

New reactions of β -diketiminatolanthanoid complexes: sterically induced self-deprotonation of β -diketiminato ligands.

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General Methods: All manipulations were carried out in an atmosphere of dry argon using standard Schlenk tube techniques or under vacuum in a sealed all-glass apparatus. Solvents were dried from the appropriate drying agent, distilled, degassed and stored over a potassium mirror. The NMR spectra were recorded on a DPX 300 or AM-500 Bruker spectrometer with residual solvent signals as internal reference (^1H and $^{13}\text{C}\{^1\text{H}\}$) or with an external reference (SiMe_4 or PbMe_4 for ^{29}Si or ^{207}Pb , respectively). Elemental analyses were carried out at the University of North London. KL ,¹ KL' ,² $[\text{YbL}'_2]$,² $\text{TmI}_2(\text{dme})_3$,³ $\text{TmI}_3(\text{thf})_{3.5}$ ⁴ and $[\text{HNEt}_3][\text{BPh}_4]$ ⁵ were prepared according to literature procedures. $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (Strem) was used as received.

*Synthesis of $[\text{TmL}(\text{L}^{\text{dep}})]$ (**1**):* KL (1.212 g, 2.67 mmol) was added to a suspension of $\text{TmI}_3(\text{thf})_{3.5}$ (0.766 g, 0.95 mol) in thf (10 mL) at 0°C . The mixture was stirred for 2 h at room temperature and the solvent was removed in a vacuum. The residue was extracted with toluene (2×5 mL), the combined toluene solution was concentrated to *ca.* 1 mL and covered with hexanes. Storing at 5°C overnight gave 0.779 g (57%) of $\mathbf{1}\cdot\text{LH}\cdot 0.5\text{PhMe}$ as yellow prisms suitable for X-ray crystallography. Drying the crystals in a vacuum at 100°C gave the toluene-free product, mp $235\text{--}240^\circ\text{C}$ (sublimation of LH from the crystals was observed at $155\text{--}160^\circ\text{C}$). Anal. Calc. for $\text{C}_{87}\text{H}_{123}\text{N}_6\text{Tm}$: C, 73.5; H, 8.72; N, 5.91. Found: C, 73.3,

H, 8.82, N, 5.81%. $^1\text{H-NMR}$ (C_6D_6 , δ): 240.8 (s, 3 H, CH_3), 177.6 (s, 3 H, CH_3), 170.7 (s, 3 H, CH_3), 138.3 (s, 3 H, CH_3), 124.8 (s, 1 H, CH), 120.1 (s, 1 H, CH), 105.8 (s, 1 H, CH), 105.9 (s, 1 H, CH), 86.6 (s, 1 H, CH), 80.7 (s, 3 H, CH_3), 66.3 (s, 3 H, CH_3), 65.3 (s, 3 H, CH_3), 57.0 (s, 1 H, CH), 26.7 (s, 3 H, CH_3), 17.8 (s, 1 H, CH), 13.0 (s, 1 H, CH), -9.4 (s, 3 H, CH_3), -10.4 (s, 3 H, CH_3), -22.9 (s, 1 H, CH), -29.1 (s, 1 H, CH), -37.2 (s, 1 H, CH), -37.8 (s, 3 H, CH_3), -38.7 (s, 1 H, CH), -44.5 (s, 3 H, CH_3), -47.7 (s, 3 H, CH_3), -56.2 (s, 1 H, CH), -72.0 (s, 3 H, CH_3), -77.5 (s, 3 H, CH_3), -87.2 (s, 3 H, CH_3), -96.9 (two s, 6 H, 2 CH_3), -101.3 (s, 3 H, CH_3), -147.3 (s, 1 H, CH), -160.0 (s, 1 H, CH), -220.8 (s, 1 H, CH), -245.2 (s, 1 H, CH); some of the low-intensity signals were not found due to line broadening (Fig. 1S).

Isolation of 1 from a Tm(II) precursor: KL (0.566 g, 1.24 mmol) was added to a suspension of $\text{TmI}_2(\text{dme})_3$ (0.427 g, 0.61 mol) in thf (10 mL) at $-40\text{ }^\circ\text{C}$. The mixture was stirred for 2 h at $-30\text{ }^\circ\text{C}$ to $-20\text{ }^\circ\text{C}$ while the starting materials dissolved giving a dark red-brown solution with precipitate of KI. The solvent was removed in a vacuum, the residue was extracted with pentane ($2 \times 10\text{ mL}$). The solvent from the extract was removed in a vacuum producing a yellow crystalline material with a brown oil. It was dissolved in a minimum amount of toluene and covered with hexane to yield **1**·LH·0.5PhMe (first crop 0.178 g, 20%). The $^1\text{H-NMR}$ spectrum was identical to that obtained in the previous experiment.

Synthesis of 2b: $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.198 g, 0.25 mmol) was added to a solution of **1**·LH (0.354 g, 0.25 mmol) in toluene (10 mL) at room temperature. A yellow oil separated immediately and solidified after stirring overnight. The precipitate was washed with toluene and dried in a vacuum, quantitatively yielding nearly pure ($^1\text{H NMR}$) complex **2b**. To obtain X-ray quality crystals, the product was dissolved in a minimum amount of thf, layered with toluene and stored at $-27\text{ }^\circ\text{C}$ for 1 week, producing 0.301 g (0.20 mmol, 80%) of lemon yellow crystals. Anal. Calc. for $\text{C}_{82}\text{H}_{82}\text{BF}_{20}\text{N}_4\text{Tm}$: C, 58.5; H, 4.91; N, 3.33. Found: C, 58.4, H, 5.12, N, 3.28%. $^1\text{H-NMR}$ (C_6D_6 , δ): 170.1 (s, 3 H, CH_3), 74.1 (s, 3 H, CH_3), 67.4 (s, 1 H, CH), 63.7 (s, 3 H, CH_3), 62.4 (s, 1 H, CH), 55.9 (s, 1 H, CH), 40.3 (s, 1 H, CH), 38.2 (s, 3 H, CH_3), 9.1 (s, 3 H, CH_3), -12.4 (s, 3 H, CH_3), -38.9 (s, 1 H, CH), -57.4 (s, 3 H, CH_3), -60.2 (s, 3 H, CH_3), -60.8 (s, 1 H, CH), -73.5 (s, 3 H, CH_3), -108.4 (s, 3 H, CH_3); some of the low-intensity signals were not found due to line broadening (Fig. 2S).

Synthesis of 2a: [HNEt₃][BPh₄] (0.062 g, 0.15 mmol) was added to a solution of **1**·LH (0.191 g, 0.13 mmol) in toluene (10 mL) at room temperature and the mixture was stirred overnight. No visible change occurred and the ¹H NMR spectrum of the solution showed only signals of the starting complex **1**. The solvent was removed in a vacuum and the residue was dissolved completely in thf (5 mL). After 5 h at room temperature the solvent was removed in a vacuum, pentane was added to the oily residue and the mixture was stored at -27 °C for 1 day, yielding light yellow sticky crystals of complex **2a**. The ¹H NMR spectrum of the product (Fig. 2S) was very similar to that of complex **2b** but contained signals of LH and of the [BPh₄] anion (multiplet at 7.4-6.6 ppm). Attempts to obtain X-ray quality crystals were unsuccessful.

Synthesis of [PbL'₂] 3: Potassium β-diketiminato KL' (0.667 g, 1.65 mmol) was added to a stirred suspension of PbI₂ (0.380 g, 0.82 mmol) in thf (20 mL) at room temperature and the mixture was stirred overnight. The solvent was removed in a vacuum and the residue was extracted with hexane (2×10 mL). The resulting deep yellow solution was slowly evaporated in a vacuum until crystallisation began and was cooled to -30 °C. The solution was decanted from yellow crystals, concentrated and cooled again giving second crop of product; overall yield was 0.555 g (0.59 mmol, 72%), mp 132 – 135 °C (decomposition). EI MS (*m/z* (%), assignment): 938 (0.8, [M]⁺), 573 (90, [M – L']⁺), 365 (80, [L']⁺). Anal. Calc. for C₄₂H₅₈N₄Si₄Pb: C, 53.8; H, 6.23; N, 5.97. Found: C, 53.9, H, 6.37, N, 5.95%. ¹H-NMR (C₆D₆, δ): 7.66 (m, 8 H, *m*-H), 6.97 (m, 12 H, *o*- and *p*-H), 6.02 (s, 2 H, middle CH), 0.26 [s, with ²⁰⁷Pb satellites, *J*(²⁰⁷Pb-¹H) = 6.6 Hz, 36 H, SiMe₃]. ¹³C-NMR (C₆D₆, δ): 172.90 [s, with ²⁰⁷Pb satellites, *J*(²⁰⁷Pb-¹H) = 28.5 Hz, NC(Ph)CH], 146.40 (s, *ipso*-C of Ph ring), 129.96, 129.01, 128.33 (three s, C of Ph ring), 118.38 [s, with ²⁰⁷Pb satellites, *J*(²⁰⁷Pb-¹H) = 41.4 Hz, CH], 3.81 [s, with ²⁰⁷Pb satellites, *J*(²⁰⁷Pb-¹H) = 53.3 Hz, SiMe₃]; ²⁹Si-NMR (C₆D₆, δ): 0.80 [s, with ²⁰⁷Pb satellites, *J*(²⁰⁷Pb-¹H) = 56.4 Hz, SiMe₃]; ²⁰⁷Pb-NMR (C₆D₆, δ): 1060.0 (broad s, line width *w*_{1/2} 200 Hz).

Synthesis of 4 and 4a (method 1): [PbL'₂] (0.110g, 0.12 mmol) was added to a green-brown solution of [YbL'₂] (0.151 g, 0.17 mmol) in C₆H₆ (5 mL). The mixture was kept at 80 °C for 3 h. The yellow-brown solution was filtered, the filtrate was concentrated in a vacuum to give a brown oil; addition of a few drops of hexane yielded 0.080 g (53%) of brown crystals of **4a** (co-crystals of **4** with [YbL'₂] in a 76:24 ratio) suitable for X-ray crystallography. Washing these crystals with pentane gave **4** as a yellow powder. When the reaction time was increased to 6 h, the isolated product was free of starting material.

Anal. Calc. for $C_{42}H_{57}N_4Si_4Yb$: C, 55.8; H, 6.36; N, 6.20. Found: C, 52.7, H, 6.12, N, 6.14% [*Note: a low carbon content is often observed in organolanthanoid complexes due to Ln carbide formation*]. 1H -NMR (C_6D_6 , δ): 107.9 (s, 9 H, SiMe₃), 74.1 (s, 9 H, SiMe₃), 5.7 (s, 2 H, CH), 2.6 (s, 1 H, CH), 1.3 (s, 2 H, CH), 0.9 (s, 1 H, CH), 0.3 (s, 1 H, CH), -0.5 (s, 2 H, CH), -1.0 (s, 3 H, CH₃), -1.5 (s, 1 H, CH), -2.2 (s, 2 H, CH), -11.1 (s, 2 H, CH), -19.5 (s, 2 H, CH), -26.1 (s, 1 H, CH), -30.5 (s, 9 H, SiMe₃), -46.2 (s, 3 H, CH₃), -56.5 (s, 1 H, CH), -62.4 (s, 1 H, CH), -78.7 (s, 1 H, CH); some of the low-intensity signals were not found due to line broadening (Fig. 3S).

In a control experiment, an NMR tube containing a C_6D_6 solution of [PbL'₂] was stored at 80 °C for 3 days; no change in the 1H -NMR spectrum was observed in spite of the solution becoming slightly darker.

Synthesis of 4 (method 2): [Pb{N(SiMe₃)₂}₂] (0.130 g, 0.25 mmol) was added to a green-brown solution of [YbL'₂] (0.354 g, 0.39 mmol) in C_6H_6 (10 mL). The mixture was kept at 80 °C for 0.5 h (precipitation of Pb metal started at 50 °C). The dark yellow solution was filtered, the filtrate was concentrated in a vacuum to ca. 1 mL and covered with hexane. Storing at 5 °C overnight gave 0.225 g (64%) of **4** as orange hexagonal prisms, mp 220-224 °C (decomposition). The 1H -NMR spectrum was identical to that obtained in method 1.

Crystallographic information: CCDC 254749 (**1**), 254750 (**2b**), 254751 (**3**), 254752 (**4**) and 254753 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The molecular structures of **2b** and **3** are shown in Figures 4S and 5S, respectively.

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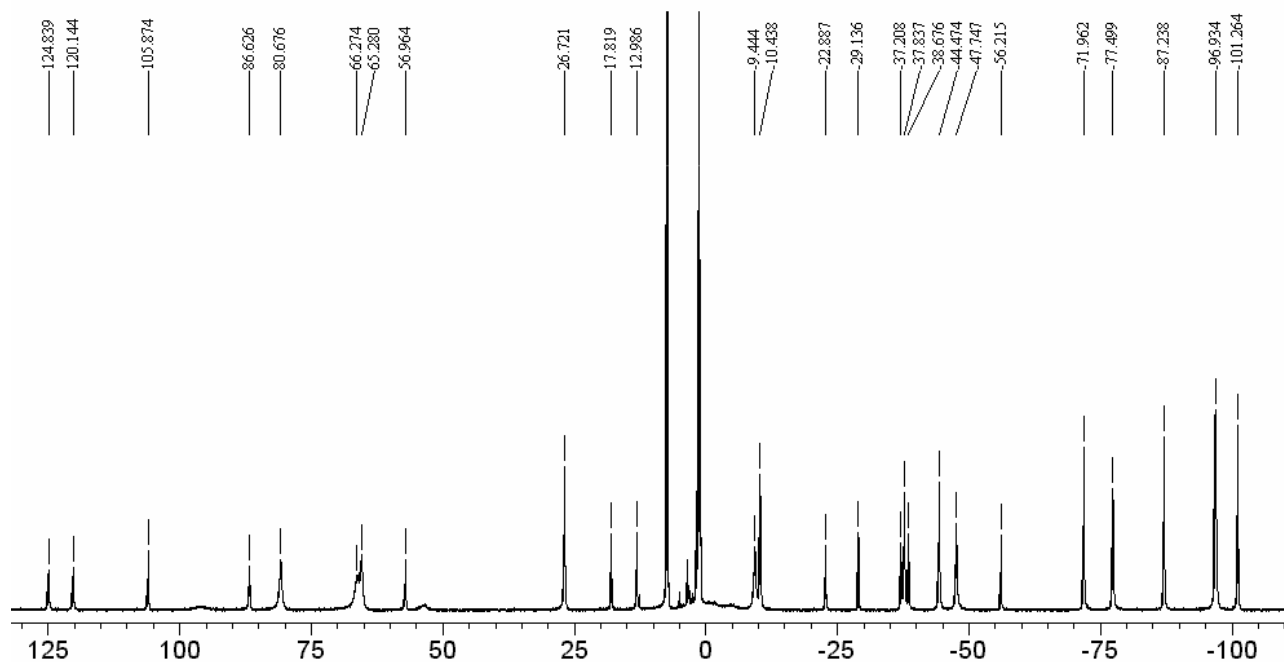


Fig. 1S. The central part of the ¹H NMR spectrum (250 ppm range) of complex **1**.

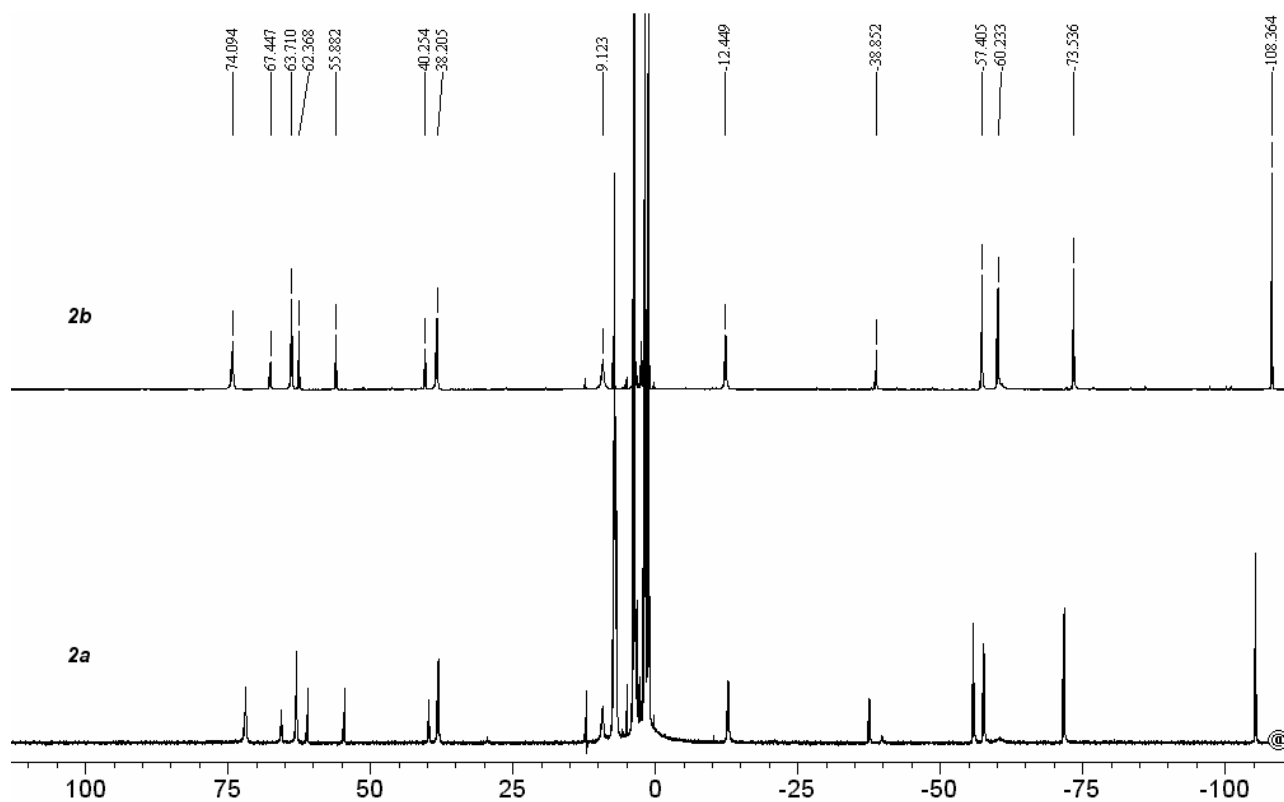


Fig. 2S. The central part of the ¹H NMR spectra (250 ppm range) of complexes **2a** (contains LH by-product) and **2b** (recrystallised sample).

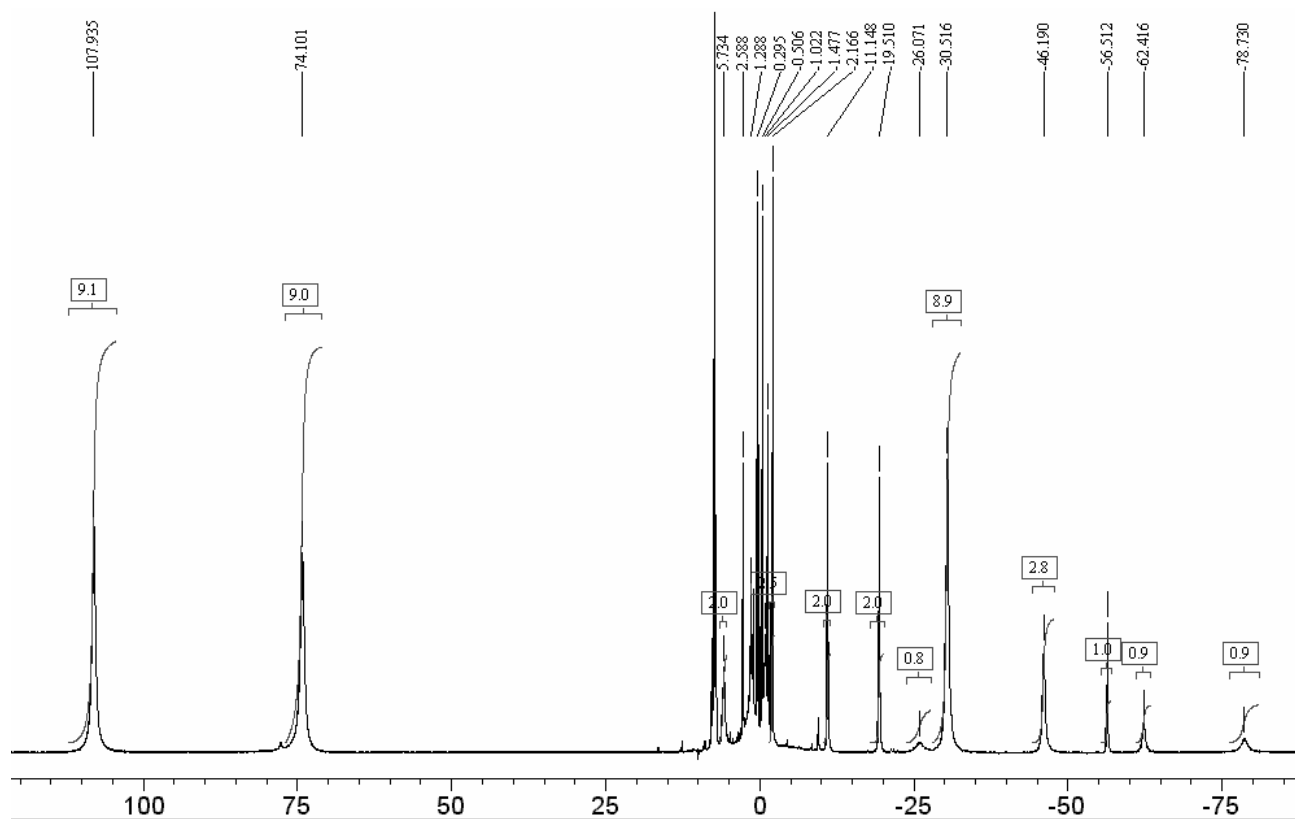


Fig. 3S. The ^1H NMR spectrum of complex **4**.

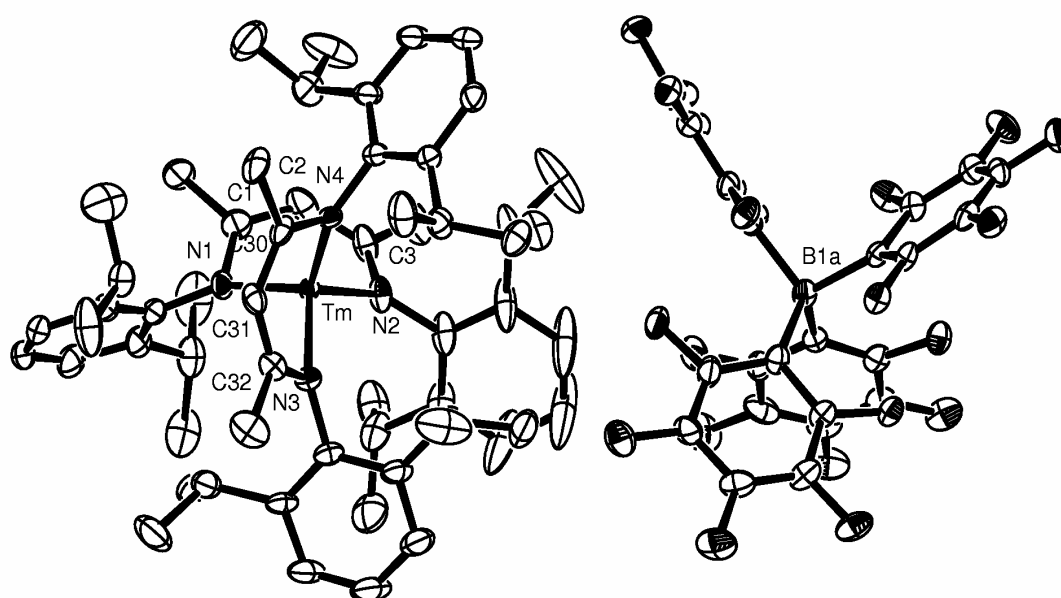


Fig. 4S. ORTEP drawing and atom numbering scheme for complex **2b** (20% ellipsoids).

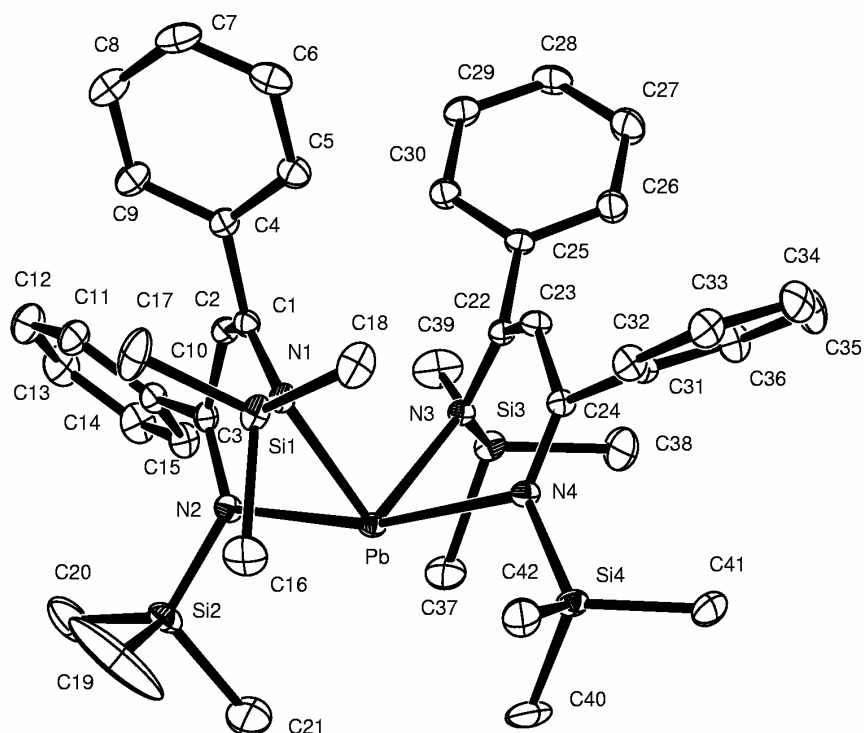


Fig. 5S. ORTEP drawing and atom numbering scheme for complex **3** (20% ellipsoids). Selected bond lengths (Å) and angles (°): Pb–N1 2.315(3), Pb–N2 2.548(3), Pb–N3 2.311(3), Pb–N4 2.669(3), N1–C1 1.351(5), N2–C3 1.317(5), N3–C22 1.353(5), N4–C24 1.291(5), C1–C2 1.398(5), C2–C3 1.413(5), C22–C23 1.378(5), C23–C24 1.446(5), N1–Pb–N3 93.87(10), N2–Pb–N4 166.20(10).