Extremely bulky β-diketiminate complexes of calcium(II) and ytterbium(II)†

Brant Maitland[A], Andreas Stasch[A] and Cameron Jones[A,*]

ABSTRACT

The potassium salt of an extremely bulky β-diketiminate, [K(^{Ar*}Nacnac)] (^{Ar*}Nacnac, [(Ar*NCMe)$_2$CH]$^-$; Ar*, C$_6$H$_2$Me{C(H)Ph$_2$}$_2$-4,2,6) was reacted with either CaI$_2$ or YbI$_2$(THF)$_2$, which afforded [(^{Ar*}Nacnac)MI] (M = Ca or Yb). These are the first examples of structurally characterised, donor solvent-free, N-arene substituted β-diketiminato calcium and ytterbium complexes that incorporate a terminal iodide ligand. Reduction of [(^{Ar*}Nacnac)CaI] with sodium metal gave a complex product mixture, from which a few crystals of the β-diketiminate C–H activated product, [{Ca(μ-^{Ar*}Nacnac^{-H})}$_2$], were obtained and crystallographically characterised. In an attempt to form a terminal ytterbium hydride compound, treatment of [(^{Ar*}Nacnac)YbI] with K[HBEt$_3$] gave a good yield of the contact ion pair compound [(^{Ar*}Nacnac)Yb(HBEt$_3$)].

Keywords: β-diketiminate, bulky ligand, calcium, C–H activation, metal hydrides, metal–metal bonding, reduction, ytterbium.

Introduction

Over the past 50 years or so, the β-diketiminate (Nacnac) class of chelating, anionic N-donor ligand has proved invaluable to inorganic and organometallic chemists for the kinetic stabilisation of highly reactive complexes of metals from across the periodic table.[1] Of most relevance to the present study is the use of very bulky β-diketiminates to stabilise low-oxidation-state s-block metal complexes, e.g. [(Nacnac)MM(Nacnac)], from undergoing disproportionation to elemental metal and [M(Nacnac)$_2$], and to prevent β-diketiminato s-block metal hydride compounds, [{(Nacnac)MH}$_n$], from redistributing via the Schlenk equilibrium to saline metal hydrides, MH$_2$, and [M(Nacnac)$_2$].

Most success in low-oxidation-state s-block chemistry has come from dimagnesium(I) systems, the first bulky β-diketiminate coordinated example of which, [{(^{Dip}Nacnac)Mg}$_2$] (^{Dip}Nacnac, [(DipNCMe)$_2$CH]$^-$; Dip, 2,6-diisopropylphenyl), was reported in 2007.[2] Since that time, more than 20 other examples have emerged.[3] These display various substitution patterns, including N-aryl substituents that vary in steric bulk from xylyl[4] to 2,4,6-tricyclohexylphenyl (TCHP)[5] or 2,6-di(3-pentyl)phenyl (DiPep).[6] Indeed, the latter substituent has recently been utilised in the stabilisation of the first magnesium(0) complexes, [Na$_2${(^{ButDiPep}Nacnac)Mg}$_2$] and [(^{ButDiPep}Nacnac)MgMgMg(^{ButDiPep}Nacnac)] (^{ButDiPep}Nacnac, [(DiPepNCBu^t)$_2$CH]$^-$.[7] More than just chemical curiosities, low-oxidation-state magnesium complexes have been widely used around the globe as soluble, selective reducing agents in numerous inorganic and synthetic transformations.[3] Although no β-diketiminate complexes of other Group 2 metals in the 0 or +1 oxidation states have been isolated, it has been suggested that a calcium(I) complex is a transient intermediate in the reduction of N$_2$, which yields the only known examples of homometallic Group 2 dinitrogen complexes, e.g. [{(^{DiPep}Nacnac)(THF)Ca}$_2$(μ-N$_2$)] (^{DiPep}Nacnac, [(DiPepNCMe)$_2$CH]$^-$).[1][8]

---

†This invited submission is associated with the special issue of the *Australian Journal of Chemistry* that celebrates the 85th birthday of Professor Glen B. Deacon.

[1]N.B. one formally calcium(I) complex which does not contain a β-diketiminate ligand has been reported. See: Krieck S, Görls H, Yu L, Reiher M, Westerhausen M. *J. Am. Chem. Soc.* 2009, 131, 2977. doi:10.1021/ja808524y

β-Diketiminato Group 2 metal hydride complexes are more widespread than their low-oxidation-state counterparts. A good number of β-diketiminato magnesium[9] and calcium hydride complexes[10] have been reported, and these are finding increasing use in a variety of stoichiometric and catalytic synthetic transformations.[11] To date, there are no crystallographically characterised examples of β-diketiminato beryllium or barium hydrides, though one strontium hydride analogue has been reported.[12] In order to increase the reactivity of β-diketiminato Group 2 metal hydrides, it would be advantageous to have access to three-coordinate, terminal hydride examples, which should be more Lewis acidic and hydridic than their hydride bridged counterparts. There is, however, only one such compound known, [(Ar*Nacnac)MgH] (Ar*Nacnac, [(Ar*NCMe)$_2$CH]$^-$; Ar*, C$_6$H$_2$Me{C(H)Ph$_2$}$_2$-4,2,6), and this is prevented from dimerising through hydride bridges by the imposing steric bulk of its β-diketiminate ligand.[13]

Given the stability of [(Ar*Nacnac)MgH], it seemed that the Ar*Nacnac ligand might be able to stabilise other low-coordinate Group 2 metal hydride systems, or compounds that contain Group 2 metal–metal bonds. In this respect, β-diketiminato dicalcium(I) and terminal calcium(II) hydride complexes were targeted, as these compound types are unknown. Moreover, given the almost identical ionic radii of calcium(II) and ytterbium(II) (1.00 Å and 1.02 Å for six-coordinate complexes, respectively[14]), and the well-documented similar coordination chemistry of the metals,[15] attempts were made to prepare closely related ytterbium(I) and ytterbium(II) hydride complexes. Although none of the target complexes were accessible, rare examples of terminal iodo complexes of calcium(II) and ytterbium(II), bearing β-diketiminate ligands, were prepared. The characterisation of these precursor complexes, and the outcomes of their reductions, are described herein.

Results and discussion

As potential precursors to the target low-oxidation-state and hydrido complexes of calcium and ytterbium, β-diketiminato metal(II) iodides were synthesised. This involved the 1:1 reactions of [K(Ar*Nacnac)] with either CaI$_2$ or YbI$_2$(THF)$_2$ in THF. These reactions afforded compounds **1** and **2** in isolated yields of 70% and 64% respectively, as pale yellow or red crystalline solids, after workup (Scheme 1). Both compounds are thermally stable in solutions of normal organic solvents and in the solid state for weeks at ambient temperature under a dinitrogen atmosphere. They have moderate solubility in arene solvents, but are poorly soluble in aliphatics.

NMR spectra of **1** and **2** confirmed that there is no THF coordinated to the metal centres, despite the reactions being carried out in that strong donor solvent. This is unusual for such Lewis acidic metals, and suggests that intramolecular
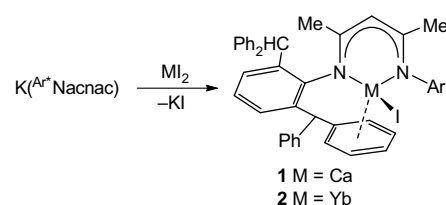
Scheme 1. Synthesis of compounds **1** and **2**.

metal–arene coordination, as seen in the solid-state structures, is preferable to THF coordination. However, in C$_6$D$_6$ solutions, the NMR spectra of the two compounds suggest more symmetrical solution state structures than in the solid state. That is, one signal each is seen for the ligand backbone methyl groups, and for the benzhydryl methine protons. One possibility for this observation is that there is fluxional exchange of coordination between the phenyl substituents of the Ar*Nacnac ligand, which is rapid on the NMR timescale. Attempts to probe the nature of this exchange by carrying out variable-temperature NMR spectroscopic studies on d_8-toluene solutions of the compounds were thwarted by their poor solubilities in this solvent at temperatures below 0°C. Moreover, no resonance was observed in the ^{171}Yb NMR spectrum of **2**.

The molecular structures of **1** and **2** are depicted in Fig. 1. The compounds are essentially isostructural, with the metal centres being chelated by the N centres of the Ar*Nacnac ligand, in addition to having a skewed η^6-interaction with one of its phenyl groups. As far as we are aware, there are no other examples of donor solvent-free, N-arene substituted β-diketiminato calcium and ytterbium complexes that incorporate a terminal iodide ligand. However, one related THF coordinated triketiminato complex has been recently structurally characterised.[16] Given the very similar ionic radii and coordination chemistry of Ca^{2+} and Yb^{2+}, it is not surprising that the bond lengths and angles involving both metal centres are very similar, and the majority of bond lengths lie within the known ranges for β-diketiminato calcium(II) and ytterbium(II) complexes (as determined from a survey of the Cambridge Crystallographic Database, version 2.0.4, October, 2021).[17] The exceptions here are the metal–iodine distances, which are shorter than in any other examples of this compound class, presumably owing to the fact that the iodide ligands are terminal.

With **1** and **2** in hand, their reductions with a variety of reducing agents, e.g. Na metal or KC$_8$, in both coordinating and non-coordinating solvents, were attempted. In each case, complex product mixtures were obtained, as determined by NMR spectroscopic analyses of the reaction solutions. In only one instance were a few crystals of the phenyl C–H activated calcium(II) product, **3**, obtained (Scheme 2). While it cannot be certain how **3** was formed, it seems reasonable that an initial reductive iodide elimination process yields a short-lived radical, (Ar*Nacnac)Ca. Instead of dimerising to give the
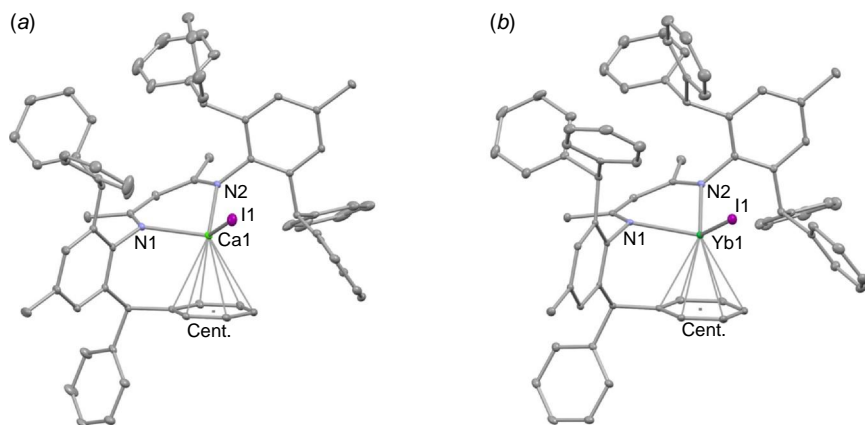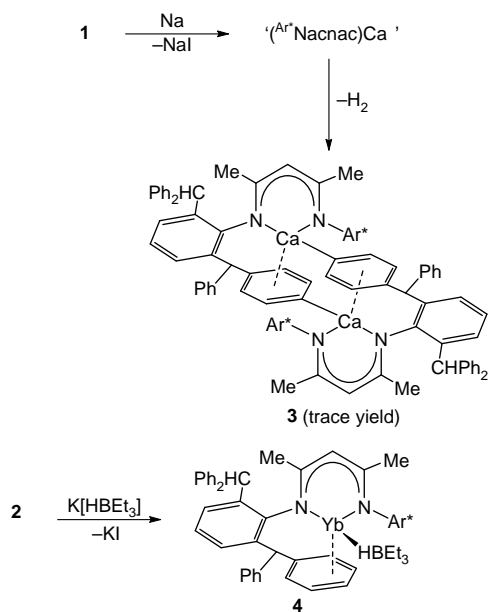
(a)

(b)

Fig. 1. ORTEP diagrams of (a) **1** and (b) **2** (20% thermal ellipsoids; hydrogen atoms omitted; Cent. = centroid). Selected bond lengths (Å) and angles (°) for **1**: I(1)–Ca(1) 2.9516(5), Ca(1)–N(2) 2.3275(19), Ca(1)–N(1) 2.3562(19), Ca(1)–Cent. 2.617(2), Ca–C$_{Ph}$ range: 2.852(2)–3.075(2), N(2)–Ca(1)–N(1) 82.30(6), I(1)–Ca(1)–Cent. 112.58 (5). Selected bond lengths (Å) and angles (°) for **2**: Yb(1)–N(2) 2.343(2), Yb(1)–N(1) 2.360(2), Yb(1)–I(1) 2.9630(2), Yb(1)–Cent. 2.537(3), Yb–C$_{Ph}$ range: 2.831(3)–2.964(3), N(2)–Yb(1)–N(1) 80.77(7), I(1)–Yb(1)–Cent. 113.82(1).

Scheme 2. Synthesis of compounds **3** and **4**.

Fig. 2. Molecular structure of **3** (20% thermal ellipsoids where shown; hydrogen atoms omitted, sections of Ar* substituents shown as wireframe for clarity). Selected bond lengths (Å) and angles (°): Ca(1)–N(1) 2.3333(15), Ca(1)–N(2) 2.4032(16), Ca(1)–C(17)′ 2.549(2), Ca(1)–Cent. 2.540(2), Ca(1)–C$_{Ph}$ range: 2.800(2)–3.012(2), N(1)–Ca(1)–N(2) 80.63(5), C(17)′–Ca(1)–Cent. 104.18(5).

target Ca–Ca bonded compound, the Ca centre of one radical attacks a phenyl ring of another, leading to loss of dihydrogen, and the formation of **3**. It is noteworthy that all previous attempts by us,[17] and others,[8] to prepare calcium(I) compounds bearing Ca–Ca bonds have met with failure.

Owing to the very low yield of **3**, no spectroscopic data could be acquired for the compound. However, its X-ray crystal structure was obtained, and the molecular structure is depicted in Fig. 2. This shows the compound to be centrosymmetric and bimetallic, with each Ca centre N,N-chelated by one deprotonated ^{Ar*}Nacnac ligand, while having an η^1-interaction with the deprotonated phenyl carbon centre of the opposing ligand. In addition, the calcium atoms are η^6-coordinated by the deprotonated phenyl group associated with the ^{Ar*}Nacnac^{-H} ligand chelating the metal centre. The Ca–N and Ca–centroid distances in **3** are normal for such interactions, and comparable with the analogous distances found for precursor complex **1**. Moreover, the Ca–C(17)′
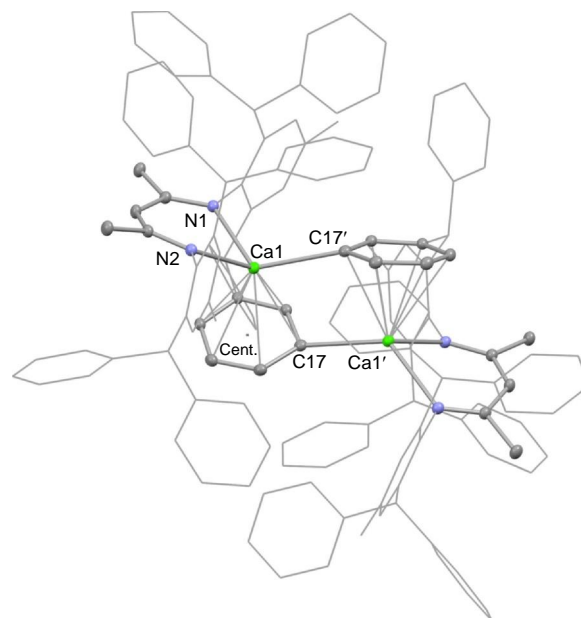
bond length (2.549(2) Å) is similar to those in related calcium phenyl compounds, e.g. 2.583(3) Å in *trans*-[CaPh (Br)(THF)$_4$].[19]

In light of the absence of β-diketiminato calcium or ytterbium terminal hydride complexes in the literature (cf. [(^{Ar*}Nacnac)MgH][13]),[20] it seemed reasonable that **1** and **2** could prove viable precursors to such target complexes. To this end, toluene solutions of either **1** or **2** were treated with the potential hydride transfer reagent K[HBEt$_3$]. Although no product could be isolated from the reaction involving **1**, that with **2** gave a good isolated yield (78%) of the purple crystalline ytterbium-borate contact ion pair **4**, on workup (Scheme 2). Therefore, the reaction did not proceed via
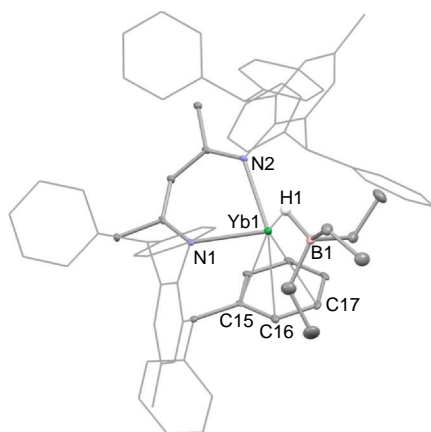
Fig. 3. Molecular structure of **4** (20% thermal ellipsoids where shown; hydrogen atoms omitted, sections of Ar* substituents shown as wireframe for clarity). Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.405(4), Yb(1)–N(2) 2.418(4), Yb(1)–C(16) 2.906(5), Yb(1)–C(15) 2.996(5), Yb(1)–C(17) 3.061(5), Yb(1)–H(1) 2.23(10), B(1)–H(1) 1.23(9), N(1)–Yb(1)–N(2) 79.96(13), C(16)–Yb(1)–H(1) 127(2).

hydride transfer, as initially predicted, but instead ceased after elimination of KI from the mixture of reagents. Although this is similar to the situation in related reactions between less bulky β-diketiminato calcium iodide compounds and K[HBR₃],[21] it was thought that the extreme steric bulk of the ^{Ar*}Nacnac ligand might force elimination of BEt₃, and formation of (^{Ar*}Nacnac)YbH. Clearly, this did not prove to be the case.

Compound **4** is thermally stable in solutions of common organic solvents, and in the solid state, for weeks at ambient temperature under a dinitrogen atmosphere. As was the situation with the precursor complex **2**, the NMR spectra for the ytterbium borate species suggest a more symmetrical structure in solution than was observed in the solid state. Similarly to **2**, this likely occurs owing to a dynamic exchange between ytterbium coordinated and uncoordinated phenyl groups of the ^{Ar*}Nacnac ligand. Variable-temperature NMR spectroscopic studies of **4** were hampered by the low solubility of the compound in non-coordinating deuterated solvents at temperatures below 0°C.

The molecular structure of **4** is shown in Fig. 3. The compound is a contact ion pair, involving a [(^{Ar*}Nacnac)Yb]$^+$ cation and a [HBEt₃]$^-$ anion that associate through a bridging hydride, H(1). The structure of **4** is closely related to that of the β-diketiminato calcium borate compound [(^{Dip}Nacnac)(THF)Ca(HBBu^{sec}₃)],[21] though in that system the metal centre is additionally coordinated by a THF molecule. In contrast, the ytterbium atom in **4** is N,N-chelated by the ^{Ar*}Nacnac ligand, while also having what is best described as an η³-interaction with a phenyl substituent of that ligand. The apparently weaker ytterbium–arene interaction in **4**, relative to that in **2**, probably originates from the greater steric bulk of the HBEt₃ unit, relative

to iodide, which destabilises the ytterbium–arene interaction in the former.

Conclusion

In conclusion, reactions of the potassium salt of an extremely bulky β-diketiminate ligand, [K(^{Ar*}Nacnac)], with either CaI₂ or YbI₂(THF)₂ have afforded the isostructural complexes [(^{Ar*}Nacnac)MI] (M = Ca or Yb), which represent the first examples of structurally characterised, donor solvent-free, N-arene substituted β-diketiminato calcium and ytterbium complexes that incorporate a terminal iodide ligand. Alkali metal reductions of both complexes led to complex product mixtures, from one of which a few crystals of a complex in which a C–H activated β-diketiminate ligand is coordinated to a calcium centre, were isolated. Attempts to synthesise terminal metal hydride complexes from [(^{Ar*}Nacnac)MI] were not successful, though reaction of [(^{Ar*}Nacnac)YbI] with K[HBEt₃] did give a good yield of the contact ion pair compound [(^{Ar*}Nacnac)Yb(HBEt₃)]. We continue to explore the kinetic stabilisation of low-oxidation-state and hydrido complexes of Group 2 and f-block metals.

Experimental

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high-purity dinitrogen. THF, toluene and hexane were distilled over molten potassium. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance III 400 spectrometer and are referenced to the resonances of the solvent used. The chemical shifts δ are reported in parts per million (ppm). Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid-state probe. FTIR spectra were collected for solid samples, as Nujol mulls, on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. [K(^{Ar*}Nacnac)] was prepared by the literature procedure.[13] All other reagents were used as received from commercial sources.

Preparation of [(^{Ar*}Nacnac)CaI] (1)

A suspension of [K(^{Ar*}Nacnac)] (3.20 g, 3.09 mmol) and CaI₂ (1.00 g, 3.40 mmol) in THF (80 mL) was stirred overnight at room temperature. The resultant reaction mixture was dried under vaccuum, and the residue extracted with toluene (20 mL). Hexane (5 mL) was slowly added to the orange extract until an off-white solid began to precipitate. The mixture was then stored overnight at 4°C to give pale

yellow crystals of **1** (2.38 g, 70%). Mp 104–107°C. ^{1}H NMR (400 MHz, 303 K, C_6D_6): δ 1.03 (s, 6H, NCCH$_3$), 1.87 (s, 6H, ArCH$_3$), 4.54 (s, 1H, CCHC), 5.74 (s, 4H, Ph$_2$CH), 6.77 (t, ^{3}J 7.2 Hz, 4H, Ar–H), 7.03–7.08 (m, 8H, Ar–H), 7.12 (t, ^{3}J 7.2 Hz, 8H, Ar–H), 7.17–7.22 (m, 16H, Ar–H), 7.48 (d, ^{3}J 8 Hz, 8H, Ar–H). ^{13}C{^{1}H} NMR (100 MHz, 303 K, C_6D_6): δ 19.8 (NCCH$_3$), 21.6 (Ar–CH$_3$), 51.4 (Ph$_2$CH), 94.5 (CCHC), 125.5, 125.6, 127.3, 128.4, 129.0, 129.0, 129.1, 132.4, 137.7, 141.1, 143.5, 144.9 (Ar-C), 167.0 (NCCH$_3$). IR (Nujol, cm^{-1}): 1597 w, 1514 w, 1030 w, 924 w, 856 w, 834 w, 774 w, 744 m. MS (electron impact, EI) (*m/z*, %): 942.4 (^{Ar*}NacnacH^{+}, 100). Elemental analysis for $C_{77}H_{75}N_2CaI$ (**1**.hexane): calc.: 77.36; H, 6.32; N, 2.34%; found: C, 77.46; H, 6.45; N, 2.38%.

Preparation of [(^{Ar*}Nacnac)YbI] (2)

A solution of [K(^{Ar*}Nacnac)] (0.800 g, 0.819 mmol) in THF (10 mL) was added to a solution of YbI$_2$(THF)$_2$ (0.514 g, 0.9 mmol) in THF (20 mL) at 0°C. The mixture was warmed to room temperature and stirred for 12 h, before being dried under vaccuum. The residue was extracted with toluene (20 mL) and the extract cooled to −30 °C to afford dark red crystals of **2** (0.650 g, 64%). Crystals for the X-ray diffraction experiment were grown from benzene. Mp 206–210°C. ^{1}H NMR (400 MHz, 303 K, C_6D_6): δ 1.03 (s, 6H, NCCH$_3$), 1.86 (s, 6H, ArCH$_3$), 4.56 (s, 1H, CCHC), 5.78 (s, 4H, Ph$_2$CH), 6.73 (s, 4H, Ar–H), 6.90–7.30 (m, 32H, Ar–H), 7.50 (s, 8H, Ar–H). ^{13}C{^{1}H} NMR (100 MHz, 303 K, C_6D_6): δ 19.8 (NCCH$_3$), 23.1 (Ar–CH$_3$), 51.3 (Ph$_2$CH), 95.0 (CCHC), 125.3, 125.4, 127.3, 128.0, 128.8, 129.0, 129.1, 132.3, 137.7, 141.0, 142.9, 144.7 (Ar-C), 166.7 (NCCH$_3$). No signal was observed in the ^{171}Yb NMR spectrum of the compound. IR (Nujol, cm^{-1}): 1516 w, 1493 m, 1030 m, 924 w, 861 w, 764 w, 745 m, 734 m. MS/EI (*m/z*, %): 1242.7 (M^{+}, 1), 942.4 (^{Ar*}NacnacH^{+}, 26). Elemental analysis for $C_{78}H_{69}N_2YbI$ (**2**.toluene): calc.: C, 70.21; H 5.21; N, 2.10%; found: C, 70.44; H, 5.21; N, 2.38.

Preparation of [(^{Ar*}Nacnac)Yb(HBEt$_3$)] (4)

A solution of K[HBEt$_3$] in THF (1.00 M, 0.290 mmol, 0.29 mL) was added to a solution of **2** (0.300 g, 0.242 mmol) in toluene (15 mL) at −30°C. The reaction mixture was warmed to room temperature and then stirred for 1 h. The mixture was then filtered and volatiles removed under vaccum, leaving a purple reside. A hexane extract of this residue (25 mL) was cooled to −40°C to give **4** as purple crystals (0.230 g, 78%). Mp 199–202°C. ^{1}H NMR (400 MHz, 303 K, C_6D_6): δ 0.30–0.42 (m, 6H, BCH$_2$), 0.78 (s, 6H, NCCH$_3$), 1.00 (m, 9H, BCH$_2$CH$_3$), 1.95 (s, 6H, ArCH$_3$), 4.38 (s, 1H, CCHC), 5.87 (s, 4H, Ph$_2$CH), 6.86–6.94 (m, 4H, Ar–H), 6.96–7.15 (m, 20H, Ar–H), 7.16–7.28 (m, 12H, Ar–H), 7.44 (d, ^{3}J 6.8 Hz, 8H, Ar–H). The BH resonance was not observed. ^{13}C{^{1}H} NMR (100 MHz, 303 K, C_6D_6):

δ 12.3 (BCH$_2$), 15.4 (BCH$_2$CH$_3$), 19.8 (NCCH$_3$), 22.8 (ArCH$_3$), 51.7 (Ph$_2$CH), 94.5 (CCHC), 125.3, 125.7, 127.3, 127.9, 128.9, 131.8, 137.0, 141.7, 143.4, 144.2 (Ar-C), 166.7 (NCCH$_3$). IR (Nujol, cm^{-1}): 1912 m, 1494 m, 1030 m, 1014 m, 922 m, 764 s, 742 s, 733 s, 697 s. MS/EI (*m/z*, %): 942.8 (^{Ar*}NacnacH^{+}, 100). Elemental analysis for $C_{77}H_{77}BN_2Yb$: calc.: C, 76.16; H, 6.39; N, 2.31%; found: C, 76.30; H, 6.34; N, 2.39.

X-ray crystallography

Crystals suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made with either an Xcalibur Gemini Ultra diffractometer with Mo Kα radiation (λ 0.71073 Å), or the MX1 beamline of the Australian Synchrotron (λ 0.71090 Å). The software package Blu-Ice[22] was used for synchrotron data acquisition, while the program XDS[23] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-16[24]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarised in Supplementary Table S1. Crystallographic data (CIF files) for all structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2118520–2118523).

Supplementary material

Crystal data, details of data collections and refinement for all structures are available in the Supplementary material online.

References

[1] (a) Bourget-Merle L, Lappert MF, Severin JR. *Chem Rev* 2002; 102: 3031. doi:10.1021/cr010424r
(b) Tsai Y-C. *Coord Chem Rev* 2012; 256: 722. doi:10.1016/j.ccr.2011.12.012
(c) Webster RL. *Dalton Trans* 2017; 46: 4483. doi:10.1039/c7dt00319f
(d) Asay M, Jones C, Driess M. *Chem Rev* 2011; 111: 354. doi:10.1021/cr100216y
(e) Camp C, Arnold J. *Dalton Trans* 2016; 45: 14462. doi:10.1039/C6DT02013E
[2] Green S, Jones C, Stasch A. *Science* 2007; 318: 1754. doi:10.1126/science.1150856
[3] (a) Jones C. *Nat Rev Chem* 2017; 1: 0059. doi:10.1038/s41570-017-0059
(b) Stasch A, Jones C. *Dalton Trans* 2011; 40: 5659. doi:10.1039/C0DT01831G
(c) Jones C. *Commun Chem* 2020; 3: 159. doi:10.1038/s42004-020-00408-8
(d) Jones C, Stasch A. *Top Organomet Chem* 2013; 45: 73. doi:10.1007/978-3-642-36270-5_3
[4] Bonyhady SJ, Collis D, Holzmann N, Edwards AJ, Piltz RO, Frenking G, Stasch A, Jones C. *Nat Commun* 2018; 9: 3079. doi:10.1038/s41467-018-05504-x
[5] Yuvaraj K, Iskander I, Jones DDL, Maron L, Jones C. *Chem Sci* 2020; 11: 3516. doi:10.1039/d0sc00836b

[6] Gentner TX, Rösch B, Ballmann G, Langer J, Elsen H, Harder S. *Angew Chem, Int Ed* 2019; 58: 607. doi:10.1002/anie.201812051

[7] (a) Rösch B, Gentner TX, Eyselein J, Langer J, Elsen H, Harder S. *Nature* 2021; 592: 717. doi:10.1038/s41586-021-03401-w
(b) Jones C. *Nature* 2021; 592: 687. doi:10.1038/d41586-021-01014-x

[8] Rösch B, Gentner TX, Langer J, Färber G, Eyselein J, Zhao L, Ding C, Frenking G, Harder S. *Science* 2021; 371: 1125. doi:10.1126/science.abf2374

[9] (a) Green SP, Jones C, Stasch A. *Angew Chem Int Ed* 2008; 47: 9079. doi:10.1002/anie.200803960
(b) Lalrempuia R, Kefalidis CE, Bonyhady SJ, Schwarze B, Maron L, Stasch A, Jones C. *J Am Chem Soc* 2015; 137: 8944. doi:10.1021/jacs.5b06439
(c) deBruin-Dickason CN, Rosengarten CA, Deacon GB, Jones C. *Chem Commun* 2021; 57: 1599. doi:10.1039/D0CC07947B

[10] (a) Wilson ASS, Hill MS, Mahon MF, Dinoi C, Maron L. *Science* 2017; 358: 1168. doi:10.1126/science.aao5923
(b) Harder S, Brettar J. *Angew Chem Int Ed* 2006; 45: 3474. doi:10.1002/anie.200601013

[11] See, for example: (a) In: S Harder, editor. Alkaline-Earth Metal Compounds: Oddities and Applications. Heidelberg: Springer; 2013
(b) Hill MS, Liptrot DJ. *Chem Soc Rev* 2016; 45: 972. doi:10.1039/C5CS00880H
(c) Mukherjee B, Scuhknecht D, Okuda J. *Angew Chem Int Ed* 2018; 57: 9590. doi:10.1002/anie.201801869

[12] Rosch B, Gentner TX, Elsen H, Fischer CA, Langer J, Wiesinger M, Harder S. *Angew Chem Int Ed* 2019; 58: 5396. doi:10.1002/anie.201901548

[13] Arrowsmith M, Maitland B, Kociok-Kohn G, Stasch A, Jones C, Hill MS. *Inorg Chem* 2014; 53: 10543. doi:10.1021/ic501638v

[14] Shannon RD. *Acta Crystallogr* 1976; A32: 751. doi:10.1107/S0567739476001551

[15] Ruspic C, Spielmann J, Harder S. *Inorg Chem* 2007; 46: 5320. doi:10.1021/ic700403d

[16] Skvortsov GG, Fukin GK, Cherkasov AV, Kovylina TA, Trifonov AA. *Inorg Chem Acta* 2020; 508: 119623. doi:10.1016/j.ica.2020.119623

[17] Bonyhady SJ, Jones C, Nembenna S, Stasch A, Edwards AJ, McIntyre GJ. *Chem Eur J* 2010; 16: 938. doi:10.1002/chem.200902425

[18] Jones C, Nembenna S, Stasch A. *J Chem Crystallogr* 2011; 41: 1490. doi:10.1007/s10870-011-0128-1

[19] Fischer R, Gärtner M, Görls H, Westerhausen M. *Organometallics* 2006; 25: 3496. doi:10.1021/om060360g

[20] For examples of hydride bridged β-diketiminato ytterbium(II) compounds see ref. [15], and Richardson GM, Douair I, Cameron SA, Bracegirdle J, Keyzers RA, Hill MS, Maron L, Anker MD. *Nat Commun* 2021; 12: 3147. doi:10.1038/s41467-021-23444-x

[21] Sarish SP, Jana A, Roesky HW, Schulz T, John M, Stalke D. *Inorg Chem* 2010; 49: 3816. doi:10.1021/ic902338r

[22] McPhillips TM, McPhillips SE, Chiu HJ, Cohen AE, Deacon AM, Ellis PJ, Garman E, Gonzalez A, Sauter NK, Phizackerley RP, Soltis SM, Kuhn P. *J Synchrotron Rad* 2002; 9: 401. doi:10.1107/S0909049502015170

[23] Kabsch W. *J Appl Cryst* 1993; 26: 795. doi:10.1107/S0021889893005588

[24] Sheldrick GM. SHELX-16. University of Göttingen; 2016.

Author affiliation
[A]School of Chemistry, PO Box 23, Monash University, Melbourne, Vic., 3800, Australia.