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Oxidative dehydrocoupling of N–H bonds using a redox-active main group superbase $\ensuremath{^\dagger}$

Robert J. Less, Vesal Naseri,* Mary McPartlin and Dominic S. Wright*

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Reaction of the redox-active base $Sn(NMe_2)_2/"BuLi$ with *o*-phenylene diamine leads to oxidative dehydrocoupling and rearrangement into the triazolyl anion.

The applications of superbases in a range of deprotonation reactions are long-established in organic chemistry, such as the well known Schlosser base consisting of 'BuOK and RLi.¹ The past two decades has seen a growing interest in *synergic bases* of this type, in which the presence of two metals results in enhancement in the basicity and specificity of deprotonation over and above that found for the separate components.² The use of a range of synergic bases, followed by the addition of an electrophile, is increasingly being employed as a standard methodology in the modification of organic molecules. Mulvey in particular has focused on the relationship between the structures of an extensive series of heterometallic amide bases, revealing remarkable reactivity and selectivity towards various organic and inorganic species which can be tuned by the choice of metals present.³

Heterometallic p-block reagents $E(NMe_2)_n/RM$ (E = Sn^{II}. $As^{III}, Sb^{III}, Bi^{III}; M =$ alkali metal) also function as superbases, for example, in the quadruple deprotonation of 2-amino-phenylphosphine.⁴ However, the presence of redox-active metals (E) means that reactions may not simply stop at deprotonation: subsequent bond-forming and bond-breaking reactions can also occur. The resulting ability for p-block bases of this type to dehydrocouple P-H bonds into P-P bonds is similar to the activity of a range of transition metal organometallics.^{5,6} A case in point are reactions involving the diphosphine $1,2-(PH_2)_2-C_6H_4$. Stephan and coworkers have shown that the dehydrocoupling reaction with the single-site catalyst [Cp*2ZrH3] gives the dimeric tetraphosphane [(C₆H₄P)PH]₂ as an intermediate, which then couples into the cyclic octamer $[C_6H_4P_2]_8$ (Scheme 1, top).⁷ Under the more basic and reducing conditions involved, the analogous reaction involving the mixed-metal main group system Sb(NMe₂)₃/ⁿBuLi initially gives the dianion $[(C_6H_4P)P]_2^{2-}$, which



then undergoes reductive C–P bond cleavage to finally produce the 1,2,3-triphospholide anion $[C_6H_4P_3]^-$ (Scheme 1, bottom).⁸

Given the broad applications of dehydrocoupling reactions to a wide variety of bonds,⁶ it is surprising that dehydrocoupling of amines (formally 2N–H \rightarrow N–N + H–H) has attracted so little attention.⁹ Recently, Corma *et al.*¹⁰ and Zhang and Jiao¹¹ have made significant breakthroughs in this area by showing that catalytic oxidative coupling of a range of aromatic amines (ArNH₂) into diazo compounds (RN=NR) can be achieved using a Cu^IBr/pyridine complex or Au nanoparticles as catalysts, with air as the oxidant. We show in this communication for the first time that the redox-active superbase Sn(NMe₂)₂/^{*n*-} BuLi is also useful in the oxidative coupling of amines.

The reaction of *o*-phenylene diamine $[1,2-(NH_2)_2-C_6H_4]$ (1H₄) with a 1 : 2 stoichiometric mixture of Sn(NMe₂)₂ and "BuLi in thf at reflux (16 h) gives a deep, blood-red solution together with tin metal.[‡] The ¹H NMR spectrum of the CH₂Cl₂ extract of the hydrolysed mixture showed that benzotriazole [C₆H₄N₃H] (**2**H) (Fig. 1) is the main product, together with a minor amount of 2,3-diamino-phenazene (**3**) (Fig. 1) (ESI[†]). The formation of **3** was also confirmed by the isolation and structural characterization of the crystalline hydrochloride salt [**3**][**3**H]⁺Cl⁻·7H₂O,§ obtained by storage of the acidified aqueous extract (ESI[†]).



Fig. 1 The products 2 and 3 generated from reaction of $1H_4$.

Chemistry Department, Cambridge University, Lensfield Road, Cambridge CB2 1EW, UK. E-mail: vn226@cam.ac.uk, dsw1000@cam.ac.uk

[†] Electronic supplementary information (ESI) available: Details of the structural solutions and X-ray data for [3][3H]⁺Cl⁻⁻7H₂O, [Sn₇(1H)₂(1)₄][2-LiPMDETA]₂ and [(1H)SnLi-PMDETA]₂. CCDC 796653 ([Sn₇(1H)₂(1)₄][2-LiPMDETA]₂), 796654 ([(1H)SnLi-PMDETA]₂) and 796655 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/clcc00053e

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The formation of **3** in this reaction is readily understood in terms of the redox-active, superbase properties of the heterometallic reagent employed. It can be noted that **3** is also formed in the reaction of *o*-phenylene diamine with Cu^{II} in air and a similar mechanism is probably involved here (ESI†).¹² Notably, however, there are *no* reports of the formation of **2**H in this or related reactions involving transition metals.¹³

Although the reaction producing **2H** is clearly closely related to that seen previously in the 1,2,3-triphospholide (Scheme 1), the formation of N–N bonds at the expense of seemingly more thermodynamically stable C–N bonds is a surprising feature of this transformation. In order to understand more about the mechanism of formation of **2H**, we next attempted to characterize intermediates in the reaction. The reaction in thf was repeated as before, but this time at room temperature (14 h). Layering with PMDETA [=(Me₂NCH₂CH₂)₂NMe] at room temperature for a week led to the gradual deposition of yellow crystals of [(1H)SnLi·PMDETA]₂ (Fig. 2), together with a small number of orange crystals of the salt [Sn₇(1H)₂(1)₄][**2** (Li·PMDETA)₂]₂ (Fig. 3).‡ More of this second product is generated if the reaction is stirred for longer at room temperature prior to layering with PMDETA.

The centrosymmetric dimer [(1H)SnLi·PMDETA]₂ (Fig. 2) contains the triply-deprotonated [1H]³⁻ trianion.§ The imido nitrogen of each trianion ($-N^{2-}$) is involved in bonding within the central Sn₂N₂ ring unit, while the amido nitrogen ($-NH^{-}$) chelates the Sn^{II} centres *exo* to the ring. The bonding of the Li⁺ counterions to the N-atoms of the Sn₂N₂ units is augmented by a relatively short π -arene interaction to the α -C atoms of the C₆H₄ group [Li···C(6) 2.708(7) Å].¹⁴ This gives Li a nominal five-coordination number.

The solid-state structure of $[Sn_7(1H)_2(1)_4][2(Li PMDETA)_2]_2$ contains a heptanuclear Sn_7 dianion, in which both the trianion $[1H]^{3-}$ and tetraanion $[1]^{4-}$ are present (Fig. 3a), and two crystallographically-independent cations, in which two PMDETA-solvated Li⁺ ions coordinate a triazolyl anion, $[2]^-$ (Fig. 3b). The double-cubane arrangement of the $[Sn_7(1H)_2(1)_4]^{2-}$ dianion is reminiscent of neutral $[Sn_7(NR)_8]$ cages.¹⁵ Like these neutral cages, the central Sn^{IV} centre [Sn(1)] bridges the two cubane





Fig. 3 Structures of (a) the Sn₇ dianion $[Sn_7(1H)_2(1)_4]^{2-}$ and (b) one of the two independent $[2(\text{Li-PMDETA})_2]^+$ cations. Selected bond lengths (Å) and angles (°); in the $[Sn_7(1H)_2(1)_4]^{2-}$ dianion, Sn(1)–N range 2.131(4)–2.215(4), Sn(2,3,4,5,6,7)–N range 2.130(5)–2.273(5), Sn(2,5)···N(4,7) 2.655(5)–2.819(6), N(10,80)–Sn(5,2) range 2.281(6)–2.287(5), N–SN–N (core) range 78.0(2)–91.1(1), SN–N–Sn range 92.2(2)–108.9(2); in the $[2(\text{Li-PMDETA})_2]^+$ cations, N=N range 1.328(8)–1.375(8), N(triazolyl)–Li range 1.92(2)–2.01(1), N=N=N range 116.0(8)–116.1(6).

halves of the dianion together, with the remaining metal atoms all being Sn^{II}. There is a very broad range of SN–N bond lengths within the SN–N core, ranging from 2.130(5)–2.273(5) Å for the majority of the Sn^{II}/Sn^{IV}–N bonds to 2.655(5)–2.819(6) Å for the very weak Sn(2,5)···N(4,7) interactions [*trans* to the chelate bonding to N(10) and N(80)]. The [**2**·(Li·PMDETA)₂]⁺ cations are similar conceptually to other inverse sandwich cations of this type, such as [PMDETA·Li–(μ -Cl)–Li·PMDETA]⁺,¹⁶ while the N=N bond lengths [range 1.328(8)–1.375(8) Å] and N=N=N angles [range 116.0(8)–116.1(6)°] in this unit are typical of other structurally characterized triazolyl complexes.¹⁷

Given the combined experimental observations, one potential mechanism for the formation of the triazolyl anion of $[2]^-$ is outlined in Scheme 2 in which the formation of a diazo intermediate occurs *via* oxidation of the highly electron-rich imido N atoms of the $[1H]^-$ anion. It is noteworthy in this regard that we find that the room-temperature reaction of $Sn(NMe_2)_2$ alone with PhNH₂ produces PhN=NPh (m/z = 182.1). The simplest way by which this oxidation can be achieved is through $2Sn^{II} + 2e \rightarrow 2Sn^0$. However, the observation of Sn^{IV} in the structure of $[Sn_7(1H)_2(1)_4][2(Li-PMDETA)_2]_2$ (Fig. 3) suggests that more complicated redox chemistry may be operating, *e.g.*, $2Sn^{II} \rightarrow Sn^0 + Sn^{IV}$, $Sn^{IV} + 2e \rightarrow Sn^{II}$. The potential

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Scheme 2 Proposed mechanism of formation of the triazolyl anion from *o*-phenylene diamine (the Li⁺ counterions have been omitted for clarity).



Fig. 4 Heterocycles that are potentially accessible by oxidative dehydrocoupling.

intermediacy of a tetraazopentalyl dianion $[(C_6H_4N)N]_2^{2-}$ (the N analogue of the tetraphosphane dianion in Scheme 1) cannot be discounted in this case but does not appear to be necessary for the formation of the $[2]^-$ anion.

In summary, we have revealed for the first time the potential of redox-active main group $E(NMe_2)_n/RM$ superbases to oxidatively dehydrocouple N–H bonds. In the current study this provides access to 1,2,3-triazole through a series of reactions which is unknown with transition metal counterparts. This new methodology might well be useful for other ring systems such as imidazoles (A), oxadiazoles (B) and diazaphospholes (C) (Fig. 4) and we are exploring this potential.

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Notes and references

[‡] Synthesis of 2H: a mixture of *o*-phenylene diamine (208 mg, 2.0 mmol) and Sn(NMe₂)₂ (414 mg, 2.0 mmol) was dissolved in 30 mL thf at 25 °C and stirred for 20 min. To the orange solution at 25 °C was added ^{*t*}BuLi (1.7 mol L^{-1} in heptane, 2.4 mL, 4.0 mmol). The mixture was brought to reflux (16 h), turning deep blood red (after ca. 1 h). The mixture was cooled to room temperature and the solvent removed under vacuum and replaced with DCM (30 mL). This solution was hydrolyzed with 30 mL of distilled water and dilute HCl(aq) added until the aqueous phase was of pH 8. The organic phase was separated and dried with MgSO4. Removal of the solvent gave a yellow semi-solid. ¹H NMR spectroscopy (see ESI[†]) showed that this consists of a mixture of 1H₄, 2H and 3. Deep red crystals of [3][3H]⁺Cl⁻·7H₂O were deposited from the acidified aqueous residue after storage for 1 week at room temperature. [(1H)SnLi·PMDETA]₂; Sn(NMe₂)₂ (1 mol L^{-1} solution in toluene, 0.45 mL, 0.45 mmol) was added dropwise to a solution of o-phenylene diamine (45 mg, 0.42 mmol) in 1.5 mL thf at room temperature and stirred for 1.5 h. nBuLi (1.6 mol L⁻ in hexanes, 0.62 mL, 1.0 mmol) was then added dropwise at room temperature, producing a clear, orange solution. After stirring for a

further 14 h, PMDETA (3 mL) was layered carefully onto the reaction mixture. After 1 week, large yellow-orange, block-shaped crystals of $[(1H)SnLi \cdot PMDETA]_2$ had formed, in which a few yellow-orange crystals of $[Sn_7(1H)_2(1)_4][2(LiPMDETA)_2]_2$ are also present. Analytically-pure samples of $[(1H)SnLi \cdot PMDETA]_2$ can be manually separated. (Elemental analysis, found C 43.9, H 6.9, N 16.3, calcd for $[(1H)SnLi \cdot PMDETA]_2$ C 44.6, H 7.0, N 17.3.) However, crystalline $[(1H)SnLi \cdot PMDETA]_2$ and $[Sn_7(1H)_2(1)_4][2(LiPMDETA)_2]_2$ proved to be too insoluble to obtain solution ¹H or ¹³C NMR spectra (only hydrolysis products were observed).

§ Crystal data: $[3][3H]^+Cl^-.7H_2O$, $C_{24}H_{35}ClN_8O_7$, M = 583.05, triclinic, space group PI, Z = 2, a = 7.0826(2), b = 12.5439(4), c = 16.0868(6) Å, $\alpha = 82.669(1)$, $\beta = 78.708(2)$, $\gamma = 84.163(2)^\circ$, V = 1385.75(8) Å³, μ (Mo-K α) = 0.196 mm⁻¹, $\rho_{calc} = 1.397$ Mg m⁻³, T = 180(2) K. Total reflections 14267, unique 6208 ($R_{int} = 0.053$). $R_1 = 0.076 [I > 2\sigma(I)]$ and $wR_2 = 0.237$ (all data). [(1H)SnLi· PMDETA]₂: $C_{30}H_{56}Li_2N_{10}Sn_2$, M = 808.11, monoclinic, space group $\begin{array}{l} P21/n, \ Z = 2, \ a = 13.9707(3), \ b = 9.3155(2), \ c = 14.8029(3) \ \text{Å}, \\ \beta = 106.888(1)^\circ, \ V = 1843.43(7) \ \text{\AA}^3, \ \mu(\text{Mo-K}\alpha) = 1.389 \ \text{mm}^{-1}, \end{array}$ $\rho_{\text{calc}} = 1.456 \text{ Mg m}^{-3}, T = 180(2) \text{ K}.$ Total reflections 23029, unique $3760 (R_{int} = 0.060). R_1 = 0.036 [I > 2\sigma(I)] \text{ and } wR_2 = 0.087 \text{ (all data)}.$ $[Sn_7(1H)_2(1)_4][2 \cdot LiPMDETA]_2: C_{78}H_{122}Li_4N_{28}Sn_7, M = 2310.63,$ triclinic, space group $P\bar{1}$, Z = 2, a = 13.86730(10), b = 18.7128(2), thermite, space group 11, Z = 2, α = 10.00150(10), β = 10.121(2), c = 20.1729(3) Å, $\alpha = 97.4860(10)$, $\beta = 104.4300(10)$, $\gamma = 103.9620(10)^{\circ}$, V = 4817.83(9) Å³, μ (Mo-K α) = 1.839 mm⁻¹, $\rho_{calc} = 1.593$ Mg m⁻³, $\mu_{calc} = 1.593$ Mg m⁻³, T = 180(2) K. Total reflections 41 657, unique 13 382 ($R_{int} = 0.045$). $R_1 = 0.056 [I > 2\sigma(I)]$ and $wR_2 = 0.185$ (all data). Nonius KappaCCD diffractometer, solved by direct methods and refined by full-matrix least squares on F² (G. M. Sheldrick, SHELX-97, Göttingen, 1997). CCDC 796653, 796654 and 796655.

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