

## Supplementary Information

### Self-assembly of gold(I) with diphosphine and bitopic nitrogen donor linkers in the presence of trifluoroacetate anion: Formation of coordination polymer versus discrete macrocycle

Andrea Deák,<sup>\*a</sup> Tünde Tunyogi,<sup>a</sup> Gábor Tárkányi,<sup>a</sup> Péter Király<sup>a</sup> and Gábor Pálinkás<sup>\*a</sup>

<sup>a</sup>*Institute of Structural Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Budapest, Hungary.*

*E-mails: deak@chemres.hu and palg@chemres.hu*

#### 1. Synthesis

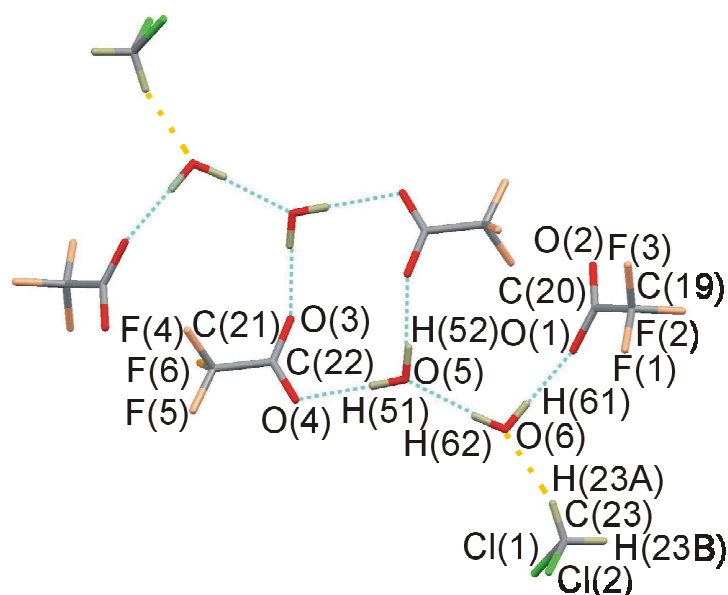
All chemicals and solvents used for the syntheses were of reagent grade.

Synthesis of [(AuCl)<sub>2</sub>(dppbz)]: A solution of dppbz (0.227 g, 0.508 mmol) in 10 mL dichloromethane was added to a suspension of Au(SMe<sub>2</sub>)Cl (0.30 g, 1.01 mmol) in 10 mL dichloromethane. A clear solution was formed, and after 5 hours of stirring shielded from light, the solution was filtered through Celite and the solvent was removed to yield an off-white product. The complex was washed with dichloromethane, diethyl ether and dried under vacuum. Yield: 0.43 g (92.7 %); m.p. 165-169°C.

#### 2. Single Crystal X-ray Diffraction

Crystals of **1–3** were mounted in Paratone-N oil within a conventional cryo-loop, and intensity data were collected on a Rigaku R-AXIS RAPID image plate diffractometer ( $\lambda(\text{Mo-}K_{\alpha}\text{ radiation}) = 0.71070 \text{ \AA}$ ), fitted with an X-stream low temperature attachment. Several scans in the  $\varphi$  and  $\omega$  direction were made to increase the number of redundant reflections, which were averaged over the refinement cycles. The structures were solved by direct method

(SIR92)<sup>1</sup> and refined by full-matrix least-squares (SHELXL-97).<sup>2</sup> All calculations were carried out using the *WinGX* package of crystallographic programs.<sup>3</sup> All non-hydrogen atoms were refined anisotropically in  $F^2$  mode. Hydrogen atomic positions were generated from assumed geometries. The riding model was applied for the hydrogen atoms.



**Fig. S1** The centrosymmetric O–H $\cdots$ O and C–H $\cdots$ O hydrogen-bonded aggregate of four trifluoroacetate counterions, four water and two dichloromethane solvent molecules in the crystal structure of **3**.

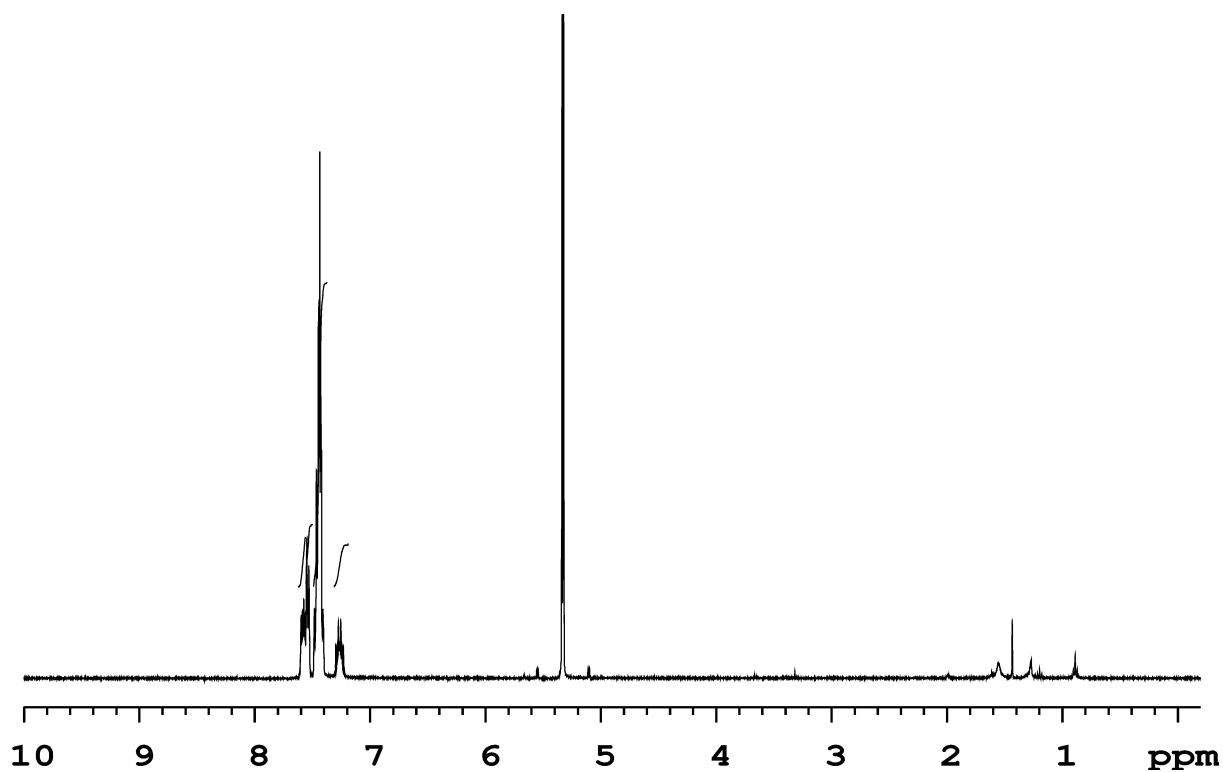
Table S1. Selected interatomic distances (Å) and angles (°) for the O–H $\cdots$ O and C–H $\cdots$ O hydrogen bonding in complex **2**.

D–H $\cdots$ A	Symmetry code (i)	H $\cdots$ A (Å)	D $\cdots$ A (Å)	D–H $\cdots$ A (°)
O(5)–H(51) $\cdots$ O(4)	–	2.00(2)	2.851(9)	179(10)
O(5)–H(52) $\cdots$ O(3) <sup>i</sup>	1 – x, 1 – y, –z	1.97(5)	2.810(9)	174(8)
O(6)–H(61) $\cdots$ O(1)	– 1 + x, y, z	2.09(7)	2.906(9)	160(7)
O(6)–H(62) $\cdots$ O(5)	– x, – ½ + y, ½ – z	2.05(6)	2.896(9)	174(6)
C(23)–H(23A) $\cdots$ O(6)	–	2.5000	3.400(13)	151.00

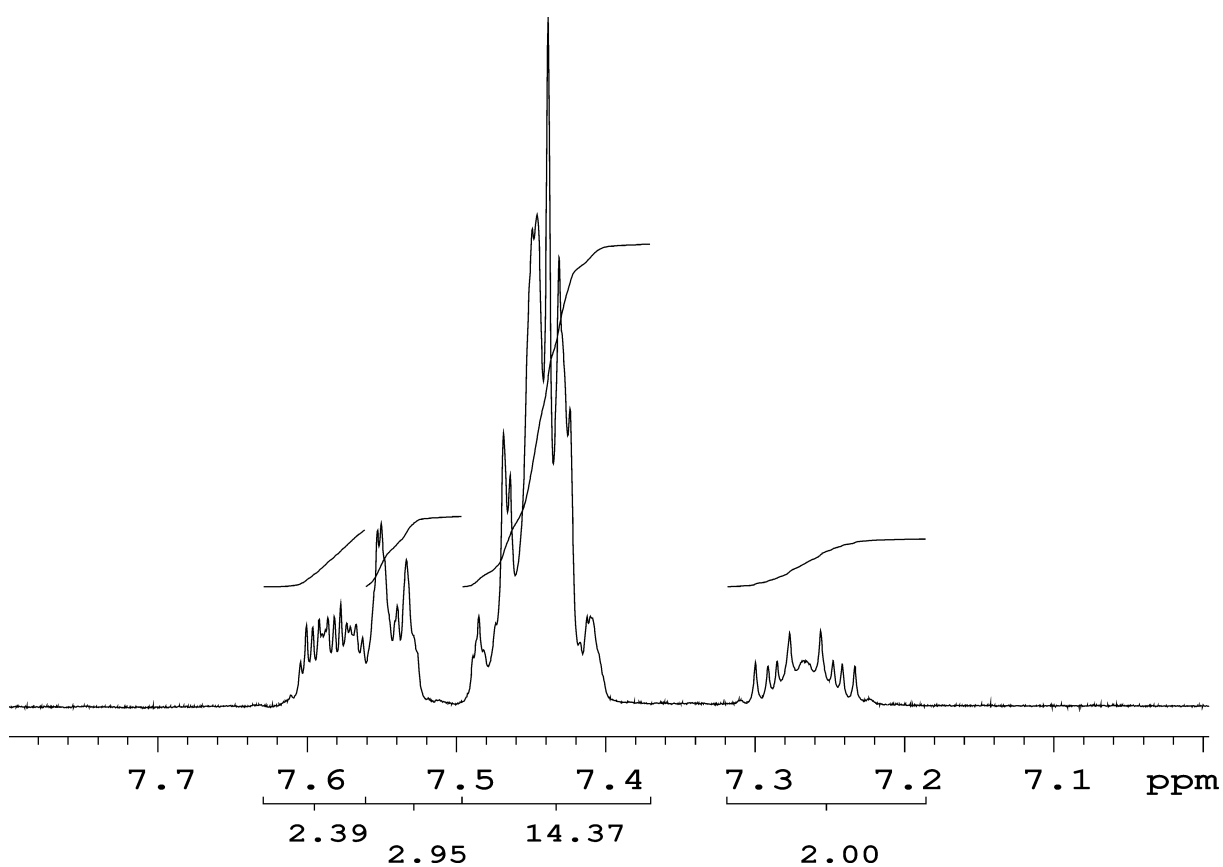
### 3. NMR Experiments

Solution NMR experiments were carried out on *Varian Inova* (400 MHz for  $^1\text{H}$ ) and *Varian NMR SYSTEM* (600 MHz for  $^1\text{H}$ ) spectrometers using a switchable broadband X $\{^1\text{H}\}$ , and an inverse detection triple tuneable pfg 5 mm  $^1\text{H}^{13}\text{C}\{X\}$  probe ( $X = ^{31}\text{P}$ ) respectively. Samples were placed into 5 mm and 3 mm NMR tubes, using 2 mm capillaries with the latter.  $^1\text{H}$  chemical shifts are referenced to the residual solvent signals ( $\text{CDCl}_2\text{CDCl}_2$ : 5.91 ppm;  $\text{CD}_2\text{Cl}_2$ : 5.32 ppm).  $^{31}\text{P}$  shifts are given relative to the external reference 85 %  $\text{H}_3\text{PO}_4$ . Deuterated (99.98 atom%) solvents were purchased from Merck<sup>®</sup> GmbH, Germany. Phosphorous spectra were recorded by using 5 seconds recycle delay and WALTZ proton decoupling.  $^1\text{H}$ -DOSY experiments were carried out in a 3 mm tube at 25°C to minimize convection effects. Performa I. gradient amplifier was used. The gradient strength was calibrated by using 5w/w % sucrose in  $\text{D}_2\text{O}$  at 25°C ( $D = 5.22\text{E}-10 \text{ m}^2/\text{s}$ ). The bipolar pulse-pair stimulated echo pulse-sequence was used for acquiring diffusion data with 50 ms diffusion delay, 8 squared increments for gradient levels. The Varian DOSY package was used for the processing. Spectra were processed in VnmrJ<sup>®</sup> 2.1B.

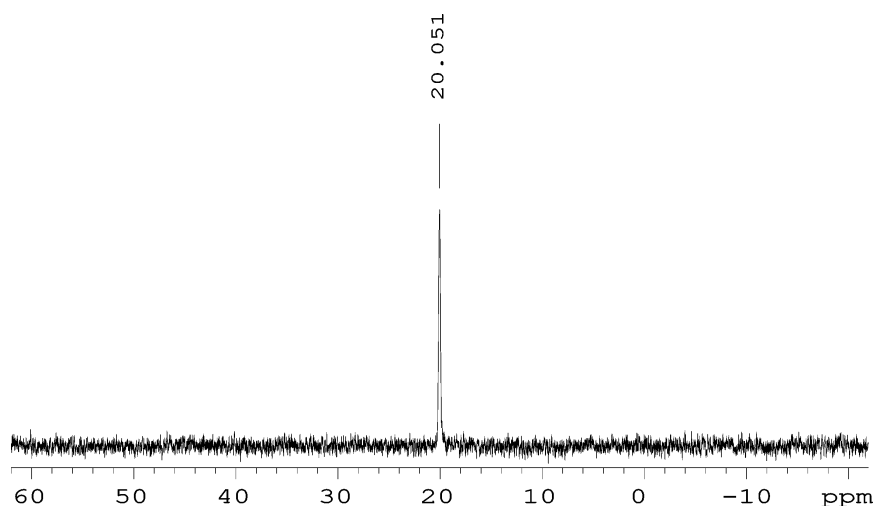
Solid-state MAS spectra were recorded by using a 3.2 mm HXY Varian Chemagnetics tunable MAS probe in HX double resonance (DR) mode. Chemical shifts in the solid state were referenced to  $(\text{NH}_4)\text{H}_2\text{PO}_4$  ( $\delta_{^{31}\text{P}} = 0.81 \text{ ppm}$ ) for phosphorous and to adamantane ( $\delta_{^{13}\text{C}} = 38.55, 29.50 \text{ ppm}$ ). For  $^{31}\text{P}$  MAS experiments recycle delay of 100 seconds and TPPM  $^1\text{H}$  decoupling field strength of 85 kHz were used. When recording the 125 kHz wide  $^{13}\text{C}$  ramped CP/MAS spectra, 5 ms contact time and 10 seconds recycle delay were used with TPPM proton decoupling field strength of 100 kHz.



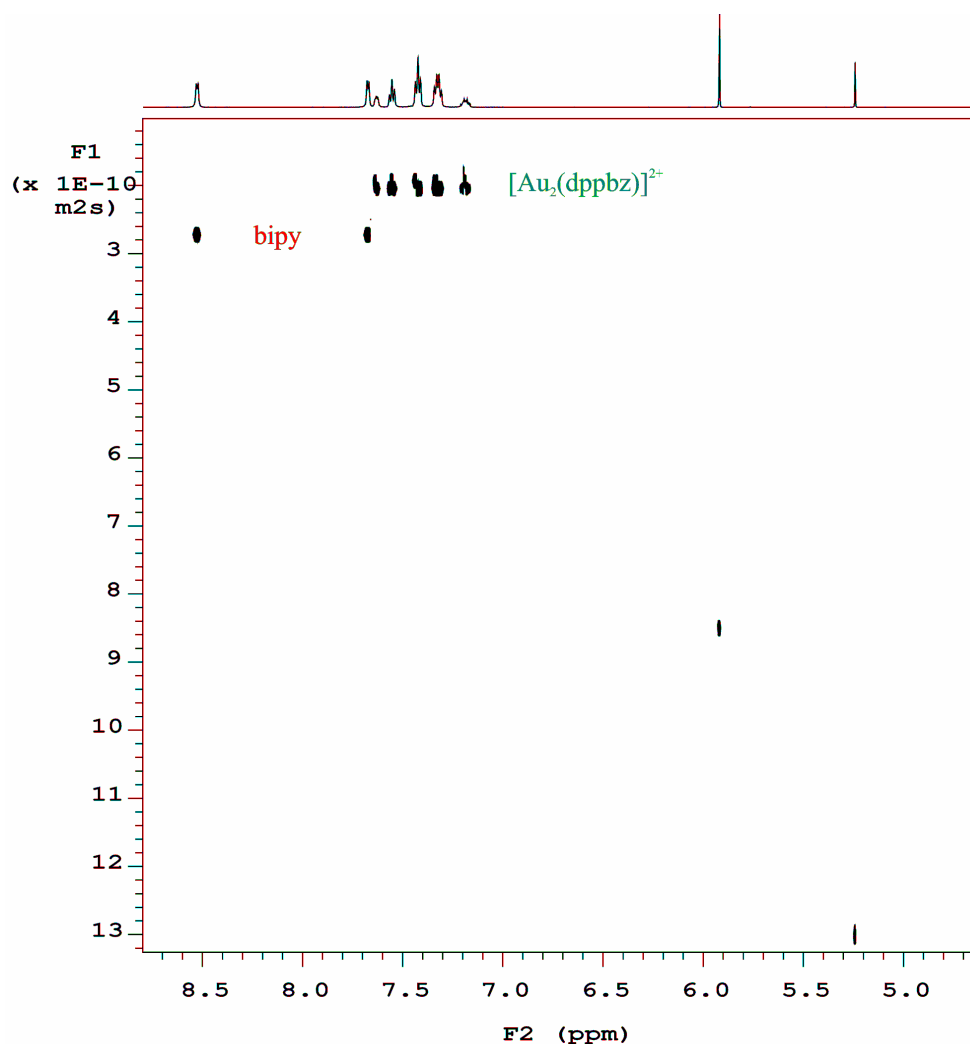
**Fig. S2** <sup>1</sup>H-NMR (399.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of **1** in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C (10 mM).



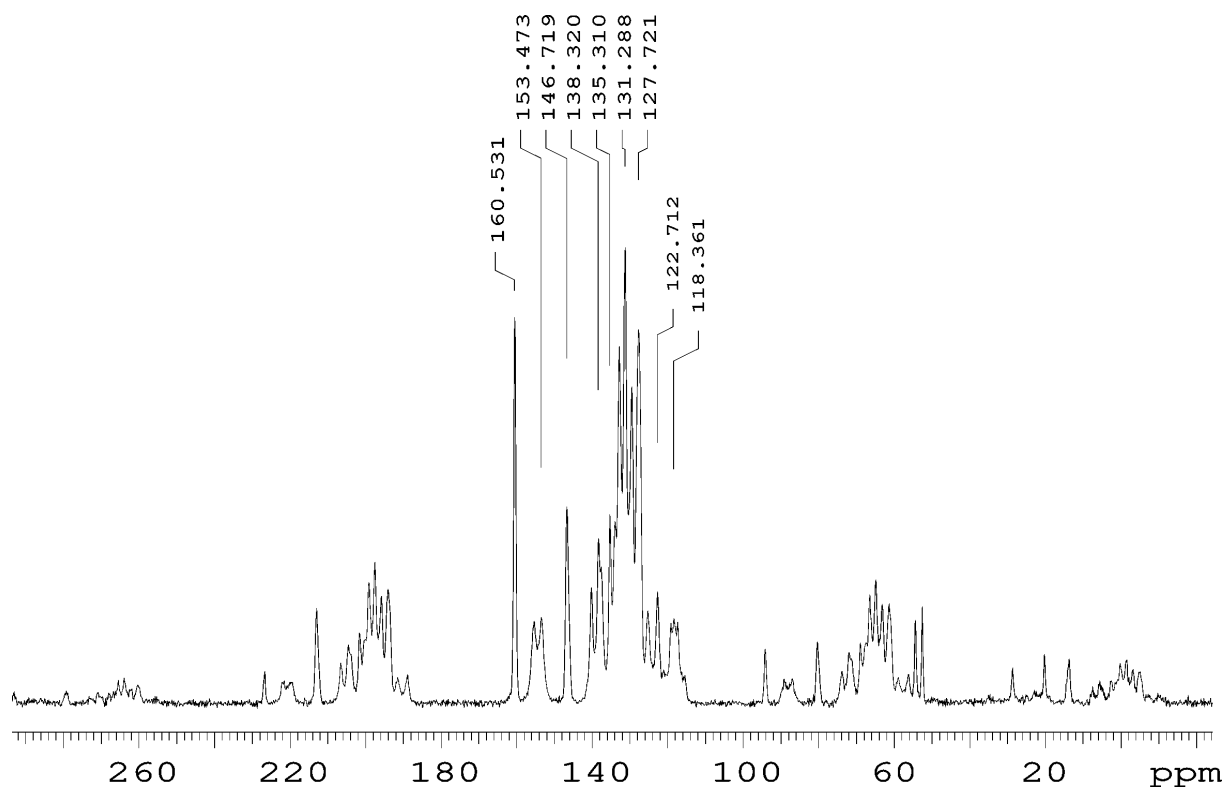
**Fig. S3** Aromatic region of the <sup>1</sup>H-NMR (399.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of **1** in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C (10 mM).



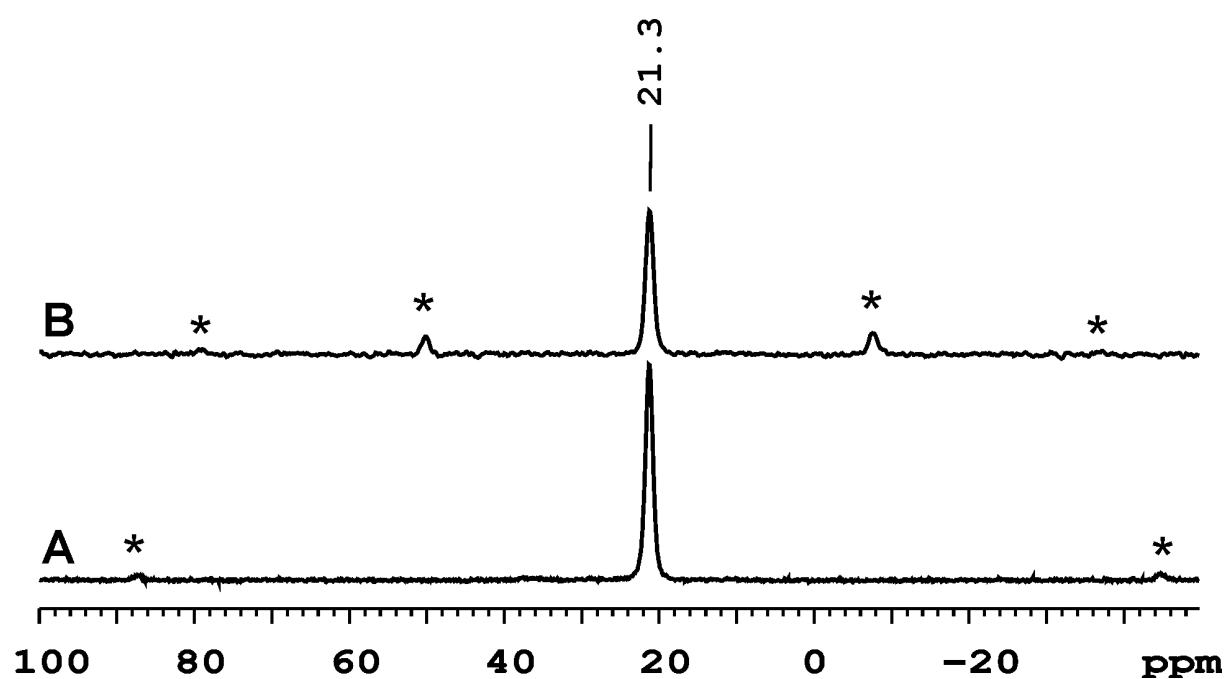
**Fig. S4**  $^{31}\text{P}$ -NMR (161.9 MHz) of **1** (10 mM) in  $\text{CD}_2\text{Cl}_2$  at 25 °C.



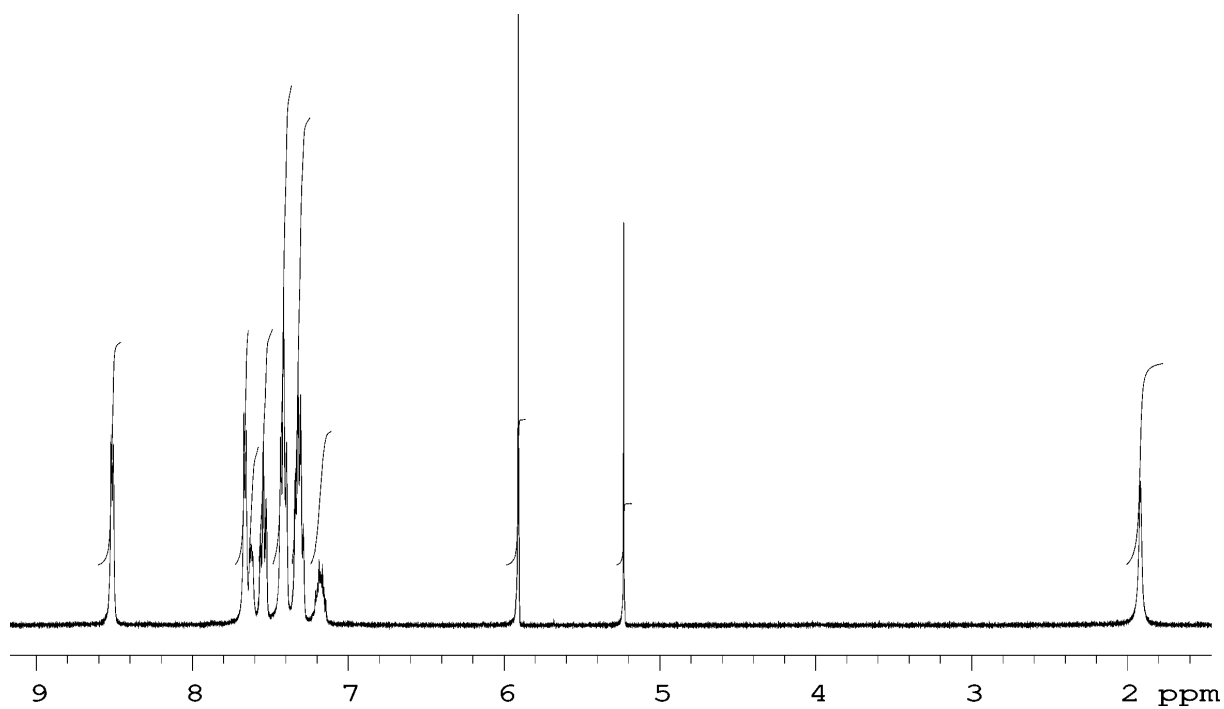
**Fig. S5** The  $^1\text{H}$  2D-DOSY NMR spectrum of **2** measured at 25 °C after being dissolved in hot (70 °C) tetrachloroethane- $\text{d}_2$  (< 10 mM). The horizontal scale shows the  $^1\text{H}$  chemical shifts (ppm) whereas the vertical dimension shows the diffusion scale ( $\text{m}^2/\text{s}$ ). Diffusion cross-peaks for the solvents (5.91 ppm, 5.32 ppm  $\{\text{CH}_2\text{Cl}_2\}$ ) are also present. Number of scans: 16.<sup>4</sup>



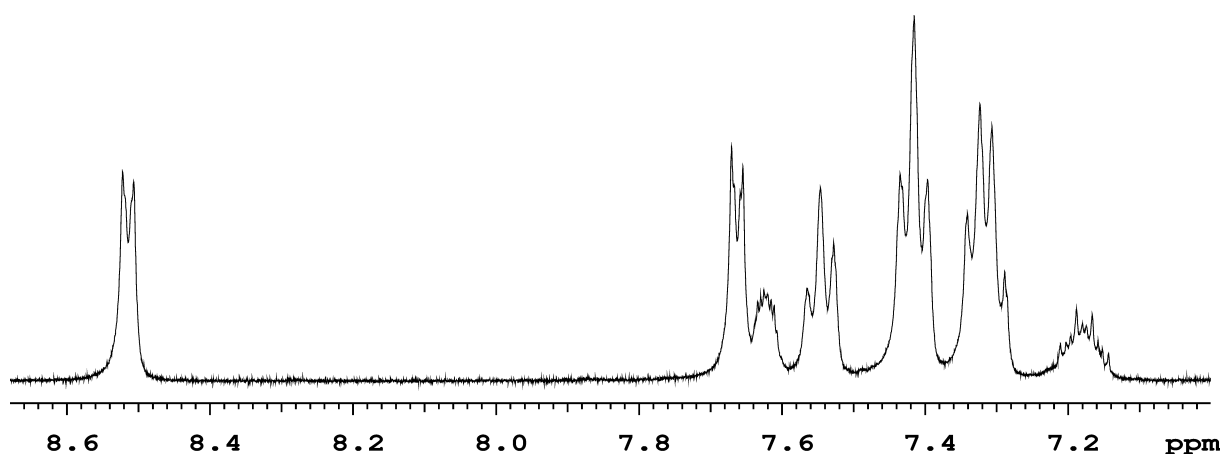
**Fig. S6** Solid-state  $^{13}\text{C}\{^1\text{H}\}$  CP/MAS (150.8 MHz, 10 kHz MAS) spectrum of **2** at 25 °C.



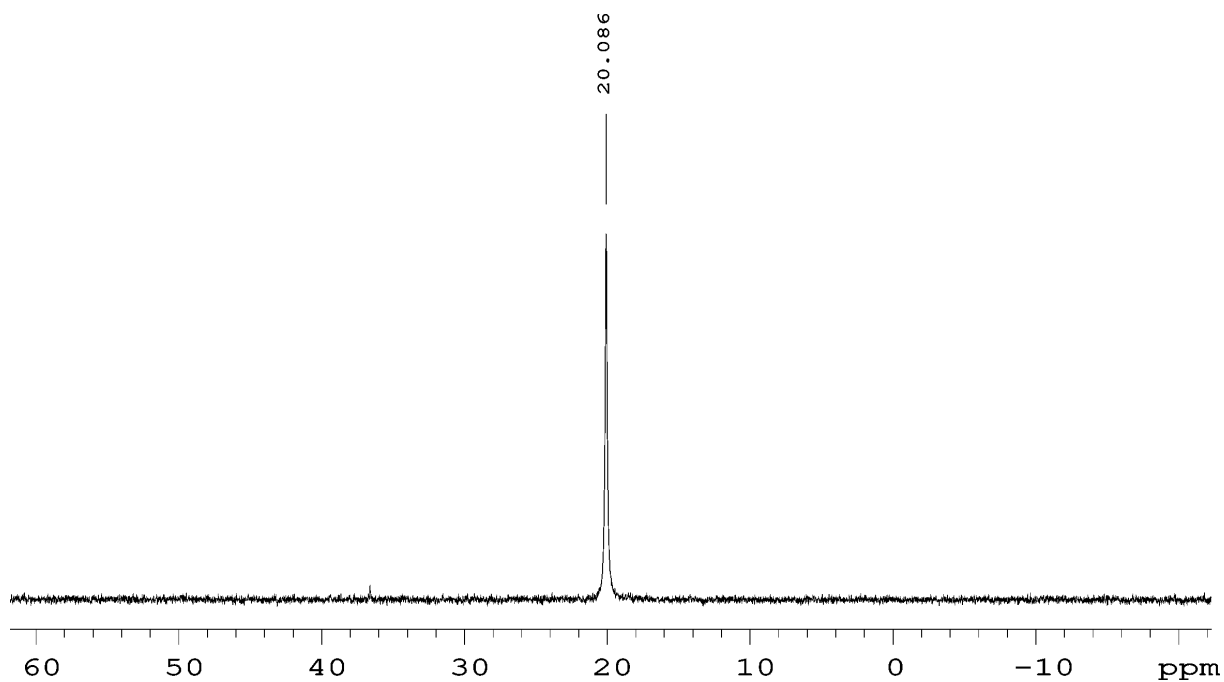
**Fig. S7** Solid-state  $^{31}\text{P}$ -MAS NMR spectra (242.7 MHz) of complex **2** at 16 kHz (A) and 7 kHz (B) MAS frequency. Spinning sidebands are indicated by asterisks.



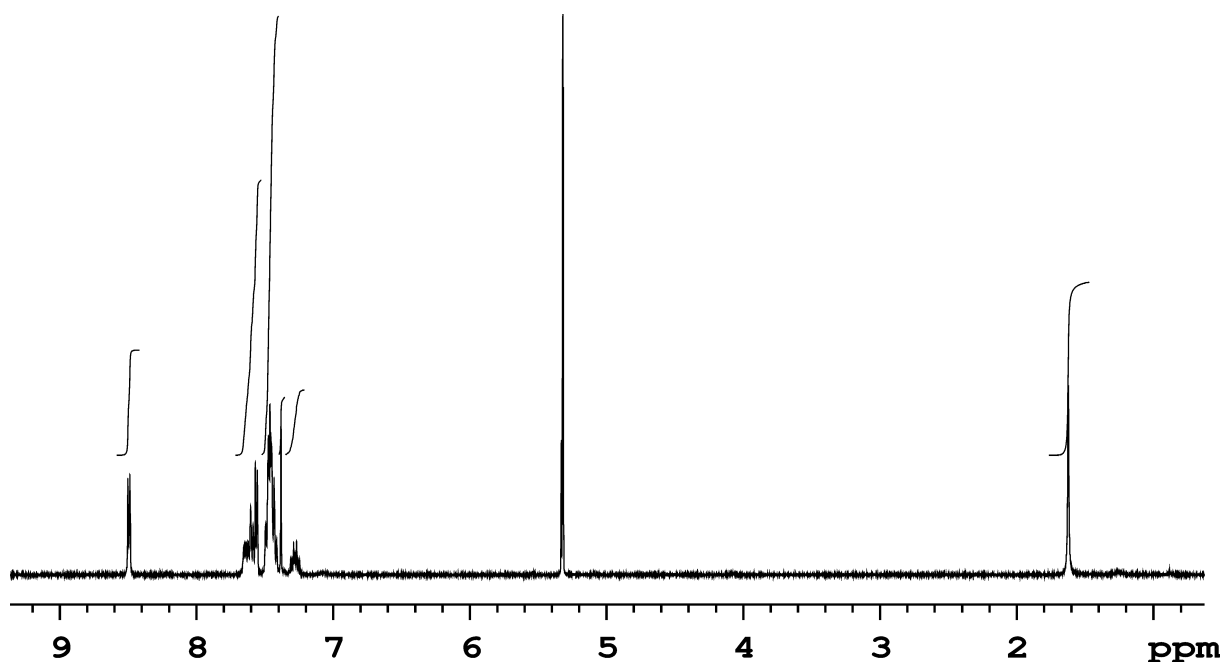
**Fig. S8**  $^1\text{H-NMR}$  (399.9 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ) of **2** measured at 25 °C after being dissolved in hot (70 °C) tetrachloroethane- $d_2$  (< 10 mM).



**Fig. S9** Aromatic region of the  $^1\text{H-NMR}$  (399.9 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ) of **2** measured at 25 °C after being dissolved in hot (70 °C) tetrachloroethane- $d_2$  (< 10 mM).

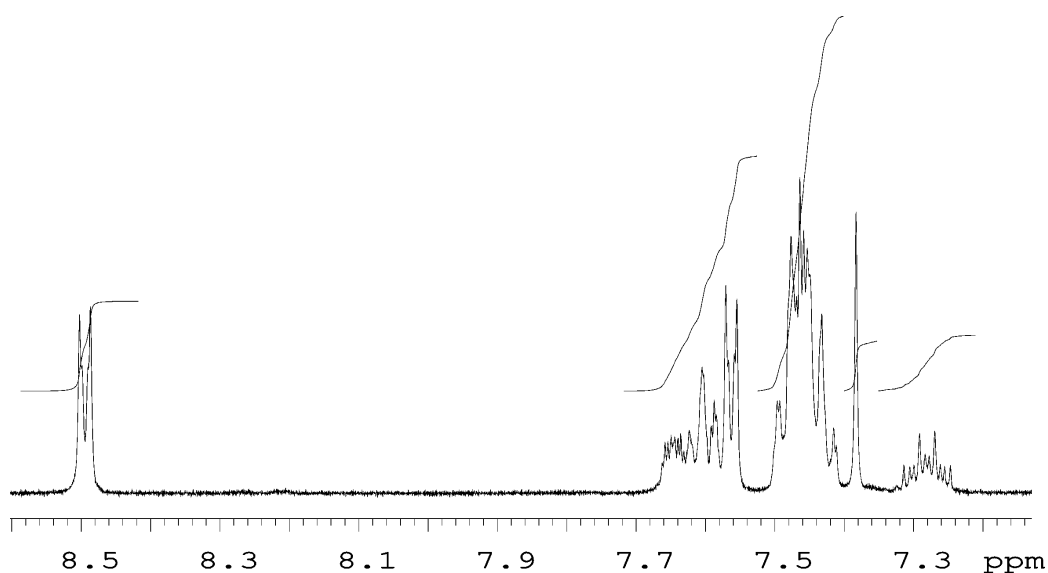


**Fig. S10**  $^{31}\text{P}$ -NMR (161.9 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ) of **2** measured at 25 °C after being dissolved in hot (70 °C) tetrachloroethane- $d_2$  (< 10 mM).

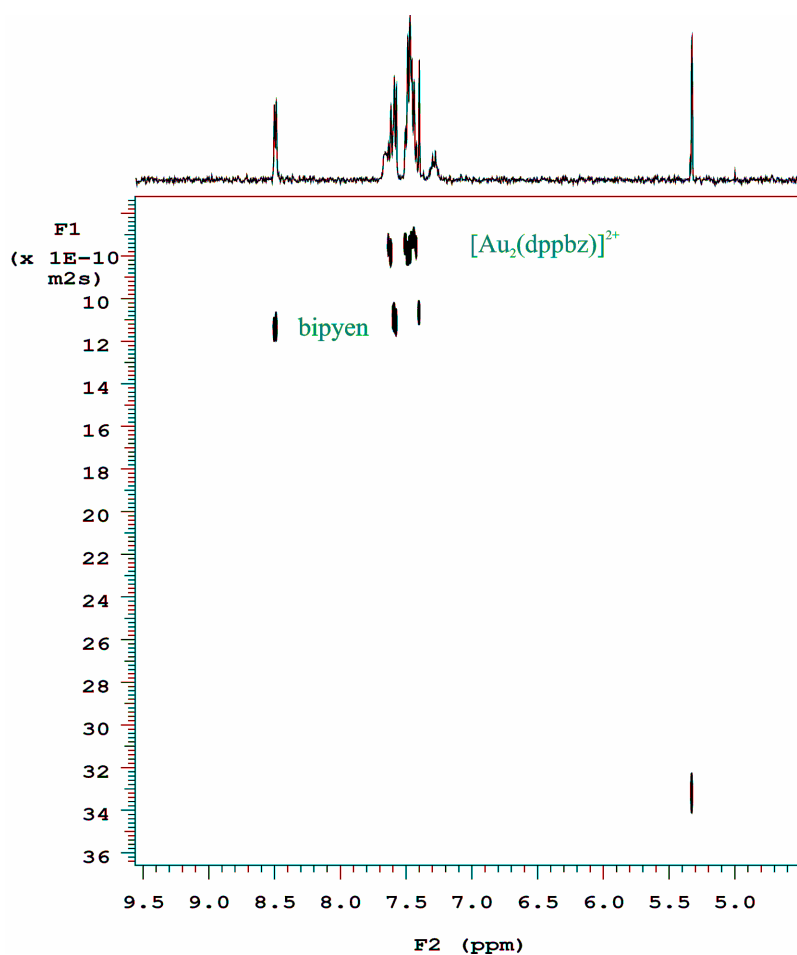


**Fig. S11**  $^1\text{H}$ -NMR (399.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **3** measured at 25 °C (1 mM).

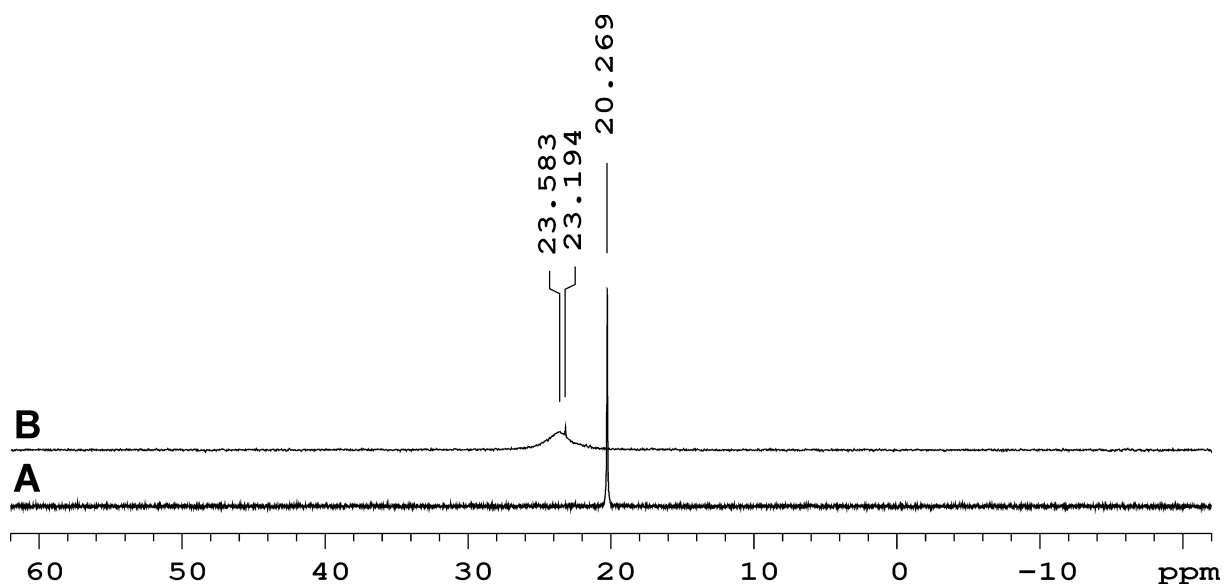




**Fig. S12** Aromatic region  $^1\text{H}$ -NMR (399.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **3** measured at 25 °C (1 mM).



**Fig. S13** The  $^1\text{H}$  2D-DOSY NMR spectrum of **3** in dichloromethane- $d_2$ . The horizontal scale shows the  $^1\text{H}$  chemical shifts (ppm) whereas the vertical dimension shows the diffusion scale ( $\text{m}^2/\text{s}$ ). Diffusion cross-peak of the solvent is at 5.32 ppm. Number of scans: 64.<sup>4</sup>



**Fig. S14** <sup>31</sup>P-NMR (161.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectra of **3** measured at (A) 25 °C and (B) -80 °C (1 mM).

## References

- (1) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
- (2) G. M. Sheldrick, *SHELXL97*-Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
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- (4) (a) K. F. Morris and C. S. Johnson Jr., *J. Am. Chem. Soc.*, 1992, **114**, 3139; (b) C. S. Johnson Jr., *Progr. Nucl. Magn. Res.*, 1999, **34**, 203; (c) J. T. Edward, *J. Chem. Educ.*, 1970, **47**, 261; (d) D. Wu, A. Chen and C. S. Johnson Jr., *J. Magn. Reson. A*, 1995, **115**, 260; (e) A. Deák and G. Tárkányi, *J. Organomet. Chem.*, 2006, **691**, 1693.