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Synthesis and characterization of β-diketiminate lanthanide complexes: the effect of the bulkiness of ancillary ligand on the reaction

Yingming Yao [a], Mingqiang Xue [a], Yunjie Luo [a], Zhenqin Zhang [a], Rui Jiao [a], Yong Zhang [a], Qi Shen [a,*], Wingtak Wong [b], Kaibei Yu [c], Jie Sun [d]

[a] *Department of Chemistry and Chemical Engineering, Suzhou University, 1 Shizi Street, Suzhou 215006, PR China*
[b] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China*
[c] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, PR China*
[d] *Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China*

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Abstract

The reactions of ytterbium dichlorides with different β-diketiminate ligand ((Ar)NC(Me)CHC(Me)N(Ar′), Ar = Ar′ = C_6H_5 (L^1); Ar = Ar′ = 2,6-Me_2–C_6H_3 (L^2); Ar = C_6H_5, Ar′ = 2, 6-Pr^i_2-C_6H_3 (L^3)) with 1 equiv of Cp′Na were studied. It was found that the bulkiness of β-diketiminate ligand and cyclopentadienyl group both have significant effect on the above reaction. For less bulky ligands L^1 and L^2, the reaction affords not the expected mixed-ligand ytterbium chloride, (C_5H_5)YbLCl or $(CH_3C_5H_4)$YbCl, but the ligand-redistributed product $(C_5H_5)_2$YbL or $(CH_3C_5H_4)_2$YbL. For bulkier ligand L^3, the desired anionic ytterbium chloride $(C_5H_5)YbL^3(\mu\text{-}Cl)_2Li(THF)_2$ is obtained. For the smallest ligand L^1, the expected ytterbium monochloride can also be obtained using bulky C_5Me_5Na as reactant. Each of these complexes was well characterized, while several have been characterized by X-ray diffraction structure determination.

Keywords: Organolanthanides; β-Diketiminate ligand; Synthesis; Reactivity; Crystal structures

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1. Introduction

The β-diketiminates have been the subject of intense interest in recent years [1] and complexes incorporating main group metals [2–17], and transition metals [18–39], and lanthanides [40–45] have been reported. These ligands have several attractive features. β-Diketiminate ligands and cyclopentadienyl anions are isoelectronic, and both of them are monoanions in their deprotonated forms; the steric and electronic properties of β-diketiminate ligands can be readily altered through an appropriate choice of amine and β-diketone used in their synthesis, and they can coordinate to the metal center in different bonding models ranging from purely σ to a combination of σ and π donation [46]. In particular, some of these β-diketiminate complexes have found potential applications as homogeneous polymerization catalysts. For example, β-diketiminate zinc complexes can catalyze the alternating copolymerization of CO_2 and epoxides [18,22], and stereocontrol polymerization of lactide [23]; cationic β-diketiminate scandium methyl complexes have ethylene polymerization activities comparable to those of metallocenes [19]. However, the synthesis and reactivity of mixed–ligand complexes containing β-diketiminate and cyclopentadienyl groups have received scant attention [30,36].

We have recently reported that β-diketiminate ligand $(DIPPh)_2$nacnac ($(DIPPh)_2$nacnac = *N*,*N*-2,6-diisopropylphenyl-2,4-pentanediimine anion) with two 2,6-dii-

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* Corresponding author. Tel.: +86-512-65112513; fax: +86-512-65112371.
E-mail address: qshen@suda.edu.cn (Q. Shen).

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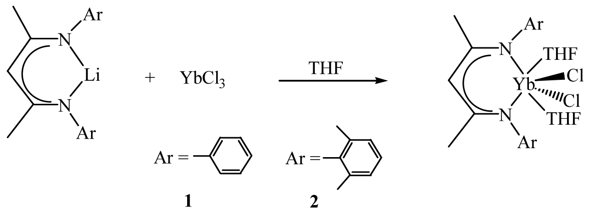
sopropylphenyl groups on the nitrogen atoms is a ideal ligand for the synthesis of mixed-ligand lanthanide chloride with β-diketiminate and cyclopentadienyl. These kinds of complexes are important precursors for the synthesis of the corresponding alkyl, or amido complexes [40]. Therefore, it is interesting to further study on the synthesis of these complexes with different β-diketiminates in understanding the relationship between the coordination environment of metal center and their reactivity. It is unexpected that the ligand redistribution occurred when ytterbium dichloride with less bulky β-diketiminate (here, R′ = Ph or 2,6-Me_2Ph) reacted with 1 equiv of C_5H_5Na, and the product $(C_5H_5)_2YbL$ in stead of the desired $(C_5H_5)YbLCl$ was obtained. Thus, the effect of the bulkiness of β-diketiminate and cyclopentadienyl groups on the reaction pathway was studied, respectively. In this paper, we report these results.

2. Results and discussion

2.1. Synthesis

The metathesis reaction with anhydrous ytterbium chloride was carried out smoothly with freshly prepared LLi to give the desired dichlorides $LYbCl_2(THF)_2$ (L = PhNC(Me)CHC(Me)NPh (L^1, **1**), L = (2,6-Me_2)PhNC(Me)CHC(Me)NPh(2,6-Me_2) (L^2, **2**) in high yield even for β-diketiminate (L^1), which has no substituent on the arene rings. Complex **1** was directly isolated as red precipitate from the reaction solution due to its sparing solubility in THF. For complex **2**, red microcrystals were obtained after crystallization from toluene. The IR spectra of these complexes exhibited the strong absorptions near 1550 and 1530 cm^{-1}, which were consistent with partial C=N double bond character [47]. Complex **2** was also characterized by X-ray structure analysis (Scheme 1).

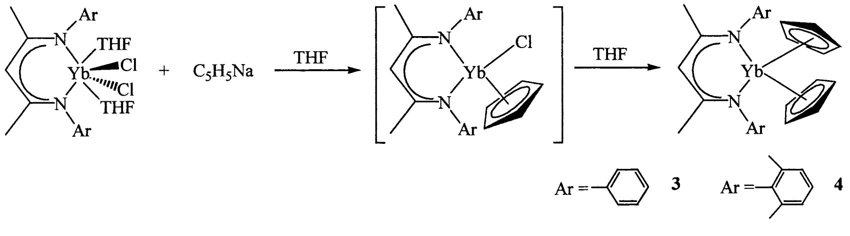


Scheme 1.

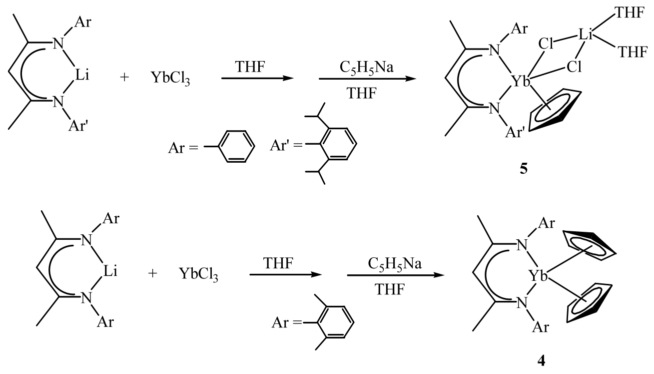
The further reaction of above ytterbium dichlorides with 1 equiv of C_5H_5Na in THF at room temperature, after workup, gave orange–red crystals. Quite surprisingly, the crystals were identified to be $(C_5H_5)_2YbL$ (L = L^1, **3**; L^2, **4**), not the desired products $(C_5H_5)YbLCl$. It seems that in our present case, the chloride $(C_5H_5)YbLCl$ is not stable enough, and will transform immediately to the most stable one $(C_5H_5)_2YbL$ (Scheme 2). In comparison with the results by the similar reaction with $[(DIPPh)_2nacnac]YbCl_2(THF)_2$, in which the mixed ligand ytterbium chloride can be isolated in high yields [40], it can be supposed that the bulkiness of β-diketiminate ligand is the key point for the synthesis of mixed-ligand lanthanide chloride with β-diketiminate and cyclopentadienyl.

In order to confirm further, we design a new more bulky β-diketimine L^3H (**9**) with a phenyl and a 2,6-diisopropylphenyl on the two N atoms, respectively, and did the reaction of $YbCl_3$ with freshly prepared L^3Li (from L^3H with *n*-BuLi in toluene), followed with C_5H_5Na in THF. After workup, the expected chloride stabilized by lithium chloride, $(C_5H_5)YbL^3(\mu\text{-}Cl)_2Li(THF)_2$ (**5**), was really obtained in good yield as orange microcrystals. In order to elucidate the effect of the coordinated lithium chloride, we also tried the one pot reaction of $YbCl_3$ with L^2Li and C_5H_5Na. However, the product isolated for this reaction is still a ligand-redistributed product $(C_5H_5)_2YbL^2$ (**4**) (Section 4.6.2) (Scheme 3). From these results it might be concluded that to construct a suitable coordination environment around the central metal is crucial for stabilizing the β-diketiminate-cyclopentadienyl ytterbium chloride.

We considered that the desired steric congestion around the lanthanide metal should also be constructed by change the bulkiness of the other ancillary ligand, i.e. choosing a suitable substituted cyclopentadienyl as another ancillary ligand, the ligand redistribution should also be suppressed. First, we tried the reaction of complex **2** with 1 equiv of $CH_3C_5H_4Na$ in THF. After workup, still the unexpected products, $(CH_3C_5H_4)_2YbL^2$ (**6**) was isolated. This result indicated that the $CH_3C_5H_4^-$ group is still not bulky enough. Then, we did another reaction with complex **1** (the smallest β-diketiminate as ancillary ligand) and bulky



Scheme 2.



Scheme 3.

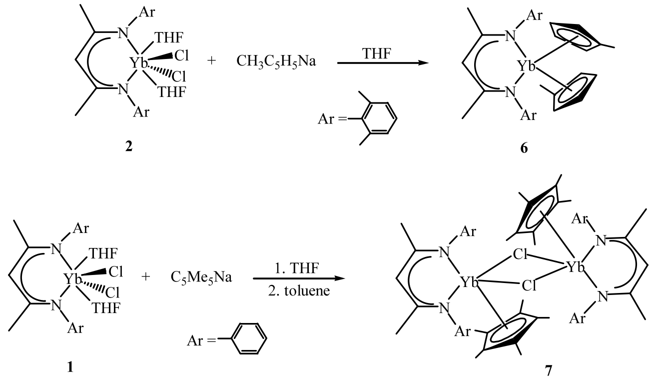
C_5Me_5Na as the reactants. At last, a desired complex $[(C_5Me_5)YbL^1(\mu\text{-}Cl)]_2$ (**7**) was really obtained as an only product (Scheme 4). These results reveal that choice suitable bulkiness of β-diketiminate and cyclopentadienyl are both important for the synthesis of mixed-ligand lanthanide chloride supported by β-diketiminate and cyclopentadienyl.

2.2. Crystal structure determination

*2.2.1. $L^2YbCl_2(THF)_2$ (**2**)*

The molecular structure of complex **2** is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. The ytterbium atom is six-coordinate with two nitrogen atoms of the β-diketiminate ligand, two chloride, and two THF molecules in a distorted octahedron. The molecular structure establishes cis disposition of the THF molecules, and trans disposition of the chlorine atoms.

The β-diketiminate ligand is symmetrically coordinated to the ytterbium atom with the variation in Yb–N bond lengths of 0.004 Å (2.300(4) and 2.304(4) Å, respectively), which is similar to that found in $L^1GdBr_2(THF)_2$ [45]. Two Yb–Cl bond lengths of 2.557(1) and 2.538(1) Å are apparently shorter than that in $[(DIPPh)_2nacnac]YbCl(\mu\text{-}Cl)_3Yb[(DIPPh)_2nacnac](THF)$ [40]. The bond distances of C(1)–C(2), C(2)–C(3), N(1)–C(1) and N(2)–C(3) lie intermediate between the corresponding single- and double-bond distances (see Table 1), which suggest significant delocalization within the π-system of β-diketiminate backbone. The Yb–C(1, 2, 3) distances are quite long, suggesting a negligible π contribution to the β-diketiminate–Yb bonding in this complex.



Scheme 4.

*2.2.2. $(C_5H_5)_2YbL^1$ (**3**) and $(CH_3C_5H_4)_2YbL^2$ (**6**)*

The molecular structures of complexes **3** and **6** are shown in Figs. 2 and 3, and their selected bond lengths and angles are listed in Tables 2 and 3, respectively. Both complexes **3** and **6** have unsolvated monomeric structure in the solid state with ytterbium atom bound to two nitrogen atoms of the β-diketiminate ligand, and two cyclopentadienyl rings. The geometry about the ytterbium center is best described as a distorted tetrahedron. In complex **6**, two methyl groups of the methylcyclopentadienyl adopt trans conformation.

The β-diketiminate ligand is symmetrically coordinated to the ytterbium atom in **3** and **6**. There is the expected pattern of delocalization within the β-diketiminate ligand. The backbone of the ligand (NC_3N) and ytterbium atom form a stable six-membered ring which adopts a boat conformation. In complex **3**, C(8) and Yb lying 0.14 and 0.90 Å out of the NC_2N plane, respectively; in complex **6**, C(10) and Yb lying 0.19 and 1.12 Å out of the NC_2N plane, respectively. The quite long distances between Yb and the carbon atoms of the backbone of the β-diketiminate ligand in these two complexes reveal that the β-diketiminate ligand is only an N,N′-bonded chelate.

*2.2.3. $(C_5H_5)YbL^3(\mu\text{-}Cl)_2Li(THF)_2$ (**5**)*

A drawing of complex **5** is shown in Fig. 4, and selected bond distances and angles are listed in Table 4. Complex **5** is a lithium chloride stabilized mixed-ligand ytterbium chloride. The coordination sphere of the Yb center is composed of two nitrogen atoms of a β-diketiminate anion, and the cyclopentadienyl group, and two chloride to form a distorted pyramidal geometry with Cl(1), Cl(2), N(1), and N(2) coplanar, and the Cp centroid vertex, the formal coordination number of the central metal is seven.

In complex **5**, the β-diketiminate ligand has some η^5-character. The Yb–C(13, 14, 15), distances are 2.904(4), 2.840(4), and 2.780(4) Å, respectively, which are well comparable with the Yb–C bond distances in the indisputably π-arene bonded $Yb(\eta^6\text{-}C_6Me_6)(AlCl_4)_3\text{-}(MeC_6H_5)$ [48]. This indicates that the complex involves π coordination of the β-diketiminate ligand to the ytterbium atom, which is different from those found in complexes **2**, **3**, and **6**.

The Yb–C(ring) distances range from 2.605(4) to 2.616(4) Å. The averaged Yb–C(ring) distance of 2.609(5) Å is comparable with those in $[(C_5H_5)_2YbCl]_2$

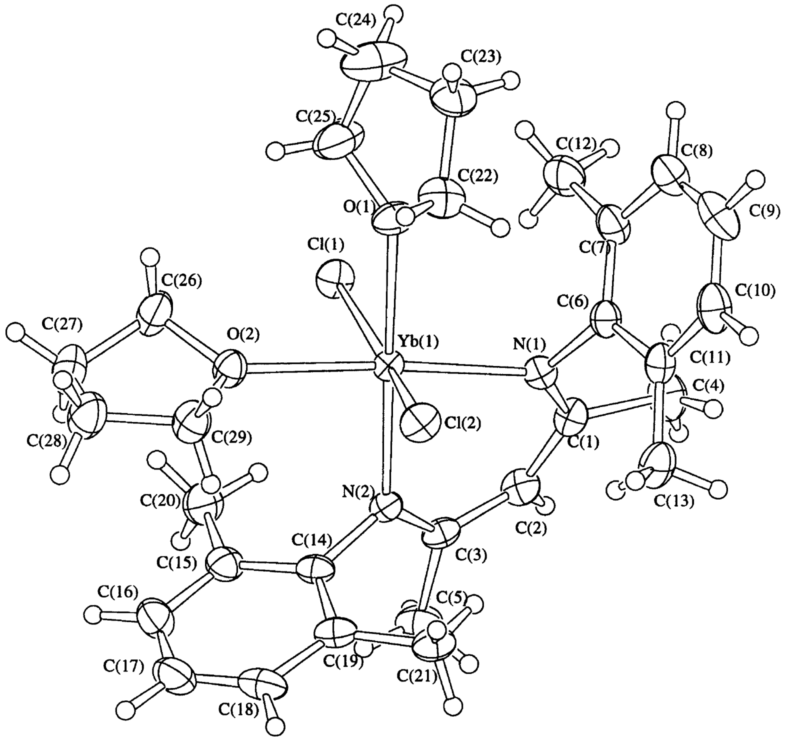


Fig. 1. Molecular structure of complex **2**.

(2.58(6) Å) [49], and $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(Et_2O)_2$ (2.610(3) Å) [50]. The Yb–Cl bond lengths of 2.629(1), and 2.681(1) Å in complex **5** are apparently longer than those in $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(Et_2O)_2$ [50], which suggests that the steric repulsion play an important role.

2.2.4. $[(C_5Me_5)YbL^1(\mu\text{-}Cl)]_2$ (7)

The X-ray structure of complex **7** was also determined, and the molecular structure is depicted in Fig. 5, and selected bond lengths and angles are listed in Table 5. Complex **7** has dimeric structure in solid state, which is different from that of $(CH_3C_5H_4)Yb[(DIPPh)_2nacnac]Cl$ [40].

Table 1
Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths			
Yb–N(1)	2.300(4)	Yb–O(2)	2.368(4)
Yb–N(2)	2.304(4)	N(1)–C(1)	1.337(6)
Yb–Cl(1)	2.557(1)	N(2)–C(3)	1.337(6)
Yb–Cl(2)	2.538(1)	C(1)–C(2)	1.407(7)
Yb–O(1)	2.383(4)	C(2)–C(3)	1.388(7)
Bond angles			
N(1)–Yb–N(2)	80.3(1)	Cl(1)–Yb–Cl(2)	166.57(5)
N(1)–Yb–Cl(1)	93.0(1)	N(1)–Yb–Cl(2)	96.0(1)
N(2)–Yb–Cl(1)	94.1(1)	N(2)–Yb–Cl(2)	97.2(1)
O(1)–Yb–O(2)	85.9(1)	O(1)–Yb–N(1)	98.7(1)
O(1)–Yb–N(2)	178.8(1)	O(2)–Yb–N(1)	175.3(1)
O(2)–Yb–N(2)	95.0(1)	O(1)–Yb–Cl(1)	85.31(9)
O(1)–Yb–Cl(2)	83.49(9)	O(2)–Yb–Cl(1)	86.51(9)
O(2)–Yb–Cl(2)	85.32(9)	C(1)–C(2)–C(3)	129.3(5)

The β-diketiminate ligand is η^2-bonded to the ytterbium atom in this structure. The Yb–C(1), Yb–C(2), and Yb–C(3) distances are quite long, which indicates that there is only purely σ bonding. The β-diketiminate ligand is also symmetrically coordinated to ytterbium atom in complex **7**. The averaged Yb–C(ring) distance is 2.618(7) Å, which is comparable with those in complex **5**, and $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(Et_2O)_2$ [50]. The averaged Yb–Cl bond length of 2.571(3) Å in complex **7** is apparently shorter than that of 2.655(1) Å in complex **5**.

3. Conclusion

The reaction chemistry of β-diketiminate ytterbium complexes has been studied. The bulkiness of β-diketi-

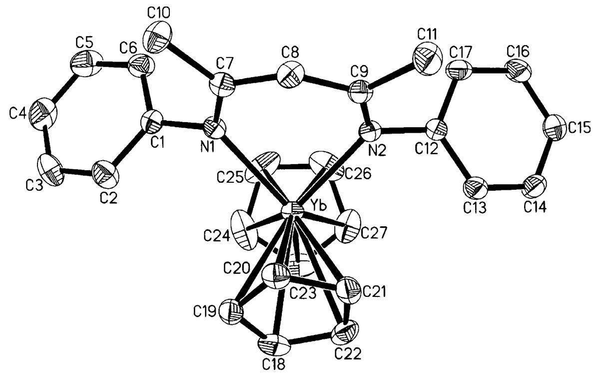


Fig. 2. Molecular structure of complex **3**.

Table 2
Selected bond lengths (Å) and angles (°) for complex **3**

Bond lengths			
Yb–N(1)	2.307(3)	N(1)–C(7)	1.325(5)
Yb–N(2)	2.290(3)	N(2)–C(9)	1.329(5)
Yb–Cent(1)	2.348	C(7)–C(8)	1.401(5)
Yb–Cent(2)	2.325	C(8)–C(9)	1.395(5)
Bond angles			
N(1)–Yb–N(2)	80.5(1)	C(7)–C(8)–C(9)	129.3(4)
Cent(1)–Yb–Cent(2)	128.2	Cent(1)–Yb–N(1)	110.3
Cent(1)–Yb–N(2)	106.6	Cent(2)–Yb–N(1)	110.6
Cent(2)–Yb–N(2)	110.3		

Cent(1) is the center of ring C(18)–C(22), Cent(2) is the center of ring C(23)–C(27).

Table 3
Selected bond lengths (Å) and angles (°) for complex **6**

Bond lengths			
Yb–N(1)	2.345(4)	N(1)–C(9)	1.324(6)
Yb–N(2)	2.301(4)	N(2)–C(11)	1.332(5)
Yb–Cent(1)	2.331	C(9)–C(10)	1.402(6)
Yb–Cent(2)	2.380	C(10)–C(11)	1.405(6)
Bond angles			
N(1)–Yb–N(2)	83.4(1)	C(9)–C(10)–C(11)	130.9(4)
Cent(1)–Yb–Cent(2)	127.3	Cent(1)–Yb–N(1)	110.6
Cent(1)–Yb–N(2)	105.3	Cent(2)–Yb–N(1)	107.9
Cent(2)–Yb–N(2)	113.6		

Cent(1) is the center of ring C(22)–C(26), Cent(2) is the center of ring C(28)–C(32).

minate ligand and cyclopentadienyl group has significant effect on the reaction pathway of the β-diketiminate ytterbium dichloride. Using less bulky β-diketiminate as ancillary ligands, the ligand redistribution occurred, when the ytterbium dichloride reacted with C_5H_5Na or $CH_3C_5H_4Na$ in 1:1 molar ratio in THF. There are two ways to suppress the ligand redistribution, the bulky β-diketiminate ligand was used or $C_5Me_5^-$ was used instead of $C_5H_5^-$ or $CH_3C_5H_4^-$. It also was already evident that there was a diversity of bonding modes possible for the β-diketiminate ligands in their ytterbium complexes: in complex **5**, the ligand is being η^5-bonded to the metal, whereas in complexes **2**, **3**, **6**, and **7**, it is an N,N′-bonded chelate.

4. Experimental

Reactions were performed under pure argon with exclusion of air and moisture by Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over Na or sodium benzophenone ketyl and distilled under argon prior to use. Anhydrous $YbCl_3$ [51], L^1Li [39] and L^2Li [38] were prepared according to the literature methods.

Melting points were determined in sealed argon filled capillaries and are uncorrected. Metal analyses were carried out using complexometric titration. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on an EA-1110 instrument, quoted data are the average of at least two independent determinations. The IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. ^{1}H-NMR spectra were recorded on a Varian-400 spectrometer in $CDCl_3$.

4.1. 2-(2,6-Diisopropylphenyl)aminopent-2-en-4-one (*8*)

A 20.0 cm^3 amount of 2,6-diisopropylaniline (0.106 mol) was added to a solution of 2,4-pentanedione (16.4 cm^3, 0.159 mol) in toluene (100 cm^3) in a round-bottomed flask. The resulting mixture was heated to reflux for 8 h, and water was removed as a toluene azeotrope using a Dean and Stark apparatus. The reaction mixture was then evaporated to dryness. The resulting solid was recrystallized from hexane to afford 2-(2,6-diisopropylphenyl)aminopent-2-en-4-one (**8**) (23.9 g, 87%). Anal. Calc. for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.80; H, 9.78; N, 5.33%. ^{1}H-

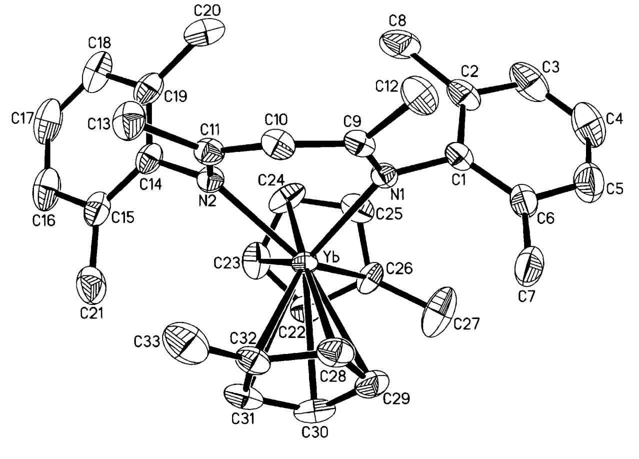


Fig. 3. Molecular structure of complex **6**.

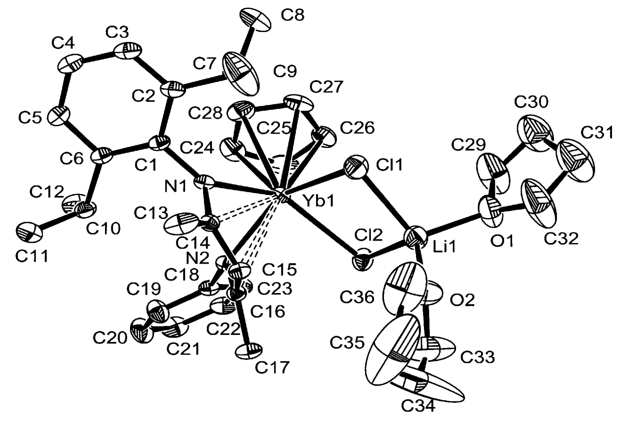


Fig. 4. Molecular structure of complex **5**.

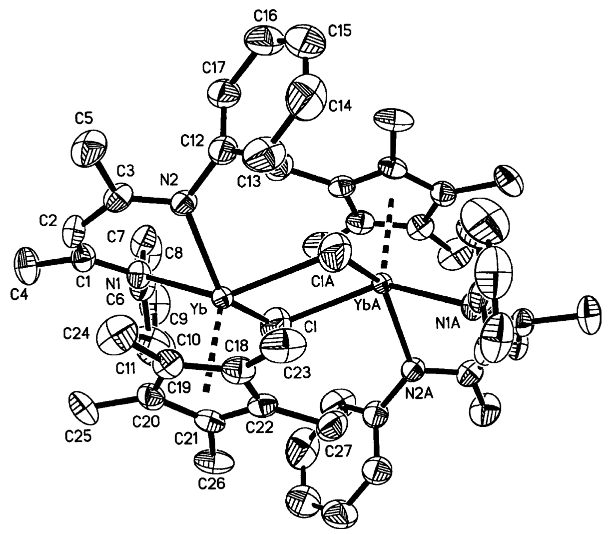


Fig. 5. Molecular structure of complex **7**.

NMR (400 MHz; $CDCl_3$): 1.14 (d, 6H, *CH_3*$CHCH_3$), 1.20 (d, 6H, CH_3CH*CH_3*), 1.64 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.99–3.06 (m, 2H, CH_3*CH*CH_3), 5.21 (s, 1H, C*H*=C(CH_3)N), 7.18 (d, 2H, aromatic protons), 7.28–7.32 (m, 1H, aromatic proton), 12.06 (s, 1H, N*H*).

4.2. 2-(2,6-Diisopropylphenyl)aminopent-2-en-4-(phenyl)imine L^3H (**9**)

Aniline hydrochloride (11.0 g, 0.085 mol), compound **8** (22 g, 0.085 mol), and 100 cm^3 of absolute EtOH were added to a 250 cm^3 round-bottomed flask. The reaction mixture was allowed to reflux for 4 h. The reaction solution was then evaporated to dryness. After stirring with 40 cm^3 saturated sodium carbonate, 2-(2,6-diisopropylphenyl)aminopent-2-en-4-(phenyl)imine L^3H was extracted into ethyl ether. Evaporation of solvent and recrystallization from hexane afforded L^3H as a white crystalline solid (17.0 g, 60%). Anal. Calc. for $C_{23}H_{30}N_2$: C, 82.59; H, 9.04; N, 8.37. Found: C, 82.52; H, 9.07; N, 8.37%. ^1H-NMR (400 MHz; $CDCl_3$): 1.12 (d, 6H, *CH_3*$CHCH_3$), 1.26 (d, 6H, CH_3CH*CH_3*), 1.72 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.96–3.03 (m, 2H, CH_3*CH*CH_3), 4.88 (s, 1H, C*H*=C(CH_3)N), 6.93–7.28 (m, 8H, aromatic protons), 12.70 (s, 1H, N*H*).

4.3. $L^1YbCl_2(THF)_2$ (**1**)

A solution of L^1Li (25 cm^3, 4.58 mmol) in toluene–hexane was slowly added to a suspension of $YbCl_3$ (1.28 g, 4.58 mmol) in 40 cm^3 THF at room temperature (r.t.). The color of the solution gradually changed to red. The reaction mixture was stirred overnight at r.t., then centrifugation to remove the solution. Complex **1** was obtained as a red powder (2.48 g, 85%). M.p. 175–178 °C (dec.). Anal. Calc. for $C_{25}H_{33}Cl_2N_2O_2Yb$: C, 47.10; H, 5.18; N, 4.39; Yb, 27.16. Found: C, 46.43; H, 5.22; N, 4.26; Yb, 27.62%. IR (KBr pellet, cm^{-1}) 3422(m), 2974(s), 2927(m), 2859(m), 1620(s), 1556(vs), 1535(vs), 1489(s), 1439(s), 1373(w), 1364(s), 1300(s), 1038(m), 760(m), 694(s).

4.4. $L^2YbCl_2(THF)_2$ (**2**)

A solution of L^2Li (35 cm^3, 5.47 mmol) in toluene–hexane was slowly added to a suspension of $YbCl_3$ (1.53 g, 5.47 mmol) in 50 cm^3 THF at r.t. The color of the solution gradually changed to red. The reaction mixture was stirred overnight at r.t. The solvent was removed in vacuum and toluene was added to extract the product. The dissolved portion was removed by centrifugation. The red micro crystals were obtained from the concentrated toluene solution at r.t. (2.96 g, 78%). M.p. 172–174 °C (dec.). Anal. Calc. for $C_{25}H_{33}Cl_2N_2O_2Yb$: C, 50.00; H, 6.37; N, 4.02; Yb, 24.83. Found: C, 49.66; H, 5.91; N, 4.08; Yb, 24.37%. IR (KBr pellet, cm^{-1}) 3418(m), 2967(s), 2923(m), 2847(m), 1597(m), 1559(vs), 1539(vs), 1474(s), 1443(m), 1381(m), 1364(s), 1300(s), 1044(m), 1096(w), 922(w), 764(m). Crystals suitable for X-ray crystal structure studies were obtained by recrystallization from toluene at r.t. in a few days.

4.5. $(C_5H_5)_2YbL^1$ (**3**)

To a THF suspension (30 cm^3) of compound **1** (3.29 g, 5.17 mmol) was slowly added a solution of C_5H_5Na (5.37 cm^3, 5.17 mmol) in THF at r.t. After being stirred for 24 h, the precipitate was separated by centrifugation and the solvent was evaporated completely under reduce pressure. Then ether was added to extract the product and the dissolved portion was separated by centrifugation. The orange–red crystals were obtained from concentrated ether solution at −10 °C for 3 days (1.08 g, 38%). M.p. 132–135 °C (dec.). Anal. Calc. for $C_{27}H_{27}N_2Yb$: C, 58.69; H, 4.92; N, 5.07; Yb, 31.32. Found: C, 59.01; H, 4.94; N, 5.07; Yb, 31.42%. IR (KBr pellet, cm^{-1}) 3445(m), 1632(s), 1597(s), 1559(vs), 1485(s), 1435(m), 1381(s), 1366(s), 1281(s), 1188(m), 1026(m), 748(s), 698(m). The crystals suitable for single crystal structure studies were obtained by recrystallization from ether solution at −10 °C for a week.

4.6. $(C_5H_5)_2YbL^2$ (**4**)

4.6.1. Method 1

The synthesis of compound **4** was carried out as described for **3**, but $L^2YbCl_2(THF)_2$ (**2**) (2.76 g, 3.98 mmol) was used in place of $L^1YbCl_2(THF)_2$ (**1**). The product was collected as orange–red microcrystals in two crops by filtration (0.78 g, 32%). M.p. 186–188 °C (dec.). Anal. Calc. for $C_{31}H_{35}N_2Yb$: C, 61.16; H, 5.80; N, 4.60; Yb, 28.43. Found: C, 61.06; H, 5.75; N, 4.60; Yb, 28.24%. IR (KBr pellet, cm^{-1}) 3449(m), 2920(w),

Table 4
Selected bond lengths (Å) and angles (°) for complex **5**

Bond lengths			
Yb–N(1)	2.330(2)	Yb–Cent(1)	2.320
Yb–N(2)	2.275(2)	Yb–C(14)	2.906(3)
Yb–Cl(1)	2.630(1)	Yb–C(15)	2.840(3)
Yb–Cl(2)	2.680(1)	Yb–C(16)	2.781(3)
Yb–C(24)	2.613(3)	Yb–Cent(2)	1.679
Yb–C(25)	2.605(3)	N(1)–C(14)	1.317(4)
Yb–C(26)	2.610(3)	N(2)–C(16)	1.343(4)
Yb–C(27)	2.606(3)	C(14)–C(15)	1.432(4)
Yb–C(28)	2.611(3)	C(15)–C(16)	1.403(4)
Yb–C(av)	2.609(3)		
Bond angles			
N(1)–Yb(1)–N(2)	78.34(8)	N(1)–Yb(1)–Cl(1)	89.56(6)
Cl(1)–Yb(1)–Cl(2)	82.38(3)	N(2)–Yb(1)–Cl(2)	82.91(6)
Cl(1)–Yb(1)–N(2)	136.49(6)	N(1)–Yb(1)–Cl(2)	142.90(6)
Yb(1)–Cl(1)–Li(1)	90.1(2)	Yb(1)–Cl(2)–Li(1)	89.1(2)
Cent(1)–Yb(1)–Cent(2)	97.57		

Cent(1) is the center of ring C(24)–C(28), Cent(2) is the center of ring N1, C(14)–C(16), N(2).

1624(s), 1555(vs), 1466(s), 1435(s), 1377(m), 1281(s), 1181(s), 1096(m), 1026(m), 768(s).

4.6.2. Method 2

To a slurry of anhydrous $YbCl_3$ (1.75 g, 6.26 mmol) in about 40 cm^3 THF was slowly added the solution of L^2Li (20 cm^3, 6.26 mmol) in toluene–hexane at r.t. After $YbCl_3$ disappeared completely, the THF solution of C_5H_5Na (9.8 cm^3, 6.26 mmol) was added slowly. The mixture was stirred at r.t. for another 48 h, and then the precipitate was removed from the reaction mixture by centrifugation. THF was completely removed in vacuum and ether was added to extract the product. The precipitation was removed again by centrifugation. The orange–red microcrystals were obtained from the concentrated ether solution at −10 °C (1.26 g, 33%).

4.7. $(C_5H_5)YbL^3(\mu\text{-}Cl)_2Li(THF)_2$ (**5**)

The synthesis of compound **5** was carried out as described for **4** (Section 4.6.2), but L^3Li (3.76 mmol) was used in place of L^2Li. The product was collected as orange microcrystals in two crops by filtration (2.0 g, 67%). M.p. 186–188 °C (dec.). Anal. Calc. for $C_{36}H_{50}Cl_2LiN_2O_2Yb$: C, 54.48; H, 6.35; N, 3.53; Yb, 21.80. Found: C, 54.23; H, 6.36; N, 3.49; Yb, 21.98%. IR (KBr pellet, cm^{-1}) 3441(s), 2963(m), 1628(s), 1559(vs), 1493(m), 1439(m), 1385(m), 1292(s), 1177(m), 1038(m), 752(m). The crystals suitable for single crystal structure studies were obtained by recrystallization from ether solution at −10 °C for a few days.

Table 5
Selected bond lengths (Å) and angles (°) for complex **7**

Bond lengths			
Yb–N(1)	2.340(5)	Yb–C(22)	2.594(7)
Yb–N(2)	2.328(5)	Yb–C(av)	2.618(7)
Yb–Cl(1)	2.563(3)	Yb–C(1)	3.210(7)
Yb–Cl(1A)	2.580(3)	Yb–C(3)	3.179(7)
Yb–C(18)	2.609(7)	N(1)–C(1)	1.329(8)
Yb–C(19)	2.634(7)	N(2)–C(3)	1.338(9)
Yb–C(20)	2.639(7)	C(1)–C(2)	1.38(1)
Yb–C(21)	2.617(6)	C(2)–C(3)	1.39(1)
Bond angles			
N(1)–Yb–N(2)	78.4(2)	N(1)–Yb–Cl(2)	84.3(2)
Cl(1)–Yb–Cl(2)	83.0(1)	N(2)–Yb–Cl(2)	135.9(2)
N(1)–Yb–Cl(1)	139.0(2)	C(1)–C(2)–C(3)	129.1(7)
N(2)–Yb–Cl(1)	84.2(2)		

4.8. $(CH_3C_5H_4)_2YbL^2$ (**6**)

The synthesis of complex **6** was carried out as described for **4**, but $(CH_3C_5H_4)Na$ (7.2 cm^3, 3.56 mmol) was used instead of C_5H_5Na. The product was collected as orange–red microcrystals (0.68 g, 30%). M.p. 186–188 °C (dec.). Anal. Calc. for $C_{33}H_{36}N_2Yb$: C, 62.55; H, 5.73; N, 4.42; Yb, 27.30. Found: C, 62.31; H, 5.61; N, 4.35; Yb, 27.53%. IR (KBr pellet, cm^{-1}) 3445(s), 2961(m), 1627(s), 1559(vs), 1496(m), 1438(m), 1382(m), 1290(s), 1176(m), 1039(m), 756(m). The crystals suitable for single crystal structure studies were obtained by recrystallization from toluene solution at r.t. for a few days.

4.9. $[(C_5Me_5)YbL^1(\mu\text{-}Cl)]_2$ (**7**)

To a THF solution (20 cm^3) of compound **1** (1.51 g, 2.37 mmol) was slowly added a solution of C_5Me_5Na (3.6 cm^3, 2.37 mmol) in THF at r.t. After being stirred at 30 °C for 48 h, the precipitate was separated by centrifugation and the solvent was evaporated completely under reduce pressure. Then toluene was added to extract the product and the dissolved portion was separated by centrifugation. The red crystals suitable for single crystal structure studies were obtained from concentrated toluene solution at r.t. for a few weeks (0.74 g, 53%). M.p. 152–155 °C (dec.). Anal. Calc. for $C_{27}H_{32}ClN_2Yb$: C, 54.68; H, 5.44; N, 4.72; Yb, 29.17. Found: C, 54.32; H, 5.53; N, 4.58; Yb, 28.75%. IR (KBr pellet, cm^{-1}) 3440(s), 1624(s), 1566(s), 1481(s), 1432(s), 1312(s), 1107(m), 1026(m), 751(s), 682(m).

4.10. Crystal structure determination

Suitable single crystals of complexes **2**, **3**, **5**, **6** and **7** were sealed in thin-walled glass capillary for single-crystal structure determination. Intensity data were collected at ambient temperature on a MSC/AFC

Table 6
Crystallographic data for complexes **2**, **3**, **5**, **6** and **7**

Compound	**2**	**3**	**5**	**6**	**7**
Empirical formula	$C_{29}H_{41}Cl_2N_2O_2Yb$	$C_{27}H_{27}N_2Yb$	$C_{36}H_{50}Cl_2LiN_2O_2Yb$	$C_{33}H_{36}N_2Yb$	$C_{27}H_{32}ClN_2Yb$
M	693.60	552.55	793.69	633.68	593.04
Temperature (K)	298(1)	290(2)	193(1)	293(2)	293(2)
Radiation (Å)	0.71069	0.71073	0.71070	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$Pbca$	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
Unit cell dimensions					
a (Å)	19.040(1)	9.428(2)	11.436(2)	14.717(2)	9.9668(6)
b (Å)	15.104(2)	17.317(5)	12.036(2)	10.299(2)	11.9749(7)
c (Å)	21.130(2)	14.469(4)	14.905(3)	19.118(3)	12.4949(7)
α (°)	90	90	94.049(2)	90	109.758(1)
β (°)	90	95.17(2)	106.357(3)	99.26(1)	104.928(1)
γ (°)	90	90	109.577(2)	90	107.024(1)
V (Å^3)	6076.6(8)	2353(1)	1823.6(5)	2860.0(8)	1232.1(1)
Z	8	4	2	4	2
ρ_{calc} (g cm^{-3})	1.516	1.560	1.445	1.472	1.598
μ (Mo–K$_\alpha$) (cm^{-1})	32.80	39.90	27.42	32.93	39.20
$F(000)$	2792	1092	806	1272	590
Reflections collected	37 000	5016	19 177	5756	7499
Unique reflections (R_{int})	7574 (0.033)	4377 (0.0214)	8013 (0.023)	5032 (0.0185)	5449 (0.0783)
Goodness-of-fit	0.97	0.917	0.988	0.925	1.043
R	0.033	0.0247	0.027	0.0281	0.0482
WR	0.035	0.0524	0.036	0.0608	0.1202

diffractometer (for **2**), Siemens P4 diffractometer (for **3** and **6**), Rigaku Mercury CCD (for **5**), and Bruker SMART CCD area detector (for **7**) equipped with graphite monochromatized Mo–K$_\alpha$ radiation. Crystal data, data collection and refinement parameters are summarized in Table 6.

The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.95 Å), with assigned appropriate isotropic thermal parameters.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center CCDC nos. 200112-174632 for complexes **2**, **3**, **5**, **6**, **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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