Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Unique and contrasting structures of homoleptic lanthanum(III) and cerium(III) 3,5-dimethylpyrazolates

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Experimental Details

General procedures: Complexes **1** and **2** are air and moisture sensitive. Thus, all manipulations were performed using glovebox (MBraun 200B; <0.1 ppm O_2, <0.1 ppm H_2O) or Schlenk techniques under an atmosphere of purified argon/nitrogen gas in oven-dried glassware. Me_2pzH was purchased from Sigma Aldrich and used as received. Lanthanum and cerium metals were purchased from Rhone Poulenc or Santoku as a metal ingot, and were manually filed under an inert atmosphere before use. Solvents (*n*-hexane, and toluene) were purified by either Grubbs columns (MBraun SPS, solvent purification system), or by distillation over sodium/benzophenone and stored in a glovebox. ^{1}H NMR spectra were recorded on a Bruker 400MHz spectrometer. Infrared spectra were recorded on a Nicolet 6700 FTIR spectrometer ($\tilde{\nu}$ = 4000-600 cm^{-1}) using a DRIFT chamber with dry KBr/sample mixtures and KBr windows, or as Nujol mulls with a Nicolet-Nexus FT-IR spectrometer(4000-400 cm^{-1}). Elemental analysis (C, H, N) were performed on the bulk sample with London Metropolitan University, England, or with an Elementar Vario Micro cube at the Tübingen University. The synthesis of amorphous [Ce(Me_2pz)$_3$] has been previously reported.[8]

[La(Me_2pz)$_3$] (1):

Method a) elevated temperature reaction: lanthanum metal (0.140 g, 1.01 mmol), Me_2pzH (0.150 g, 1.56 mmol) and 1,2,4,5-tetramethylbenzene (0.200 g, 1.50 mmol, used as flux) were sealed in a Carius glass tube under vacuum. The tube was heated at 220 °C for 78 h. The reaction mixture was extracted with hot toluene (10 mL) to give a colourless solution, which was reduced in volume (*in vacuo*). After a few hours, colourless single crystals of [La(Me_2pz)$_3$]$_n$ (**1**) formed and were suitable for X-ray structure analysis. Yield: 0.072g (48%); m.p.: 259-261 °C; IR (Nujol): ν = 3106 (vw), ~3000-2800 (peaks hidden under Nujol), 2721 (vw), 1516 (s), 1412 (s), 1316 (vw), 1301 (w), 1285 (vw), 1036(w), 1004 (m), 957 (w), 867 (vw), 800 (sh w), 793 (m), 777 (m), 728 (m), 682 (vw), 651 cm^{-1} (vw).Pure crystalline material was hard to obtain due to contamination of the crystals with excess metal fillings. No NMR spectroscopic data could be obtained due to insolubility of the crystals in non-coordinating solvents.

Method b) protonolysis reaction: La[N(SiMe$_3$)$_2$]$_3$ (0.140 g, 0.226 mmol) was dissolved in toluene (3 mL) and a toluene solution (3 mL) of Me_2pzH (0.0650 g, 0.670 mmol) added dropwise. Within minutes a white precipitate formed. After 30 min the solution was agitated by swirling, and then evaporated to dryness, giving a colourless powder. An extract of the powder was dissolved in THF-D$_8$, and analysed by ^{1}H NMR, indicating complete consumption of Me_2pzH. ^{1}H NMR (THF-d$_8$, 400 MHz, 300 K): δ = 0.05 (s, 0.32 H, trace La[N(SiMe$_3$)$_2$]$_3$), 2.20 (s, 18H, Me_2pz-CH$_3$), 5.85 ppm (s, 3 H, Me_2pz-C(4)H). The powder was washed with *n*-hexane and the supernatant solution discarded. Further drying gave an amorphous white powder (0.067 g, 70%). 3104 (vw), 2967 (br), 2919 (m), 2867 (m), 2796 (vw), 2714 (vw), 1515 (vs), 1412 (s), 1364 (m), 1316(vw), 1301 (vw), 1287 (w), 1245 (vw), 1037 (w), 1005 (m), 956 (w), 869 (vw), 837 (vw), 801 (sh w), 793 (m), 777 (m), 727 (m), 676 cm^{-1} (vw), matching well with that prepared by method a.
IR (DRIFT) ν = 3105 (w), 2918 (m), 1515 (vs), 1411 (s), 1364(w), 1286(vw), 1245 (vw), 1036(w), 1006(m), 957(w), 866(w), 792(m), 776(m), 730(m), 676 (vw), 658 (w), 588 cm^{-1}(w). Calcd. (%) for $C_{15}H_{21}LaN_6$ (424.28 g mol^{-1}): C 42.46, H 4.99, N 19.81; found: C 42.21, H 5.09, N 19.03. %. Although the nitrogen result is outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

[Ce$_4$(Me_2pz)$_{12}$] **(2)**:

Method a), elevated temperature reaction: cerium metal (0.070 g, 0.51 mmol), one drop of mercury, Me_2pzH (0.150 g, 1.56 mmol), and 1,2,4,5-tetramethylbenzene (0.200 g, 1.50 mmol), were sealed in a Carius glass tube under vacuum, and heated at 220 °C-270 °C in a furnace for a total of 336 h. The reaction mixture was extracted with hot toluene (10 mL) which gave a yellow amorphous powder. The suspension was heated for three days and concentrated under vacuum to 5mL. The suspension was slowly cooled to room temperature and stored at -35 °C for a week leading to no crystal formation. Afterwards, the colour slowly changed to dark red without any product suitable for X-ray crystallography. IR (Nujol): ν = 3200 (w), 3131 (vw), 3102 (w), 2725 (vw), 1596(vw), 1567(w), 1518 (m), 1305(m), 1154 (m), 1099(vw), 1023(m), 964(vw), 866(m), 783(m), 727(w), 661 cm^{-1}(w). The resulting yellow powder was insoluble in both C_6D_6, toluene and THF-d$_8$, and the IR spectrum did not correspond to any identifiable product.

Method b, protonolysis reaction: Me_2pzH (0.0720 g, 0.749 mmol) was dissolved in toluene (1-2 mL) and added dropwise to a toluene (1-2 ml) solution of [Ce{N(SiMe$_3$)$_2$}$_3$] (0.1571 g, 0.253 mmol). After one day the light yellow solution was concentrated (under *vacuo*) and stored at -35 °C producing large yellow block crystals of [Ce$_4$(Me_2pz)$_{12}$]·PhMe (**2**·PhMe, 0.0586 g, 69%), which was identified by X-ray crystallography. Drying the crystals caused them to fracture giving a light-yellow powder. When the reaction was repeated, the reagents were stirred for 30 min and the reaction mixture was dried (*in vacuo*). *n*-Hexane (1 mL) was added, and over time yellow block crystals formed of [Ce$_4$(Me_2pz)$_{12}$]·$^3/_4$*n*-hexane (**2**·0.75hex), identified by X-ray crystallography and IR spectroscopy. The reaction mixture was briefly dried, and a small amount was dissolved in THF-d$_8$ and analysed by ^{1}H NMR, giving a similar spectrum to [Ce(Me_2pz)$_3$] that was previously reported,[7] indicating all Me_2pzH was consumed. ^{1}H NMR (THF-d$_8$, 400 MHz, 300 K, trace impurities were not included): δ = 0.28 (s, 0.6 H, HN(SiMe$_3$)$_2$)), 6.41 (s, 18 H, Me_2pz-CH$_3$), 11.94 ppm (s, 3 H, Me_2pz-C(4)H). The sample was further dried under vacuum to remove volatile impurities. DRIFT (dried under vacuum): ν = 3103 (w), 2953 (m), 2927 (m), 1520 (vs), 1473 (w), 1432 (m), 1412 (m), 1368 (vw), 1310 (m), 1287(w), 1246 (vw), 1056 (vw), 1020 (m), 1009 (m), 967 (w), 824 (m), 784(m), 730 (m), 676 (vw), 658 (w), 588 cm^{-1} (vw). ^{1}H NMR (toluene-d$_8$, 500 MHz, 300 K): δ = -30.71 (s), -11.94 (s), -11.62 (s), -11.08 (s), -10.64 (s), -7.91 (s), -4.27 (s), -3.72 (s), -3.40 (s), -1.73 (s), 0.92 (*n*-hexane), 1.34 (*n*-hexane), 2.74 (br s), 4.63 (br s), 5.63 (s), 6.28 (s), 6.48 (s), 9.94 (s), 13.39 (br s), 16.03 ppm (br s).

Conversion of [Ce$_4$(Me$_2$pz)$_{12}$]·$^3/_4$*n*-hexane to unsolvated [Ce$_4$(Me$_2$pz)$_{12}$] and [Ce(Me$_2$pz)$_3$]$_n$: a sample of complex **2**·0.75hex (0.150 g, 0.085 mmol) was placed into a Schlenk flask and toluene (10 mL) was added. The colourless suspension was heated at 120 °C for several days giving a colourless powder and a light-yellow supernatant. The supernatant was separated and concentrated. After several days, when no crystallisation occurred, the solution was allowed to evaporate to dryness giving a yellow oil. *n*-Hexane (1 mL) was added, resulting in formation of slight yellow/colourless crystals of unsolvated [Ce$_4$(Me$_2$pz)$_{12}$] (**2**). Yield (0.110 g, 76%). IR (DRIFT): ν = 3101 (w), 2922 (s), 2854 (m), 1520 (vs), 1473 (m), 1432 (m), 1410 (m), 1368 (w), 1310 (m), 1286 (w), 1245 (vw), 1056 (vw), 1056 (vw), 1020 (m), 1010 (m), 960 (w), 829 (w), 816 (w), 783(m), 770 (m), 729 (w), 658 (vw), 588 cm^{-1} (vw). Calcd. (%) for $C_{60}H_{84}Ce_4N_{24}$ (1701.93 g mol^{-1}): C 42.34, H 4.97, N 19.75; found: C 42.27, H 4.89, N 19.01. The precipitated white powder which also formed after addition of *n*-hexane, was washed twice in *n*-hexane to remove molecular **2**, and was then dried under vacuum. A small amount of powder was added to a ^{1}H NMR tube and C_6D_6 was added, the suspension was measured by ^{1}H NMR indicating the presence of only *n*-hexane. Analysis by IR spectroscopy indicated a spectrum nearly identical to **1**. IR (DRIFT): ν = 2919 (m), 2852(w), 1516 (vs), 1474 (w), 1415 (s), 1373 (w), 1361 (w), 1312 (vw), 1289 (w), 1034 (vw), 1002 (m), 953 (s), 794 (s), 775 (w), 728 cm^{-1}(w). Elemental analysis indicated a degree of *n*-hexane to be present. Calcd. (%) for $C_{16.5}H_{24.5}CeN_6$ (447.03 g mol^{-1}, [Ce(Me$_2$pz)$_3$]·0.25 *n*-hexane): C 44.33, H 5.52, N 18.79; found C 44.49, H 5.59, N 18.70. Calcd. (%) for $C_{15}H_{21}CeN_6$ (425.49 g mol^{-1}): C 42.34, H 4.97, N 19.75. Repeatedly, co-crystallized *n*-hexane could not be fully removed by prolonged treatment under vacuum. This is also indicated by the NMR spectra. Although the elemental analysis results are outside the range expected for "*n*-hexane-free" **2**, they are satisfactory for a partial *n*-hexane solvate **2**·0.25 *n*-hexane.

X-Ray crystallography: All compounds were examined on either a ADSC Quantum 210r (**1**) or a 'Bruker APEX-II CCD' diffractometer (**2**) at 100 K, mounted on a fibre loop in *n*-paratone crystallography oil. The radiation source was Mo $\underline{K\alpha}$ radiation (λ = 0.71073 Å). Absorption corrections were completed using with either XDS[1] or the Apex II program suite.[2] Structural solutions were obtained by charge flipping (**2**)[3] or direct methods (**1**)[4] and refined using full matrix least squares methods against F^2 using SHELX2015,[5] within the OLEX 2 graphical interface.[6]

Table S1. X-ray crystallographic parameters for complexes **1** and **2**

Sample Code:	**1**	**2**·PhMe	**2**·0.75*n*-hexane	**2**
CCDC Number:	1813156	1441020	1813158	1813157
Formula	$C_{15}H_{21}LaN_6$	$C_{60}H_{84}Ce_4N_{24}\cdot C_7H_8$	$C_{60}H_{84}Ce_4N_{24}\cdot 0.75(C_6H_{14})$	$C_{60}H_{84}Ce_4N_{24}$
Molecular weight	424.29	1794.12	1766.62	1702.00
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	*P*-1	*P*-1	$P2_1/n$	*P21/c*
a (Å)	7.9960(16)	14.583(4)	16.5130(3)	21.3632(18)
b (Å)	10.246(2)	15.851(4)	20.6361(4)	13.4207(11)
c (Å)	10.755(2)	16.822(4)	22.3828(4)	25.122(2)
α (°)	71.42(3)	103.244(4)	90	90
β (°)	79.55(3)	91.321(7)	95.2323(9)	100.5122(15)
γ (°)	81.91(3)	90.869(5)	90	90
V (Å^3)	818.1 (3)	3783.0(17)	7595.5	7081.8(10)
Z	2	2	4	4
F(000)	420	1788	3526	3376.0
D_x (mg m^{-3})	1.722	1.575	1.545	1.596
μ = (mm^{-1})	2.62	2.42	2.40	2.576
Data/restraints/parameters	2858/0/205	13315/1344[d]/879	13384/6/873	19065/0/8
Goodness-of-fit[a] on F^2[a]	1.15	1.08	1.00	1.105
Final R indexes [I>=2σ (I)][b,c]	$R_1 = 0.027$ $wR_2 = 0.070$	$R_1 = 0.0658$ $wR_2 = 0.1016$	$R_1 = 0.037$ $wR_2 = 0.1$	$R_1 = 0.0495$ $wR_2 = 0.0841$

[a]GOF = $[\Sigma w(F_0^2 - F_c^2)^2 / (n_0 - n_p)]^{1/2}$. [b]R1 = $\Sigma(||F_0| - |F_c||) / \Sigma|F_0|$, $F_0 > 4\sigma(F_0)$. [c]wR$_2$ = $\{\Sigma[w(F_0^2 - F_c^2)^2 / \Sigma[w(F_0^2)^2]]^{1/2}$.[d] ISOR commands were used to remove APD atoms generated from the poor crystal quality, RIGU command used on all data.

Additional structural information for $[La(Me_2pz)_3]_n$ (1) and $[Ce_4(Me_2pz)_{12}]$ (2)

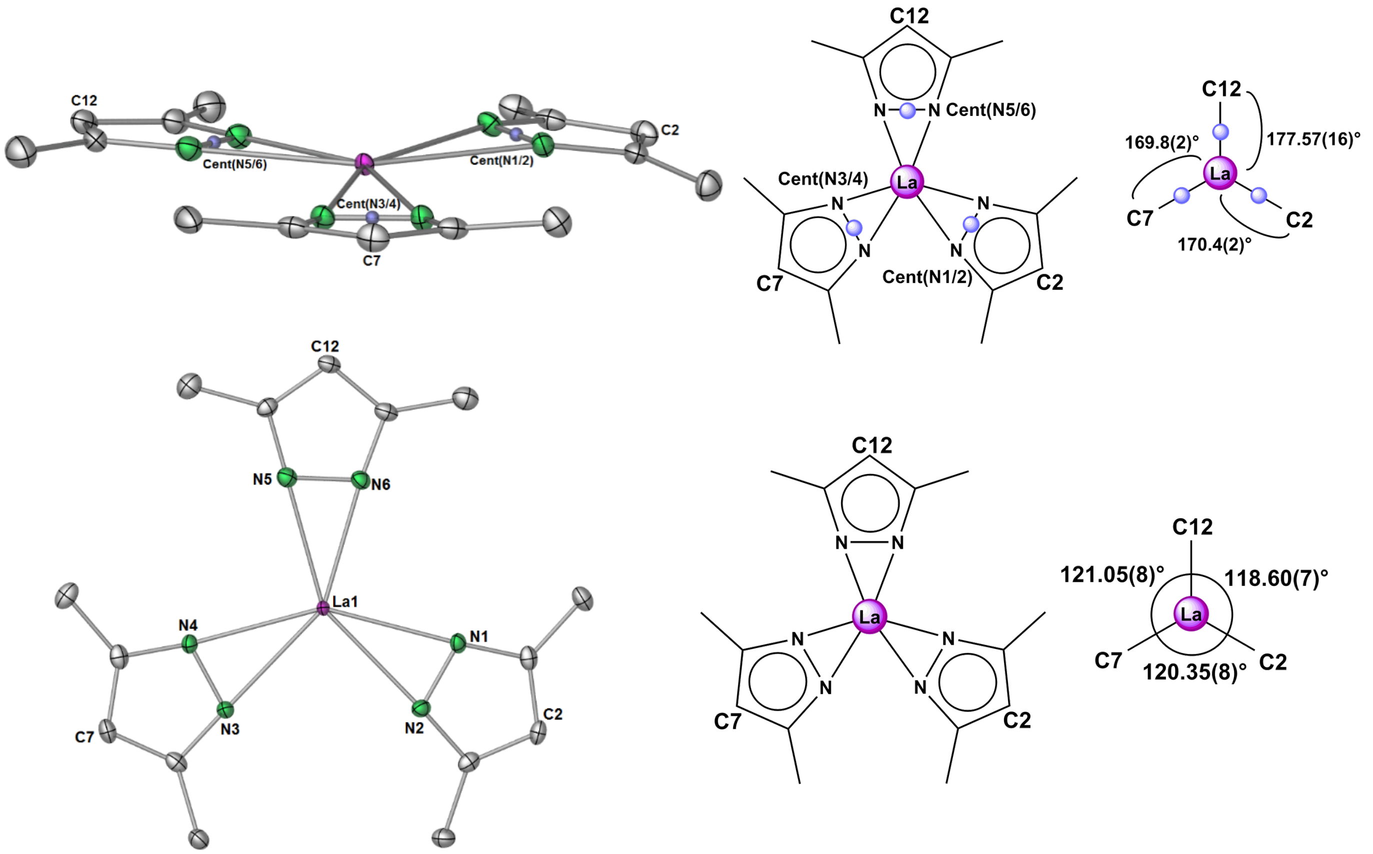


Figure S1. Asymmetric unit of **1** showing the Me_2pz ligands are not flat (top), but the N,N′ donor atoms are arranged in a near trigonal planar fashion around the La centre (bottom).

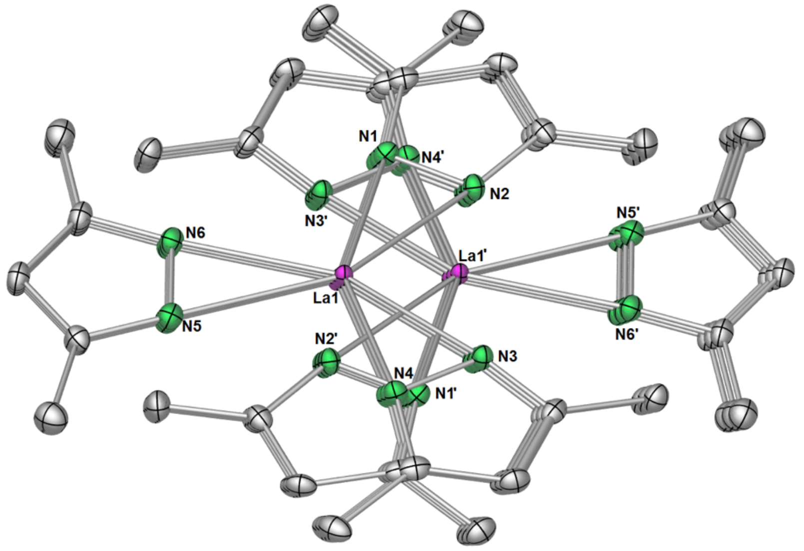
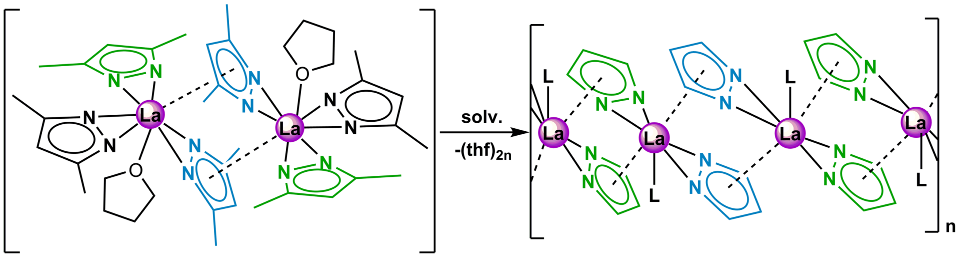


Figure S2. Structure of polymeric **1** as observed from the *a* axis.



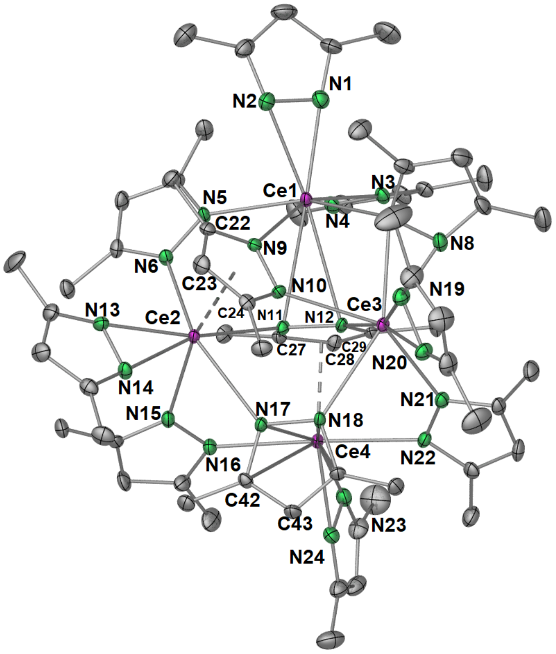
n[La(Me$_2$pz)$_3$(thf)]$_2$

[La(Me$_2$pz)$_3$]$_\infty$ (1)

solv. = non-coordinating solvents
L = Me$_2$pz (η^2-bound)

Scheme S1. Change in coordination mode of one terminal η^2(*N,N′)* Me$_2$pz ligand in [La(Me$_2$pz)$_3$(thf)]$_2$ to a *μ*-η^2(*N,N′*):η^5(*N$_2$C$_3$*) ligand, generating polymeric **1**. Me groups have been removed from the pictures on the *right*. (L = Me$_2$pz).

Atoms		Bond length (Å)	Atoms		Bond length (Å)
Ce1	N1	2.368(4)	Ce3	N8	2.534(4)
Ce1	N2	2.531(4)	Ce3	N10	2.585(4)
Ce1	N3	2.446(4)	Ce3	N12	2.710(4)
Ce1	N4	2.448(4)	Ce3	N18	2.670(4)
Ce1	N5	2.536(4)	Ce3	N19	2.408(4)
Ce1	N7	2.716(4)	Ce3	N20	2.463(4)
Ce1	N9	2.638(4)	Ce3	N21	2.540(4)
Ce1	N11	3.077(4)	Ce4	N11	2.774(4)
Ce1	N12	3.051(4)	Ce4	N12	2.772(4)
Ce2	N6	2.563(4)	Ce4	C27	2.972(5)
Ce2	N9	2.697(4)	Ce4	C28	3.038(9)
Ce2	N10	2.697(4)	Ce4	C29	2.968(9)
Ce2	N11	2.739(4)	Ce4	N16	2.610(4)
Ce2	N13	2.433(4)	Ce4	N17	2.671(4)
Ce2	N14	2.463(4)	Ce4	N18	2.687(4)
Ce2	N15	2.550(4)	Ce4	C42	3.112(5)
Ce2	N17	2.671(4)	Ce4	C43	3.355(5)
Ce2	C22	2.976(5)	Ce4	C44	3.130(5)
Ce2	C23	3.147(5)	Ce4	N22	2.574(4)
Ce2	C24	2.999(5)	Ce4	N23	2.408(4)
Ce3	N7	2.560(4)	Ce4	N24	2.393(4)



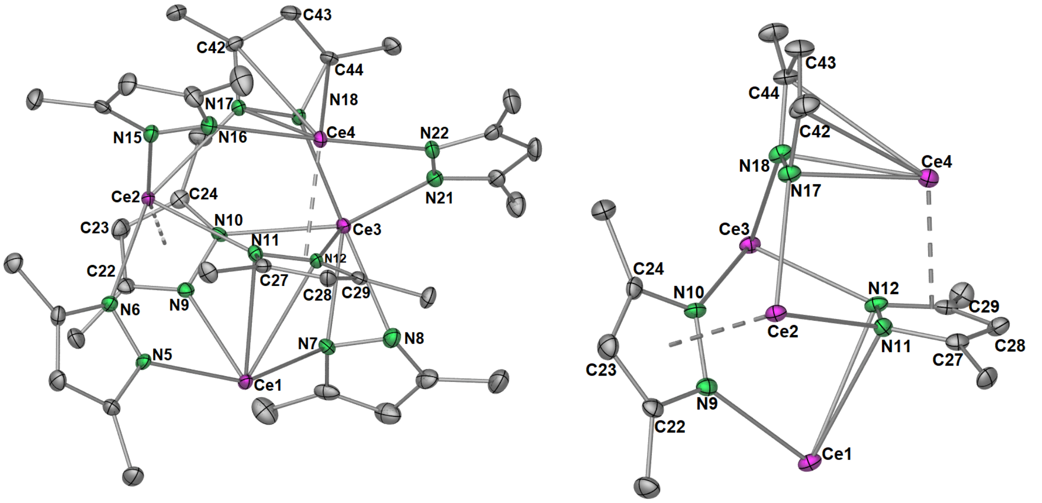
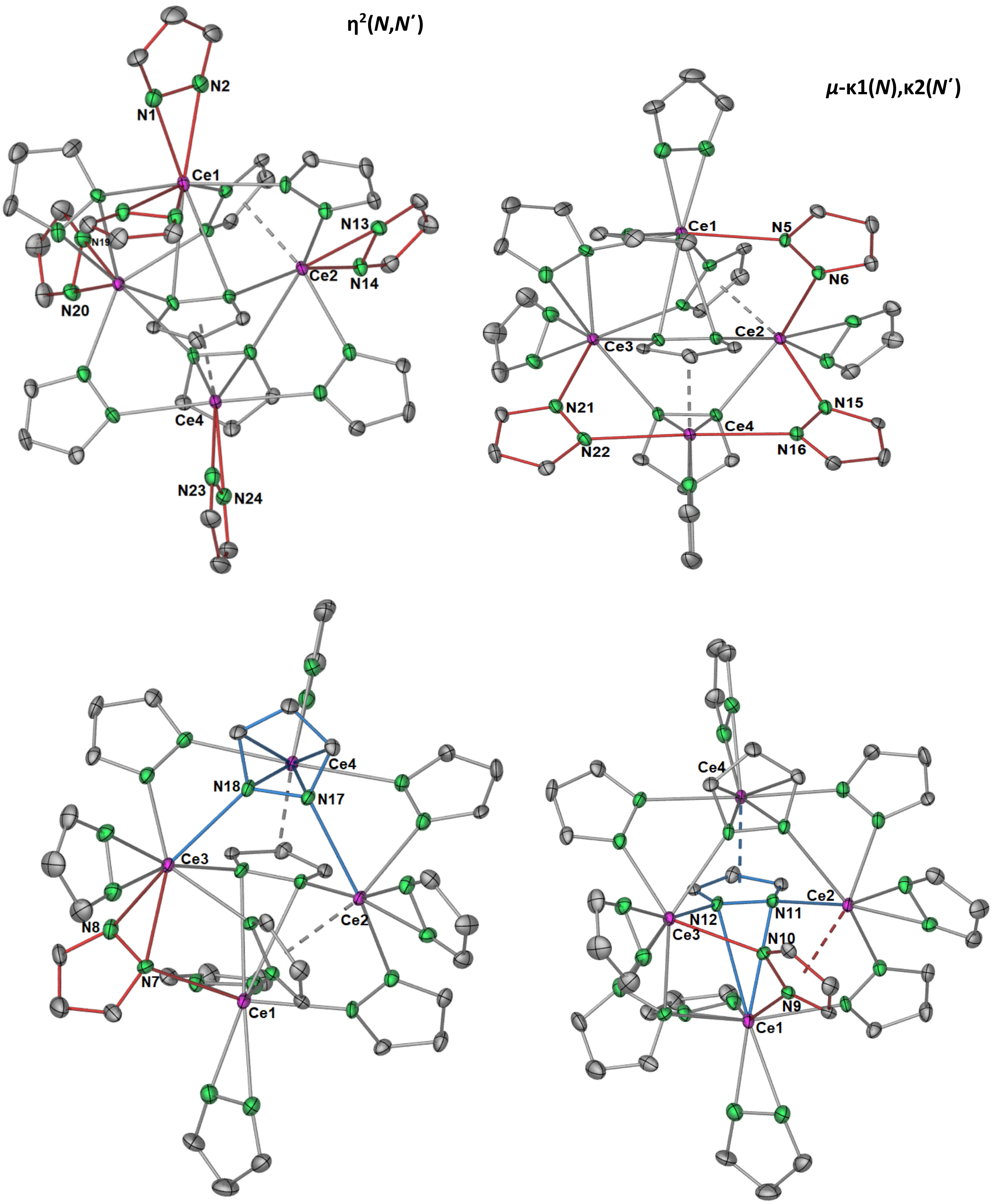


Figure S3.1. TOP: Molecular structure of [Ce$_4$(Me$_2$pz)$_{12}$]·$^3/_4$*n*-hexane (**2**·*n*-hexane) viewed from another angle and table of bond lengths. BOTTOM: *left*, only bridging ligands; *right*: only ligands bridging between three or more metals.



μ-η^2(*N*,*N′*):2κ(*N*) (red)μ_3-
η^4(*C*,*N*,*N′*,*C′*):2κ(*N*):3κ(*N′*) (blue)

μ_3-η^5(N_2C_3):2κ(*N*):3κ(*N′*) (red)
μ_4-η^5(N_2C_3):η^2(*N*,*N′*):3κ(*N*):4κ(*N′*) (blue)

Figure S3.2. Highlighted bonding of different ligand environments in **2**, Me groups of pz ligands are omitted for clarity.

Relevant NMR spectra for complexes [La(Me$_2$pz)$_3$]$_n$ (1) and [Ce$_4$(Me$_2$pz)$_{12}$] (2)

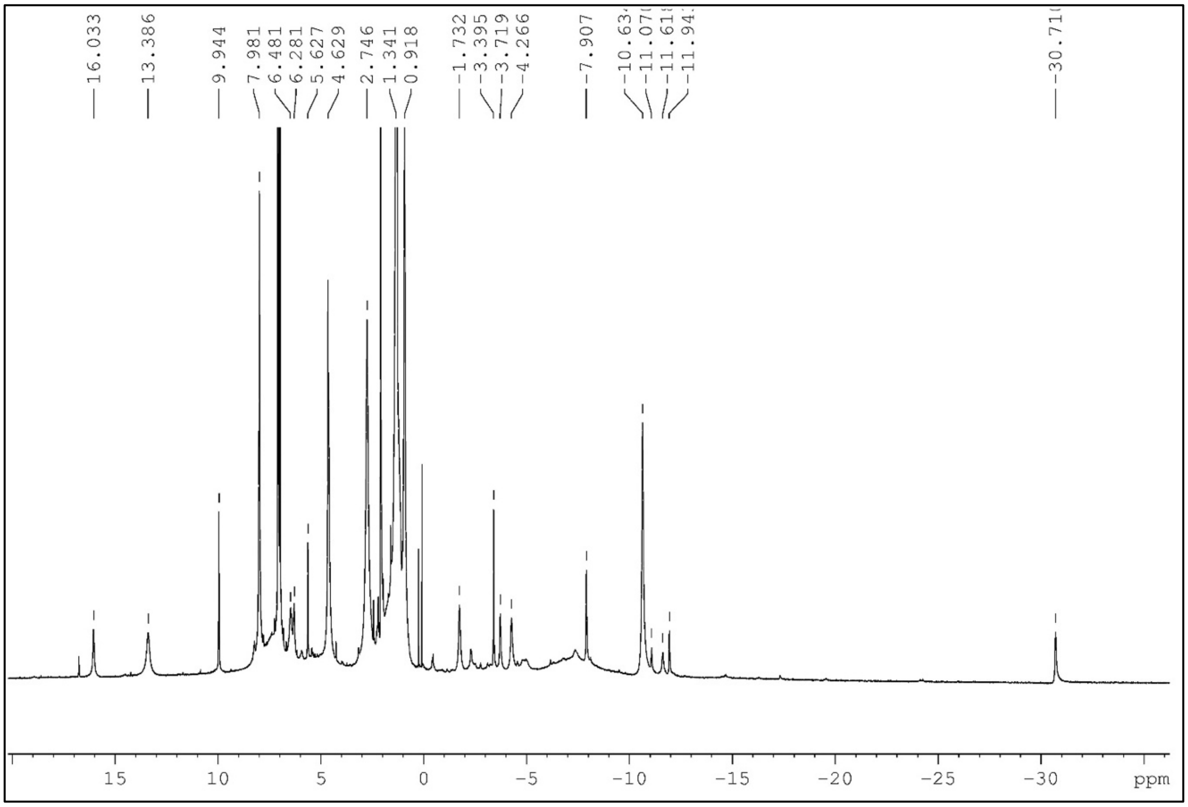


Figure S4. ^{1}H NMR spectrum (toluene-d$_8$, 400 MHz, 300 K) of molecular [Ce$_4$(Me$_2$pz)$_{12}$]·$^3/_4$*n*-hexane (**2**·*n*-hexane).

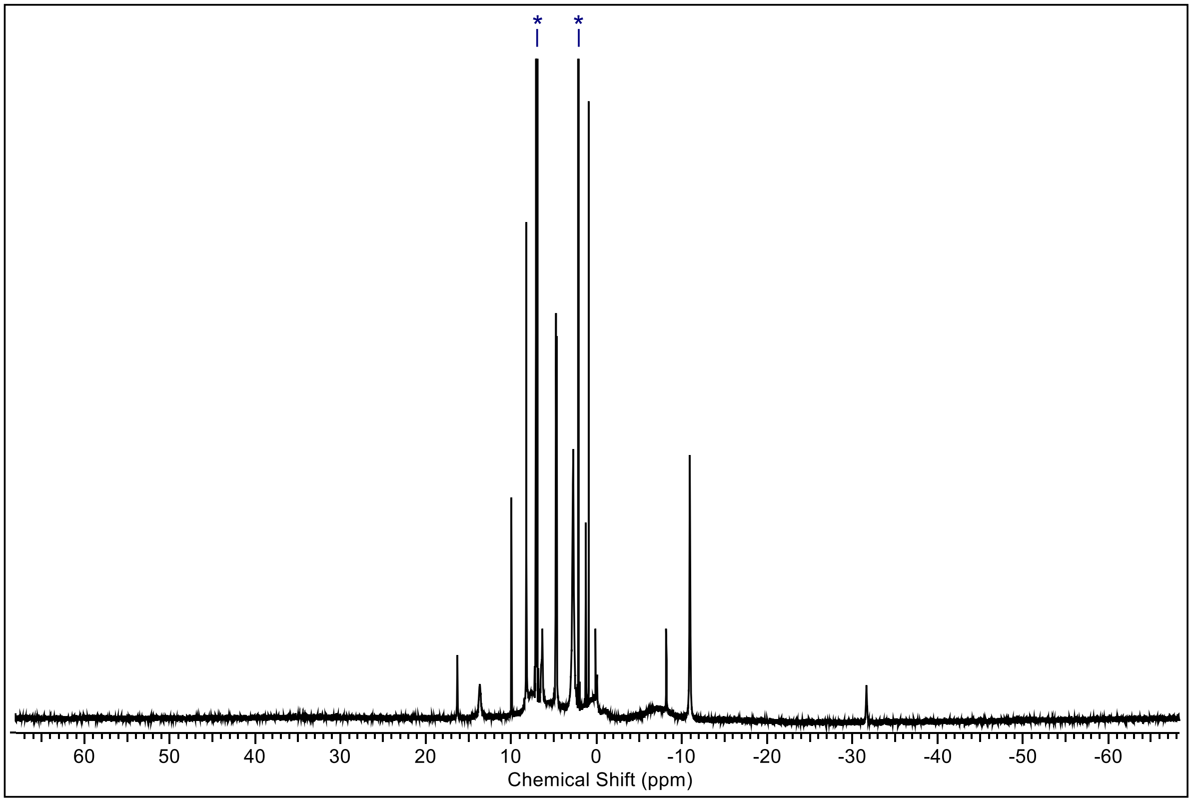


Figure S5. ^{1}H NMR spectrum (toluene-d$_8$, 500 MHz, 293 K) of [Ce$_4$(Me$_2$pz)$_{12}$]·$^3/_4$*n*-hexane (**2**·*n*-hexane), recrystallized.

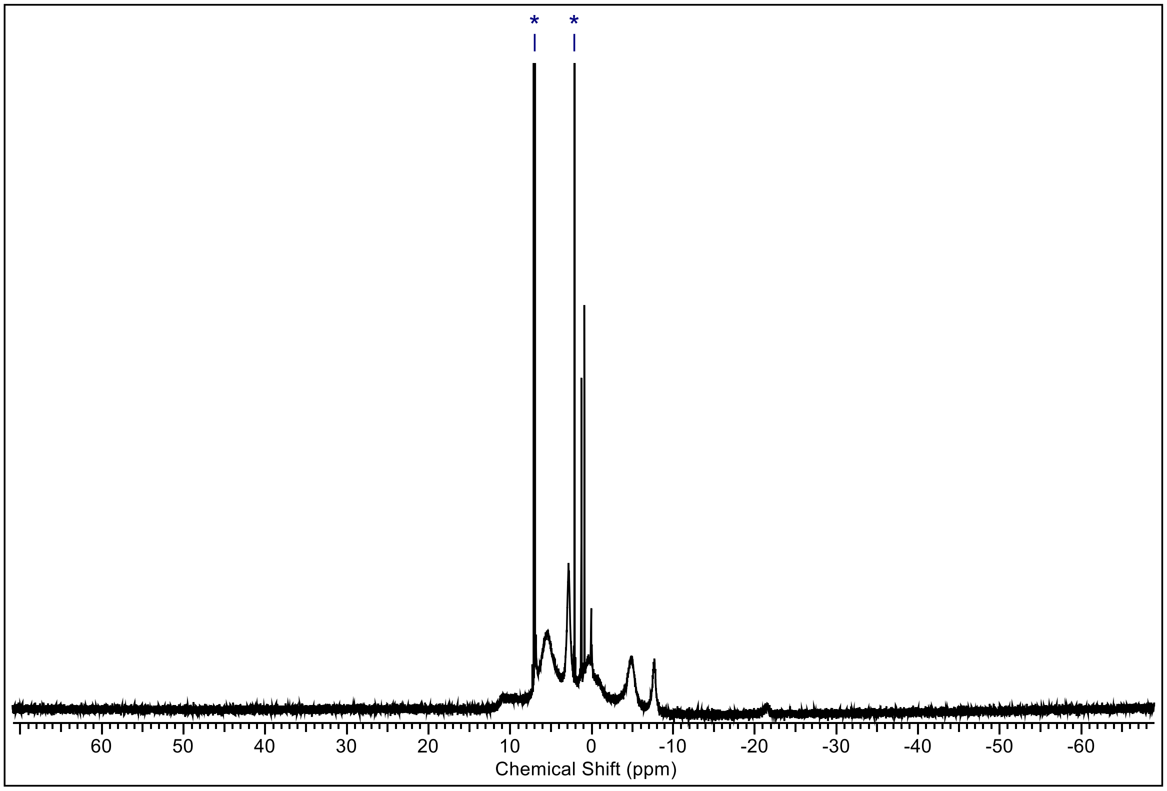


Figure S6. ^{1}H NMR spectrum (toluene-d$_8$, 500 MHz, 353 K) of [Ce$_4$(Me$_2$pz)$_{12}$]·$^3/_4$*n*-hexane (**2**· *n*-hexane), recrystallized.

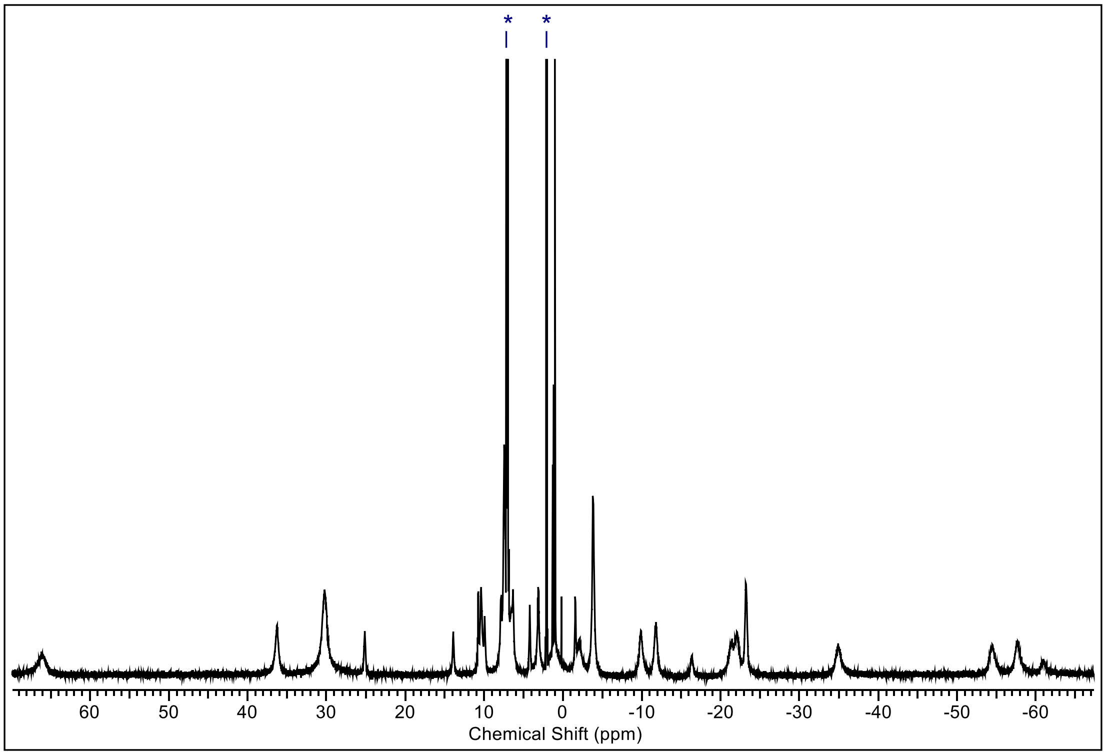


Figure S7. ^{1}H NMR spectrum (toluene-d$_8$, 500 MHz, 193 K) of [Ce$_4$(Me$_2$pz)$_{12}$]·$^3/_4$*n*-hexane (**2**·*n*-hexane), recrystallized.

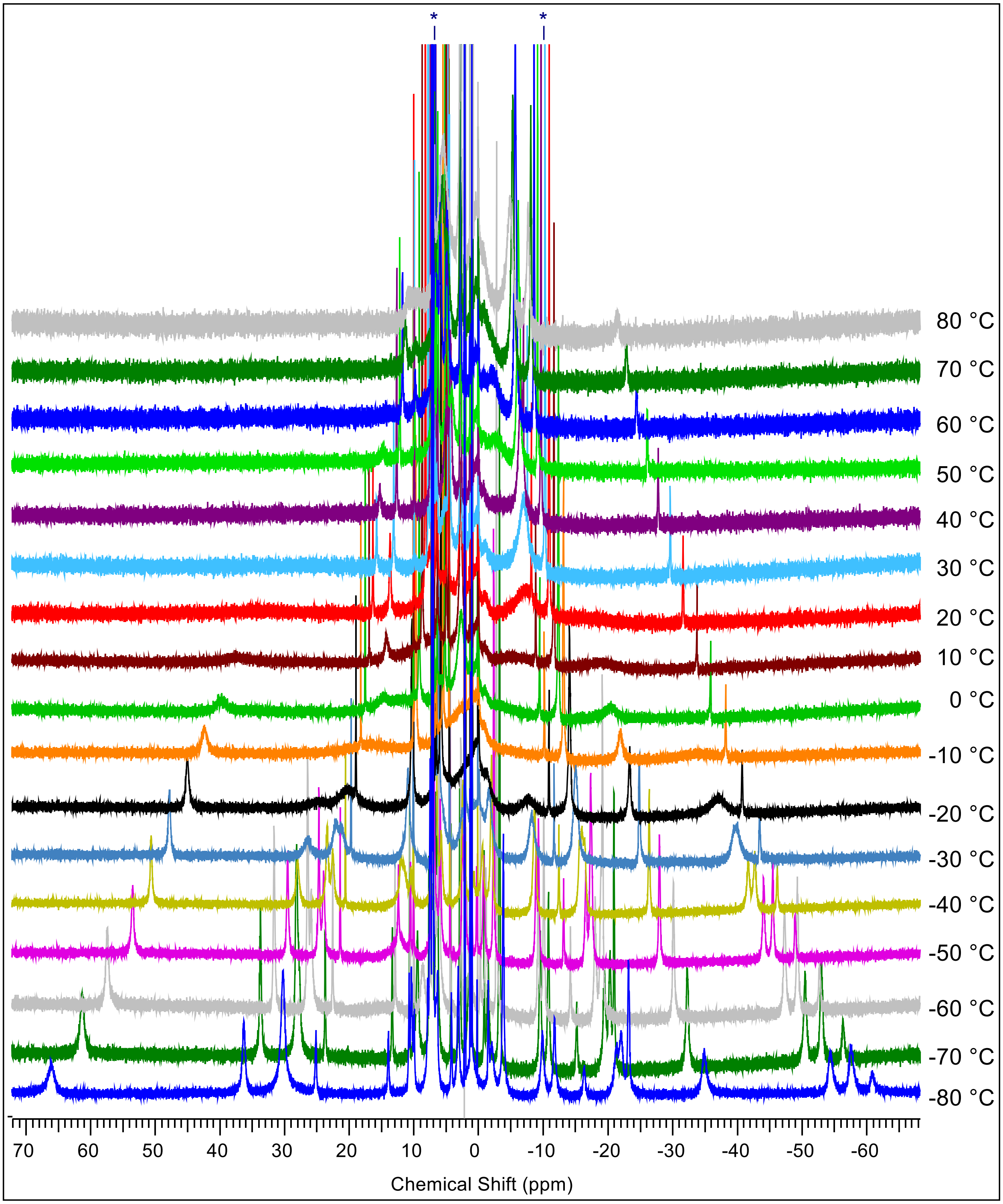


Figure S8. VT ^{1}H NMR spectra (toluene-d$_8$, 500 MHz) of [Ce$_4$(Me$_2$pz)$_{12}$]·$^3/_4$*n*-hexane (**2**·*n*-hexane), recrystallized.

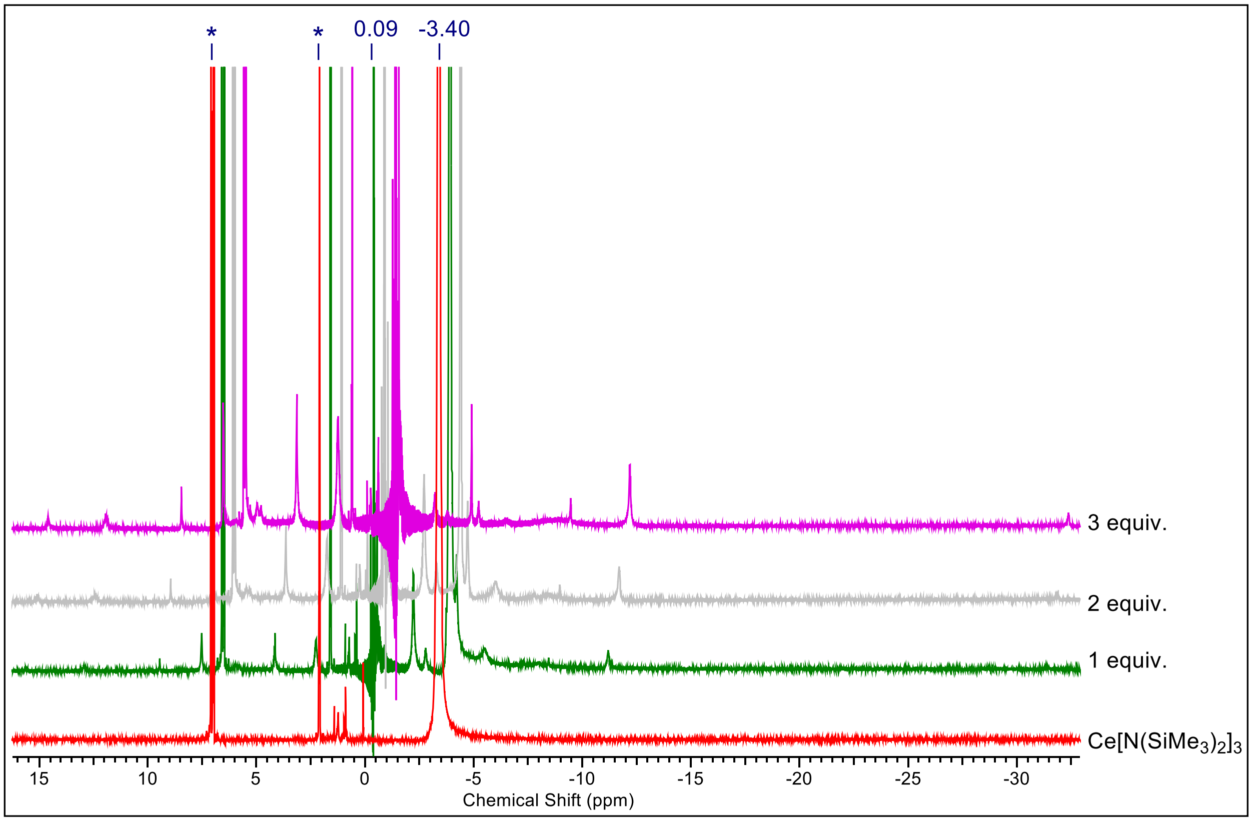


Figure S9. Stacked ^{1}H NMR spectra (toluene-d_8, 400 MHz, 300 K) of the protonolysis reaction of Ce[N(SiMe$_3$)$_2$]$_3$ with varying amounts of Me$_2$pzH. Solvent signals are marked with *. The red spectrum shows Ce[N(SiMe$_3$)$_2$]$_3$ with minor impurities of K[N(SiMe$_3$)$_2$] and *n*-hexane. Upon addition of one (green), two (gray) or three (purple) equivalents of Me$_2$pzH, HN(SiMe$_3$)$_2$ at 0.09 ppm, Ce[N(SiMe$_3$)$_2$]$_3$ at -3.40 ppm and [Ce$_4$(Me$_2$pz)$_{12}$]·(**2**) can be identified.

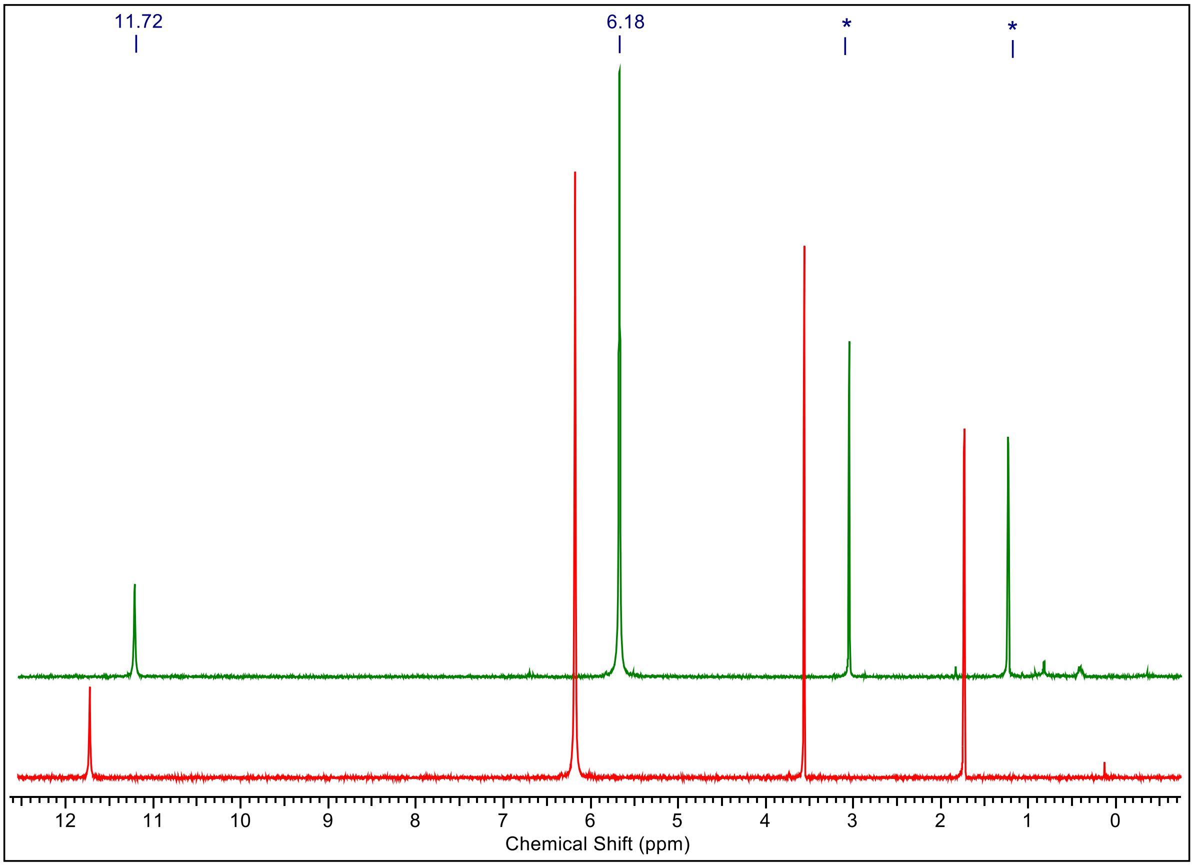


Figure S10. Stacked ^{1}H NMR spectra (THF-d_8, 400 MHz, 300 K) of [$Ce_4(Me_2pz)_{12}$] (**2**, red) and of the white precipitate which is formed upon heating to 120 °C in toluene (green), indicating the formation of [$Ce(Me_2pz)_3(thf)_2$]. ^{1}H NMR spectra are in accordance with literature.[7]

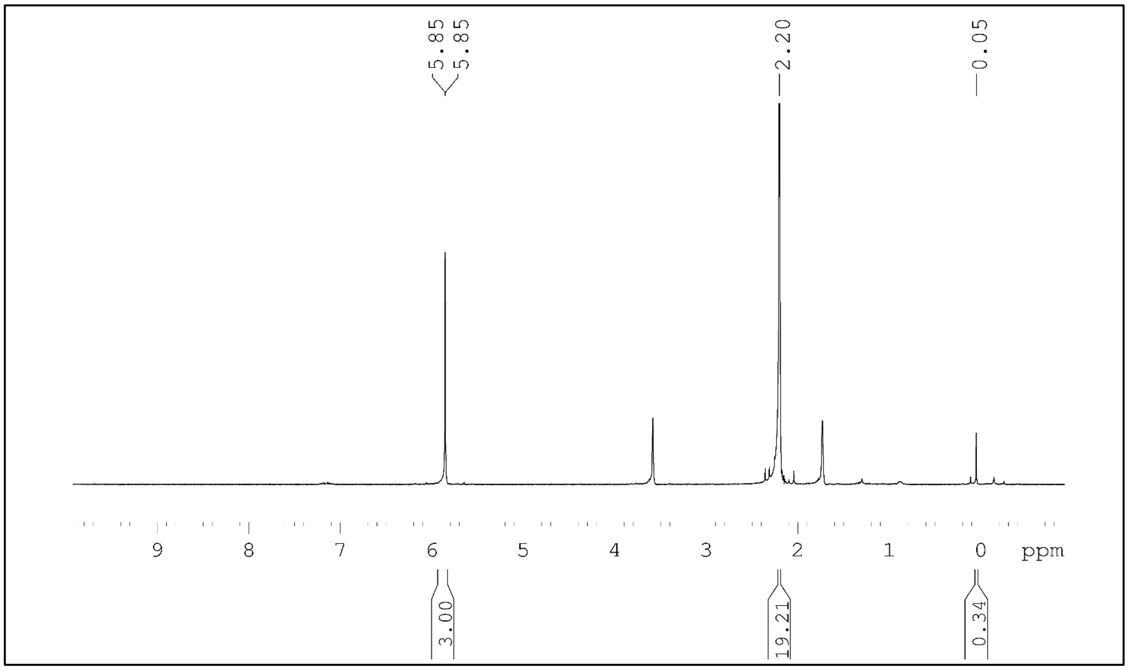


Figure S11. ^{1}H NMR spectrum (THF-d_8, 400 MHz, 300 K) of **1** (synthesized by method b), dissolved in THF-d_8 (trace impurities not included).

Relevant IR spectra for complexes [La(Me₂pz)₃]*ₙ* (1) and [Ce₄(Me₂pz)₁₂] (2)

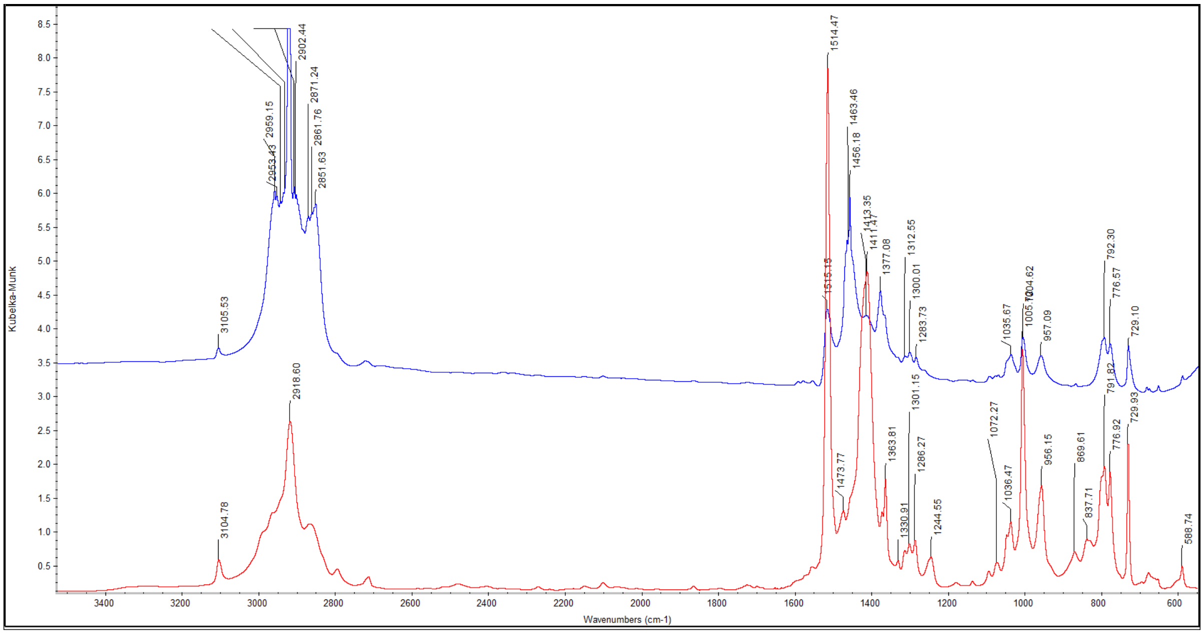


Figure S12. Stacked IR spectra of [La(Me₂pz)₃] (**1**, blue, obtained from high-temperature reaction, in Nujol) and "[La(Me₂pz)₃]" (**1**, red, obtained from protonolysis reactions, by DRIFT (KBr)), indicating very similar spectra.

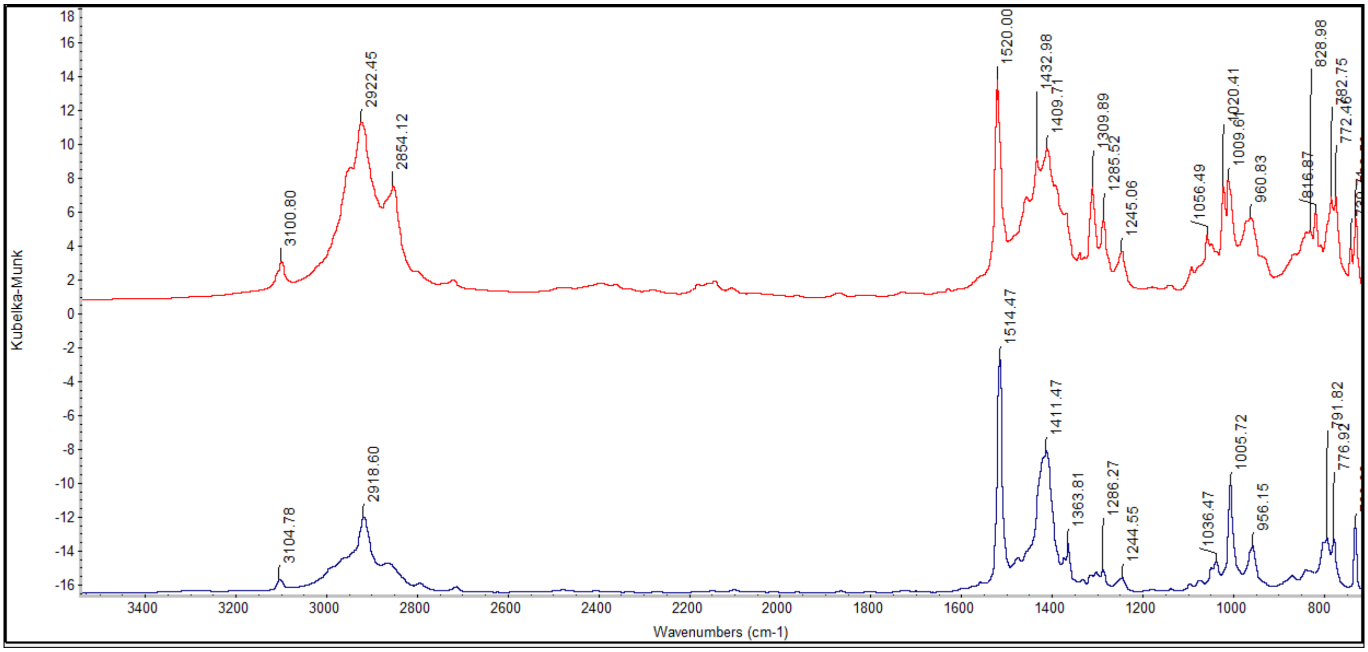


Figure S13. Stacked IR (DRIFT) spectra of [Ce₄(Me₂pz)₁₂] (**2**, red) and "[La(Me₂pz)₃]" (**1**, blue, obtained from protonolysis reaction), indicating differences in the IR bands between the structures of molecular **2** and polymeric **1**.

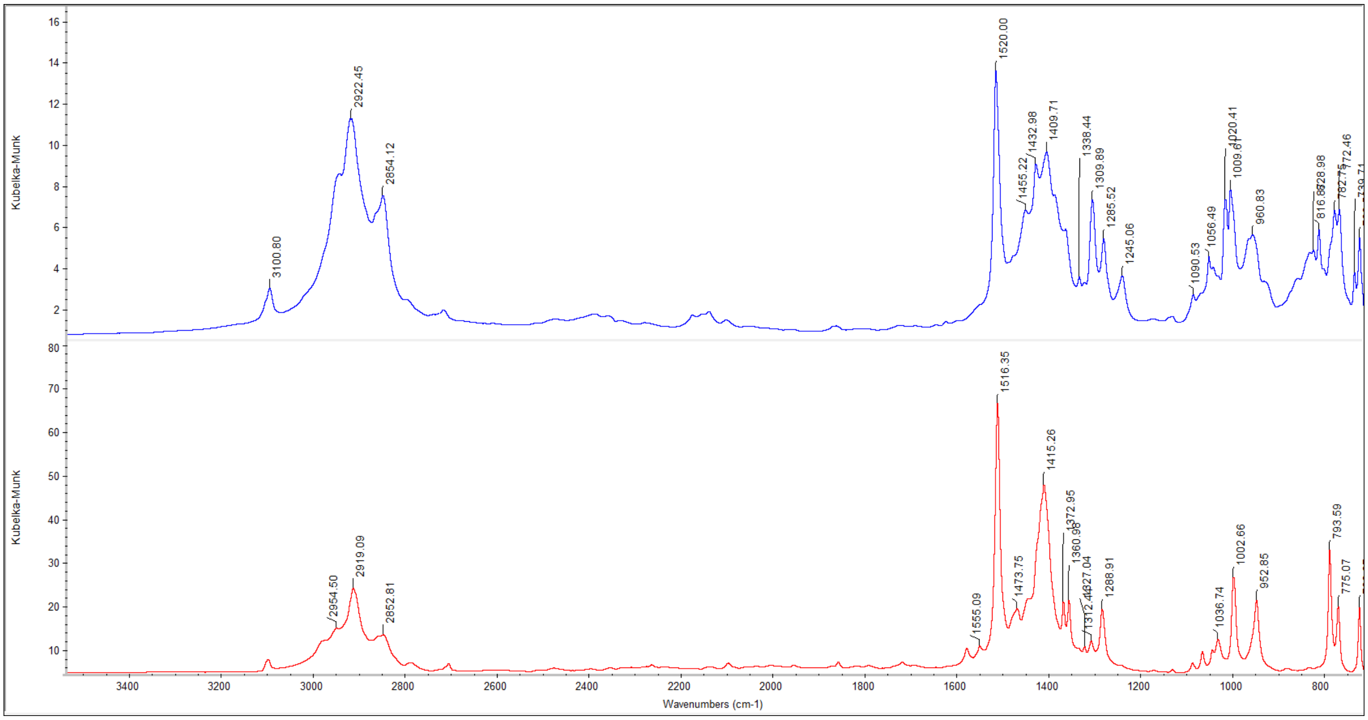


Figure S14. Stacked IR (DRIFT) spectra of [$Ce_4(Me_2pz)_{12}$] (**2**, blue) and the white powder of "[$Ce(Me_2pz)_3$]$_n$" (red) obtained from the conversion of **2** to [$Ce(Me_2pz)_3$]$_n$ by heating, revealing distinct band patterns.

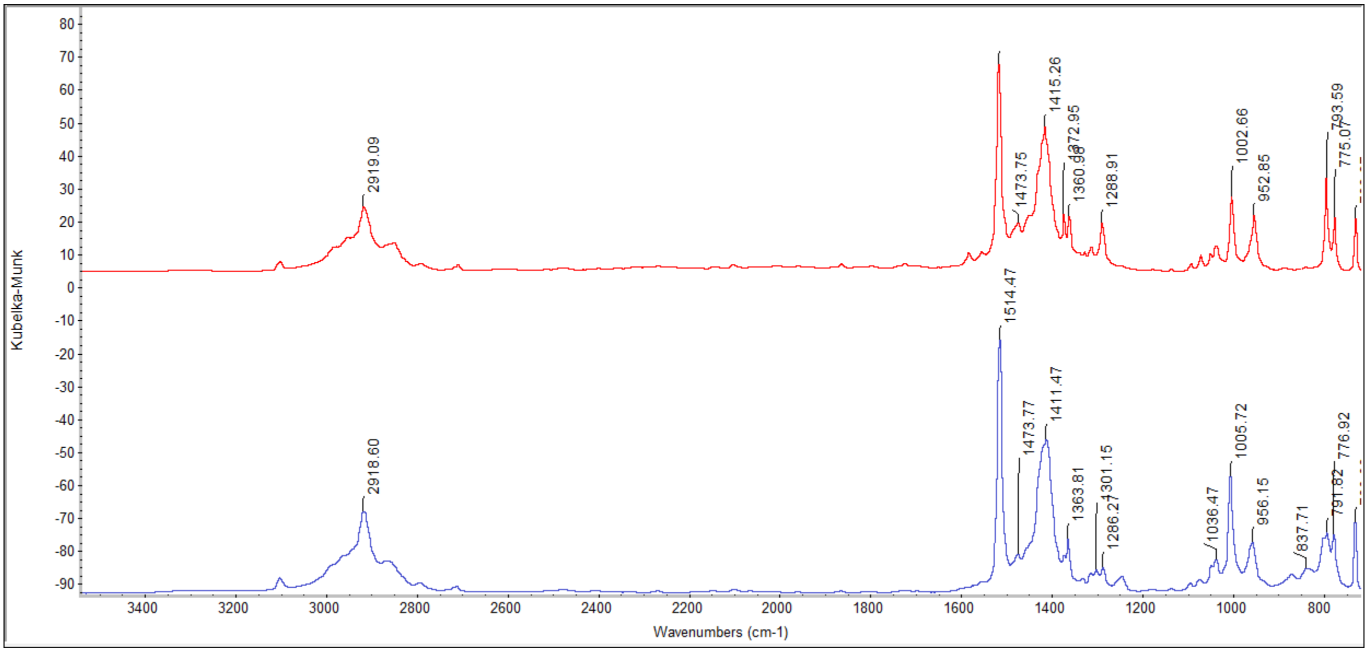


Figure S15. Stacked IR spectra of "[$Ce(Me_2pz)_3$]" (red, obtained as the white powder from heating crystalline **2**·*n*-hexane), and "[$La(Me_2pz)_3$]" (**1**, blue, obtained from protonolysis reaction), indicating a near identical IR spectra and, hence, suggesting both are polymeric [$Ln(Me_2pz)_3$]$_n$.

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