

Chem. Commun.

Supplementary Information

Cubane and dicubane complexes stabilised by sterically demanding *m*-terphenyl ligands

Benjamin M. Gridley, Toby J. Blundell, Graeme J. Moxey, William Lewis, Alexander J. Blake and Deborah L. Kays*

Supporting Information (6 pages)

Details of Synthesis, Characterising Data and Refinement Details for 1-3

Synthesis and Characterisation of 1-3	S2
Refinement Details and Structural Data for 1·THF-3·2THF	S4
References	S6

Synthesis and Characterisation of 1-3

General Procedures

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or glove box techniques. Hexane, toluene and THF were pre-dried over Na wire prior to passing through a column of alumina (hexane), distillation from molten Na (toluene) or sodium-benzophenone ketyl (THF). Hexane and toluene were stored over a potassium mirror, THF was stored over activated 4 Å molecular sieves and all solvents were degassed prior to use. Benzene-*d*₆ was dried over potassium and degassed with three freeze-pump-thaw cycles prior to use. [2,6-Ar₂C₆H₃Li]₂ (Ar = Mes, Pmp) and anhydrous CdCl₂ were prepared by minor modification of literature methods.¹⁻³ CdI₂ was dried *in vacuo* at room temperature for 24 hours prior to use. Mass spectra were measured by the departmental service at the University of Nottingham and at the EPSRC National Mass Spectrometry Service Facility, University of Wales, Swansea. Elemental microanalysis was performed by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK. ¹H and ¹³C{¹H} NMR spectra were collected on Bruker DPX400, AV(III)400 and AV(III)500 spectrometers, ⁷Li{¹H} NMR and ¹¹³Cd{¹H} NMR spectra were collected on a Bruker AV400 spectrometer. Chemical shifts are quoted in ppm relative to TMS (¹H and ¹³C{¹H}), LiCl/D₂O solution (⁷Li{¹H}) and to 0.1 M Cd(ClO₄)₂/D₂O (¹¹³Cd{¹H}).

Synthesis of 1

A solution of [2,6-Pmp₂C₆H₃Li]₂ (0.20 g, 0.27 mmol) in toluene (30 cm³) was added dropwise to a solution of CdI₂ (0.22 g, 0.6 mmol) in a mixture of toluene and THF (30 cm³/5 cm³) cooled to -78 °C with vigorous stirring. The pale yellow mixture was left to warm to room temperature overnight. The supernatant was removed *in vacuo* and the resulting pale yellow sticky solid was extracted into hexane (3 × 20 cm³). Filtration and storage at -30 °C resulted in colourless crystals of pure 1·THF (102 mg, 11%). THF of crystallisation was not observed in the ¹H and ¹³C{¹H} NMR spectra of this compound. ¹H NMR (400 MHz, C₆D₆, 300 K): δ 1.38 (m, trace, CH₂ of THF), 1.93 (s, 24H, *o*-CH₃), 2.27 (s, 12H, *p*-CH₃), 2.36 (s, 24H, *m*-CH₃), 3.47 (m, trace, CH₂ of THF), 7.05 (d, 4H, *J* = 7.5 Hz, *m*-CH), 7.30 (t, 2H, *J* = 7.5 Hz, *p*-CH_{Ar}). ¹³C{¹H} NMR (100 MHz, C₆D₆, 300 K): δ 16.3 (*m*-Me and *p*-Me of Pmp), 18.7 (*o*-Me of Pmp), 25.2 (CH₂ of THF), 68.4 (CH₂ of THF), 127.6 (*m*-CH of C₆H₃), 128.5 (*p*-CH of C₆H₃), 131.1 (*o*-C of Pmp), 131.9 (*m*-C of Pmp), 133.5 (*p*-C of Pmp), 140.0 (*o*-C of

C₆H₃), 142.9 (*i*-C of Pmp), 151.5 (*i*-C of C₆H₃). ⁷Li{¹H} NMR (155 MHz, C₆D₆, 300 K): δ – 0.81. ¹¹³Cd{¹H} NMR (C₆D₆, 88.7 MHz, 300K): δ 393.4. EI-MS: M⁺ not observed, fragment ion peaks at *m/z* 853 [((2,6-Pmp₂C₆H₃)₂Cd)⁺, 4%], 608 [(2,6-Pmp₂C₆H₃CdI)⁺, 4%], 481 [(2,6-Pmp₂C₆H₃Cd)⁺, 1%], 369 [(2,6-Pmp₂C₆H₃)⁺, 67%], 354 [(2,6-Pmp₂C₆H₃ – Me)⁺, 23%], 339 [(2,6-Pmp₂C₆H₃ – 2Me)⁺, 18%], 325 [(2,6-Pmp₂C₆H₃ – 3Me)⁺, 8%], 309 [(2,6-Pmp₂C₆H₃ – 4Me)⁺, 10%]. Elemental analysis has been obtained on a powdered sample: C₆₄H₈₂Cd₂I₄Li₂O₂: calcd. C 47.06, H 5.06; found C 47.38, H 5.02 and a crystalline sample: C₆₈H₉₀Cd₂I₄Li₂O₃: calcd. C 47.99, H 5.33; found C 48.18, H 5.48.

Synthesis of mixture of **2** and **3**

A solution of [2,6-Mes₂C₆H₃Li]₂ (0.64 g, 1.0 mmol) was added dropwise to a stirred suspension of CdCl₂ (0.37 g, 2.0 mmol) in a toluene/THF solution (30 cm³/5 cm³) at –78 °C. The resulting suspension was warmed slowly to room temperature and stirred for 16 h, after which the solvent was removed *in vacuo*, and the yellow residue extracted into hexane (30 cm³) and concentrated *in vacuo*. The resulting yellow precipitate was isolated, dissolved in hexane (20 cm³) and following controlled cooling to –30 °C, colourless crystals with two distinct morphologies were isolated (50 mg). Single crystal X-ray diffraction measurements revealed a mixture of **2**·0.25C₆H₁₄ and **3**·2THF, which could not be separated. Solvent of crystallisation molecules were not observed in the ¹H and ¹³C{¹H} NMR spectra of this mixture. The ratios of **2** and **3** could not be discerned in the solid state, and there is only one ligand environment in solution, as shown by the ¹H NMR below, and assignments have been based on this. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 1.42 (m, trace, CH₂ of THF), 1.80 (s, 12 H, *o*-CH₃), 2.20 (s, 6H, *p*-CH₃), 3.34 (m, trace, CH₂ of THF), 6.84 (s, 4H, *m*-CH of Mes), 6.92 (d, 2H, *J* = 7.5 Hz, *m*-CH of C₆H₃), 7.17 (t, 1H, *J* = 7.5 Hz, *p*-CH of C₆H₃). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ 20.9 (*p*-CH₃), 21.0 (*o*-CH₃), 25.1 (CH₂ of THF), 68.2 (CH₂ of THF), 125.0 (*m*-CH of Mes), 128.0 (*p*-CH of C₆H₃), 128.5 (*m*-CH of C₆H₃), 135.5 (*p*-C of Mes), 135.8 (*o*-C of Mes), 144.0 (*i*-C of Mes), 149.4 (*o*-C of C₆H₃), 162.6 (*i*-C of C₆H₃). ⁷Li{¹H} NMR (155 MHz, C₆D₆, 298 K): δ –0.72, –0.53. ¹¹³Cd{¹H} NMR (88 MHz, C₆D₆, 298 K): δ 401.3. EI-MS: M⁺ not observed, fragment ion peaks at *m/z* 427 [(2,6-Mes₂C₆H₃Cd)⁺, 50%], 314 [(2,6-Mes₂C₆H₃)⁺, 100%], 299 [(2,6-Mes₂C₆H₃ – Me)⁺, 30%], 284 [(2,6-Mes₂C₆H₃ – 2Me)⁺, 10%], 269 [(2,6-Mes₂C₆H₃ – 3Me)⁺, 5%], 119 [(2,6-Mes₂C₆H₃ – Mes)⁺, 5%].

Refinement Details and Structural Data for 1·THF-3·2THF

Refinement Details for 1·THF-3·2THF

Crystals of 1·THF-3·2THF were mounted on Micromounts using YR-1800 perfluoropolyether oil and cooled rapidly to 90 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device.⁴ Data for compounds 1·THF, 2·0.25C₆H₁₄ and 3·2THF were collected on a SMART APEX diffractometer equipped with a graphite-monochromated Mo-*K*_α radiation source ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied using a multiscan method (SADABS).⁵ All non-H atoms were located using direct methods⁶ and difference Fourier syntheses. All fully occupied non-H atoms were refined with anisotropic displacement parameters. In the case of 1·THF, O(1) and C(29)-C(32) of the Li(1) bound THF were disordered over two positions and their occupancies competitively refined to a 51(2):49(2) ratio. Chemically-equivalent 1,2-distances related to the disordered sections of the THF molecules were restrained to be approximately equal. Rigid-bond and similarity restraints were applied to both THF molecules in the structure. It was not possible to model the lithium anisotropically. In the case of 2·0.25C₆H₁₄ the Cl(4) and Cl(8) sites were found to be partially occupied by I(4) and I(8) in 70.2(3):29.8(3) and 66.7(3):33.3(3) ratios, respectively. The C(92)-C(100) and C(125)-C(133) mesityl groups were each disordered over two positions, and the occupancies competitively refined to a 52(3):48(3) and 35.3(8):64.7(8) ratio, respectively. The bond lengths and angles in the disordered mesityl groups were restrained to be approximately equal. C(74) and C(75) of the Li(1)-bound THF molecule were disordered over two positions - their occupancies were competitively refined to a 49(2):51(2) and 54(3):46(3) ratio, respectively. C(169) of the Li(2)-bound THF molecule was also disordered over two positions, with their occupancies in an 81(2):19(2) ratio. A global rigid bond restraint was applied to all atoms. In the case of 3·2THF disordered THF was removed using PLATON SQUEEZE.⁷ Hydrogen atoms were placed in calculated positions and refined using a riding model; methyl groups were refined as rigid rotors, except for C(23) and C(23A), which were modelled as having two possible, half-occupied, fixed positions. The molecule exhibits significant disorder in all the exterior ligands. Chemically equivalent bonds of the different disorder components of the coordinated THF molecule were restrained to be equivalent. The C(16)-C(24), C(16A)-C(24A), C(40)-C(48) and C(40A)-C(48A) mesityl groups were restrained to be approximately flat. All mesityl groups were also restrained to have equivalent 1-2 and 1-3 distances. Rigid bond and similarity restraints were

applied to the thermal parameters of all atoms. Sensible anisotropic models could not be developed for C(22), C(22A), C(37A) and C(46A), so these atoms were refined isotropically. CCDC 956481-956483 contain the supplementary data for **1·THF-3·2THF**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

References

1. K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer and P. P. Power, *J. Am. Chem. Soc.*, 1993, **115**, 11353.
2. S. Hino, M. M. Olmstead, J. C. Fettinger and P. P. Power, *J. Organomet. Chem.*, 2005, **690**, 1638.
3. P. Boudjouk and J.-H. So, *Inorg. Synth.*, 1992, **29**, 108.
4. J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
5. G. M. Sheldrick, *SADABS, Program for Area Detector Absorption Correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
6. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.
7. A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148.