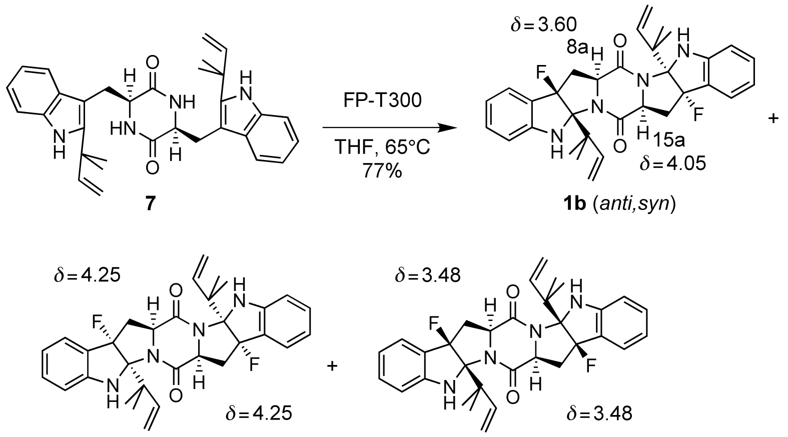

7 **1b** (*anti,syn*)

bis(*epi*)fluorogypsetin (**8**) (*syn,syn*) bis(*epi*)fluorogypsetin (**9**) (*anti,anti*)

(2)

rolo[2,3-*b*]indole-1,4-diones based on an electrophilic fluorination–cyclization sequence. We have demonstrated the utility of this procedure by the efficient syntheses of **1b** and **2b**. The biological activities of these alkaloid isosteres will be evaluated and reported subsequently. In addition, we plan to extend application of this new methodology to the synthesis of fluorinated analogues of other indole alkaloids, including himastatin and asperlicin.

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The First Alkaline Earth Metal Complex Containing a μ-η^1:η^1 Allyl Ligand: Structure of $[\{HC[C(t\mathrm{Bu})NC_6H_3(CHMe_2)_2]_2Mg(C_3H_5)\}_6]$**

Philip J. Bailey,* Stephen T. Liddle,*
Carole A. Morrison, and Simon Parsons

Recent times have witnessed a surge of interest in the use of β-diketiminates[1] as ancillary ligands in transition metal[2] and main group[3] coordination chemistry. The flexible steric and electronic properties of β-diketiminate ligands, such as **1** (see Scheme 1), make them ideal candidates for the synthesis of well-defined magnesium monoalkyl [(L-X)-Mg-R] complexes; an area that has been recently highlighted as relatively undeveloped,[4] and one which we,[3d, 3g] and others,[3i] have been addressing. Given that there is precedent for the oligomerization and polymerization of ethene by diakylmag-

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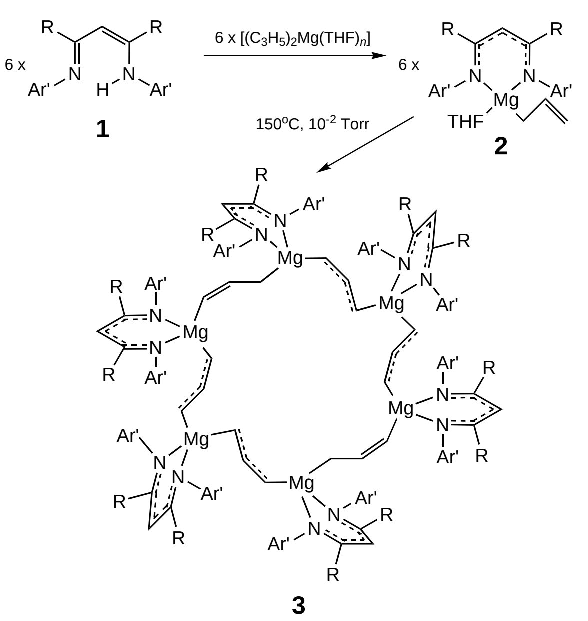
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



Scheme 1. Synthesis of **2** and **3**. Ar′ = 2,6-diisopropylphenyl, R = *t*Bu.

nesium compounds,[5] we have embarked upon a study of well-defined magnesium monoalkyl compounds with β-diketiminate ancillary ligands as potential catalytic agents. As part of this study we have investigated allyl complexes in the hope that they might protect a vacant coordination site without preventing reaction with ethene. A further incentive for this avenue of work is that, outside of transition metal coordination chemistry, there is a dearth of allyl complexes. Indeed, there are relatively few structurally characterized p-block metal allyl compounds,[6] and only a handful of Group I[7] and Group II[8] complexes. Herein we report the synthesis and characterization of the mono-THF solvated β-diketiminate magnesium allyl complex **2** , and its solvent-free form **3**, which adopts a remarkable cyclic hexanuclear structure, in which the allyl ligand adopts a μ-η^1:η^1 coordination mode that is unprecedented for alkaline-earth metal chemistry (Scheme 1).

$[\mathrm{HC\{C(}t\mathrm{Bu)NAr'\}_2Mg(C_3H_5)(thf)}]$ **2**

$[\{\mathrm{HC[C(}t\mathrm{Bu)NAr']_2Mg(C_3H_5)\}_6}]$ **3**

Treatment of **1** with one equivalent of $[(\mathrm{C_3H_5})_2\mathrm{Mg(THF)}_n]$ in toluene gave a yellow solution (Scheme 1). Upon standing at 5 °C overnight crystals formed, which were identified as **2** by NMR spectroscopy. A single-crystal X-ray structure analysis[9] of these crystals confirmed that **2** is a monomeric species in which the allyl ligand is bound to the four-coordinate magnesium center in a η^1 mode; a chelating β-diketiminate ligand and a molecule of THF complete the coordination sphere of the magnesium atom.

Thermal treatment of **2** (150 °C, 10^{-2} Torr) resulted in an orange oil (Scheme 1). Storage of a concentrated solution of this oil in toluene at −30 °C over three days gave crystals of **3**, which were shown by NMR spectroscopy to be free of THF. Although the best crystals of **3** that could be obtained diffracted only weakly, the essential features of the complex were determined unambiguously by an X-ray structure analysis,[10] which revealed that **3** is a hexanuclear cyclic species, in which magnesium centers are linked by *trans* μ-η^1:η^1 allyl groups. A chelating β-diketiminate ligand completes the coordination sphere of each magnesium center (Figure 1). Within transition metal coordination chemistry η^3 and η^1 coordination by allyl dominates. Although a relatively small number of complexes displaying *cis* μ-η^1:η^1 coordination are known,[11] there are very few examples of *trans* μ-η^1:η^1 coordination known for allyl.[12] Within main group chemistry there is only one example of *trans* μ-η^1:η^1 coordination, namely the tetramethylethylenediamine (TMEDA) solvate of allyllithium.[7e] Hence the coordination mode of allyl in **3** is, to the best of our knowledge, unprecedented in alkaline earth metal chemistry. The observed N-Mg-N chelate bite angles range between 95.4(2) and 97.2(2)°; a modest increase from

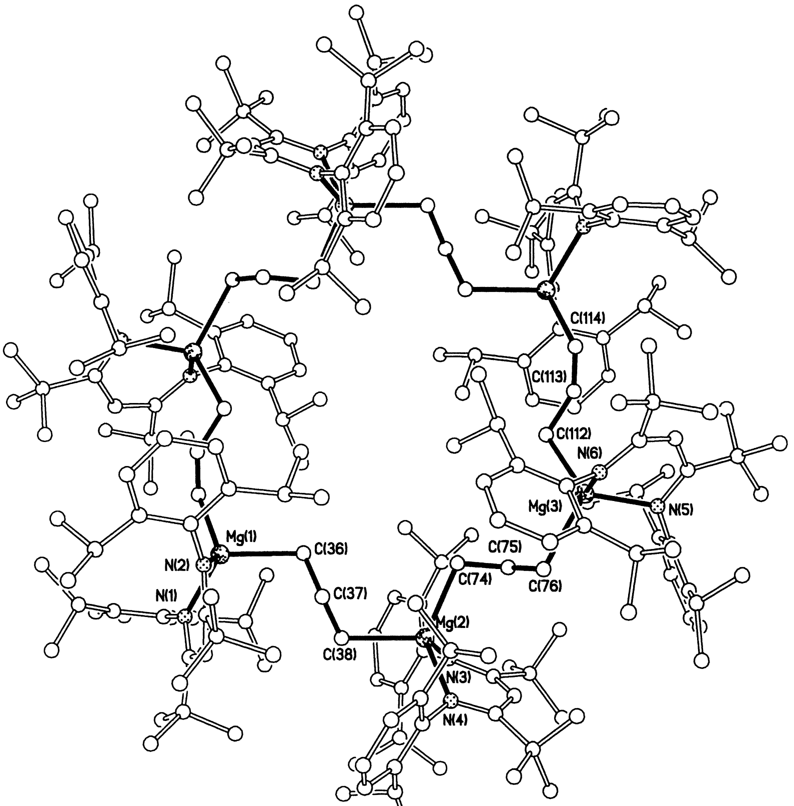


Figure 1. Crystal structure of **3**; hydrogen atoms are omitted for clarity. Only symmetry unique atoms are labeled. Selected bond lengths [Å] and angles [°]: Mg(1)-N(1) 2.056(5), Mg(1)-N(2) 2.067(5), Mg(1)-C(36) 2.327(5), Mg(1)-C(114) 2.328(16), Mg(2)-N(3) 2.039(5), Mg(2)-N(4) 2.075(4), Mg(2)-C(38) 2.290(5), Mg(2)-C(74) 2.308(6), Mg(3)-N(5) 2.058(5), Mg(3)-N(6) 2.048(5), Mg(3)-C(76) 2.304(5), Mg(3)-C(112) 2.252(6); Mg(1)-C(36)-C(37) 106.0(4), Mg(1)-C(114)-C(113) 111.5(10), Mg(2)-C(38)-C(37) 111.7(4), Mg(2)-C(74)-C(75) 107.6(4), Mg(3)-C(76)-C(75) 108.9(4), Mg(3)-C(112)-C(113) 109.4(4).

that observed in **2**.[9] The substitution of THF by additional allyl coordination results in angles at each magnesium center close to the tetrahedral ideal. The six-membered chelate rings adopt a distorted cyclohexane boat conformation in which the magnesium atom and central backbone carbon atoms deviate by mean distances of 0.3377 and 0.2488 Å, respectively, from the mean plane of the ring. The observed Mg–N bond lengths (mean 2.057(5) Å) are unremarkable and the Mg–C bonds range between 2.214(12) and 2.327(5) Å; these are correspondingly longer bonds than reported for the TMEDA solvate of allylmagnesium chloride (Mg–C bond length of 2.1793(3) Å),[8] the only other structurally reported allylmagnesium species, in which the allyl group bonds in an η^1 mode. Inspection of the allyl C–C bond lengths reveals that four of the six allyl groups are present as resonance-delocalized ligands with essentially identical C–C bond lengths (mean 1.396(7) Å), whereas the other two exhibit more localized long and short C–C bonds (C(112)–C(113) 1.4145(8), C(113)–C(114) 1.2901(11) Å). However, irrespective of internal allyl C–C bond lengths, the Mg-C-C bond angles span a narrow range (107.6(4)–111.7(4)°) close to the tetrahedral ideal. The allyl groups in **3** could be regarded as β-carbocations in which a negative charge is localized on each sp^2-hybridized CH$_2$ group. Although the Mg-C-C bond angles suggest sp^3 hybridization of the CH$_2$ groups, the requirement for conjugative stabilization of the carbocationic β-carbon atom would preclude such an arrangement, and we rationalize the electronic structure on the basis of sp^2 hybridization with distorted coordination caused by the steric demands of the β-diketiminate ligand.[13] Despite the structural data, NMR spectroscopic experiments at room temperature reveal that all allyl ligands are equivalent for **3**, with CH$_2$ hydrogen atoms appearing as a doublet at $\delta = 2.37$ and the β-CH hydrogen atom as a quintet at $\delta = 5.44$. The differences between the allyl ligands found in the solid state as outlined above must therefore be attributed to solid-state effects, and this is supported by preliminary density functional theory (DFT) calculations on a model system which show equivalent C–C bond lengths.[13]

Our aim in undertaking this work was to induce η^3 coordination of allyl groups to magnesium centers to protect the fourth coordination site by weak β-intramolecular ligation. However, the reluctance of magnesium to partake in π bonding results in an unusual μ-η^1:η^1 coordination mode in which the Mg–C bonding may be regarded as effectively σ in nature.

Experimental Section

2: Diallylmagnesium (0.23 g, 5.0 mmol) in THF (3.5 mL) was added dropwise to a solution of **1** in toluene (30 mL) at room temperature and was stirred for 2 h. The solution was filtered and concentrated to about 10 mL. Storage of the solution at 5 °C overnight gave **2** as colorless blocks in 44 % yield. M.p. 141–144 °C. ^{1}H NMR (360 MHz, C$_6$D$_5$CD$_3$, 293 K): $\delta = 1.28$ (s, 18 H; C(CH$_3$)$_3$), 1.31 (m, 4 H; C*H*$_2$-THF), 1.42 (d, ^3J(H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 1.48 (d, ^3J(H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 2.75 (d, ^3J(H,H) = 11.1 Hz, 4 H; CH$_2$-allyl), 3.44 (spt, ^3J(H,H) = 6.8 Hz, 4 H; C*H*(CH$_3$)), 3.89 (m, 4 H; OC*H*$_2$-THF), 5.48 (s, 1 H; CH), 6.16 (quin, ^3J(H,H) = 11.1 Hz, 1 H; C*H*-allyl), 7.22 (t, ^3J(H,H) = 5.6 Hz 4 H; *meta*-CH), 7.26 (d, ^3J(H,H) = 5.3 Hz, 2 H; *para*-CH); satisfactory C, H, and N analyses.

3: Crystals of **2** (1.278 g, 2.0 mmol) were heated to 150 °C under vacuum (10^{-2} Torr) for 1 h to give **3** as an orange oil in quantitative yield. Crystals of **3** were grown from a solution in toluene at −30 °C; yield 38 %. M.p. 138–140 °C. ^{1}H NMR (360 MHz, C$_6$D$_5$CD$_3$, 293 K): $\delta = 1.21$ (s, 108 H; C(CH$_3$)$_3$), 1.28 (d, ^3J(H,H) = 6.5 Hz, 72 H; CH(C*H*$_3$)$_2$), 1.30 (d, ^3J(H,H) = 6.5 Hz, 72 H; CH(C*H*$_3$)$_2$), 2.37 (d, ^3J(H,H) = 11.2 Hz, 24 H; C*H*$_2$-allyl), 3.24 (spt, ^3J(H,H) = 6.8 Hz, 24 H; C*H*(CH$_3$)), 5.38 (s, 6 H; CH), 5.44 (quin, ^3J(H,H) = 11.2 Hz, 6 H; C*H*-allyl), 7.04 (t, ^3J(H,H) = 6.2 Hz, 12 H; *meta*-CH), 7.13 (d, ^3J(H,H) = 6.3 Hz, 24 H; *para*-CH); satisfactory C, H, and N analyses.

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[10] Crystal data for **3**$\cdot 4\,C_6H_5CH_3$: $C_{232}H_{348}N_{12}Mg_6 \cdot 4\,C_6H_5CH_3$, $M_r = 3771.58$, triclinic, space group $P\bar{1}$, $a = 18.028(6)$, $b = 20.271(7)$, $c = 21.948(7)$ Å, $\alpha = 110.365(4)$, $\beta = 98.789(5)$, $\gamma = 109.543(5)^\circ$, $V = 6749.0(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 0.928$ g cm^{-3}; Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.065$ mm^{-1}, $T = 150$ K. A total of 38910 data (17554 unique, $R_{int} = 0.0998$, $\theta < 22.52^\circ$, reflections at higher angle were very weak or absent due to the severe disorder of solvent molecules; see below) were collected on a Bruker SMART APEX CCD diffractometer equipped with a Bruker Monocap capillary optic using narrow

frames (0.3° in ω) and were corrected semiempirically for absorption (transmission 0.709 – 0.928). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2202$ conventional $R = 0.0830$ for F values of 6700 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 0.927$ for 1159 parameters. Residual electron density extremes were 0.267 and −0.221 e Å^{-3}. Highly disordered toluene solvent molecules were treated by the SQUEEZE procedure of PLATON (A. L. Spek, University of Utrecht, The Netherlands, **2000**), which indicated the correct total electron density for four molecules of toluene per molecule of **3**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166394 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[13] Preliminary DFT calculations (B3LYP/6 – 31G*) for the simplified model system $[\{HC(CHNH)_2MgCH_3\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_3H_5)]^-$ were performed to obtain supporting evidence for sp^2 hybridization of the allyl CH$_2$ groups. The C–C bond lengths (1.403 Å) obtained clearly indicate an unsaturated bonding environment; in addition Mulliken charge assignments yield a positive charge to the central CH group, and negative charges to the neighboring CH$_2$ groups. The highest occupied molecular orbital (HOMO) can be largely attributed to p-type character orbitals located on the CH$_2$ carbon atoms, pointing in the direction of the Mg centers. Further details are provided in the Supporting Information.

An Unorthodox Conformation of [18]porphyrin-(1.1.1.1) Heteroanalogue—21,23-Ditelluraporphyrin with a Flipped Tellurophene Ring**

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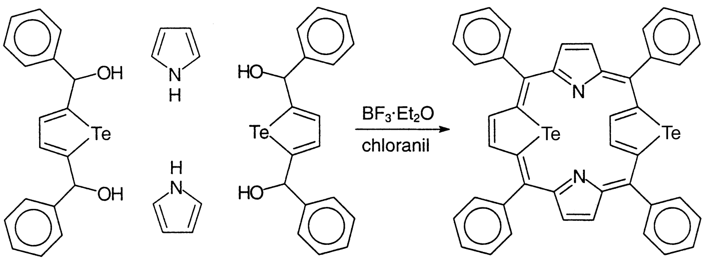
Conformational flexibility of tetrapyrrole macrocycles is currently appreciated as an important factor in the fine-tuning of porphyrin and metalloporphyrin properties.[1] Thus, introduction of sterically demanding residues (including nitrogen atom protonation) in the porphyrin core or at the outer rim (alkylation, arylation), as well as coordination of metal ions, can result in a nonplanar porphyrin conformation. Core-modified porphyrins, formed by replacement of one or more nitrogen atoms by other heteroatom(s), also demonstrate severe nonplanar arrangements once the size and/or number of heteroatoms in the core increases, even though the basic framework of the porphyrin skeleton is preserved.[2] On the whole, [18]porphyrins-(1.1.1.1) and their heteroanalogues contain a similar framework of four essentially planar five-membered rings linked by methine carbon atoms with all the nitrogen atoms or other heteroatoms pointing toward the center of the macrocycle. Even the most severe distortion of a macrocycle preserves such an "in"-macrocycle orientation of the five-membered rings.[1]

An enlargement of the macrocycle by the addition of heterocyclic moiety(s) and/or methine carbon atoms introduces a novel structural motif. Thus a five-membered ring—axiomatic for porphyrins (heteroporphyrins)—can be oriented in such a way that one nitrogen or other heteroatom is located at the outer perimeter and two β-atoms are found in the core or just over the center. An inversion of this type has been detected for the following expanded porphyrins and expanded heteroporphyrins:[3] tetrathia[22]porphyrin-(2.2.2.2),[4] tetrathia[24]porphyrin-(2.2.2.2),[5] *meso*-substituted [22]pentaphyrin-(1.1.1.1.0) (sapphyrins)[6] and its heteroanalogues,[7, 8] [26]hexaphyrin-(1.1.1.1.1.1),[9] heteroanalogues of [26]hexaphyrin-(1.1.0.1.1.0) (rubyrin),[3, 10] and heteroanalogues of [30]heptaphyrins-(1.1.0.0.1.1.0) and [30]heptaphyrins-(1.1.0.1.0.1.0).[11] The lowest limit of the macrocycle size permitting the flipped geometry is exemplified by [18]annulene bridged by three sulfur atoms (which formally may be named trithia[18]porphyrin-(2.2.2)), but it behaves only as an array of isolated thiophene units which are totally out of plane in the solid state.[5] It was also postulated that a 180° rotation of the *N*-confused pyrrole ring of 2-aza-21-carbaporphyrin is necessary to produce the "fused" porphyrin.[12] The conformation of 2-aza-21-carbaporphyrin with the flipped pyrrole ring is energetically accessible as demonstrated by DFT calculations.[13]

Here we report on the synthesis and characterization of 5,10,15,20-tetraphenyl-21,23-ditelluraporphyrin (Te$_2$TPP, **2**) which is the first heteroanalogue of [18]porphyrin-(1.1.1.1) with the nonplanar macrocyclic conformation containing the flipped five-membered ring.

The 21,23-ditelluraporphyrin **2** was synthesized by condensation of pyrrole and 2,5-bis(phenylhydroxymethyl)tellurophene[14c] (**1** Scheme 1). This procedure follows the methodology previously used for the preparation of 5,10,15,20-



1 **2**

Scheme 1. Synthesis of Te$_2$TPP.

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