

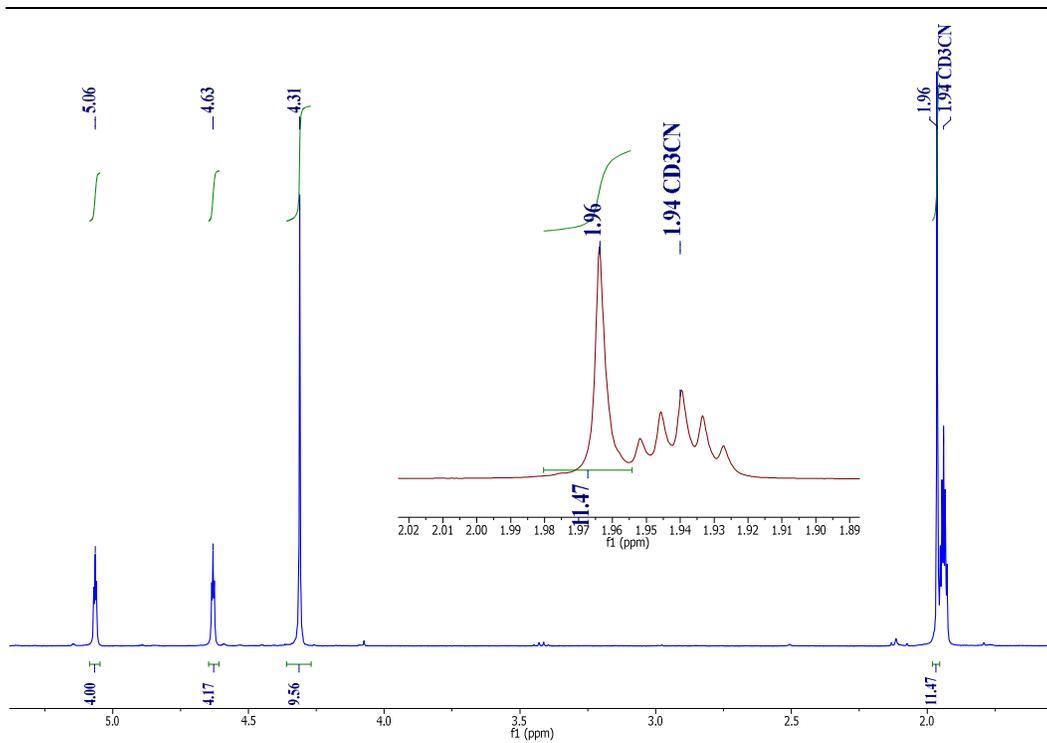
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**Supporting Information for****Synthesis and Characterization of Dimolybdenum(II) Complexes  
Connected by Carboxylate Linkers**

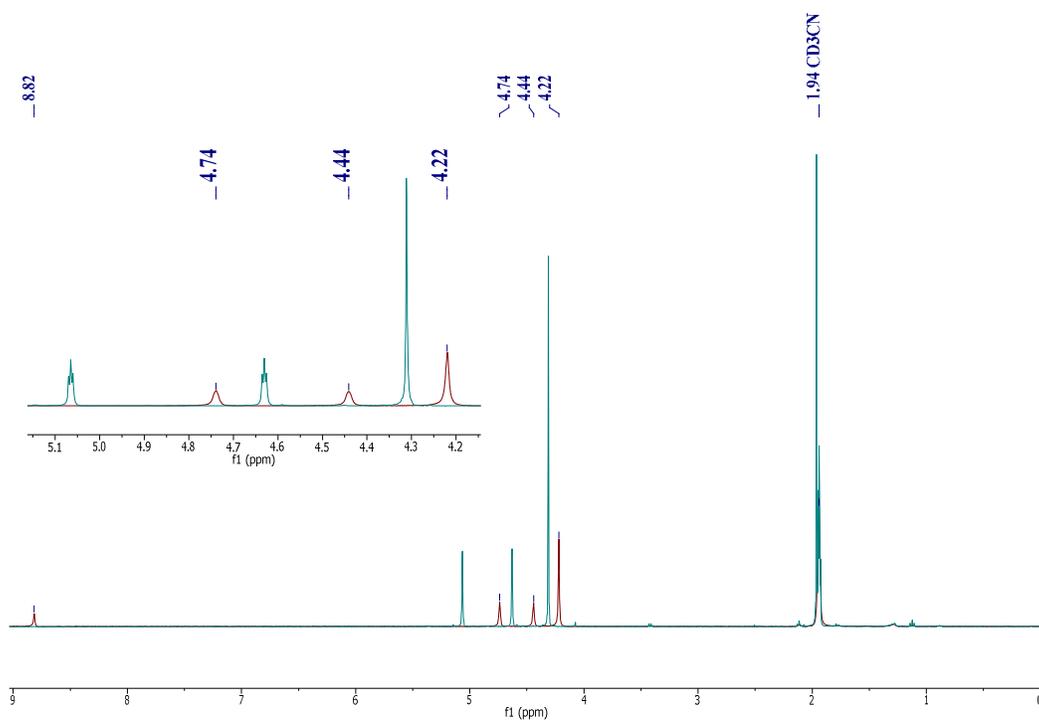
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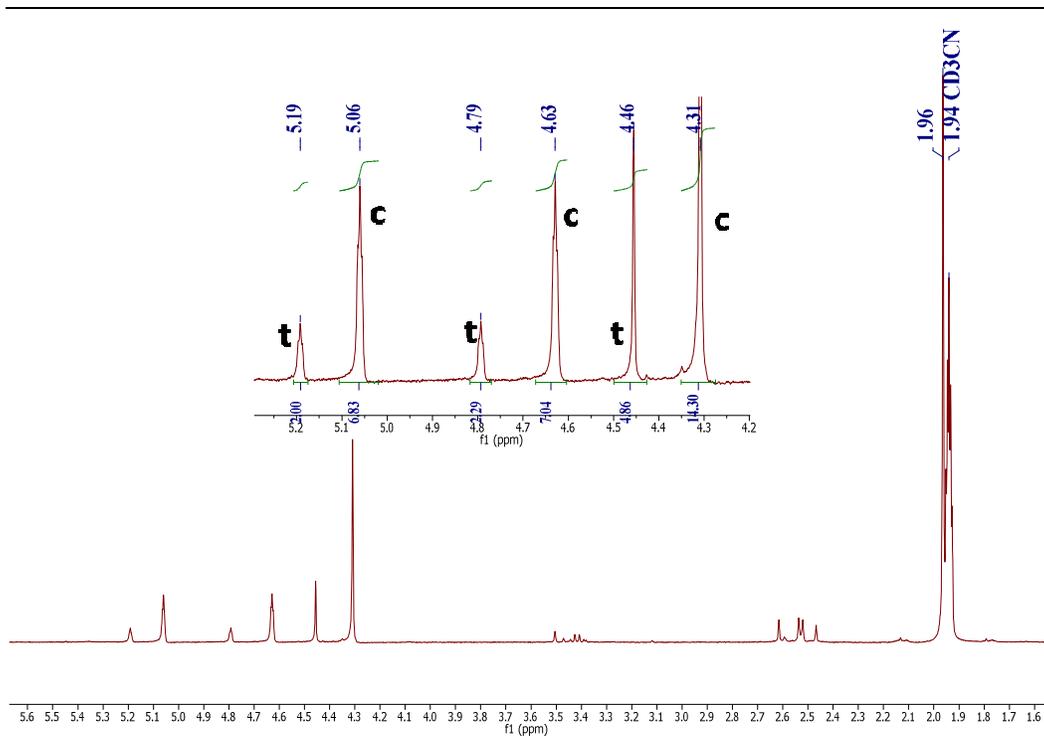
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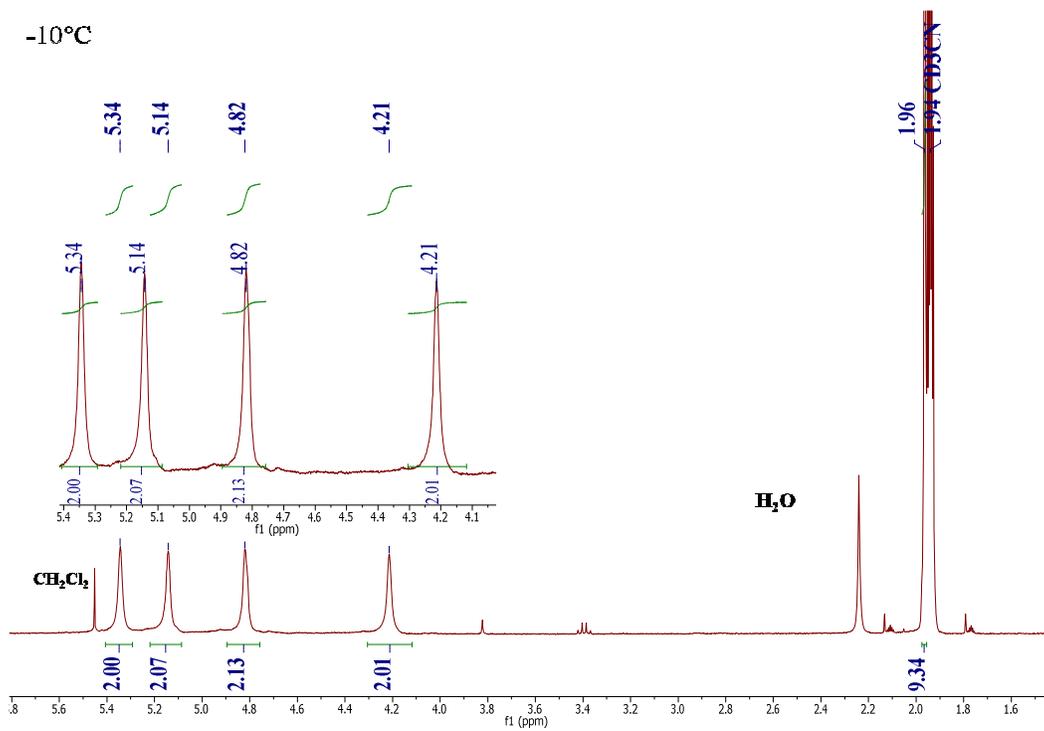
**Figure S1.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$ .



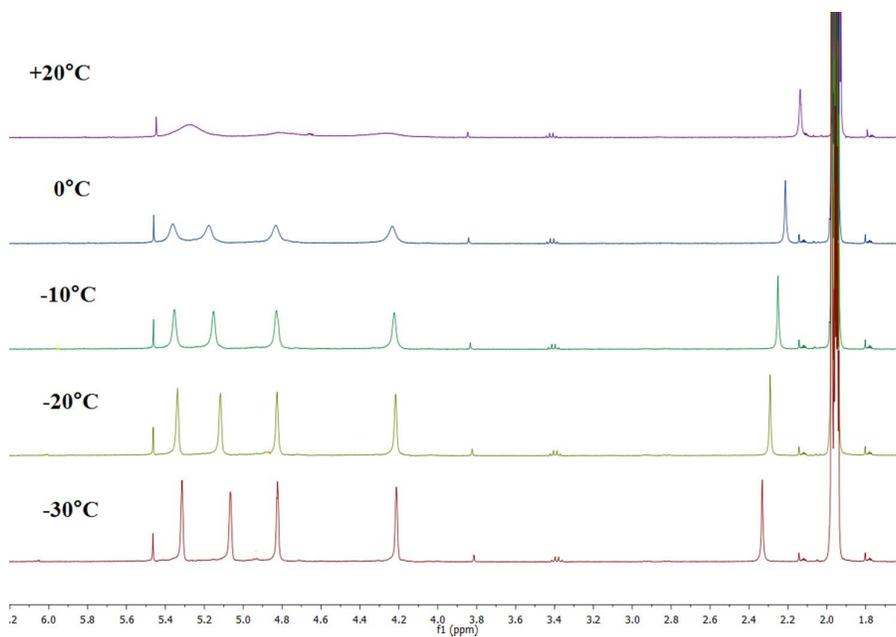
**Figure S2.**  $^1\text{H}$  NMR spectra of FMCA (red) and **2** (blue) in  $\text{CD}_3\text{CN}$ .



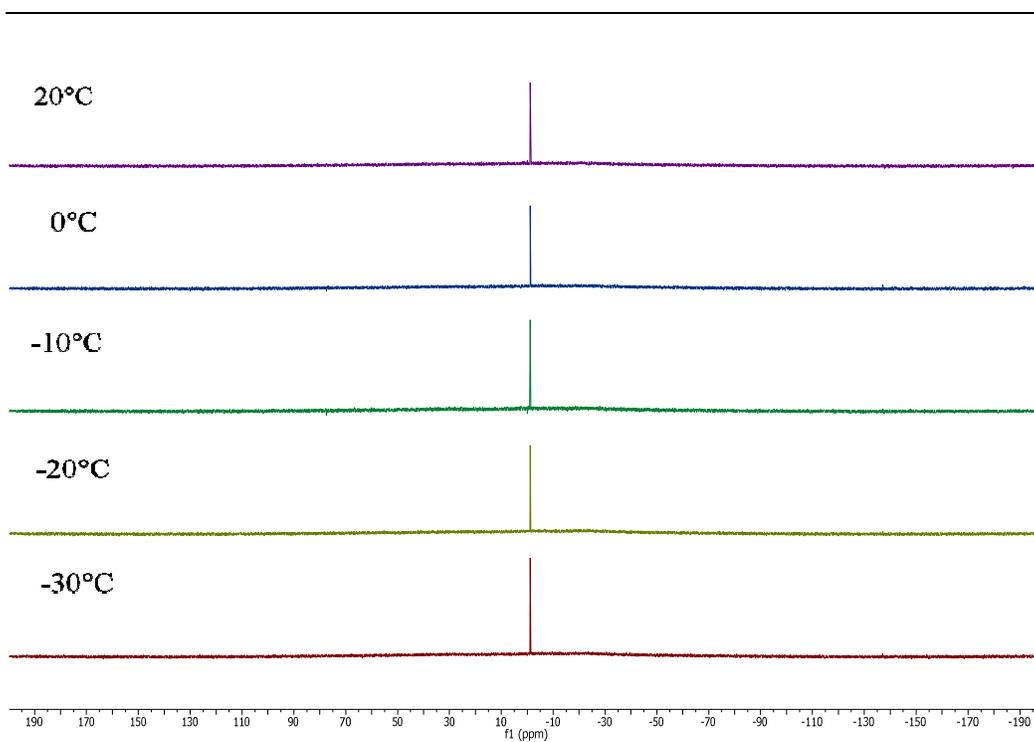
**Figure S3.**  $^1\text{H}$  NMR spectrum of the unpurified product **2** after 20h in  $\text{CD}_3\text{CN}$ . (t: trans-structure; c: cis-structure).



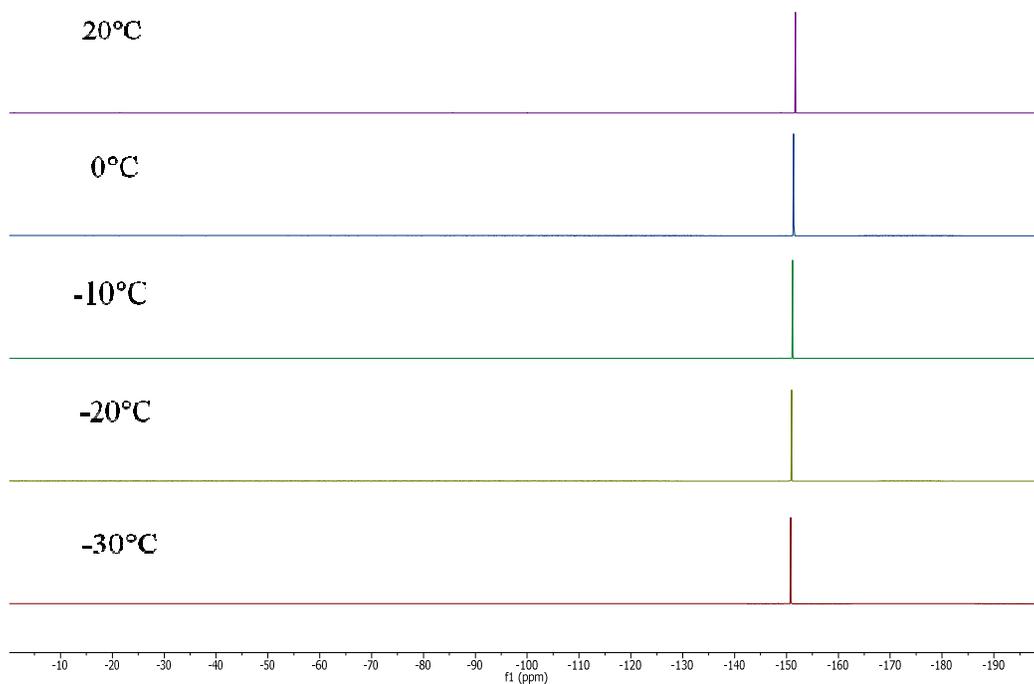
**Figure S4.**  $^1\text{H}$  NMR spectrum of **3** at  $-10^\circ\text{C}$  in  $\text{CD}_3\text{CN}$ .



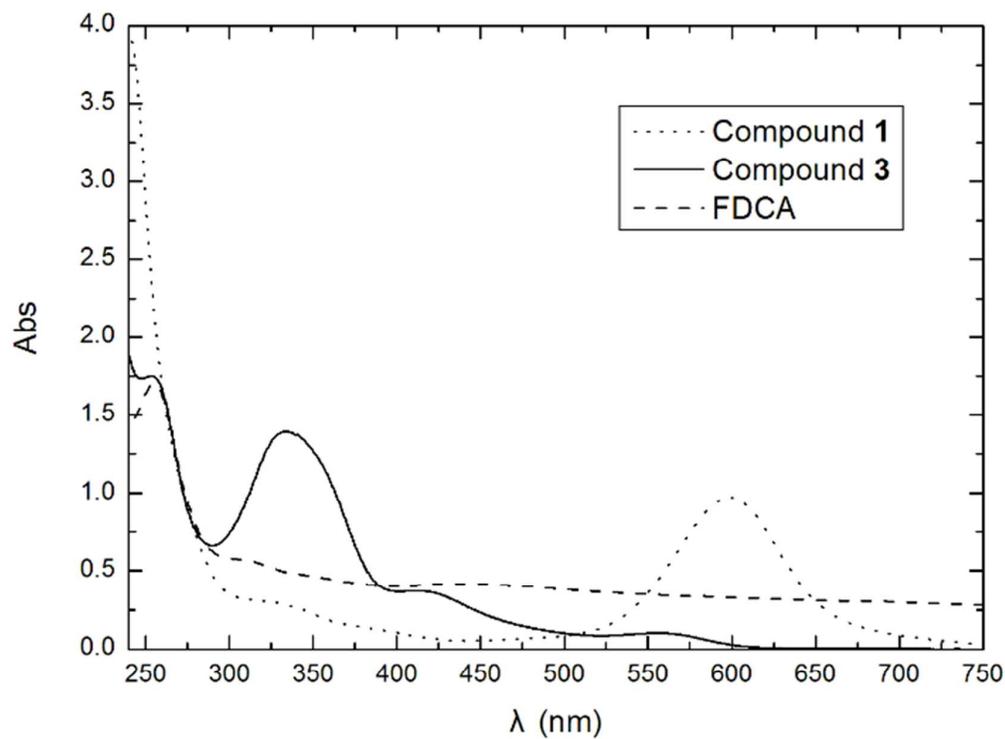
**Figure S5.** Variable-temperature <sup>1</sup>H NMR spectra of compound **3** in CD<sub>3</sub>CN at temperatures from +20 °C to -30 °C. The scrambling of the ferrocene (4.21-5.34 ppm) ligand can be stopped at around 0 °C.



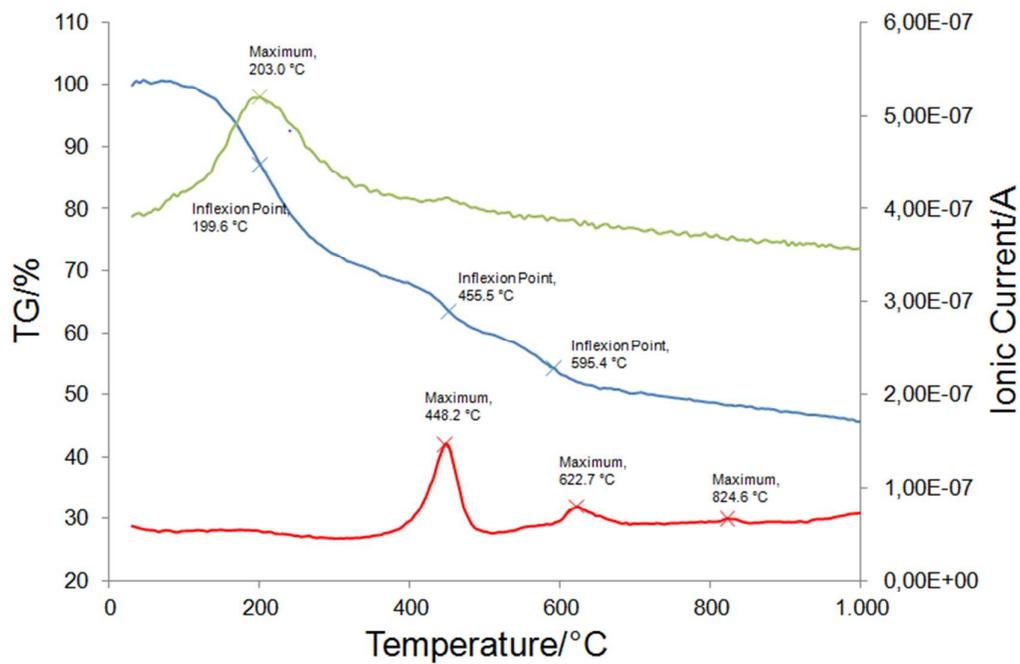
**Figure S6.** Variable-temperature  $^{11}\text{B}$  NMR spectra of compound **3** at temperatures from  $+20^\circ\text{C}$  to  $-30^\circ\text{C}$  in  $\text{CD}_3\text{CN}$ .



**Figure S7.** Variable-temperature  $^{19}\text{F}$  NMR spectra of compound **3** at temperatures from  $+20^\circ\text{C}$  to  $-30^\circ\text{C}$  in  $\text{CD}_3\text{CN}$ .



**Figure S8.** Absorption spectra of FDCA, **1** and **3** in CH<sub>3</sub>CN.



**Figure S9.** TGA (blue) and MS curves (green acetonitrile, red CO<sub>2</sub>) of compound **3**.

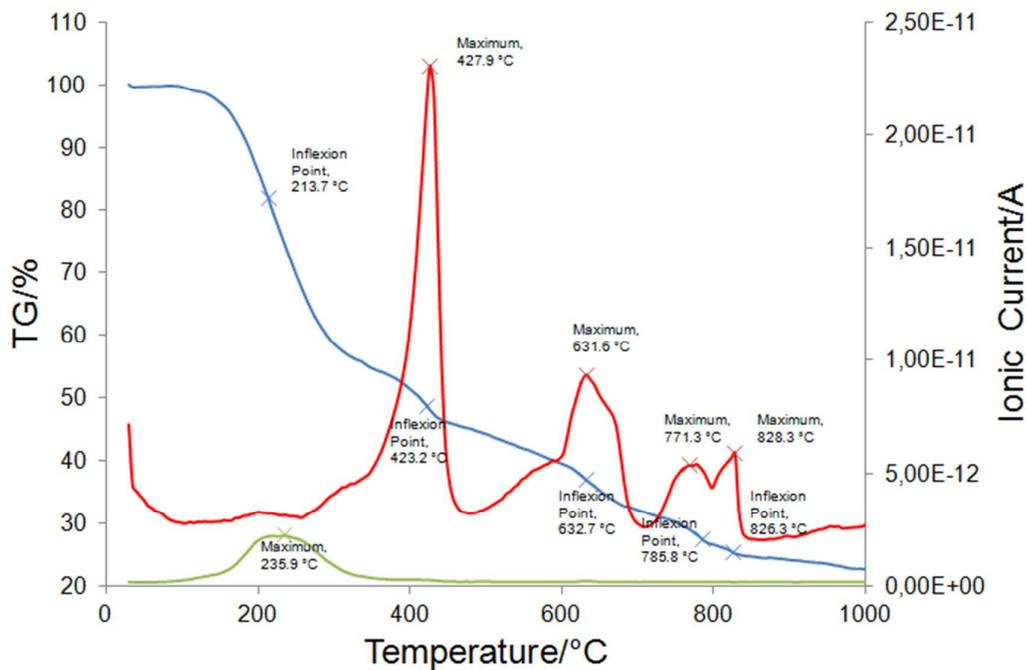


Figure S10. TGA (blue) and MS curves (green propionitrile, red CO<sub>2</sub>) of compound 4.

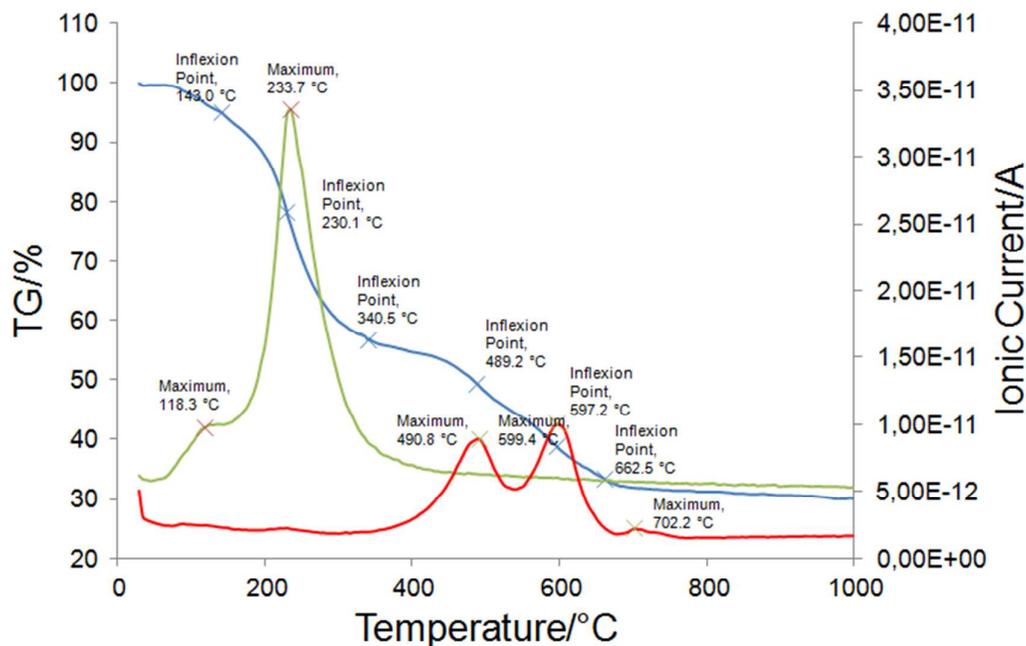
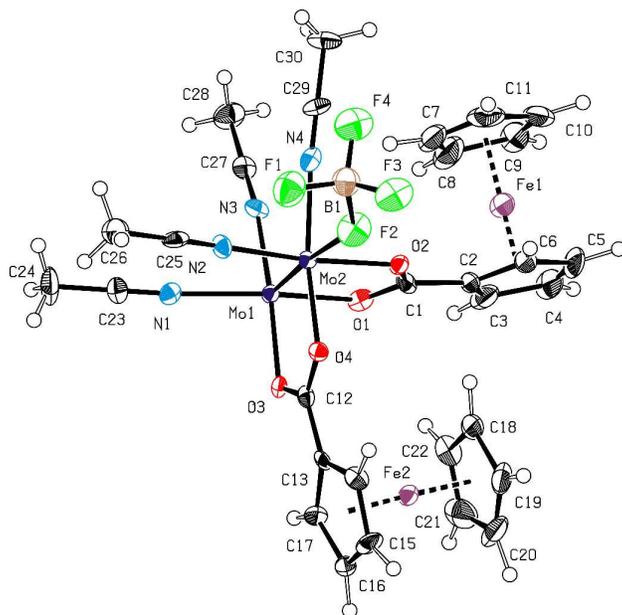


Figure S11. TGA (blue) and MS curves (green acetonitrile, red CO<sub>2</sub>) of compound 5.

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**Single Crystal X-Ray Structure Determination of Compound 2 and 5****General:**

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker APEX II,  $\kappa$ -CCD), a rotating anode (Bruker AXS, FR591) (compound **5**) or a fine-focussed sealed tube (compound **2**) with MoK $_{\alpha}$  radiation ( $\lambda = 0.71073$  Å), and a graphite monochromator by using the SMART software package. [1] The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a glass fiber and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT. [2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. [2] Space group assignments were based upon systematic absences,  $E$  statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX [7] based on SIR-92 [3], or SHELXLE [8] in conjunction with SHELXL-97 [5] (for compound **2**). Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing  $\Sigma w(F_o^2 - F_c^2)^2$  with SHELXL-97 [5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. [4] Images of the crystal structures were generated by PLATON. [6]

**Compound 2:** (CCDC 942543)**Figure S12** – Ortep drawing drawing of compound **2** with 50% ellipsoids. [6]

## Crystal Data

Formula	C <sub>30</sub> H <sub>30</sub> B F <sub>4</sub> Fe <sub>2</sub> Mo <sub>2</sub> N <sub>4</sub> O <sub>4</sub> , 2(C <sub>2</sub> H <sub>3</sub> N), B F <sub>4</sub>		
Formula Weight	1069.89		
Crystal System	Orthorhombic		
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	(No. 19)	
a, b, c [Angstrom]	9.3889 (2)	11.2996 (2)	44.7144 (8)
V [Ang**3]	4743.79 (16)		
Z	4		
D(calc) [g/cm**3]	1.498		
Mu(MoKa) [ /mm ]	1.186		
F(000)	2128		
Crystal Size [mm]	0.09 x 0.12 x 0.30		

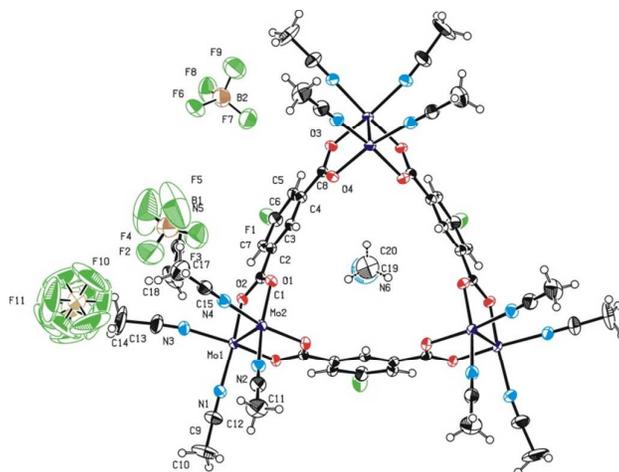
## Data Collection

Temperature (K)	123		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	1.8, 25.4		
Dataset	-11: 11 ; 0: 13 ; 0: 53		
Tot., Uniq. Data, R(int)	8658,	8658,	0.000
Observed data [I > 2.0 sigma(I)]	6891		

## Refinement

Nref, Npar	8658, 530
R, wR2, S	0.0524, 0.1182, 1.04
w = 1/[\s^2(Fo^2)+(0.0537P)^2+8.8786P] where P=(Fo^2+2Fc^2)/3	
Max. and Av. Shift/Error	0.00, 0.00
Flack x	0.0(5)
Min. and Max. Resd. Dens. [e/Å <sup>3</sup> ]	-0.91, 2.86

Due to physical meaningless ADP the ISOR-restraint was applied for the refinement of the B1 atom. The large positive residual electron density is located on the molybdenum-molybdenum bond, not unusual for the IAM-refinement of the metal-centers. The unit cell contains 5 methylene chloride molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[6]

**Compound 5:** (CCDC 904006)

**Figure S13** – Ortep drawing drawing of compound **5** with 50% ellipsoids. [6]

Operator:	*** Herdtweck ***
Molecular Formula:	C <sub>56</sub> H <sub>57</sub> B <sub>6</sub> F <sub>27</sub> Mo <sub>6</sub> N <sub>16</sub> O <sub>12</sub> [(C <sub>48</sub> H <sub>45</sub> F <sub>3</sub> Mo <sub>6</sub> N <sub>12</sub> O <sub>12</sub> ) <sup>6+</sup> ], [6(B F <sub>4</sub> ) <sup>-</sup> ], 4(C <sub>2</sub> H <sub>3</sub> N)
Crystal Color / Shape	Red fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.18 × 0.36 × 0.51 mm
Molecular Weight:	2299.80 a.m.u.
F <sub>000</sub> :	2252
Systematic Absences:	none

Space Group:	Trigonal	$P\bar{3}$	(I.T.-No.: 147)
Cell Constants:	Least-squares refinement of 9212 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $1.14^\circ < \theta < 25.41^\circ$ ; Mo(K $\bar{\alpha}$ ): $\lambda = 71.073$ pm		
	$a =$	2063.55(3) pm	$\alpha = 90^\circ$
	$b =$	2063.55(3) pm	$\beta = 90^\circ$
	$c =$	1366.58(2) pm	$\gamma = 120^\circ$
	$V = 5039.60(13) \cdot 10^6$ pm <sup>3</sup> ; $Z = 2$ ; $D_{\text{calc}} = 1.516$ g cm <sup>-3</sup> ; Mos. = 0.69		
Diffraction:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 40 kV; 30 mA; $\lambda = 71.073$ pm; Mo(K $\bar{\alpha}$ )		
Temperature:	(-150±1) °C;	(123±1) K	
Measurement Range:	$1.14^\circ < \theta < 25.41^\circ$ ; h: -24/24, k: -24/24, l: -16/16		
Measurement Time:	2 × 5 s per film		
Measurement Mode:	measured: 7 runs; 3969 films / scaled: 7 runs; 3969 films $\varphi$ - and $\omega$ -movement; Increment: $\Delta\varphi/\Delta\omega = 0.50^\circ$ ; dx = 50.0 mm		
LP - Correction:	Yes [2]		
Intensity Correction	No/Yes; during scaling [2]		
Absorption Correction:	Multi-scan; during scaling; $\mu = 0.826$ mm <sup>-1</sup> [2]		
	Correction Factors:	$T_{\text{min}} = 0.6490$	$T_{\text{max}} = 0.7452$
Removing solvent molecules	Besides the solvent molecule, well located in the difference Fourier maps, unresolved solvent molecules remained and had to be removed with the SQUEEZE procedure. [6]		
Reflection Data:	123391	reflections were integrated and scaled	
	123391	reflections to be merged	
	6214	independent reflections	
	0.022	$R_{\text{int}}$ : (basis $F_o^2$ )	
	6214	independent reflections (all) were used in refinements	
	5935	independent reflections with $I_o > 2\sigma(I_o)$	
	100 %	completeness of the data set	
	398	parameter full-matrix refinement	
	15.6	reflections per parameter	
Solution:	Direct Methods [3, 7]; Difference Fourier syntheses		
Refinement Parameters:	In the asymmetric unit:		
	41	Non-hydrogen atoms with anisotropic displacement parameters	
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ( $d_{\text{C-H}} = 95, 98$ pm). Isotropic		

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	displacement parameters were calculated from the parent carbon atom ( $U_H = 1.2/1.5 U_C$ ). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4, 5, 7]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a*P)^2 + b*P$ with a: 0.0593; b: 21.0221; P: $[\text{Maximum}(0 \text{ or } F_o^2) + 2*F_c^2]/3$	
Shift/Err:	Less than 0.001 in the last cycle of refinement	
Resid. Electron Density:	+2.18 e <sub>0</sub> <sup>-</sup> /Å <sup>3</sup> ; -0.91 e <sub>0</sub> <sup>-</sup> /Å <sup>3</sup>	
R1:	$\Sigma( F_o  -  F_c ) / \Sigma F_o $	
[ $F_o > 4\sigma(F_o)$ ; N=5935]:	0.0437	=
[all reflctns; N=6214]:	0.0450	=
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	
[ $F_o > 4\sigma(F_o)$ ; N=5935]:	0.1199	=
[all reflctns; N=6214]:	0.1207	=
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO} - \text{NV})]^{1/2}$	=
	1.063	
Remarks:	Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$	

### References:

- [1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- [2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- [3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli M. "SIR92", *J. Appl. Cryst.* **1994**, *27*, 435-436.
- [4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.
- [5] Sheldrick, G. M. "SHELXL-97", University of Göttingen, Göttingen, Germany, (1998).
- [6] Spek, A. L. "PLATON", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).
- [7] L. J. Farrugia, "WinGX (Version 1.70.01 January 2005)", *J. Appl. Cryst.* **1999**, *32*, 837-838.
- [8] Huebschle, C. B., Sheldrick, G. M. & Dittrich, B. "SHELXLE", *J. Appl. Cryst.* **2011**, *44*, 1281-1284.