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Chiral Lanthanoid Dimers Ligated by Carbohydrate-Based Diketonates: Catalytic and Luminescent Properties

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The reaction of hydrated lanthanoid chlorides (Ln = La, Eu) with chiral, carbohydrate-based diketonate ligands has yielded dimeric species with Ln_2L_6 composition as determined by MALDI mass spectrometry and single-crystal X-ray crystallography. The X-ray crystallographic analysis identified a chiral cavity formed by interligand repulsion able to coordinate dimethylformamide, prompting investigation of the catalytic properties of the dimers. Preliminary results indicate that the dimers display catalytic activity in thio-Michael addition reactions as well as metal-based luminescence in the case of europium.

Introduction

The synthesis of new, enantiopure catalysts incorporating the lanthanoid elements constitutes a fascinating challenge revolving around the search for chiral ligands suited to desired applications.[1] The lanthanoid series, replete with a highly electropositive nature coupled with a flexible coordination sphere, have been shown to catalyse a range of chemo- and stereoselective reactions, varying according to ligand class.[1b] Such reactions include hydrosilylations,[2] hydroaminations,[2,3] polymerisations,[4] Mukaiyama aldol reactions[5] and thio-Michael reactions,[6] to name but a few. Prior ligand classes investigated include alkoxide complexes,[1b] heterometallic BINOL complexes,[1c] phosphate complexes[1b] and a range of neutral O- and N-donor complexes.[7] Diketonate ligands have been largely overlooked since the early inception of asymmetric lanthanoid catalysis.[1b] Similarly, with the notable exception of a range of D-glucose-derived bifunctional asymmetric catalysts reported by Shibasaki et al.,[1e–1g] the potential of lanthanoid carbohydrate complexes has remained largely unexplored. Carbohydrates represent the most abundant group of natural products known and hence have the ability to impart versatility and cost-effectiveness to a catalyst series. Furthermore, the isolation of polynuclear chiral lanthanoid species, either by chelation of ligands containing a chiral centre or by induced chirality through coordination, has been garnering increasing attention over the past decade, owing to their potential application to carbon dioxide fixation[8] and molecular magnetism.[9] Such species have been synthesised by ligation of amino acids,[9b,10] chiral amine chelates[8,11] and coordination-induced species.[9a,9c]

Herein we report the synthesis of lanthanum and europium dimers ligated by diketonate ligands incorporating a chiral protected galactose moiety. The dimers contain a binding pocket which has been visualised in the solid state by X-ray crystallography, while possessing luminescent properties measured for the europium species. An investigation of the catalytic properties of both dimers in the 1,4-addition of thiols to α,β-unsaturated carbonyl compounds revealed high catalytic activity, at low catalyst loadings, whilst employing mild conditions.

Results and Discussion

The asymmetric diketonate ligand central to this study incorporates both a chiral terminus, to promote asymmetric induction, and an achiral phenyl terminus to ease steric constraints within the coordination environment. The core of the ligand, D-Galactose, imparts a source of chiral diols that have been extended to give greater steric bulk by simple conversion to acetonide groups.[12] Subsequent oxidation, acid chloride formation and direct coupling to lithium 1-phenylenolate yields the chiral diketone Hhpp (Scheme 1).[13] Each step of the ligand synthesis was monitored using optical rotation measurements, with values similar to these reported for intermediate species. The reaction of Hhpp with hydrated lanthanoid chloride salts using established methodologies for cluster synthesis[14] yielded chiral dimers with the composition $[Ln_2(hpp)_6]$ [Ln = La (**1**), Eu (**2**)]. The solid-state structure of lanthanum species **1** was elucidated by X-ray diffraction studies performed on single crystals generated by the slow infusion of hexane into

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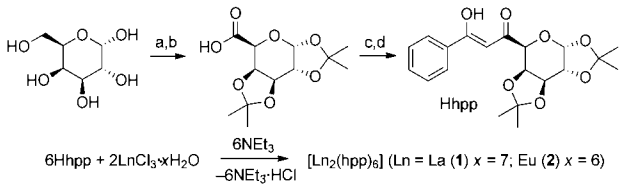
a toluene solution of **1** containing 1% dimethylformamide (Figure 1). The compound was found to crystallise in the chiral space group $P4_12_12$.



Scheme 1. *Reagents and conditions:* (a) acetone, $ZnCl_2$, 8 h; (b) 0.5 M aqueous NaOH, $KMnO_4$, 12 h; (c) neat $SOCl_2$, reflux, 3 h; (d) 1 equiv. lithium 1-phenylenolate, –78 °C→room temp., 2 h.

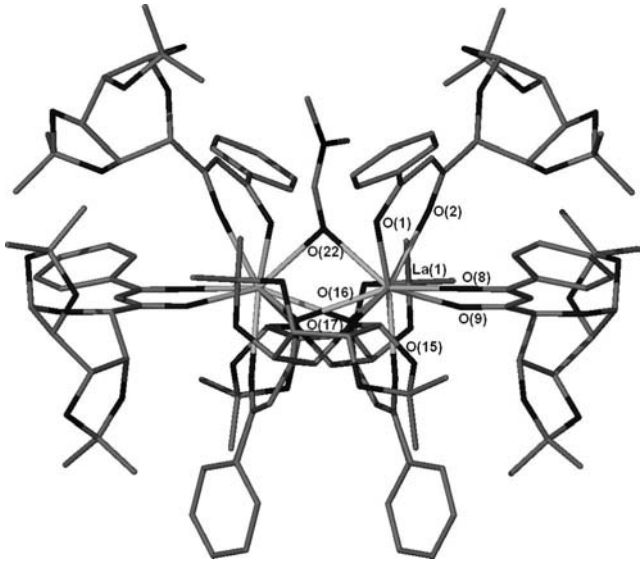


Figure 1. The molecular structure of **1** coordinating a molecule of DMF. Hydrogen atoms have been omitted for clarity.

Performing the symmetry operation (y, x, $-z$) generated the anticipated $[La_2(hpp)_6]$ dimeric motif containing an unexpected bridging DMF molecule. The bridging DMF is disordered over two positions with symmetry transformations generating the reciprocal molecule. Each of the metal centres has a coordination number of nine and is μ_2-bridged by both O(22) of the DMF, and the central oxygen atoms [O(17), O′(17)] of two ligands. The La–O–La angles vary only slightly between that of the ligands and that of the DMF [102.3(9)° and 103.3(8)°, respectively]. The two bridging ligands are tridentate, coordinating through both oxygen atoms of the diketonate and the oxygen of the pyranose ring, giving an overall coordination mode of μ_2-η^2(O,O′)η^2(O′,PyO). The solely chelating diketonates give the closest oxygen-to-metal contacts, with La–O distances averaging 2.46 Å. This compares with a bridging diketonate La–O distance of 2.485(3) Å for the outer ketone, 2.62 Å (averaged) for the bridging ketone and 2.703(2) Å for the pyranose oxygen. The bridging ketone oxygen slightly favours one of the lanthanum atoms with La–O and La′–O distances of 2.587(3) and 2.656(2) Å, respectively. Removal of the DMF molecule allows visualisation of the binding pocket containing two lanthanum atoms (Figure 2). It is postulated that the sterically bulky acetonide groups inhibit the regular ligand spacing around the exterior that can be seen for analogous lanthanoid dimers.[15]

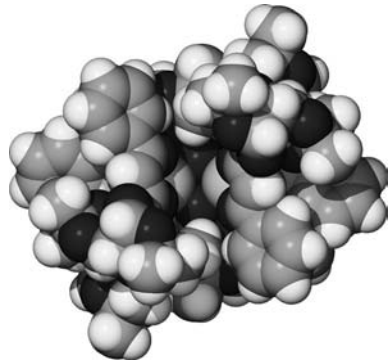


Figure 2. Space-filling model of the binding pocket of **1** viewed from above. The coordinating DMF molecule has been omitted to highlight the exposed lanthanoid atoms.

A crystallographic structural determination could not be made for europium species **2**, however there is considerable evidence supporting retention of the dimeric motif. Aside from consistent infrared and elemental analyses, MALDI mass spectrometry yielded a dominant cationic fragment consistent with the $[Ln_2(hpp)_5]^+$ species in each case (Table 1). The observed isotopic profiles were in each instance consistent with the dimeric form. Analysis of crystalline **1** by ^{1}H NMR spectroscopy gave a spectrum consistent with the crystal structure shown in Figure 1. Evidence for both the enolic proton, determined from Hhpp to be located at δ = 15.99 ppm, and resonances derived from the keto tautomer were absent. The greatest shifts in resonances relative to the free ligand corresponded to protons assigned to the pyranose ring, owing to the changes in the local magnetic environment caused by metal coordination for two of the six tridentate ligands. Nonequivalence of the methyl resonances of the acetonide groups also suggests two distinct magnetic environments for the ligand groups, although assignment of the signals proved impossible. Methyl resonances for the coordinated DMF molecule were observed at δ = 2.88 and 2.94 ppm, while the aldehyde proton was shifted upfield to 6.65 ppm. The latter resonance, corresponding to the DMF aldehyde proton, represents a significant shift relative to the aldehyde of a noncoordinated solvent sample, which is located at δ = 8.02 ppm.[16] The upfield shift can be justified as increased imine character over the C–N bond in response to polarisation of the aldehyde carbonyl group. The crystallographic evidence supports this assertion, with a longer C–O distance of 1.289(10) Å, and shorter C–N distance of 1.268(10) Å observed relative to a noncoordinated DMF molecule [C–O: 1.221 Å; C–N: 1.315(7) Å].[17] The europium dimer **2** exhibited an analogous ^{1}H spectrum to the lanthanum species, however protons located in closer proximity to the europium centres exhibited an increasing degree of upfield paramagnetic

shifting (see Supporting Information). The shifts in the NMR resonances observed for the europium species arise from low-lying excited states and are typical of such systems.

Table 1. Observed MALDI fragments for dimers **1** and **2**.

Cation	Predicted *m*/*z* (relative intensity %)[a]	Observed *m*/*z* (relative intensity %)[a]
$[La_2(hpp)_5]^+$	2154.5379 (100)	2154.6017 (100)
	2153.5346 (90)	2153.6297 (90)
	2155.5413 (61)	2155.5664 (60)
$[Eu_2(hpp)_5]^+$	2179.5630 (100)	2180.4300 (100)
	2181.5697 (97)	2182.4214 (99)
	2180.5663 (95)	2181.4241 (94)
	2182.5677 (70)	2183.4165 (70)

[a] Only peaks with relative intensities greater than 50% have been listed.

The luminescent properties of europium dimer **2** were next investigated by fluorescence spectroscopy. Excitation of a chloroform solution of the europium dimer with ultraviolet radiation (λ = 396 nm) resulted in characteristic red emission of the $^5D_0$ excited state to a suitable end state ^7F_J (J = 0–6).[18] The first five transitions corresponding to photon emission from $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) are shown in Figure 3. Low intensity transitions, $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$, have been omitted. The $^5D_0 \rightarrow {}^7F_1$ transition has a low intensity, attributed to the noncentrosymmetrical position of Eu^{3+} atoms, which is consistent with prior reports.[15]

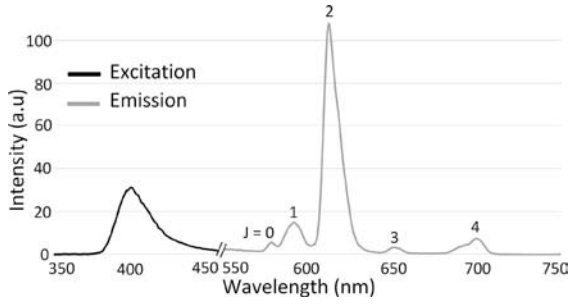
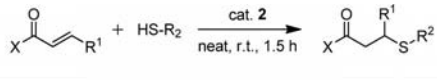
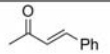
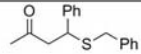
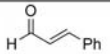
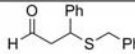
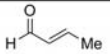
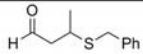
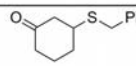
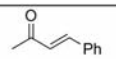
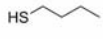
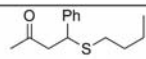
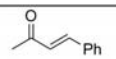
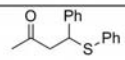


Figure 3. Emission spectra of europium dimer **2** with an excitation wavelength of 396 nm.

Lanthanoid species have been shown to act as reliable catalysts in thio-Michael addition reactions, which is attributed to their Lewis acidity and oxophilic nature.[6] To investigate the catalytic activity of the dimers the addition of benzyl mercaptan to benzalacetone was initially studied. To eliminate competitive DMF binding in the chiral pocket the catalysts were precipitated as amorphous powders in the absence of DMF. Both MALDI and elemental analyses for both lanthanum and europium powders remained consistent with the $[Ln_2(hpp)_6]$ motif. It was found that the reaction proceeded smoothly at room temperature under noninert conditions without the need for solvent, yielding selectively the β-addition product (Table 2, entry 1). Whilst a catalyst loading of 5 mol-% gave complete conversion in 90 min with both dimers **1** and **2** (isolated yields 96% and 91%, respectively), the loading could be lowered to 1 mol-% without significant loss of reactivity (Table 2, entries 1a–c). A control experiment omitting the catalyst confirmed only minor uncatalysed thio-Michael addition (Table 2, entry 1d). The optimised reaction conditions, using 5 mol-% lanthanum dimer **1**, were employed with both ketone- and aldehyde-derived α,β-unsaturated carbonyl compounds (Table 2, entries 1a, 2–4), with constantly high isolated yields. Furthermore, both aliphatic and aromatic thiols were shown to be competent nucleophiles (Table 2, entries 1a, 5–6).

Table 2. Dimers **1** and **2** as catalysts in thio-Michael addition reactions.

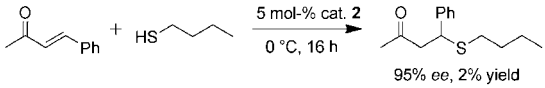


Entry	Unsaturated carbonyl	Thiol	Catalyst loading (mol-%)	Product	Yield (%)
1a			5		96
b			5[b]		91
c			1		92[c]
d			0		4[d]
2			5		75
3			5		94
4			5		98
5			5		81
6		HS–Ph	5		96

[a] Isolated yield following flash column chromatography. (b) 5 mol-% **1** used as catalyst. (c) Reaction time 6 h. (d) Reaction stopped after 24 h.

As the chiral nature of the binding cavity suggests potential for asymmetric induction, the enantiomeric excess of the thio-Michael products were evaluated. Unfortunately, using the described reaction conditions (Table 2, entry 1a) the thio-Michael adduct was obtained in <10% *ee*. Decreasing the reaction temperature to 0 °C increased the enantioselectivity, with the adduct being formed in 95% *ee*, however the yield was now very modest (Scheme 2). Further optimisation did not lead to reaction conditions capable of both good yields and high enantioselectivities.

We postulate that at lower temperatures the ligand conformation and binding pocket corresponds to that shown in Figures 1 and 2 promoting enantioselectivity. Unfortunately at these temperatures the thio-Michael reaction is kinetically disfavoured when catalysed by dimers **1** or **2**. At higher temperatures the thio-Michael reaction becomes ki-



Scheme 2. Low-yielding synthesis of thio-Michael addition product (Table 2, entry 5) at 0 °C in 95% *ee*.

netically favourable, however ligand lability, which has been reported for analogous species at this temperature,[14c] likely negates the selectivity of the chiral binding pocket, allowing indiscriminate reaction.

While these studies have achieved moderate enantioselectivities they provide important proof of principle that chiral β-diketone carbohydrate lanthanoid complexes are capable of enantioselective catalysis. Currently several strategies to improving the enantioselectivity at elevated temperatures are under investigation. They include screening a greater range of lanthanoid elements to observe the effects of ionic size on enantioselectivity, and altering the acetonide groups to incorporate more bulky functionalities such as phenyl rings. We believe that future generations of such catalysts have the potential for widespread application to a range of asymmetric lanthanoid-catalysed reactions.

Conclusions

We have synthesised the first example of a diketonate ligand bearing a protected carbohydrate group chelating a lanthanoid species. A single crystal diffraction study of the resultant lanthanoid adducts identified a $[La_2(hpp)_6]$ motif containing a chiral cavity occupied by a coordinated molecule of DMF. MALDI mass spectrometry and elemental analyses confirmed the europium moiety to be isostructural, with a luminescence study on dimer **2** identifying a characteristic red wavelength emission when exposed to ultraviolet radiation (λ = 396 nm). Both **1** and **2** show excellent activity as Lewis acid catalysts. However, the transfer of chiral information during the catalyzed reactions under optimal reaction conditions remains a challenge. These findings define a new range of chiral lanthanoid complexes with vast potential for modification and tuning to act as chiral catalysts.

Experimental Section

General Considerations: 1,2:3,4-Di-*O*-isopropylidene-α-D-galacturonyl chloride was obtained by refluxing 1,2:3,4-di-*O*-isopropylidene-α-D-galacturonic acid in thionyl chloride for 3 h followed by removal of volatile impurities under high vacuum. All other chemicals were obtained from Sigma–Aldrich and were used as received. Flash chromatography was performed on silica gel (Davisil LC60A, 40–63-μm silica media) using compressed air. The solvent system employed was an increasing gradient of ethyl acetate in hexane initiating from neat hexane unless otherwise stated. TLC was performed using aluminium-backed plates coated with 0.2 mm silica (Merck; 60 F_{254} plates). Eluted plates were visualised using a 254-nm UV lamp or by treatment with a suitable stain. ^1H and ^{13}C NMR spectra were recorded with a Varian Unity Nova 500 spectrometer. Chemical shifts were recorded on the δ scale and referenced to the solvent. Solid-state IR spectra were recorded with a Perkin–Elmer 1600 series FTIR or a Bruker Equinox 55 Infrared Spectrometer fitted with a Specac Diamond ATR source. Infrared band frequencies are reported in wavenumbers (cm^{-1}) and intensities are reported as strong (s), medium (m) or weak (w). Solution Real-Time Infrared (RTIR) scanning measurements were recorded with a Mettler Toledo ReactIR 10 spectrometer fitted with a DiComp probe connected to an MCT detector by a K6 Conduit and scanning in the region of 4000 to 650 wavenumbers at 8 wavenumber resolution. HRMS were recorded with a Bruker BioApex 47e FTMS fitted with an Analytica electrospray source using NaI for accurate mass calibration. Melting points were measured with a Stuart Scientific Melting Point Apparatus in an open capillary. Elemental analyses were performed by Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. Optical rotation was measured with a PolAAr 2001 automatic polarimeter at the sodium D line (587 nm) at 25 °C. HPLC analysis was performed with a Perkin–Elmer LC200 and a Daicel AD-H column.

Synthesis of (*Z*)-3-Hydroxy-3-phenyl-1-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose)prop-2-en-1-one (Hhpp): The ligand Hhpp was obtained by a modified literature procedure.[13] 1,2:3,4-Di-*O*-isopropylidene-α-D-galacturonyl chloride (2.00 g, 7.30 mmol) was dissolved in dry THF (5 mL) and rapidly stirred under nitrogen. In a separate flask cooled to –78 °C a solution of dry acetophenone (1.64 mL, 14.00 mmol) in dry THF (10 mL) was lithiated with freshly prepared LiHMDS (14.2 mmol) under nitrogen. The solution of enolate was transferred in one portion to the acid chloride solution at –78 °C with rapid stirring. The reaction was then warmed to room temperature, after which time the solution was quenched with water (ca. 30 mL) and neutralized with hydrochloric acid (10%) and extracted with ethyl acetate (3 × 100 mL). The organic washes were combined, dried ($MgSO_4$) and concentrated to dryness under reduced pressure yielding a brown oil. Purification was done by gradient column chromatography (*n*-hexane → EtOAc/*n*-hexane, 1:2) to yield the title compound as a pale yellow crystalline solid; yield 2.08 g (76%); m.p. 88.8–90.2 °C. $[\alpha]_D$ = –170.2. $C_{20}H_{24}O_7$ (376.41): calcd. C 63.8, H 6.4; found C 64.1, H 6.5. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.34 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 4.31–4.49 (m, 2 H, H^2 H^3), 4.61–4.80 (m, 2 H, H^4 H^5), 5.67 (d, J = 5.0 Hz, 1 H, H^1), 6.63 (s, J = 7.5 Hz, 1 H, H^7), 7.44 (t, J = 7.5 Hz, 2 H, H^{10}), 7.51 (t, J = 7.5 Hz, 1 H, H^{12}), 7.91 (d, J = 7.5 Hz, 2 H, H^{11}), 15.99 (s, 1 H, O*H*) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.59, 25.01, 26.02, 26.08, 70.23, 70.86, 70.89, 72.15, 94.55, 96.71, 109.20, 109.92, 127.40, 128.72, 132.54, 134.58, 182.06, 194.81 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 2987 (m), 2938 (m), 1599 (s), 1569 (s), 1493 (m), 1459 (s), 1379 (s), 1324 (w), 1259 (s), 1208 (s), 1166 (s), 1143 (w), 1114 (m), 1064 (s), 1001 (s), 930 (s), 900 (w), 869 (m), 849 (m), 836 (m), 817 (m), 770 (s), 693 (s), 658 (w) cm^{-1}. MS (ESI) calcd. for $[M + Na]^+$: 399.1, found: 399.3; for $[M + H]^+$: 377.2, found 377.2.

Synthesis of Dimers 1 and 2: To a round-bottomed flask equipped with a stirrer bead were added Hhpp and the appropriate lanthanoid trichloride in a 1:1 molar ratio. The starting materials were dissolved in methanol, followed by a slow, dropwise addition of 4 equiv. of triethylamine. The reactions were stirred for 16 h. After this time the solvent was removed and the residue stirred in toluene (ca. 5 mL) for 1 h. The solution was then filtered to remove triethylammonium chloride, and the toluene removed under high vacuum yielding the dimeric complex.

$[La_2(hpp)_6(DMF)]$ (1): Colourless crystals were obtained after the slow infusion of hexane into a toluene solution of **1** infused with

1% dimethylformamide; yield 63%; m.p. 145–151 °C (dec.). $C_{123}H_{145}La_2NO_{43}$ (2603.29): calcd. C 56.7, H 5.6, N 0.5; found C 56.6, H 5.3, N 0.4. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.26–1.54 (m, 72 H, 24× CH_3), 2.88 [s, 3 H, CH_3(DMF)], 2.95 [s, 3 H, CH_3(DMF)], 4.25–4.75 (m, 24 H, H^5 H^6 H^7 H^8), 5.65 (s, 6 H, H^9), 6.46–6.66 (m, 6 H, H^3), 6.65 (s, 1 H, DMF), 7.20–7.70 (m, 18 H, Ph*H*), 7.76–8.19 (m, 12 H, Ph*H*) ppm. IR (ATR): $\tilde{\nu}_{max}$ = 2983 (m), 2929 (m), 1654 (w), 1598 (s), 1570 (m), 1517 (s), 1485 (m), 1453 (s), 1425 (s), 1377 (s), 1252 (m), 1208 (s), 1165 (m), 1064 (s), 1000 (s), 899 (m), 767 (m), 695 (m), 667 (w) cm^{-1}. HRMS (MALDI) calcd. for $[La_2(gph)_5]^+$: 2154.54 (100), 2153.53 (90), 2155.54 (61), 2156.54 (25), 2157.55 (9); found 2154.60 (100), 2153.63 (90), 2155.57 (60), 2156.55 (23), 2157.53 (7).

[Eu_2(hpp)$_6$] (2): Removal of toluene yielded **2** as a yellow powder; yield 57%; m.p. 102–116 °C (dec.). $C_{120}H_{138}Eu_2O_{42}$ (2556.31): calcd. C 56.4, H 5.4; found C 56.0, H 5.3. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = –1.43 (s, 6 H, H^9), 0.43 (s, 18 H, 6× CH_3), 0.83 (s, 18 H, 6× CH_3), 1.24–1.53 (m, 36 H, 12× CH_3), 3.96–4.78 (m, 24 H, H^5 H^6 H^7 H^8), 5.77 (m, 6 H, H^3), 6.20–6.26 (m, 12 H, Ph*H*), 6.26–6.48 (m, 6 H, Ph*H*), 7.39–7.45 (m, 12 H, Ph*H*) ppm. IR (ATR): $\tilde{\nu}_{max}$ = 2984 (m), 2936 (m), 1595 (s), 1565 (s), 1517 (s), 1486 (m), 1452 (m), 1413 (s), 1378 (s), 1288 (w), 1251 (m), 1209 (m), 1165 (s), 1139 (m), 1107 (w), 1062 (s), 991 (s), 939 (m), 899 (m), 871 (m), 842 (m), 782 (m), 711 (m) cm^{-1}. HRMS (MALDI) calcd. for $[Eu_2(gph)_5]^+$: 2180.56 (100), 2182.56 (98), 2181.56 (94), 2183.57 (69), 2179.56 (40), 2184.57 (37), 2178.56 (37); found 2180.43 (100), 2182.42 (98), 2181.42 (94), 2183.42 (69), 2179.43 (40), 2184.43 (37), 2178.44 (37).

General Synthetic Procedure for Thio-Michael Additions: To a vial equipped with a stirrer bead was added the α,β-unsaturated carbonyl compound (0.5 mmol), thiol (1.0 mmol) and [Eu_2(hpp)$_6$] **2** (64 mg, 25 μmol, 5 mol-%). The mixture was stirred at room temperature until TLC analysis indicated complete conversion. The product was purified via flash column chromatography (EtOAc/*n*-hexane, 1:9).

4-(Benzylthio)-4-phenylbutan-2-one:[19] (Table 2, Entry 1), yield 96%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.00 (s, 3 H), 2.91–2.93 (m, 2 H), 3.45 (d, J = 13.2 Hz, 1 H), 3.52 (d, J = 13.2 Hz, 1 H), 4.20 (t, J = 7.2 Hz, 1 H), 7.19–7.32 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 30.62, 35.89, 44.10, 50.16, 127.16, 127.53, 128.09, 128.59, 128.72, 129.06, 137.97, 141.67, 205.42 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3027 (w), 2915 (w), 1714 (s), 1601 (w), 1493 (m), 1452 (m), 1416 (m), 1359 (m), 1154 (m), 1073 (m), 1025 (m), 762 (m), 699 (s) cm^{-1}.

3-(Benzylthio)-3-phenylpropanal: (Table 2, Entry 2), yield 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.82 (ddd, J = 7.6, 3.2, 2.0 Hz, 2 H), 3.40 (d, J = 13.6 Hz, 1 H), 3.50 (d, J = 13.6 Hz, 1 H), 4.11 (t, J = 7.6 Hz, 1 H), 7.13–7.28 (m, 10 H), 9.52 (t, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.74, 42.93, 49.75, 127.30, 127.82, 128.04, 128.67, 128.92, 129.09, 137.79, 141.04, 199.51 ppm. IR (NaCl): $\tilde{\nu}_{max}$ = 3061 (w), 3028 (m), 2918 (w), 2826 (w), 2727 (w), 1723 (s), 1677 (m), 1601 (w), 1493 (s), 1453 (s), 1071 (m), 1028 (m), 751 (m), 699 (s) cm^{-1}. HRMS (ESI) calcd. for [M + NH_4]$^+$: 274.1266; found 274.1260.

3-(Benzylthio)butanal:[20] (Table 2, Entry 3), yield 94%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (d, J = 7.2 Hz, 3 H), 2.51–2.65 (m, 2 H), 3.16 (sext, J = 7.2 Hz, 1 H), 3.78 (s, 2 H), 7.24–7.33 (m, 5 H), 9.67 (t, J = 2.0 Hz. 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.58, 33.84, 35.44, 50.33, 127.28, 128.73, 128.93, 138.15, 200.66 ppm. IR (NaCl): $\tilde{\nu}_{max}$ = 3028 (m), 2961 (m), 2923 (m), 2825 (m), 2726 (m), 1720 (s), 1601 (m), 1494 (s), 1453 (s), 1377 (m), 1240 (m), 1116 (m), 1070 (m), 1028 (m), 769 (m), 704 (s) cm^{-1}.

3-(Benzylthio)cyclohexanone:[19] (Table 2, Entry 4), yield 98%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.57–1.65 (m, 2 H), 2.00–2.05 (m, 2 H), 2.22–2.26 (m, 2 H), 2.30 (ddd, J = 14.0, 10.4, 0.8 Hz, 1 H), 2.57–2.62 (m, 1 H), 2.83–2.89 (m, 1 H), 3.69 (s, 2 H), 7.14–7.24 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.21, 31.41, 35.05, 41.03, 42.08, 47.91, 127.24, 128.70, 128.82, 138.01, 208.75 ppm. IR (NaCl): $\tilde{\nu}_{max}$ = 3028 (w), 2941 (m), 1712 (s), 1601 (w), 1494 (m), 1453 (m), 1421 (w), 1314 (m), 1221 (m), 1175 (w), 1069 (m), 703 (m) cm^{-1}.

4-(Butylthio)-4-phenylbutan-2-one:[6c] (Table 2, Entry 5), yield 81%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.83 (t, J = 7.6 Hz, 3 H), 1.27–1.34 (m, 2 H), 1.42–1.51 (m, 2 H), 2.08 (s, 3 H), 2.19–2.36 (m, 2 H), 2.96 (d, J = 7.2 Hz, 2 H), 4.31 (t, J = 7.2 Hz, 1 H), 7.20–7.28 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.72, 22.06, 30.86, 31.16, 31.36, 44.30, 50.33, 127.39, 127.85, 128.66, 142.19, 205.68 ppm. IR (NaCl): $\tilde{\nu}_{max}$ = 2957 (s), 2929 (s), 2872 (m), 1716 (s), 1600 (w), 1492 (m), 1453 (m), 1359 (m), 1152 (m), 1021 (w), 699 (s) cm^{-1}. HRMS (ESI) calcd. for [M + Na]$^+$: 259.1133; found 259.1123; HPLC Daicel AD-H, λ = 238 nm, hexane/*i*PrOH, 98:2, 0.5 mL/min, fraction t_r = 13.6 (major enantiomer) and 14.7 (minor enantiomer).

4-Phenyl-4-(phenylthio)butan-2-one:[19] (Table 2, Entry 6), yield 96%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.05 (s, 3 H), 3.02–3.05 (m, 2 H), 4.69 (t, J = 7.2 Hz, 1 H), 7.18–7.29 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 30.80, 48.19, 49.64, 127.55, 127.73, 127.82, 128.60, 128.95, 133.01, 134.17, 141.16, 205.60 ppm. IR (NaCl): $\tilde{\nu}_{max}$ = 3059 (m), 3029 (m), 1715 (s), 1600 (w), 1582 (m), 1480 (m), 1453 (m), 1438 (m), 1359 (m), 1152 (m), 1023 (m), 748 (s), 696 (s) cm^{-1}.

X-ray Crystallography: Crystal data was collected at 123(2) K at the Australian synchrotron MX1 beam-line. The data collection and integration were performed within Blu-Ice[21] and XDS[22] software programs. Structural solution and refinement was carried out with SHELXL-97[23] utilising the graphical interface X-Seed.[24] Data were corrected for absorption using the SADABS[25] or SORTAV[26] packages.

Refinement of F^2 was carried out against ALL reflections. The weighted R factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc., and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. There are considerable solvent accessible voids within the asymmetric unit (4919 Å^3). However, the low concentration of electron density compared to the cluster core combined with a large amount of thermal motions and disorder meant that the solvent could not be adequately modelled and therefore the residual electron density was removed using Platon[27] squeeze. The electron count within the void is 462. Two of the phenyl rings, attached to ligands one and three are disordered over two positions with occupancies of the major component of 70% and 50%, respectively. Because of this disorder the rings on ligand three could not sustain anisotropic refinement.

CCDC-822445 contains the supplementary crystallographic data for this publication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Additional X-ray crystallographic data for complex **1**, MALDI mass spectra and ^{1}H NMR spectra of complexes **1** and

2, as well as the HPLC trace for the stereoselective thio-Michael reaction.

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