Lanthanide/actinide differentiation with sterically encumbered N-heterocyclic carbene ligands

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Supplementary information

NMR spectra of the reaction of $UN"_3$ with HL^D:

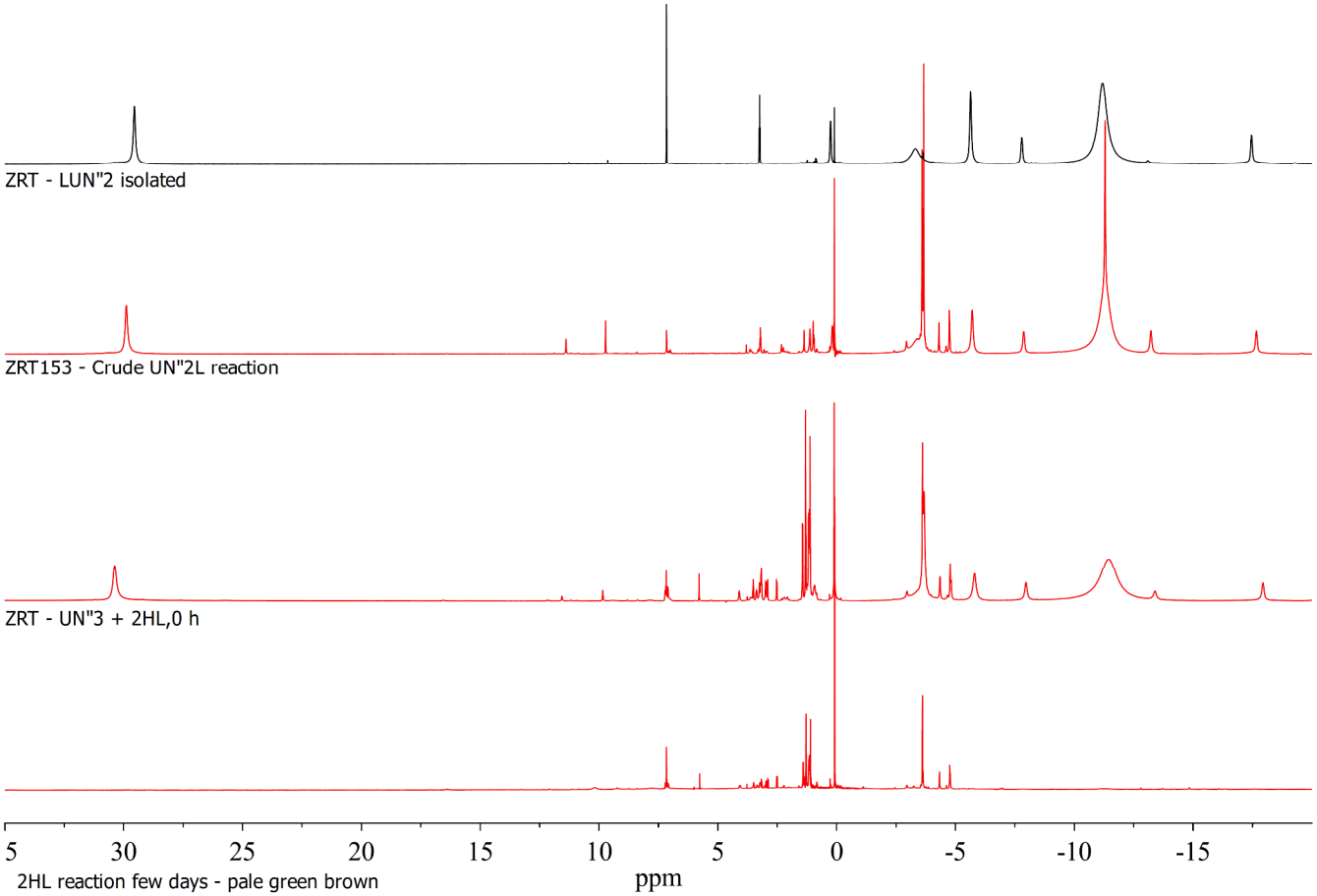

Figure ESI.1. ^{1}H NMR spectra of reactions carried out in the attempt to make $U(L^D)_2N"$.
(top) is a pure, isolated samples of $U(L^D)N"_2$. (second) The reaction of $UN"_3$ with HL^D: Crude $U(L^D)N"_2$ is formed instantly. (third) The reaction of $UN"_3$ with two equivalents of HL^D: Crude $U(L^D)N"_2$ is formed instantly and then the reaction mixture decomposes over the course of a few days to afford (bottom) the ligand HL^D, HN" and a few paramagnetic resonances (3 that persist and the rest are small in the base line across the spectral width 60 to -40 ppm). The colour changes from dark blue to clear green-brown in this time

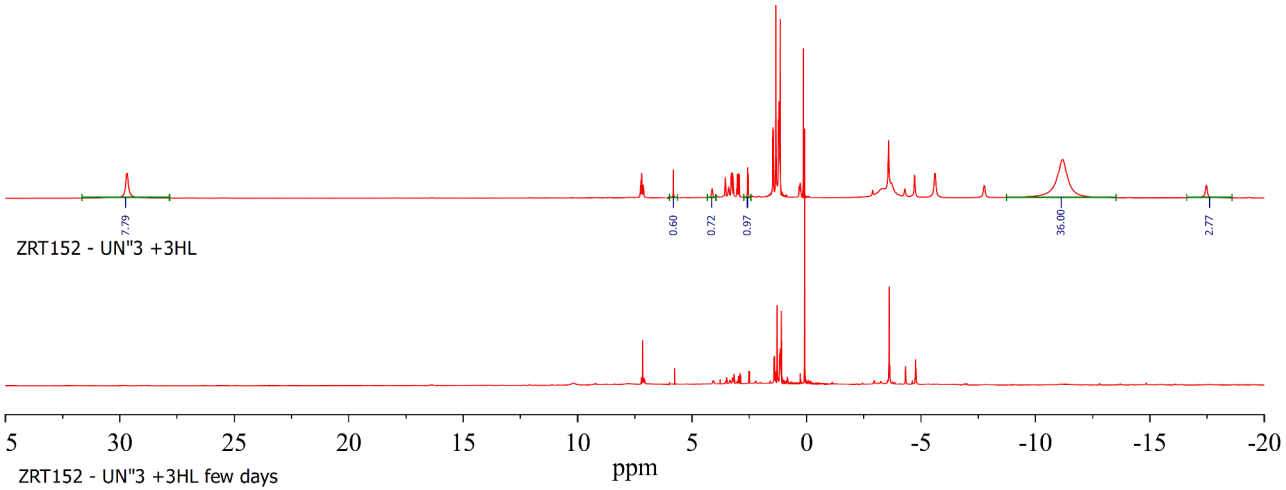

Figure ESI.2. ^{1}H NMR spectra of reactions carried out in the attempt to make U(L^{D})$_2$N".
(upper) The reaction of UN"$_3$ with three equivalents of HL^{D}: Crude U(L^{D})N"$_2$ and HL^{D} are formed instantly, and then the reaction mixture decomposes over the course of a few days to afford (bottom) the ligand HL^{D}, HN" and a few paramagnetic resonances. The colour changes from dark blue to clear green-brown in this time.

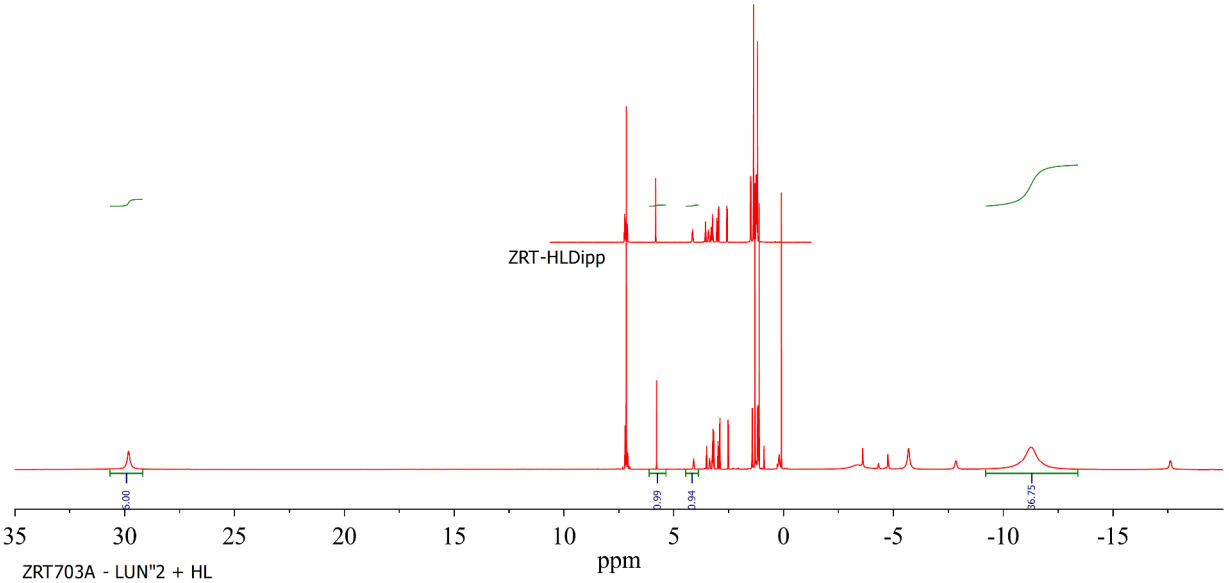

Figure ESI.3. ^{1}H NMR spectra of the reaction of U(L^{D})N"$_2$ with HL^{D}: initially, crude U(L^{D})N"$_2$ and HL^{D} only are observed (HL^{D} is shown in the upper inset). As above, the reaction mixture decomposes over the course of a few days to afford the ligand HL^{D}, HN" and a few small, unassignable paramagnetic resonances (spectrum not shown). The colour changes from dark blue to clear green-brown in this time.

X-ray Crystallographic details

Experiments were carried out on crystals mounted on the end of a glass fibre in fomblin oil, at 150 K on a Bruker *SMART APEX* CCD area detector diffractometer, with Mo *K*α radiation. Riding.

	$[Ce(L^M)N''_2]$	$[Ce(L^M)_2N'']$	$[Ce(L^D)_2N'']$	$[U(L^M)_2I_2]$
Crystal data				
Chemical formula	$C_{33}H_{64}CeN_5OSi_4C_5H_5N$	$C_{38}H_{64}CeN_5O_2Si_2$	$C_{47}H_{79}CeN_5O_2Si_2$	$C_{32}H_{46}I_2N_4O_2U$
M_r	878.47	819.24	942.45	1010.56
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a, *b*, *c* (Å)	16.1984 (6), 13.4476 (5), 22.0515 (9)	11.1139 (4), 18.0530 (6), 11.5188 (4)	19.9366 (6), 12.7554 (4), 20.3716 (6)	12.1805 (4), 12.0395 (4), 12.3962 (4)
α, β, γ (°)	90, 98.384 (2), 90	89.924 (2), 112.910 (2), 89.187 (2)	90, 92.147 (2), 90	90, 101.881 (2), 90
V (Å^3)	4752.1 (3)	2128.54 (13)	5176.8 (3)	1778.92 (10)
Z	4	2	4	2
μ (mm^{-1})	1.09	1.16	0.96	6.33
Crystal size (mm)	0.37 × 0.31 × 0.29	0.4 × 0.2 × 0.17	0.38 × 0.25 × 0.25	0.67 × 0.45 × 0.42
Data collection				
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi scan *SADABS*
T_{min}, T_{max}	0.535, 0.745	0.627, 0.820	0.609, 0.746	0.041, 0.069
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30810, 9754, 7308	17055, 17055, 15887	66609, 14500, 11504	18933, 4693, 4138
R_{int}	0.064	0.0000	0.061	0.034
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.055, 0.132, 1.05	0.056, 0.132, 1.15	0.046, 0.097, 1.10	0.033, 0.075, 1.16
No. of reflections	9754	17055	14500	4693
No. of parameters	427	449	547	192
No. of restraints	6	0	48	0
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.99, -0.88	1.51, -1.83	1.38, -0.70	2.23, -0.83

Computer programs: *SMART* (Siemens, 1993); *SAINT* (Siemens, 1995); *SIR-92* (Giacovazzo, 1994); *SHELXL-97* (Sheldrick, 1997); *ORTEP* (Farrugia, 1997); *enCIFer* (Allen et al., 2004).

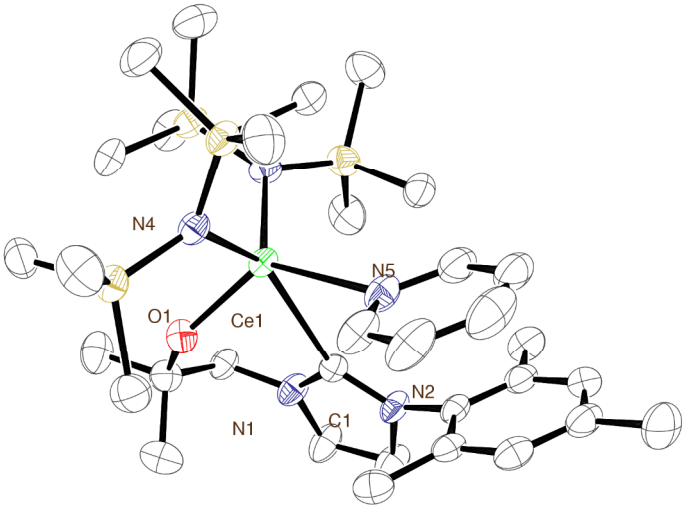

Figure ESI.4. Displacement ellipsoid (50 % probability) drawing for [Ce(L^M)N"$_2$(NC_5H_5)] Hydrogen atoms and lattice pyridine molecule omitted for clarity.