

Note

# An amido lithium tetra-zinc oxo complex: Synthesis and X-ray crystal structure of ( $\mu_4$ -oxo)-pentakis( $\mu_2$ -diethylamido)-bis(N(ethyl)CHCH<sub>2</sub>)-lithium-tetrazinc

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Received 21 July 2006; received in revised form 4 September 2006; accepted 3 October 2006

Available online 10 October 2006

## Abstract

The synthesis of an unusual cyclometallated amido lithium-tetra-zinc complex, ( $\mu_4$ -oxo)-pentakis( $\mu_2$ -diethylamido)-bis(N(ethyl)CHCH<sub>2</sub>)-lithium-tetrazinc, was achieved in reasonable yield by the reaction of zinc chloride and lithium diethylamide. The new complex was characterised and an X-ray crystal structure was reported.

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*Keywords:* Zinc; Amide; Oxo; Lithium

## 1. Background

Zinc amide complexes are an important class of compounds for use in inorganic and organometallic synthesis, catalytic chemistry and materials synthesis. Whilst considerable attention has been paid to zinc alkyl and zinc alkoxide complexes, the majority of the research with zinc amides has focused on the commercially available [bis{bis(trimethylsilyl)amido}zinc]. It is a useful precursor for organometallic and inorganic syntheses as it reacts with acidic ligands to liberate bis(trimethylsilyl)amine and enable the clean synthesis of mononuclear zinc compounds [1]. These complexes have also been used as catalysts for Lewis acid catalysed transformations, for example the Aldol reaction and ring opening polymerisations [1,2]. Zinc amides have also been used as molecular precursors for inorganic materials synthesis, either through CVD or by controlled hydrolysis to generate zinc oxide nanomaterials [3,4].

The first reported alkyl(amido)zinc complexes [ZnR(NR'<sub>2</sub>)] (1856) were formed by direct combination

of diethyl zinc and a range of amines, including diethylamine [5]. Several subsequent publications detail the syntheses of [ZnR(NR'<sub>2</sub>)] [6–9] with special emphasis being paid to the bulky bis(trimethylsilyl)amide [10,11]. Less attention has been paid to more basic and less sterically hindered amines such as the di(alkyl)amines, although the syntheses of the [alkyl{di(alkyl)amido}zinc] complexes are well documented [9,12–14]. A recent report highlights the utility of [aryl{di(alkyl)amido}zinc] complexes, generated *in situ*, for the preparation of  $\alpha$ -functionalised organozincs [15].

[Bis{di(alkyl)amido}zinc] complexes would be interesting precursors for both organometallic and inorganic syntheses, but have received scant attention. There are only two previous literature reports: Rees and co-workers described the synthesis of [bis(tetramethylpiperidido)zinc] [16] and O'Brien and Malik reacted zinc chloride with 2 equivalents of lithium di(alkyl)amide to generate three novel [bis{di(alkyl)amido}zinc] compounds, where alkyl includes ethyl, iso-propyl and iso-butyl groups [3]. During our investigations into [bis{di(alkyl)amido}zinc] complexes [17], an unusual cyclometallated amido lithium tetra zinc complex was discovered whereby the [bis{di(alkyl)amido}-zinc] had undergone an unexpected cyclometallation and

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oxo capture reaction, thus ( $\mu_4$ -oxo)-pentakis( $\mu_2$ -diethylamido)-bis(*N*(ethyl)CHCH<sub>2</sub>)-lithium-tetrazinc was synthesised and its X-ray structure determined.

## 2. Experimental

### 2.1. Materials and instrumentation

The reaction was performed using standard techniques on a nitrogen line and in an MBraun nitrogen filled glove box. Hexane and diethyl ether were dried by distillation from sodium benzophenone ketyl. Anhydrous zinc chloride (>99%) and *n*-butyl lithium were purchased from Aldrich and used as received. Diethyl amine was purchased from VWR and distilled from CaH<sub>2</sub> immediately prior to use. The <sup>1</sup>H NMR spectrum was recorded on a JOEL 270 MHz NMR spectrometer, chemical shifts are given in ppm relative to the residual CHCl<sub>3</sub> in the CDCl<sub>3</sub>. The elemental analysis was performed by Mr Steven Boyer, London Metropolitan University.

### 2.2. Synthesis of ( $\mu_4$ -oxo)-pentakis ( $\mu_2$ -diethylamido)-bis(*N*(ethyl)CHCH<sub>2</sub>)-lithium-tetrazinc

Diethylamine (0.89 mL, 8.60 mmol, 2.5 equiv.) was dissolved in hexane (10 mL) and cooled to  $-78^\circ\text{C}$ . A solution of *n*-butyl lithium (5.40 mL of a 1.6 M solution in pentane, 8.60 mmol, 2.5 equiv.) was added resulting in immediate formation of a white precipitate. The precipitate was filtered and washed with hexane (3  $\times$  20 mL). Lithium diethylamide was dissolved in diethyl ether (10 mL) and added slowly to a solution of anhydrous zinc chloride (0.46 g, 3.50 mmol, 1 equiv.) in diethyl ether (15 mL) at  $0^\circ\text{C}$ . The solution was kept at  $0^\circ\text{C}$  for 20 h during which time a white precipitate formed. The solution was filtered and stirred for a further 24 h at room temperature which resulted in a colour change to yellow and further formation of lithium chloride. The lithium chloride was removed and the filtrate was evaporated to yield a yellow solid which was crystallised from cold hexane to yield white crystals (0.56 g, 1.4 mmol, 20%).

Anal. Calc. for C<sub>28</sub>H<sub>66</sub>LiN<sub>7</sub>OZn<sub>4</sub>: C, 42.5; H, 8.4; N, 12.4. Found: C, 43.0; H, 8.9; N, 12.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz, ppm) 0.28 (2H, m, Zn-CH<sub>2</sub>), 1.08–1.14 (18H, m, CH<sub>3</sub>), 3.02–3.28 (12H, m, CH<sub>2</sub>), 8.06 (1H, t, <sup>3</sup>J<sub>HH</sub> 8 Hz, CH=N).

### 2.3. X-ray crystal data

C<sub>28</sub>H<sub>66</sub>LiN<sub>7</sub>OZn<sub>4</sub> ·  $\frac{1}{36}$ Et<sub>2</sub>O, *M* = 787.32, trigonal, P3<sub>1</sub>21 (no. 152), *a* = 18.1905(6) Å, *c* = 11.6032(4) Å, *V* = 3325.04(19) Å<sup>3</sup>, *Z* = 3, *D*<sub>c</sub> = 1.180 g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha)$  = 2.163 mm<sup>-1</sup>, *T* = 173 K, colourless needles, Oxford Diffraction Xcalibur 3 diffractometer; 7780 independent measured reflections, *F*<sup>2</sup> refinement, *R*<sub>1</sub> = 0.049, *wR*<sub>2</sub> = 0.099, 7526 independent observed absorption-corrected reflections [*F*<sub>o</sub>] > 4σ(*F*<sub>o</sub>), 2θ<sub>max</sub> = 65°, 192 parameters. The absolute

structure was determined by a combination of *R*-factor tests [*R*<sub>1</sub><sup>+</sup> = 0.0486, *R*<sub>1</sub><sup>-</sup> = 0.0592] and by use of the Flack parameter [*x*<sup>+</sup> = +0.000(16), *x*<sup>-</sup> = +1.007(16)]. The solvent present was disordered, and was handled using the SQUEEZE procedure (see supporting information).

## 3. Results and discussion

[Bis{di(ethyl)amido}zinc] was targeted as a useful precursor for the synthesis of well defined zinc amide complexes for use in catalysis and as a molecular precursor to zinc oxide via mild and controllable hydrolysis. Despite some reports detailing its preparation by direct combination of diethyl zinc and diethylamine [13]. We, and others, have found that this led exclusively to the formation of [di(ethyl)amido]ethylzinc [3,8]. This was due to the kinetic stability of diethylzinc and [di(ethyl)amido]ethylzinc. We observed that the reaction of two and a half equivalents of freshly prepared lithium diethylamide with anhydrous zinc chloride, at low temperature over 1 h, led initially to the formation of a mixture of lithium diethyl amide, Zn(NEt<sub>2</sub>)Cl and Zn(NEt<sub>2</sub>)<sub>2</sub> in approximately a 2:2:1 ratio, determined by <sup>1</sup>H NMR spectroscopy. When the mixture of lithium diethyl amide, Zn(NEt<sub>2</sub>)Cl and Zn(NEt<sub>2</sub>)<sub>2</sub> was stirred at room temperature for one day, more lithium chloride was precipitated and the filtrate was evaporated to yield a yellow gum. Crystallisation from hexane produced white crystals in 20% yield. The filtrate from the crystallisation was evaporated to yield Zn(NEt<sub>2</sub>)<sub>2</sub>, a tacky solid, in approximately 80% yield and with analysis consistent with the published reports [3]. The white crystals, analysed by elemental analysis were not consistent with the Zn(NEt<sub>2</sub>)<sub>2</sub> minimal formula, but the analysis was consistent with incorporation of an oxo ligand. The <sup>1</sup>H NMR of the new compound showed peaks at 8.06, 3.24, 1.12 and 0.22 ppm integrating to 1, 12, 18 and 2 protons, respectively. All the peaks were broadened and could not be further resolved even at  $-90^\circ\text{C}$  (in CD<sub>2</sub>Cl<sub>2</sub>). The peaks are assigned to the imine, methylene, methyl and zinc-methylene protons, respectively. The broad peaks could indicate rapid exchange or fluxional processes are occurring in the tetrazinc cluster, these could involve changes to the aggregation state of the cluster. Crystals suitable for X-ray diffraction were grown by slow cooling of the hexane solution and representations of the structure are shown in Figs. 1 and 2. The X-ray structure showed that a rare cyclometallated amido lithium tetra zinc complex had formed. It also sheds light on the <sup>1</sup>H NMR, the peak at 8.06 ppm being assigned to the imine protons, the multiplet at 0.46 ppm being assigned to the methylenes in the N(Et)CHCH<sub>2</sub> unit, the peaks at 3.24 and 1.12 are assigned to the methylene and methyl protons on the ethyl groups.

## 4. X-ray crystal structure

X-ray analysis of crystals of **1** revealed an unusual and unexpected tetrazinc cluster with a central five-coordinate

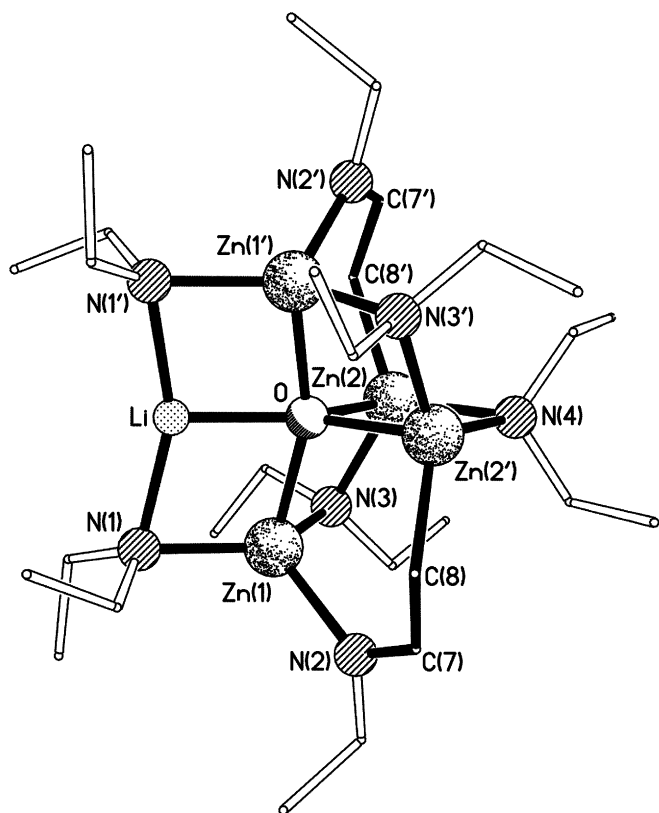


Fig. 1. The molecular structure of the  $C_2$ -symmetric tetrazinc cluster **1**. The atoms labelled with primes are related to their non-primed analogues by the  $C_2$  axis which is coincident with the  $\text{Li} \cdots \text{O}$  vector.

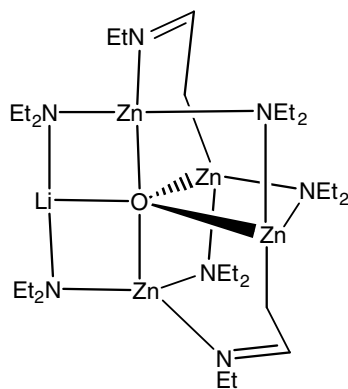


Fig. 2. Representation of the tetrazinc cluster **1**.

oxygen atom and an incorporated lithium ion (Fig. 1). The  $C_2$ -symmetric cluster consists of three  $\text{Zn}_2\text{ON}$  and two  $\text{ZnONLi}$  4-membered rings, and two 6-membered  $\text{Zn}_2\text{ONC}_2$  chelate rings all sharing the same sole oxygen atom, giving the cluster a unique  $\text{LiZn}_4\text{O}$  core [18]. Probably the most notable feature of the cluster is the transformation of an  $\text{Et}_2\text{N}$  moiety into an  $\text{EtN}=\text{C}(\text{H})-\text{CH}_2-$  unit [ $\text{N}(2)-\text{C}(7)$  1.301(4),  $\text{C}(7)-\text{C}(8)$  1.431(4) Å] which bridges between two zinc centres using the nitrogen and terminal  $\text{CH}_2$  carbon atoms [ $\text{N}(2)$  and  $\text{C}(8)$ ] [19]. The inner core of this structure has a topology very similar to that of the tetramagnesium species ( $\mu_4$ -oxo)-pentakis( $\mu_2$ -2-methyl-

phenoxy)-bis( $\mu_2$ -2-methylphenoxy)-tetrakis(tetrahydrofuran)-lithium-tetramagnesium [20], though the literature structure has seven 4-membered rings. The geometry at the central oxygen atom in **1** is distorted trigonal bipyramidal,  $\text{Zn}(1)$  and  $\text{Zn}(1')$  occupying the axial positions with a *trans* axial angle of  $161.10(17)^\circ$ ; the axial–equatorial *cis* angles are in the range  $80.55(8)$ – $106.98(6)^\circ$ , and the unique equatorial–equatorial *cis* angles are  $86.26(12)^\circ$  and  $136.87(6)^\circ$  (Table 1). The  $\text{Zn}-\text{O}$  bonds differ by less than 2%, being 2.0818(6) and 2.054(2) Å to  $\text{Zn}(1)$  and  $\text{Zn}(2)$ , respectively, and are noticeably longer than the  $\text{Zn}-\text{O}$  bond distances typically seen in clusters with  $\text{Zn}_4\text{O}$  moieties [21–23]. The severe angular distortions at the oxygen are a consequence of the 4-membered chelate rings at this oxygen atom, which have bite angles of  $86.26(12)^\circ$ ,  $87.00(5)^\circ$  and  $80.55(8)^\circ$ . This is particularly noticeable in the equatorial plane where the  $86.26(12)^\circ$   $\text{Zn}(2)-\text{O}-\text{Zn}(2')$  bite angle causes a ca.  $34^\circ$  contraction from ideal, and an associated ca.  $17^\circ$  enlargement of both the  $\text{Zn}(2)-\text{O}-\text{Li}$  and  $\text{Zn}(2')-\text{O}-\text{Li}$  angles. The two unique  $\text{Zn}_2\text{ON}$  rings have noticeably different geometries; for the  $\{\text{Zn}(2), \text{Zn}(2'), \text{O}, \text{N}(4)\}$  ring, the four atoms are perfectly coplanar, a consequence of the  $C_2$  symmetry, whilst for the  $\{\text{Zn}(1), \text{Zn}(2), \text{O}, \text{N}(3)\}$  ring there is a ca.  $20^\circ$  fold about the  $\text{Zn}(1) \cdots \text{Zn}(2)$  vector. This fold is reflected in a ca.  $3^\circ$  contraction of the  $\text{O}-\text{Zn}-\text{N}$  angles from  $93.77(9)^\circ$  in the  $\{\text{Zn}(2), \text{Zn}(2'), \text{O}, \text{N}(4)\}$  ring to  $90.37(8)^\circ$  and  $90.94(8)^\circ$  in the  $\{\text{Zn}(1), \text{Zn}(2), \text{O}, \text{N}(3)\}$  ring. At the same time there is a ca.  $2^\circ$  enlargement of the  $\text{Zn}-\text{N}-\text{Zn}$  angle at  $\text{N}(3)$  [ $88.04(9)^\circ$ ] cf. that at  $\text{N}(4)$  [ $86.20(15)^\circ$ ]. The bite angles for the two rings are similar, being  $86.26(12)^\circ$  and  $87.00(5)^\circ$  for the

Table 1  
Selected bond lengths (Å) and angles ( $^\circ$ ) for **1**

Bond length (Å)			
$\text{Zn}(1)-\text{O}$	2.0818(6)	$\text{Zn}(1)-\text{N}(1)$	1.973(3)
$\text{Zn}(1)-\text{N}(2)$	2.057(3)	$\text{Zn}(1)-\text{N}(3)$	2.044(3)
$\text{Zn}(2)-\text{O}$	2.054(2)	$\text{Zn}(2)-\text{N}(3)$	2.052(2)
$\text{Zn}(2)-\text{N}(4)$	2.055(3)	$\text{Zn}(2)-\text{C}(8')$	2.067(3)
$\text{Li}-\text{O}$	1.921(9)	$\text{Li}-\text{N}(1)$	2.000(3)
$\text{Li}-\text{N}(1')$	2.000(3)	$\text{O}-\text{Zn}(1')$	2.0818(6)
$\text{O}-\text{Zn}(2')$	2.054(2)	$\text{N}(2)-\text{C}(7)$	1.301(4)
$\text{C}(7)-\text{C}(8)$	1.431(4)	$\text{Zn}(1) \cdots \text{Zn}(2)$	2.8468(5)
$\text{Zn}(1) \cdots \text{Zn}(2')$	3.3242(5)	$\text{Zn}(2) \cdots \text{Zn}(2')$	2.8082(7)
$\text{Zn}(1) \cdots \text{Li}$	2.591(5)	$\text{Zn}(1') \cdots \text{Li}$	2.591(5)
Bond angle ( $^\circ$ )			
$\text{O}-\text{Zn}(1)-\text{N}(1)$	96.42(11)	$\text{O}-\text{Zn}(1)-\text{N}(2)$	110.77(9)
$\text{O}-\text{Zn}(1)-\text{N}(3)$	90.37(8)	$\text{N}(1)-\text{Zn}(1)-\text{N}(2)$	114.87(11)
$\text{N}(1)-\text{Zn}(1)-\text{N}(3)$	130.34(11)	$\text{N}(2)-\text{Zn}(1)-\text{N}(3)$	108.14(11)
$\text{O}-\text{Zn}(2)-\text{N}(3)$	90.94(8)	$\text{O}-\text{Zn}(2)-\text{N}(4)$	93.77(9)
$\text{O}-\text{Zn}(2)-\text{C}(8')$	102.88(11)	$\text{N}(3)-\text{Zn}(2)-\text{N}(4)$	121.42(8)
$\text{N}(3)-\text{Zn}(2)-\text{C}(8')$	113.77(12)	$\text{N}(4)-\text{Zn}(2)-\text{C}(8')$	121.73(11)
$\text{O}-\text{Li}-\text{N}(1)$	100.9(3)	$\text{O}-\text{Li}-\text{N}(1')$	100.9(3)
$\text{N}(1)-\text{Li}-\text{N}(1')$	158.2(5)	$\text{Zn}(1)-\text{O}-\text{Zn}(2)$	87.00(5)
$\text{Zn}(1)-\text{O}-\text{Li}$	80.55(8)	$\text{Zn}(1)-\text{O}-\text{Zn}(1')$	161.10(17)
$\text{Zn}(1)-\text{O}-\text{Zn}(2')$	106.98(6)	$\text{Zn}(2)-\text{O}-\text{Li}$	136.87(6)
$\text{Zn}(2)-\text{O}-\text{Zn}(1')$	106.98(6)	$\text{Zn}(2)-\text{O}-\text{Zn}(2')$	86.26(12)
$\text{Li}-\text{O}-\text{Zn}(1')$	80.55(8)	$\text{Li}-\text{O}-\text{Zn}(2')$	136.87(6)
$\text{Zn}(1')-\text{O}-\text{Zn}(2')$	87.00(5)		

{Zn(2), Zn(2'), O, N(4)} and {Zn(1), Zn(2), O, N(3)} rings, respectively. The only noticeable difference in the bond lengths within the two rings is that the Zn(1)–O bond [2.0818(6) Å] is longer than that to Zn(2) [2.054(2) Å], though given that the actual difference is less than 0.03 Å it is unlikely to have a major effect on the geometry of the 4-membered rings. The unique ZnONLi ring has a much more asymmetric geometry; though the Li–N(1) and Zn(1)–N(1) bond lengths are very similar [2.000(3) and 1.973(3) Å, respectively], the Li–O and Zn(1)–O bonds differ by ca. 0.16 Å [1.921(9) and 2.0818(6) Å, respectively]. It is noticeable that the Zn(1)–N(1) bond length here [1.973(3) Å] is significantly shorter than the other Zn–N bonds in the cluster which range between 2.044(3) and 2.057(3) Å, though it is not immediately clear why this should be the case. Whilst the intra-ring angles at the oxygen and the nitrogen are fairly similar [80.55(8)° and 81.4(3)°, respectively], those at the lithium [100.9(3)°] and Zn(1) [96.42(11)°] differ by ca. 4°. The ZnLiNO ring is slightly folded, the {Zn(1), O, Li} and {Zn(1), N(1), Li} planes being inclined by ca. 9°. The bite angle subtended at the oxygen centre by this ring is substantially contracted compared to the Zn<sub>2</sub>ON rings, being 80.55(8)° cf. 86.26(12)° and 87.00(5)° (*vide supra*). The 6-membered Zn<sub>2</sub>ONC<sub>2</sub> ring has a severely twisted geometry, C(8) and Zn(2') lying ca. +0.56 and –0.48 Å out of the {Zn(1), O<sub>2</sub>, N(2), C(7)} plane which is coplanar to within ca. 0.05 Å (a positive deviation being in the direction of the lithium centre). The geometry at the lithium centre is T-shaped planar, all four atoms being perfectly coplanar due to the C<sub>2</sub> axis, the two O–Li–N angles being 100.9(3)°, and the N(1)–Li–N(1') angle being 158.2(5)°. Both Zn(1) and Zn(2) have distorted tetrahedral geometries with angles in the ranges 90.37(8)° to 130.34(11)° and 90.94(8)° to 121.73(11)°, respectively.

Although the formation of this unusual compound was fortuitous and is not yet fully understood, it is reproducible and the oxo ligand is postulated to derive from small quantities of water in the diethyl ether solvent. The complex is highly unusual for two reasons: firstly the enhanced reactivity of the [bis{di(alkyl)amido}zinc] is highlighted by the ability of the complex to attack its own dialkylamide ligands to form the unprecedented chelate ring and secondly in the ability of these complexes to abstract oxide ligands from water. The formation of the two N(Et)CHCH<sub>2</sub> chelate rings is without precedent and represents a potential route to functionalised alkyl zincs. Functionalised alkyl zincs are synthesised by the lithiation of haloalkanes or by the Reformatsky reaction. Amido zinc oxo complexes with an M<sub>4</sub>O core have been previously formed by the reaction of [alkyl(amido)zinc] complexes with water [21] or by the direct addition of azaindoles to zinc acetate dihydrate [22] but these structures do not include a lithium ion. Lithium zincates are known and have attracted attention recently in a number of catalytic transformations and structural studies [24]. Furthermore lithium zinc oxo clusters can be synthesised by the reaction of lithium alkylzincates with

oxygen [23] but amongst these lithium zinc oxo clusters the LiZn<sub>4</sub>O core unit is unknown. The only related structure, that of an LiMg<sub>4</sub>O core, was reported by Mulvey and co-workers by reaction of *o*-cresol with dibutylmagnesium and *n*-butyllithium [20]. Future investigations will focus on the rational synthesis of the novel complex by the controlled hydrolysis of [bis{di(alkyl)amido}zinc] complexes and on their utility in a range of catalytic processes.

### Acknowledgements

This material is based on work funded by the EPSRC grants GR/T17960/01, EP/C544846 and the Nuffield foundation grant NAL/00893/G.

### Appendix A. Supplementary material

Further details of the X-ray crystallography can be found in the supporting information. CCDC 612589 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.10.002](https://doi.org/10.1016/j.jorganchem.2006.10.002).

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