ( $\text{CH}_2$ ), 83.5 ( $\text{CpC}$ ), 73.0 (C), 33.8 ( $\text{CH}_3$ ); IR (KBr):  $\nu$ [ $\text{cm}^{-1}$ ] = 3075, 2959, 2916, 2852, 1844, 1707, 1636, 1424, 1409, 1368, 1352, 1288, 1261, 1135, 1104, 1011, 998, 947, 917, 890, 834, 800, 737, 731, 686, 556, 474, 409.



**Fig. S1:**  $^1\text{H}$  NMR spectra of  $[\text{Cp}_2\text{Mo}\{\text{Bi}(\text{OC}(\text{CH}_3)_2\text{CH}=\text{CH}_2)_2\}_2]$ , **2**, in benzene- $d_6$ ; § denotes the residual proton resonance of benzene- $d_6$  ( $\text{C}_6\text{D}_5\text{H}$ ).

**$^1\text{H}$  NMR Spectroscopic Data of  $[\text{Cp}_2\text{Mo}(\text{OCH}_2\text{CH}=\text{CH}_2)_2]$ :** Equimolar Reactions of  $[\text{Cp}_2\text{MoH}_2]$  with  $[\text{Bi}\{\text{OCH}_2\text{CH}=\text{CH}_2\}_3]$ , **I**, led to the initial formation of a red solution, that darkened to black within few minutes. While stirring the solution at ambient temperature the color of the solution changed back to red, and the latter was accompanied by the formation of elemental Bi in form of a metallic mirror at the vascular wall as well as amorphous solid. Filtration of the reaction mixture and removal of all volatile compounds led to a red solid, whose  $^1\text{H}$  NMR spectroscopic investigations revealed the formation of  $[\text{Cp}_2\text{Mo}(\text{OCH}_2\text{CH}=\text{CH}_2)_2]$ .

$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$ [ppm] = 5.82 (m, 2H,  $^3J_{\text{H}^E\text{H}^Z} = 17.1, 10.3$  Hz,  $^3J_{\text{HH}} = 5.4$  Hz, CH), 5.39 (s, 10H,  $\text{CpH}$ ), 5.00 (dd, 2H,  $^3J_{\text{HH}^E} = 17.1$  Hz,  $^2J_{\text{H}^E\text{H}^Z} = 1.7$  Hz,  $\text{CH}^2\text{H}^E$ ), 4.83 (d br, 2H,  $^3J_{\text{HH}^Z} = 10.3$  Hz,  $\text{CH}^2\text{H}^Z$ ), 3.77 (d, 4H,  $^3J_{\text{H}^E\text{H}^Z} = 5.4$  Hz,  $\text{CH}_2$ ).



**Fig. S2:** TA-MS curves of **3**. (25,25 mg, layered by  $\alpha\text{-Al}_2\text{O}_3$ ) in  $\text{N}_2$  with IC curves for  $m/z = 66$  ( $\text{C}_3\text{H}_6^+$ ,  $\text{M}^+ \rightarrow \text{Cp}$ ) and 92 ( $\text{C}_7\text{H}_8^+$ ,  $\text{M}^+ \rightarrow \text{toluene}$ ).

## References

- S1 W.-D. Emmerich, E. Post, *J. Therm. Anal.* **49** (1997) 1007-12.  
S2 E. Kaisersberger, E. Post, *Thermochim. Acta* **295** (1997) 73-93.

- S3 J. O. Hill (Ed.), *For Better Thermal Analysis III*, Special Edn. of the Intern.Confederation for Thermal Analysis (ICTA), 1991.
- S4 C. Knispel, C. Limberg and B. Ziemer, *Inorg. Chem.*, 2010, **49**, 4313.
- S5 a) T. K. Panda, M. T. Gamer and P. W. Roesky, *Organometallics*, 2003, **22**, 877. b) N. D. Silavwe, M. P. Castellani and D. R. Tyler, *Inorg. Synth.*, 1992, **29**, 204.