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Unsymmetrical bis(anilido)xanthene ligands: development and use in the preparation of magnesium diamide complexes†

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Unsymmetrical bis(anilido)xanthene ligands, decorated by a 2,4,6-tricyclohexylanilido substituent and a less bulky anilido group, are readily prepared in moderate yields from a 4,5-dibromo-substituted xanthene. These ligands are used for the preparation of magnesium(II) complexes, the reductions of which in methylcyclohexane and benzene are described.

Xanthene bridged scaffolds feature diverse and tuneable structural and electronic properties that have led to their application in materials,¹ medicinal² and chemical sciences.³ Within the context of organometallic chemistry, substituted derivatives of xanthene have been widely utilised as neutral, monoanionic and dianionic ligands, which are suitable for the stabilisation of metals in various oxidation states. Their rigidity and amenability to modification enables control over the coordination environment at the metal centre(s). An archetypal example here is the neutral xanthphos ligand (**I**, Fig. 1), transition metal complexes of which have been extensively employed in homogeneous catalysis (e.g. Suzuki–Miyaura and Buchwald–Hartwig reactions).⁴ With regard to related anionic ligand systems, and of most relevance to this study, the first bis(anilido)xanthene ligand (**II**, R = ⁱPr, R' = H) was prepared by Emslie and co-workers in 2007.⁵ This, and similar bis(anilido)xanthenes, were subsequently used to form complexes with metals from across the periodic table (e.g. Mg,⁶ Al,⁷ K,⁸ Ca,^{6,9} Sr,⁹ Ba,^{9b} Mn,¹⁰ Fe,¹¹ Co,¹¹ Y,⁷ Zr,¹² La,¹³ Sm,¹⁴ Dy,¹⁴ Yb,¹⁴ Lu,¹³ Th,^{5,15} U¹⁶).

Recently, bis(anilido)xanthenes have further shown their value with the stabilisation of main group elements in low oxidation states. For example, Aldridge and Goicoechea enlisted Emslie's ligand **II** (R = ⁱPr, R' = H) to prepare the first isolable alumanyl anion (an Al^I species) and a gallyl anion (a Ga^I species) in 2018,^{17–19} with the In^I analogue soon to follow.²⁰

Several years later, the same ligand system featured in neutral Ge^{II} and Sn^{II} diamide complexes, the reduction of which afforded anionic Ge^I and Sn^I radicals.²¹ In 2022, our group developed a much bulkier analogue of Emslie's ligand, viz. **II** (R/R' = Cy, NON^{TCHP}), and a derived calcium complex [(NON^{TCHP})-Ca(η⁶-toluene)], which when reduced with potassium metal, under dinitrogen, gave a rare calcium-dinitrogen compound K₂[(NON^{TCHP})Ca]₂(μ-η²,η²-N₂).²² The next year, the first example of a magnesium–dinitrogen complex K₂[(NON^{TCHP})Mg]₂(μ-κ¹,κ¹-N₂) **III** was similarly synthesized.²³ Both reduction reactions were calculated to proceed *via* metal(I) radicals, K[(NON^{TCHP})M•], which are sterically frustrated from forming metal–metal bonds due to the bulk of the diamide ligand, and therefore preferentially reduce dinitrogen to [N₂]²⁻. Strong evidence for this came in 2024, when we reduced a less bulky magnesium diamide, [(NON^{Trip})Mg] (NON^{Trip} = **II** R/R' = ⁱPr), which did not give an [N₂]²⁻ complex, but instead a magnesium(I) system, K₂[(NON^{Trip})Mg]₂ **IV**, with a very long Mg–Mg covalent bond (3.137(2) Å).²⁴ Both **III** and **IV** have proved powerful reagents for the reductive activation of gaseous small molecules (e.g. H₂, CO, CO₂, C₂H₄), P₄ and typically inert arenes.^{9b,23–25}

Given that the contrasting nature of the reduction products **III** and **IV** results from steric differences between their *N*-aryl

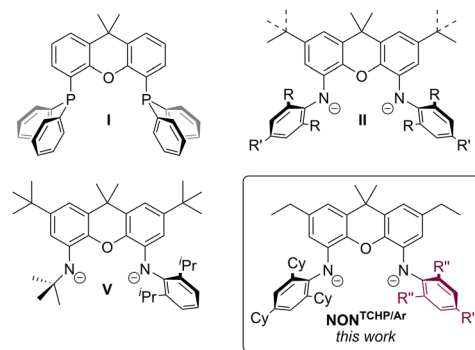
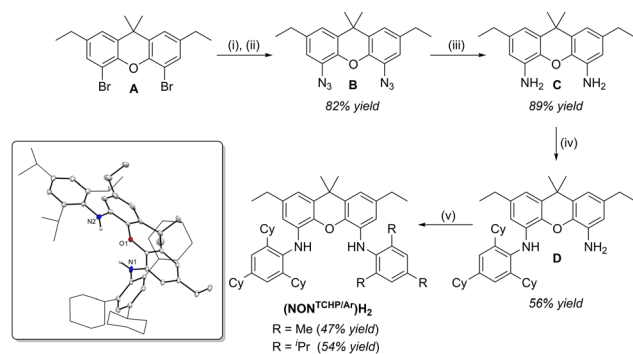


Fig. 1 Selected examples of previously reported xanthene bridged ligand systems.

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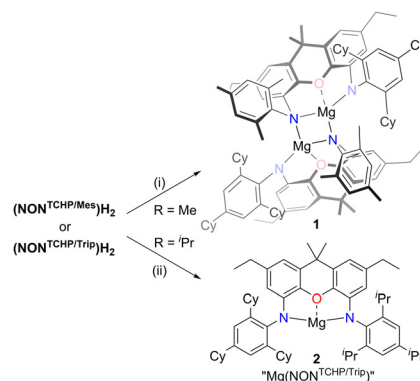


Scheme 1 Synthesis of unsymmetrical bis(aniline)xanthene pro-ligands. (i) $^n\text{BuLi}$ (2 equiv.), THF, -78°C . (ii) Tosylazide (2 equiv.), THF, -78°C – RT, 18 h. (iii) LiAlH_4 (3 equiv.), Et_2O , reflux, 2 h. (iv) (TCHP)Br (1 equiv.), $\text{Pd}(\text{OAc})_2$ (4 mol%), DPEPhos (6 mol%), NaO^tBu (1.4 equiv.). (v) (Mes)Br (1 equiv.) or (Trip)Br (1 equiv.), $\text{Pd}(\text{OAc})_2$ (4 mol%), DPEPhos (6 mol%), NaO^tBu (1.4 equiv.). Inset: Molecular structure of $(\text{NON}^{\text{TCHP/Trip}})\text{H}_2$. R = Me (47% yield), R = ^iPr (54% yield). Thermal ellipsoids shown at 15% probability; hydrogen atoms (except amine protons) omitted; cyclohexyl and isopropyl groups shown in wireframe for clarity.

substituents, it seemed a logical extension to investigate the outcome of the reduction of a magnesium complex incorporating a bis(anilido)xanthene ligand that is unsymmetrically substituted with one TCHP (2,4,6-tricyclohexylphenyl) and one Trip (2,4,6-triisopropylphenyl), or smaller, aryl group. However, although there is one report on an unsymmetrical amido/anilido-xanthene ligand (V),²⁶ unsymmetrical bis(anilido)xanthene ligands are unknown. In this contribution, we detail the straightforward syntheses of such ligands, and the formation and reduction of their magnesium(II) complexes.

The synthesis of unsymmetrical bis(aniline)xanthene pro-ligands, $(\text{NON}^{\text{TCHP/Ar}})\text{H}_2$ (4-(TCHP-NH)-5-(Ar-NH)-2,7-diethyl-9,9-dimethylxanthene; Ar = Mes or Trip; Mes = 2,4,6-trimethylphenyl), is depicted in Scheme 1. Dibromoxanthene **A**²² is first converted to 4,5-diazido-2,7-diethyl-9,9-dimethylxanthene (**B**) and then subsequently reduced with lithium aluminium hydride to yield 4,5-diamino-2,7-diethyl-9,9-dimethylxanthene (**C**) in moderate to high yields over 2 steps. This route to **C** is achievable on a 10 gram scale, and is based on a previous report by Metz and co-workers who detailed a similar smaller scale (< 1 g) route to 4,5-diaminoxanthene directly from xanthene.²⁷ Moreover, previous syntheses of 2,7-disubstituted-4,5-diaminoxanthenes are generally low yielding and/or utilise precious metal catalysts,^{11,28} while our method is convenient, high yielding, cheap and does not require catalysts.

Syntheses of symmetrical bis(aniline)xanthene pro-ligands such as $(\text{NON}^{\text{TCHP}})\text{H}_2$ normally proceed *via* cross-coupling reactions between dibromoxanthenes, *e.g.* **A**, and an aniline. However, we have found that preparing unsymmetrical systems, $(\text{NON}^{\text{TCHP/Trip}})\text{H}_2$, by sequential cross-coupling reactions of **A** with (TCHP) NH_2 and another aniline is problematic. Hence, an alternative route was developed whereby diaminoxanthene **C** was cross-coupled with one equivalent of (TCHP)Br, affording a moderate yield of the mono-substituted product **D**. Subsequent cross-coupling reactions with the aryl bromides, (Mes)Br or (Trip)Br, gave the unsymmetrical bis(aniline)xanthene pro-



Scheme 2 Synthesis of magnesium(II) complexes **1** and **2**. (i) $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$, C_6H_6 , 80°C . (ii) $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$, methylcyclohexane, 80°C .

ligands, $(\text{NON}^{\text{TCHP/Ar}})\text{H}_2$ (Ar = Mes or Trip), as colourless solids in moderate yields after work-up (see ESI† for further details).

So as to draw comparisons with the aforementioned reduced species, **III** and **IV**, we sought to prepare magnesium(II) precursor complexes containing bis(anilido)xanthene ligands of intermediate steric bulk, which could be subsequently reduced with potassium metal. To this end, the pro-ligands $(\text{NON}^{\text{TCHP/Ar}})\text{H}_2$ were deprotonated with one equivalent of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ to give **1** (Ar = Mes, 65% yield) and **2** (Ar = Trip, 98% yield) as colourless and pale yellow solids respectively (Scheme 2). The ^1H NMR spectrum (C_6D_6) of each complex exhibits signals for four chemically inequivalent xanthene arene protons, which is consistent with the proposed dimeric solid-state structure of **1**, but would also be expected if the compounds are monomeric in solution.

Suitable crystals of **2** could not be obtained from hexane or benzene solutions due to its high solubility in these solvents, but **1** could be crystallised from benzene. The molecular structure of **1** (see Fig. S47, ESI†) reveals it to be an *N*-mesityl bridged dimer, which is similar to that previously reported for propane bridged dianilido complexes $[\text{Mg}(\text{NCN}^{\text{Ar}})]_2$ ($\text{NCN}^{\text{Ar}} = [(\text{Ar})\text{NCH}_2]_2\text{CH}_2]^{2-}$, Ar = Trip or TCHP).²⁹ This is in contrast to the related complex $[\text{Mg}(\text{NON}^{\text{Dip}})]_2$ ($\text{NON}^{\text{Dip}} = \text{II}$, R = ^iPr , R' = H) which dimerises through bridging $\text{Mg} \cdots \pi(\text{Dip})$ arene contacts,⁶ and to the arene capped magnesium(II) complex $\text{Mg}(\text{NON}^{\text{TCHP}})(\eta^2\text{-C}_6\text{H}_6)$,^{9b} both of which are crystallised from benzene. The inability of both **1** and **2** to form isolable benzene-capped complexes may suggest that they exist as *N*- or arene-bridged dimers in both aliphatic and arene solutions. If this is the case for **2**, any intermolecular association can be disrupted by addition of the Lewis bases 1,3,4,5-tetramethylimidazol-2-ylidene (TMC) or THF to the compound. This results in the formation of the corresponding monomeric Lewis adducts $\text{Mg}(\text{NON}^{\text{TCHP/Trip}})(\text{TMC})_2$ (**3**) and $\text{Mg}(\text{NON}^{\text{TCHP/Trip}})(\text{THF})_2$ (**4**), respectively (Scheme S1, ESI†). Both complexes were characterised in the solid-state by X-ray diffraction measurements, which showed them to have similar heavily distorted square-based pyramidal magnesium geometries (see Fig. S48 and S49, ESI†).

With **1** and **2** in hand, reductions of the compounds were investigated, in order to compare the nature of the products

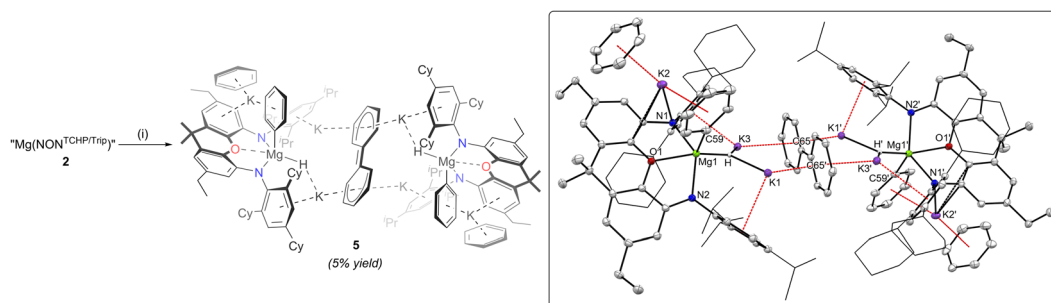
with **III** and **IV**. Accordingly, complexes **1** and **2** were treated with K/KI³⁰ (5% w/w, 4 equivalents) in methylcyclohexane over 18 hours. Compound **1** was found to be unreactive towards K/KI under these reaction conditions, presumably as the strength of its dimeric structure towards dissociation protects its Mg centres from reaction with potassium. In contrast, **2** does react with K/KI, but this generated a complex mixture of products, none of which could be identified by NMR spectroscopy or crystallised from the reaction mixture. Given that **1** and **2** do not form complexes with benzene, we turned to that solvent to further assess their reduction. That is, solutions of compounds **1** and **2** in benzene were reacted with K/KI (4 equivalents), resulting in intensely dark red coloured reaction solutions after 18 hours. Analysing the reaction mixtures by ¹H NMR spectroscopy revealed mixtures of ill-defined products, including dihydrogen, in both cases. For sake of comparison, the reduction of Mg(NON^{TCHP}) in benzene was also shown to give a complex mixture of products, with dissolved dihydrogen present. Although the reduction of **1** failed to give any crystalline products after work-up, single crystals of **5** could be obtained from the reaction involving **2** in a low (5%) but reproducible yield (Scheme 3).

The solid-state structure of **5** shows it to comprise two formally dianionic [(NON^{TCHP/Trip})Mg(H)(Ph)]^{2−} units which exhibit distorted square pyramidal geometries ($\tau_5 = 0.30$) at each magnesium centre. A partially delocalised biphenyl dianion, [C₁₂H₁₀]^{2−}, bridges the two units, through interactions with four potassium cations, while each of the two remaining K⁺ centres exhibit arene coordination to a [(NON^{TCHP/Trip})Mg(H)(Ph)]^{2−} unit and a molecule of benzene. The structure of **5** is related to reported complexes of rare earth and alkaline earth metals (Y,³¹ Sm,³² Yb,³² Ca,³³ Sr³³), which incorporate the biphenyl dianion ligand. Furthermore, and similar to the formation of **5**, an electride, “K⁺[Li{N(SiMe₃)₂}e[−]]”, prepared by ball-milling, has recently been shown by Lu and co-workers to react with benzene to give a black solution, from which the biphenyl dianion bridged complex [(Li)(K)₂{N(SiMe₃)₂}₂][μ-η¹²-(C₁₂H₁₀)] was isolated.³⁴

It is not clear what the mechanism of formation of **5** entails, but the complexity of the product, which incorporates three

anionic fragments seemingly derived from benzene, makes a meaningful computational analysis of the reaction pathway improbable. With that said, it likely involves an initial reduction of **2** to give a magnesium(i) radical K[(NON^{TCHP/Trip})Mg[•]], similar to the calculated intermediate in the formation of **III**.²³ This could then doubly reduce benzene to give a “Birch-like” intermediate K₂[(NON^{TCHP/Trip})Mg]₂(μ-C₆H₆), analogous to the reaction of **III** with benzene, which yields more sterically protected K₂[(NON^{TCHP})Mg]₂(μ-C₆H₆).^{25a} The reduced intermediate K₂[(NON^{TCHP/Trip})Mg]₂(μ-C₆H₆) could then undergo a benzene C–H activation reaction, yielding magnesium hydride and magnesium phenyl products, *e.g.* K[(NON^{TCHP/Trip})MgH] and K[(NON^{TCHP/Trip})MgPh], ultimately leading to the observed dianionic units [(NON^{TCHP/Trip})Mg(H)(Ph)]^{2−} in **5** (see Scheme S2, ESI[†]). Indeed, it has been previously shown that *in situ* generated magnesium(i) radicals can similarly reduce benzene to isolable [C₆H₆]^{2−} containing products, the reduced benzene fragment of which can then be C–H activated, yielding magnesium hydride and magnesium phenyl compounds.³⁵ With regard to the formation of the biphenyl dianion in **5**, the proposed intermediate K₂[(NON^{TCHP/Trip})Mg]₂(μ-C₆H₆) could alternatively react with a further molecule of benzene to give the biphenyl dianion *via* C–C bond formation and dihydrogen elimination processes. This enhanced reactivity, relative to alkali metal free magnesium “Birch-like” products,³⁵ could be explained by Mg/K mixed-metal cooperativity, which has been previously shown to boost reactivity relative to monometallic systems.³⁶ Further precedent for this mechanistic proposal comes from a study by Harder and co-workers, who showed that calcium and strontium complexes of the benzene dianion [C₆H₆]^{2−} can similarly react with benzene to give the biphenyl dianion and H₂.³³ Whatever the mechanism is for the formation of **5**, it most likely involves a number of potentially competing pathways and intermediate redistribution steps, which is consistent with the low yield of the compound.

In summary, we have presented a convenient approach to synthesise the first examples of unsymmetrical bis(anilido)xanthene ligands, NON^{TCHP/Ar}. It is likely that this method should be readily adaptable to access a variety of other unsymmetrical bis(anilido)xanthenes, which will allow an expansion of



Scheme 3 Reduction of complex **2** with K/KI to give **5** and other unidentified reduction products. (i) K/KI (3 equiv.), C₆H₆, 16 h, RT. Inset: Molecular structure of **5**. Thermal ellipsoids shown at 20% probability; hydrogen atoms omitted; cyclohexyl and isopropyl groups shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): Mg1–N1 2.169(3), Mg1–N2 2.157(3), Mg1–C59 2.204(5), Mg1–O1 2.142(3), Mg1–H 1.855(15), C65–C65' 1.399(7), C65–C66 1.470(4), C65–C70 1.454(5), C66–C67 1.365(5), C67–C68 1.421(6), C68–C69 1.418(6), N1–Mg–N2 138.12(13), O1–Mg1–H 155.9(7).

the already broad coordination chemistry of related symmetrical bis(anilido)xanthenes. Preliminary investigations into the coordination chemistry of $\text{NON}^{\text{TCHP/Ar}}$ have yielded four magnesium(II) complexes of the ligands. The reduction of one of these ($\text{NON}^{\text{TCHP/Trip}}$)Mg **2** with K/KI in benzene affords a low yield of the unusual complex **5**, which contains two dianionic magnesium(II) fragments $[(\text{NON}^{\text{TCHP/Ar}})\text{Mg}(\text{H})(\text{Ph})]^{2-}$ bearing phenyl and hydride ligands. These are bridged by a biphenyl dianion, with the charges on all anionic units being balanced by six potassium cations. Mechanisms for the formations of the anions in **5** have been proposed. We are currently investigating the application of unsymmetrical bis(anilido)xanthene ligands for the stabilisation of low oxidation state main-group compounds.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

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