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Efficient Ni$^{II}_2$Ln$^{III}_2$ electrocyclization catalysts for the synthesis of trans-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines

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Abstract: A series of heterometallic Coordination Clusters (CCs) [Ni$^{II}_2$Ln$^{III}_2$(L$_1$)$_4$Cl$_2$(CH$_3$CN)$_2$]2CH$_3$CN [Ln is Y (1Y), Sm (1Sm), Eu (1Eu), Gd (1Gd), or Tb (1Tb)] were synthesized by the reaction of (E)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol (H$_2$L$_1$) with NiCl$_2$·6(H$_2$O) and LnCl$_3$·x(H$_2$O) in the presence of Et$_3$N at room temperature. These air-stable CCs can be obtained in very high yields from commercially available materials and are efficient catalysts for
the room-temperature domino ring-opening electrocyclization synthesis of trans-4,5-
diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines under a non
inert atmosphere. Structural modification of the catalyst to achieve immobilization or
photosensitivity is possible without deterioration in catalytic activity.
Introduction

Polynuclear Coordination Clusters (CCs),\textsuperscript{1,2} assembled from organic ligands, transition metal (3d) and/or lanthanide (4f) elements, are a burgeoning class of functional materials with fascinating structures.\textsuperscript{3–8} These materials are already used in areas ranging from molecular magnetism,\textsuperscript{9–17} biology,\textsuperscript{18–20} molecular imaging,\textsuperscript{21} magnetic resonance\textsuperscript{22} and luminescence.\textsuperscript{23–27} However, one of the most common applications for coordination compounds, catalysis, is much less studied for polynuclear 3d/4f heterometallic CCs with classical N,O-donor ligands,\textsuperscript{28–34} than for organometallic compounds.\textsuperscript{35,36} The difference in the growth rates between the two research fields may reflect the fact that organometallic compounds are mainly of low nuclearity and so it is easier to determine a possible mechanism for the catalytic procedure.

Electrocyclizations are one of the most valuable transformations for the construction of carbon–carbon bonds. The Nazarov cyclization exemplifies such an electrocyclization providing access to important and useful cyclopentones and Lewis acids catalyze this cyclization.\textsuperscript{37–39} The interest in bifunctionalized cyclopentenones arises from the fact that they are versatile building blocks in the synthesis of natural products such as (+)-Nakadomarin A.\textsuperscript{40} Batey and Li used a variety of Lewis acids for the synthesis of trans-4,5-diaminocyclopentanones (Scheme 1) from the domino condensation/ring-opening/electrocyclization reaction of furfuraldehyde with amines.\textsuperscript{41} In this study, Dy(OTf)\textsubscript{3} and Sc(OTf)\textsubscript{3} were found to be the best catalysts, with 10\% loadings. However Sc(OTf)\textsubscript{3} gave higher yields with primary anilines (R\textsuperscript{2}=H, Scheme 1) than Dy(OTf)\textsubscript{3}. This reaction proceeds in high yields with the use of acidic ionic liquids under solvent-free conditions\textsuperscript{42} or with the use of N-sulfonylimine, with p-toluenesulfonamide acting as a leaving group.\textsuperscript{43} However in both cases the reaction works only for secondary amines.
Scheme 1. A schematic representation of trans-4,5-diaminocyclopentanones

We have recently developed a new generation of 3d/4f CCs and have explored their catalytic behavior. The Schiff base $\text{H}_2\text{L}_1^{44}$ (Scheme S1), along with 3d and 4f ions affords tetranuclear $\text{M}^{\text{II}}_2\text{Ln}^{\text{III}}_2$, (M = Co or Ni) CCs possessing a defect dicubane topology with two divalent 3d ions (center) and two trivalent 4f ions (wings) (Scheme S1, middle).$^{45,46}$ In this specific topology, five out of six, and six out of seven or eight, coordination sites are occupied by $\text{H}_2\text{L}_1$ for the 3d and the Dy$^{\text{III}}$ centers, respectively (Scheme S1, right). Recently, we reported that compound $[\text{Ni}^{\text{II}}_2\text{Dy}^{\text{III}}_2(\text{L}_1)_4\text{Cl}_2(\text{CH}_3\text{CN})_2] \ 2\text{CH}_3\text{CN}$ (1Dy) exhibits similar catalytic efficiency, with only 1% loading. This CC, unlike Dy(OTf)$_3$, could catalyze the reaction with secondary and primary amines.$^{41,47}$ In our quest to develop these catalytic species further and to a) seek lower cost materials and b) investigate its possibility of immobilization, we decided to i) extend our study to other lanthanides and ii) to tune the organic periphery of the $\text{H}_2\text{L}_1$ ligand. Synthetic, catalytic and theoretical issues are discussed in this report.

Experimental Section

Materials and methods

Materials. Chemicals (reagent grade) were purchased from Sigma Aldrich and Alfa Aesar. All experiments were performed under aerobic conditions using materials and solvents as received.

Instrumentation. NMR spectra were recorded on a Varian VNMRS solution-state spectrometer at 500 MHz at 30°C using residual isotopic solvent (DMSO, $\delta_\text{H} = 2.50$ ppm) as internal reference. Chemical shifts are quoted in ppm. Coupling constants (J) are recorded in Hz. IR spectra of the
samples were recorded over the range of 4000-650 cm\(^{-1}\) on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with an UATR polarization accessory. ESI-MS data were obtained on a VG Autospec Fissions instrument (EI at 70 eV). TGA analysis was performed on a TA Instruments Q-50 model (TA, Surrey, UK) under nitrogen and at a scan rate of 10 °C/min.

**Synthetic procedures.** For ligand’s synthesis see ESI.

**Synthesis of 1Ln (Ln=Y, Sm, Eu, Gd, Tb, Dy)**

To a solution of MeCN (20 mL), H\(_2\)L1 (0.2 mmol, 48 mg) and Et\(_3\)N (0.5 mmol, 69 µL) were added and its mixture was stirred for 10 minutes. NiCl\(_2\).6H\(_2\)O (0.1 mmol, 24 mg) and LnCl\(_3\)·xH\(_2\)O (0.1 mmol) (Ln=Y, Nd, Sm, Eu, Gd, Tb, Dy) were added and the resultant solution was heated under reflux for 2h. In this time a green precipitate was formed from the yellow solution. The precipitant was filtered off, washed with cold MeCN (20 mL) and Et\(_2\)O (10 mL). The precipitate (1Ln) was then collected and dried overnight at 60 °C. Yield = 69-95% based on Ln (for 1Ln).

Elemental analysis for Ni\(_2\)Dy\(_2\)(C\(_{14}\)H\(_{11}\)NO\(_3\))\(_4\)Cl\(_2\)(CH\(_3\)CN)\(_2\) (1Dy): C 46.55, H 3.23, N 5.38; found C 46.84, H 3.21, N 5.16. Elemental analysis for Ni\(_2\)Y\(_2\)(C\(_{14}\)H\(_{11}\)NO\(_3\))\(_4\)Cl\(_2\)(CH\(_3\)CN)\(_2\) (1Y): C 51.06, H 3.57, N 5.95.; found C 51.32, H 3.51, N 6.09. Elemental analysis for Ni\(_2\)Gd\(_2\)(C\(_{14}\)H\(_{11}\)NO\(_3\))\(_4\)Cl\(_2\)(CH\(_3\)CN)\(_2\) (1Gd): C 46.15, H 3.25, N 5.42; found C 46.51, H 3.18, N 4.82. Elemental analysis for Ni\(_2\)Eu\(_2\)(C\(_{14}\)H\(_{11}\)NO\(_3\))\(_4\)Cl\(_2\)(CH\(_3\)CN)\(_2\) (1Eu): C 46.81, H 3.47, N 5.46.; found C 47.08, H 3.79, N 5.52. Elemental analysis for Ni\(_2\)Tb\(_2\)(C\(_{14}\)H\(_{11}\)NO\(_3\))\(_4\)Cl\(_2\)(CH\(_3\)CN)\(_2\) (1Tb): C 46.85, H 3.25, N 5.42.; found C 47.20, H 3.33, N 4.98. Elemental analysis for Ni\(_2\)Sm\(_2\)(C\(_{14}\)H\(_{11}\)NO\(_3\))\(_4\)Cl\(_2\)(CH\(_3\)CN)\(_2\) (1Sm): C 46.87, H 3.28, N 5.16.; found: C 46.81, H 3.22, N 4.91.

**Synthesis of Compounds 2Y, 3Y and 4Y**
**Compound 2Y.** To a solution of MeCN (20 mL), H$_2$L$_2$ (0.2 mmol,) and Et$_3$N (0.5 mmol, 69 µL) were added and the mixture was stirred for 10 minutes. NiCl$_2$.6H$_2$O (0.1 mmol, 24 mg) and YCl$_3$.xH$_2$O (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2h. The brown precipitate that settled as the mixture was left to cool was filtered and washed off with cold MeCN (20 mL) and Et$_2$O (10 mL). The precipitate was then collected and dried overnight at 60°C. Yield 65% based on Y. Crystals for single crystal X-ray diffraction were obtained by dissolving 2Y (25mg) in DMF (10 mL). The solution was stirred for 10 minutes before filtration. The filtrate underwent vapor diffusion with Et$_2$O; after 7 days large brown crystals suitable for X-ray diffraction were obtained. Elemental analysis for Ni$_2$Y$_2$(C$_{17}$H$_{15}$NO$_3$)$_4$Cl$_2$(CH$_3$CN)$_2$ (2Y): C 55.02, H 4.23, N 5.35; found: C 55.04, H 4.64, N 5.16.

**Compound 3Y.** To a solution of MeCN (20 mL), H$_2$L$_3$ (0.2 mmol,) and Et$_3$N (0.5 mmol, 69 µL) were added and the mixture was stirred for 10 minutes. NiCl$_2$.6H$_2$O (0.1 mmol, 24 mg) and YCl$_3$.xH$_2$O (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2H. The brown/yellow precipitate that settled as the mixture was left to cool was filtered and washed off with cold MeCN (20 mL) and Et$_2$O (10 mL). The precipitate was then collected and dried overnight at 60 °C. Yield =74% based on Y. Crystals for single crystal X-ray diffraction were obtained by dissolving 3Y (25 mg) in DMF (10 mL). The solution was stirred for 10 minutes before filtration. The filtrate underwent vapor diffusion with Et$_2$O; after 12 days clear green crystals suitable for X-ray diffraction were obtained. Elemental analysis for Ni$_2$Y$_2$(C$_{18}$H$_{13}$NO$_3$)$_4$Cl$_2$(CH$_3$CN)$_2$ (3Y): C 56.31, H 3.97, N 5.02; found: C 56.64, H 3.63, N 5.21.

**Compound 4Y.** To a solution of MeCN (20mL), H$_2$L$_4$ (0.2 mmol,) and Et$_3$N (0.5 mmol, 69 µL) were added and the mixture was stirred for 10 minutes. NiCl$_2$.6H$_2$O (0.1 mmol, 24 mg) and YCl$_3$.xH$_2$O (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for
The brown/red precipitate that settled as the mixture was left to cool was filtered and washed off with cold MeCN (20 mL) and Et₂O (10 mL). The precipitate was then collected and dried overnight at 60°C. Yield 90% based on Y. Crystals for single crystal X-ray diffraction were obtained by dissolving 4Y (25 mg) in DMF (10 mL). The solution was stirred for 10 min before filtration. The filtrate underwent vapor diffusion with Et₂O; after 3 weeks small green crystals suitable for X-ray diffraction were obtained. Elemental analysis for Ni₂Y₂(C₂₁H₁₇NO₃)₄Cl₂(CH₃CN)₂: C 59.65, H 4.21, N 4.74; found: C 59.84, H 3.60, N 4.92.

General Catalytic Protocol. In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vials equipped with magnetic stirring bars. The use of molecular sieves is crucial for the reaction, since one equivalent of water is generated as a side product. MeCN (dry, 4 mL), furfural (0.5 mmol, 41 μL), secondary amine (1 mmol) and the appropriate amount of catalyst (10 – 1% total Dy) were added. The mixture was stirred at room temperature from 2 to 24 h and the reaction was followed by TLC. The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (20-30% ethyl acetate in hexanes). The products were obtained as red or yellow oils which solidified on standing.

Crystallography. Data for 2Y, 3Y and 4Y (ω- scans) were obtained at the University of Sussex by use of an Agilent Xcalibur Eos Gemini Ultra difractometer with CCD plate detector under a flow of nitrogen gas at 173(2) K using Mo Kα radiation (λ = 0.71073 Å). CRYSALIS CCD and RED software was used respectively for data collection and processing. Reflection intensities were corrected for absorption by the multi-scan method. Data for 1Sm-A, 1Sm-B, 1Sm-C, and 1Eu-A were collected at the National Crystallography Service, University of Southampton on a Rigaku Saturn 724+ area detector mounted at the window of an FR-E+ rotating anode generator with a
Mo anode ($\lambda=0.71075\AA$) under a flow of nitrogen gas at 100(2) K. The X-ray data were collected and processed using Rigaku CrystalClear except 1Eu-A where Rigaku Oxford Diffraction CrystallisPro was used for data processing. Crystal structures 1Sm-B, 2Y and 4Y were solved by dual-space methods with SHELXT,\(^{49}\) whereas 1Sm-A, 1Sm-C, 1Eu-A and 3Y were solved using charge flipping methods with Superflip.\(^{50}\) All crystal structures were then refined on Fo2 by full-matrix least-squares refinements using SHELXL.\(^{49}\) All non-H atoms were refined with anisotropic thermal parameters, and H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms. Geometric/crystallographic calculations were performed using PLATON,\(^{51}\) Olex2,\(^{52}\) and WINGX\(^{53}\) packages; graphics were prepared with Crystal Maker.\(^{54}\) Crystallographic details are given in Table S1. CCDC 1442674-1442680.

**Computational details.** Energy minimization calculations on strategically designed model compounds (see Results and Discussion) were made within the Kohn-Sham Density Functional Theory (DFT) approach at the B3LYP/SDD and B3LYP/6-311G* levels,\(^{56-66}\) with the Gaussian09\(^{67}\) software. The Jmol program was used for visualization purposes.\(^{68}\)

**Results and Discussion**

With the goal of developing effective molecular catalysts with low cost, we reasoned that replacement of Dy\(^{\text{III}}\) with lanthanides of lower cost would allow us to evaluate the relationship between cost and effectiveness. Thus, we attempted to isolate and characterize the analogues of compound 1Dy with Y (1Y), Sm (1Sm), Eu (1Eu), Gd (1Gd), and Tb (1Tb) following the similar reaction procedure that gave 1Dy.\(^{47}\) The synthetic protocol specifies that when the blend Dy(OTf)\(_3\) / Ni(ClO\(_4\))\(_2\)-6H\(_2\)O or NiCl\(_2\)-6H\(_2\)O / H\(_2\)L\(_1\) / Et\(_3\)N (molecular ratio 1 / 1 / 2 / 5) in CH\(_3\)CN (20 mL) is refluxed for one hour results, after filtration, in yellow-greenish crystals in moderate yield. As the reactions to produce the 1Y, 1Sm, 1Eu, 1Gd, and 1Tb gave a large amounts of filtrate we
decided to further characterize the constituent species. A range of techniques such as ESI-MS, elemental analysis, IR and TGA showed that these filtrates were similar to that from \textbf{1Dy}. IR spectra of \textbf{1Y}, \textbf{1Sm}, \textbf{1Eu}, \textbf{1Gd}, and \textbf{1Tb} are similar to that of \textbf{1Dy} (see ESI). The TGA data (Figures S12 to S17) for all solid compounds indicated the loss of four CH$_3$CN molecules (lattice and coordinated) up to 290 °C and decomposition at higher temperatures. ESI-MS spectra of all species were similar, with two main peaks corresponding to the \{[Ni$^{II}_2$Ln$^{III}_2$(L1)$_4$Cl(CH$_3$CN)(CH$_3$OH)]+4H$^+$ and \{[Ni$^{II}_2$Ln$^{III}_2$(L1)$_4$]\}$_2^+$ fragments (Figures S1-7). Finally, elemental analysis are consistent with the calculated values without lattice CH$_3$CN molecules. The IR, TGA and ESI-MS analyses were performed three times from different batches, with similar results.

In our attempts to grow crystals, several unexpected products were structurally characterized, indicating that the synthesis of these species is not a simple task.\textsuperscript{69} For example, our effort to obtain crystals of \textbf{1Sm} resulted in the structural characterization of three different compounds formulated as [Ni$^{II}_5$Sm$^{III}_3$(CO$_3$)(L1)$_7$(L')(H$_2$O)$_3$] (\textbf{1Sm-A}), [Ni$^{II}_2$Sm$^{III}_3$(L1)$_4$(O-Van)$_2$(H$_2$O)$_2$] 4CH$_3$CN (\textbf{1Sm-B}) and [Sm$^{III}_4$(OH)$_2$(L1)$_4$(HL1)$_2$] 2CH$_3$CN (\textbf{1Sm-C}) (See ESI) where L' is 2-aminophenol and O-Van is ortho-vanillin. In our attempt to obtain crystals of \textbf{1Eu} a compound formulated as [Ni$^{II}_8$Eu$^{III}_4$(L1)$_8$(CO$_3$)$_4$Cl$_4$(H$_2$O)$_{14}$] (\textbf{1Eu-A}) was obtained. The latter molecule is isoskeletal to recently reported compounds by Ke et al.\textsuperscript{70}

The next step was to characterize the catalytic activity of these species using the catalytic protocol developed in our previous study.\textsuperscript{47} In order to ascertain that the catalytic activity of these species is driven solely by the 4f ions, various blank tests were performed (Table S1). First, three Ni$^{II}$ salts with three different loadings (Table S1, Entries 2-10) were used in the prototype reaction. NiCl$_2$ was found to catalyze the reaction with very high loadings and very low yields after 24 hours
(Table S2, Entry 2) reflecting that its contribution is negligible for the shorter time period. An in situ mixture of Ni salt and ligand (Table S2, Entries 11-13) gave none of the anticipated product after 24h. In Batey’s protocol,\textsuperscript{41} as Dy(OTf)\textsubscript{3} was found to be an excellent catalyst using a loading of 10 mol\%, our next step was to employ other lanthanide salts (Table S1, Entries 14-20) along with Yttrium salts. Y\textsuperscript{III} has a size and Lewis acidity similar to Ho\textsuperscript{III}, and the use allows a catalytic reaction to be monitored with NMR (\textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{15}N or \textsuperscript{89}Y) due to its diamagnetic character. Astonishingly, Y(OTf)\textsubscript{3} showed similar excellent catalytic performance (Table S1, entry 14) to Dy(OTf)\textsubscript{3},\textsuperscript{41} and the lanthanide chlorides showed poorest performance (Table S1, Entries 15-20).

The next task was to utilize a mixture of Ni and Ln salts (Table S1, entries 21-26) which showed that the presence of the Ni salt had almost negligible influence in the catalytic performance. Finally, the use of Ni(ClO\textsubscript{4})\textsubscript{2} and Dy(OTf)\textsubscript{3} or Y(OTf)\textsubscript{3} (Table S1, entries S27-28), showed an insignificant influence of the Ni source on the catalytic performance. The Y salt was better than the Dy salt. All these experiments demonstrated the superior catalytic behavior of 1Dy\textsuperscript{47} (use of only 1 mol\%, Table 1, entry 1) over the simple metal salts as catalysts and the insignificant role of Ni\textsuperscript{II} in the catalysis. As shown in Table 1, 1Sm, 1Eu, 1Tb and 1Gd (entries 2 – 5) catalyze the reaction in moderate to good yields in comparison to 1Dy but show higher yields than to simple salts. When 1Y (Table 1, entry 6) was involved, a catalytic performance similar to 1Dy was observed. A further decrease of the catalytic amount of 1Y to 0.5% loading results in excellent conversion (Table 1, entry 7). The higher efficacy of Y\textsuperscript{III} than Ln\textsuperscript{III} in Lewis acid catalysis, has been previously reported,\textsuperscript{71,72} but no rationale has been proposed. All attempts to recover the 1Ln catalyst in order to reuse it, were unsuccessful.
Table 1. Comparison of 1Ln source catalytic activity

| Entries | Catalyst | T         | Loading (mol%) | Time (h) | Yield (%) |
|---------|----------|-----------|----------------|----------|-----------|
| 1       | 1Dy      | r.t.      | 1              | 2        | quantitative<sup>47</sup> |
| 2       | 1Sm      | r.t.      | 1              | 2 (24)   | 55 (75)   |
| 3       | 1Eu      | r.t.      | 1              | 2 (24)   | 60 (99)   |
| 4       | 1Gd      | r.t.      | 1              | 2 (24)   | 63 (99)   |
| 5       | 1Tb      | r.t.      | 1              | 2 (24)   | 63 (86)   |
| 6       | 1Y       | r.t.      | 1              | 2        | quantitative |
| 7       | 1Y       | r.t.      | 0.5            | 2 (24)   | 98 (100)  |

<sup>a</sup> Reaction conditions: amine, 1 mmol; 2-furaldehyde, 0.5 mmol; 4 Å MS, 100 mg; catalyst; anhydrous MeCN, 4 mL; room temperature; <sup>b</sup>Catalyst loading calculated per equivalent of Dy; <sup>c</sup>Determined by <sup>1</sup>H NMR spectroscopy.

Taking into account the cost of the metal salts, the yttrium derivative (1Y) was used in further experiments. <sup>73</sup> Compound 1Y shows similar or better catalytic behavior than 1Dy along with various secondary or primary amines (Table 2). <sup>47</sup>
| Entry | Product | Yield/ % | Yield/ % | Yield/ % | Yield/ % | Yield/ % |
|-------|---------|----------|----------|----------|----------|----------|
| 1     | ![Product 1] | Quantitative | Quantitative | 91 | Quantitative | 85 |
| 2     | ![Product 2] | 99 | 96 | 85 | 95 | 80 |
| 3     | ![Product 3] | 95 | 99 | 70 | 94 | 64 |
| 4     | ![Product 4] | 61 | 53 | 58 | 51 | 52 |
| 5     | ![Product 5] | 63 | 71 | 69 | 69 | 62 |
| 6     | ![Product 6] | 96 | 99 | 96 | 99 | 94 |
| 7     | ![Product 7] | 62 | 91 | 91 | 93 | 91 |
| 8     | ![Product 8] | 70 | 95 | 94 | 94 | 92 |
| 9     | ![Product 9] | 26 | 90 | 81 | 86 | 81 |

| Compound | 1Dy | 1Y | 2Y | 3Y | 4Y |
|----------|-----|----|----|----|----|
| Loading/ % | 1 | 0.5 | 1 | 0.5 | 1 |
| Time/h | 16 | 8 | 12 | 8 | 12 |

Table 2. Comparison of catalytic activity of 1Y, 2Y, 3Y and 4Y with secondary and primary substrates along with 1Dy, for comparison.

*Reaction conditions: amine, 1 mmol; 2-furaldehyde, 0.5 mmol; 4 Å MS, 100 mg; catalyst; anhydrous MeCN, 4 mL; room temperature; Catalyst loading calculated per equivalent of 1Ln; Determined by 1H NMR spectroscopy.*
The excellent results using even lower catalyst loadings (0.5% for 1Y instead of 1.0% for 1Dy) and the cheaper lanthanide source, led us to consider the possibility that 1Y could be structural modified to achieve immobilization and demonstrate photosensitivity. We recently reported a library of nineteen modified Schiff-base organic ligands that offer coordination environment similar to that in \( \text{H}_2\text{L1} \). Among these, the three organic ligands shown in Scheme 2 were selected for the synthesis of the corresponding tetranuclear CCs. Other considerations were i) to increase the solubility as well to offer the possibility for deposition of these species on surfaces by the introduction of an allyl group (\( \text{H}_2\text{L2} \)) and ii) to create “photosensitive” catalysts by inclusion of a naphtho group (\( \text{H}_2\text{L3} \)) and iii) to combine both these features (\( \text{H}_2\text{L4} \)).

Scheme 2 The three modified organic ligands \( \text{H}_2\text{L2}, \text{H}_2\text{L3} \) and \( \text{H}_2\text{L4} \) used for the synthesis of 2Y, 3Y and 4Y, respectively.

From ligand \( \text{H}_2\text{L2} \) (Scheme 2, left), in a slightly different synthetic ratio to 1Y, a compound formulated as \([\text{Ni}^{II}_2\text{Y}^{III}_2(\text{L2})_4\text{Cl}_2(\text{DMF})_2]\) (2Y) (Figure 1A) was obtained. Also, the ligands \( \text{H}_2\text{L3} \) and \( \text{H}_2\text{L4} \) (Scheme 2, center and right), with slightly different synthetic ratios, gave \([\text{Ni}^{II}_2\text{Y}^{III}_2(\text{L3})_4\text{Cl}_2(\text{DMF})_2]\) 2DMF 2Et\text{O} (3Y 2DMF 2Et\text{O}) (Figure 1B) and \([\text{Ni}^{II}_2\text{Y}^{III}_2(\text{L4})_4\text{Cl}_2(\text{DMF})_2]\) (4Y) (Figure 1C), respectively. These compounds were characterized by X-Ray crystallography (Figure 1), IR, ESI-MS, and TGA (see ESI). Single crystal studies indicate that compounds 2Y, 3Y and 4Y are isoskeletal\(^{69}\) to 1Dy, while the ESI-MS data indicate
that all three compounds retain their core structures in solution, shown by two main peaks corresponding to the \([\text{Ni}^{II}_2\text{Y}^{III}_2(\text{L})_4\text{Cl}_2]^+\) and \([\text{Ni}^{II}_2\text{Y}^{III}_2(\text{L})_4]^2^+\) fragments. Each Ni^{II} center coordinates to six atoms (O_{5}N environment) possessing an octahedral geometry and each Y^{III} center coordinates to seven atoms (O_{5}NCl environment) possessing a pentagonal bipyramidal geometry.

Figure 1. X-ray crystal structures of 2Y (upper, left), 3Y (upper right) and 4Y (lower). Color code; green = Ni^{II}; Light blue = Y^{III}; yellow = C; Red = O; Pale blue= N; light green = Cl. Hydrogen atoms and disordered solvent molecules omitted for clarity.
The catalytic activity of \textbf{2Y}, \textbf{3Y} and \textbf{4Y} towards the prototype reaction is shown in Table 2. Compounds \textbf{2Y} and \textbf{4Y} are not so efficient as to \textbf{1Y} (1.0\% instead of 0.5\% loading and slightly lower yields), but these results can be attributed to the presence of the sterically demanding naphtho groups. When \textbf{3Y} was employed as catalyst (Table 2) yields similar to those with \textbf{1Y} were obtained. As we reported before,\textsuperscript{47} when the reaction takes place with primary amines the corresponding deprotonated Stenhouse salts are formed (Entries 6-9). The ring-closing of the salt is promoted by the use of very dilute HCl leading to the corresponding trans-4,5-diaminocyclopent-2-enones.

To explore further the possible immobilization of these catalysts, we attempted to synthesize the novel organic ligands \textbf{H_4L5} and \textbf{H_4L6} shown in Scheme 3 (see ESI for synthetic details). Ligand \textbf{H_4L5} offers a coordination environment similar to that in \textbf{H_2L1} and thus it was expected to form coordination polymers upon complexation with the Ni\textsuperscript{II} and Y\textsuperscript{III} salts. However, \textbf{H_4L5} is only slightly soluble in polar solvents such as N,N’-DMF or DMSO. Organic ligand \textbf{H_4L6} was synthesized expecting a higher solubility, but like \textbf{H_4L5} it is only slightly soluble in polar solvents. Our efforts to synthesize the corresponding coordination polymers have not yet been successful.

![Scheme 3](image)

\textbf{Scheme 3.} The protonated form of the modified organic ligands \textbf{H_4L5} (R=H) and \textbf{H_4L6} [R=C(CH_3)_3]
Computational studies showed that it was possible to modify ligand sterics without compromising the electrostatic properties that one key to the activities of the complexes. The results also suggest that the charge distribution within the O-O-N-O core pattern directly interacting with the metals is a function of the conformation of the ligands.

**Figure 2.** Rendition of the molecular electrostatic potential (MEP) of $H_2L_2$ (upper), $H_2L_3$ (middle) and $H_2L_4$ (lower) and bound (left) and its free conformation (right).

**Conclusions**

The collective data on this simple and high yielding isoskeletal series of $\text{Ni}^{\text{II}}_2\text{Ln}^{\text{III}}_2$ CCs, supported by structurally homologous Schiff base ligands, shows remarkable catalytic activity in the formation of trans-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines. The $\text{Ni}^{\text{II}}$ contribution is negligible and therefore it is safe to deduce that the domino reaction is driven solely by the 4f or Y ion. Remarkably, the employment of Y$^{\text{III}}$ instead
of DyIII makes possible a lower loading and lower cost catalyst. We show that the functionalization of the organic skeleton is feasible (2Y, 3Y and 4Y), without impairing the catalytic activity. Moreover, our results suggest that the modified species 2Y and 4Y, that bear allyl groups, can be immobilized by deposition on surfaces. Further work on this aspect is in progress. We are currently exploring the possibilities of utilizing 3d/4f or 3d/Y CCs as tandem catalysts in other organic transformations.

Supporting Information.

ESI-MS, TGA and IR of 1Ln. ESI-MS, TGA and IR of 2Y-4Y. 1H NMR and ESI-MS of H2L1, H2L2, H2L3, H2L4 and H4L5. 1H NMR of Catalytic Products from Table 2. CIF Files. Tables S1-S2, Scheme S1-S2, Figures S1-S22. The supporting information is available free of charge on the ACS publications website at DOI...

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A series of isoskeletal Ni$^{II}_2$Ln$^{III}_2$ coordination clusters possessing defect dicubane topology were tested as catalysts in a domino reaction leading to the synthesis of trans-4,5-diaminocyclopent-2-enones.