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Synthesis and structural characterization of imido–lanthanide complexes with a metal–nitrogen multiple bond

Hoi-Shan Chan, Hung-Wing Li and Zuowei Xie*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China. E-mail: zxie@cuhk.edu.hk

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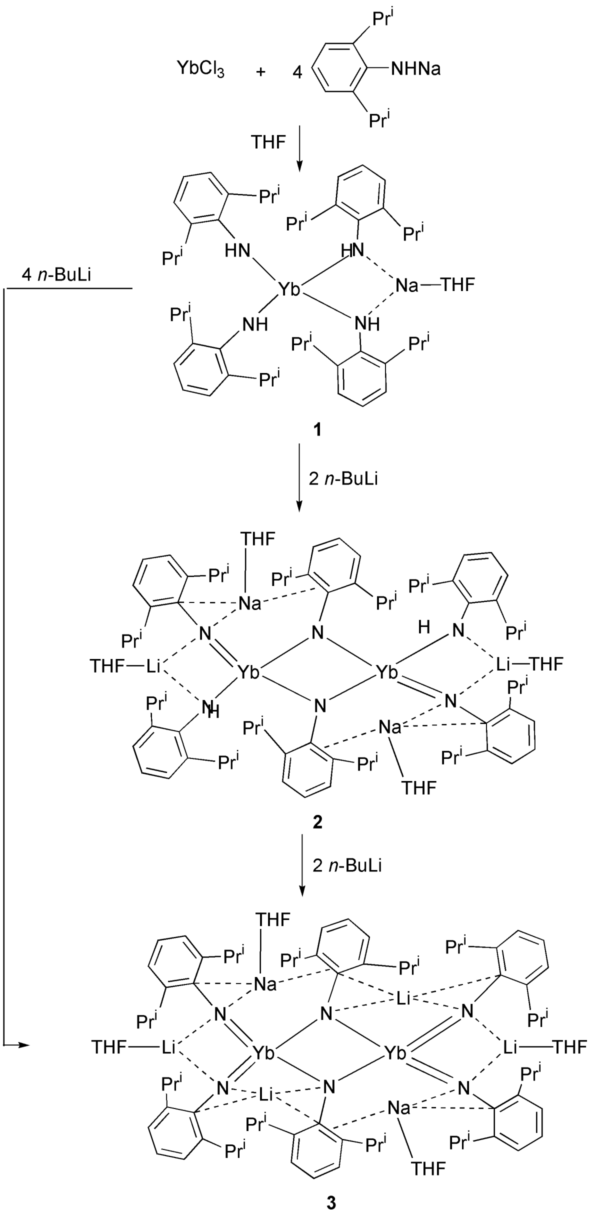
Treatment of an amido–ytterbium complex with *n*-BuLi leads to the isolation and structural characterization of a mixed amido–imido–ytterbium or imido–ytterbium complex, respectively, depending upon the molar ratios of the reactants; the Yb–N distance and the linearity of the imido N atom strongly suggest the presence of a formal Yb=N multiple bond in these novel complexes.

Imido–d-transition-metal complexes play an important role both in biological processes such as nitrogen fixation and in a series of industrial processes.[1] Cycloadditions, C–H bond activations, and ring-opening polymerizations can all be catalyzed by various imido complexes.[1–3] Numerous imido–d-transition-metal complexes have been reported; however, imido–lanthanide complexes are largely unexplored.[1–4] Very recently, a samarium complex with a Sm=C bond was communicated.[5] Homoleptic complexes $Ln[NPPh_3]_3$ were also very recently reported to have La–N multiple bonding for Ln = La with an average La–N–P angle of 166.0(5)°. This angle is dramatically reduced to only 158.3(3)° when Ln = Yb,[6] suggesting that the lone pair of the nitrogen is mainly localized on the N itself. We report herein novel imido–ytterbium complexes with a linear Yb–N–C angle and a formal Yb=N bond stabilized by sterically demanding 2,6-diisopropylphenyl groups.

Treatment of $(Pr^i_2C_6H_3NH)_2Yb(\mu\text{-}NHC_6H_3Pr^i_2)_2Na(THF)$ (**1**) with 2 or 4 equiv. of *n*-BuLi in THF at room temperature gave the mixed amido–imido–ytterbium complex $\{(Pr^i_2C_6H_3N)(Pr^i_2C_6H_3NH)Yb(\mu\text{-}NC_6H_3Pr^i_2)\}_2\{[Li(THF)][Na(THF)]\}_2$ (**2**) or the imido–ytterbium complex $\{(Pr^i_2C_6H_3N)_2Yb(\mu\text{-}NC_6H_3Pr^i_2)\}_2\{[Li_2(THF)][Na(THF)]\}_2$ (**3**), respectively.† **3** was also prepared by reaction of **2** with 2 equiv. of *n*-BuLi, shown in Scheme 1. These complexes are extremely air- and moisture-sensitive but remain stable for months at room temperature under an inert atmosphere. All three new ytterbium complexes were fully characterized by various spectroscopic data, elemental analyses and X-ray diffraction studies.‡

The solid-state structures of **2** and **3** are shown in Figs. 1 and 2, respectively. Both **2** and **3** are dimeric complexes in which each Yb^{3+} ion bonds to four N atoms in a distorted-tetrahedral geometry. The two Yb and two doubly bridging N atoms are coplanar; the two terminal N atoms are *ca.* 0.90 Å in **2** or *ca.* 0.96 Å in **3** above this plane and the other two are *ca.* 1.63 Å in **2** or *ca.* 1.35 Å in **3** below this plane. The relatively longer Yb–N(terminal) distances and smaller C–N–Yb angles in **2** suggest that both N(4) and N(5) are amido N atoms since the imido N atoms are superior to the amido ones in bonding with two lanthanide ions.

The most interesting structural features are the very short Yb–N(imido) distances and very large C–N(imido)–Yb angles. The Yb–N(3,6) distances of 2.101(4) and 2.126(4) Å in **2** and the Yb–N(2,3) distances of 2.122(2) Å in **3** are among the shortest Yb–N distances reported in the literature, for example, the shortest known Yb–N distances are 2.107(4) and 2.137(4) Å in $[(Ph_3PN)_2Yb(\mu\text{-}NPPh_3)]_2$[6] and 2.142(6) Å in $(C_5H_5)_3Yb_2(NPPh_3)_3$.[7] It is noteworthy that the short bonded N atoms [N(3,6) in **2** and N(2,3) in **3**] in the present complexes are also weakly linked by bridging to Li^+ or Na^+ ions, which would lengthen the Yb–N distances. The Yb–N(3,6)–C angles are 172.3(3) and 172.5(3)° in **2**, and the Yb–N(2,3)–C angles are 167.5(2) and 171.4(1)° in **3**, respectively. The short U–N distance and large U–N–C angle have been described as an indication of multiple bonding between uranium and nitrogen in imido–uranium complexes such as $(MeC_5H_4)_3U(NPh)$[8] and $[(Me_3Si)_2N]_3U(NPh)F$.[9] The relatively short Sm–C distance in $Sm\{C(Ph_2P{=}NSiMe_3)_2\}\{N(C_6H_{11})_2\}(THF)$ has been attributed to the presence of a Sm=C bond.[5,10] The very short Yb–N distances and linear Yb–N–C angles in the imido complexes **2**



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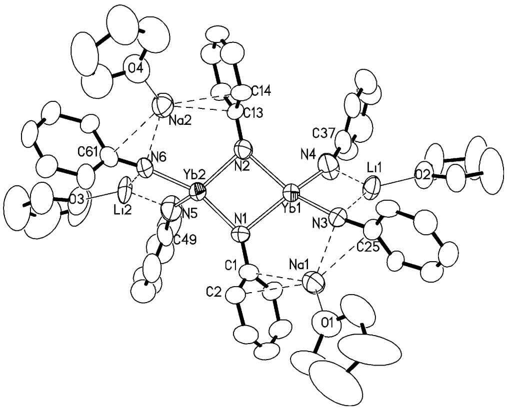

Fig. 1 ORTEP illustration of **2** with thermal ellipsoids drawn at the 35% probability level (all H atoms and ^{i}Pr groups are omitted for clarity). Selected bond lengths (Å) and angles (°): Yb1–N1 2.316(3), Yb1–N2 2.286(4), Yb1–N3 2.101(4), Yb1–N4 2.179(5), Yb2–N1 2.166(3), Yb2–N2 2.221(4), Yb2–N5 2.196(5), Yb2–N6 2.126(4), Yb1–N3–C25 172.3(3), Yb1–N4–C37 161.1(4), Yb2–N5–C49 150.6(3), Yb2–N6–C61 172.5(3).

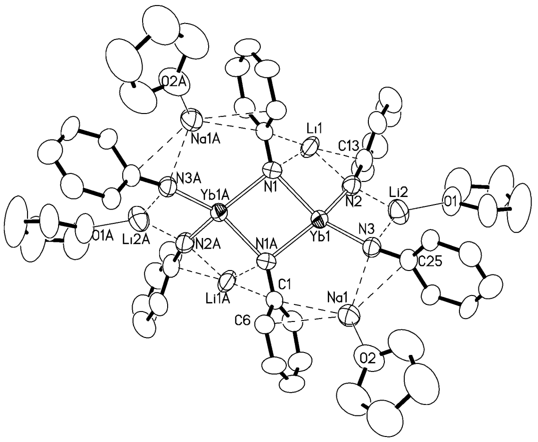

Fig. 2 ORTEP illustration of **3** with thermal ellipsoids drawn at the 35% probability level (all H atoms and ^{i}Pr groups are omitted for clarity). Selected bond lengths (Å) and angles (°): Yb1–N1 2.304(2), Yb1–N1A 2.288(2), Yb1–N2 2.122(2), Yb1–N3 2.122(2), Yb1–N2–C13 167.5(2), Yb1–N3–C25 171.4(1).

and **3** strongly suggest the presence of multiple bonding between Yb and the imido N with the lone pairs of the nitrogen being presumably donated into metal d orbitals to form a formal Yb=N bond.

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Notes and references

† *Preparation of* **1**: a THF solution (5 mL) of $NaNHC_6H_3Pr^i_2$ (0.57 g, 2.86 mmol) was added to a suspension of $YbCl_3$ (0.20 g, 0.71 mmol) in THF (10 mL) at room temperature, and the reaction mixture was refluxed for 2 days. Removal of THF and hexane extraction (3 × 10 mL) gave a red solution from which **1** was isolated as red crystals upon evaporation (0.46 g, 67%). ^{1}H NMR (C_6D_6): δ 8.19 (br, aryl H), 3.56 (m, THF), 1.41 (m, THF), 0.51 (br, ^{i}Pr); ^{13}C NMR (C_6D_6): δ 139.50, 123.06, 119.33, 118.81 (aryl C), 65.03, 23.95 (THF), 29.40, 28.09, 22.53 (^{i}Pr); IR (KBr, cm^{-1}): ν 3054 (w), 3024 (w), 2958 (s), 2872 (s), 1589 (s), 1419 (s), 1259 (s), 1046 (s), 842 (s). Anal. Calc. for $C_{52}H_{80}N_4NaOYb$: C, 64.17; H, 8.28; N, 5.75. Found: C, 63.86; H, 8.54; N, 5.52%. **2**·$0.5C_6H_6$: A 0.16 M solution of *n*-BuLi in hexane (4.60 mL, 0.74 mmol) was slowly added to a THF solution (5 mL) of **1** (0.36 g, 0.37 mmol), and the mixture was stirred at room temperature overnight. The solvents were removed under vacuum, and the residue was extracted with hexane (3 × 10 mL). The hexane solutions were combined and concentrated to about 10 mL from which **2**·$0.5C_6H_6$ was isolated as red crystals upon addition of a few drops of benzene (0.15 g, 46%). ^{1}H NMR (C_6D_6): δ 10.92 (br, aryl H), 3.63 (m, THF), 1.63 (m, THF), 1.25 (br, ^{i}Pr); ^{13}C NMR (C_6D_6): δ 160.30, 130.74, 122.84, 106.29 (aryl C), 68.39, 26.36 (THF), 27.50, 24.00, 14.95 (^{i}Pr); IR (KBr, cm^{-1}): ν 3025 (m), 2956 (s), 2870 (s), 1590 (s), 1458 (s), 1391 (s), 1252 (s), 1039 (s), 886 (s). Anal. Calc. for $C_{72}H_{104}Li_2N_6Na_2Yb_2$ (**2**·$0.5C_6H_6$ − 4THF − $0.5C_6H_6$): C, 59.25; H, 7.18; N, 5.76. Found: C, 59.49; H, 6.90; N, 5.91%. **3**·$0.5C_6H_6$: A 0.16 M solution of *n*-BuLi in hexane (8.50 mL, 1.36 mmol) was slowly added to a THF solution (5 mL) of **1** (0.33 g, 0.34 mmol) at room temperature, followed by procedures similar to those used in the synthesis of **2** affording **3**·$0.5C_6H_6$ as red crystals (0.24 g, 78%). ^{1}H NMR (C_6D_6): δ 10.62 (br, aryl H), 3.49 (m, THF), 1.44 (m, THF), 1.10 (br, ^{i}Pr); ^{13}C NMR (C_6D_6): δ 160.39, 130.61, 122.81, 106.19 (aryl C), 68.27, 26.24 (THF), 28.41, 23.94, 14.67 (^{i}Pr); IR (KBr, cm^{-1}): ν 3033 (m), 2958 (s), 2870 (s), 1620 (m), 1583 (s), 1458 (s), 1390 (s), 1318 (s), 1251 (s), 1043 (s), 747 (s). Anal. Calc. for $C_{91}H_{137}Li_4N_6Na_2O_4Yb_2$: C, 60.76; H, 7.68; N, 4.67. Found: C, 60.69; H, 7.85; N, 4.52%.

‡ *Crystal data*: for **1**: $C_{52}H_{80}N_4NaOYb$, M = 973.23, monoclinic, space group $P2_1/n$, a = 24.516(1), b = 19.815(1), c = 24.541(1) Å, β = 117.68(1)°, V = 10557.3(9) Å^3, D_c = 1.225 g cm^{-3}, Z = 8, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 1.817 mm^{-1}, 58633 reflections used, 18578 unique, R_1 = 0.043 ($I > 2.0\sigma(I)$), wR_2 = 0.077 on F^2. For **2**·$0.5C_6H_6$: $C_{91}H_{139}Li_2N_6Na_2O_4Yb_2$, M = 1787.02, monoclinic, space group $P2_1/n$, a = 17.839(4), b = 22.603(5), c = 25.919(5) Å, β = 93.75(3)°, V = 10428(4) Å^3, D_c = 1.138 g cm^{-3}, Z = 4, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 1.834 mm^{-1}, 11887 reflections used, 11887 unique, R_1 = 0.089 ($I > 2.0\sigma(I)$), wR_2 = 0.223 on F^2. For **3**·$0.5C_6H_6$: $C_{91}H_{137}Li_4N_6Na_2O_4Yb_2$, M = 1798.89, orthorhombic, space group $Pbcn$, a = 17.912(4), b = 25.454(5), c = 22.850(5) Å, V = 10418(4) Å^3, D_c = 1.147 g cm^{-3}, Z = 4, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 1.836 mm^{-1}, 18983 reflections used, 6245 unique, R_1 = 0.071 ($I > 2.0\sigma(I)$), wR_2 = 0.177 on F^2. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation. An empirical correction was applied using the SADABS program.[11] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[12] CCDC reference numbers 175639–175641. See http://www.rsc.org/suppdata/cc/b1/b110793c/ for crystallographic data in CIF or other electronic format.

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