ORGANOMETALLICS

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Yttrium Complexes Featuring Different Y−C Bonds. Comparative Reactivity Studies: Toward Terminal Imido Complexes

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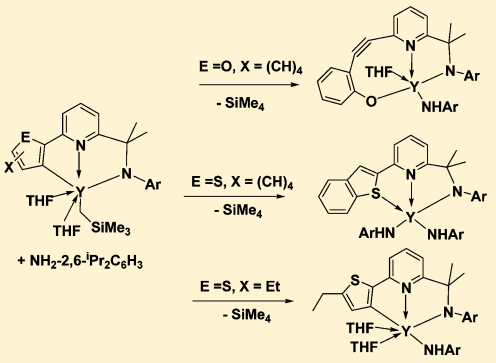
Supporting Information

ABSTRACT: The reactions of 2,6-diisopropylaniline with equimolar amounts of alkyl−heteroaryl yttrium complexes containing Y−C(sp^3, alkyl) along with Y−C(sp^2, heteroaryl) bonds resulting from intramolecular C−H bond activation of the amido−pyridinate ligands [NNO^{BzFur}]YCH$_2$SiMe$_3$(THF)$_2$, [NNS^{BzTh}]YCH$_2$SiMe$_3$(THF)$_2$, and [NNS^{EtTh}]YCH$_2$SiMe$_3$(THF)$_2$ have been scrutinized with the aim of synthesizing yttrium terminal imido species. These reactions occur at ambient temperature with the protonolysis of the Y−C(sp^3, alkyl) bond, thus affording anilido−heteroaryl species and maintaining the residual Y−C(sp^2, heteroaryl) bond untouched. However, the subsequent transformation of the as-synthesized anilido−heteroaryl complexes depends on the nature of the substituent on the 6-position of the pyridyl ring. In the case of the benzofuryl yttrium derivative [NNO^{BzFur}]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(THF)$_2$ (**4**), heating to 50 °C results in benzofuran ring opening with the formation of an anilido species supported by a dianionic amido−yne−phenolate ligand framework, [NNC≡CO]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(THF) (**6**). In contrast, a complex containing a benzothiophenyl moiety, [NNS^{BzTh}]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(THF)$_2$ (**7**), slowly undergoes protonation of the Y−C(sp^2, heteroaryl) bond and a ligand redistribution reaction takes place, affording an yttrium bis(anilido) species supported by a monoanionic amido−pyridinate ligand featuring intramolecular Y−S heteroaryl coordination, [NNS^{BzTh}]Y[NH-2,6-^{i}Pr$_2$C$_6$H$_3$]$_2$ (**9**). It is worth noting that an yttrium complex containing α-thiophenyl fragment, [NNS^{EtTh}]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(THF)$_2$ (**10**), turned out to be extraordinarily robust and no transformation was ever detected even upon heating the complex at 100 °C for prolonged times.



INTRODUCTION

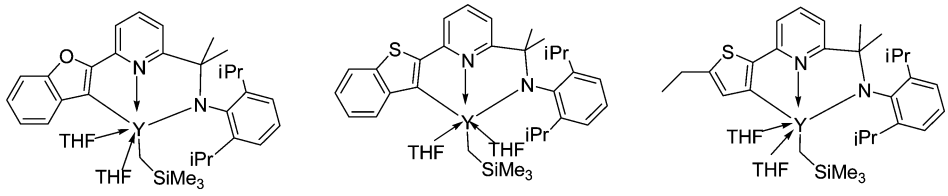
Rare-earth complexes containing M−C σ bonds still deserve particular interest as highly active species that exhibit unique reactivity[1] and ability to promote activation and derivatization of unsaturated[2] and saturated[3] substrates. Recently we have reported how the reaction of an equimolar amount of [Y(CH$_2$SiMe$_3$)$_3$(thf)$_2$] with aminopyridine ligands bearing aryl or heteroaryl substituents at the 6-position of the pyridine ring results in quantitative intramolecular sp^2 or sp^3 C−H bond activations. These reactions proved to be a useful synthetic approach, allowing for the convenient synthesis of novel yttrium complexes featuring the simultaneous presence of two different Y−C bonds (Y−benzyl, Y−aryl, or Y−heteroaryl together with Y−alkyl).[4] Notably, the Y−C bonds in the isolated complexes showed different reactivities: i.e., upon complex treatment with an excess of PhSiH$_3$, a σ-bond metathesis reaction took place selectively on the residual Y−alkyl bonds, leading to the formation of unique yttrium aryl−-hydrido, benzyl−hydrido, and heteroaryl−hydrido species.

Chen et al. reported in 2010 on the synthesis and characterization of the first (and still the only) example of a rare-earth complex with a terminal imido ligand.[5] Complexes containing a double nitrogen−metal bond have important synthetic potentialities due to the ability of the M═N functional group to undergo several reactions/transformations (metathesis of imines and carbodiimides, metallacycle formation with alkynes and alkenes, and C−H bond activation).[6] It is worth noting that, unlike the well-established imido chemistry based on transition metals,[7] that of rare-earth metals is still in its infancy.[8] Synthetic difficulties are basically related to the pronounced tendency of these large metal ions to assemble in the form of more stable bi- or polymetallic complexes with μ_2-imido ligands.[8,9] Several examples of C−H bond activation resulting from the transformation of terminal imido rare-earth complexes have been also documented.[8d,f] Bulky polydentate ligands able to provide kinetic stability to the final imido species may be employed in order to overcome these synthetic limitations. Accordingly, the aforementioned alkyl−heteroaryl yttrium complexes[4] coordinated by amidopyr-

Received: February 4, 2013

   dx.doi.org/10.1021/om400099z | *Organometallics* XXXX, XXX, XXX−XXX

Chart 1. Yttrium Alkyl−Heteroaryl Complexes Containing Potentially Coordinative S and O Donor Sites



idinate ligands represent good candidates for the synthesis of related derivatives bearing terminal imido fragments via reaction with sterically demanding anilines. Indeed, the stabilization of the terminal imido species would potentially be assisted from an intramolecular coordination of either S (soft) or O (hard) donors belonging to the tridentate amidopyridinate system (N,N,O or N,N,S) itself; the Y−C(heteroaryl) bond protonolysis carried out by the aniline reagent would render accessible those ligand donor sites not available in the former species. In this regard, inspired by the challenging synthesis of rare-earth terminal imido complexes, we have explored the reactions of yttrium alkyl−heteroaryl complexes with 2,6-diisopropylaniline.

RESULTS AND DISCUSSION

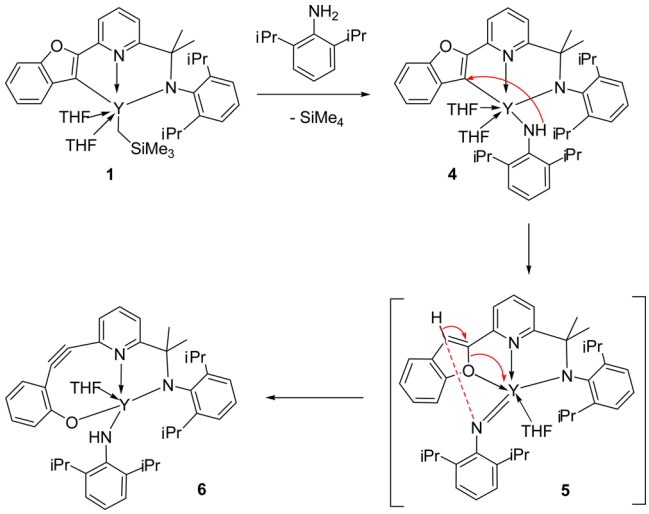
In order to prepare terminal imido yttrium species, we attempted the reactions of equimolar amounts of alkyl−heteroaryl complexes **1**−**3** (Chart 1) with 2,6-diisopropylaniline. As the crucial role of a Lewis base coordination to the metal center is emphasized as a prerequisite for the formation of terminal imido complexes,[5] we fix upon the use of tridentate ligands combining both hard/hard (N,O) and hard/soft (N,S) basic centers (Chart 1).

The NMR-tube reaction of **1** with 2,6-diisopropylaniline was carried in C_6D_6 at ambient temperature. The disappearance of the doublet at −0.69 ppm (attributed to the hydrogen atoms of the residual methylene group bound to the yttrium center) and the concomitant release of $SiMe_4$ were indicative of Y−C(alkyl) bond protonolysis. Furthermore, the persistence (in the $^{13}C\{^1H\}$ NMR spectrum) of a doublet centered at 157.3 ppm ($^1J_{YC}$ = 40.0 Hz) assigned to the sp^2 carbon of the benzofuryl moiety σ-bonded to the metal center, together with the appearance (in the ^1H NMR spectrum) of a doublet at 5.10 ppm ($^2J_{YH}$ = 2.2 Hz), characteristic for an NH anilido proton,[17] supported the formation of the benzofuryl−anilido species **4** (Scheme 1).

Complex **4** was isolated and completely characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and microanalysis. Following the behavior of **4** in C_6D_6 solution at room temperature by ^1H NMR spectroscopy revealed that neither decomposition nor further transformation took place even after several days. In contrast, when the complex solution temperature was raised to 50 °C, a relatively rapid conversion of **4** into a new species was observed (50% of conversion within 15 h).

The preparative-scale reaction of **1** with 2,6-diisopropylaniline was carried out in a toluene/hexane mixture (toluene/hexane 1/4) at room temperature, and the mixture was then heated at 50 °C for 30 h. The reaction mixture turned from yellow to deep red, and yellowish orange crystals suitable for X-ray analysis were isolated in 54% yield after cooling the mixture to −20 °C.

Scheme 1. Synthesis of the Anilido Complex 4 and Its Subsequent Thermal Rearrangement (Furyl Ring Opening) to Complex 6 Stabilized by a Dianionic Amido−Yne−Phenolate Ligand



An X-ray diffraction study showed that the anilido complex **6** contains a dianionic amido−yne−phenolate ligand (Figure 1). Complex **6** crystallizes as a solvate species (**6**·C_7H_8). Due to the furyl fragment ring opening an 11-membered chelating amido−yne−phenolate group metallacycle was formed. This metallocycle is not planar, the maximum deviation of the atoms from its plane being 0.690(1) Å. The yttrium atom in **6** is covalently bonded with one oxygen and one nitrogen atom from the amido−yne−phenolate framework (Y(1)−O(1) = 2.1808(9) Å, Y(1)−N(1) = 2.244(1) Å), while the nitrogen of the pyridine fragment forms with yttrium a coordinative bond (Y(1)−N(2) = 2.409(1) Å). Due to covalent bonding with the anilido fragment (Y(1)−N(3) = 2.203(1) Å) and coordination of one THF molecule, the coordination number at the yttrium is 5. The complex adopts a distorted-square-pyramidal coordination geometry, whose base is set up by the N and O atoms from the amido−yne−phenolate moiety and one O atom from a THF molecule. The covalent Y−N bonds in **6** are somewhat nonequivalent, but their values are comparable to those reported for related amides on five-coordinated yttrium[10] complexes. The Y−O bond length is also in a good agreement with the values reported for five-coordinated yttrium alkoxides.[10b,11] The angles around carbon atoms C(21) and C(22) (C(21)−C(22)−C(23) = 173.3(2)°, C(20)−C(21)−C(22) = 163.9(2)°) are consistent with a C_{sp} hybridization of the acetylenic moiety. The corresponding C(21)−C(22) bond distance of 1.200(2) Å is also in agreement with triple-bond character.[12] The C(23)−C(24) bond length (1.410(2) Å) is

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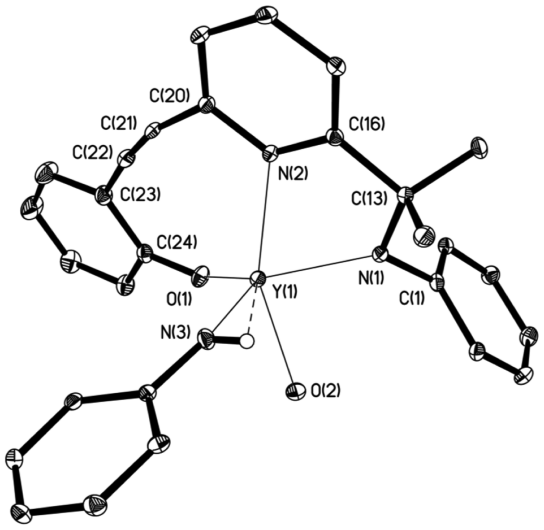


Figure 1. Molecular structure of complex **6** with 30% probability ellipsoids. The ^{i}Pr substituents of the aminopyridinate ligand, the methylene groups of THF molecules, and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y(1)−O(1) = 2.1808(9), Y(1)−O(2) = 2.361(1), Y(1)−N(1) = 2.244(1), Y(1)−N(2) = 2.409(1), Y(1)−N(3) = 2.203(1), O(1)−C(24) = 1.321(2), C(20)−C(21) = 1.432(2), C(21)−C(22) = 1.200(2), C(22)−C(23) = 1.425(2), C(23)−C(24) = 1.410(2); C(20)−C(21)−C(22) = 163.9(2), C(21)−C(22)−C(23) = 173.3(2).

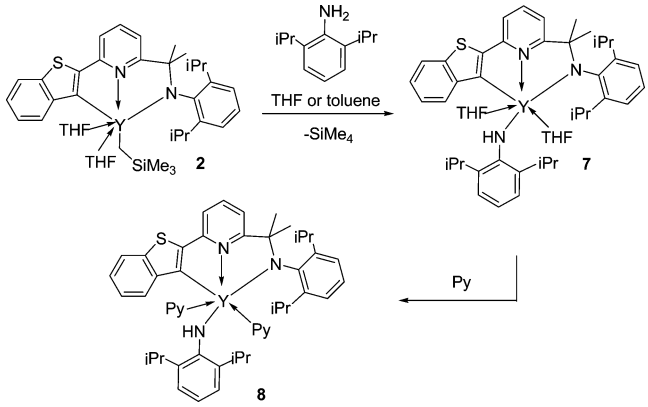
characteristic for aromatic C−C bonds.[12] The single bonds next to the triple bond (C(22)−C(23) = 1.425(2) Å) and C(20)−C(21) = 1.432(2) Å) show distances within the range for those in eneynes.[13]

Additionally, an intense band at 2250 cm^{-1} in the Raman spectrum of complex **6** gives further evidence of the presence of a triple bond.[29]

Furan ring-opening reactions, triggered by intramolecular C−H bond activation in alkyl and heteroaryl species, have been reported in a few cases.[14] Formation of complex **6** can be rationalized by a sequence of transformations of the benzofuryl−amido species **4**, a reliable representation of which is provided in Scheme 1. First, an intramolecular protonolysis of the Y−C(heteroaryl) bond promoted by the residual proton of the NH amido function takes place, leading to the formation of the terminal imido complex **5** (Scheme 1). Afterward, the transient terminal imido complex undergoes rapid intramolecular C−H bond activation, leading to the ring opening of the furyl cycle with the generation of **6**. It is worth noting that, when the reaction course of the thermal rearrangement of **4** is followed by NMR spectroscopy, no signals attributed to the transient terminal imido species **5** were ever detected, thus revealing an extremely short lifetime (on the NMR time scale) of the imido intermediate itself.

Aiming at stabilizing the terminal imido species as well as evaluating the general character of this heterocycle ring-opening reaction, we have investigated the reaction of 2,6-diisopropylaniline with the analogous thio analogue **2** (Scheme 2). The coordination of a soft Lewis base along with a lower energy of the covalent Y−S bond (in comparison to that of Y−O)[15] was thought to be beneficial to the final stabilization of the expected terminal imido yttrium species. It is worth noting that we found a dramatic impact on the reaction outcome by the replacement of the benzofuryl fragment with the benzothiophenyl fragment. Indeed, the reaction of **2** with 2,6-diisopropylaniline in both

Scheme 2. Synthesis of the Anilido Complexes 7 and 8



toluene and THF afforded the benzothiophenyl−amido complex **7**, which was isolated as a yellow crystalline solid in 78% yield (Scheme 2). Complex **7** was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and microanalysis. Unfortunately, all our attempts to obtain single crystals of **7** suitable for X-ray diffraction studies failed. Nevertheless, the treatment of **7** with pyridine and its subsequent recrystallization from benzene allowed for the isolation of the bis(pyridine) adduct **8**, which was characterized by an X-ray diffraction study (Figure 2). The

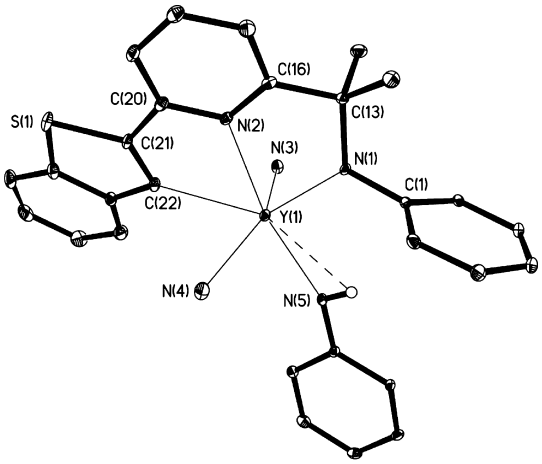


Figure 2. Molecular structure of complex **8** with 30% probability ellipsoids. The ^{i}Pr substituents in the aminopyridinate and aniline ligands, the CH groups of the Py molecules, and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y(1)−N(1) = 2.253(2), Y(1)−N(2) = 2.475(2), Y(1)−N(3) = 2.481(2), Y(1)−N(4) = 2.506(3), Y(1)−N(5) = 2.293(2), Y(1)−C(22) = 2.551(3); N(1)−Y(1)−N(2) = 67.64(8), N(1)−Y(1)−N(5) = 94.81(9), N(1)−Y(1)−N(3) = 102.73(8), N(1)−Y(1)−N(4) = 107.18(9), N(2)−Y(1)−N(3) = 98.81(8), N(2)−Y(1)−N(4) = 90.03(9), N(2)−Y(1)−N(5) = 160.90(8), N(3)−Y(1)−N(5) = 92.22(9), N(4)−Y(1)−N(5) = 88.10(9).

proton of the NH group in **7** was clearly evidenced by a singlet at 4.46 ppm, while the presence of a doublet at 194.7 ppm in the ^{13}C{^{1}H} NMR spectrum ($^{1}J_{YC}$ = 40.3 Hz) was consistent with the sp^{2}-carbon atom of the benzothiophene ring still covalently bound to the yttrium center.

The X-ray diffraction study of **8** revealed that it crystallizes as a solvate (**8**·C_6H_6). The yttrium atom in **8** is covalently bound by the amido nitrogen of the amidopyridinate ligand, the sp^{2} carbon of the thiophenyl ring, and a nitrogen atom of the

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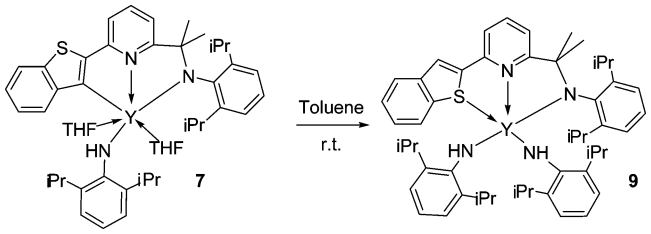
anilido fragment (Figure 2). Moreover, yttrium is coordinated by one nitrogen from the pyridyl central unit and two nitrogens from the ancillary pyridine molecules. The coordination number of yttrium in **8** is 6, with a distorted-square-bipyramidal coordination geometry. The Y−C bond length in **8** (2.551(3) Å) is slightly longer in comparison to that measured in related heteroaryl−hydrido complexes (2.514(3) Å).[4b] The distances between yttrium and nitrogen atoms of the amidopyridinate ligand (Y(1)−N(1) = 2.253(2) Å, Y(1)−N(2) = 2.475(2) Å) are close to those previously reported for related six-coordinated yttrium complexes[4a,b] (2.202(1)−2.254(1) and 2.420(1)−2.462(2) Å, respectively). The amidopyridinate ligand is not planar, showing a maximum deviation of atoms from the eight-membered metallacycle of 0.343(2) Å (C(13)). The angle between the planes containing the pyridine central unit and the benzothiophenyl fragments is 13.6°. The measured covalent Y−N(5) bond distance is 2.293(2) Å.

When a yellow solution of **7** in toluene was kept at room temperature for 1 week, the precipitation of orange crystals took place. Notably, an X-ray diffraction study of the isolated crystals revealed the formation of a bis(anilido) yttrium compound **9** supported by the tridentate amidopyridinate ligand (Scheme 3). Isolation of **9** was continued after the

Scheme 3. Synthesis of the Bis-Anilido Complex 9



separation of the first batch of crystals ,and an overall 30% yield of **9** were collected from the mother liquor after maintaining the solution for 2 weeks at room temperature.

Complex **9** crystallizes as a solvate with one molecule of toluene per unit. In **9** the yttrium atom is coordinated by a monoanionic tridentate amidopyridinate ligand, the latter resulting from the intramolecular protonolysis of the Y−C(heteroaryl) bond on precursor **7** (Scheme 3 and Figure 3).

The Y−C(heteroaryl) bond protonolysis allows the sulfur atom to coordinate the yttrium center. As Figure 3 shows, the coordination number of yttrium is 5. Unlike the case in complex **7**, the amidopyridinate ligand in **9** is bound to the yttrium center via one covalent Y−N bond, while both sulfur and nitrogen atoms form coordinative bonds with the metal center. The length of the covalent Y−N(1) bond (2.177(3) Å) in **9** is slightly shorter than that measured in related six-coordinated yttrium complexes stabilized by dianionic amidopyridinate ligands (2.206(2)−2.254(2) Å),[4] but it falls into the range of values reported for five-coordinate yttrium amides.[10] The length of the coordination bond between yttrium and the nitrogen atom of the amidopyridinate ligand (Y(1)−N(2) = 2.475(2) Å) is close to those previously reported for related six-coordinated yttrium complexes (2.420(1)−2.462(2) Å).[4a,b] Finally, the Y−S bond distance in **9** (3.0755(9) Å) is much longer in comparison to the distances measured in five-coordinated yttrium complexes with either chelating bis(thiophosphinic amide) (2.7910(6) Å)[16a] or bis(thiophosphinic amidate) (2.718(1) and 2.741(1) Å) ligands.[16b] The Y−S

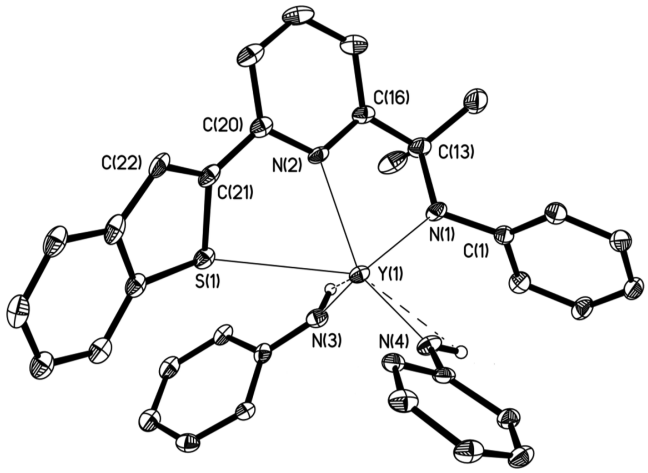


Figure 3. Molecular structure of complex **9** with 30% probability ellipsoids. The ^{i}Pr substituents of the aminopyridinate ligand, the aniline ligands, and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y(1)−N(1) = 2.177(3), Y(1)−N(2) = 2.475(2), Y(1)−N(3) = 2.236(3), Y(1)−N(4) = 2.231(2), Y(1)−S(1) = 3.0755(9); N(1)−Y(1)−N(2) = 70.70(9), N(1)−Y(1)−S(1) = 132.79(7), N(2)−Y(1)−S(1) = 65.26(6), N(3)−Y(1)−N(4) = 116.36(9).

distance in **9** significantly exceeds the sum of the covalent radii of these atoms (2.82 Å); nevertheless, it still lies below the sum of van der Waals radii (4.25 Å) (Y, R_{coval} = 1.68, R_{VdW} = 2.4; S, R_{coval} = 1.14, R_{VdW} = 1.85).[22] It is worth noting that complexes containing Y−S coordination bonds are still rather rare. The bond lengths between yttrium and anilido nitrogens (Y−N(3,4) = 2.231(2) and 2.236(3) Å, respectively) slightly exceed those measured in **6** (2.203(1) Å) but are somewhat longer than those found in **8** (2.293(2) Å). The dihedral angle between the pyridinate and benzothiophenyl fragments (29.8°) is significantly larger in comparison to that measured in **8** (13.6°) as well as those found in other related yttrium complexes.[4b]

The generation of a bis(anilido) species, in pursuit of the synthesis of rare-earth terminal imido complexes, has been already documented.[17] Complex **9** may result from a hydrogen abstraction by a transient terminal imido complex followed by a ligand redistribution reaction. Unfortunately, all our attempts to isolate the imido intermediate still failed. The source for hydrogen abstraction also remains unclear, but THF seems to be a plausible candidate for that role. The intermolecular protonolysis and ligand redistribution reactions can be also evoked as possible routes of formation of **9**.

All these data taken together make reasonable the assumption of the crucial role played by the nature of the heterocyclic group at the amidopyridinate ligand in controlling/driving the evolution path of the intermediate terminal imido complexes. While in the case of a benzofuryl-containing system a concerted intramolecular C−H bond activation and ring-opening reaction occur, when a benzothiophene-containing analogue (having similar steric and electronic properties) is employed, the reaction pathway changes dramatically: no heterocycle ring opening is observed, while protonolysis and ligand redistribution reactions take place. Such a different behavior could originate in the contribution of either different Lewis base softness/hardness of the oxygen and the sulfur atoms or by a substantial difference of in terms of energies of Y−O and Y−S covalent bonds (Y−O, 692.5−719.0 kJ/mol; Y−

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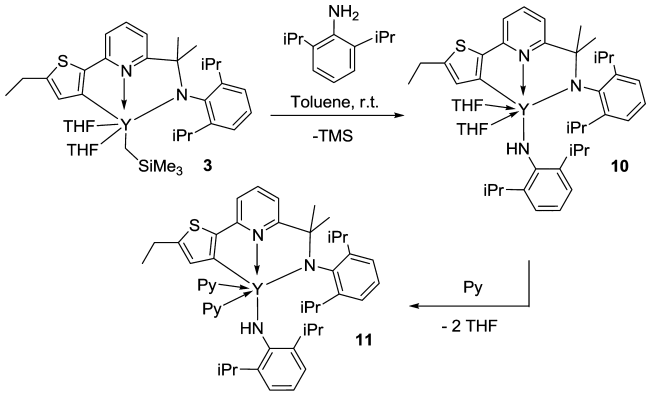
S, 528.4 ± 10.5 kJ/mol).[15] In our opinion, the formation of a strong covalent Y−O bond is largely responsible for the ring-opening reaction occurring at the benzofuryl moiety and leading to complex **6**.

As an additional proof of the relevant contribution played by the ligand's heteroaromatic group on the transformation/rearrangement path of the rare-earth terminal imido intermediates, we finally investigated the reaction of 2,6-diisopropylaniline with complex **3** (containing an α-ethylthiophene substituent at the 6-position of the pyridine ring; see Chart 1). The NMR-tube reaction of **3** with an equimolar amount of 2,6-diisopropylaniline in C_6D_6 at room temperature showed the occurrence of a selective protonolysis of the Y−C(alkyl) bond exclusively while the Y−C(thien-2-yl) bond remained untouched (as confirmed by a clear doublet at 202.1 ppm (d, $^1J_{YC}$ = 36.2 Hz) in the $^{13}C\{^1H\}$ NMR spectrum). The reaction takes place with the simultaneous release of $SiMe_4$ and formation of the anilido species **10**. A similar reactivity between 2,6-diisopropylaniline and yttrium complexes containing both Y−C(alkyl) and Y−C(aryl) bonds has been recently documented by Chen et al.[5] Complex **10** was characterized by spectroscopic analysis and microanalysis. Unfortunately, all attempts to obtain suitable crystals of **10** for X-ray analysis failed. However, the treatment of **10** with an excess of pyridine and the subsequent recrystallization from toluene allowed us to obtain high-quality crystals of the pyridine adduct **11** (Scheme 4).

Scheme 4. Synthesis of the Anilido Complexes 10 and 11



An X-ray diffraction study of **11** (Figure 4) revealed that the coordination environment at the yttrium center was set up by two nitrogen atoms and one carbon atom from the dianionic tridentate amidopyridinate ligand, one nitrogen atom from the monoanionic anilido group, and two nitrogen atoms from the two pyridine molecules. The coordination number of yttrium in **11** is 6. The coordination environment around the yttrium ion can be considered as a distorted octahedron where the amidopyridinate and anilido ligands are located in the equatorial plane, while two pyridine molecules occupy the apical positions. Complex **11** crystallizes as a solvate with one toluene molecule and contains two crystallographically independent molecules in the asymmetric unit. Both molecules have similar parameters, and therefore only one of them will be discussed.

The coordination mode of the amidopyridinate ligand in **11** is similar to that observed in the parent alkyl species.[4b] The Y−amidopyridinate fragment is planar (the maximum deviation from the plane is 0.047(1) Å). The Y−C(22) bond (2.506(2)

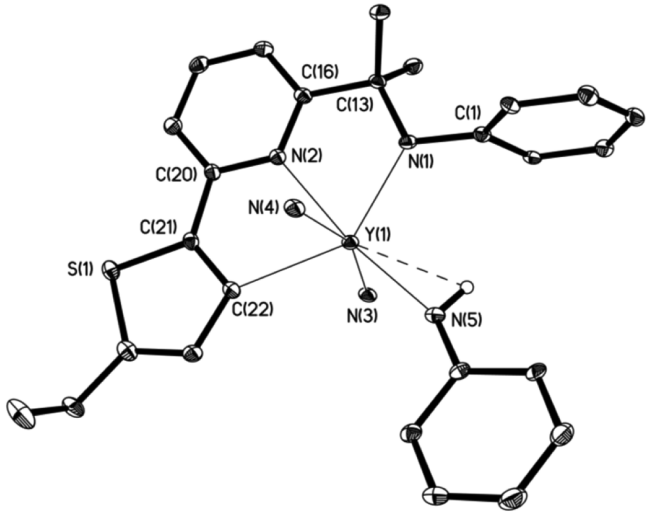


Figure 4. Molecular structure of complex **11** with 30% probability ellipsoids; the ^{i}Pr substituents in amidopyridinate and aniline ligands, the CH groups of the Py molecules, and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y(1)−N(1) = 2.247(2), Y(1)−N(5) = 2.289(2), Y(1)−N(2) = 2.452(2), Y(1)−N(3) = 2.496(2), Y(1)−N(4) = 2.495(2), Y(1)−C(22) = 2.506(2); N(1)−Y(1)−N(2) = 68.17(7), N(1)−Y(1)−C(2) = 137.13(8), N(3)−Y(1)−N(4) = 161.97(7).

Å) in **11** is slightly longer than those measured in both the alkyl precursor **3** (2.482(2) Å)[4b] and in the related yttrium monoalkyl thien-2-yl species, the latter featuring an analogue intramolecular C−H bond activation at the β position of the thienyl moiety (2.423(3) Å).[19] The distance between the Y center and the anilido nitrogen atom (2.289(2) Å) is slightly longer than that measured for the amido Y−N bond, the latter being similar to those observed in related structures.[17a,20] The dihedral angle between the pyridinate and thiophenyl fragments is 1.7°, and it is significantly lower than that observed in **8**.

For all compounds (**6**, **8**, **9**, and **11**) featuring anilido fragments, the observed bond distances between the Y atom and the centers of N−H bonds (2.27−2.37 Å) together with the measured Y−N−H angles (85.4−101.2°) suggest the presence of agostic Y−NH bond interactions.[23]

It is worth noting that complex **10** is distinguished by its extraordinary stability. Unlike complexes **4** and **7**, neither intramolecular protonolysis of Y−C(thien-2-yl) bond by the anilido NH group nor a ligand redistribution reaction takes place both at room temperature (for prolonged times—up to 1 month) and upon heating at 80 °C for several hours. No decomposition/rearrangement takes place even after heating at 100 °C for 3 h. Such a result demonstrates, once more, how small modifications on the ligand framework can change the reactivity at the metal center remarkably, driving the reaction course toward different (and differently stable) organolanthanide species.

■ CONCLUSION

In this paper we have described the reactions of alkyl−heteroaryl complexes **1**−**3**, containing Y−C(sp^3, alkyl) and Y−C(sp^2, heteroaryl) bonds, with an equimolar amount of 2,6-diisopropylaniline. For all scrutinized systems the protonolysis of the Y−C(alkyl) bond takes place selectively at room temperature, leading to the formation of the corresponding anilido−heteroaryl species which keep the Y−C(sp^2, hetero-

dx.doi.org/10.1021/om400099z | Organometallics XXXX, XXX, XXX−XXX

aryl) bonds untouched. Notably, both the stability of the anilido−heteroaryl derivatives and their potential transformation/rearrangement paths remarkably differentiate one from the other upon heating the complexes at elevated temperatures. In this regard, we have demonstrated how the nature of the heteroaryl framework attached to the 6-position of the pyridine ring can strongly influence both the reaction course and the complex stability. Thus, in the case of the anilido complex **4** a furyl ring opening takes place, leading to the unprecedented amido−yne−phenolate derivative **6**. Supposedly, complex **6** results from an intramolecular protonolysis of the Y−C(heteroaryl) bond (promoted by the residual proton of the NH anilido group), formation of the terminal imido complex, and its subsequent and rapid intramolecular hydrogen abstraction at the β-position of the heteroaromatic moiety. For the analogous complex **7**, containing a benzothiopheyl fragment with stereoelectronic properties similar to those of **4**, no heteroaryl ring opening takes place. It seems reasonable to invoke the formation of a strong covalent Y−O bond as the main driving force toward the generation of **6**. Unlike **4**, a solution of complex **7** undergoes slow Y−C(heteroaryl) bond protonolysis, leading to the formation of a complex stabilized by a monoanionic amidopyridinate ligand featuring a coordinative intramolecular Y−S interaction. Finally, the anilido−heteroaryl complex **10** featuring an α-ethylthiophenyl group turns out to be extraordinarily inert, since no reaction/rearrangement takes place even after prolonged heating at high temperatures (up to 100 °C). Further studies are currently ongoing in our laboratories with the aim at exploring the role of both the multidentate ancillary ligands and the rare-earth metal ion sizes on the formation and stability of terminal imido species.

EXPERIMENTAL SECTION

All experiments were performed in evacuated tubes by using standard Schlenk techniques, with rigorous exclusion of traces of moisture and air. After being dried over KOH, THF was purified by distillation from sodium/benzophenone ketyl; hexane and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. C_6D_6 was dried with sodium and condensed under vacuum into NMR tubes prior to use. 2,6-Diisopropylaniline was purchased from Acros and was dried over CaH_2 and molecular sieves. Anhydrous $(Me_3SiCH_2)_3Y(THF)_2$[24] and compounds **1** and **3**[4] were prepared according to literature procedures. The imino precursor (N^{2BTh}) to the benzothiophene-containing aminopyridinate ligand (N^2H^{BTh}) was prepared according to similar procedures reported in the literature.[25] All other commercially available chemicals were used after the appropriate purifications. NMR spectra were recorded with either a Bruker DPX 200 or a Bruker Avance DRX-400 spectrometer in $CDCl_3$ or C_6D_6 at 25 °C, unless otherwise stated. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced internally to the residual solvent resonances and are reported in ppm relative to TMS. IR spectra were recorded as Nujol mulls with a Bruker Vertex 70 instrument. Raman spectra were recorded with the RAM II accessory module coupled to the Bruker Vertex 70, equipped with a InGaAs detector and an Nd:YAG laser source (1064 nm) for sample excitation at a power of ∼450 mW and resolution of 4 cm^{-1}. All of the Raman spectra were recorded in the wavenumber range 50−3500 cm^{-1}. Lanthanide metal analyses were carried out by complexometric titrations. The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of the Benzothiophene-Containing Aminopyridinate Ligand (N_2H^{BzTh}). A solution of the iminopyridine ligand N_2^{BTh} (1.00 g, 2.49 mmol) in dry and degassed toluene (20 mL) was cooled to 0 °C in an ice bath and treated dropwise with a 2.0 M toluene solution of trimethylaluminum (TMA; 1.86 mL, 3.73 mmol). The reaction mixture was stirred at room temperature for 12 h and then was quenched with 20 mL of water. The aqueous phase was extracted with 3 × 15 mL of AcOEt, and the combined organic layers were dried over Na_2SO_4. Removal of the solvent under reduced pressure gave the amidopyridinate ligand as a crude pale yellow solid. The ligand was purified by crystallization from hot MeOH, by cooling the resulting solution to −20 °C overnight to afford white crystals in 89% yield (0.95 g). ^1H NMR (200 MHz, CD_2Cl_2, 293 K): 1.12 (12H, d, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)$); 1.52 (6H, s, $C(CH_3)_2$); 3.38 (2H, sept, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)$); 4.40 (1H, bs, NH); 7.10 (3H, m, Ar); 7.40−7.35 (2H, m, Ar); 7.51 (1H, m, Ar); 7.92−7.75 (5H, Ar). $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2, 293 K): 23.9 ($CH(CH_3)_2$); 28.3 ($CH(CH_3)_2$); 28.9 ($C(CH_3)_2$); 59.3 ($C(CH_3)_2$); 117.0 (Ar); 118.4 (Ar); 120.7 (Ar); 122.4 (Ar); 123.0 (Ar); 124.0 (Ar); 124.0 (Ar); 124.4 (Ar); 124.5 (Ar); 124.9 (Ar); 137.1 (Ar); 140.3 (Ar); 140.7 (Ar); 145.7 (Ar); 146.8 (Ar); 150.8 (Ar); 168.1 (Ar). IR (KBr): 573 (m); 645 (s); 713 (s); 742 (s); 750 (s); 781 (m); 805 (s); 829 (s); 838 (m); 860 (m); 897 (w); 931 (m); 938 (m); 995 (s); 1089 (s); 1124 (s); 1154 (s); 1180 (m); 1203 (s); 1248 (s); 1256 (s); 1330 (m); 1359 (s); 1240 (s); 1440 (s); 1528 (m); 1570 (s); 1583 (s); 1645 (w); 3054 (w); 3343 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{32}N_2S$: C, 78.46; H, 7.52; N, 6.54; S, 7.48. Found: C, 79.01; H, 7.58; N, 6.50; S, 6.91.

Synthesis of $[NNS^{BzTh}]YCH_2SiMe_3(THF)_2$ (2). To a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.4284 g, 0.87 mmol) in hexane (25 mL) was added a solution of N_2H^{BTh} (0.3526 g, 0.82 mmol) in hexane (15 mL) at 0 °C, and the reaction mixture was stirred for 0.5 h. The product crystallized from the reaction mixture as a pale yellow microcrystalline solid and was isolated in a yield of 91% (0.5475 g). ^1H NMR (400 MHz, C_6D_6, 293 K): −0.62 (2H, d, $^2J_{YH}$ = 2.6 Hz, YCH_2); 0.18 (9H, s, $SiMe_3$); 0.94 (8H, m, THF); 1.28 (6H, s, $C(CH_3)_2$); 1.31 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3(i-Pr)); 1.35 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3(i-Pr)); 3.62 (8H, m, THF); 3.80 (2H, sept, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$); 6.62 (1H, d, $^3J_{HH}$ = 7.9 Hz, m-Py); 7.07−7.15 (3H, m, p-Py, p-NPh, BTh); 7.30 (1H, d, $^3J_{HH}$ = 7.6 Hz, m-Py); 7.31 (1H, d, $^3J_{HH}$ = 6.0 Hz, BTh); 7.34−7.37 (2H, m, m-NPh); 7.95 (1H, d, $^3J_{HH}$ = 7.9 Hz, BTh); 8.60 (1H, d, $^3J_{HH}$ = 7.8 Hz, BTh). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293 K): 4.3 ($SiMe_3$); 23.7 (CH_3(i-Pr)); 24.4 (THF); 27.8 (CH(i-Pr)); 28.3-(CH_3(i-Pr)); 31.2 ($C(CH_3)_2$); 31.6 (YCH_2); 69.2 (d, $^2J_{YC}$ = 2.3 Hz, $C(CH_3)_2$); 70.0 (THF); 116.0 (m-Py); 117.6 (m-Py); 122.1 (Ar); 123.9 (Ar); 124.0 (Ar); 124.1 (Ar); 124.6 (Ar); 129.7 (Ar); 139.1 (p-Py); 143.7 (d, $^3J_{YC}$ = 1.8 Hz, YCCCS); 143.8 (d, $^2J_{YC}$ = 3.1 Hz, YCC); 144.2 (Ar); 149.7 (Ar); 152.0 (d, $^2J_{YC}$ = 2.4 Hz, Ar); 158.5 (Ar); 174.8 (Ar); 195.9 (d, $^1J_{YC}$ = 37.2 Hz, Y−C). IR (KBr): 479 (w); 574 (w); 669 (w); 724 (s); 740 (s); 805 (s); 838 (m); 862 (s); 934 (w); 970 (w); 1026 (m); 1073 (w); 1090 (m); 1125 (m); 1159 (w); 1178 (m); 1226 (w); 1234 (w); 1247 (w); 1307 (m); 1530 (w); 1570 (s); 1590 (m) cm^{-1}. Anal. Calcd for $C_{40}H_{57}N_2O_2SSiY$: C, 64.32; H, 7.69; N, 3.75; Y, 11.90. Found: C, 64.51; H, 7.64; N, 3.54; Y, 11.92.

Synthesis of $[NNO^{BzFur}]YNH\text{-}2,6\text{-}^iPr_2C_6H_3(THF)_2$ (4). A solution of 2,6-diisopropylaniline (0.0517 g, 0.29 mmol) in hexane (10 mL) was added to a solution of **1** (0.2132 g, 0.29 mmol) in a hexane/toluene mixture (20 mL, 4/1) at room temperature, and the reaction mixture was stirred for 0.5 h. The reaction mixture changed from yellow to red. The reaction mixture was kept at −18 °C overnight. Complex **4** was isolated as a yellow-orange microcrystalline solid in 76% yield (0.182 g). ^1H NMR (400 MHz, C_6D_6, 293 K): 1.16−1.18 (14H, m, CH_3(i-Pr), THF); 1.33 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3(i-Pr)); 1.38 (12H, d, $^3J_{HH}$ = 6.5 Hz, CH_3(i-Pr)); 1.23 (6H, s, $C(CH_3)_2$); 2.71−2.84 (2H, compl m, CH(i-Pr)); 3.56 (8H, m, THF); 3.76 (2H, sept, $^3J_{HH}$ = 6.5 Hz, CH(i-Pr)); 4.13 (1H, s, NH anilido); 6.63 (1H, m, m-Py); 6.98−7.18 (6H, m, o-,p-NPh, o-,p-anilido); 7.19−7.22 (1H, m-,p-Py); 7.25 (1H, m, Ph); 7.32 (1H, m, Ph); 7.68 (1H, m, Ph); 8.27 (1H, m, Ph); 7.66 (1H, m, m-Py). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293K): 24.1 (CH_3(i-Pr)); 24.9 (CH_3(i-Pr)); 26.3 (THF); 27.4 (CH_3(i-Pr)); 27.9 (CH(i-Pr)); 31.1 ($C(CH_3)_2$); 68.3 ($C(CH_3)_2$); 68.6 (THF); 113.9 (Ar); 114.4 (m-Py); 117.5 (m-Py); 121.5 (Ar); 122.5 (Ar, anilido); 122.8 (Ar, anilido); 124.6 (Ar, anilido); 124.2 (Ar); 127.1 (Ar); 132.8 (Ar, anilido); 133.4 (Ar, anilido); 139.0 (p-Py); 140.4 (Ar); 148.4 (Ar, anilido); 149.0 (Ar, anilido); 151.8 (Ar);

dx.doi.org/10.1021/om400099z | Organometallics XXXX, XXX, XXX−XXX

156.6 (Ap); 157.2 (d, $^1J_{YC}$ = 40.9 Hz, Y−C); 161.0 (Ar); 175.1 (Ar). IR (KBr): 467 (w); 484 (w); 514 (w); 552 (w); 570 (w); 617 (w); 635 (w); 649 (w); 678 (w); 695 (w); 743 (s); 775 (w); 799 (m); 810 (m); 840 (m); 852 (m); 880 (m); 894(m); 926 (w); 936 (m); 960 (w); 967 (w); 990 (w); 1007 (w); 1026 (m); 1046 (m); 1084 (m); 1095 (w); 1107 (w); 1122 (m); 1170 (m); 1178 (m); 1197 (w); 1229 (w); 1254 (s); 1303 (w); 1318 (w); 1341 (w); 1363 (w); 1424 (s); 1462 (s); 1506 (w); 1573 (m); 1588 (w); 1601 (w); 3405 (w); 3482 (w) cm^{-1}. Anal. Calcd for $C_{48}H_{64}N_3O_3Y$: C, 70.31; H, 7.87; N, 5.12; Y, 10.84. Found: C, 70.42; H, N, 4.75; 7.98; Y, 10.77.

Synthesis of [NNC≡CO]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(THF) (6). A solution of 2,6-diisopropylaniline (0.0869 g, 0.49 mmol) in hexane (10 mL) was added to a solution of **1** (0.3582 g, 0.49 mmol) in a hexane/toluene mixture (30 mL, 4/1) at room temperature, and the reaction mixture was stirred for 0.5 h and then was heated to 50 °C for 30 h. The reaction mixture turned from yellow to deep red. The solution was kept at −18 °C overnight. Complex **6** was isolated as yellow-orange crystals in 54% yield (0.1981 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): 1.06−1.18 (10H, m, CH_3(i-Pr), THF); 1.27 (12H, d, $^3J_{HH}$ = 6.7 Hz, CH_3(i-Pr)); 1.37−1.50 (6H, broad m, CH_3(i-Pr)); 1.98 (6H, s, $C(CH_3)_2$); 2.95−3.63 (7H, compl m, CH(i-Pr), THF); 4.42 (1H, broad m, CH(i-Pr)); 5.31 (1H, s, NH); 6.50−6.58 (2H, m, m-Py, p-Ph); 6.60 (2H, t, $^3J_{HH}$ = 8.3 Hz, m-Ph); 6.74−6.83 (2H, m, p-Py, p-Ph); 7.08−7.15 (6H, m, o-NPh, o-anilido, p-NPh, p-anilido); 7.42 (1H, dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 1.4 Hz, m-Py). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 22.6−24.6 (broad s, Ar, anilido); 24.9 (THF); 25.3−27.0 (broad s, Ar, anilido); 27.0−28.9 (broad s, Ar, anilido); 29.8 (broad s, Ar, anilido); 64.7 (d, $^3J_{YC}$ = 2.6 Hz, Ar); 69.6 (broad s, THF); 93.4 (Ph-*C*C); 101.2 (Ph−*C*C); 115.5 (Ar); 115.8 (Ar); 118.2 (m-Py); 118.7 (Ar); 119.9 (Ar); 122.7 (Ar, anilido); 123.3 (Ar, anilido); 123.4 (Ar, anilido); 127.9 (Ar); 129.3 (m-Py); 132.3 (Ar, anilido); 133.0 (Ar, anilido); 137.5 (Ar, anilido); 138.8 (p-Py); 140.5 (Ar); 148.0 (Ar); 151.4 (d, $^2J_{YC}$ = 4.5 Hz, Ar anilido); 171.6 (d, $^2J_{YC}$ = 3.5 Hz, Ar); 177.3 (Y−O−C). IR (KBr): 569 (w); 605 (w); 743 (s); 806 (s); 850 (m); 935 (m); 1027 (s); 1044 (s); 1096 (s); 1147 (w); 1170 (w); 1193 (w); 1260 (s); 1308 (s); 1323 (m); 1364 (m); 1439 (s); 1564 (m); 1573 (s); 1589 (m); 1618 (m); 2196 (m); 3342 (w); 3404 (w); 3482 (w) cm^{-1}. Anal. Calcd for $C_{44}H_{56}N_3O_2Y$: C, 70.67; H, 7.55; N, 5.62; Y, 11.89. Found: C, 70.32; H, 7.61; N, 5.20; Y, 11.79.

Synthesis of [NNS^{BzTh}]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(THF)$_2$ (7). A solution of 2,6-diisopropylaniline (0.0803 g, 0.45 mmol) in hexane (10 mL) was added to a solution of **2** (0.3384 g, 0.45 mmol) in a toluene/hexane mixture (30 mL) at room temperature, and the reaction mixture was stirred for 0.5 h. The volatiles were removed under vacuum, and the solid residue was recrystallized from toluene to give 0.2952 g (78% yield) of **7** as a yellow microcrystalline solid. ^{1}H NMR (400 MHz, C_6D_6, 293 K): 1.10 (8H, m, THF); 1.17 (6H, d, $^3J_{HH}$ = 6.5 Hz, CH_3(i-Pr)); 1.25 (12H, d, $^3J_{HH}$ = 6.6 Hz, CH_3(i-Pr) anilido); 1.29 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3(i-Pr)); 1.36 (6H, s, $C(CH_3)_2$); 2.96 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH(i-Pr) anilido); 3.55 (8H, m, THF); 3.73 (2H, sept, $^3J_{HH}$ = 6.82 Hz, CH(i-Pr)); 4.52 (1H, s, NH anilido); 6.63 (1H, d, $^3J_{HH}$ = 7.9 Hz, m-Py); 6.81 (1H, t, $^3J_{HH}$ = 7.5 Hz, p-anilido); 7.07−7.12 (2H, m, p-Py, m-Ph); 7.16−7.19 (3H, m, p-NPh, m-anilido); 7.21−7.25 (2H, m, m-NPh); 7.33 (2H, d, $^3J_{HH}$ = 7.9 Hz, o-Ph, m-Py); 7.96 (1H, d, $^3J_{HH}$ = 7.5 Hz, o-Ph); 8.22 (1H, d, $^3J_{HH}$ = 7.8 Hz, p-Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 292 K): 24.0 (*C*H$_3$(i-Pr) anilido); 24.4 (*C*H$_3$(i-Pr)); 24.9 (THF); 27.0 (*C*H$_3$(i-Pr)); 27.8 (*C*H(i-Pr)); 29.1 (*C*H(i-Pr) anilido); 31.8 (*C*(CH$_3$)$_2$); 67.5 (*C*(CH$_3$)$_2$); 69.4 (THF); 114.7 (anilido); 116.3 (m-Py); 116.6 (m-Py); 122.2, (Ar); 122.5 (Ar); 122.6 (Ar); 123.3 (Ar); 123.6 (Ar); 123.9 (Ar); 129.6 (Ar); 133.1 (Ar); 139.6 (p-Py); 143.5 (Ar); 145.6 (Ar); 147.5 (Ar); 149.1 (Ar); 152.1 (Ar); 152.4 (Ar); 158.4 (Ar); 175.5 (Ar); 194.6 ppm (d, $^1J_{YC}$ = 40.4 Hz, Y−C). IR (KBr): 479 (w); 519 (w); 555 (w); 644 (w); 727 (m); 743 (s); 805 (s); 839 (m); 846 (w); 883 (m); 913 (w); 931 (w); 962 (w); 944 (w); 1027 (w); 1042 (w); 1074 (w); 1096 (w); 1124 (w); 1156 (w); 1181(m); 1200 (w); 1246 (s); 1257 (s); 1302 (w); 1321 (w); 1363 (m); 1425 (s); 1445 (s); 1528 (w); 1571 (s); 1588 (s); 1621 (w); 3342 (w); 3354 (w); 3473 (w) cm^{-1}. Anal. Calcd for $C_{48}H_{64}N_3O_2SY$: C, 68.96; H, N, 5.02; 7.72; Y, 10.63. Found: C, 69.01; H, 7.75; N, 4.69; Y, 10.72.

Synthesis of [NNS^{BzTh}]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(py)$_2$ (8). A 0.2516 g amount (0.30 mmol) of **7** was dissolved in pyridine (4 mL). The solution was kept at room temperature for 0.5 h, and the volatiles were removed under vacuum. The orange-yellow solid residue was dissolved in a minimum volume of toluene, and the solution was slowly concentrated at ambient temperature. Complex **8** was isolated as orange-yellow crystals in 77% yield (0.1968 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): 0.83 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3(i-Pr)); 1.22 (6H, d, $^3J_{HH}$ = 7.1 Hz, CH_3(i-Pr)); 1.23 (12H, d, $^3J_{HH}$ = 6.7 Hz, CH_3(i-Pr)); 1.29 (6H, s, $C(CH_3)_2$); 2.87 (2H, sept, $^3J_{HH}$ = 6.5 Hz, CH(i-Pr)); 3.71 (2H, sept, $^3J_{HH}$ = 6.6 Hz, CH(i-Pr)); 4.73 (1H, s, NH anilido); 6.30 (4H, t, $^3J_{HH}$ = 6.3 Hz, Py); 6.60 (2H, t, $^3J_{HH}$ = 7.6 Hz, Py); 6.72 (1H, d, $^3J_{HH}$ = 7.9 Hz, m-Py); 6.87 (1H, t, $^3J_{HH}$ = 7.3 Hz, p-anilido); 6.99 (1H, dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.9 Hz, m-Ph); 7.09 (1H, dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.8 Hz, m-Ph); 7.12 (1H, m, p-NPh); 7.18−7.22 (3H, compl. m, m-NPh, p-Py); 7.25 (2H, d, $^3J_{HH}$ = 6.8 Hz, m-Ph); 7.44 (1H, d, $^3J_{HH}$ = 7.7 Hz, m-Py); 7.80 (1H, d, $^3J_{HH}$ = 7.8 Hz, o-Ph); 7.96 (1H, d, $^3J_{HH}$ = 7.9 Hz, p-Ph); 8.62 (4H, s, Py). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 24.9 (*C*H$_3$(i-Pr)); 25.0 (*C*H$_3$(i-Pr)); 26.6 (*C*H$_3$(i-Pr)); 27.8 (*C*H(i-Pr)); 28.4 (*C*H(i-Pr)); 32.1 (*C*(CH$_3$)$_2$); 67.7 (d, $^2J_{YC}$ = 2.0 Hz, *C*(CH$_3$)$_2$); 114.6 (Ar); 115.0 (m-Py); 116.5 (m-Py); 121.8 (Ar); 122.6 (Ar); 122.8 (Ar); 123.3 (Ar)); 123.6 (Py); 124.1 (Ar); 124.4 (Ar); 129.8 (Ar); 133.7 (Ar)); 137.2 (Py); 139.9 (p-Py); 143.4 (d, $^3J_{YC}$ = 1.5 Hz, YCCCS); 143.9 (d, $^2J_{YC}$ = 2.2 Hz, YCCS); 148.5 (Ar); 149.9 (Py); 149.9 (Ar); 151.9 (d, $^2J_{YC}$ = 2.0 Hz, YCCCS); 152.5 (d, $^2J_{YC}$ = 3.9 Hz, ipso-Ar); 159.2 (Py Ar); 176.1 (Py); 199.9 ppm (d, $^1J_{YC}$ = 34.4 Hz, Y−C). IR (KBr): 556 (w); 626 (m); 675 (m); 683 (m); 703 (s); 728 (w); 748 (s); 798 (m); 807 (m); 842 (m); 884 (w); 952 (w); 1006 (m); 1017 (w); 1038 (s); 1069 (m); 1092 (w); 1109 (w); 1125 (w); 1152 (m); 1179 (m); 1216 (m); 1225 (m); 1259 (s); 1308 (w); 1319 (w); 1324 (s); 1343 (s); 1568 (s); 1590 (s); 1599 (s); 1622 (w); 3455 (w); 3467 (w) cm^{-1}. Anal. Calcd for $C_{50}H_{58}N_5SY$: C, 70.65; H, 6.88; N, 8.24; Y, 10.46. Found: C, 70.78; H, 7.14; N, 7.89; Y, 10.51.

Synthesis of [NNS^{BzThH}]Y(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$ (9). A solution of **7** (0.2785 g, 0.33 mmol) in a toluene/hexane mixture (5 mL, 3/2) was kept at room temperature for 2 weeks. Complex **9** slowly formed as fine bright-orange crystals and was isolated in 30% yield (0.0864 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): 1.06 (24H, d, $^3J_{HH}$ = 6.7 Hz, CH_3(i-Pr)); 1.28 (6H, d, $^3J_{HH}$ = 6.9 Hz, CH_3(i-Pr)); 1.48 (6H, d, $^3J_{HH}$ = 6.9 Hz, CH_3(i-Pr)); 1.56 (6H, s, $C(CH_3)_2$); 2.66 (4H, sept, $^3J_{HH}$ = 6.4 Hz, CH(i-Pr)); 3.72 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH(i-Pr)); 5.01 (2H, s, NH anilido); 6.79 (3H, t, $^3J_{HH}$ = 7.6 Hz, p-Ph, m-Py); 6.84 (1H, dd, $^3J_{HH}$ = 7.30 Hz, $^3J_{HH}$ = 7.10 Hz, Ar); 6.91 (1H, dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.6 Hz, m-Py); 6.98 (3H, compl m, p-Py); 7.07(4H, d, $^3J_{HH}$ = 7.6 Hz, m-Ph); 7.09−7.14 (2H, compl m, p-NPh); 7.21 (2H, d, $^3J_{HH}$ = 7.5 Hz, m-NPh); 7.37 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 23.1 (*C*H$_3$(i-Pr)); 24.3 (*C*H$_3$(i-Pr)); 26.4 (*C*H$_3$(i-Pr)); 28.5 (*C*H(i-Pr)); 30.3 (*C*H(i-Pr)); 32.6 (*C*(CH$_3$)$_2$); 63.9 (d, $^2J_{YC}$ = 2.1 Hz, *C*(CH$_3$)$_2$); 1154.0 (Ar); 118.6 (m-Py); 119.7 (m-Py); 122.5 (Ar); 123.2 (Ar); 123.8 (Ar); 124.6 (Ar); 126.9 (Ar); 127.0 (Ar); 132.8 (Ar); 137.0 (Ar); 139.3 (Ar);139.7 (Ar); 140.4 (Ar); 141.2 (Ar); 147.6 (Ar); 150.1 (Ar); 152.0 (d, $^2J_{YC}$ = 4.1 Hz, ipso-anilido); 178.6 (Ar). IR (KBr): 464 (m); 515 (w); 537 (w); 557 (w); 695 (s); 728 (s); 747 (s); 794 (m); 809 (m); 841 (m); 866 (w); 881 (w); 891 (w); 960 (w); 1007 (w); 1036 (m); 1079 (w); 1096 (m); 1122 (w); 1148 (w); 1181 (m); 1217 (w); 1230 (w); 1247 (w); 1263 (s); 1304 (w); 1340 (w); 1423 (s); 1461 (s); 1495 (w); 1563 (w); 1571 (m); 1588 (s); 3356 (w) cm^{-1}. Anal. Calcd for $C_{52}H_{67}N_4SY$: C, 71.86; H, 7.77; N, 6.44; Y, 10.23. Found: C, 71.84; H, 7.80; N, 6.75; Y, 10.31.

Synthesis of [NNS^{EtTh}]YNH-2,6-^{i}Pr$_2$C$_6$H$_3$(py)$_2$ (11). A solution of 2,6-diisopropylaniline (0.0812 g, 0.46 mmol) in toluene (10 mL) was added to a solution of **3** (0.3320 g, 0.46 mmol) in toluene (30 mL) at room temperature, and the reaction mixture was stirred for 0.5 h. The volatiles were removed under vacuum, and the solid residue was treated with pyridine. The resulting orange oil was dried under vacuum for 0.5 h and was dissolved in toluene. Slow concentration of the resulting solution at ambient temperature afforded crystals of **11** in 64% yield (0.2427 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): 0.78 (12H, broad d, $^3J_{HH}$ = 6.2 Hz, CH_3(i-Pr)); 1.06 (3H, t, $^3J_{HH}$ = 7.4 Hz, Et-

dx.doi.org/10.1021/om400099z | *Organometallics* XXXX, XXX, XXX−XXX

Table 1. Crystallographic Data and Structure Refinement Details for Complexes 6, 8, 9, and 11

	6	8	9	11
empirical formula	$C_{51}H_{64}N_3O_2Y$	$C_{56}H_{64}N_5SY$	$C_{55.50}H_{71}N_4SY$	$C_{55}H_{68}N_5SY$
formula wt	839.96	928.09	915.13	920.11
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pbca*	$P2_1/c$	$P2_1/c$
a, Å	10.0359(6)	10.51965(15)	21.976(2)	16.9665(3)
b, Å	11.6546(8)	19.8913(4)	13.4831(13)	19.4635(3)
c, Å	20.5907(13)	47.7557(7)	17.1832(17)	30.0634(4)
α, deg	95.8550(10)	90	90	90
β, deg	90.2040(10)	90	104.695(2)	90.1406(13)
γ, deg	112.8730(10)	90	90	90
V, Å^3	2205.0(2)	9992.9(3)	4924.9(8)	9927.7(3)
Z	2	8	4	8
P_{calcd} (g/cm^3)	1.265	1.234	1.234	1.231
abs coeff (mm^{-1})	1.365	1.250	1.266	1.257
F(000)	892	3920	1948	3904
cryst size, mm	0.55 × 0.22 × 0.12	0.40 × 0.30 × 0.10	0.28 × 0.18 × 0.12	0.40 × 0.40 × 0.40
2*θ*, deg	52	60	52	60
index ranges	$-12 \le h \le 12$	$-14 \le h \le 14$	$-27 \le h \le 27$	$-23 \le h \le 23$
	$-12 \le k \le 14$	$-27 \le k \le 27$	$-16 \le k \le 16$	$-27 \le k \le 27$
	$-23 \le l \le 25$	$-67 \le l \le 67$	$-21 \le l \le 21$	$-42 \le l \le 42$
no. of rflns collected	10883	184929	41090	203301
no. of indep rflns (R_{int})	8215 (0.0226)	14479 (0.1038)	9646 (0.1332)	28866 (0.1638)
completeness to *θ*, %	94.6	99.3	99.6	99.7
max/min transmission	0.8533/0.5206	0.8852/0.6347	0.8629/0.7181	0.6332/0.6332
no. of data/restraints/params	8215/4/532	14479/0/582	9646/46/567	28866/4/1146
GOF on F^2	1.017	1.249	0.982	0.964
final *R* index ($I > 2\sigma(I)$)	0.0423	0.0748	0.0692	0.0677
R index (all data)	0.0978	0.1270	0.1613	0.1695
largest diff in peak/hole, e/Å^3	1.187/−0.924	0.718/−2.452	1.016/−0.544	1.503/−1.316

CH_3,); 1.17 (12H, broad d, $^3J_{HH}$ = 6.5 Hz, CH_3(i-Pr)); 1.36 (6H, s, $C(CH_3)_2$); 2.62 (2H, q, $^3J_{HH}$ = 7.4 Hz, Et-CH_2); 3.62 (4H, sept, $^3J_{HH}$ = 6.5 Hz, CH(i-Pr)); 4.62 (1H, s, NH); 6.25 (4H, m, Py); 6.59, (2H, m, Py); 6.76, (1H, d, $^3J_{HH}$ = 7.9 Hz, m-CH Py); 6.91 (1H, $^3J_{HH}$ = 7.4 Hz, p-Ph); 7.05 (1H, s, Ar); 7.19−7.30 (4H, compl m, p-Py, m- and p-NPh); 7.30 (2H, d, $^3J_{HH}$ = 7.4 Hz, m-Ph); 7.40 (1H, d, $^3J_{HH}$ = 7.8 Hz, m-Py); 8.59 (4H, m, Py). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293 K): 15.7 (CH_3(Et)); 23.2 (CH_2(Et)); 24.4, (CH_3(i-Pr)); 27.7 (CH_3(i-Pr)); 28.0 (CH(i-Pr)); 31.8 ($C(CH_3)_2$); 69.1 (d, $^2J_{YC}$ = 2.4 Hz, $C(CH_3)_2$); 114.4 (anilido); 1154.0 (Ar); 115.3, (Ar); 123.3 (Ar); 123.5 (Py); 123.6 (Ar); 124.2 (Ar); 133.4 (Ar); 134.9 (d, $^2J_{YC}$ = 2.0 Hz, SCCH); 137.5 (Py); 137.5 (Ar); 139.5 (Ar); 143.2 (d, $^2J_{YC}$ = 2.3 Hz, YCCS); 148.6 (Ar); 149.1 (Ar); 149.7 (Py); 152.6 (d, $^2J_{YC}$ = 3.9 Hz, ipso-anilido), 159.7 (Ar); 175.4 (Ar); 202.1 (d, $^1J_{YC}$ = 36.2 Hz, Y−C). IR (KBr): 464 (m); 523 (w); 565 (w); 601 (w); 625 (w); 677 (w); 696 (s); 702 (s); 729 (s); 744 (s); 800 (s); 843 (m); 888 (w); 931 (w); 965 (w); 977 (m); 1009 (m); 1030 (s); 1039 (s); 1069 (m); 1096 (m); 1126 (w); 1162 (m); 1180 (m); 1219 (w); 1261 (s); 1303 (w); 1322 (w); 1362 (m); 1425 (m); 1443 (s); 1479 (m); 1496 (m); 1571 (s); 1587 (s); 1600 (m); 1621 (w); 1800 (w); 1859 (w); 1939 (w); 3343 (w); 3406 (w); 3485 (w) cm^{-1}. Anal. Calcd for $C_{48}H_{60}N_5SY$: C, 69.63; H, 7.30; N, 8.46; Y, 10.74. Found: C, 69.70; H, 7.34; N, 8.95; Y, 10.78.

X-ray Crystallography. The X-ray data were collected on a Smart Apex diffractometer (for **6** and **9**, graphite-monochromated Mo K*α* radiation, *ω*-scan technique, *λ* = 0.71073 Å, *T* = 100(2) K) and a Agilent Xcalibur E diffractometer (for **8** and **11**, graphite-monochromated Mo K*α* radiation, *ω*-scan technique, *λ* = 0.71073 Å, *T* = 100(2) K). The structures were solved by direct methods and were refined on F^2 using SHELXTL[26] (**6** and **9**) and CrysAlis Pro[27] (**8** and **11**) package. All non-hydrogen atoms and H atoms in NH groups of anilido fragments were found from Fourier syntheses of electron density and were refined anisotropically and isotropically for hydrogens. All other hydrogen atoms were placed in calculated positions and were refined in the riding model. SADABS[28] (**6** and **9**) and ABSPACK (CrysAlis Pro)[27] (**8** and **11**) were used to perform area-detector scaling and absorption corrections. Details of crystallographic, collection, and refinement data are reported in Table 1. CCDC files 909588 (**6**), 909589 (**8**), 909590 (**9**), and 909592 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The study was supported by the Ministry of education and science of Russian Federation, Project No. 8445, the Russian Foundation for Basic Research (grant 12-03-31865 mol_a), the Program of the Presidium of the Russian Academy of Science (RAS), and the RAS Chemistry and Material Science Division. We also thank the Groupe de Recherche International (GDRI) "Homogeneous Catalysis for Sustainable Development" for support.

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