

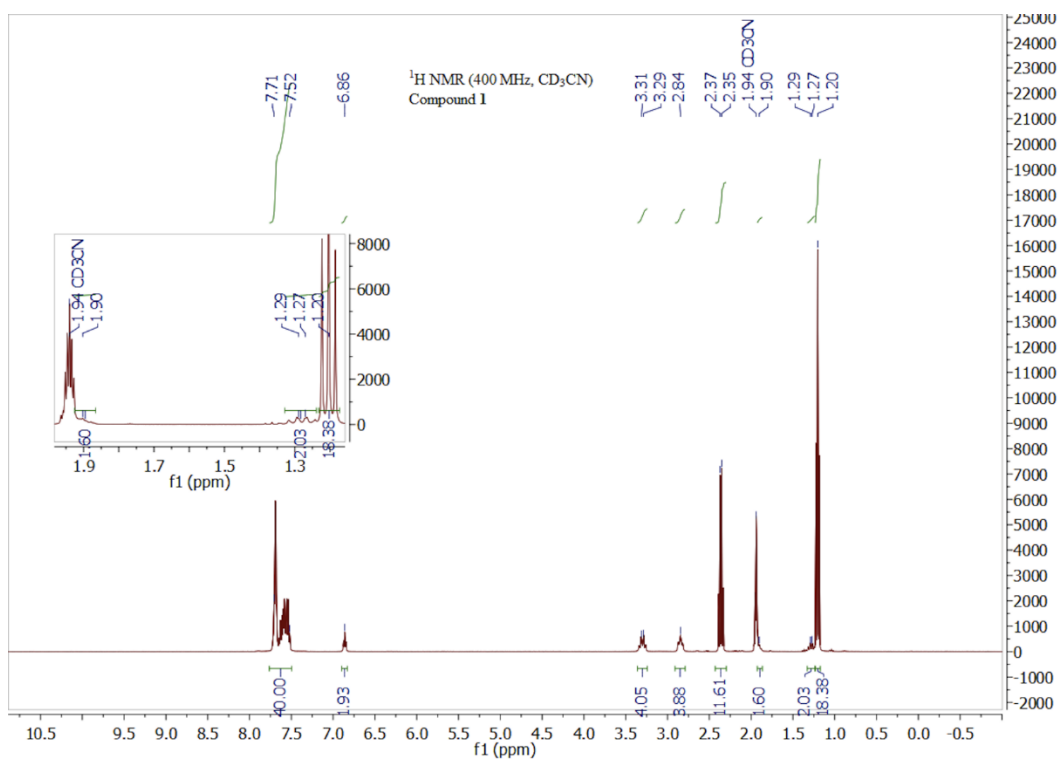
# Supporting Information for

## Loop Shaped Dicarboxylate-bridged Dimolybdenum(II) Bisphosphine Compounds – a Rational Synthesis

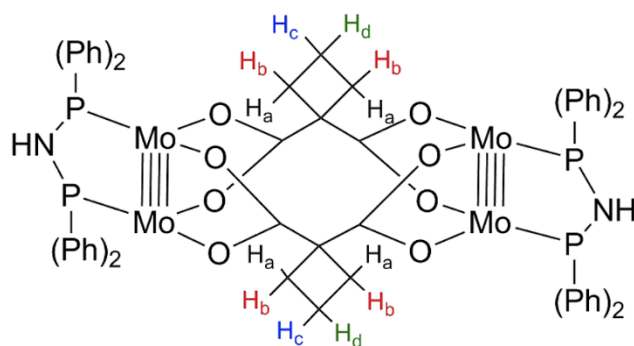
*Dominik Höhne, Eberhardt Herdtweck, Alexander Pöthig and Fritz. E. Kühn\**

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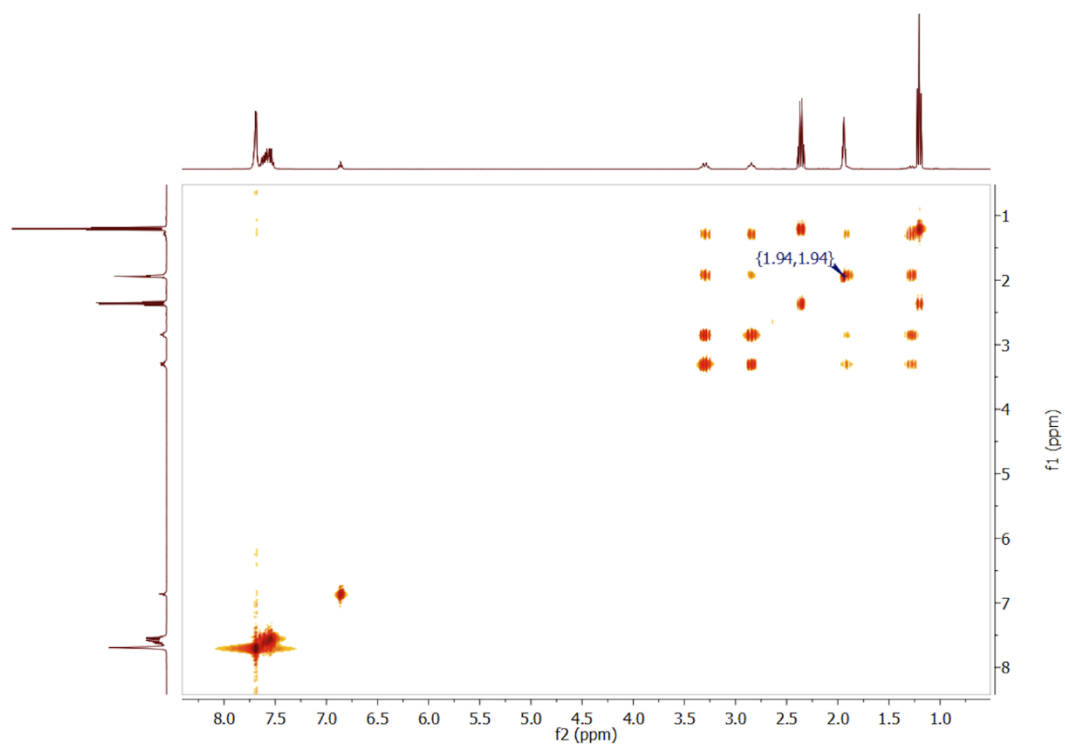
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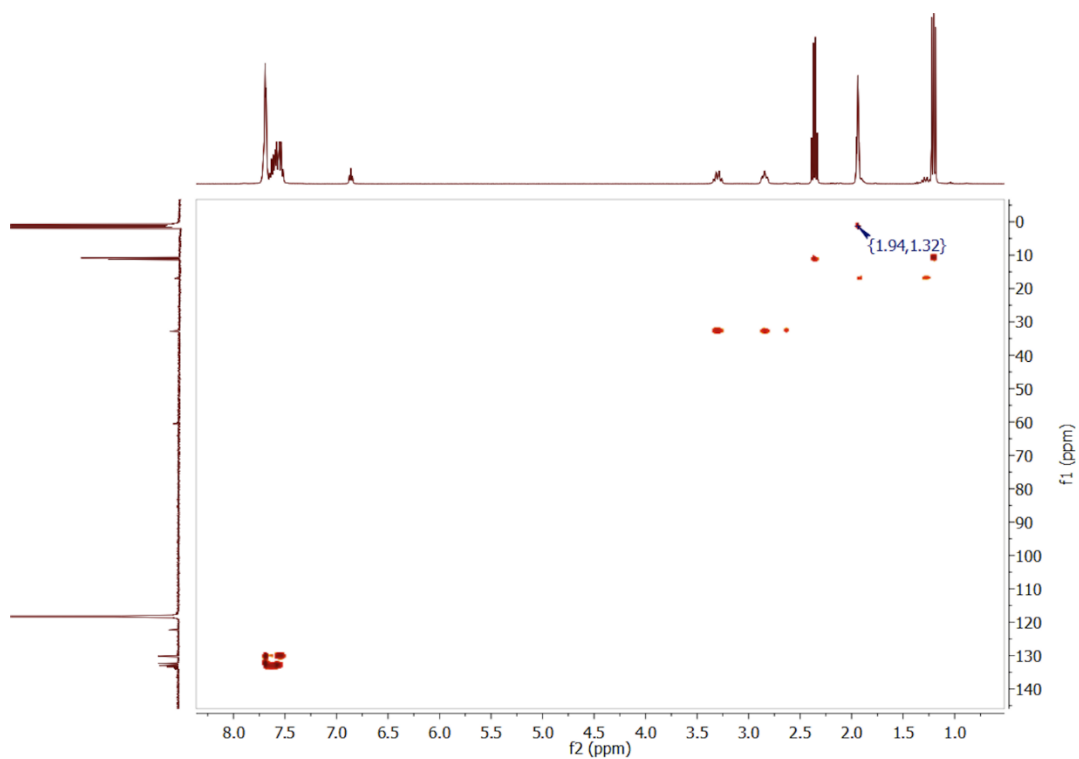
**Fig. S1** <sup>1</sup>H NMR spectrum of **2** in CD<sub>3</sub>CN.



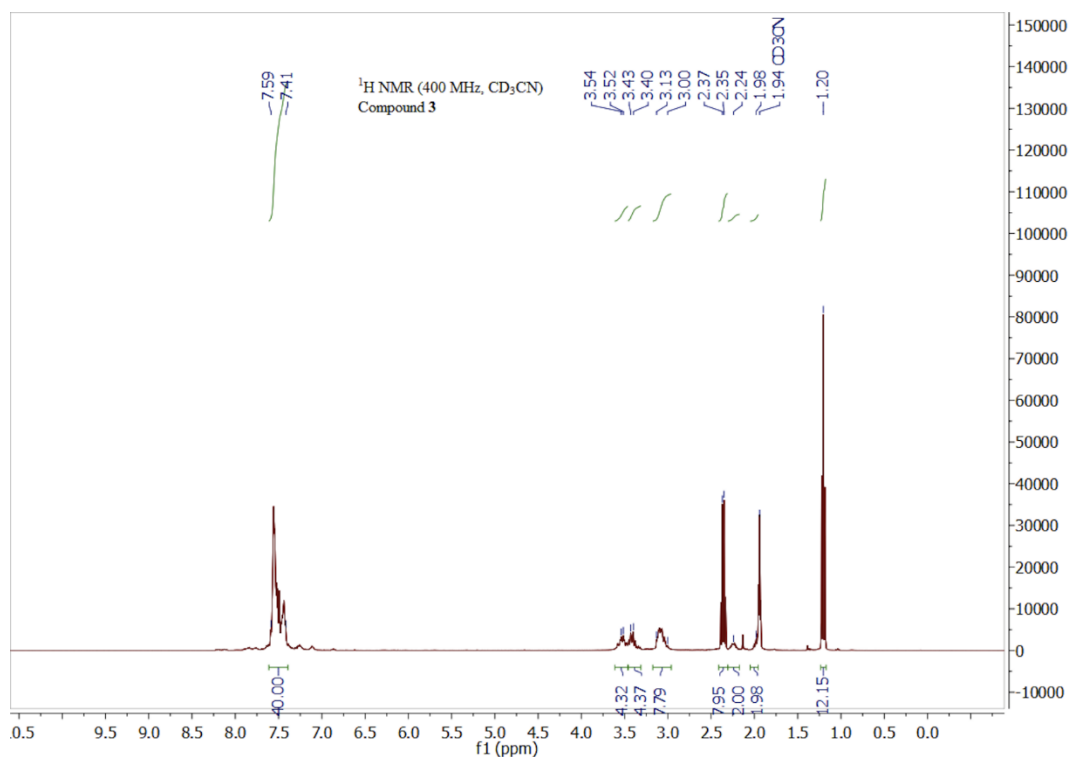
**Fig. S2** Different proton species of the cyclobutane rings in **2**.



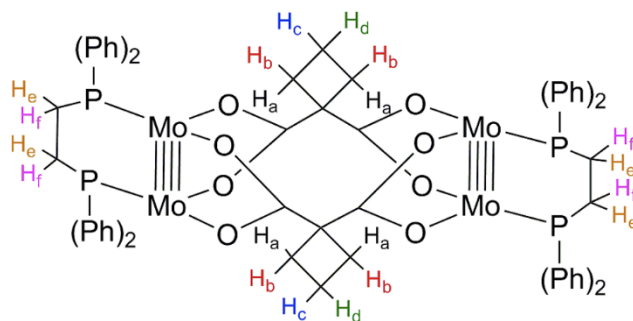
**Fig. S3** COSY spectrum of **2** in CD<sub>3</sub>CN.



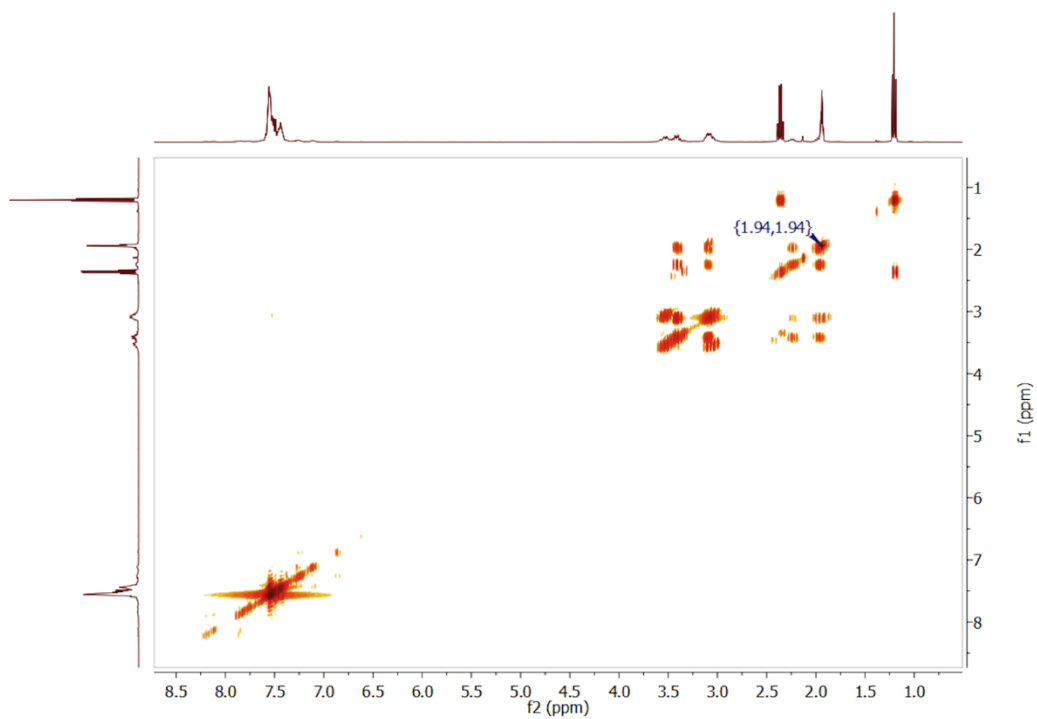
**Fig. S4** HSQC spectrum of **2** in CD<sub>3</sub>CN.



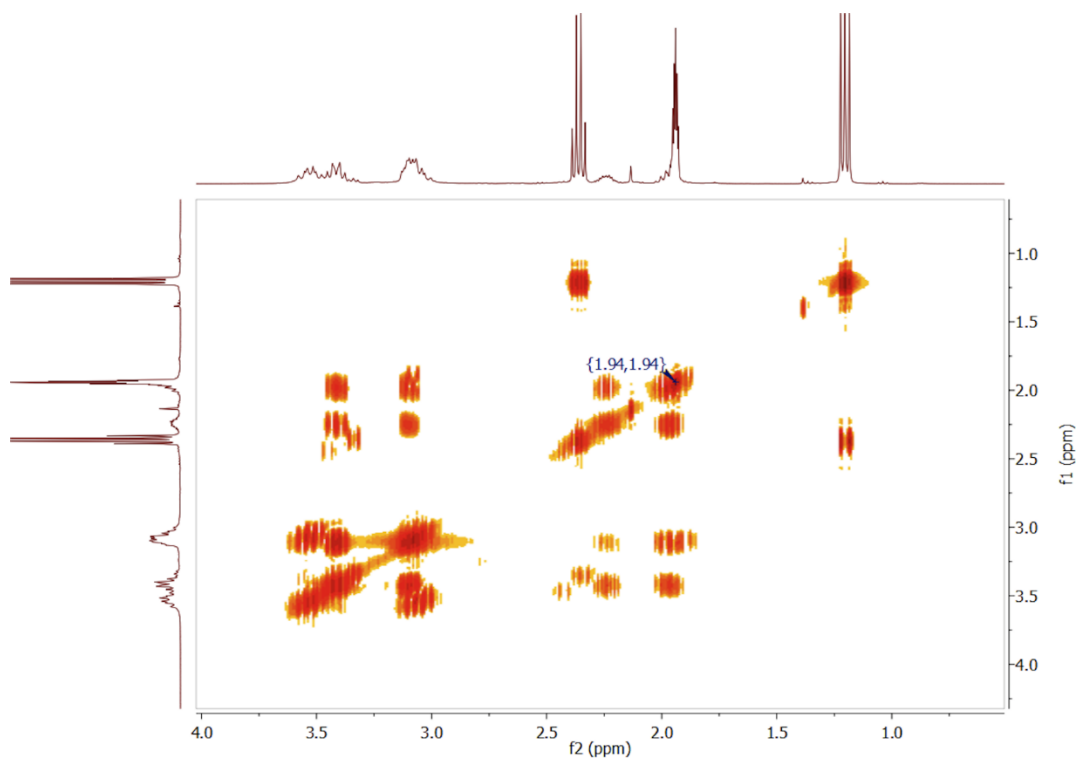
**Fig. S5** <sup>1</sup>H NMR spectrum of **3** in CD<sub>3</sub>CN.



**Fig. S6** Different proton species of the cyclobutane rings and the ethylene bridges in **3**.



**Fig. S7** COSY spectrum of **3** in CD<sub>3</sub>CN.



**Fig. S8** Excerpt of the COSY spectrum of **3** in CD<sub>3</sub>CN.

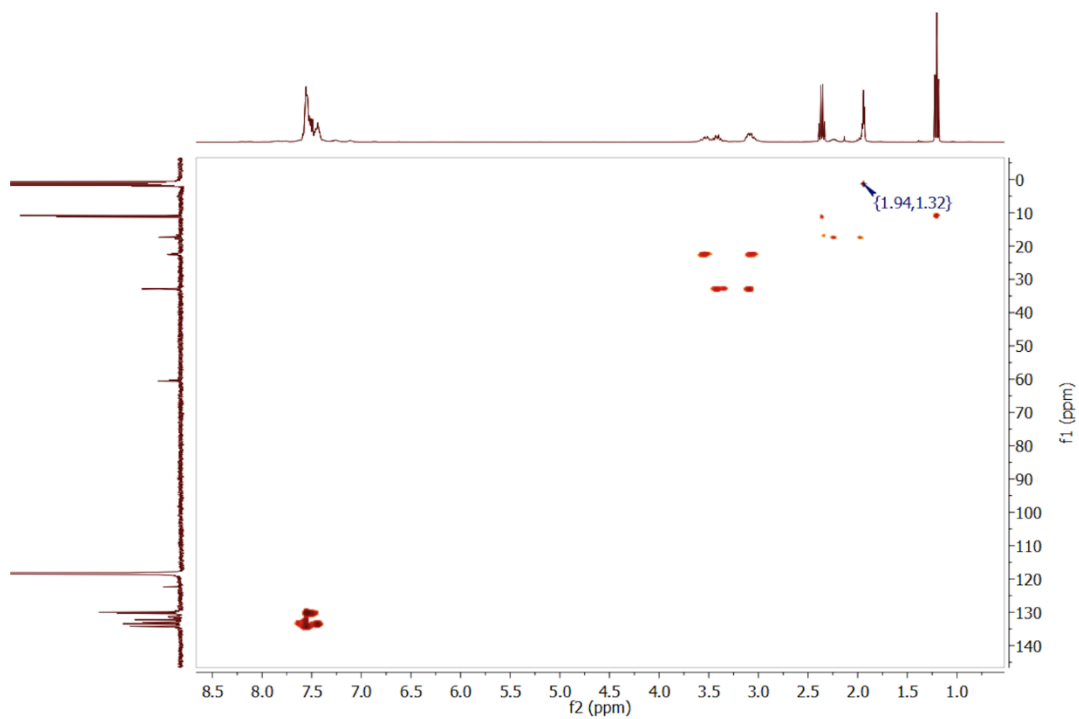


Fig. S9 HSQC spectrum of 3 in CD<sub>3</sub>CN.

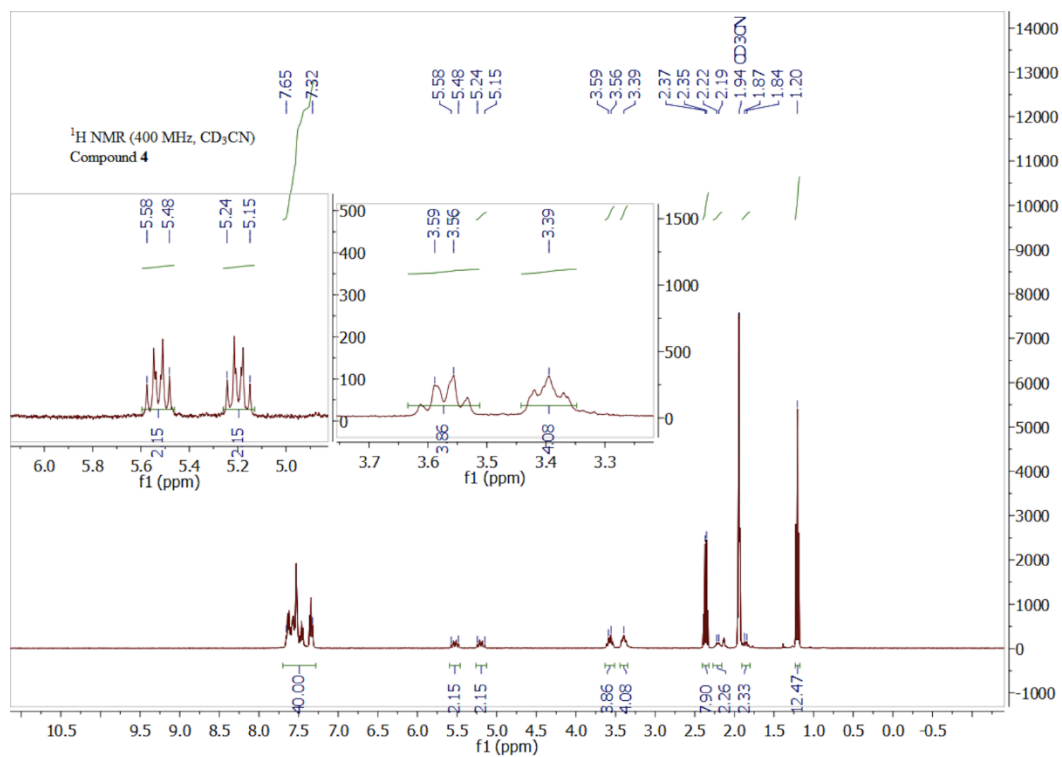
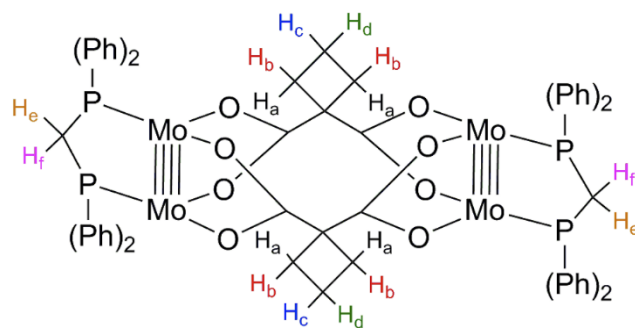
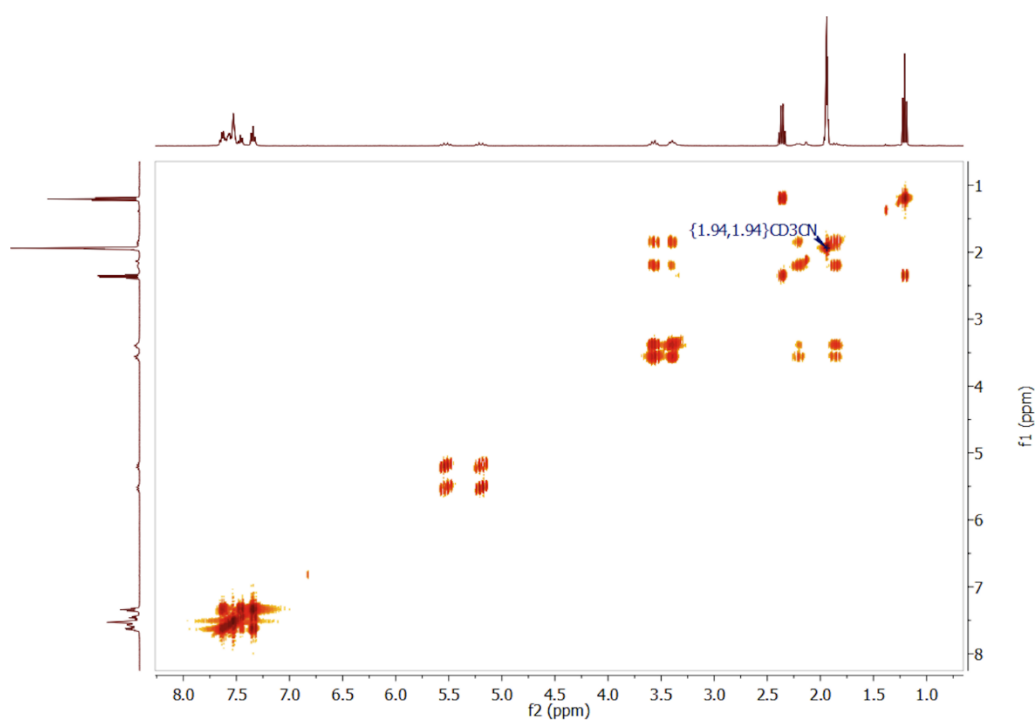


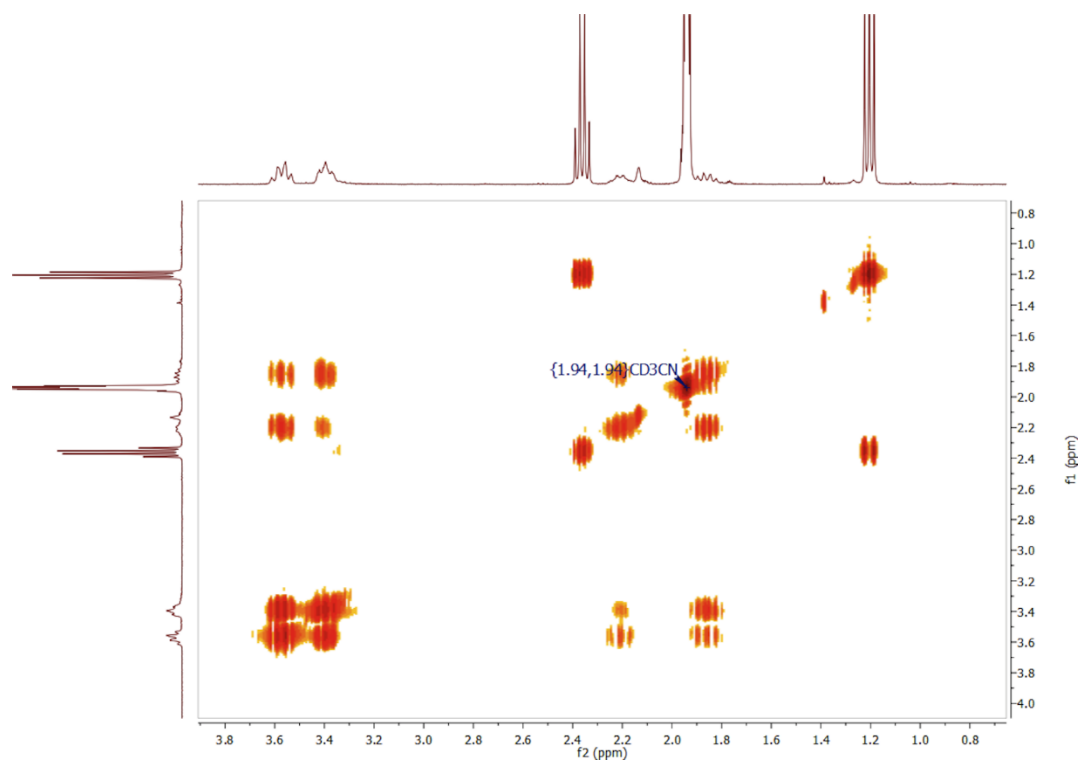
Fig. S10 <sup>1</sup>H NMR spectrum of 4 in CD<sub>3</sub>CN.



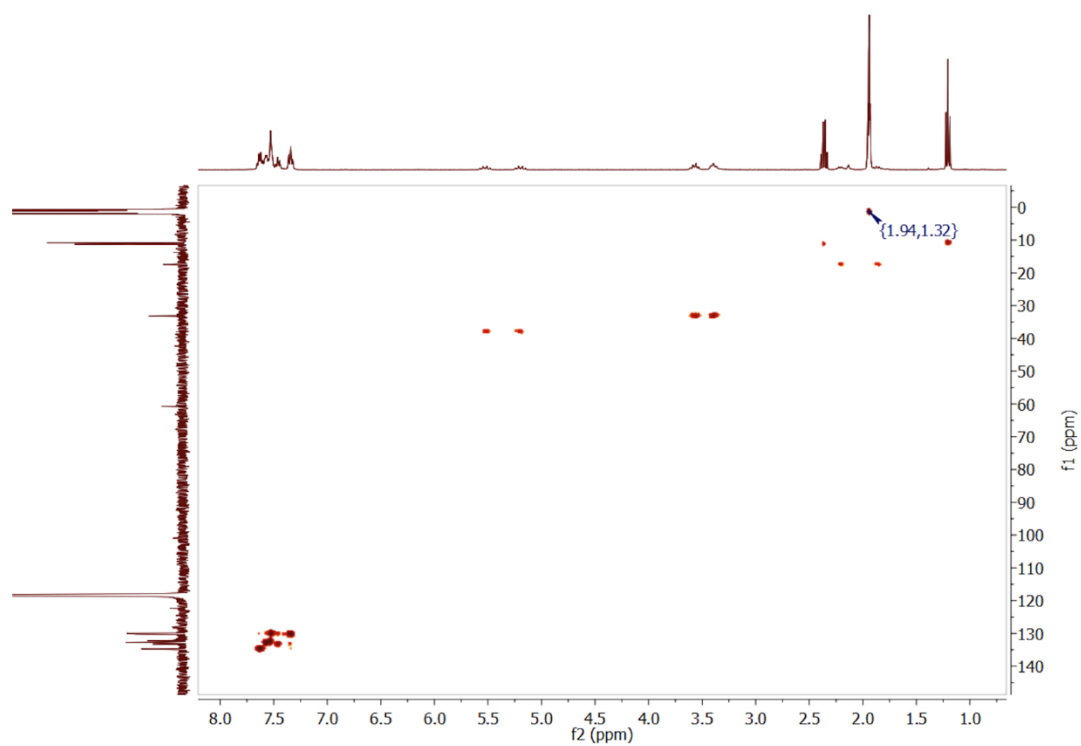
**Fig. S11** Different proton species of the cyclobutane rings and the methylene bridges in **4**.



**Fig. S12** COSY spectrum of **4** in CD<sub>3</sub>CN.

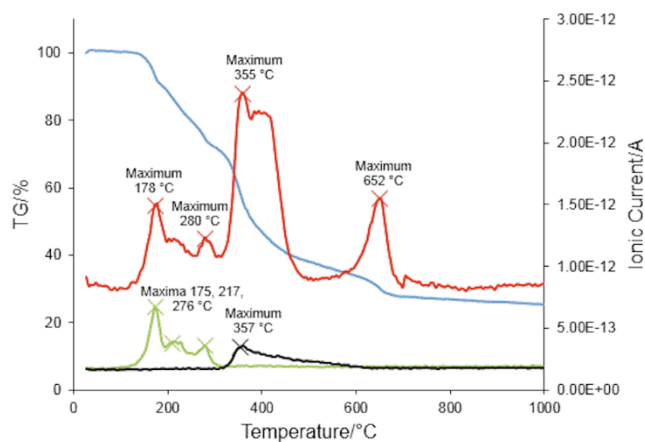


**Fig. S13** Excerpt of the COSY spectrum of **4** in CD<sub>3</sub>CN.

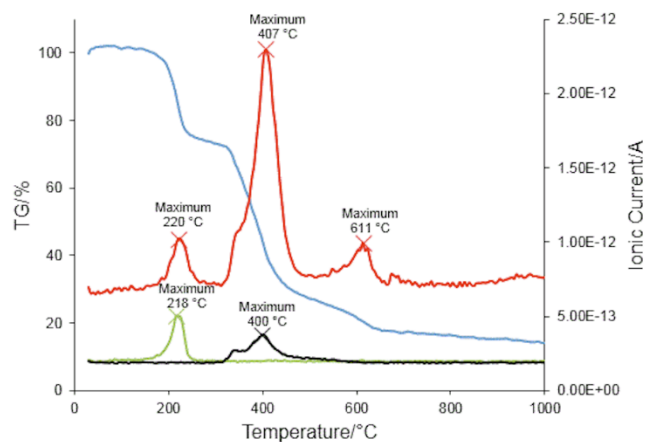


**Fig. S14** HSQC spectrum of **4** in CD<sub>3</sub>CN.





**Fig. S15** TGA (blue) and MS curves (green for propionitrile, red for CO<sub>2</sub> and black for phenyl group) of compound 2.



**Fig. S16** TGA (blue) and MS curves (green for propionitrile, red for CO<sub>2</sub> and black for phenyl group) of compound 3.

## Single Crystal X-Ray Structure Determination of Compounds 2, and 3

### **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) with MoK $_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), and a graphite monochromator by using the SMART software package. [1] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a cactus prickly (Opuntia ficus-india) and transferred to the diffractometer. The crystals were 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 [3a] or SIR-97 [3b] in conjunction with SHELXL-97 [5]. Unless otherwise noticed, methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of  $0.98 \text{ \AA}$  and  $U_{\text{iso(H)}} = 1.5 \cdot U_{\text{eq(C)}}$ . Other H atoms were placed in calculated positions and refined using a riding model, with aromatic C–H distances of  $0.95 \text{ \AA}$  and with methylene C–H distances of  $0.99 \text{ \AA}$ , and  $U_{\text{iso(H)}} = 1.2 \cdot U_{\text{eq(C)}}$ . For compound **2** the N–H distances was fixed to  $0.88 \text{ \AA}$  and  $U_{\text{iso(H)}} = 1.2 \cdot U_{\text{eq(N)}}$ . If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  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]

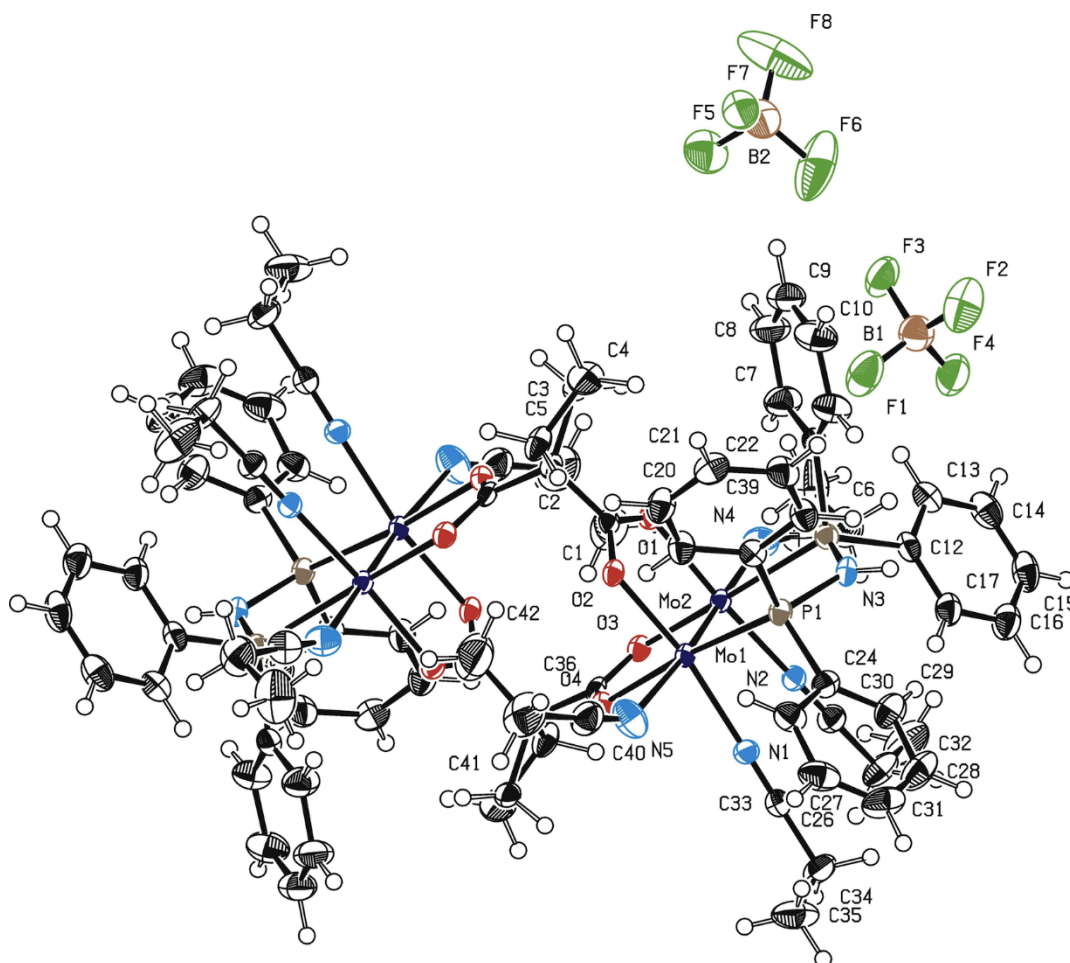
### **Special:**

**2:** As all crystals appeared to be twinned, two components were identified using CELL NOW [8]. The data were integrated using two domains (domain 1 and 2 each 50.0% and unit cell relationships  $a' = -a$ ;  $b'=b$ ;  $c'=-c$ ) and scaled using TWINABS. [9] Absorption corrections, including odd and even ordered spherical harmonics were

performed using TWINABS. HKLF4 was used for solution, HKLF5 for structure refinement.

3: Full refinement was possible without running into problems.

### Compound 2



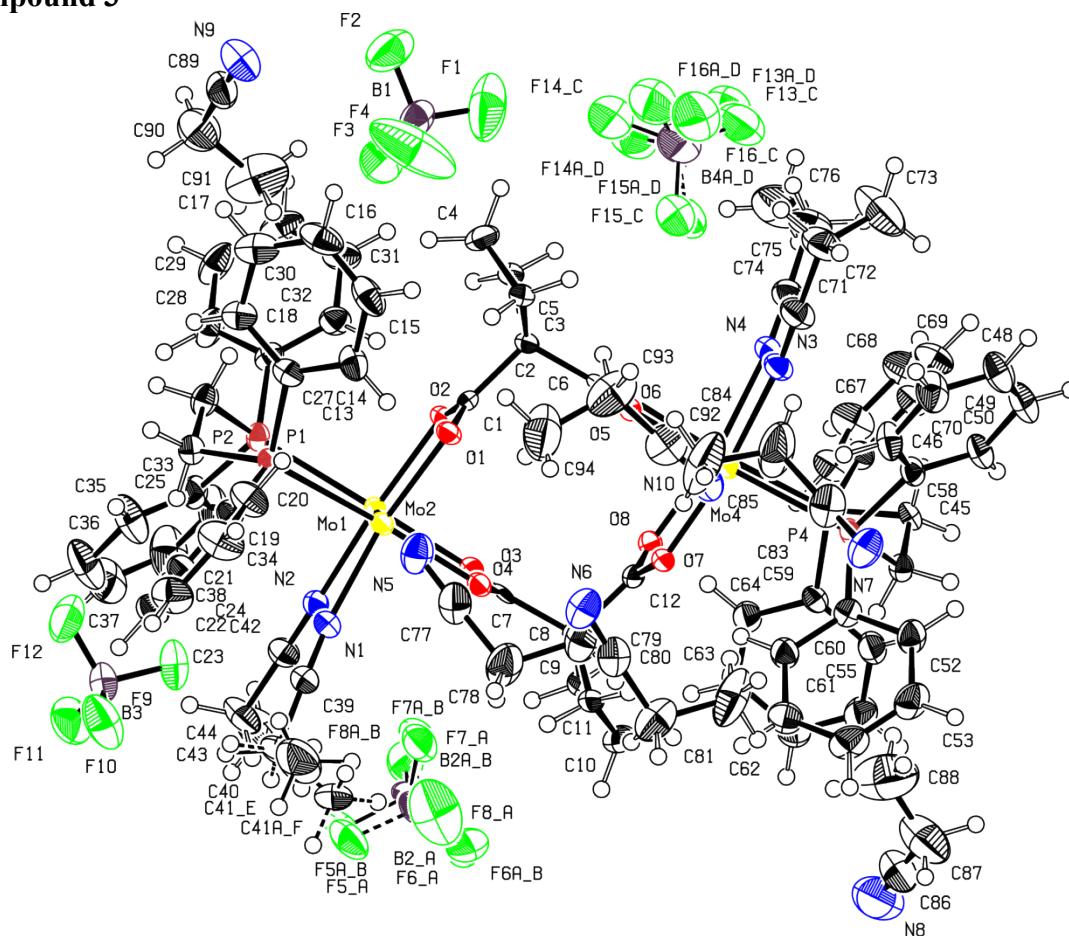
**Fig. F1** – Ortep drawing of compound 2 with 50% ellipsoids. [6]

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{84} H_{94} B_4 F_{16} Mo_4 N_{10} O_8 P_4$ $[(C_{84} H_{94} Mo_4 N_{10} O_8 P_4)^{4+}], 4[(B F_4)^-]$
Crystal Color / Shape	Red fragment
Crystal Size	Approximate size of crystal fragment used for data collection: $0.18 \times 0.38 \times 0.51$ mm
Molecular Weight:	2226.57 a.m.u.
$F_{000}$ :	2248
Systematic Absences:	$h0l: l \neq 2n; 0k0: k \neq 2n$
Space Group:	Monoclinic $P 2_1/c$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9487 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range $1.25^\circ < \theta < 25.47^\circ$ ; $Mo(K\alpha)$ ; $\lambda = 0.71073 \text{ \AA}$

$a = 18.183(2) \text{ \AA}$   
 $b = 15.535(2) \text{ \AA}$        $\beta = 116.427(3)^\circ$   
 $c = 18.873(2) \text{ \AA}$   
 $V = 4774.0(10) \cdot 10^6 \text{ pm}^3$ ;  $Z = 2$ ;  $D_{\text{calc}} = 1.549 \text{ g cm}^{-3}$ ;  $Mos. = 0.66$   
 Diffractometer: Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA;  $\lambda = 0.71073 \text{ \AA}$ ; Mo(K $\bar{\alpha}$ )  
 Temperature:  $(-150 \pm 1)^\circ\text{C}$ ;  $(123 \pm 1) \text{ K}$   
 Measurement Range:  $1.25^\circ < \theta < 25.47^\circ$ ; h: -21/19, k: 0/18, l: 0/22  
 Measurement Time:  $2 \times 5 \text{ s per film}$   
 Measurement Mode: measured: 10 runs; 5011 films / scaled: 10 runs; 5011 films  
 $\phi$ - and  $\omega$ -movement; Increment:  $\Delta\phi/\Delta\omega = 0.50^\circ$ ; dx = 100.0 mm  
 LP - Correction: Yes [2]  
 Intensity Correction: No/Yes; during scaling [2]  
 Absorption Correction: Multi-scan; during scaling;  $\mu = 0.669 \text{ mm}^{-1}$  [2]  
 Correction Factors:  $T_{\text{min}} = 0.5812$        $T_{\text{max}} = 0.7452$   
 Reflection Data: 16083 reflections were integrated and scaled  
 576 reflections systematic absent and rejected  
 15507 reflections to be merged  
 8832 independent reflections  
 0.047  $R_{\text{int}}$ : (basis  $F_o^2$ )  
 15507 reflections (all) were used in **HKLF5** refinements  
 14292 independent reflections with  $I_o > 2\sigma(I_o)$   
 99.8 % completeness of the data set  
 585 parameter full-matrix refinement  
 26.5 reflections per parameter  
 Solution: Direct Methods [3a]; Difference Fourier syntheses  
 Refinement Parameters: In the asymmetric unit:  
 65 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 ( $d_{\text{C-H}} = 0.95, 0.98, 0.99 \text{ \AA}$ ;  $d_{\text{N-H}} = 0.88 \text{ \AA}$ ). Isotropic displacement parameters were calculated from the parent carbon atom ( $U_{\text{H}} = 1.2/1.5 U_{\text{C}}$ ;  $U_{\text{H}} = 1.2 U_{\text{N}}$ ). The hydrogen atoms were included in the structure factor calculations but not refined.  
 Atomic Form Factors: For neutral atoms and anomalous dispersion [4]  
 Extinction Correction: no  
 Weighting Scheme:  $w^{-1} = \sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P$   
 with a: 0.0657; b: 5.8818; P:  $[\text{Maximum}(0 \text{ or } F_o^2) + 2 \cdot F_c^2]/3$   
 Shift/Err: Less than 0.001 in the last cycle of refinement:  
 Resid. Electron Density:  $+1.07 \text{ eError!/\AA}^3$ ;  $-0.65 \text{ eError!/\AA}^3$   
 R1:  $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$   
 $[F_o > 4\sigma(F_o)$ ; N=14292]: = 0.0361  
 $[\text{all reflctns}$ ; N=15507]: = 0.0389  
 R2:  $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

$[F_o > 4\sigma(F_o); N=14292]:$  = 0.1008  
 [all refltns; N=15507]: = 0.1036  
 Goodness of fit:  $[\Sigma w(F_o^2 - F_c^2)^2 / (\text{NO} - \text{NV})]^{1/2}$  = 1.034  
 Remarks: Refinement expression  $\Sigma w(F_o^2 - F_c^2)^2$

### Compound 3



**Fig. F2** – Ortep drawing of compound 3 with 50% ellipsoids. [6]

Operator: \*\*\* Herdtweck \*\*\*  
 Molecular Formula:  $C_{94} H_{110} B_4 F_{16} Mo_4 N_{10} O_8 P_4$   
 $[(C_{76} H_{80} Mo_4 N_4 O_8 P_4)^{4+}], 4[(B F_4)^-], 6(C_3 H_5 N)$   
 Crystal Color / Shape: Red prism  
 Crystal Size: Approximate size of crystal fragment used for data collection:  
 $0.20 \times 0.21 \times 0.34$  mm  
 Molecular Weight: 2362.81 a.m.u.  
 $F_{000}$ : 2400  
 Systematic Absences: none  
 Space Group: Triclinic  $P \bar{1}$  (I.T.-No.: 2)  
 Cell Constants: Least-squares refinement of 9004 reflections with the programs  
 "APEX suite" and "SAINT" [1,2]; theta range  $0.86^\circ < \theta < 25.44^\circ$ ;  
 $Mo(K\alpha)$ ;  $\lambda = 0.71073 \text{ \AA}$   
 $a = 12.4049(5) \text{ \AA}$   $\alpha = 74.092(2)^\circ$   
 $b = 18.0187(7) \text{ \AA}$   $\beta = 88.172(2)^\circ$

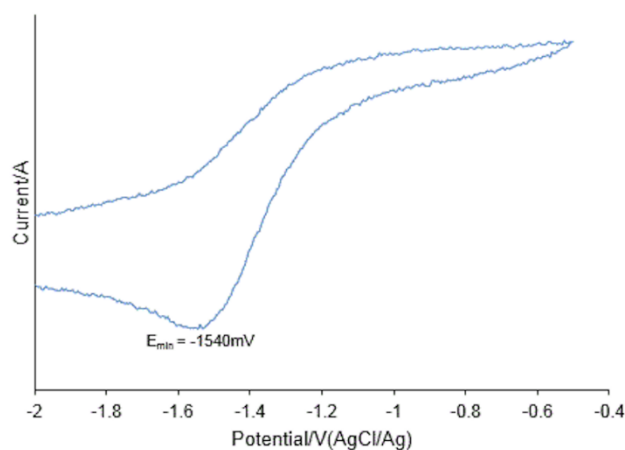
$c = 24.6268(10) \text{ \AA}$       $\gamma = 81.785(2)^\circ$   
 $V = 5239.3(4) \text{ \AA}^3$ ;  $Z = 2$ ;  $D_{\text{calc}} = 1.498 \text{ g cm}^{-3}$ ;  $Mos. = 0.77$   
 Diffractometer: Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA;  $\lambda = 0.71073 \text{ \AA}$ ; Mo(K $\alpha$ )  
 Temperature:  $(-150 \pm 1)^\circ\text{C}$ ;  $(123 \pm 1) \text{ K}$   
 Measurement Range:  $0.86^\circ < \theta < 25.44^\circ$ ; h: -14/14, k: -21/21, l: -29/29  
 Measurement Time:  $2 \times 10 \text{ s per film}$   
 Measurement Mode: measured: 12 runs; 3229 films / scaled: 12 runs; 3229 films  $\varphi$ - and  $\omega$ -movement; Increment:  $\Delta\varphi/\Delta\omega = 0.50^\circ$ ;  $dx = 60.0 \text{ mm}$   
 LP - Correction: Yes [2]  
 Intensity Correction: No/Yes; during scaling [2]  
 Absorption Correction: Multi-scan; during scaling;  $\mu = 0.614 \text{ mm}^{-1}$  [2]  
 Correction Factors:  $T_{\text{min}} = 0.6351$       $T_{\text{max}} = 0.7452$   
 Reflection Data: 92311 reflections were integrated and scaled  
 9 obvious wrong intensity and rejected (two hkl)  
 92302 reflections to be merged  
 19172 independent reflections  
 0.049  $R_{\text{int}}$ : (basis  $F_o^2$ )  
 19172 independent reflections (all) were used in refinements  
 15071 independent reflections with  $I_o > 2\sigma(I_o)$   
 99.1 % completeness of the data set  
 1281 parameter full-matrix refinement  
 15.0 reflections per parameter  
 Solution: Direct Methods [3b]; Difference Fourier syntheses  
 Refinement Parameters: In the asymmetric unit:  
 141 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 ( $d_{\text{C-H}} = 0.95, 0.98, 0.99 \text{ \AA}$ ). Isotropic displacement parameters were calculated from the parent carbon atom ( $U_{\text{H}} = 1.2/1.5 U_{\text{C}}$ ). The hydrogen atoms were included in the structure factor calculations but not refined.  
 Atomic Form Factors: For neutral atoms and anomalous dispersion [4]  
 Extinction Correction: no  
 Weighting Scheme:  $w^{-1} = \sigma^2(F_o^2) + (a * P)^2 + b * P$   
 with a: 0.0463; b: 26.3199; 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:  $+2.07 \text{ eError!/\AA}^3$ ;  $-1.46 \text{ eError!/\AA}^3$   
 R1:  $\sum(|F_o| - |F_c|) / \sum|F_o|$   
 [ $F_o > 4\sigma(F_o)$ ; N=15071]: = 0.0533  
 [all refltns; N=19172]: = 0.0717  
 wR2:  $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$   
 [ $F_o > 4\sigma(F_o)$ ; N=15071]: = 0.1247  
 [all refltns; N=19172]: = 0.1408

Goodness of fit:  $[\sum w(F_o^2 - F_c^2)^2 / (\text{NO} - \text{NV})]^{1/2} = 1.066$   
Remarks: Refinement expression  $\sum w(F_o^2 - F_c^2)^2$

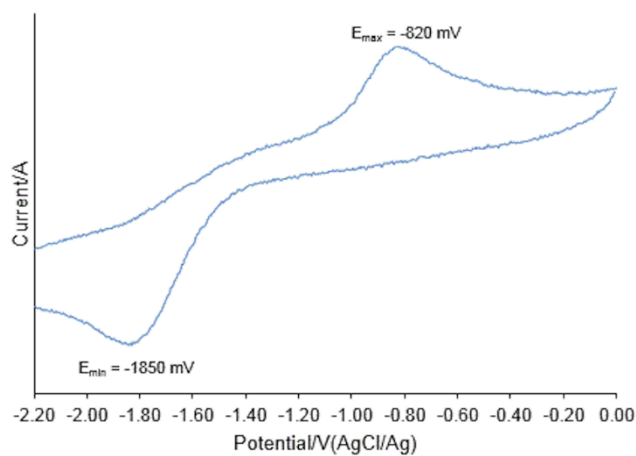
**References:**

- [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).
- [3a] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. "SIR92", *J. Appl. Crystallogr.* **1994**, 27, 435-436.
- [3b] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni A. G. G.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. "SIR97", A New Tool for Crystal Structure Determination and Refinement; *J. Appl. Crystallogr.* **1999**, 32, 115-119.
- [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. Crystallogr.* **1999**, 32, 837-838.
- [8] CELL NOW, Version 2008-2. Bruker AXS Inc., Madison, Wisconsin (USA) **2008**
- [9] SAINT, Version 8.27b and TWINABS (version 2012/1). Bruker AXS Inc., Madison, Wisconsin (USA) **2012**.

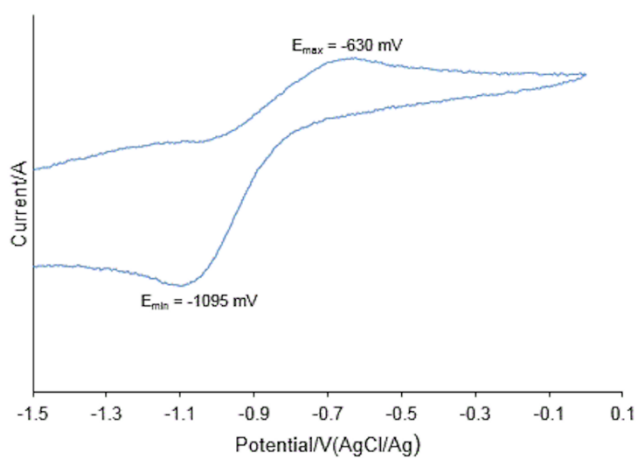
**Cyclic voltammograms of 2-4 and parameters of CV measurements**



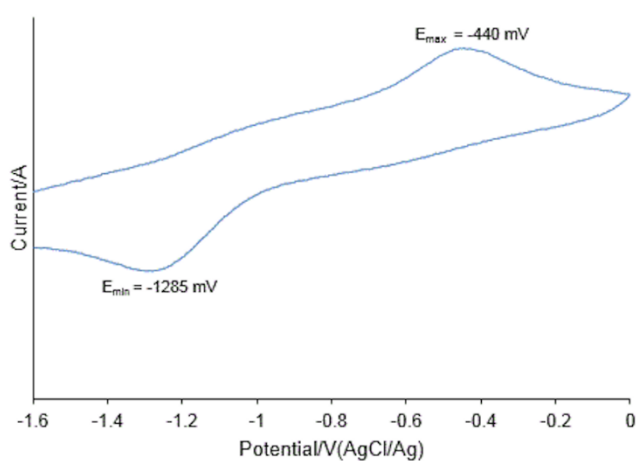
**Fig. S17** Cyclic voltammogram of compound **2** (scan rate: 100 mV/s).



**Fig. S18** Cyclic voltammogram of compound **2** (scan rate: 1000 mV/s).

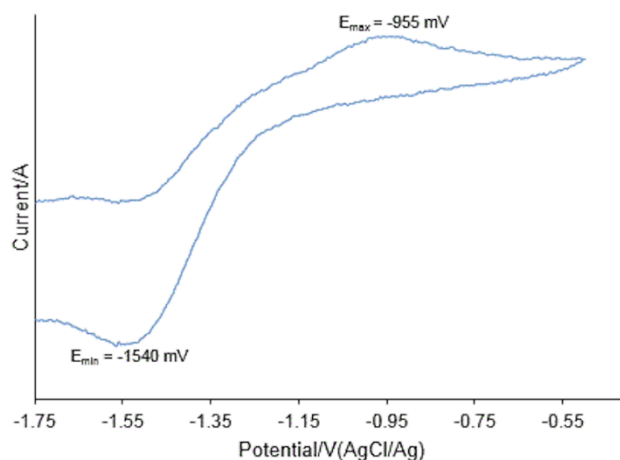


**Fig. S19** Cyclic voltammogram of compound **3** (scan rate: 100 mV/s).

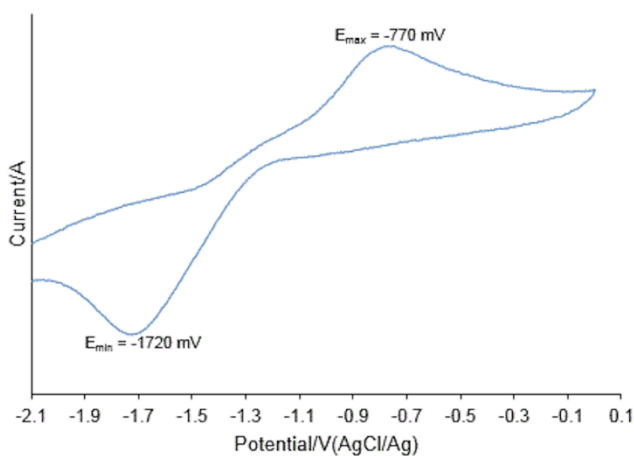


**Fig. S20** Cyclic voltammogram of compound **3** (scan rate: 1000 mV/s).





**Fig. S21** Cyclic voltammogram of compound **4** (scan rate: 100 mV/s).



**Fig. S22** Cyclic voltammogram of compound **4** (scan rate: 1000 mV/s).

CV measurements of complexes **2-4** were carried out on a Gamry potentiostat using a three-electrode cell. The working electrode was a platinum electrode (1 mm diameter), which was polished before each measurement. As a counter electrode, a Pt/Ti electrode was utilized. The potential was measured against Ag/AgCl with a scan rate of 100 and 1000 mV/s, respectively.  $[\text{Bu}_4\text{N}][\text{BF}_4]$  was used as electrolyte (0.025 mol/L in dry and degassed MeCN) and the concentration of the complexes was around  $0.25 \times 10^{-3}$  mol/L.

For all complexes **2-4** a reversible oxidation/reduction process can be excluded since, amongst others, the following requirements for a reversible process do not apply [10]:

1. For a one electron process  $\Delta E = E^A - E^C = 59$  mV
2. The position of the peak maxima  $E_p$  is independent of the scan rate  $v$

**Reference:**

- [10] R. Greef, R. Peat, L. M. Peter, D. Pletcher, J. Robinson, in *Instrumental Methods in Electrochemistry*, ed. T. J. Kemp, Ellis Horwood Limited, Halsted Press, Chichester/New York, 1985.