DOI: 10.1002/ejic.200701098

Small Steric Variations in Ligands with Large Synthetic and Structural Consequences

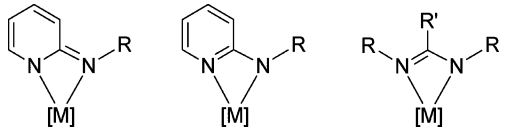
Sadaf Qayyum,[a] Kristina Haberland,[a] Craig M. Forsyth,[b] Peter C. Junk,[b] Glen B. Deacon,*[b] and Rhett Kempe*[a]

Keywords: Agostic interactions / Amidopyridine ligands / Aminopyridinato ligands / N ligands / Ytterbium

The reaction of ytterbium metal with the aminopyridines 2,6-(diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]-amine (**1**, Ap′H) and (2,4,6-trimethylphenyl)-[6-(2,4,6-trimethylphenyl)pyridin-2-yl]amine (**2**, $Ap^{Me}H$) at elevated temperature under vacuum in the presence of mercury gave rise to divalent [$Yb(Ap')_2$] (**3**) and trivalent [$Yb(Ap^{Me})_3$] (**4**), respectively. The single-crystal X-ray structure analysis of **3** revealed a four-coordinate ytterbium atom with two chelating (N,N′) Ap′ ligands inclined to each other at an angle of 126.93(7)° (Cl–Yb–C26). Additionally the complex forms intermolecular C^{Aryl}–H agostic interactions [Yb1···C17 2.981(2) Å and Yb1···H17 2.56(3) Å] (all H atoms refined). Complex **4** contains a six-coordinate ytterbium atom having three chelating (N,N′) Ap^{Me} ligands and has distorted octahedral stereochemistry. The reaction of the potassium salts of Ap′H (**5**) and $Ap^{Me}H$ (**6**) with [YbI_2 $(thf)_4$] in thf gave rise to the divalent lanthanoid complexes [$Yb(Ap')_2(thf)$] (**7**), and [$Yb(Ap^{Me})_2(thf)_2$] (**8**), respectively, and **7** was also obtained by redox transmetallation/ligand exchange from Yb metal, $HgPh_2$ and Ap′H. X-ray crystal structures show that **7** and **8** have five- and six-coordinate ytterbium atoms and distorted trigonal-bipyramidal and distorted octahedral stereochemistry, respectively, the difference in coordination number reflecting the difference in steric demand of the Ap′ and Ap^{Me} ligands.

Introduction

Agostic bonding has been found to play a major role in the ligand reactivity of transition-metal complexes, particularly in α-olefin polymerization.[1,2] The nature of the interaction was interpreted by Brookhart and Green in terms of a three-centre, two-electron bond between the C–H bond and a vacant d-orbital of the transition metal atom.[3,4] The presence of an agostic interaction is commonly indicated by the resulting geometric deformation of the agostic ligand, as shown by an elongation of the C–H bond, rather short M···H contacts, and a distortion of the ligand spatial arrangement.[5,6] Aminopyridinato ligands[7,8] are of interest due to the flexibility of their binding mode (amidopyridine vs. aminopyridinato form)[9] and the ligand "asymmetry". Such ligands (Scheme 1, left) are structurally related to amidinates[10] (Scheme 1, right).



Scheme 1. Aminopyridinato form (left), amidopyridine form (centre) and amidinato ligands (right).

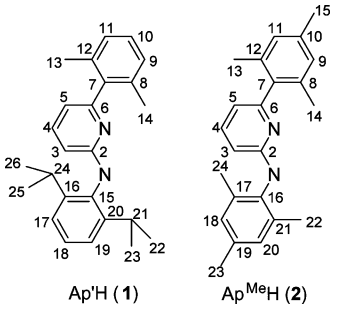
We have begun investigations of very bulky versions of such ligands.[11] Here we report that small variations in very bulky ligands have large synthetic and structural consequences including a rare example of a C^{Aryl}–H intermolecular agostic interaction and a small steric range in which such an interaction could be stabilized.

Results and Discussion

The aminopyridines **1**[11a] and **2**[12] [Equation (1), Scheme 2] were prepared by palladium-catalyzed arylamination,[13] and appeared suitable for conversion into the corresponding (amidopyridine)lanthanoid complexes by reaction of lanthanoid metals with the ligands at elevated temperatures.

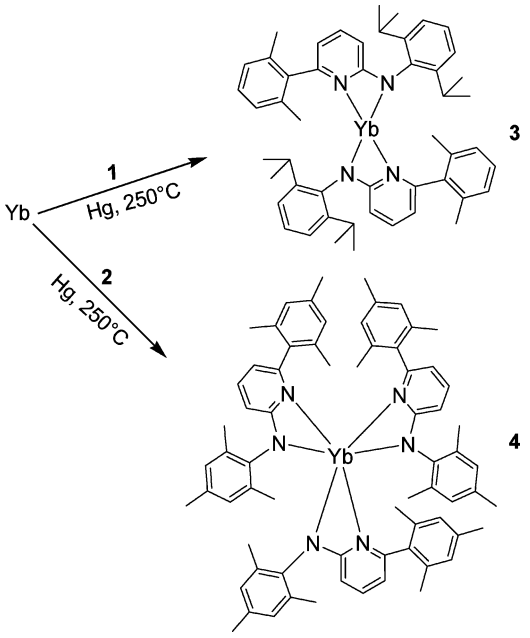
$$Ln + n\,ApH \longrightarrow LnAp_n + n/2\,H_2 \quad (Ap = Ap' \text{ or } Ap^{Me}) \qquad (1)$$

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany
Fax: +49-921-55-2157
E-mail: kempe@uni-bayreuth.de
[b] School of Chemistry, Monash University, Clayton, Victoria 3800, Australia
Fax: +61-3-99054597
E-mail: glen.deacon@sci.monash.edu.au



Scheme 2. 2,6-Dialkylphenyl-substituted aminopyridines and the numbering scheme used for NMR assignments.

This "direct" synthetic method[14] is especially valuable for homoleptic lanthanoid organoamides and phenolates[15] and has recently been extended to analogous alkaline earth complexes.[16] Direct reaction of **1** with ytterbium metal activated by mercury metal under vacuum at 250 °C gave rise to divalent [Yb(Ap′)$_2$] (**3**) (Scheme 3). Mercury assists by way of metal surface amalgamation/cleaning, while the molten ligand possibly acts initially as a solvent until the reaction mixture solidifies.



Scheme 3. Synthesis of the ytterbium complexes **3** and **4**.

Suitable crystals of **3** could be grown during the complex synthesis. For crystallographic details see Table 1. The molecular structure of divalent homoleptic **3** (Figure 1) exhibits a bent structure as observed for the metallocenes [Yb{η-C$_5$H$_3$(1,3-SiMe$_3$)$_2$}$_2$][17] and [Ln(η-C$_5$Me$_5$)$_2$] (Ln = Sm,[18,19] Eu[19]). The C1–Yb–C26 angle for **3** is 126.93°, rather small when compared with the centroid–Yb–centroid angle of bulky [Yb{η-C$_5$H$_3$(1,3-SiMe$_3$)$_2$}$_2$] (138.0°). The ytterbium atom is four-coordinate with two chelating Ap′ ligands. The Yb–N bond lengths suggest that both ligands are in the amidopyridine form.

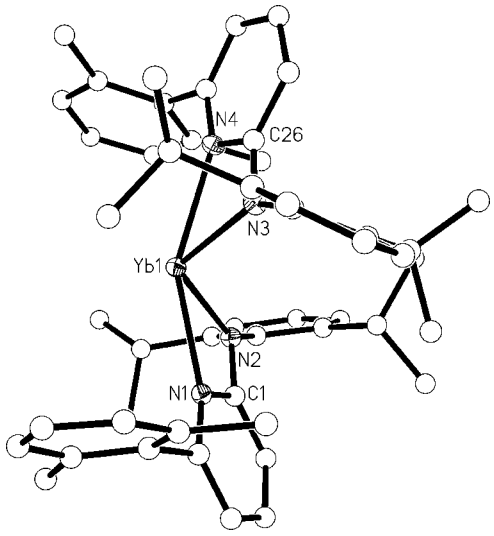


Figure 1. Molecular structure of [Yb(Ap′)$_2$] (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Yb1 2.4323(18), N2–Yb1 2.4041(18), N3–Yb1 2.3708(18), N4–Yb1 2.4489(18); N1–Yb1–N2 56.05(6), N1–Yb1–N3 105.89(6), N1–Yb1–N4 151.90(6), N2–Yb1–N3 116.20(6), N2–Yb1–N4 109.36(6), N3–Yb1–N4 56.02(6), C1–Yb1–C26 126.93(6).

This open sandwich structure leaves a vacant face on the Yb atom. To compensate for this, there is a close contact between a carbon–hydrogen bond of one of the phenyl rings of one YbAp′$_2$ molecule and a neighbouring Yb atom, with Yb1···C17 bonding distances of 2.981(2) Å and Yb1···H17 distances of 2.56(3) Å (all H atoms refined; Figure 2). Sterically crowded homoleptic (NacNac)Yb^{II} complexes adopt a highly symmetric non-bent structure.[20] Thus, we conclude that for anionic bidentate N,N ligands the thermodynamically more stable form is the highly symmetric and not the bent conformation. The ligand inclination may result from these unique intermolecular agostic interactions. Structurally characterized mononuclear homoleptic (amidinato/aminopyridinato/amidopyridine)Yb^{II} complexes have not yet been described to the best of our knowledge.

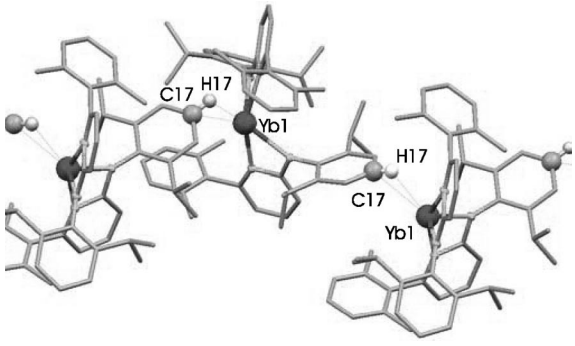


Figure 2. X-ray structure of **3** showing intermolecular agostic interactions [Yb1···C17 2.981(2), Yb1···H17 2.56(3) Å].

Reduction of the steric bulk, by applying **2** – a ligand which is smaller than **1** – according to Equation (1) led to a trivalent homoleptic Yb complex (Scheme 3). The forma-

Table 1. Details of the X-ray crystal structure analyses of **3**, **4**, **7** and **8**.

	3	**4**	**7**·2C_7H_8	**7**·0.5C_6H_{14}	**8**·C_6H_{14}
Empirical formula	$C_{50}H_{58}N_4Yb$	$C_{69}H_{75}N_6Yb$	$C_{68}H_{82}N_4OYb$	$C_{57}H_{73}N_4OYb$	$C_{30}H_{40}N_2OYb$
Formula mass	888.04	1161.39	1144.42	1003.23	531.16
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2/c$
a [Å]	12.1463(3)	11.4580(7)	11.1460(7)	10.8483(2)	12.4800(7)
b [Å]	22.6968(6)	11.4970(7)	27.6330(19)	24.2933(5)	12.2840(8)
c [Å]	15.5101(4)	26.6150(18)	19.960(15)	19.7081(3)	18.6520(12)
α [°]	90	101.131(5)	90	90	90
β [°]	95.608(1)	90.670(5)	103.037(5)	101.643(1)	104.689(5)
γ [°]	90	118.141(4)	90	90	90
V [Å^3]	4255.39(19)	3011.8(3)	5991.3(7)	5087.02(16)	2766.0(3)
Z	4	2	4	4	4
Crystal size [mm]	0.18×0.10×0.08	0.19×0.18×0.17	0.17×0.15×0.10	0.25×0.25×0.25	0.39×0.17×0.11
$\rho_{calcd.}$ [g cm^{-3}]	1.386	1.281	1.269	1.310	1.276
$\mu_{calcd.}$ [mm^{-1}] (Mo-K_α)	2.236	1.598	1.605	1.880	1.734
T [K]	123(2)	193(2)	193(2)	123(2)	193(2)
θ range [°]	1.60–30.00	1.57–25.82	1.28–25.85	2.51–27.50	1.66–25.71
No. of obsd. refl. [$I > 2\sigma(I)$]	11605	5573	6844	10516	3364
No. of unique refl.	12400	11144	11392	11681	5237
No.of parameters	728	685	667	581	303
R [$I>2\sigma(I)$]	0.0321	0.0606	0.0408	0.0379	0.0447
wR^2	0.0590	0.1193	0.0993	0.0793	0.0860

tion of bis- or tris(amidopyridine)ytterbium complexes and thus the formation of di- or trivalent complexes can be explained in terms of the steric bulk of the corresponding ligands. The rare earth metal atom can bind three ligands of the less bulky version, Ap^{Me}, and thus the thermodynamically favoured trivalent oxidation state is accessible. Ytterbium can only bind two ligands of the slightly bulkier version, and thus the redox process stops at the oxidation state of two. X-ray analysis of **4** (for crystal and refinement data, see Table 1) reveals a distorted octahedral coordination for the ytterbium atom (Figure 3).

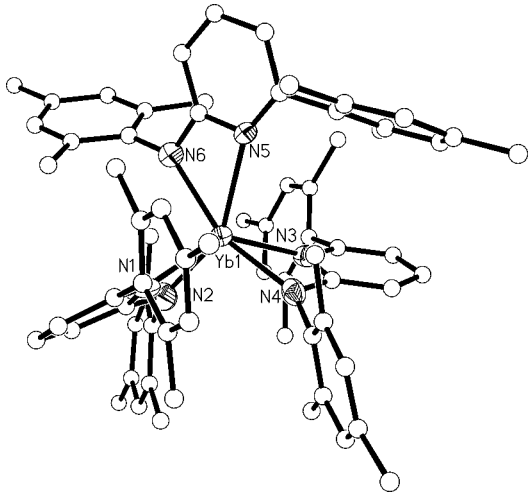
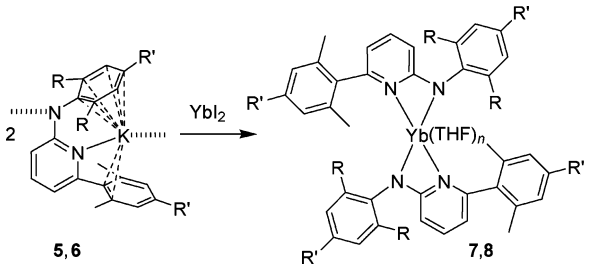


Figure 3. Molecular structure of [Yb(Ap^{Me})$_3$] (**4**). Selected bond lengths [Å] and angles [°]: N1–Yb1 2.357(8), N2–Yb1 2.264(7), N3–Yb1 2.395(7), N4–Yb1 2.263(7), N5–Yb1 2.543(7), N6–Yb1 2.299(7); N4–Yb1–N2 106.1(2), N4–Yb1–N6 158.4(2), N2–Yb1–N6 95.5(3), N4–Yb1–N1 92.5(3), N2–Yb1–N1 58.4(3), N6–Yb1–N1 98.7(2) N4–Yb1–N3 59.0(3), N2–Yb1–N3 98.9(3), N6–Yb1–N3 118.7(3), N1–Yb1–N3 138.8(2), N4–Yb1–N5 102.1(2), N2–Yb1–N5 151.2(2), N6–Yb1–N5 56.3(2), N1–Yb1–N5 115.6(2), N3–Yb1–N5 100.2(2).

It is noteworthy that the ligands are coordinated in the amidopyridine binding mode to the metal atom. The different bond lengths for Yb–$N1_{pyridine}$ [2.357(8) Å] and Yb–$N2_{amido}$ [2.264(7) Å] indicate an amidopyridine binding mode where the anionic function is localized at the amido N-atom. A similar situation is noticeable with the bond length Yb–$N5_{pyridine}$ [2.543(7) Å] and Yb–$N6_{amido}$ [2.299(7) Å]. The ligand N3,N4 is also in the amidopyridine form, but the difference in appropriate bond lengths is smaller (0.13 Å). It is noteworthy that, for one of the ligands, the Yb–$N_{pyridine}$ bond (2.543 Å) is much longer than the averaged Yb–$N_{pyridine}$ bond for the two others (2.376 Å) indicating weak bonding due to steric saturation. Ligands N3,N4 and N1,N2 are the ligands containing the respective donor atoms.

Salt metathesis reactions of **5** (potassium salt of **1**)[11a] with [YbI_2(thf)$_4$] in thf solution resulted in the formation of the bis(amidopyridine)Yb^{II} complex **7** (Scheme 4). In addition, **7** was prepared from Yb metal by redox transmetallation/ligand exchange in thf [Equation (2)].

$$Yb + 2\,Ap'H + HgPh_2 \xrightarrow{thf} [Yb(Ap')_2(thf)] + 2\,PhH + Hg^0 \quad (2)$$



Scheme 4. Synthesis of **7** and **8** (**5**, **7**: n = 1, R = *i*Pr; R′ = H; **6**, **8**: n = 2, R = R′ = Me) by metathesis reactions.

X-ray quality crystals of **7**·$2C_7H_8$ were grown from concentrated toluene solution. In addition, crystals of **7**·$0.5C_6H_{14}$ were grown from hexane. In the case of the sterically more demanding ligand Ap′, only one thf molecule coordinates to the central metal atom. The resulting five-coordination can be best described as very distorted trigonal-bipyramidal, with the N2, N4 and O1 atoms in the Yb plane and N1 and N3 apical [N1–Yb1–N3 157.59(14)°] (Figure 4). The Yb–$N_{pyridine}$ [2.479(4), 2.466(4) Å] bonds are significantly longer than the Yb–N_{amido} bonds [2.380(4), 2.384(3) Å] indicating an amidopyridine bonding mode.

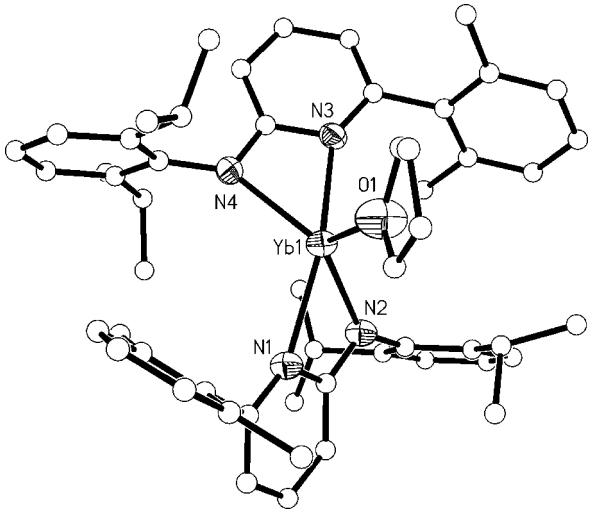


Figure 4. Molecular structure of [Yb(Ap′)$_2$(thf)] (**7**). Hydrogen atoms and two toluene molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: N1–Yb1 2.479(4), N2–Yb1 2.380(4), N3–Yb1 2.466(4), N4–Yb1 2.384(3), O1–Yb1 2.362(4); N4–Yb1–N1 113.38(15), O1–Yb1–N1 101.37(15), O1–Yb1–N4 114.73(16), N3–Yb1–N1 157.59(14), N4–Yb1–N3 55.82(15), O1–Yb1–N3 101.05(15), N2–Yb1–N1 56.17(14), N2–Yb1–N4 126.99(15), O1–Yb1–N2 118.28(16), N2–Yb1–N3 112.02(16).

The reactant **6** was prepared in a similar fashion to **5**[11a] and was treated with [$YbI_2(thf)_4$] in thf. Product **8** was extracted with hexane, and crystallisation afforded red crystals. Complex **8** was characterized by X-ray crystal-structure analysis and contains one hexane molecule per Yb atom in the crystal lattice. Crystal and refinement details are listed in Table 1. The molecular structure of **8** is shown in Figure 5.

The reduction of the steric bulk of the amidopyridine from **7** to **8** allows for the coordination of the two thf ligands which bind to the metal centre in a *cisoid* manner, and the coordination arrangement can be best described as distorted octahedral. The Yb–$N_{pyridine}$ (2.544 Å), Yb–N_{amide} (2.396 Å) and Yb–O distances are comparable to other related thf complexes,[11b] and the bonding mode is amidopyridine in character. Considering the lability of the coordinated thf molecules, it is surprising that the Yb–O distance (Figure 5) lies close to the mean value for those in all previously reported Yb–O_{thf} interactions (2.43 Å).[21] The small chelating angle N_{amido}–Yb–$N_{pyridine}$ (average

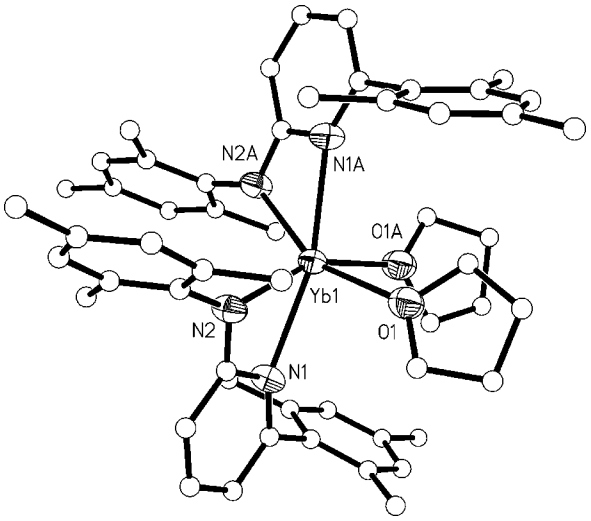


Figure 5. Molecular structure of [Yb(Ap^{Me})$_2$(thf)$_2$] (**8**). Hydrogen atoms and hexane molecule are omitted for clarity; selected bond lengths [Å] and angles [°]: N1–Yb1 2.544(4), N2–Yb1 2.396(5), O1–Yb1 2.428(4); N2–Yb1–N2A 105.7(2), N2–Yb1–N1 54.76(15), O1A–Yb1–O1 78.1(2).

54.76°) underlines the strained nature of the amidopyridine ligand binding. The Yb–$N_{pyridine}$ and Yb–O_{thf} bonds of **8** are longer than those of **7** by amounts consistent with a change of one in the coordination number,[22] but the differences in the Yb–N_{amido} distances is much smaller (ca. 0.02 Å).

The nature of the products depends highly on the size of the ligands as the steric bulk is in the order Ap*–H > Ap′–H > Ap^{Me}–H. In the present study, the formation of the solvent-free complexes **3** and **4** has been enforced by the use of solvent-free conditions. The smallest ligand, Ap^{Me}–H, yields a six-coordinate Yb^{III} complex, and the slightly bulkier Ap′–H yields a 4-coordinate Yb^{II} complex with rare intermolecular agostic interactions. This indicates that the coordination sphere is large enough to induce the presence of an agostic interaction but not large enough to accommodate a third ligand. Agostic complexes are often unstable, and substrate coordination and/or chelation generally seem to be necessary to bring the C–H bond and the coordinatively unsaturated metal centre into close proximity.[23] The reaction of the sterically more demanding aminopyridine Ap*–H (**9**), {(2,6-diisopropylphenyl)[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine}[11a] directly with Yb metal mainly gave starting material. Salt metathesis reactions of the potassium salt of **9** with [$YbI_2(thf)_4$] in thf solution resulted in the formation of a heteroleptic ytterbium iodide dimer [$Yb_2(Ap^*)_2I_2(thf)_4$],[11b] notably with an Ap*/Yb ratio of 1:1. This outcome is driven by the extreme bulk of Ap* and contrasts the present metathesis reactions (Scheme 4).

Conclusions and Outlook

The direct reaction between lanthanoid metal and bulky aminopyridines is an effective and simple way to synthesize

true homoleptic "monomeric" amidopyridine complexes of Yb. The complexes predominantly adopt the amidopyridine binding mode. Relatively less bulky **2** results in the formation of a six-coordinate trivalent Yb complex, whereas more bulky **1** afforded a low-coordinate divalent Yb compound showing intermolecular C_{Aryl}–H agostic interactions, which do not persist in thf, from which five-coordinate [Yb(Ap′)$_2$(thf)] (**7**) is isolated. A further increase of the steric bulk leads to different chemistry, such as mixed amido/iodo complexes in salt metathesis chemistry. Further studies are directed towards the exploration of the differences in reactivity of the low-valent ytterbium complexes introduced here.

Experimental Section

General Procedures: All reactions and manipulations with air-sensitive compounds were performed under dry argon or N_2, using standard Schlenk and glovebox techniques. Non halogenated solvents were distilled from sodium/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled from sodium/benzophenone prior to use. All chemicals were purchased from commercial vendors and used without further purification. Ytterbium metal was obtained from Santoku. NMR spectra were obtained using either a 250 or 400 MHz Bruker ARX spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. X-ray crystal structure analyses were performed with a STOE-IPDS II or an Enraf–Nonius KAPPA CCD diffractometer equipped with a low-temperature unit. Structure solution and refinement were accomplished using SIR97,[24] SHELXL-97[25] and WinGX.[26] Crystallographic details are summarised in Table 1. Elemental analyses were carried out with Vario Elementar EL III or Leco CHNS-932 elemental analysers. CCDC-663340 to -663344 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [Yb(Ap′)$_2$] (3): Ap′H (0.50 g, 1.4 mmol), Yb powder (0.40 g, 2.31 mmol) and a drop of mercury metal were heated together at 250 °C in a vacuum-sealed glass tube for 16 d. The glass tube was gradually cooled to room temperature. After cooling, some red crystals of [Yb(Ap′)$_2$] were observed and handpicked for X-ray crystallography. Yield (0.476 g, 77%). $C_{50}H_{58}N_4Yb$ (888.04): calcd. C 67.62, H 6.58, N 6.31; found C 68.13, H 6.40, N 5.87. ^{1}H NMR (C_6D_6, 296 K): δ = 1.04 [br. d, 12 H, H^{22,23,25,26} Me$_2$(CH)], 1.32 [br. d, 12 H, H^{22,23,25,26} Me$_2$(CH)], 1.56 [br. s, 6 H, H^{13,14} Me(Ar)], 2.11 [br. s, 6 H, H^{13,14} Me(Ar)], 3.41 [br. m, 4 H, H^{21,24}], 5.60 [d, 2 H, H^3 *m*-H(py)], 5.67 [dd, 2 H, H^5 *m*-H(py)], 6.72 [t, 2 H, H^4 *p*-H(py)], 7.26–7.32 [m, 12 H, H^{9,10,11,17,18,19} H(Ar)] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.6 (s, C^{13,14}), 24.3 (C^{22,23,25,26}), 25.3 (C^{22,23,25,26}), 25.8 (s, C^{13,14}), 25.71 (C^{21,24}), 27.5 (C^{21,24}), 96.94 (C$^{3\text{ or }5}$), 106.73 (C$^{3\text{ or }5}$), 123.51 (C^{17,19}), 123.73 (C^{9,11}), 124.4 (C^{18}), 137.1 (C^{10}), 138.0 (C^{16,20}), 142.6 (C^7), 143.1 (C^4), 145.4 (C^{15}), 146.8 (C^{8,12}), 155.5 (C^6), 169.1 (C^2) ppm.

Synthesis of [Yb(Ap^{Me})$_3$] (4): Yb powder (0.262 g, 1.51 mmol), Ap^{Me}H (0.500 g, 1.51 mmol), and mercury metal (two drops) were heated together at 250 °C in a vacuum-sealed glass tube for 9 d. The glass tube was gradually cooled to 150 °C over 1 d, and further cooling to room temperature yielded light orange crystals of [Yb(Ap^{Me})$_3$]. Yield (0.200 g, 60%). $C_{69}H_{75}N_6Yb$ (1161.41): calcd. C 71.36, H 6.51, N 7.24; found C 72.02, H 7.35, N 6.92. ^{1}H NMR (C_6D_6, 298 K, paramagnetic species): δ = –5.20 (br. s), 1.11 (d), 2.19 (m), 11.96 (s), 20.17 (s), 34.95 (br. s), 67.05 (br. s) ppm.

Synthesis of [(Ap^{Me}K)] (6): Ap^{Me}H, (3.00 g, 9.08 mmol), and KH (0.364 g, 9.08 mmol) were placed into a Schlenk flask in a glove box. Diethyl ether (50 mL) was added to this mixture at 0 °C. The yellow reaction mixture was stirred at room temperature overnight, then filtered and the solvent removed in vacuo to dryness. The resulting yellow precipitate was washed with hexane and then dried under vacuum. Yield (3.240 g, 97%). $C_{23}H_{25}KN_2$ (368.56): calcd. C 74.95, H 6.84, N 7.60; found C 74.70, H 6.73, N 7.03. ^{1}H NMR (C_6D_6, 298 K): δ = 2.02 [s, 6 H, H^{13,14,22,24} *o*-Me], 2.17 [s, 6 H, H^{13,14,22,24} *o*-Me], 2.24 [s, 3 H, H$^{15\text{ or }23}$ *p*-Me], 2.33 [s, 3 H, H$^{15\text{ or }23}$ *p*-Me], 5.74 [dd, 1 H, H$^{3\text{ or }5}$ *m*-H(py)], 5.77 [dd, 1 H, H$^{3\text{ or }5}$ *m*-H(py)], 6.85 [s, 2 H, H^{18,20} H(Ar)], 6.96 [s, 2 H, H^{9,11} H(Ar)], 6.98 [t, 1 H, H^4 *p*-H(py)] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.2 (d, C^{13,14,22,24}), 20.1 (d, C^{13,14,22,24}), 20.9 (C^{15,23}), 21.2 (C^{15,23}), 103.9 (d, C$^{3/5}$), 105.4 (d, C$^{3/5}$), 129.3 (d, C^{9,11}), 129.4 (C^{19}), 129.5 (C^{18,20}), 131.2 (C^{17,21}), 135.2 (C^{8,12}), 135.5 (C^7), 138.1 (C^{10}), 140.1 (C^{22}), 141.3 (C^4), 158.4 (C^6), 165.5 (C^2) ppm.

Synthesis of [Yb(Ap′)$_2$(thf)] (7). Method I (Toluene Co-Crystallized): $YbI_2(thf)_4$ (1.072 g, 1.50 mmol) and **4** (1.10 g, 3.00 mmol) were placed into a Schlenk flask in a glove box; thf (40 mL) was added to the dark maroon-coloured reaction mixture which was stirred overnight. The solvent was evaporated under vacuum. The product was extracted with toluene (30 mL). The mixture was filtered and the filtrate concentrated to afford dark red crystals suitable for X-ray analysis after 24 h at –20 °C. Yield (0.600 g, 45%). $C_{54}H_{66}N_4OYb$ (960.17): calcd. C 67.55, H 6.93, N 5.84; found C 66.99, H 6.76, N 5.65. ^{1}H NMR (C_6D_6, 298 K): δ = 1.13 [d, 12 H, H^{22,23,25,26} Me$_2$(CH)], 1.29 [br. m, 16 H, H^{22,23,25,26} Me$_2$(CH), β-CH$_2$, thf], 1.90 [s, 12 H, H^{13,14} Me(Ar)], 3.41 [br. s, 8 H, H^{21,24}, α-CH$_2$, thf], 5.70 [dd, 2 H, H^3 *m*-H(py)], 6.82 [dd, 2 H, H^5 *m*-H(py)], 6.96 [t, 2 H, H^4 *p*-H(py)], 7.26–7.32 [m, 12 H, H^{9,10,11,17,18,19} H(Ar)] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.8 (d, C^{13,14}), 24.5 (C^{22,23,25,26}), 24.8 (C^{22,23,25,26}), 25.5 (C$^{\beta\text{-thf}}$), 28.4 (C^{21,24}), 31.9 (C^{21,24}), 68.0 (C$^{\alpha\text{-thf}}$), 105.9 (C$^{3/5}$), 123.4 (C^{17,19}), 123.8 (C^{9,11}), 128.2 (C^{18}), 135.8 (C^{10}), 138.2 (C^{16,20}), 142.2 (C^7), 142.3 (C^4), 143.5 (C^{15}), 146.9 (C^{8,12}), 155.8 (C^6), 168.9 (C^2) ppm. Analysis and NMR samples toluene-free. **Method II (Hexane Co-Crystallized):** A mixture of Yb metal (1.04 g, 6.0 mmol), $HgPh_2$ (0.71 g 2.0 mmol) and Ap′H (1.37 g, 4.0 mmol) in thf (40 mL) was heated to 65 °C while being stirred for 24 h. After cooling, the reaction mixture was filtered and the red-orange solution concentrated to dryness. Recrystallization of the residue from hexane gave the title compound as red needles Yield (1.24 g, 62%). ^{1}H NMR (C_6D_6, 298 K): δ = 0.94 [m, 2 H, CH$_2$ (hexane)], 1.14 [br. s, 12 H, H^{22,23,25,26} Me$_2$(CH)], 1.27 [br. m, 21 H, H^{22,23,25,26} Me$_2$(CH), β-CH$_2$, CH$_2$/CH$_3$(hexane)], 1.88 [br. s, 12 H, H^{13,14} Me(Ar)], 3.40 [br. s, 8 H, H^{21,24}, α-CH$_2$, thf], 5.71 [dd, ^3J = 6.9, ^4J = 0.9 Hz, 4 H, H$^{3\text{ or }5}$ *m*-H(py)], 6.81 [br. s, 6 H, H^{17,18,19} H(Ar)], 6.99 [br. m, 2 H, H^4 *p*-H(py)], 7.29 [br. m, 6 H, H^{9,10,11} H(Ar)] ppm.

Synthesis of [Yb(Ap^{Me})$_2$(thf)$_2$] (8): [$YbI_2(thf)_4$] (1.072 g, 1.50 mmol) and **6** (1.100 g, 3.00 mmol) were placed into a Schlenk flask in a glove box; thf (40 mL) was added to the reaction mixture being of dark maroon colour at the time of addition. The reaction mixture was stirred overnight. The solvent was removed under vacuum, and hexane (30 mL) was added. The mixture was filtered and the filtrate concentrated to afford dark red crystals suitable for X-ray analysis after 24 h at –20 °C. Yield (1.00 g, 85.57%). $C_{54}H_{66}N_4O_2Yb{\cdot}C_6H_{14}$ (1062.34): calcd. C 67.84, H 7.59, N 5.27; found C 67.57, H 7.87, N 5.72. ^{1}H NMR (C_6D_6, 298 K): δ = 1.23 (br. s, 8 H, β-CH$_2$, thf), 2.05 (s, 12 H, H^{13,14,22,24} *o*-Me), 2.12 (s, 6 H, H^{15,23} *p*-Me), 2.20 (s,

12 H, $H^{13,14,22,24}$ *o*-Me), 2.38 (s, 6 H, $H^{15,23}$ *p*-Me), 3.33 (br. s, 8 H, α-CH_2, thf), 5.81 [dd, 4 H, $H^{3/5}$ *m*-H(py)], 6.69 [s, 4 H, $H^{18,20}$ H(Ar)], 6.93 [t, 2 H, H^4 *p*-H(py)], 6.96 [s, 4 H, $H^{9,11}$ H(Ar)] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.2 (d, $C^{13,14,22,24}$), 20.1 (d, $C^{13,14,22,24}$), 21.2 ($C^{15,23}$), 23.0 ($C^{15,23}$), 25.4 (β-CH_2, thf), 68.3 (α-CH_2, thf), 105.9 (d, $C^{3/5}$), 105.7 (d, $C^{3/5}$), 129.3 (d, $C^{9,11}$), 130.0 ($C^{18,20}$), 132.5 ($C^{17,21}$), 135.8 (C^{19}), 136.1 ($C^{8,12}$), 137.9 (C^7), 138.1 (C^{10}), 140.1 (C^{22}), 147.5 (C^4), 156.3 (C^6), 167.9 (C^2) ppm.

Attempted Synthesis of [Yb(Ap*)$_2$] (10): Yb powder (0.189 g, 1.09 mmol), Ap*H (0.500 g, 1.09 mmol), and mercury metal (two drops) were heated together at 250 °C in a vacuum-sealed glass tube for 15 d. Progressive heating at 270 and 300 °C failed to achieve any reaction.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm 1166 "Lanthanoid-spezifische Funktionalitäten in Molekül und Material), the Fonds der Chemischen Industrie and the Australian Research Council is gratefully acknowledged.

[1] a) B. J. Burger, M. E. Thomson, W. D. Cotter, J. E. Bercaw, *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577; b) W. J. Piers, J. E. Bercaw, *J. Am. Chem. Soc.* **1990**, *112*, 9406–9407; c) R. H. Grubbs, G. W. Coates, *Acc. Chem. Res.* **1996**, *29*, 85–93.

[2] a) P. Margl, J. C. W. Lohrenz, T. Ziegler, P. E. Blöch, *J. Am. Chem. Soc.* **1996**, *118*, 4434–4441; b) A. C. Cooper, J. C. Huffman, K. Folting, R. G. Caulton, *Organometallics* **1996**, *15*, 3990–3997.

[3] a) M. Brookhart, M. L. H. Green, *J. Organomet. Chem.* **1983**, *250*, 395–408; b) M. Brookhart, M. L. H. Green, L.-L. Wong, *Prog. Inorg. Chem.* **1988**, *36*, 1–24.

[4] Z. Dawoodi, M. L. H. Green, V. S. B. Metetwa, K. J. Prout, *J. Chem. Soc. Chem. Commun.* **1982**, 802–803.

[5] For the sensitivity to steric effects and explanations based on molecular orbital analysis, electron delocalization and topological analysis of the electron density, see: E. Clot, O. Eisenstein, *Struct. Bonding (Berlin)* **2004**, *113*, 1–36.

[6] For the importance of local charge concentrations especially in d^0-metal–alkyl systems, see W. Scherer, G. S. Mc Grady, *Angew. Chem.* **2004**, *116*, 1816–1842; *Angew. Chem. Int. Ed.* **2004**, *43*, 1782–1806.

[7] Review article on aminopyridinato ligands:R. Kempe, *Eur. J. Inorg. Chem.* **2003**, 791–803.

[8] Review article on (aminopyridinato)lanthanoid chemistry:R. Kempe, H. Noss, T. Irrgang, *J. Organomet. Chem.* **2002**, *647*, 12–20.

[9] S. Deeken, G. Motz, R. Kempe, *Z. Anorg. Allg. Chem.* **2007**, *633*, 320–325.

[10] Selected reviews on amidinato coordination chemistry: a) J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219–300; b) F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403–481; c) N. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondo, S. Masuda, K. Miyazaki, K. Matsubara, K. Kirchner, *Coord. Chem. Rev.* **2003**, *245*, 177–190; d) P. C. Junk, M. L. Cole, *Chem. Commun.* **2007**, 1579–1590.

[11] a) N. M. Scott, T. Schareina, O. Tok, R. Kempe, *Eur. J. Inorg. Chem.* **2004**, 3297–3304; b) N. M. Scott, R. Kempe, *Eur. J. Inorg. Chem.* **2005**, 1319–1324; c) W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978; d) W. P. Kretschmer, A. Meetsma, B. Hessen, N. M. Scott, S. Qayyum, R. Kempe, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1936–1938; W. P. Kretschmer, B. Hessen, A. Noor, N. M. Scott, R. Kempe, *J. Organomet. Chem.* **2007**, *692*, 4569–4579.

[12] T. Schmalz, J. Burkhardt, T. Irrgang, R. Kempe, *Z. Kristallogr. - New Cryst. Struct.* **2005**, *220*, 405–406.

[13] a) S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 7240–7241; b) J. F. Hartwig, *Synlett* **1996**, 329–340; c) J. P. Wolfe, H. Tomori, J. P. Sadihghi, J. Yin, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1158–1174; d) T. Schareina, G. Hillebrand, R. Kempe, *Eur. J. Inorg. Chem.* **2001**, 2421–2426; e) J. Silberg, T. Schareina, R. Kempe, K. Wurst, M. R. Buchmeiser, *J. Organomet. Chem.* **2001**, *622*, 6–18; f) M. R. Buchmeiser, T. Schareina, R. Kempe, K. Wurst, *J. Organomet. Chem.* **2001**, *634*, 39–46; g) N. M. Scott, T. Schareina, O. Tok, R. Kempe, *Eur. J. Inorg. Chem.* **2004**, 3297–3304.

[14] For reviews, see a) G. B. Deacon, C. M. Forsyth, in *Inorganic Chemistry Highlights* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2002**, chapter 7, p. 139–153; b) K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2005**, *631*, 811–828; c) G. Meyer, *Z. Anorg. Allg. Chem.*, in press.

[15] See, for example: a) G. B. Deacon, C. M. Forsyth, P. C. Junk, B. W. Skelton, A. H. White, *Chem. Eur. J.* **1999**, *5*, 1452–1459; b) G. B. Deacon, T. Feng, C. M. Forsyth, A. Gitlits, D. C. R. Hockless, Q. Shen, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **2000**, 961–966; c) G. B. Deacon, A. Gitlits, P. W. Roesky, M. K. Burgstein, K. C. Lim, B. W. Skelton, A. H. White, *Chem. Eur. J.* **2001**, *7*, 127–128; d) G. B. Deacon, C. M. Forsyth, A. Gitlits, R. Harika, P. C. Junk, B. W. Skelton, A. H. White, *Angew. Chem.* **2002**, *114*, 1383–1385; *Angew. Chem. Int. Ed.* **2002**, *41*, 3249–3251; e) K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2127–2132; f) G. B. Deacon, C. M. Forsyth, A. Gitlits, B. W. Skelton, A. H. White, *Dalton Trans.* **2004**, 1239–1247; g) K. Müller-Buschbaum, C. Quitmann, *Inorg. Chem.* **2006**, *45*, 2678–2687; h) G. B. Deacon, C. M. Forsyth, P. C. Junk, S. G. Leary, *New J. Chem.* **2006**, *30*, 592–596; i) C. C. Quitmann, V. Bezugly, F. R. Wagner, K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1173–1186.

[16] See, for example a) J. Hitzbleck, A. T. O'Brien, C. M. Forsyth, G. B. Deacon, K. Ruhlandt-Senge, *Chem. Eur. J.* **2004**, *10*, 3315–3323; b) J. Hitzbleck, G. B. Deacon, K. Ruhlandt-Senge, *Angew. Chem.* **2004**, *116*, 5330–5332; *Angew. Chem. Int. Ed.* **2004**, *43*, 5218–5230.

[17] P. B. Hitchcock, J. A. K. Howard, M. F. Lappert, S. Prashar, *J. Organomet. Chem.* **1992**, *437*, 177–189.

[18] W. J. Evans, L. A. Hughes, T. P. Hanusa, *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272.

[19] W. J. Evans, L. A. Hughes, T. P. Hanusa, *Organometallics* **1986**, *5*, 1285–1291.

[20] S. Harder, *Angew. Chem. Int. Ed.* **2004**, *43*, 2714–2718.

[21] As determined from a survey of the Cambridge Crystallographic Database, August, **2006**.

[22] R. D. Shannon, *Acta Crystallogr.* **1976**, *32*, 751–767.

[23] M. E. van der Boom, M. A. Iron, O. Atasoylu, L. J. W. Shimon, H. Rozenberg, Y. Ben-David, L. Konstantinovski, J. M. L. Martin, D. Milstein, *Inorg. Chim. Acta* **2004**, *357*, 1854–1864.

[24] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[25] G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Analysis*, release 97–2, Institut für Anorganische Chemie, University of Göttingen, Germany, **1998**.

[26] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: October 11, 2007
Published Online: December 7, 2007

