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Evidence for Substrate Binding by the Lanthanide Centers in $[Li_3(thf)_n(binolate)_3Ln]$: Solution and Solid-State Characterization of Seven- and Eight-Coordinate $[Li_3(sol)_n(binolate)_3Ln(S)_m]$ Adducts**

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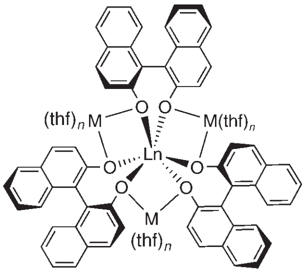
Dedicated to Professor Larry Sneddon on the occasion of his 60th birthday.

The heterobimetallic $[M_3(thf)_n(binolate)_3Ln]$ (binol = 1,1′-bi-2-naphthol; M = Li, Na, K; thf = tetrahydrofuran) catalysts (Figure 1) developed by Shibasaki and co-workers have proven to be among the most versatile and successful asymmetric Lewis acid catalysts introduced to date.[1–3] Central to mechanistic proposals involving $[M_3(thf)_n(binolate)_3Ln]$ heterobimetallic compounds is Lewis acid activation of the substrate by the lanthanide.[2–4] Prior efforts to detect lanthanide–substrate interactions, however, have not been successful. Herein, we disclose solid-state and solution evidence that $[Li_3(thf)_n(binolate)_3Ln]$ catalysts can bind organic substrates and substrate analogues to form seven- and eight-coordinate Ln centers.



Ln = lanthanide(III)
M = Li, Na, or K
n = 1 or 2

Figure 1. $[M_3(thf)_n(binolate)_3Ln]$ catalysts developed by Shibasaki and co-workers.

Several $[M_3(thf)_n(binolate)_3Ln]$[5,6] and $[M_3(thf)_n(binolate)_3Ln(OH_2)]$[1,5,7,8] complexes have been characterized crystallographically.[9] The lanthanide centers in these structures are either six-coordinate (Figure 1) or seven-coordinate when bound to a water molecule. Each main-group-metal center is bound by one or two organic solvent molecules. The lanthanide centers in sterically hindered $[M_3(thf)_n(binolate)_3Ln]$ complexes have a much higher affinity for water than for organic ligands, evidence for which was found by crystallization of the hydrates above from THF and Et_2O. In this regard, the absence of structurally characterized $[M_3(thf)_n(binolate)_3Ln(S)]$ (S = substrate or solvent) complexes with Lewis basic organic ligands bound to the lanthanide atom raises questions concerning the ability of the lanthanide center to bind and activate substrates in asymmetric catalysis.

One approach used by prior investigators to address these concerns involved probing Ln–substrate binding interactions in solution by using paramagnetic Pr, Eu, and Yb analogues. Paramagnetic complexes provide greater chemical-shift dispersions than their diamagnetic counterparts, thereby allowing the study of normally unobservable metal–substrate interactions.[10] Previously reported ^{1}H NMR spectroscopic binding studies of $[Na_3(thf)_6(binolate)_3Pr]$ and $[Na_3(thf)_6(binolate)_3Eu]$ with cyclohexenone showed small chemical-shift differences for the α-vinyl proton of 0.1 and 0 ppm, respectively.[8] Similarly, addition of pivalaldehyde to $[Li_3(thf)_6(binolate)_3Pr]$ resulted in a shift of the signal for the formyl hydrogen atom of only 0.1 ppm.[11] These small lanthanide-induced shifts (LISs) could be attributed to coordination of the carbonyl groups to the main-group atoms. Alternatively, the small LIS may indicate weak, reversible substrate binding to the lanthanide center. A related NMR spectroscopic study with paramagnetic $[Na_3(thf)_6(binolate)_3Yb]$ showed that the small Yb center does not even bind water.[6]

To reconcile some of the differences in proposed mechanisms and experimental observations for this important class of catalysts, we set out 1) to assess whether the lanthanide in $[Li_3(sol)_n(binolate)_3Ln]$ complexes could bind organic substrates and substrate analogues in solution and in the solid state, and 2) to examine the coordination numbers and geometries of the resultant adducts.

Binding studies of $[Li_3(thf)_6(binolate)_3Eu]$ in solution are complicated by the presence of two different Lewis acidic metal centers, both of which can bind the substrate, thus causing a LIS. To simplify the analysis of our binding studies, we sought to inhibit substrate binding to the lithium centers by addition of a tightly binding diamine. Thus, addition of *N*,*N*′-dimethylethylenediamine (dmeda) to $[Li_3(thf)_6(binolate)_3Ln]$ (**1**: Ln = Eu, **2**: Ln = La)[1] in THF resulted in the formation of $[Li_3(dmeda)_3(binolate)_3Ln]$ (**3**: Ln = Eu, **4**: Ln = La) as crystalline solids. The ^{1}H NMR spectra of **3** and **4** suggest that they are single diastereomers. Importantly, the diamine backbone of **3** experiences a LIS to lower frequencies with the resonances being observed as two broad singlets at $\delta = -3.59$ and -3.82 ppm. The diamine backbone is diastereotopic due to the chiral environment of the binolate ligands and indicates that the diamine is not dissociating from the lithium on the NMR timescale.

A comparison of the LISs of **1** and **3** could reveal whether the cyclohexenone carbonyl group binds to the lithium or the

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lanthanide centers. If cyclohexenone binds to the lithium centers, the LISs of **1** and **3** will be significantly different because the lithium centers in **3** are coordinatively saturated and cannot bind the substrate. If binding takes place at the lanthanide center, however, cyclohexenone will exhibit similar LISs with both **1** and **3**. The addition of 6 equivalents of cyclohexenone to **1** in [D$_8$]THF resulted in significant LIS of the vinyl α- and β-hydrogen atoms to higher frequencies, giving chemical-shift differences consistent with reversible substrate binding of 0.56 and 0.16 ppm, respectively (Table 1). At the same concentration ratio for the dmeda adduct **3**, the resonances of the cyclohexenone vinyl α- and β-hydrogen atoms shifted to similarly high frequencies, giving LISs of 0.66 and 0.18 ppm, with the diamine backbone remaining diastereotopic.

Table 1: Measured induced shifts of cyclohexenone and DMF with various shift reagents at given concentration ratios.[a]

Shift reagent and substrate	[SR]/[Sub] [M/M]			LIS		
		$\Delta\delta$ H$_\alpha$ [ppm]	$\Delta\delta$ H$_\beta$ [ppm]	$\Delta\delta$ H (formyl) [ppm]	$\Delta\delta$ CH$_3$ [ppm]	$\Delta\delta$ CH$_3$ [ppm]
1 + cyclohexenone	0.032/0.193	0.56	0.16	–	–	–
3 + cyclohexenone	0.037/0.186	0.66	0.18	–	–	–
5 + cyclohexenone	0.032/0.193	0.46	0.28	–	–	–
[Eu(hfc)$_3$] + cyclohexenone	0.032/0.193	0.05	0.00	–	–	–
[Eu(hfc)$_3$] + cyclohexenone	0.193/0.193	0.30	0.06	–	–	–
4 + cyclohexenone	0.032/0.194	0.03	0.02	–	–	–
1 + DMF	0.032/0.258	–	–	1.14	1.26	0.61
3 + DMF	0.032/0.258	–	–	2.30	1.06	0.77
4 + DMF	0.032/0.258	–	–	0.09	0.04	0.02

[a] Internal reference: mesitylene at $\delta = 6.73$ ppm (H) and $\delta = 2.22$ ppm (CH$_3$). Solvent: [D$_8$]THF at $\delta = 3.58$ and 1.73 ppm.

Further support for substrate binding was obtained with [Li$_3$(thf)$_6$(binolate)$_3$Pr] (**5**), which induced LISs to lower frequencies for the vinyl α- and β-hydrogen atoms of cyclohexenone of 0.46 and 0.28 ppm, respectively. The contrasting effect of Pr and Eu complexes on the chemical shifts of bound substrates to lower and higher frequencies, respectively, is well-known.[10,12] The LISs observed with cyclohexenone and **1**, **3**, and **5** can only arise from binding of the carbonyl oxygen atom to the lanthanide centers. To put these LISs in perspective, the LISs of cyclohexenone was examined in the presence of the well-known chiral shift reagent [Eu(hfc)$_3$] (hfc = 3-(heptafluoropropylhydroxymethylene)-*d*-camphorato). At the above concentration ratio in [D$_8$]THF, [Eu(hfc)$_3$] caused only a small LIS for the vinyl α-hydrogen atom (0.05 ppm, Table 1). A 1:1 molar ratio of [Eu(hfc)$_3$] to cyclohexenone, however, resulted in a LIS of 0.30 ppm. These shifts are smaller than would be observed in non-coordinating solvents owing to competition between [D$_8$]THF and cyclohexenone for binding at the europium center. We attribute the larger LIS of the Eu–binolate-based complexes over [Eu(hfc)$_3$] to the greater steric hindrance about the lanthanide center in the binolate derivatives, which results in a greater selectivity for the less-crowded carbonyl oxygen atom over the THF oxygen atom. For comparison, diamagnetic **4** induced shifts of < 0.03 ppm in the resonances of the vinyl group of cyclohexenone.

To obtain a larger LIS, we examined a substrate analogue that would have an affinity for the lanthanide center greater than that of cyclohexenone. Addition of 8 equivalents of *N,N*-dimethylformamide (DMF) to **1** and **3** resulted in a LIS of 1.14 and 2.30 ppm, respectively, for the signals of the formyl hydrogen atom. In contrast, addition of DMF to diamagnetic **4** resulted in a shift of 0.09 ppm. The binding studies with cyclohexenone and DMF attest to the advantages of using paramagnetic lanthanides to probe interactions that would be otherwise difficult to evaluate.

Additional support for lanthanide–substrate binding in solution was obtained by demonstrating that **4**, which contains coordinatively saturated lithium atoms, is an active catalyst. Complex **2** often gives the highest enantioselectivities and product yields.[3] Therefore, the reaction of 1.2 equivalents of dimethyl phosphite with benzaldehyde[13] in the presence of **4** (10 mol %) at -78 °C in THF produced the α-hydroxy phosphonate in 92 % yield with 78 % *ee*. In the asymmetric Henry reaction,[14] nitromethane (10 equiv) was added to benzaldehyde in the presence of **4** (10 mol %) at -50 °C in THF to generate the nitroaldol product in 76 % yield with 25 % *ee*. Finally, addition of 1,3-cyclopentadiene (10 equiv) to 3-(1-oxo-2-propenyl)-2-oxazolidinone in CH$_2$Cl$_2$ at 0 °C in the presence of **4** (10 mol %) produced the Diels–Alder product in 54 % yield with 32 % *ee*.[15]

Inspired by the observation of substrate binding to the lanthanide center in THF, we explored the solid-state structure of the substrate adducts. Pentane was diffused into THF solutions of **1** and **2** at room temperature. Pale crystals were obtained, and their structures determined. An ORTEP diagram of seven-coordinate [Li$_3$(thf)$_4$(binolate)$_3$La(thf)] (**7**) is shown in Figure 2.[16] Isostructural [Li$_3$(thf)$_4$(binolate)$_3$Eu(thf)][17] (**6**) is illustrated in the Supporting Information. These structures are consistent with competitive binding of [D$_8$]THF in the solution studies outlined above.

The gross structural features of **6** and **7** consist of a LnO$_7$ core that can be described as a trigonally compressed capped octahedron with THF as the capping group. In addition to the chirality of the binolate ligands, the lanthanide ions are stereogenic centers. As observed with the hydrates, use of (*R*)-binol led to the Δ configuration at the lanthanide. Slight differences in the bond lengths of **6** and **7** were observed owing to the smaller ionic radius of Eu (1.09 Å) relative to La (1.17 Å). The binolate La–O bond lengths in **7** ranged from 2.403(5) to 2.485(3) Å, and the dative La–O$_{\mathrm{THF}}$ bond length was 2.567(5) Å. The Eu–O bond lengths for the binolate ligands ranged from 2.302(3) to 2.400(4) Å, with a Eu–O$_{\mathrm{THF}}$ bond length of 2.482(4) Å. Binding of THF to the lanthanide pulled the La 0.767(4) Å out of the Li$_3$ plane, whereas the smaller Eu was displaced by 0.737(3) Å. Smaller displace-

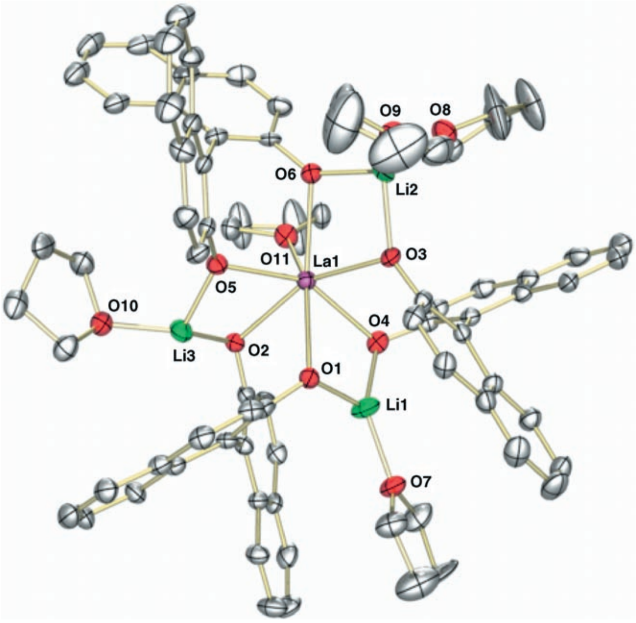

Figure 2. Structure of [$Li_3(thf)_4(binolate)_3La(thf)$] (**7**).

ments were observed for the seven-coordinate aqua adducts [$Na_3(thf)_6(binolate)_3Eu(OH_2)$] (0.387 Å) and [$Li_3(OEt_2)_3(binolate)_3Eu(OH_2)$] (0.326 Å).[5]

To probe the binding of softer ligands to the lanthanide center, we crystallized [$Li_3(py)_5(binolate)_3La(py)_2$] (**8**) (py = pyridine) by diffusion of pentane into a solution of **2** in pyridine at room temperature. An ORTEP diagram of **8** is shown in Figure 3.[18] The complex consists of an eight-coordinate lanthanum center with two pseudo-*trans* pyridine molecules (N−La−N = 150.87(8)°; La−N bond lengths: La1−N6 = 2.812(3) Å, La1−N7 = 2.773(3) Å). The observed *trans* coordination may explain why the chelating diamine dmeda does not bind to the lanthanide centers in **3** and **4**. The binolate La−O bond lengths in **8** ranged from 2.439(2)–2.536(2) Å and were, on average, longer than the La−O bond lengths in THF adduct **7** (2.403(5)–2.485(3) Å). The La atom in eight-coordinate **8** was displaced by only 0.042 Å from the Li_3 plane. Although the eight-coordinate pyridine adduct has not been used in asymmetric reactions to date, it is quite relevant, because it clearly demonstrates that sterically hindered [$Li_3(thf)_n(binolate)_3Ln$] catalysts can achieve a coordination number of eight. In solution, there is probably rapid equilibria between six-, seven-, and eight-coordinate complexes that result in signal averaging on the NMR timescale.[19]

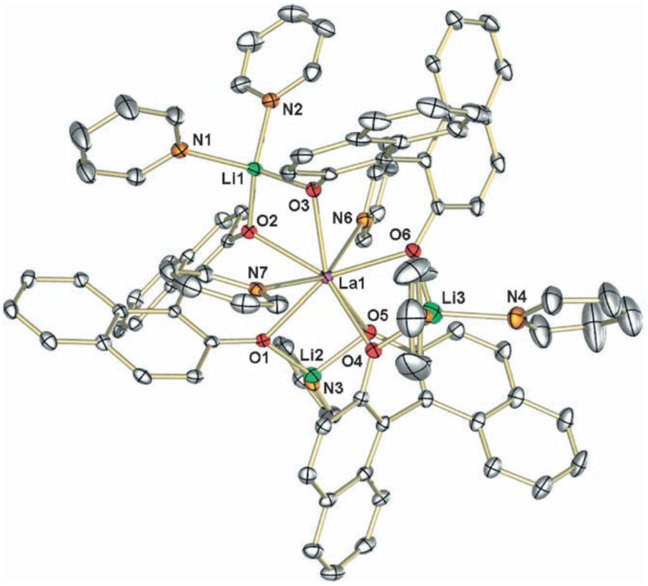

Figure 3. Structure of [$Li_3(py)_5(binolate)_3La(py)_2$] (**8**).

In summary, the solution and solid-state structures of the seven- and eight-coordinate complexes described herein provide the first definitive evidence that the lanthanide in [$Li_3(thf)_n(binolate)_3Ln$] complexes can bind substrates and substrate analogues. Furthermore, several reactions catalyzed by [$Li_3(thf)_n(binolate)_3Ln$] complexes require an additive, such as water, to allow high enantioselectivity. It has been proposed that in the aldol reaction, the seven-coordinate water adduct, [$Li_3(thf)_6(binolate)_3La(OH_2)$], binds the substrate to give eight-coordinate [$Li_3(thf)_6(binolate)_3La(OH_2)(substrate)$].[20,21] The characterization of eight-coordinate [$Li_3(py)_5(binolate)_3La(py)_2$] lends support to this proposal for larger lanthanides and indicates that the lanthanide centers can expand their coordination number beyond seven, the proposed maximum for this important class of compounds.[22]

Experimental Section

Determination of induced chemical shifts: The ^{1}H NMR spectra in this study were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz. Mesitylene was used as an internal-referencing standard for all experiments, and [D$_8$]THF was used as the solvent. Induced chemical shifts of cyclohexenone and DMF were obtained by incremental addition of known masses of the solid lanthanide complex to a substrate solution of known concentration. The first shift reagent (SR) used with cyclohexenone and DMF was [$Li_3(thf)_3(binolate)_3Eu$], at a concentration ratio ([SR]:[Substrate]) of 0.032 M:0.193 M and 0.032 M:0.258 M, respectively. [$Li_3(dmeda)_3(binolate)_3Eu$] was then used with cyclohexenone and DMF at a concentration ratio of 0.037 M:0.186 M and 0.032 M:0.258 M, respectively. Finally, [$Li_3(thf)_3(binolate)_3Pr$] was used with cyclohexenone at a concentration ratio of 0.032 M:0.193 M. Each sample was allowed to equilibrate for 15 min before acquisition of NMR data. All spectra can be found in the Supporting Information.

4: Under nitrogen, dmeda (0.143 mL, 0.118 g, 1.34 mmol) was added to a solution of **2** (0.500 g, 0.407 mmol) in THF (40 mL). This solution was stirred at room temperature for 4 h, after which all volatile materials were removed in vacuo. The remaining white solid was placed on a frit and washed with diethyl ether (3 × 5 mL) to afford the desired compound after drying under reduced pressure (0.470 g, 91% yield based on **2**). ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C, tetramethylsilane (TMS)): $\delta = 0.61$ (br s, 2H; NH), 1.60 (s, 6H; $N{-}CH_3$), 1.69 (br d, 2H; $N{-}CH_2$), 1.96 (br d, 2H; $N{-}CH_2$), 6.83 (d, 2H), 6.91 (m, 4H), 7.23 (d, 2H), 7.67 ppm (t, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_8$]THF): $\delta = 36.1$ ($N{-}CH_3$), 50.7 ($N{-}CH_2$), 119.4, 120.4, 125.0, 126.1, 127.2, 127.9, 128.2, 128.6, 136.6, 163.8 ppm; IR (KBr): $\tilde{\nu} =$ 3341, 3299, 3043, 2981,2952, 2890, 2855, 2802, 1612, 1588, 1553, 1499, 1463, 1422, 1342, 1283, 1247, 1177, 1140, 1096, 1069, 994, 959, 935, 882, 822, 746, 665, 632, 591, 574 cm^{-1}; elemental analysis: calcd (%) for $C_{72}H_{72}Li_3O_6N_6La$ (1277.11 $g\,mol^{-1}$): C 67.71, H 5.68, N 6.58; found: C 67.35, H 5.67, N 6.30.

3: Under nitrogen, dmeda (0.141 mL, 0.117 g, 1.33 mmol) was added to a solution of **1** (0.500 g, 0.403 mmol) in THF (40 mL). This solution was stirred at room temperature for 4 h, after which all volatile materials were removed in vacuo. The remaining solid was placed on a frit and washed with diethyl ether (3 × 5 mL) to afford the desired compound after drying under reduced pressure (0.440 g, 85 % yield based on **1**). ^1H NMR (300 MHz, $[D_8]$THF, 25 °C, TMS): $\delta = -9.16$ (br s, 2H; NH), -3.82 (br s, 2H; $N-CH_2$), -3.59 (br s, 2H; $N-CH_2$), 0.366 (s, 6H; $N-CH_3$), -1.69 (d, 2H), 3.04 (t, 2H), 5.56 (t, 2H), 7.65 (d, 2H), 13.76 (br s, 2H), 40.56 ppm (br s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_8]$THF): $\delta = 33.2$ ($N-CH_3$), 43.8 ($N-CH_2$), 85.99, 116.43, 116.86, 122.07, 122.58, 128.64, 130.49, 132.39, 134.54, 180.40 ppm; IR (KBr): $\tilde{\nu} = 3342$, 3299, 3043, 2985, 2952, 2875, 2856, 2803, 1612, 1589, 1554, 1501, 1463, 1423, 1342, 1283, 1248, 1175, 1138, 1096, 1069, 995, 959, 935, 898, 821, 746, 665, 642, 591, 574 cm^{-1}; elemental analysis: calcd (%) for $C_{72}H_{72}Li_3O_6N_6Eu\cdot THF$ (1362.27 $g\,mol^{-1}$): C 67.01, H 5.92, N 6.17; found: C 67.26, H 6.35, N 5.99.

8: Complex **2** (30 mg) was added to a vial and dissolved in pyridine (1.0 mL). This vial was then placed within a 20-mL screw-capped vial that was half-filled with dry pentane. After several days, pale crystals suitable for an X-ray diffraction study were formed. ^1H NMR (500 MHz, $[D_8]$THF, 25 °C, TMS): $\delta = 6.79$ (m, 4H), 6.89 (m, 2H), 6.98 (d, $J(H,H) = 8.7$ Hz, 2H), 7.22 (m, 7H), 7.58 (d, $J(H,H) = 8.8$ Hz, 2H), 7.60 (d, $J(H,H) = 8.0$ Hz, 2H), 7.65 (m, 3H), 8.52 ppm (m, 7H); $^{13}C\{^1H\}$ NMR (125 MHz, $[D_8]$THF): $\delta = 119.1$, 120.4, 124.4, 124.8, 126.8, 126.9, 128.1, 128.4, 128.5, 136.4, 136.7, 150.9, 163.5 ppm; elemental analysis: calcd (%) for $C_{95}H_{71}Li_3O_6N_7La$ (1566.35 $g\,mol^{-1}$): C 72.85, H 4.57, N 6.26; found: C 72.98, H 4.78, N 6.12.

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[16] Crystal data for **7**: $C_{80}H_{76}O_{11}LaLi_3$, $M_r = 1373.18$; monoclinic, space group $P21$, $a = 18.532(4)$, $b = 11.479(3)$, $c = 19.262(5)$ Å, $\beta = 101.379(2)^o$, $V = 4017(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.135\ g\,cm^{-3}$, μ $(Mo_{K\alpha}) = 5.84\ cm^{-1}$, $F_{000} = 1420$, 2θ range = 5.24–54.94°, crystal size = $0.25 \times 0.12 \times 0.05\ mm^3$, $T = 143$ K; 28983 reflections measured with 14622 used in refinement; $R_1 = 0.0585$, $wR_2 = 0.1237$ (11601 reflections with $F > 4\sigma(F)$); $R_1 = 0.0767$, $wR_2 = 0.1357$, GoF = 1.035 (14622 unique, nonzero reflections and 857 variables).

[17] Crystal data for **6**: $C_{80}H_{76}O_{11}EuLi_3$, $M_r = 1386.24$; monoclinic, space group $P21$, $a = 18.2048(6)$, $b = 11.4818(4)$, $c = 18.9389(7)$ Å, $\beta = 100.190(1)($, V=3896.2(2) Å^3, $Z = 2$, $\rho_{calcd} = 1.182\ g\,cm^{-3}$, μ $(Mo_{K\alpha}) = 8.59\ cm^{-1}$, $F_{000} = 1432$, 2θ range = 5.28–55.12°, crystal size = $0.38 \times 0.27 \times 0.08\ mm^3$, $T = 143$ K; 28807 reflections measured with 28807 used in refinement; $R_1 = 0.0518$, $wR_2 = 0.1584$ (28033 reflections with $F > 4\sigma(F)$); $R_1 = 0.0536$, $wR_2 = 0.1608$, GoF = 1.151 (28807 unique, nonzero reflections and 858 variables).

[18] Crystal data for **8**: $C_{100}H_{76}O_6N_8LaLi_3$, $M_r = 1645.45$; monoclinic, space group $P21$, $a = 13.3600(8)$, $b = 13.5347(8)$, $c = 23.066(2)$ Å, $\beta = 101.9270(10)^o$, $V = 4080.9(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.316\ g\,cm^{-3}$, μ $(Mo_{K\alpha}) = 5.84\ cm^{-1}$, $F_{000} = 1664$, 2θ range = 5.22–54.96°, crystal size = $0.42 \times 0.40 \times 0.22\ mm^3$, $T = 143$ K; 23262 reflections measured with 13727 used in refinement; $R_1 = 0.0308$, $wR_2 = 0.0742$ (13052 reflections with $F > 4\sigma(F)$); $R_1 = 0.0334$, $wR_2 = 0.0768$, GoF = 1.082 (13727 unique, nonzero reflections and 1064 variables). CCDC-284685, -284686, and -284687 (**7, 8, 6**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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