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# Introduction

Mechanochemical synthesis, in which solid starting materials are ground together to induce chemical reactions, is emerging

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# One-pot two-step mechanochemical synthesis: ligand and complex preparation without isolating intermediates<sup>+</sup>

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Although the use of ball milling to induce reactions between solids (mechanochemical synthesis) can provide lower-waste routes to chemical products by avoiding solvent during the reaction, there are further potential advantages in using one-pot multistep syntheses to avoid the use of bulk solvents for the purification of intermediates. We report here two-step syntheses involving formation of salen-type ligands from diamines and hydroxyaldehydes followed directly by reactions with metal salts to provide the corresponding metal complexes. Five salen-type ligands 2,2'-[1,2-ethanediylbis[(E)-nitrilomethylidyne]]bisphenol, 'salenH<sub>2</sub>', **1**; 2,2'-[(+)-1,2-cyclohexanediylbis-[(E)-nitrilomethylidyne]]bis-phenol, **2**; 2,2'-[1,2-phenylenebis(nitrilomethylidyne)]-bis-phenol, 'salphenH<sub>2</sub>' **3**; 2-[[(2-aminophenyl)imino]methyl]-phenol, **4**; 2,2'-[(+)-1,2-cyclohexanediylbis[(E)-nitrilomethylidyne]]-bis[4,6-bis(1,1-dimethylethyl)]-phenol, 'Jacobsen ligand',  $\mathbf{5}$ ) were found to form readily in a shaker-type ball mill at 0.5 to 3 g scale from their corresponding diamine and aldehyde precursors. Although in some cases both starting materials were liquids, ball milling was still necessary to drive those reactions to completion because precipitation of the product and or intermediates rapidly gave in thick pastes which could not be stirred conventionally. The only ligand which required the addition of solvent was the Jacobsen ligand 5 which required 1.75 mol equivalents of methanol to go to completion. Ligands 1-5 were thus obtained directly in 30-60 minutes in their hydrated forms, due to the presence of water by-product, as free-flowing yellow powders which could be dried by heating to give analytically pure products. The one-armed salphen ligand 4 could also be obtained selectively by changing the reaction stoichiometry to 1:1. SalenH<sub>2</sub>  $\mathbf{1}$  was explored for the onepot two-step synthesis of metal complexes. In particular, after in situ formation of the ligand by ball milling, metal salts (ZnO, Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O or Cu(OAc)<sub>2</sub>·H<sub>2</sub>O) were added directly to the jar and milling continued for a further 30 minutes. Small amounts of methanol (0.4-1.1 mol equivalents) were needed for these reactions to run to completion. The corresponding metal complexes [M(salen)] (M = Zn, 6; Ni, 7; or Cu, 8) were thus obtained quantitatively after 30 minutes in hydrated form, and could be heated briefly to give analytically pure dehydrated products. The all-at-once 'tandem' synthesis of [Zn(salen)] 6 was also explored by milling ZnO, ethylene diamine and salicylaldehyde together in the appropriate mole ratio for 60 minutes. This approach also gave the target complex selectively with no solvent needing to be added. Overall, these syntheses were found to be highly efficient in terms of time and the in avoidance of bulk solvent both during the reaction and for the isolation of intermediates. The work demonstrates the applicability of mechanochemical synthesis to one-pot multi-step strategies.

> as a general way to synthesise chemical products whilst avoiding, or greatly reducing, the use of solvents as reaction media.<sup>1</sup> However, even if solventless reaction conditions are used, the issue of solvent use in the purification and isolation of the product remains as has been discussed in a recent review.<sup>1k</sup> Mechanochemical reactions which provide quantitative conversion with no by-products can potentially give analytically pure products directly, although in practice such by-product-free reactions will be in the minority.<sup>2</sup> More common are quantitative mechanochemical reactions in which the product and by products differ significantly in their boiling points or vapour

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pressures. The products are then amenable to isolation by distillation or sublimation. Many such examples only require the removal of condensates such as water or acetic acidic from solid products by heating, or in favourable cases the sublimation of the product.<sup>3</sup>

However, often the use of bulk solvents may be unavoidable for effective isolation or purification of the product. In such cases mechanochemical synthesis can still provide an advantage over conventional solution-based synthesis if the reaction solvent is particularly undesirable compared to those needed for purification. Examples include the use of mechanochemical synthesis to avoid the use of dimethylformamide and pyridine in nucleotide protection reactions, thus reducing the solvents required to ethylacetate and hexane, as used in the work-up.<sup>4</sup> Also, the groups of Wang<sup>5a,b</sup> and Lamaty<sup>5c</sup> have developed solventless mechanochemical syntheses for which only simple aqueous-based washing is needed to give the products in analytically pure form. Mack and coworkers demonstrated how two-step mechanochemical reactions could simplify the work up stage and reduce solvent usage.<sup>5d</sup> However, despite the overall efficiency gains which mechanochemistry can provide in these cases, it would clearly be more desirable still to avoid bulk solvents both as reaction media as well as for work-up procedures.

Here we explore a way to address this problem in the context of ligand synthesis followed by metal complexation either by sequentially adding reagents for each step to the reaction vessel (sometimes known as telescoping<sup>6</sup>), or by simply adding all reagents for all steps at the start (sometimes known as tandem reactions<sup>7</sup>). One-pot multistep reactions under mechanochemical conditions have been developed by the groups of Wang and Mack, but remain rare.4,5d-g In addition to the general issues associated with compatibility of reagents, products and conditions, additional issues particular to mechanochemical synthesis in this regard include *i*. the possible build-up of (solid) by products which could reduce the effectiveness of the milling as well as dilute the reactants, and *ii*. the build-up of liquid by products which could be helpful in assisting mass transfer by acting as 'internal solvent' (similar or liquid-assisted grinding, or LAG).

In this work, we have investigated the mechanochemical synthesis of a widely-used class of organic imine-based ligands. Specifically, salen-type ligands are formed from their corresponding hydroxyaldehydes and diamines under ball milling conditions. We then investigated *in situ* ligand synthesis followed directly by metal complexation to Zn(n), Ni(n) or Cu(n) (see Schemes 1 and 2) as test cases for one-pot two step mechanochemical syntheses. Salen complexes are of wide interest for example for biological mimics,<sup>8</sup> fluorescent indicators,<sup>9</sup> 'Jacobsen' epoxidation catalysts,<sup>10</sup> ring-opening polymerisation catalysts,<sup>11</sup> extraction of metal ions from water<sup>12</sup> and organic light emitting diode (OLED) applications.<sup>13</sup> Therefore, low-waste routes to such materials are of practical as well as academic interest.

# Results and discussion

# Synthesis of salen-type ligands

The formation of imines from primary amines and aldehydes is traditionally performed in alcohol solvents under reflux conditions.<sup>14</sup> The reaction has also been reported under solventless mechanochemical conditions,<sup>15</sup> including its use for the synthesis of construction of large cage compounds.<sup>16</sup> However, solventless mechanochemical synthesis of salen-type ligands by this reaction has not been reported to our knowledge. For the synthesis of salenH<sub>2</sub> itself, the starting materials (ethylene diamine and salicylaldehyde) are both liquids. Therefore in principle, such a reaction might be performed readily without using solvent by simply mixing these two liquids with conventional stirring. However, we found that in practice this led only to partial reactions, most likely because precipitation of the product (and potentially the mono-substituted intermediate) from the reaction mixture rapidly lead to a thick paste which could not be stirred.

Thus, in an unconventional application of ball milling, it was found that the two liquid reactants could be advantageously milled together without solvent for 30 minutes at 25 Hz to give a quantitative yield of salenH<sub>2</sub>, 1. The crucial role of the milling is most likely after the initial precipitation in that it provides superior mixing. The product was obtained as a free-flowing yellow powder containing variable amounts of residual water by-product as shown by TGA (thermogravimetric analysis). At this stage the product was removed, dried by heating (80 °C, 36 h) and characterised by PXRD (powder X-ray diffraction), solution state <sup>1</sup>H NMR, solid state MAS NMR, elemental analysis, TGA and solid state IR spectroscopy. TGA confirmed that the dried product contained no residual water. All other analytical data were consistent with a quantitative reaction to give an analytically pure product. In particular, IR spectroscopy clearly showed the expected imine peak at 1637 cm<sup>-1</sup>.<sup>14b</sup> For comparison, a sample was also synthesised by the conventional method<sup>14b</sup> of refluxing in alcoholic solution for 1-2 hours. The fingerprint regions for the ball milled and solution-prepared samples were identical (see ESI Fig. S4<sup>†</sup>). The solution state <sup>1</sup>H NMR spectrum also showed only peaks due to salenH<sub>2</sub> (see ESI Fig. S1<sup>†</sup>) although it must be recognised that in dissolving the product into CDCl<sub>3</sub> it is possible that the reaction continued after dissolution. More definitive is the solid state <sup>13</sup>C MAS NMR spectrum which was identical to that of a spectrum of salenH<sub>2</sub> prepared by the conventional solution-based method (Fig. 1). Each spectrum exhibits six peaks which we assign to the CH<sub>2</sub> carbons (61.5 ppm), the C=N carbon (166.9 ppm) and aromatic carbons (162.3, 131.9, 120.0 and 117.3 ppm). The simplicity of the spectra also suggests that the local crystal symmetry is high. The material was found to be highly crystalline by PXRD, and its PXRD pattern was consistent with the pattern simulated from single crystal structure data obtained from the Cambridge Structural Database (ESALIM) (see ESI Fig. S5<sup>†</sup>). The material also gave a satisfactory elemental analysis (see ESI<sup>†</sup>). The chiral cyclohexane-backboned ligand 2<sup>17</sup> was also prepared in a similar





RCHO	H <sub>2</sub> N NH <sub>2</sub>	Product	Conditions	Product Number
ОН	H <sub>2</sub> N NH <sub>2</sub>	ОН НО-	30mins Neat	1
он	H <sub>2</sub> N NH <sub>2</sub>		30mins Neat	2
ОН	H <sub>2</sub> N NH <sub>2</sub>	ЛИНИСТИИНА	60mins Neat	3
Он	H <sub>2</sub> N NH <sub>2</sub>		60mins Neat	4
он	H <sub>2</sub> N NH <sub>2</sub>		30mins LAG MeOH (1.75 equiv.)	5

Scheme 1 General scheme for the mechanochemical synthesis of salen-type ligands 1–5. For compound 4 equimolar amounts of reactants were used.

way as a free-flowing yellow powder starting from trans±-1,2diaminocyclohexane. The aryl-backboned ligand 3<sup>18</sup> was also successfully prepared although a longer reaction time of 60 min was required in this case. This may reflect the fact that the starting diamine is itself a solid. Shorter reaction times lead to mixtures of the diimine 3 and the monoamine 4. This led us to investigate whether the known monoamine,<sup>19</sup> which could be a useful precursor to unsymmetrical ligands, could be prepared selectively under mechanochemical conditions. It was indeed found that use of equimolar amounts of aldehyde and 1,2-diaminobenzene gave monoamine 4 quantitatively after 60 minutes grinding. No evidence for contamination of the product by diimine 3 or starting materials was observed in the <sup>1</sup>H solution state NMR spectrum. Friscic *et al.* have recently reported a related and facile mono-functionalisation of 1,2-diaminobenzene to yield mixed amine-thioureas.<sup>20</sup> For each of compounds 2-4 solid state IR, elemental analysis and solution

state  ${}^{1}$ H NMR (CDCl<sub>3</sub>) were all in accord with the expected structures and literature data.<sup>17–19</sup>

The bulky chiral ligand 5 ('Jacobsen' ligand) is widely used in conjunction with Mn(m) for enantioselective epoxidation catalysis.<sup>10,21</sup> The starting aldehyde is a solid (m.p. 59–61 °C) and the diamine is a liquid. Only partial reactions were observed between these reactants after 30 minutes milling at 25 Hz. However, LAG (liquid-assisted grinding) using 30  $\mu$ L of methanol (1.75 molar equivalents) did give the target diimine 5 quantitatively as a yellow powder after milling for 30 minutes under the same conditions. Analysis by solid state IR, solution state <sup>1</sup>H NMR, TGA and elemental analysis all pointed to a quantitative conversion to 5 under these conditions. TGA performed rapidly after removal from the reaction vessel suggested that one equivalent of water by-product remained in the product. However, on heating (80 °C, 36 h) complete loss of the water occurred to give a material with satisfactory



Scheme 2 General reaction scheme for the formation of salenH<sub>2</sub> from salicylaldehyde and ethylene diamine followed directly by metal complexation of salenH<sub>2</sub> under liquid assisted grinding conditions.



Fig. 1 Comparison of solid state  $^{13}$ C MAS NMR spectra of salenH<sub>2</sub> obtained from conventional solution state synthesis (top) and the solventless mechanochemical method (bottom, compound 1).

elemental analysis. The solid state IR spectrum showed the expected imine peak at  $1630.5 \text{ cm}^{-1}$ , and the fingerprint region was identical to that of a sample synthesised by the conventional solvent-based method (see ESI Fig. S24<sup>†</sup>).

Overall, in comparison to the conventional solution-based methods of synthesising these ligands (typically reflux in ethanol to give 70–90% isolated yields)<sup>10,14,17–19,22</sup> the mechanochemical methods are not only solvent-free but analysis of the solid product suggests that conversion is quantitative, with the only loss of product due to mechanical losses during transfer. It is also notable that the products are obtained in good purity, so that no purification, for example by recrystallisation or extraction, is actually required. Heating to remove the water by-product is needed however, if the fully dehydrated forms are needed. Overall, we suggest that these methods are preferable to the conventional solution-based syntheses.

#### One-pot two-step synthesis of complexes

A growing variety of metal complexes has been synthesised under mechanochemical conditions.<sup>1k</sup> However, there are relatively few examples based on chelating polydentate ligands. Examples include complexes of bidentate dimethylglyoxime (dmg) [Ni(H<sub>2</sub>dmg)<sub>2</sub>]X<sub>2</sub> (X = Cl, NO<sub>3</sub>),<sup>23</sup> cobalt, manganese and nickel complexes of tridentate tris(pyrazolyl)borates,<sup>24</sup> the aluminium quinolinate complex 'Alq<sub>3</sub>'<sup>3b</sup> a range of functionalised acac complexes and N–O chelates.<sup>25</sup> To our knowledge there are no examples of the complexation of tetradentate ligands under mechanochemical conditions. The conventional solution based method of forming metal–salen complexes is to reflux alcoholic solutions of salenH<sub>2</sub> and metal salts for 2 hours, which typically gives yields of 80–90%.<sup>14a,b</sup>

Metal salts, specifically ZnO,  $Ni(OAc)_2 \cdot 4H_2O$  or Cu-(OAc)<sub>2</sub>·H<sub>2</sub>O, were added directly to the reaction vessel after formation of salenH<sub>2</sub> as described above, without isolating or drying of the ligand at that stage. In each case, milling was performed for a further 30 minutes at 25 Hz to induce complexation.

Using ZnO, only a partial formation of Zn(salen)had occurred after this time as suggested by solution state <sup>1</sup>H NMR analysis. Therefore LAG conditions were employed using 0.5 ml of methanol (1.1 molar equivalents). These conditions were more effective, causing a clear change in colour to give a paler yellow powder product. Analysis by solution state <sup>1</sup>H NMR indicated that complexation had occurred quantitatively. Specifically, no peak due to the phenolic group was observed and other peaks had also shifted slightly. However, as stated above, caution must be applied in using solution-based NMR to ascertain reaction progress especially with labile systems due to the possibility of further reaction in solution in the NMR solvent itself. More definitively, the solid state MAS <sup>13</sup>C NMR spectrum for the as obtained product showed new peaks attributable to the Zn complex and no peaks due to the free ligand. Metal coordination caused the CH<sub>2</sub> carbons to shift from 61.5 to 56.1 ppm and the spectrum was identical to that of the complex prepared by the conventional solution-based route (see ESI<sup>†</sup>). Elemental analysis of the as-obtained product matched well for the known *aquo* complex  $[Zn(salen)(H_2O)]^{26}$ (CSD code SAEDZN10) TGA of the product confirmed one equivalent of water to be present by a mass loss of 5.9% at 154 °C (theoretical loss 5.1%)(see ESI<sup>†</sup>). IR spectroscopy showed the expected complexation-induced shift in the imine peak to 1641 cm<sup>-1</sup> (see ESI Fig. S27<sup>†</sup>),<sup>14b</sup> and the spectrum was identical to that of a sample prepared by the conventional method.<sup>14a</sup> The product could be heated to remove the included water (80 °C, 36 h), after which the PXRD pattern was consistent with the known dimeric solid state structure in which the Zn centres are bridged by phenolic oxygen atoms, as established by comparison with the PXRD pattern simulated

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from the single crystal X-ray diffraction data in the Cambridge Structural Database (CSD code, MEHBEH) (see ESI Fig. 29<sup>†</sup>).

Similarly, reaction of the in situ generated ligand with Ni-(OAc)·4H<sub>2</sub>O was also investigated under LAG with methanol, although because of the hydrated nature of the metal salt the amount of methanol was reduced to 0.4 molar equivalents (0.2 ml). Milling resulted in a red clay-like product which presumably still contained water and acetic acid by-product. After drying (80 °C, 36 h), the material became brittle and was easily ground to form a dry, free-flowing powder. At this stage it gave a satisfactory elemental analysis for [Ni(salen)]. The solid state IR spectrum was identical to that of a sample prepared by the conventional solution-based method (see ESI<sup>†</sup>) and showed the expected complexation-induced shift in the imine peak (to 1625 cm<sup>-1</sup>). The complex is diamagnetic and therefore amenable to analysis by NMR spectroscopy. Solution-state <sup>1</sup>H NMR spectroscopy indicated that complexation was quantitative by the absence of a phenolic peak as well as the expected small shifts in peaks due to the other protons.

Solid state MAS <sup>13</sup>C NMR spectroscopy confirmed the absence of any remaining salenH<sub>2</sub> starting material, and showed the expected complexation induced change in chemical shift of the CH<sub>2</sub> carbons (from 61.5 to 59.3 ppm). The aromatic/imine region showed more than the five peaks observed for salenH<sub>2</sub> which may indicate less symmetrical crystal packing than for the Zn complex. Interestingly, the spectrum was distinctly different to that of a sample of Ni(salen) prepared by the conventional solution based method (Fig. 2), which showed fewer peaks presumably because of higher local symmetry.<sup>14a</sup>

Consistent with this, the PXRD pattern of 7 was also different to the predicted patterns based on single crystal X-ray data for the known monomeric and dimeric forms of this complex (CCD codes SAENNI and RITMUD respectively, Fig. 3) suggesting that it is a new solid form of this complex. This further illustrates the ability of mechanochemical preparation



Fig. 2 Comparison of solid state  $^{13}$ C MAS NMR spectra of Ni(salen) obtained from conventional solution state synthesis (top) and the mechanochemical method (bottom, compound 7).



Fig. 3 Comparison of PXRD patterns for Ni(salen) obtained from the mechanochemical reaction (top, compound 7), with the predicted patterns for the known dimeric (middle, CSD code RITMUD) and monomeric (bottom, CSD code SAENNI) forms of Ni(salen).

to give alternative solid forms to those made by solution-based methods because of the unusual crystallisation conditions.<sup>3b,27</sup>

The sequential two-step complexation was also investigated with  $copper(\pi)$ , by adding  $copper(\pi)$  acetate monohydrate to a vessel containing preformed salenH2 and subsequent milling for 30 minutes at 25 Hz under LAG conditions. The amount of methanol used for the copper complexation was the same as for the nickel complexation (0.2 ml, 0.43 molar equivalents). This resulted in a colour change to dark green and the formation of product with, initially, clay-like texture, similar to the initial texture of the nickel complex. Upon drying the material became brittle and was readily crushed to form a dry, free-flowing powder in quantitative yield which gave a satisfactory elemental analysis for [Cu(salen)]. As expected, the solid state IR spectrum showed a distinct shift in the imine band from that in the starting material (from 1637 to 1649  $\text{cm}^{-1}$ )<sup>14a</sup> and the fingerprint region was indistinguishable from that of a sample prepared by the conventional solvent-based method (see ESI<sup>†</sup>).<sup>14a</sup> PXRD showed the dried product to be highly crystalline and the pattern obtained was very similar to that simulated from a single-crystal X-ray diffraction data for the complex (CSD code PIFKIY) (see ESI Fig. S45†). In this structure the complex is dimeric with Cu-O-Cu bridging by phenolic O atoms.

### All-at-once multicomponent synthesis

Given the success of the two-step sequential reactions, attempts were also made to perform both steps of the reaction by simply milling together ethylenediamine, salicylaldehyde and ZnO directly (Scheme 3).

This approach gave Zn(salen), denoted **6**', after 60 minutes milling, which is the same total period required for the twostep sequential method. Interestingly, in contrast to the above stepwise reactions, no solvent needed to be added for this reaction to go to completion. This may reflect the fact that since the jar did not need to be opened for addition of reagents, the





**Fig. 4** Comparison of <sup>13</sup>C SSNMR of Zn(salen) obtained from the all-atonce mechanochemical synthesis of **6**', (red) and the hydrated product from the two-step mechanochemical reaction, **6**. Peaks marked \* are located on either side of the centreband and separated from it by a frequency equal to the sample spin rate. They are therefore assigned to spinning sidebands.

water by-product was not able to evaporate and thus stayed in the vessel accelerating the reaction.

The analytical data for 6' (solid state <sup>13</sup>C NMR spectrum, Fig. 4, and PXRD pattern, Fig. S45<sup>†</sup>) matched very closely with the corresponding data for 6 and the product gave a satisfactory elemental analysis.

# Conclusions

In this work we have demonstrated the mechanochemical synthesis of salen-type ligands and their complexes. In all cases, analytically pure materials were obtained using this method.

As stated in the introduction, mechanochemical synthesis provides a way to avoid (or greatly reduce) the consumption of solvents conventionally used in reactions. However, it needs to be recognised that any purification of the products may still require solvents, and this can detract from the 'solvent-free' advantages of performing the reactions mechanochemically. The current study highlights the fact that mechanochemical synthesis is amenable to one-pot multi-step synthesis approaches, providing a way to reduce the need for solvents both as reaction media and for purification.

# Experimental

### Physical measurements

Solution state NMR spectra were recorded on a Bruker AM 300 MHz referenced to the residual <sup>1</sup>H containing solvent. Chemical shifts ( $\delta$ ) are given in parts per million (ppm) and coupling constants are given in hertz. Solid-state <sup>13</sup>C spectra were recorded at 100.56 MHz using a Varian VNMRS spectrometer and a 6 mm (rotor o.d.) magic-angle spinning probe. They were obtained using cross-polarisation and TOSS spinning sideband suppression with recycle delays varying from 10 to 120 s, a contact time of 3 or 5 ms, at ambient probe temperature (~25 °C) and at a sample spin-rate of 6.8 kHz. Spectral referencing was with respect to an external sample of neat tetramethylsilane (carried out by setting the high-frequency signal from adamantane to 38.5 ppm). Solid state IR spectra were recorded on a Perkin-Elmer FTIR Spectrum-One, samples were recorded as KBr discs. Elemental analyses were determined by the Analytical Service Department of the School of Chemistry (ASEP) using a Perkin-Elmer 2400 CHN microanalyser. PXRD measurements were carried out on a PANanalytical X'Pert Pro X-ray diffractometer. Copper was used as the X-ray source with a wavelength of 1.5405 Å. All experiments were carried out ex-situ using a spinning stage. Diffractograms were typically carried out from 5-50° with a step size of 0.0167°. TGA were carried out by ASEP on a Perkin-Elmer Diamond TG/ DTA. The instrument was placed inside an argon filled glovebox in order to analyse samples with virtually no exposure to air and moisture.

#### Materials

The materials used in this study were obtained from Sigma Aldrich UK in >98% purity. All materials were used as obtained without further purification.

#### Mechanochemical synthesis

All mechanochemical reactions were carried out using a Retsch MM400 vibrational ball mill, equipped with Retsch 25 ml screw top vessels, containing one 13.6 g stainless steel ball of 15 mm diameter unless otherwise stated. The operating frequency was set at 25 Hz for each experiment. The products were dried in a Carbolite PF60 oven set at 80 °C.

#### 2,2'-[1,2-Ethanediylbis[(E)-nitrilomethylidyne]]bis-phenol; 1

2-Hydroxybenzaldehyde (2.5 ml,  $2.29 \times 10^{-2}$  mol) and ethylenediamine (0.776 ml,  $1.15 \times 10^{-2}$  mol) were added to the vessel and set to shake for 30 minutes. The bright yellow product was dried in the oven for 36 hours to obtain a yield of 2.99 g, 96.8%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, CDCl<sub>3</sub>): 13.23 (s, 2H), 8.36 (s, 2H), 7.32–7.22 (m, 5H), 6.96–6.93 (d, 2H, J = 9 Hz), 6.89–6.84 (t, 2H,  ${}^{2}J$  = 7.5 Hz,  ${}^{3}J$  = 15 Hz), 3.95 (s, 4H).<sup>28</sup>

# 2,2'-[(±)-1,2-Cyclohexanediylbis[(*E*)-nitrilomethylidyne]]bis-phenol; 2

2-Hydroxybenzaldehyde (0.3865 g,  $3.102\times10^{-3}$  mol) and trans ±-1,2-diaminocyclohexane (0.1789 ml,  $1.551\times10^{-3}$  mol) were

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added to the vessel and set to shake for 30 minutes. The resulting light yellow compound was dried in the oven for 36 hours to obtain a dry yield of 0.3944 g, 78.88%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, CDCl<sub>3</sub>) 13.35 (s, 2H), 8.26 (s, 2H), 7.28–7.20 (m, 3H), 7.15 (dd, 2H, *J* = 7.7 Hz, *J* = 1.6 Hz), 6.88 (d, 2H, *J* = 8.2 Hz), 6.79 (t, 1H, *J* = 7.5 Hz), 3.32 (d, 2H, *J* = 9.5 Hz), 1.91 (s, 4H), 1.74 (s, 2H), 1.57 (s, 2H, H<sub>2</sub>O), 1.47 (s, 2H).<sup>29</sup>

### 2,2'-[1,2-Phenylenebis(nitrilomethylidyne)]bis-phenol; 3

2-Hydroxybenzaldehyde (2.292 g,  $1.839 \times 10^{-2}$  mol) and 1,2phenylenediamine (1.990 g,  $1.839 \times 10^{-2}$  mol) were added to a Retsch 50 ml screw top vessel equipped with a 20 mm stainless steel ball, and set to shake for 60 minutes. The resulting yellow compound was dried in the oven for 36 hours to obtain a dry yield of 3.2089 g, 89.9%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, CDCl<sub>3</sub>) 13.07 (s, 2H), 8.64 (s, 2H), 7.43–7.32 (m, 6H), 7.28–7.20 (m, 2H), 7.06 (d, 2H, *J* = 8.0 Hz), 6.93 (td, 2H, *J* = 7.5 Hz, *J* = 1.0 Hz), 1.59 (s, 2H, H<sub>2</sub>O).<sup>29</sup>

#### 2-[[(2-Aminophenyl)imino]methyl]-phenol; 4

2-Hydroxybenzaldehyde (2.292 g,  $1.839 \times 10^{-2}$  mol) and 1,2phenylenediamine (0.9995 g,  $9.196 \times 10^{-3}$  mol) were added to the vessel and set to shake for 60 minutes. The resulting yellow compound was dried in the oven for 36 hours to obtain a dry yield of 3.704 g, 94.53%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, CDCl<sub>3</sub>) 13.03 (s, 1H), 8.62 (s, 1H), 7.40 (dd, 2H, *J* = 12.1 Hz, *J* = 7.9 Hz), 7.04 (tt, 4H, *J* = 23.3 Hz, *J* = 7.6 Hz), 6.80 (t, 2H, *J* = 6.7 Hz), 4.01 (s, 2H), 1.57 (s, 1H, H<sub>2</sub>O).<sup>30</sup>

### 2,2'-[(±)-1,2-Cyclohexanediylbis[(*E*)-nitrilomethylidyne]]bis[4,6-bis(1,1-dimethylethyl)]-phenol; 5

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (0.2000 g,  $8.45 \times 10^{-4}$  mol), *trans*±-1,2-diaminocyclohexane (0.0512 ml,  $4.225 \times 10^{-4}$  mol) and methanol (0.03 ml,  $7.414 \times 10^{-4}$  mol) were added to the vessel and set to shake for 30 minutes. The resulting yellow compound was dried in the oven for 36 hours to obtain a dry yield of 0.1604 g, 77.0%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, CDCl<sub>3</sub>) 13.73 (s, 2H), 8.30 (s, 2H), 7.28 d, 6H, *J* = 9.3 Hz), 6.98 (s, 2H), 3.50 (s, 2H), 3.30 (s, 2H, MeOH), 1.92 (s, 4H), 1.79–1.67 (m, 2H) 1.57 (s, 6H, H<sub>2</sub>O), 1.41 (s, 18H), 1.33 (s, 2H), 1.23 (s, 18H).<sup>31</sup>

### 2,2'-[1,2-Ethanediylbis[(*E*)nitrilomethylidyne]]bis[phenolato]-κ*N*,*N*',*O*,*O*'-zinc(π); 6

2-Hydroxybenzaldehyde (2.5 ml,  $2.29 \times 10^{-2}$  mol), and ethylene-diamine (0.776 ml,  $1.15 \times 10^{-2}$  mol) were added to the vessel and set to shake for 30 minutes. To the resulting bright yellow powder zinc oxide (0.9370 g,  $1.15 \times 10^{-2}$  mol) and methanol (0.5 ml,  $1.23 \times 10^{-2}$  mol) were added and set to shake for a further 30 minutes. The pale yellow product was dried in the over for 36 hours to obtain a yield of 3.639 g 96%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, DMSO<sub>d6</sub>): 8.43 (s, 2H), 7.15–7.10 (m, 4 Hz), 6.62–6.60 (d, 2H, J = 6 Hz), 6.44–6.39 (t, 2H,  ${}^{2}J =$ 6 Hz,  ${}^{3}J = 15$  Hz, 3.72 (s, 4H).<sup>32</sup>

## 2,2'-[1,2-Ethanediylbis[(*E*)nitrilomethylidyne]]bis[phenolato]-κ*N*,*N*',*O*,*O*'-nickel(π); 7

2-Hydroxybenzaldehyde (2.5 ml,  $2.29 \times 10^{-2}$  mol) and ethylene-diamine (0.776 ml,  $1.15 \times 10^{-2}$  mol) were added to the vessel and set to shake for 30 minutes. To the resulting bright yellow powder nickel acetate tetrahydrate (2.9188 g,  $1.15 \times 10^{-2}$ mol) and methanol (0.2 ml,  $4.94 \times 10^{-3}$  mol) were added and set to shake for a further 30 minutes. The brick red product was dried in the oven for 36 hours to obtain a yield of 3.652 g, 97.7%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, DMSO<sub>d6</sub>): 7.91 (s, 2H), 7.28–7.26 (s, 2H, *J* = 6 Hz), 7.20–7.15, (t, 2H, <sup>2</sup>*J* = 7.5 Hz, <sup>3</sup>*J* = 15z), 6.71–6.69 (d, 2H, *J* = 6 Hz), 6.54–6.49 (t, 2H, <sup>2</sup>*J* = 7.5 Hz, <sup>3</sup>*J* = 15 Hz), 3.42 (s, 4H).<sup>33</sup>

# 2,2'-[1,2-Ethanediylbis[(*E*)nitrilomethylidyne]]bis[phenolato]-κ*N*,*N*',*O*,*O*'-copper(II); 8

2-Hydroxybenzaldehyde (2.5 ml,  $2.29 \times 10^{-2}$  mol) and ethylene-diamine (0.776 ml,  $1.15 \times 10^{-2}$  mol) were added to the vessel and set to shake for 30 minutes. To the resulting bright yellow powder copper acetate monohydrate (2.2953,  $1.15 \times 10^{-2}$ mol) and methanol (0.2 ml,  $4.94 \times 10^{-3}$  mol) were added and set to shake for a further 30 minutes. The dark green product was dried in the oven for 36 hours to obtain at yield of 3.699 g, 97.5%.

### 'All-at-once' 2,2'-[1,2-ethanediylbis[(*E*)nitrilomethylidyne]]bis[phenolato]-κ*N*,*N*',*O*,*O*'-zinc(π); 6'

2-Hydroxybenzaldehyde (2.5 ml,  $2.29 \times 10^{-2}$  mol), and ethylene-diamine (0.776 ml,  $1.15 \times 10^{-2}$  mol) and zinc oxide (0.9366 g,  $1.15 \times 10^{-2}$  mol) were added to the vessel and set to shake for 60 minutes. The pale yellow product was dried in the oven for 36 hours to obtain a yield of 3.600 g 94.4%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, DMSO) 8.43 (s, 1H), 7.12 (dd, 2H, *J* = 12.8 Hz, *J* = 4.7 Hz), 6.61 (d, 1H, *J* = 8.2 Hz), 6.42 (t, 1H, *J* = 7.3 Hz), 3.72 (s, 2H).

### Solution based synthesis

All solution based reactions were carried out in a 250 ml twonecked round bottomed flask equipped with a magnetic stirrer, a reflux condenser and a 100 ml dropping funnel. Products were obtained by vacuum filtration and dried in a desiccator over silica crystals for 36 hours.

#### 2,2'-[1,2-Ethanediylbis[(E)-nitrilomethylidyne]]bis-phenol

To the flask 2-hydroxybenzaldehyde (2.5 ml,  $2.29 \times 10^{-2}$  mol) dissolved in 25 ml of methanol was added and brought to reflux. Once refluxing a solution of ethylenediamine (0.776 ml,  $1.15 \times 10^{-2}$  mol) dissolved in 25 ml of methanol was added dropwise over 30 seconds. The solution changed from colourless to yellow upon addition. The mixture was brought to reflux for 1 hour, at this point the heat was removed and the reaction was allowed to cool to room temperature. Upon cooling bright yellow flaky crystals formed, which were obtained with a dry yield of 2.932 g, 95%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, CDCl<sub>3</sub>): 13.22 (s, 2H), 8.36 (s, 2H), 7.37–7.13

(m, 5H), 6.94 (d, 2H, J = 6 Hz), 6.86 (t, 2H,  ${}^{2}J$  = 6 Hz,  ${}^{3}J$  = 15 Hz), 3.95 (s, 4H).

# 2,2'-[1,2-Ethanediylbis[(*E*)-nitrilomethylidyne]]bis[phenolato]- $\kappa N,N',O,O'$ -zinc( $\pi$ )

2,2'-[1,2-Ethanediylbis[(*E*)-nitrilomethylidyne]]bis-phenol (2 g, 7.454 × 10<sup>-4</sup> mol) dissolved in ethanol (50 ml)was brought to reflux. A solution of zinc acetate dihydrate (1.67 g, 7.454 × 10<sup>-4</sup> mol) in methanol (50 ml) was added dropwise over 30 seconds. The solution changed from bright yellow to pale yellow. The mixture was brought to reflux for 1 hour, and allowed to cool to room temperature. Upon cooling yellow crystals formed, which were obtained in a dry yield of 2.1017 g, 85.0%. <sup>1</sup>H NMR  $\delta$ H (300 MHz, DMSO<sub>d6</sub>): 8.43 (s, 2H), 7.16–7.10 (m, 4H), 6.62–6.60 (d, 2H, 6 Hz), 6.44–6.39 (t, 2H, <sup>2</sup>J = 6 Hz, <sup>3</sup>J = 15 Hz), 3.72 (s, 4H).

## 2,2'-[1,2-Ethanediylbis[(*E*)nitrilomethylidyne]]bis[phenolato]-κ*N*,*N*',*O*,*O*'-nickel(II)

2,2'-[1,2-Ethanediylbis[(*E*)-nitrilomethylidyne]]bis-phenol (2 g, 7.454 × 10<sup>-4</sup> mol) dissolved in ethanol (50 ml) was brought to reflux. A solution of nickel acetate tetrahydrate (1.8930 g, 7.454 × 10<sup>-4</sup> mol) in methanol (50 ml) was added dropwise over 30 seconds. The solution changed from bright yellow to pink and finally brick red. The mixture was brought to reflux for 1 hour, and allowed to cool to room temperature. Brick red crystals were obtained, in 1.6426 g, 68% yield. <sup>1</sup>H NMR  $\delta$ H (300 MHz, DMSO<sub>d6</sub>): 7.92 (s, 2H) 7.28–7.25 (d, 2H, *J* = 9 Hz), 7.20–7.25 (t, 2H, <sup>2</sup>*J* = 7.5 Hz, <sup>3</sup>*J* = 15 Hz, 6.72–6.69 (d, 2H, *J* = 9 Hz), 6.54–6.49 (t, 2 Hz, <sup>2</sup>*J* = 7.5H, <sup>3</sup>*J* = 15 Hz), 3.42 (s, 4H).

# 2,2'-[1,2-Ethanediylbis[(E)-nitrilomethylidyne]]bis[phenolato]- $\kappa N, N', O, O'$ -copper( $\pi$ )

2,2'-[1,2-Ethanediylbis[(*E*)-nitrilomethylidyne]]bis-phenol (2 g, 7.454 × 10<sup>-4</sup> mol) dissolved in ethanol (50 ml) was brought to reflux. A solution of copper acetate monohydrate (1.4881 g, 7.454 × 10<sup>-4</sup> mol) in methanol (90 ml) was added dropwise over 30 seconds. The solution changed from bright yellow to dark green. The mixture was brought to reflux for 1 hour, and allowed to cool to room temperature. Dark green crystals were obtained in of 1.8456 g, 79% yield.

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