interaction and dipole–dipole repulsion between C–O and C=N bonds.[9]

In conclusion, we have found a unique catalytic system in which DMS enolates activated by *i*$Pr_2NH$ and $H_2O$ exhibit high reactivity to *N*-tosylimines. To the best of our knowledge, the base-catalyzed Mannich-type reaction of metal enolates is unprecedented. The present reaction provides an efficient method for the stereoselective synthesis of $\beta$-aminocarbonyl compounds, which are versatile building blocks for the synthesis of numerous, biologically significant compounds.

## *Experimental Section*

Typical procedure (entry 1 in Table 1): **1a** (94 mg, 0.60 mmol) and *i*$Pr_2NH$ (1.6 μL, 12 μmol) were added to a solution of **2a** (130 mg, 0.50 mmol) and $H_2O$ (5.4 mL, 0.30 mmol) in DMF (1.0 mL) at $-78\,^{\circ}C$. After 18 h, the resultant mixture was quenched with 2 M aqueous HCl (10 mL), then neutralized with saturated aqueous $NaHCO_3$. The aqueous phase was extracted with ethyl acetate and the combined organic phases dried over $Na_2SO_4$ before being evaporated. Purification of the residue by column chromatography on silica gel (hexane:ethyl acetate, 4:1) afforded **3a** (166 mg, 91 %). Further details can be found in the Supporting Information.

Received: January 17, 2000 [Z 14544]

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# An Unprecedented Hexapotassium-Hexamagnesium 24-Membered Macrocyclic Amide: A Polymetallic Cationic Host to Six Monodeprotonated Arene Anions[**]

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and René B. Rowlings

*In memory of Ron Snaith*[+]

We are currently developing a new concept in macrocyclic host–guest chemistry of amide-supported heterodimetallic cationic rings which formally act as hosts to anionic guests.[1–3] This idea emerged from our investigations into the effects of mixing an alkali-metal amide with a magnesium bis(amide). While some of the reaction mixtures studied follow a straightforward path leading to simple heterodimetallic compositions,[4, 5] others take an unexpected turn to behave as powerful oxygen scavengers or as regioselective dideprotonating agents to yield two distinct categories of macrocyclic complex. One type of complex is the eight-membered $[(MNMgN)_2]^{2+}$ (M = Li, Na, K) ring systems with oxo $O^{2-}$ or peroxo $(O_2)^{2-}$ cores;[1] this first category has the generalized structure **I** (shown with the oxo core). We refer to this type as "inverse crown ether" complexes, on account of their inverse relationship to conventional crown ether complexes. The single potassium[2] example **1** is strictly a poly(inverse crown ether) complex since its $(KNMgN)_2$ ring is not discrete (unlike the $(LiNMgN)_2$ or $(NaNMgN)_2$ analogues), but is linked into chains through intermolecular $K\cdots CH_3(SiMe_2)$ agostic interactions.[6] The second category have the generalized structure **II**, which are twelve-membered $[(NaNMgNNaN)_2]^{2+}$ ring systems with dianionic $[C_6H_3(CH_3)]^{2-}$ or $(C_6H_4)^{2-}$ cores derived from toluene or benzene, respectively.[2] We reveal herein the latest and most remarkable category of macrocyclic complexes yet discovered in this special family of heterodimetallic compounds. Expecting structures akin to that of **II** on replacing sodium by a larger alkali metal, our synthesis and crystallographic characterization of the new potassium 2,2,6,6-tetramethylpiperidide (tmp) complexes **2** and **3** have, in contrast, uncovered an unprecedented twenty-four membered $[(KNMgN)_6]^{6+}$ ring system, which acts as a polymetallic host to six *singly* deprotonated arene anions.

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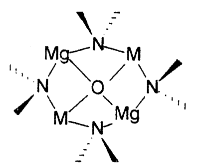
[**] This work was supported by the UK Engineering and Physical Science Research Council (Grant award No. GR/M78113). Thanks are also extended to Dr. P. J. Nichols for help with the crystallographic work.

[+] Ron Snaith was a close personal friend of R.E.M.; this dedication is in recognition of his inspired teaching and his many outstanding contributions to s-block chemistry.



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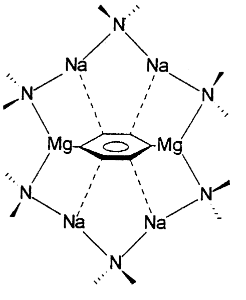

II

$[\{[(Me_3Si)_2N]_4K_2Mg_2(O_2)\}_\infty]$ **1**

$[(tmp)_{12}K_6Mg_6(C_6H_5)_6]$ **2**

$[(tmp)_{12}K_6Mg_6(C_6H_4CH_3)_6]$ **3**

In the first stage of the preparation of **2** and **3**, three equivalents of the parent amine tmpH are added to a 1:1 stoichiometric mixture of *n*BuK[7] and $Bu_2Mg$. This generates an in situ mixture of K(tmp)/Mg(tmp)$_2$.[8] This mixture smoothly converts benzene or toluene (when added in a large excess) into the new macrocyclic complexes **2** and **3**, respectively. The isolated solids of **2** and **3** each contain variable amounts of arene solvent as molecules of crystallization which complicate yield calculations; however, using the formulas obtained for the crystals studied by X-ray diffraction ($\mathbf{2}\cdot 5.07\,C_6H_6$ and $\mathbf{3}\cdot 2.15\,C_6H_5CH_3$), yields of 72.2% and 80.6%, respectively, are estimated. The substantially superior yields to that obtained previously for **II** (at best 27%) provide **2** and **3** in sufficient quantity to allow their reaction chemistry to be studied in detail.

In gross geometrical terms, **2** and **3** are essentially isostructural. For brevity, and because of disorder of the toluene groups within the latter structure, only details of the former[9] are reported here. Figure 1 shows the molecular structure of **2**.

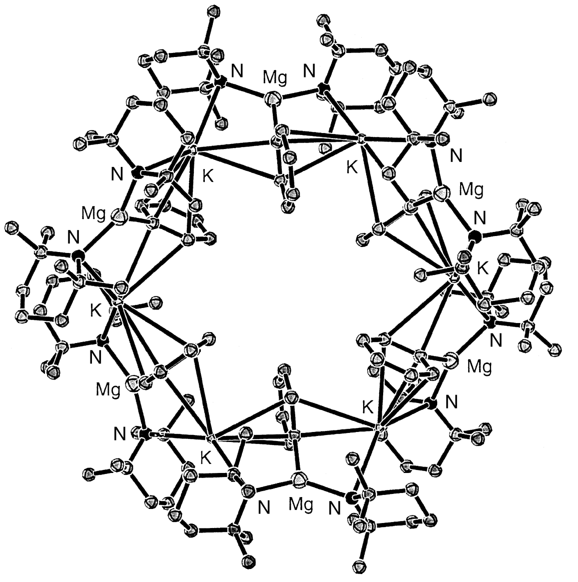

Figure 1. Molecular structure of **2** without hydrogen atoms and solvent molecules of crystallization. The (KNMgN)$_6$ ring is clearly labeled.

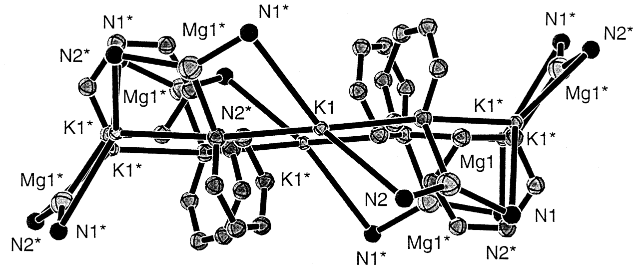

Figure 2. Alternative view of **2** emphasising the severe puckering of the twenty-four membered (KNMgN)$_6$ ring. Selected bond lengths [Å] and angles [°]: K1-N1* 3.191(4), K1-N2 3.090(4), Mg1-N1 2.016(4), Mg1-N2 2.022(4); N1*-K1-N2 141.5(1), C19-K1-C19* 124.9(2), N1*-K1-C19 123.3(2), N2-K1-C19 69.5(1), N1*-K1-C19* 67.7(1), N2-K1-C19* 139.3(2), N1-Mg-N2 136.7(2), N1-Mg-C19 110.3(2), N2-Mg-C19 113.0(2), where * is $y, -x+y, -z$.

Its 24-membered ring comprises alternating metal and nitrogen atoms in KNMgN sections, onto each a phenyl group is secured through a combination of an *ipso* C–Mg σ bond and C–K π interactions. This large ring is severely puckered (Figure 2): Although the six $K^+$ ions and six *ipso* C atoms approximate to a plane (RMS deviation 0.1379), the Mg and N atoms straddle this plane. Amide bridging within a large Mg ring system has previously been observed in the homonuclear dodecamer $[\{EtMgN(H)Dipp\}_{12}]$ (Dipp = 2,6-diisopropylphenol),[10] but it bears little resemblance otherwise to the structure of **2**. Mean K–N and Mg–N bond lengths in **2** are longer (3.141 Å) and slightly shorter (2.019 Å), respectively, than their counterparts in **1** (2.819 and 2.044 Å). Mimicking the arrangement found in the monoarene structure **II**, all the metal atoms in **2** project inwards towards the ring core—resulting in exocyclic bond angles of less than 180°, specifically 141.49(12)° at K and 136.72(18)° at Mg—while the nitrogen atoms project outwards, resulting in acute endocyclic bond angles (mean 89.32°). The interatomic distances involved suggest that the hapticity of the phenyl rings with respect to the K atoms is $\mu$-$\eta^3$:$\eta^2$, that is, three C atoms (one *ipso*, two *ortho*) on one face and two C atoms (one *ipso*, one *ortho*) on the opposing face engage in π interactions with the K atom projecting over that face at distances of 3.009(5), 3.246(5), 3.210(5), 3.083(5), and 3.354(5) Å, respectively (all other K$\cdots$C(Ph) distances exceed 3.6 Å). The distorted trigonal planar geometry at the Mg atom is completed by the aforementioned C–Mg bond, the length of which (2.196(6) Å) is equivalent to that (mean) found in **II**. It may be significant that here, as in **II**, the Mg atom occupies the same in-plane site on the arene ring as that formerly occupied by the lost proton. One might logically assume from this observation that, in the absence of any major structural reorganization, the arene deprotonation takes place at the less reactive Mg center rather than at the more reactive K center. Unfortunately, however, as yet we have not been successful in isolating the intermediate that performs this deprotonation. Interestingly, a mirror is found in the situation for the toluene-based dianions of **II**, in which the deprotonation of the toluene molecules in **3** occurs selectively on the ring (either at *meta* or *para* positions), to leave the more acidic methyl substituent intact. Conventional homometallic bases would conversely be expected to attack the latter group to generate resonance-stabilized benzyl carbanions.[11] Presumably operating through a special ring templating effect,[12] the active base(s) involved in the formation of **2** and **3** is a product of the heterodimetallic synergism taking place within the reaction mixture. In this respect, a parallel can be drawn with the chemistry of LiR · KOR′ superbases,[13] the mixed-metal reagents frequently utilized by synthetic organic chemists. More than thirty years since the first such application of superbases,[14] their mechanistic intricacies still remain to be fully unravelled, although it is established that the participation of the two distinct metal atoms is essential to the enhanced performance of superbases over that of analogous homometallic bases. Logic dictates that the mixed-metal templating ring involved in the formation of **2** and **3** must be larger and have more breadth than its counterpart in **II** given that only one end of the arene molecule experiences deprotonation, implying that the "other end" lies distant from a metal center.

## *Experimental Section*

**2** or **3**: Preparations were carried out in Schlenk tubes under a protective atmosphere of dry, oxygen-free argon. Freshly prepared but unrefined *n*BuK (15.1 or 12.3 mmol) was suspended in hexane (30 mL) and subjected to ultrasound for 5 minutes until a fine brown suspension formed. To this was added an equimolar amount of dibutylmagnesium (15.1 or 12.3 mmol, in heptane) resulting in the formation of a congealed brown/cream mass. Three molar equivalents of 2,2,6,6-tetramethylpiperidine (45.3 or 36.9 mmol) were then added. A slightly exothermic reaction ensued as most of the solid dissolved in the solvent mixture. Fine particulates were removed by filtration through Celite and the orange-brown filtrate was concentrated in vacuo to half of its original volume. At this stage 15 mL of the arene (**2**: benzene; **3**: toluene) was introduced and the solution was heated to 60°C and surrounded by a Dewar water bath. The solution cooled slowly over several hours to deposit rodlike orange/brown (**2**) or yellow (**3**) crystals. Yields **2**: 72.2 %; **3**: 80.5 %. Satisfactory C,H,N elemental analyses were obtained for both compounds. $^1$H NMR (300 MHz, [D$_8$]THF, 25°C, TMS): **2**: $\delta = 7.94$ (m, 2H, *o*-$C_6H_5$), 7.31 (s, free $C_6H_6$), 6.87 (m, 2H, *m*-$C_6H_5$), 6.72 (m, 1H, *p*-$C_6H_5$), 1.68 (m, 2H, $\alpha$-H), 1.25 (m, 4H, $\beta$-H), 1.06 (s, 12H, $\gamma$-H; **3**: $\delta = 7.83 - 7.65$ (m, 2H, bound $C_6H_4CH_3$), 7.18 – 7.10 (m, free $C_6H_5CH_3$), 6.75 – 6.63 (m, 1H, bound $C_6H_4CH_3$), 6.08 (m, 1H, bound $C_6H_4CH_3$), 2.30 (s, free $C_6H_5CH_3$), 2.16 (s, 3H, bound $C_6H_4CH_3$), 1.65 (m, 2H, $\alpha$-H), 1.25 (m, 4H, $\beta$-H) and 1.09 (s, 12H, $\gamma$-H); $^{13}$C NMR (75 MHz, [D$_8$]THF, 25°C, TMS): **2**: $\delta = 181.57$ (*ipso*-$C_6H_5$), 142.28 (*o*-$C_6H_5$), 128.84 (free $C_6H_6$), 125.10 (*m*-$C_6H_5$), 122.61 (*p*-$C_6H_5$), 52.90 (tmp $\gamma$-C), 42.47 (tmp $\alpha$-C), 36.13 (tmp $\beta$-C), 21.62 (tmp Me); **3**: $\delta = 158.64$ (bound $C_6H_4CH_3$), 143.56 (bound $C_6H_4CH_3$), 142.13 (bound $C_6H_4CH_3$), 137.94 (free $C_6H_5CH_3$), 129.48 (free $C_6H_5CH_3$), 128.71 (free $C_6H_5CH_3$), 127.61 (bound $C_6H_4CH_3$), 125.70 (free $C_6H_5CH_3$), 123.10 (bound $C_6H_4CH_3$), 112.63 (bound $C_6H_4CH_3$), 52.75 (tmp $\gamma$-C), 42.44 (tmp $\alpha$-C), 36.11 (tmp $\beta$-C), 24.64 (free $C_6H_5CH_3$), 21.14 (tmp Me), 19.98 (bound $C_6H_4CH_3$).

Received: February 7, 2000 [Z 14665]

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# Low-Temperature Hydrogenolysis of Alkanes Catalyzed by a Silica-Supported Tantalum Hydride Complex, and Evidence for a Mechanistic Switch from Group IV to Group V Metal Surface Hydride Complexes[**]

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We report herein a low-temperature hydrogenolysis of alkanes on a silica-supported tantalum hydride and the striking difference in reactivity compared to similar reactions

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[**] We are grateful to Dr. L. Lefort, Dr. O. Maury (LCOMS), Dr. C. Meric de Bellefon, and Dr. D. Schweich from the laboratory LGPC (ESCPE Lyon) for fruitful discussions. We wish to thank the CNRS, and the ESCPE-Lyon for financial support. M.C. is also grateful to the French Ministry for Education, Research, and Technology (MENRT) for a predoctoral fellowship.

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