Supplementary Material (ESI) for Chemical Communications

Supporting Information

A Porphyrin-Related Macrocycle from Carbazole and Pyridine Building Blocks: Synthesis and Metal Coordination

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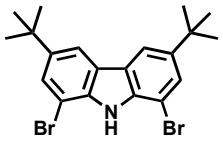
General Information

Commercially available reagents and solvents were used without further purification unless otherwise stated. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker ACS300 or Bruker AMX500 in DMF-d_7 or CD_2Cl_2, using a 5 mm broadband probe. The experiments were conducted between 413 K and 298 K and the temperatures were regulated by standard ^{1}H methanol or glycol NMR samples using the topspin 2.1 software (Bruker). All the spectra were obtained with a 90° pulse (10μs) and a sweep width between 20 ppm and 200 ppm. The kinetics were measured with a special multi scan program implanted in the Bruker software with a 30° pulse. Infrared spectroscopy was measured on a Nicolet 730 FT-IR spectrometer in the evanescence field of a diamond. Mass spectra were obtained using FD on a VG Instruments ZAB 2 SE-FPD. MALDI-TOF spectrometry was conducted on a Bruker Reflex IITOF spectrometer, utilizing a 337 nm nitrogen laser. Tetracyanoquinodimethane (TCNQ) was used as the matrix substance for solid state prepared samples. Solution UV-vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 100 spectrophotometer. Melting points were determined on a Büchi hot stage apparatus and are uncorrected. Elemental analysis was performed on a Foss Heraeus-Vario EL. X-ray crystallographic data were recorded using a Bruker AXS KCCD diffractometer with Mo Kα radiation at 120K.

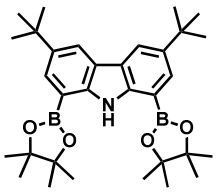
1,8-Dibromo-3,6-di-*tert*-butyl-9*H*-carbazole 1



1,8-Dibromo-3,6-di-*tert*-butyl-9*H*-carbazole **1** was synthesized following the literature procedures.[1]

^{1}H-NMR (CD_2Cl_2, 300MHz, 298K): δ = 1.44 (s, 18H), 7.67 (d, 2H), 8.04 (d, 2H), 8.26 (s, 1H) ppm. ^{13}C-NMR (CD_2Cl_2, 75MHz, 298K): δ = 32.0, 35.2, 104.2, 116.5, 125.2 , 127.1, 136.7, 145.3 ppm.

3,6-di-*tert*-butyl-1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*9H*-carbazole 2



n-BuLi (7.8 ml, 1.6 M in hexane, 12.5 mmol, 1.1 eq.) was added at 0°C to a solution of 1,8-dibromo-3,6-di-*tert*-butyl-9*H*-carbazole **1** (5 g, 11.5 mmol, 1 eq.) in degassed THF (250 ml). After stirring at this temperature for 1 h, the reaction mixture was allowed to warm to room

temperature (rt) while CO_2 gas was bubbled through the solution for 30 min. The solvent was then removed in vacuum and the residue was redissolved in degassed THF (250 ml). *t*-BuLi (29.4 ml, 1.7 M in pentane, 49.9 mmol, 4.3 eq.) was slowly added at -78°C and the reaction mixture was then stirred at 0°C for 3 h. Freshly distilled 2-isopropoxy-tetramethyl-dioxaborolane (11.6 ml, 57.5 mmol, 5 eq.) was added at -78°C and the reaction mixture was allowed to warm to rt overnight. The mixture was hydrolysed at 0°C by addition of 1M aqueous HCl and then diluted with EtOAc. The organic phase was washed twice with 1M aqueous NaOH and once with 1M $NaHCO_3$ solutions, dried over $MgSO_4$, filtered, and the solvent removed on a rotary evaporator. The crude product was purified by recrystallisation from hot hexane to afford 2.7 g (5.1 mmol, 50%) of compound **2** as a colourless solid.

Mp 387°C (from hexane); ^{1}H-NMR (CD_2Cl_2, 300 MHz, 298K): δ = 1.47 (s, 42H), 7.85 (d, 2H), 8.24 (d, 2H), 9.99 (s, 1H) ppm. ^{13}C-NMR (CD_2Cl_2, 75MHz, 298K): δ = 24.9, 31.8, 34.5, 83.76, 119.9, 121.7, 129.8, 140.9, 143.6 ppm.[1] MS (FD): *m/z* 531.37; Anal. Found: C, 71.92; H, 8.94; N, 2.63. Calcd for C32H47B2NO4: C, 72.13; H, 8.92; N, 2.64.

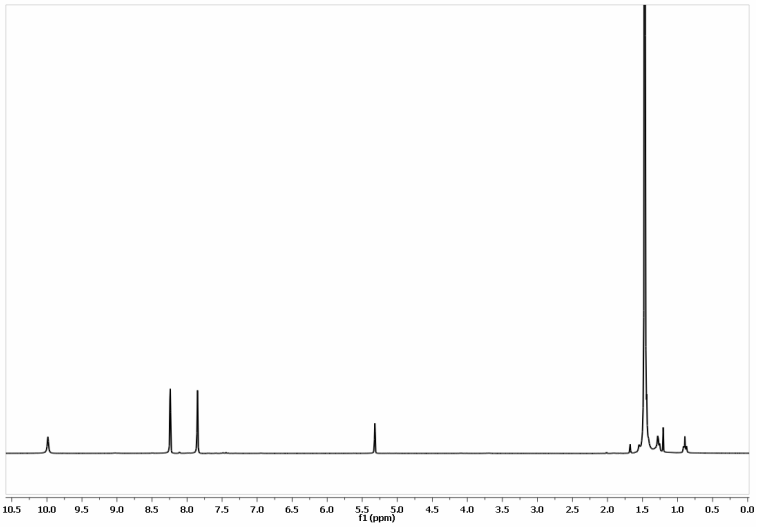


Fig. S1: ^{1}H NMR spectrum of precursor **2** recorded in CD_2Cl_2 at 298K.

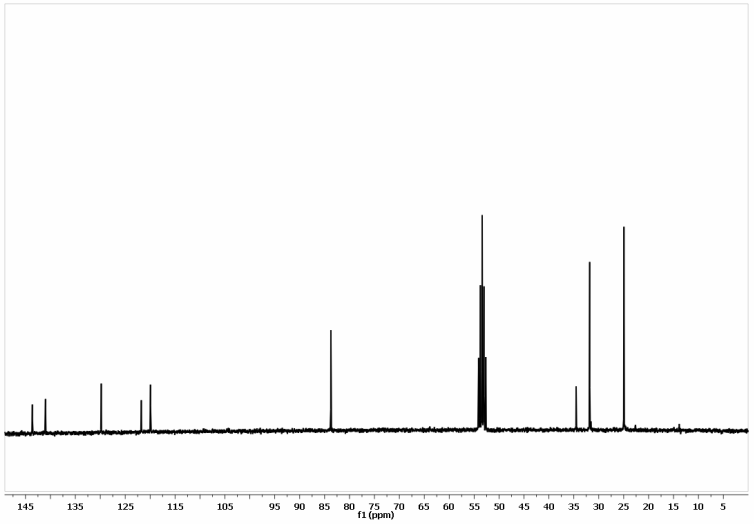
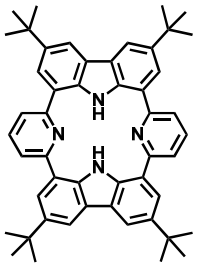


Fig. S2: ^{13}C NMR spectrum of precursor **2** recorded in CD_2Cl_2 at 298K.

[1] The quaternary atom next to the bor atom can not be observed due to the relaxation of the bor atom

Synthesis of macrocycle 3



132.8 mg (0.25 mmol, 1 eq.) of 3,6-di-*tert*-butyl-1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole **2**, 58.7 mg (0.25 mmol, 1 eq.) of 2,6-dibromopyridine and 6 mg ($5*10^{-3}$ mmol, 0.01 eq.) of $Pd(PPh_3)_4$ were dissolved in toluene (500 ml). EtOH (200 ml) and 2M K_2CO_3 (30 ml, excess) were added to the solution and the reaction mixture was degassed 3 times. The reaction mixture was stirred at 85°C for 17h. The solvents were removed on a rotary evaporator, the crude was redissolved in DCM and filtered over 1 cm silica. Crude impurities were removed by GPC chromatography in DCM. The crude product was purified by column chromatography (hexane 1:1 DCM) to yield 30 mg (0.04 mmol, 15%) of macrocycle **3** as a colourless solid.

^{1}H-NMR (CD_2Cl_2, 300 MHz, 298K): δ = 1.52 (s, 36H, 7.61 (d, 4H, ^4J=1.85 Hz), 7.68 (d, 4H, ^3J=7.83 Hz), 8.22 (t, 4H, ^3J=7.57 Hz), 8.24 (d, 4H, ^4J=1.69 Hz), 9.66 (s, 2H) ppm. ^{13}C-NMR (CD_2Cl_2, 75MHz, 298K): δ = 32.1, 35.0, 117.2, 122.6, 124.1, 124.7, 125.9, 136.1, 138.8, 143.4, 159.7 ppm. MALDI-TOF. 708.42; Found: C, 84.42; H, 7.77; N, 7.77. Anal. Calcd for C50H52N4: C, 84.70; H, 7.39; N, 7.90.

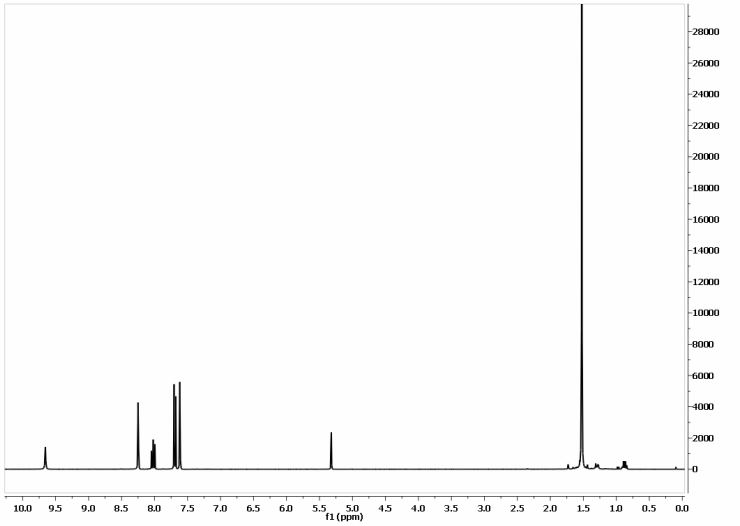


Fig. S3: ^{1}H NMR spectrum of macrocycle **3** recorded in CD_2Cl_2 at 298K.

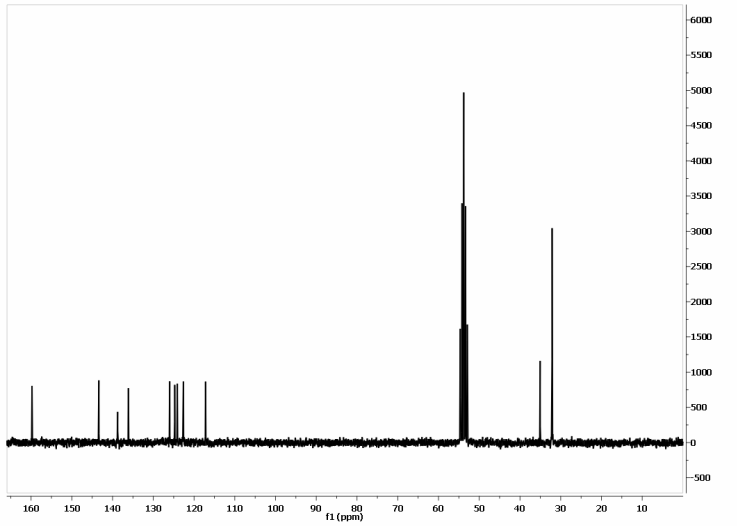
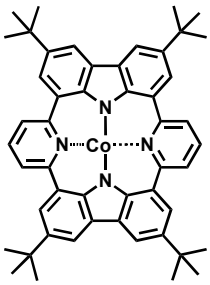


Fig. S4: ^{13}C NMR spectrum of macrocycle **3** recorded in CD_2Cl_2 at 298K.

Synthesis of cobalt complex 4



25 mg (0.035 mmol, 1 eq) of macrocycle **3** and 8 mg (0.046 mmol, 1.3 eq) of $Co(OAc)_2$ were put in a microwave-tube and dissolved in 2 ml of dry DMF. The reaction mixture was stirred for 4h in the microwave at 170°C and 300 W. It was cooled to rt and poured into ice-cold water. The precipitate was filtered of and dried under vacuum.

^{1}H-NMR (DMF-d_7, 500 MHz, 403K): δ = -8.47 (s), 5.44 (s), 8.52 (s), 11.63 (s), 45.42 (s) ppm. MALDI-TOF. 765.80.

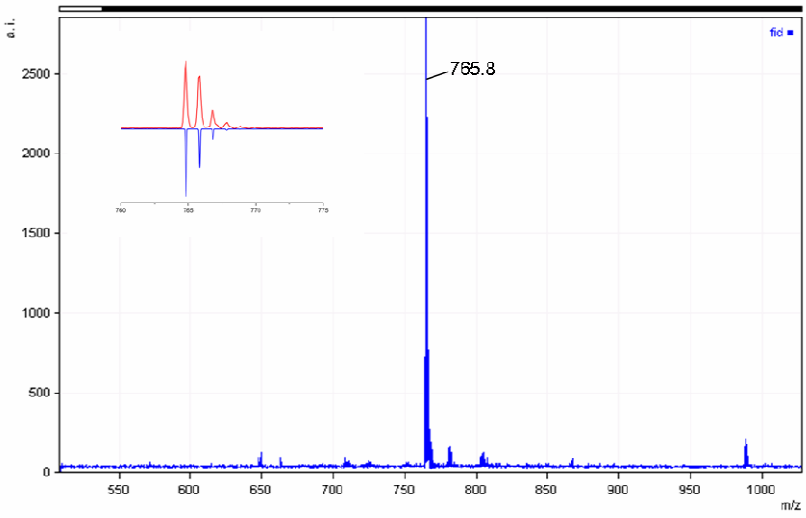


Fig. S5: MALDI-TOF mass spectrometry of cobalt complex **4**.

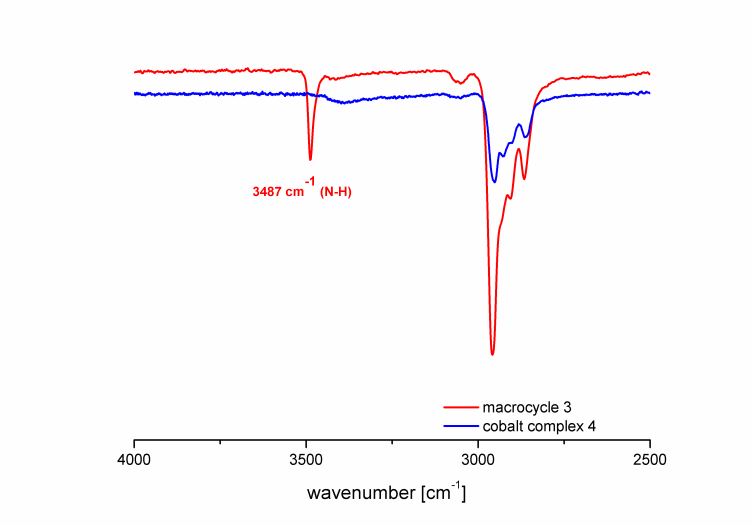


Fig. S6: FT-IR spectra of macrocycle **3** and its cobalt complex **4**.

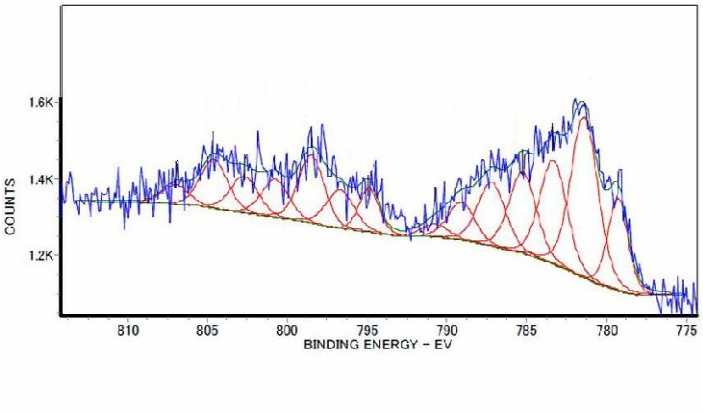


Fig. S7: XPS Co2p narrow scan for cobalt complex **4**.

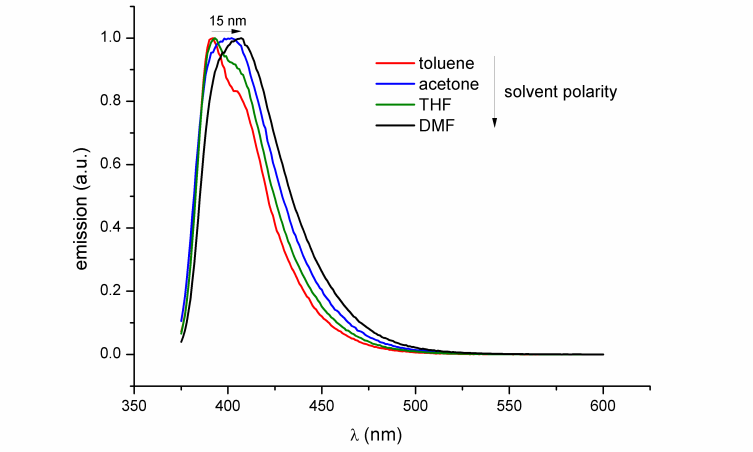


Fig. S8: Emission spectra of macrocycle **3** recorded in different solvents.

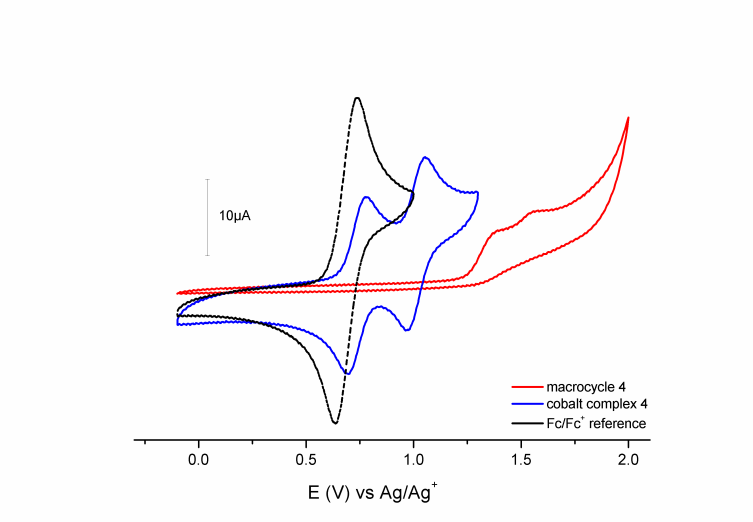


Fig. S9: Cyclic voltammogram of macrocycle **3** and cobalt complex **4**; 10^{-3} M sample solution in DMF, 10^{-1} M solution of *n*-Bu_4NPF_6 as electrolyte; working and counter electrode: Pt, reference electrode: Ag; ferrocene reference (Fc/Fc^+).

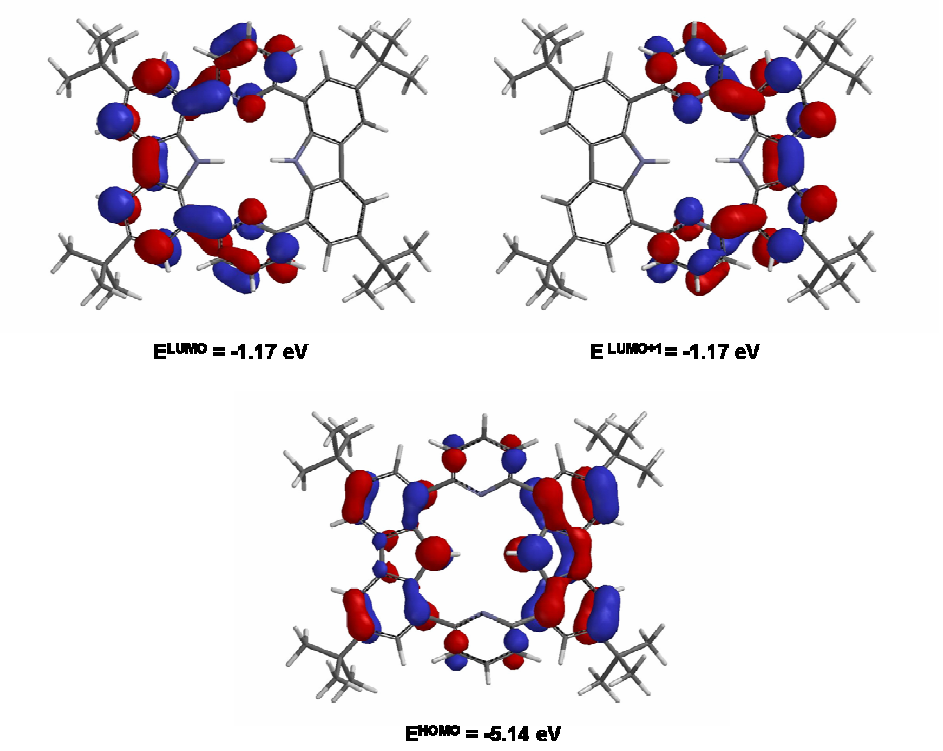


Fig. S10: Calculated HOMO, LUMO and LUMO+1 orbital energies of macrocycle **3** at B3LYP/6-31G(d) level of theory using Spartan 4.0 program.[2]

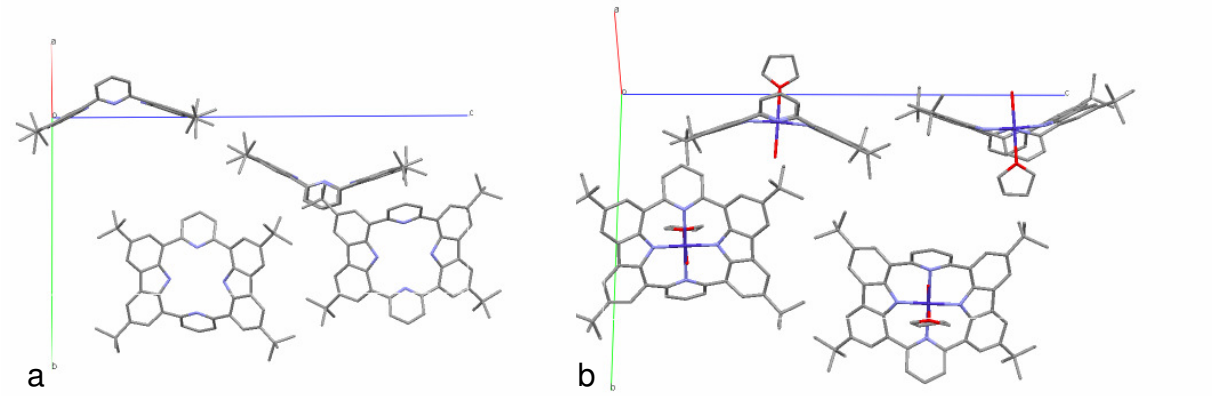


Fig. S11a, b: Crystal data for compound **3**: $C_{50}H_{52}N_4$*4.5THF ($C_{68}H_{88}N_4O_{4.5}$), M = 1032.46, orthorhombic, space group $P22_12_1$, a = 8.9009(3) Å, b = 22.2751(9) Å, c = 29.7836(9) Å, V = 5905.3(4) A^3, T = 120 K, Z = 4, D_x = 1.161 gcm^{-3}, 27036 reflections measured, 11884 unique reflections, R_{int} = 0.046, 8509 reflections observed (I > 2σ (I)). Refinement on F, R = 0.0532, Rw = 0.0578. Compound **4**: $C_{50}H_{50}N_4Co$*H_2O*4.5THF ($C_{68}H_{88}N_4CoO_{5.5}$), M = 1108.40, orthorhombic, space group $P22_12_1$, a = 9.1483(4) Å, b = 21.8882(9) Å, c = 29.7527(9) Å, V = 5957.7(4) A^3, T = 120 K, Z = 4, D_x = 1.236 gcm^-3. 29056 reflections measured, 10964 unique reflections, 9174 reflections observed (I > 2σ (I)). Refinement on F, R = 0.0625, Rw = 0.0630. THF solvate molecules and hydrogen atoms are omitted for clarity. Crystals of **3** and **4** were grown from THF by slow evaporation. The crystals turned out to be very unstable under ambient conditions by the rapid loss of solvate molecules and degraded within 10 to 30 seconds. Therefore crystals were isolated from the mother liquor in cooled Silicon oil (Riedel-de-Haën Perfluoroether 216) and mounted in sealed glass capillaries.

Data were recorded using a Bruker AXS KCCD diffractometer with Mo Kα radiation at 120 K. Owing to the large amount of solvent molecules present in the structure the diffraction was limited to a θmax of 27.5° (Temperature factors B obtained from Wilson plots were 3.62 and 3.04 Å2 for **3** and **4**, respectively). The crystal structures were solved by direct methods for **3** (Shelxs) and by heavy atom methods for **4**. Refinement was done by least-squares calculations on F with anisotropic temperature factors for all non-hydrogen atoms. The H atoms were included in the refinement with isotropic temperature factors in the riding mode. In the course of that no meaningful atomic parameters could be found. Their contributions (one THF in **3** and two THF in **4**) were taken into account using the PLATON/SQUEEZE program (P. van der Sluis, A. L. Spek, Acta Cryst. (1990) A46, 194-201). The remaining solvate molecules could be resolved but show rather high adp's indicating dynamic disorder. Also some t-butyl groups show high adp's which we interpret as rotational disorder. Projections of the structures and crystal data are shown in Figure S11.

References

1. Y. Liu, M. Nishiura, Y. Wang and Z. Hou, *J. Am. Chem. Soc.*, 2006, **128**, 5592-5593; M. S. Mudadu, A. N. Singh and R. P. Thummel, *The Journal of Organic Chemistry*, 2008, **73**, 6513-6520.
2. Spartan version 4.0, Wavefunction, Inc., 18401; Von Karman Ave. Suite 370; Irvine, CA 92612 USA