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trans-Disubstituted diamido/diamine cyclam zirconium complexes

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ABSTRACT

The reaction of H₂[1,8-dibenzyl-1,4,8,11-tetraazacyclotetradecane] (H₂Bn₂Cyclam) with 2 equiv of LiBu gives Li₂Bn₂Cyclam(L)₂ (L = Et₂O or THF) that reacts with ZrCl₄(THF)₂ to afford (Bn₂Cyclam)ZrCl₂ in 40% yield. Alternatively (Bn₂Cyclam)ZrCl₂ may be obtained via ZrCl₂(CH₂SiMe₃)₂(Et₂O)₂ in a significantly higher yield (87%), avoiding the lithiation of H₂Bn₂Cyclam. The syntheses of other H₂*Bn₂Cyclam ligand precursors (*Bn = 3,5-dimethylbenzyl and 3,5-di(*tert*-butyl)benzyl) and the corresponding Zr derivatives ({3,5-Me₂Bn₂-Cyclam)ZrCl₂ and ({3,5-^tBu₂Bn₂-Cyclam)ZrCl₂ are also reported. Results on preliminary tests of ε -caprolactone and ethylene polymerisation reactions are presented.

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The search for alternative systems to Group 4 cyclopendienylbased complexes is well documented and has been intensively explored over the last years [1]. Diamido hybrid ligands - the combination of two amido units with other neutral donors proved adequate in stabilizing early transition metal complexes that found application in numerous catalytic processes [2]. Despite the level of sophistication ligand design has reached, and though various combinations of hard and soft donors have been employed, early transition metal chemistry of saturated azamacrocycles still remains relatively unexplored. This type of ligand set is attractive to transition metal chemistry due to (i) the enhanced stability that a cyclic array presents, (ii) the flexibility to adopt different conformations and (iii) a macrocycle cavity size that forces the metal centres to sit above the plane of the donors leaving two adjacent coordination positions available at the metal coordination sphere [3]. In addition, and contrasting with azamacrocycles such as porphyrins or tetraazannulenes, saturated macrocycles are less prone to undesired secondary reactions [4]. The scarce number of diamido/diamine transition metal complexes derived from cyclam lies on the difficulty of its selective functionalisation. This difficulty was overcome by Guilard and co-workers who reported a facile and high yield method for the selective trans-functionalisation of cyclam with benzyl groups [5]. Using Guilard's procedure we have prepared ligand precursors H₂(3,5-dimethylbenzyl)Cyclam, 1, and H₂(3,5-di(*tert*-butyl)benzyl)Cyclam, **2**, in 70% and 55% global yield, respectively [6]. The benzyl bromide required for the synthesis of **2** was prepared by bromination of commercially available 3,5-di(*tert*-butyl)toluene with an aqueous H₂O₂/HBr system in *ca.* 85% yield [7]. Under these convenient and environmentally friendly conditions, multigram amounts of 3,5-di(*tert*-butyl)benzyl bromide (contaminated with residual 3,5-di(*tert*-butyl)toluene) could be directly obtained without further purification (Eq. (1)). In our hands, the known NBS-AIBN procedure (or its variants) reported in the literature [8] always gave mixtures of mono- and di-brominated material, unless conversion was halted at around 60%.

$$H_{2}O_{2,} HBr, H_{2}O_{2,} HBr, H_{2$$

Addition of 2 equiv of LiBu to a Et_2O or THF solution of $(H_2Bn_2Cyclam)$, **3**, results in the formation of $Li_2Bn_2Cyclam(Et_2O)_2$, **4**, or $Li_2Bn_2Cyclam(THF)_2$, **5**, that have been isolated in 65% and 70% yield, respectively [9,10]. The crystal structure of **5** is depicted in Fig. 1. The geometry around the lithium atoms is best described as tetrahedral, with each lithium coordinated by two amido and one amine macrocyclic moieties and one THF molecule. The lithium atoms are located at opposite faces of the macrocycle at an average distance of 0.94(32) Å from the plane containing the four macrocyclic nitrogen atoms [11].





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Fig. 1. ORTEP diagram of **5** showing thermal ellipsoids at 50% probability level. Half molecule is generated by symmetry operation -x + 3/2, y, -z + 3/2. Hydrogens are omitted for clarity. Selected bond lengths and angles: Li(1)–N(1),2.053(3) Å, Li(1)–N(2) 1.981(4) Å, Li(1)–O(1) 1.955(4) Å, Li(1)– $[N_4Plane] 0.94(32)$ Å, N(1)–Li(1)–O(1) 109.88(16)°, N(2)–Li(1)–N(1) 91.17(14)°, N(2)–Li(1)–N(2_\$1) 105.11(16)°.

As previously reported by some of us, the reaction of $ZrCl_4(THF)_2$ with **5** led to $(Bn_2Cyclam)ZrCl_2$, **6**, in 40% yield [10]. The relatively low yield obtained by the chloride metathesis reaction impelled us to investigate acid–base reactions as alternative synthetic approaches to **6**, avoiding the lithiation of $H_2Bn_2Cyclam$, **3**. Treatment of $ZrCl_2(CH_2SiMe_3)_2(Et_2O)_2$ [12] with **3** proved to be the most suitable route for the preparation of $(Bn_2Cyclam)ZrCl_2$, **6** which is reproducibly formed in 87% yield (Scheme 1) [13]. Although $ZrCl_2(CH_2SiMe_3)_2(Et_2O)_2$ presents a low thermal stability, the reaction was carried under mild THF reflux, evidencing the rapid deprotonation reaction of the macrocycle **3** and its coordination to the metal centre.

The low yield obtained in the preparation of **6** through **4** or **5** could be due to the stability of the lithium linkages in $Li_2Bn_2Cy-clam(L)_2$ and to an inadequate pre-conformation of the ligand pre-cursor to metal coordination. In fact, the square defined by the bridging lithium cations ($Li-N_{amido}-Li-N_{amido}$, see Fig. 1) is a stable motif currently observed in lithium polyamides. Furthermore, before coordinate to the zirconium, the macrocyclic ring has to undergo a structural reorganisation (equivalent to nitrogen inversion) to attain a bowl conformation and place the four nitrogen atoms in adequate position to bind to one metal centre.

Complexes $({3,5-Me_2Bn}_2-Cyclam)ZrCl_2$, **7**, and $({3,5-^tBu_2Bn}_2-Cyclam)ZrCl_2$, **8**, were obtained from the reaction of **1** or **2** with

ZrCl₂(CH₂SiMe₃)₂(Et₂O)₂ in 61% and 56% yield, respectively (Scheme 1) and characterised by ¹H, ¹³C{¹H}, COSY, HSQC and NOESY NMR experiments [14]. The ¹H NMR spectra of the compounds are similar as ten chemically non-equivalent hydrogen resonances are defined in the range 1.53-4.33 ppm for 7 and 1.46-4.29 ppm for **8**, corresponding to the twenty macrocyclic protons. The diastereotopic benzylic protons appear as AB systems for both **7** (4.66 and 4.27 ppm) and **8** (4.64 and 4.27 ppm). The average C₂ symmetry in solution is confirmed by the ¹³C{¹H} NMR spectra of 7 and 8, where five ligand core resonances and one benzylic carbon environment can be distinguished. Crystals of 7 suitable for X-ray diffraction were obtained from a concentrated dichloromethane solution at -20 °C [15]. An ORTEP depiction of the molecular structure is shown in Fig. 2, along with selected bond lengths and angles. The zirconium is coordinated to the four nitrogen atoms of the macrocycle and to two chloride ligands in a distorted trigonal prismatic geometry. The size of the cavity forces the metal to sit 1.05(16) Å above the plane defined by the four nitrogen atoms, forcing the chloride ligands to be *cis* to each other. Comparison of the molecular structures of 6 and 7 shows that the different benzylic groups have no influence on the Zr-N bonds.

Complexes **6**, **7** and **8** have been tested as catalysts for ε -caprolactone (CL) ring opening polymerisation [16]. At 80 °C, **6** is the most active catalyst showing an activity of 1.1 kg/molZr[CL]h, while **7** and **8** display much lower activities. The discrepancy between the reactivity of the three compounds is surprising and deserves further studies. Complex **6** was also tested as a catalyst precursor for ethylene (E) polymerisation in the presence of MAO [17]. The system is fairly active. The highest activity (1.7 kg/mol-



Fig. 2. ORTEP diagram of **7** showing thermal ellipsoids at 50% probability level. Half molecule is generated by symmetry operation -x + 1/2, y, -z. Hydrogens are omitted for clarity. Selected bond lengths and angles: Zr(1)-N(1) 2.441(2) Å, Zr(1)-N(2) 2.044(2) Å, Zr(1)-Cl(1) 2.5039(8) Å, $Zr(1)-[N_4Plane] 1.05(16) \text{ Å}$, $N(2)-Zr(1)-N(1) 72.32(8)^\circ$, $N(1)-Zr(1)-Cl(1) 80.00(5)^\circ$, $N(2)-Zr(1)-Cl(1) 133.92(6)^\circ$.





Zr[E]h) was observed at 18 °C with Al/Zr = 2000. At higher temperatures the system activity decreases, probably due to thermal decomposition of the active species. The Al/Zr ratio also affects the activity of **6**, increasing in the range Al/Zr 500–2000.

To the best of our knowledge, these continue to represent rare examples of Group 4 metals supported by saturated macrocyclic arrays. The reactivity and assessment of catalytic applications for these compounds are in progress.

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Appendix A. Supplementary material

CCDC 687687 and 687688 contain the supplementary crystallographic data for **5** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif.

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- [6] Compound 1: NMR (CDCl₃): ¹H δ (ppm) 6.88 (b, 4H, *p*-Ph), 6.83 (b, 2H, *o*-Ph), 3.58 (s, 4H, PhCH₂N), 2.98 (b, 2H, NH), 2.71 (m, 8H, NCH₂), 2.59 (m, 4H, NCH₂), 2.49 (m, 4H, NCH₂), 2.24 (s, 36H, Ph-(CH₃)), 1.82 (m, 4H, CH₂CH₂CH₂). ¹³Cl¹H] δ (ppm) 137.4 (*ipso*-PhCH₂N), 128.6 (*p*-Ph), 127.3 (*o*-Ph), 57.6 (PhCH₂N), 53.9, 52.1, 49.7, 47.5 (NCH₂), 26.0 (CH₂CH₂CH₂), 21.3 (Ph(CH₃)). Anal. calcd for C₂₈H₄₄N₄(CH₂Cl₂)_{0.4}: C, 72.48; H, 9.59; N, 11.90. Found: C, 72.42; H, 10.04; N, 12.38.Compound **2**: NMR (CDCl₃): ¹H δ (ppm) 7.30 (b, 2H, *p*-Ph), 7.17 (b, 4H, *o*-Ph), 3.61 (s, 4H, PhCH₂N), 2.76 (m, 8H, NCH₂), 2.57 (m, 8H, NCH₂), 2.31 (b, 2H, NH), 1.86 (m, 4H, CH₂CH₂CH₂), 133 (s, 36H, Ph-C(CH₃)₃. ¹³Cl¹H] δ (ppm) 150.4 (*ipso*-PhC(CH₃)₃), 137.2 (*ipso*-PhCH₂N), 123.3 (*o*-Ph), 120.8 (*p*-Ph), 57.9 (PhCH₂N), 53.60, 49.1, 47.4, 47.3 (NCH₂), 34.7 (PhC(CH₃)₃), 31.5 (PhC(CH₃)₃), 26.1 (CH₂CH₂CH₂). Anal. calcd for C₄₀H₆₈N₄(CH₂Cl₂)_{0.2}: C, 77.63; H, 11.08; N, 9.01. Found: C, 77.80; H, 11.62; N, 8.66.
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- [9] (1,8-Dienzyl-1,4,8,11-tetraazacyclotetradecane)Li₂(Et₂O)₂ (4): Compound 3 (1.00 g, 2.6 mmol) was dissolved in 40 mL of Et₂O and 2 equiv of a 1.6 M LiBu solution in *n*-hexane (3.28 mL, 5.3 mmol) were added drop wise at room

temperature. The white solution turned yellow and a white precipitate was instantly formed. The solution was left stirring for 1 h, concentrated to a minimum volume of ether and filtered. The white powder was washed with n hexane and isolated in 65% yield. NMR (C₆D₆): ¹H δ (ppm) 7.10–7.02 (10H, Ph), 3.80–3.58 (8H, NCH₂, NCH₂Ph), 3.40 (d, 2H, NCH₂Ph), 3.27 (m, 10H, NCH₂ e OCH₂CH₃), 3.02 (m, 2H, NCH₂), 2.89 (m, 2H, NCH₂), 2.71 (m, 2H, NCH₂), 2.42 (m, 4H, NCH₂), 2.04 (m, 2H, CCH₂C), 1.78 (m, 2H, CCH₂C), 1.12 (t, 12H, OCH₂CH₃); ¹³C{¹H} δ (ppm) 136.8, 130.2, 127.4 (Ph), 65.9 (OCH₂CH₃), 59.3, 58.9, 56.8, 55.9, 54.2 (CH₂N), 30.1 (CCH₂C), 1.56 (OCH₂CH₃), Anal. calcd for C₃₂H₅₄Li₂N₄O₂: C, 71.09; H, 10.07; N, 10.36. Found: C, 71.20; H, 9.82; N, 13.78.

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- [11] Crystallographic data for **5**: $C_{32}H_{50}N_4Li_2O_2$, $F_w = 536.64$, Triclinic, P-1, a = 8.740(2) Å, b = 9.928(3) Å, c = 10.012(3) Å, $\alpha = 64.522(13)^\circ$, $\beta = 82.339(13)^\circ$, $\gamma = 84.472(15)^\circ$, V = 776.5(4) Å³, Z = 1, F(000) = 292, Bruker AXS KAPPA APEX II difractometer, T = 150(2) K, Colourless, Plate, $0.1 \times 0.1 \times 0.2$, $\mu = 0.070$ mm⁻¹, $D_x = 1.148$ g/cm³, $\theta_{max} = 29.24$, 4178 unique reflections, 2221 with $I > 2\sigma(I)$, 181 parameters refined. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0629$, $\omega R_2 = 0.1263$, all data: $R_1 = 0.1375$, $\omega R_2 = 0.1476$.
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- [13] (1,8-Dibenzyl-1,4,8,11-tetraazacyclotetradecane)ZrCl₂ (6): Compound 3 (0.86 g, 2.3 mmol) was dissolved in 30 mL of THF and was rapidly added to a concentrated THF solution of ZrCl₂(CH₂SiMe₃)₂(Et₂O)₂ (1.10 g, 2.3 mmol). A reflux condenser was adapted and the reaction mixture was left under mild reflux. After 3 h, 90% of the THF was evaporated. The remaining THF was filtered and the bright yellow solid was rinsed with hexanes and taken to dryness (1.06 g, 87%).
- [14] (1,8–(3,5-Dimethylbenzyl)–1,4,8,11–tetraazacyclotetradecane)ZrCl₂ Compound 1 (0.50 g, 1.1 mmol) was dissolved in 15 mL of THF and was rapidly added to a concentrated THF solution of ZrCl₂(CH₂SiMe₃)₂(Et₂O)₂ (0.55 g, 1.1 mmol). A reflux condenser was adapted and the reaction mixture was left under mild reflux. After 2 h a light yellow precipitate was formed. The mixture was refluxed for further 3 h and 90% of the THF was evaporated. The remaining THF was filtered and the bright yellow solid was rinsed with hexanes and taken to dryness (0.40 g, 61%). Crystals suitable for X-ray diffraction were obtained from a dichloromethane solution stored at -20 °C. NMR (CDCl₃): ¹H δ (ppm) 6.99 (b, 2 H, *p*-Ph), 6.94 (b, 4H, *o*-Ph), 4.66 (d, 2H, PhCH₂N), 4.33 (m, 2H, NCH₂CH₂CH₂N(CH₂Ph)), 4.27 (d, 2H, PhCH₂N), 3.78 (m, 2H, NCH2CH2N(CH2Ph)), 3.55 (m, 2H, NCH2CH2CH2N(CH2Ph)), 3.35 (m, 2H, NCH₂CH₂N(CH₂Ph)), 3.15 (m, 2H, NCH₂CH₂N(CH₂Ph)), 2.78 (m, 2H $NCH_2CH_2CH_2N(CH_2Ph))$, 2.63 (m, 2H, $NCH_2CH_2CH_2N(CH_2Ph))$, 2.51 (m, 2H, $NCH_2CH_2N(CH_2Ph))$, 2.51 (m, 2H, $NCH_2N(CH_2Ph))$, 2.51 (m, 2H)), 2.51 (m, 2H)), 2.51 (m, 2H)), 2.51 (m, 2H)), 2.51 (m, 2H)) $NCH_2CH_2N(CH_2Ph)$, 2.33 (b, 12H, Ph-CH₃), 1.91 (m, 2H, CH₂CH₂CH₂), 1.53 (m, 2H, CH₂CH₂CH₂); ¹³C(¹H) δ (ppm) 137.7 (*ipso*-PhCH₃), 131.0 (*ipso*-PhCH₂N), 130.5 (o-Ph), 129.9 (p-Ph), 56.4 (NCH₂CH₂CH₂N(CH₂Ph)), 56.0 (PhCH₂N), 55.0 $(NCH_2CH_2CH_2N(CH_2Ph)), 53.6 (NCH_2CH_2N(CH_2Ph)), 49.1 (NCH_2CH_2N(CH_2Ph)),$ 24.8 (CH₂CH₂CH₂), 21.3 (CH₃PhCH₂N). Anal. calcd for C₂₈H₄₂Cl₂N₄Zr(CH₂Cl₂)₂: C, 47.00; H, 6.05; N, 7.31. Found: C, 46.97; H, 6.80; N, 7.38.(1.8-(3.5-Di-tertbutylbenzyl)-1,4,8,11-tetraazacyclotetradecane)ZrCl₂ (8): Compound 2 (0.70 g, 1.2 mmol) was dissolved in 15 mL of THF and was rapidly added to a concentrated THF solution of ZrCl₂(CH₂SiMe₃)₂(Et₂O)₂ (0.56 g, 1.2 mmol). A reflux condenser was adapted and the reaction mixture was left under mild reflux. No precipitate was formed after 6 h of reflux. The solution was taken to dryness. The resulting yellow solid was washed with toluene, resulting in a bright yellow solid that was taken to dryness (0.50 g, 56%). Crystalline material was obtained from a cold dichloromethane solution. NMR (CDCl₃): ¹H δ (ppm) was obtained non a construction obtained in the obtained in the optain (CL_3) , (CL_3) , (CL $NCH_2CH_2CH_2N(CH_2Ph))$, 2.58 (m, 2H, $NCH_2CH_2CH_2N(CH_2Ph))$, 2.39 (m, 2H, NCH₂CH₂CH₂(CH₂(H)), 2.55 (m, 2H, HCH₂CH₂CH₂(H), 1.55 (m, 2H, HCH₂CH₂(H)), 1.85 (m, 2H, CH₂CH₂(H₂), 1.46 (m, 2H, CH₂CH₂CH₂), 1.25 (b, 36H, Ph-C(CH₃)₃); $^{13}C(^{11}H) \delta$ (ppm) 150.5 (*ipso-PhC*(CH₃)₃), 129.9 (*o-Ph*), 129.9 (*o-Ph* (ipso-PhCH₂N), 122.0 (*p*-Ph), 56.9 (PhCH₂N), 126.9 56.3 (NCH₂CH₂CH₂N(CH₂Ph)), 551 (NCH₂CH₂CH₂CH₂N(CH₂Ph)), 535 (NCH₂CH₂N(CH₂Ph)), 49.0 (NCH₂CH₂N(CH₂Ph)), 34.7 (PhC(CH₃)₃), 31.5 $(PhC(H_3)_3), 24.9 (CH_2CH_2CH_2). Anal. calcd for C_{40}H_{65}Cl_2N_4Zr(CH_2Cl_2): C, 57.93; H, 8.06; N, 6.59. Found: C, 58.73; H, 8.99; N, 6.56.$
- [15] Crystallographic data for 7: $C_{28}H_{42}N_4ZrCl_2$, $F_w = 596.8$, Monoclinic, P2/a, a = 13.411(4) Å, b = 7.380(2) Å, c = 14.324(4) Å, $\alpha = 90.00^{\circ}$, $\beta = 97.722(19)^{\circ}$, $\gamma = 90.00^{\circ}$, V = 1404.8(7) Å³, Z = 2, F(000) = 624, Bruker AXS KAPPA APEX II, T = 150(2) K, Colourless, Plate, $0.05 \times 0.1 \times 0.1$, $\mu = 0.605$ mm⁻¹, $D_x = 1.411$ g/ cm³, $\theta_{max} = 32.64$, 5132 unique reflections, 3065 with $I > 2\sigma(I)$, 159 parameters refined. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0549$, $\omega R_2 = 0.0922$, all data: $R_1 = 0.1217$, $\omega R_2 = 0.1055$.
- [16] Polymerization studies were carried out using standard Schlenk techniques and the mixture was quenched with acidic methanol (1% CH₃COOH). The solution was evaporated, the polymer was precipitated by addition of water and dried in a vacuum desiccator during two days.
- [17] J.C.W. Chien, B.-P. Wang, J. Polym. Sci., Part A: Polym. Chem. 26 (1988) 3089. The polymerization mixture was quenched with acidic methanol (2% HCl) and the polymer was filtered, washed with methanol and dried in a vacuum oven at 60 °C during two days..