Steric Manipulation of the Reductive Reactivity of Ytterbocenes toward 2-(((2,6-Diisopropylphenyl)imino)methyl)pyridine: Insertion of the N=C Bond into the Yb−Indenyl Bond or Oxidative Cleavage of the η^5 Yb−Cp (Cp = $C_{13}H_9$, Cp*) Bond

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Summary: Unprecedented N=C bond insertion into the η^5 Yb−C_9H_7 bond occurs in the reaction of 2-(((2,6-diisopropylphenyl)-imino)methyl)pyridine with $(C_9H_7)_2Yb(THF)_2$ and affords the Yb(III) derivative [Yb(η^5-C_9H_7){N(2,6-i-$Pr_2C_6H_3$)CH(C_9H_7)-(C_5H_4N)}{2,6-i-$Pr_2C_6H_3NCH(C_5H_4N)^{\bullet-}$}]. For the complexes $Cp_2Yb(THF)_2$ (Cp = $C_{13}H_9$, Cp) coordinated by bulkier η^5 ligands the same reaction results in an oxidative cleavage of the η^5 Yb−Cp (Cp = $C_{13}H_9$, Cp*) bond and formation of [Yb{(2,6-i-$Pr_2C_6H_5NCH(C_5H_4N)^{\bullet-}$}$_3$] and [Yb($C_5Me_5$){(2,6-i-$Pr_2C_6H_3NCH(C_5H_4N)^{\bullet-}$}$_2$], respectively.*

Ytterbocenes have demonstrated rich and intriguing reductive reactivity toward α,α′-diimines.[1−3] These reactions are found to be strongly influenced by steric crowding in the coordination sphere of the ytterbium atom. The reaction pathway can be dramatically changed by modification of the steric demand of both carbocyclic ligands η^5 coordinated to the ytterbium atom and substituents at nitrogens of the diimine molecule. *t*-BuN=CHCH=N-*t*-Bu (DAB) oxidizes ytterbocenes $Cp_2Yb(THF)_2$ (Cp = C_5H_5,[1a] C_5Me_5,[1b] C_9H_7,[1c] CH_2-1-C_9H_6[1c]), affording the metallocene-type complexes $Cp_2Yb(DAB^{\bullet-})$ coordinated by the radical anionic diazabutadiene ligand. The bulkier diazabutadiene *i*-$Pr_2C_6H_3N$=CHCH=NC_6H_3-*i*-Pr_2-2,6 (DAD) reacts with the bis(indenyl) derivative $(C_9H_7)_2Yb(THF)_2$, affording the oxidation product $(C_9H_7)_2Yb(DAD^{-\bullet})$,[2a] while the reaction with the analogue $(C_{13}H_9)_2Yb(THF)_2$, containing more sterically demanding fluorenyl ligands, resulted in C−C coupling and formation of the unusual Yb^{II} complex [Yb{η^5-$C_{13}H_8$C(=N−C_6H_3-*i*-Pr_2-2,6)$CH_2NHC_6H_3$-*i*-Pr_2-2,6}$_2$(THF)].[2b] Moreover, ytterbocenes can act as both one- and two-electron reductants in their reactions with DAD.[2c] The complex $(C_5MeH_4)_2Yb(THF)_2$ reduces DAD to a radical anion, and the Yb^{III} derivative $(C_5MeH_4)_2Yb(DAD^{\bullet-})$ forms. In contrast, the compounds Cp^*_2-$Yb(THF)_2$ (Cp^* = C_5Me_5, C_5Me_4H), containing bulkier cyclopentadienyl ligands, under similar conditions act as two-electron reductants. The reactions lead to abstraction of one Cp* ring and afforded the Yb^{III} complexes [YbCp*(DAD)(THF)], coordinated by the dianion of DAD. Obviously the complexes Cp^*_2-$Yb(THF)_2$ demonstrate sterically induced reductive reactivity,[4] and double reduction of DAD becomes possible due to oxidation of the Yb^{II} to Yb^{III} and oxidation of one Cp* anion. In order to gain better insight into the factors determining the variety of pathways of reactions of ytterbocenes with diimines, we explored interactions of the complexes $Cp''_2Yb(THF)_2$ (Cp'' = C_9H_7 (**1**), $C_{13}H_9$ (**2**), C_5Me_5(**3**)) η^5-coordinated by monoanionic ligands possessing different size and coordination capacities with 2-(((2,6-diisopropylphenyl)imino)methyl)pyridine (**4**).

The reaction of the bis(indenyl) derivative **1** with 2 equiv of **4** (THF, 20 °C) led to formation of the Yb(III) complex [Yb(η^5-C_9H_7){N(2,6-*i*-$Pr_2C_6H_3$)CH(C_9H_7)(C_5H_5N)}{2,6-*i*-$Pr_2C_6H_3$NCH-(C_5H_5N)$^{\bullet-}$}] (**5**), which was isolated in 61% yield (Scheme 1).

The paramagnetism of complex **5** (μ_{eff} = 4.3 μB, 293 K) indicates the trivalent oxidation state of the ytterbium atom.[5] The X-ray diffraction study (Figure 1) revealed that the coordination sphere of the Yb atom in complex **5** is made up of a η^5-coordinated C_9H_7 anion, two N atoms of the amido−pyridinato ligand, and two N atoms of the iminopyridine radical anion. The chelating amido−pyridinato ligand arises from insertion of the N=C bond of **4** into the Yb−C_9H_7 bond. This insertion results in Yb−C_9H_7 bond cleavage and formation of Yb−N and C−C bonds. To the best of our knowledge, this is the sole example of such an insertion. The amido−pyridinato ligand is bound to the Yb atom by one covalent (Yb(1)−N(4) = 2.195(2) Å) and one coordination (Yb(1)−N(3) = 2.397(2) Å) Yb−N bond.[3a,6] The insertion leads to the change of hybridization of "ex"-imino C and N atoms.

The bond angles about the carbon atom C24 (N4−C24−C37 = 112.7(3)°, N4−C24−C23 = 111.7(2)°, N4−C24−H24 = 111.8(3)°) proves that, unlike the related carbon in the parent **4**, it adopts sp^3 hybridization. The noticeable difference in bond distances between the Yb ion and the C atoms of the five-membered ring indicates a partial distortion of the indenyl ligand coordination toward an η^3 type. The shortening of the average Yb−C(C_5-indenyl) bond lengths in **5** (2.670(3) Å) compared

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(1) (a) Trifonov, A. A.; Kirillov, E. N.; Bochkarev, M. N.; Schumann, H.; Muehle, S. *Russ. Chem. Bull.* **1999**, *48*, 382−384. (b) Trifonov, A. A.; Kurskii, Yu. A.; Bochkarev, M. N.; Muehle, S.; Dechert, S.; Schumann, H. *Russ. Chem. Bull.* **2003**, *52*, 601−606. (c) Trifonov, A. A.; Fedorova, E. A.; Ikorskii, V. N.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2005**, 2812−2818.

(2) (a) Trifonov, A. A.; Fedorova, E. A.; Fukin, G. K.; Ikorskii, V. N.; Kurskii, Yu. A.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Russ. Chem. Bull.* **2004**, *53*, 2736−2743. (b) Trifonov, A. A.; Fedorova, E. A.; Fukin, G. K.; Druzhkov, N. O.; Bochkarev, M. N. *Angew. Chem., Int. Ed.* **2004**, 5045−5048. (c) Trifonov, A. A.; Borovkov, I. A.; Fedorova, E. A.; Fukin, G. K.; Larionova, J.; Druzhkov, N. O.; Cherkasov, V. K. *Chem. Eur. J.*, in press.

(3) (a) Schulz, M.; Boncella, J.; Berg, D. J.; Tilley, D. T.; Andersen, R. A. *Organometallics* **2002**, *21*, 460−472. (b) Walter, M. D.; Berg, D. J.; Andersen, R. A. *Organometallics* **2006**, *25*, 3228−3237. (c) Walter, M. D.; Schulz, M.; Andersen, R. A. *New J. Chem.* **2006**, *30*, 238−246.

(4) (a) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119−2136. (b) Evans, W. J. *J. Organomet. Chem.* **2002**, *647*, 2−11.

(5) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, *326*, 299−306.

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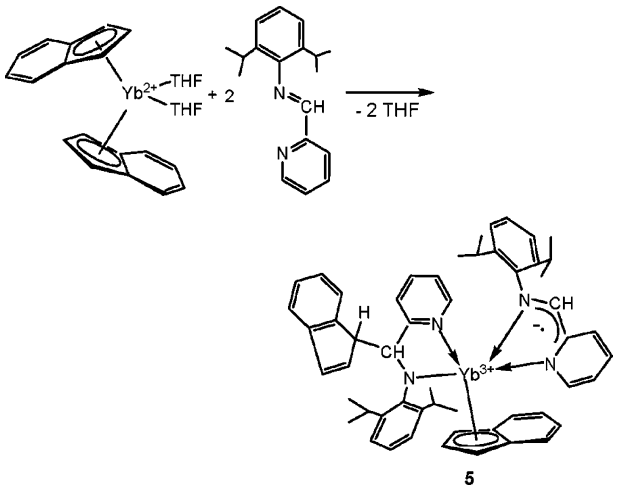
Scheme 1



5

to those in the starting ytterbocene **1** (2.73 Å)[7] reflects the oxidation of the ytterbium atom to the Yb(III) state.[8] The geometric parameters within the planar (deviation is 0.0001 Å) NCCN fragment of the iminopyridine ligand in **5** are noticeably different from those in d transition metal complexes with neutral **4**.[9] Elongation of the N2−C6 bond (1.334(4) Å) and shortening of the C5−C6 bond (1.410(4) Å) compared to the appropriate distances in the complexes [$FeCl_2${2,6-*i*-$Pr_2C_6H_5NCH(C_5H_5N)$}] (1.272(4) and 1.467(5) Å, respectively),[9a] [$PdCl_2${2,6-*i*-$Pr_2C_6H_5NCH(C_5H_5N)$}] (1.279(4) and 1.457(5) Å, respectively)[9b] give evidence for the reduced radical anion character of the iminopyridine ligand in **5**. The ytterbium−nitrogen bond lengths observed in complex **5** (Yb1−N1 = 2.326(3) Å, Yb1−N2 = 2.353(3) Å) are close to the values of Yb−N coordination bond distances reported for related Yb(III) compounds.[6] Formation of the amido−pyridinato ligand in complex **5** obviously implies rearrangement of the coordination fashion of one of the indenyl ligands in **1** from η^5 to η^1 and subsequent insertion of the N=C bond of the iminopyridine molecule coordinated to the ytterbium atom into the Yb−C_9H_7 bond.

N=C bond insertion into a η^5 Yb−C bond is very uncommon. In order to gain better insight into this process, we focused on reactions of $(C_9H_7)_2Yb(THF)_2$ with imino derivatives having similar geometries and steric demands but different substituents at the carbon atoms. Curiously, complex **1** does not react with the related imine 2,6-*i*-$Pr_2C_6H_5N{=}CHC_6H_5$ and iminothiophene 2,6-*i*-$Pr_2C_6H_5N{=}CHC_4H_4S$ (1:2 molar ratio), even with prolonged heating in THF and toluene (60 °C). Obviously, both chelating effects and electron-accepting properties of the imino compound play a crucial role in the insertion process.

The reaction of the complex $(C_{13}H_9)_2Yb(THF)_2$ (**2**), containing more sterically demanding fluorenyl ligands, with **4** under similar conditions occurs in an absolutely different way and results in cleavage of η^5 Yb−$C_{13}H_9$ bonds, oxidation of the Yb atom to the trivalent state, and formation of the tris(iminopyridine) compound [Yb{(2,6-*i*-$Pr_2C_6H_5NCH(C_5H_5N)^{\bullet-}$}$_3$] (**6**) (Scheme 2). Fluorene was found in the reaction mixture (80%).

The value of the magnetic moment of complex **6** (3.74 μB, 293 K) gives evidence for the trivalent oxidation state of the ytterbium atom. The X-ray crystal structure determination has shown that the Yb atom in **6** is coordinated by three chelating iminopyridine ligands bound to the ytterbium atom via two nitrogen atoms (Figure 2). The Yb−N bond lengths in **6** are somewhat different (2.372(3) and 2.356(2) Å), and their values are comparable to those reported for coordination Yb−N bonds[3a,5c] and appropriate distances in Yb(III) complexes with radical anionic diazadiene ligands.[1b,2a] The bonding situation within the planar (the mean deviation is 0.0151 Å) diimino fragment N1−C13−C14−N2 in **6** is consistent with the radical anionic form of the iminopyridine ligand: the C−C bond (1.382(5) Å) is shorter, while the N=C bonds are longer than the appropriate bonds in the d transition-metal complexes with neutral iminopyridine ligands.[9] The successive augmentation of the steric demand of the π-anionic ligand coordinated to the ytterbium atom and passage to the permethylated derivative $(C_5Me_5)_2Yb(THF)_2$ (**3**) changes dramatically the pathway of the reaction with iminopyridine. The reaction of **3** with a 2-fold molar excess of **4** under similar conditions occurs with abstraction of one Cp* ring and oxidation of the ytterbium atom and affords a novel half-sandwich complex of trivalent ytterbium, [Yb(C_5Me_5){(2,6-*i*-$Pr_2C_6H_3NCH(C_5H_5N)^{\bullet-}$}$_2$] (**7**) (Scheme 3). The value of the magnetic moment of complex **7** (3.71 μB, 293 K) is consistent with a trivalent oxidation state of the ytterbium atom.[5] The X-ray diffraction study (Figure 3) revealed that in complex **7** the ytterbium atom is coordinated by one C_5Me_5 ligand in a η^5 fashion and two iminopyridine radical anions. Both of the chelating iminopyridine radical anions in **7** are bound to the ytterbium atom through two coordination Yb−N bonds (Yb1−N1A = 2.356(2) Å, Yb1−N2A = 2.345(2) Å, Yb1−N1B = 2.346(2) Å, Yb1−N2B = 2.333(2) Å). There are short Yb−C contacts (Yb1−C23A = 3.142(3) Å, Yb1−C23B = 3.130(3) Å, Yb1−C24A = 3.180(2) Å, Yb1−C24B = 3.173(3) Å). The average Yb−C (Cp*) bond length in complex **7** (2.631(3) Å) is noticeably shorter than the corresponding value in the Yb^{II} complex $Cp^*_2Yb(py)_2$ (2.74 Å)[10] and comparable to those in the related Yb(III) complexes $(C_5Me_5)_2YbX(L)$ (2.628−2.65 Å), (X = Hal, L = THF),[11] giving evidence of the trivalent oxidation state of the ytterbium atom in **7**. The bond distances within the diimino fragments of both iminopyridine ligands in **7** indicate their radical anionic state. Complexes **5**−**7** are ESR silent in the solid state and THF solution (100−293 K).

Thus, the pathway of reactions of ytterbocenes with 2-(((2,6-diisopropylphenyl)imino)methyl)pyridine is mainly defined by both steric crowding in the coordination sphere of the metal atom and the coordination capacities of the π-aromatic ligands bound to ytterbium. The reactions can result in insertion of the N=C bond into the Yb−indenyl bond or oxidative cleavage of the η^5 Yb−Cp (Cp = $C_{13}H_9$, Cp*) bond. Unfortunately, at present we cannot explain which factor predominates in driving these reactions toward insertion or cleavage processes and the formation of complexes **5**−**7**. Undoubtedly, the initial act of the reaction is coordination of 2-(((2,6-diisopropylphenyl)-imino)methyl)pyridine to the ytterbium atom and formation of the mixed-ligand derivatives. We suggest that oxidation of the

(6) For comparison, see for the covalent Yb^{III}−N bond: (a) Sheng, E.; Wang, S.; Yang, G.; Zhou, S.; Cheng, L.; Zhang, K.; Huang, Z. *Organometallics* **2003**, *22*, 684−692. (b) Wang, Y.; Shen, Q.; Xue, F.; Tu, K. *J. Organomet. Chem.* **2000**, *598*, 359−364. For the coordination Yb^{III}−N bond, see: (c) Zhou, X.; Huang, Z.; Cai, R.; Zhang, L.-B.; Zhang, L.-X.; Huang, X. *Organometallics* **1999**, *18*, 4128−4133.

(7) Jin, J. Z.; Jin, Z. S.; Chen, W. Q.; Zhang, Y. *Chin. J. Struct. Chem. (Jiegou Huaxue*) **1993**, *12*, 241−245.

(8) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

(9) (a) Gibson, V. C.; O'Reily, R. K.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 2824−2830. (b) Laine, T. V.; Klinga, M.; Leskelä, M. *Eur. J. Inorg. Chem.* **1999**, 959−964. (c) Laine, T. V.; Piironen, U.; Lappalainen, K.; Klinga, M.; Aitolla, E.; Leskelä, M. *J. Organomet. Chem.* **2000**, *606*, 112−124.

(10) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2647−2649.

(11) (a) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999−2009. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 856−859.

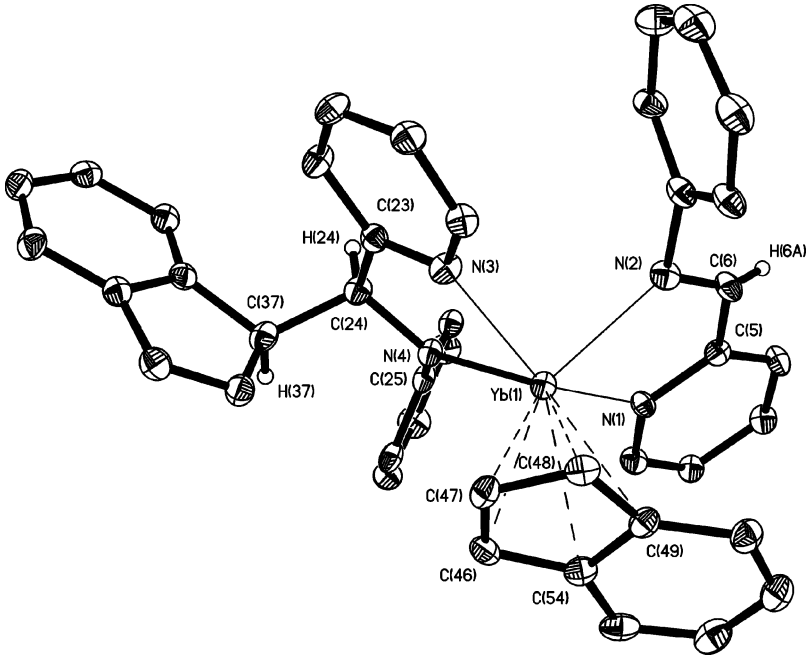
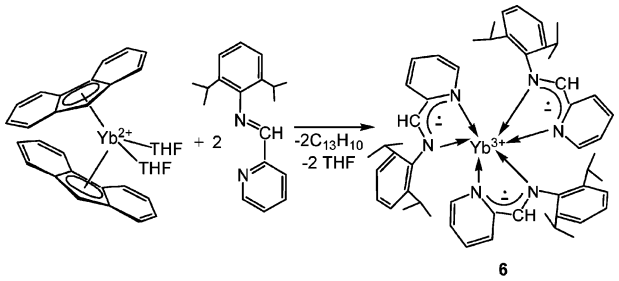


Figure 1. Molecular structure of the complex [Yb(η^5-C_9H_7){N(2,6-*i*-$Pr_2C_6H_3$)CH(C_9H_7)(C_5H_5N)}{η^4-2,6-*i*-$Pr_2C_6H_3NCH(C_5H_5N)$}] (**5**). Isopropyl groups of iminopyridine ligands are omitted for clarity. The terminal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Yb1−N4 = 2.195(2), Yb1−N3 = 2.397(2), Yb1−N1 = 2.326(2), Yb1−N2 = 2.353(3), Yb1−C47 = 2.603(3), Yb1−C46 = 2.621(3), Yb1−C48 = 2.649(3), Yb1−C54 = 2.730(3), Yb1−C49 = 2.750(3), Yb1−C5 = 3.174(3), Yb1−C6 = 3.140(3), N2−C6 = 1.334(4), C5−C6 = 1.410(4); N4−C24−C37 = 112.7(3), N4−C24−C23 = 111.7(2), N4−C24−H24 = 111.7(3), N2−C6−C5 = 121.7(3), C24−N4−C25 = 110.6(2), C25−N4−Yb1 = 126.7(2), Yb1−N4−C24 = 122.2(3), N4−C24−H24 = 111.8(2).

Scheme 2



ytterbium atom to the trivalent state occurs in this step. The tendency of the π-aromatic ligands coordinated to the ytterbium atom to haptotropic rearrangements seems to play a crucial role in these transformations. The lack of data on the bonding strength of the ytterbium atom with indenyl, fluorenyl, and pentamethylcyclopentadienyl ligands and redox potentials of Yb(II) in complexes **1**−**3** does not allow us to evaluate the influence of these factors on the reaction pathway. Further work on this subject is being actively pursued at the moment.

Experimental Section. Preparation of [Yb(η^5-C_9H_7){N(2,6-*i*-$Pr_2C_6H_3$)CH(C_9H_7)(C_5H_5N)}{2,6-*i*-$Pr_2C_6H_3NCH$ (C_5H_5N)$^{\bullet-}$}] (5). A solution of **4** (0.53 g, 1.99 mmol) in THF (5 mL) was added to a solution of **1** (0.53 g, 0.96 mmol) in THF (20 mL), and the reaction mixture was heated to 60 °C for 0.5 h. THF was evaporated in vacuo, toluene (20 mL) was added, and the reaction mixture was stirred at 60 °C for 1 h. Volatile material was evaporated in vacuo, and another portion of toluene (20 mL) was added. After the mixture was stirred at 60 °C for an additional 2 h, the solvent was evaporated in vacuo and the deep green solid residue was recrystallized from a THF−hexane mixture at −20 °C. Decanting the mother liquor, washing the crystals with cold hexane, and drying in vacuo at room temperature for 20 min afforded deep green crystals of **5**: yield 0.55 g (61%). Anal. Calcd for $C_{54}H_{58}N_4Yb$ (936.08): C, 69.28; H, 6.19; Yb, 18.48. Found: C, 68.89; H, 5.77; Yb, 18.80. IR (Nujol mull, cm^{-1}): 3060, 1620, 1600, 1565, 1275, 1169, 1103, 1046, 1015, 904, 768, 760, 750.

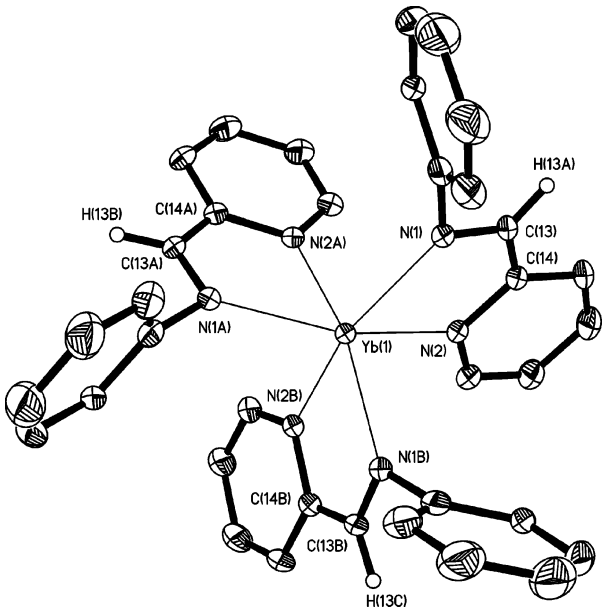
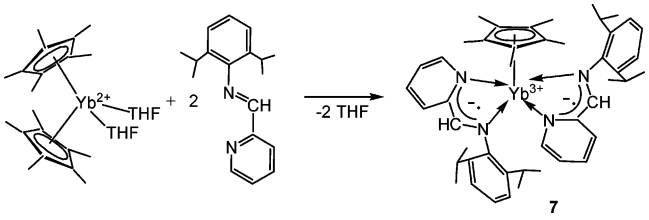


Figure 2. Molecular structure of the complex [Yb{(2,6-i-$Pr_2C_6H_5$-$NCH(C_5H_5N)^{\bullet-}$}$_3$] (**6**). Isopropyl groups of iminopyridine ligands are omitted for clarity. The terminal ellipsoids correspond to 30% probability. Selected bond lengths (Å): Yb1−N1 = 2.356(2), Yb1−N2 = 2.372(3), Yb1−C13 = 3.148(2), Yb1−C14 = 3.209(3), N1−C13 = 1.334(4), N2−C14 = 1.382(3), C13−C14 = 1.382(5).

Preparation of [Yb{(2,6-*i*-$Pr_2C_6H_5NCH(C_5H_5N)^{\bullet-}$}$_3$] (6). Similar to the procedure described for **5**, compound **6** was obtained from **4** (0.55 g, 2.06 mmol) in THF (5 mL) and **2** (0.67 g, 1.03 mmol) in THF (20 mL).The deep green solid residue was washed with hexane (2 × 15 mL). Fluorene (0.18 g, 80%) was found in the hexane extracts. Recrystallization from

Scheme 3



THF at −20 °C afforded deep green crystals of **6**: yield 0.35 g (52%). Anal. Calcd for $C_{54}H_{66}N_6Yb$ (972.17): C, 66.71; H, 6.78; Yb, 17.79. Found: C, 66.33; H, 6.54; Yb, 18.00. IR (Nujol mull, cm^{-1}): 3054, 1641, 1569, 1532, 1396, 1315, 1267, 1251, 1161, 1149, 992, 901, 801, 789, 738.

Preparation of [Yb(C_5Me_5){(2,6-*i*-$Pr_2C_6H_3NCH(C_5H_5N)^{\bullet-}$}$_2$] (7). Similar to the procedure described for **5**, compound **7** was obtained from **4** (0.58 g, 2.18 mmol) in THF (5 mL) and **3** (0.64 g, 1.09 mmol) in THF (20 mL). Recrystallization of the greenish brown solid residue from hexane at −20 °C afforded greenish brown crystals of **7**: yield 0.67 g (74%). Anal. Calcd for $C_{46}H_{59}N_4Yb$ (841.01): C, 65.69; H, 7.01; Yb, 20.57. Found: C, 65.30; H, 6.73; Yb, 20.93. IR (Nujol mull, cm^{-1}): 3060, 1620, 1600, 1565, 1275, 1169, 1103, 1046, 1015, 904, 804, 768, 742, 662.

Crystal data for **5**: $C_{54}H_{58}N_4Yb$, $M_r = 936.08$, $T = 293(2)$ K, triclinic, $P\bar{1}$, $a = 11.2187(7)$ Å, $b = 11.8654(8)$ Å, $c = 18.0649(12)$ Å, $\alpha = 94.087(2)°$, $\beta = 90.889(2)°$, $\gamma = 113.3530(10)°$, $V = 2199.6(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.413$ Mg m^{-3}, $\mu = 2.167$ mm^{-1}, $F(000) = 960$, crystal size 0.04 × 0.03 × 0.02 mm, $\theta = 1.88-25.00°$, index ranges $-12 \le h \le 13$, $-14 \le k \le 14$, $-21 \le l \le 14$, 12 097 reflections collected, 7696 independent reflections, R(int) = 0.0302, GOF = 0.952, R1 = 0.0357, wR2 = 0.0703 ($I > 2\sigma(I)$), R1 = 0.0503, wR2 = 0.0735 (all data), largest difference peak/hole (ρ_{max}/ρ_{min}) 1.339/−0.554 e Å^{-3}.

Crystal data for **6**: $C_{54}H_{66}N_6Yb$, $M_r = 972.17$, $T = 100(2)$ K, rhombohedral, $R\bar{3}$, $a = 18.5730(8)$ Å, $b = 18.5730(8)$ Å, $c = 25.1943(15)$ Å, $\alpha = \beta = 90.0°$, $\gamma = 120.0°$, $V = 7526.6(6)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.287$ Mg m^{-3}, $\mu = 1.904$ mm^{-1}, $F(000) = 3012$, crystal size 0.30 × 0.30 × 0.02 mm, $\theta = 2.05-23.00°$, index ranges $-19 \le h \le 20$, $-19 \le k \le 20$, $-27 \le l \le 27$, 11 474 reflections collected, 2310 independent reflections, R(int) = 0.0353, GOF = 1.088, R1 = 0.0304, wR2 = 0.0824 ($I > 2\sigma(I)$), R1 = 0.0365, wR2 = 0.0850 (all data), largest difference peak/hole (ρ_{max}/ρ_{min}) 0.915/−0.512 e Å^{-3}.

Crystal data for **7**: $C_{46}H_{59}N_4Yb$, $M_r = 841.01$, $T = 100(2)$ K, triclinic, $P\bar{1}$, $a = 10.8712(5)$ Å, $b = 11.5312(5)$ Å, $c = 17.6163(8)$ Å, $\alpha = 74.0000(10)°$, $\beta = 82.1300(10)°$, $\gamma = 71.8730(10)°$, $V = 2014.27(16)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.387$ Mg m^{-3}, $\mu = 2.358$ mm^{-1}, $F(000) = 866$, crystal size 0.27 × 0.22 × 0.09 mm, $\theta = 1.92-29.21°$, index ranges $-14 \le h \le 14$, $-15 \le k \le 15$, $-24 \le l \le 23$, 21 288 reflections collected, 10 535 independent reflections, R(int) = 0.0242, GOF = 1.070, R1 = 0.0299, wR2 = 0.0701 ($I > 2\sigma(I)$), R1 = 0.0356, wR2 = 0.0723 (all data), largest difference peak/hole (ρ_{max}/ρ_{min}) 2.710/−0.808 e Å^{-3}.

The data were collected on a SMART APEX diffractometer (graphite monochromated, Mo Kα radiation, $\omega-\varphi$ scan technique, $\lambda = 0.710\,73$ Å). The structures were solved by Patterson (**5**) and direct (**6**, **7**) methods and were refined on F^2 using the SHELXTL[12] package. All non-hydrogen atoms were refined anisotropically. In **5** hydrogen atoms were refined with mixed treatment. In complex **6** all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). The H atoms in **7** were located from Fourier synthesis and refined isotropically. SADABS[13] was used to perform area-detector scaling and absorption corrections. The CCDC flies 627244 (**5**), 627245 (**6**), and 627246 (**7**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) +44-1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

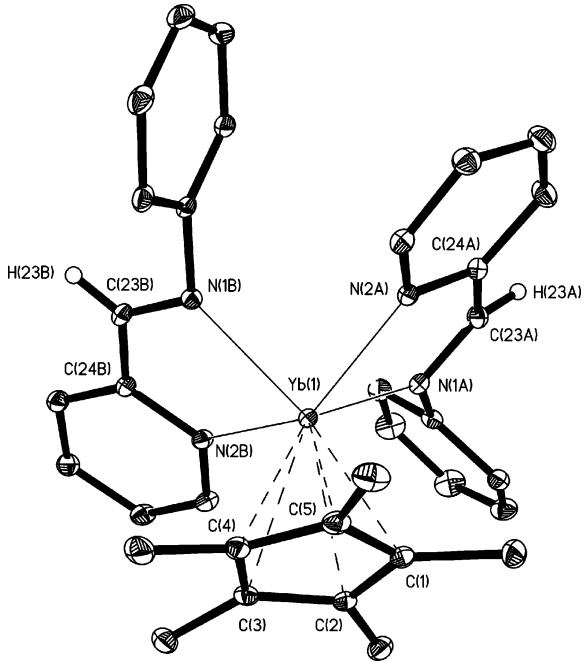


Figure 3. Molecular structure of the complex [Yb(C_5Me_5){(2,6-*i*-$Pr_2C_6H_3NCH(C_5H_5N)^{\bullet-}$}$_2$] (**7**). Isopropyl groups of iminopyridine ligands are omitted for clarity. The terminal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Yb1−C1 = 2.585(3), Yb1−C2 = 2.613(3), Yb1−C3 = 2.655(3), Yb1−C4 = 2.673(3), Yb1−C5 = 2.629(3), Yb−C_{av} = 2.631(3), Yb1−C23A = 3.142(3), Yb1−C23B = 3.130(3), Yb1−C24A = 3.180(2), Yb1−C24B = 3.173(3), Yb1−N1A = 2.356(2), Yb1−N2A = 2.345(2), Yb1−N1B = 2.346(2), Yb1−N2B = 2.333(2), N1A−C23A = 1.340(4), N2A−C24A = 1.380(3), C23A−C24A = 1.407(4), N1B−C23B = 1.342(3), N2B−C24B = 1.381(3), C23B−C24B = 1.409(4); N2B−Yb1−N1B = 71.80(7), N2A−Yb1−N1A = 71.92(8).

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Supporting Information Available: CIF files giving crystallographic data, including bond lengths and angles, of compounds **5**−**7**. This material is available free of charge via the Internet at http//pubs.acs.org.

OM070073S

(12) SMART: Bruker Molecular Analysis Research Tool, v. 5.625; Bruker AXS, Madison, WI, 2000.

(13) Sheldrick, G. M. SADABS: Bruker/Siemens Area Detector Absorption Correction Program, v.2.01; Bruker AXS, Madison, WI, 1998.