

Yttrium-Amidopyridinate Complexes: Synthesis and Characterization of Yttrium-Alkyl and Yttrium-Hydrido Derivatives

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Keywords: Amidopyridinate / Yttrium / Hydrides / Metathesis / Ethylene / Polymerization

Aryl- or heteroaryl-substituted aminopyridine ligands (N_2H^{Ar}) react with an equimolar amount of $[Y(CH_2SiMe_3)_3(thf)_2]$ to give yttrium(III)-monoalkyl complexes. The process involves the deprotonation of N_2H^{Ar} by a yttrium alkyl followed by a rapid and quantitative intramolecular sp^2 -CH bond activation of the aryl or heteroaryl pyridine substituents. As a result, new Y complexes distinguished by rare ex-

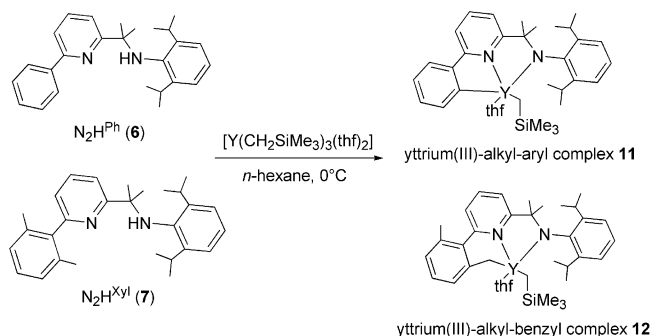
amples of CH bond activations have been isolated and completely characterized. Selective σ -bond metathesis reactions take place on the residual Y-alkyl bonds upon treatment with $PhSiH_3$. Unusual binuclear metallacyclic yttrium(III)-hydrido complexes have been obtained and characterized by NMR spectroscopy and X-ray diffraction analysis.

Introduction

Cyclopentadienyl-free rare-earth-metal alkyls or hydrides are target compounds in organometallic chemistry due to their unique properties and intriguing reactivity in polymerization catalysis.^[1] To date, rare-earth-metal complexes have been dominated by cyclopentadienyl moieties, including mono-, bis- and ansa-systems.^[2] Only recently, systems such as bidentate amidinate,^[3] guanidinate,^[4] β -diketiminate^[5] and salicylaldiminates^[6] have emerged as valuable ancillary ligands for lanthanide ions by virtue of their ability to form strong metal–ligand bonds and to allow for an easy tuning of the steric and electronic properties of the ligand. Nevertheless, lanthanide-alkyl or -hydrido complexes stabilized by these type of ligands are still fairly rare species, largely because of their troublesome preparation. Indeed, the rare-earth-metal centres in these complexes are generally both electronically and sterically less saturated than those in metallocene or half-sandwich-type derivatives. As a result, unusual reactivity paths are often observed for cyclopentadienyl-free lanthanide complexes, including dimerizations, intra- and intermolecular C–H bond activations or ligand redistributions.^[1g]

A variety of bidentate or polydentate nitrogen-containing ligands (amide, imine) have been successfully employed for the synthesis of discrete organo-rare-earth-metal complexes, although the number of reported active catalysts remain still quite limited.^[1f,7]

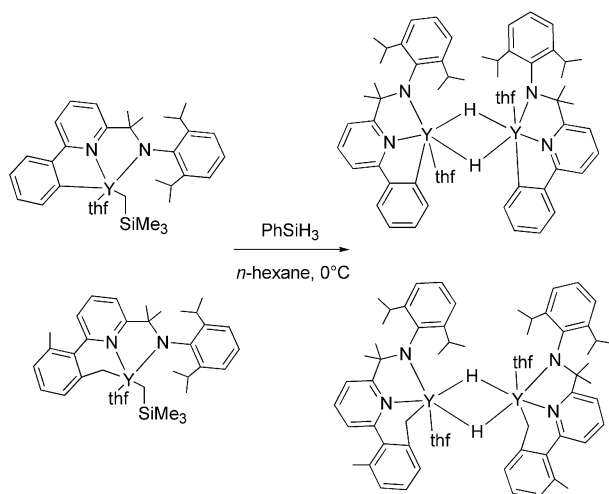
We have recently communicated on the synthesis of new yttrium(III)-monoalkyl and yttrium(III)-hydrido complexes stabilized by amidopyridinate ligands.^[8] Interesting results have been obtained from the reaction of the pyridylamine ligands N_2H^{Ph} and N_2H^{Xyl} with $[Y(CH_2SiMe_3)_3(thf)_2]$. The reactions have been found to proceed rapidly at 0 °C and independently from the dilution conditions, with the elimination of 2 equiv. of tetramethylsilane, instead of the 1 equiv. expected and the concomitant formation of the monoalkyl sp^2 or sp^3 *ortho*-metalated complexes of the type shown in Scheme 1.



Scheme 1. Synthesis of yttrium(III)-alkyl-aryl and -alkyl-benzyl complexes.

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Notably, both yttrium complexes undergo selective σ -bond metathesis on the residual CH_2SiMe_3 bond upon treatment with PhSiH_3 . As a result, binuclear aryl-hydrido and benzyl-hydrido complexes of the type shown in Scheme 2 have been isolated and characterized.



Scheme 2. Synthesis of binuclear yttrium(III)-hydrido complexes by selective σ -bond metathesis on the residual CH_2SiMe_3 group.

Much of the interest in group 4 and lanthanide-alkyl or -hydrido complexes stabilized with amidopyridinate ligands comes from their ability to undergo intramolecular C–H bond activation, thus providing metal complexes with unconventional structures. A new family of strictly related pyridylamido Hf^{IV} catalysts have been recently developed by the group of Busico and researchers at Dow as effective catalysts for the isotactic polymerization of propene in high-temperature solution processes.^[9]

One of the most notable features of these group 4 precatalysts is the *ortho*-metalation of the aryl substituent on the pyridine ring, which results in the tridentate ligation of the pyridylamido moiety and a distorted trigonal-bipyramidal metal coordination (Figure 1a). The incorporation of sp^3 -C donors into the imidopyridinate ligand framework has been successfully achieved by Coates and co-workers through an intramolecular migratory insertion of a cationic Hf^{IV} species onto a facing vinyl moiety (Figure 1b).^[10]

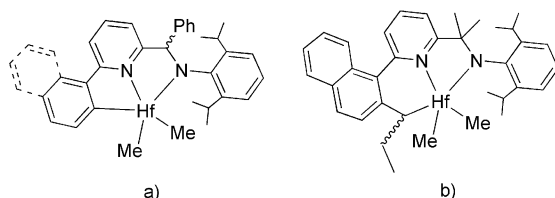


Figure 1. Group 4 metal complexes distinguished by amidopyridinate ligands showing a) sp^2 or b) sp^3 C–H bond activation.

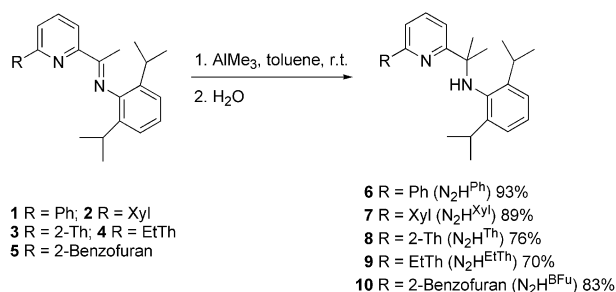
Although inter- and intramolecular metalations of sp^2 - and sp^3 -hybridized C–H bonds have been previously documented for cyclopentadienyl^[3b,11] and cyclopentadienyl-

free^[4b,12] lanthanide-alkyl and -hydride complexes, they still attract considerable interest due to the intrinsic difficulty for organometallic fragments to activate inert chemical bonds. In this paper we provide a full account on the synthesis, characterization and catalytic activity of a family of novel yttrium(III)-alkyl and -hydrido complexes distinguished by stable Y–C(aryl) or Y–C(heteroaryl) bonds.

Results and Discussion

Synthesis and Characterization of the Aminopyridinate Ligands 6–10

The 6-aryl-substituted ligands **6–10** were straightforwardly prepared, in fairly good yields (70–93% of isolated product) by reductive alkylation of the related iminopyridines (**1–5**) with a slight excess amount of trimethylaluminum in dry toluene at room temperature, followed by hydrolysis (Scheme 3).



Scheme 3. Reductive alkylation of iminopyridines **1–5**.

The imino precursors **1–5** were obtained on a multigram scale according to procedures reported in the literature,^[8,13] in some cases with little modification.^[14] All aminopyridinate ligands appear as off-white/pale-yellow solids after extractive workup and solvent evaporation. Recrystallization from hot MeOH gave the pure compounds as white/pale yellow crystals with melting points ranging from 97 to 134 °C (see the Experimental Section).

The ^1H NMR spectra of aminopyridines **6–10** confirmed the formation of saturated $-\text{C}(\text{Me})_2\text{NH}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$ moieties with the NH proton resonance appearing as a broad singlet between 4.1 and 4.6 ppm and the related $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showing the expected number of independent carbon atom signals.

Suitable crystals for X-ray diffraction studies of compounds **6–10** were isolated by successive recrystallizations from hot MeOH (Table 4). A perspective view of all ligand structures is given in Figure 2, whereas selected bond lengths and angles are listed in Table 1. All structures consist of a central pyridine unit substituted at its 6-position by an aryl (Figure 2, ligands **6** and **7**) or a heteroaryl (Figure 2, ligands **8–10**) group and at its 2-position by the same amine-containing $\text{C}(\text{Me})_2\text{NH}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$ fragment. The aryl or heteroaryl moieties are almost coplanar with respect

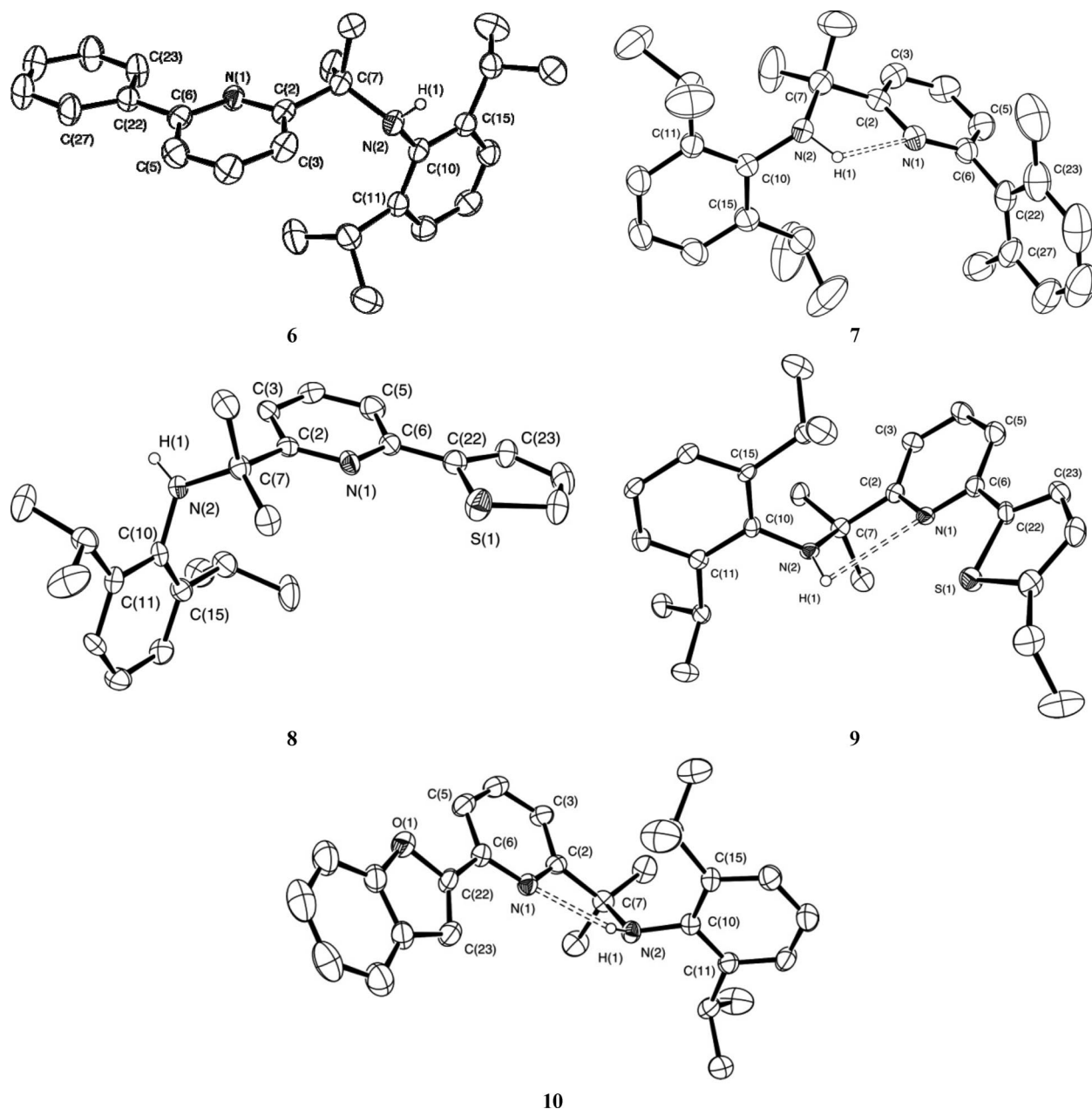


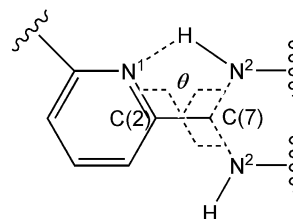
Figure 2. Crystal structures of ligands $\text{N}_2\text{H}^{\text{Ph}}$ (**6**), $\text{N}_2\text{H}^{\text{Xyl}}$ (**7**), $\text{N}_2\text{H}^{\text{Th}}$ (**8**), $\text{N}_2\text{H}^{\text{EtTh}}$ (**9**) and $\text{N}_2\text{H}^{\text{BFu}}$ (**10**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, apart from those of the N–H moiety, are omitted for clarity.

to the pyridine unit [torsion angle (θ) N(1)–C(6)–C(22)–C(23): **6**, 7.32(2)°; **8**, 177.29(2)°; **9**, 177.41(5)°; **10**, –10.8(6)°] except for ligand **7**, in which the more sterically demanding xyl group is nearly orthogonal to the pyridine plane, as expected [N(1)–C(6)–C(22)–C(23): –72.3(4)°]. The C(2)_{py}–

C(7)_{alk} bond lengths are in the typical (sp^2)–(sp^3) range of values.^[15] The C(7)–N(2) vector is rotated closer to the pyridine plane for all ligand structures, whereas the N(1)–C(2)–C(7)–N(2) torsion angle brings the N(2)H hydrogen atom

Table 1. Selected bond lengths [Å] and angles [°] for ligands **6**–**10**.

	6	7	8	9	10
N(2)–C(7)	1.492(4)	1.480(4)	1.497(9)	1.495(4)	1.493(4)
N(1)–H(1)	–	2.11(3)	–	2.61(4)	2.22(4)
N(2)–C(7)–C(2)	110.5(3)	110.0(3)	109.8(6)	108.1(3)	109.9(3)
N(1)–C(2)–C(7)	116.3(3)	115.9(3)	117.1(6)	113.9(4)	115.3(3)
N(1)–C(6)–C(22)–C(23)	7.32(2)	–72.3(4)	177.29(2)	177.41(5)	–10.8(6)



$\text{N}_2\text{H}^{\text{Ph}}$ (6);	$\theta = -148.75$
$\text{N}_2\text{H}^{\text{Xyl}}$ (7);	$\theta = -25.00$
$\text{N}_2\text{H}^{\text{Th}}$ (8);	$\theta = -142.43$
$\text{N}_2\text{H}^{\text{EtTh}}$ (9);	$\theta = 37.15$
$\text{N}_2\text{H}^{\text{BFu}}$ (10);	$\theta = -33.95$

Figure 3. N(1)–C(2)–C(7)–N(2) torsion angles on ligands **6**–**10**.

into a position in which it is able to form a hydrogen bond to the neighbouring pyridine nitrogen atom only for ligands **7**, **9** and **10** (Figure 3) [calculated N(1)⋯HN(2) distances [Å]: **7**, 2.11(3); **9**, 2.61(4); **10**, 2.22(4)].

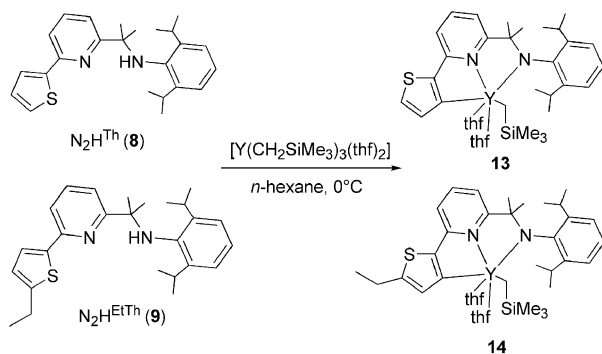
Synthesis and Characterization of the Yttrium-Alkyl-Aryl and -Alkyl-Benzyl Complexes

The reaction of the neutral aminopyridines **6** and **7** with $[Y(CH_2SiMe_3)_3(thf)_2]$ (1 equiv.) in hexane at 0 °C have been already discussed in our previous work^[8] and are mentioned here only for completeness. In both cases, the reaction is almost instantaneous and gives the mono(alkyl) complexes **11** and **12**, respectively (Scheme 1).

By following similar procedures as those reported for the preparation of **11** and **12**, the ligands containing either 2-thienyl (**8** and **9**) or 2-benzofuryl (**10**) pendant groups have been employed to study their coordination behaviour at the metal centre.

Several cyclopentadienyl-based rare-earth-metal complexes have previously been reported to yield *ortho*-metallation products in the presence of aromatic heterocycles such as furan and thiophene (Th).^[11b,16] To date, a few examples of cyclopentadienyl-free lanthanide complexes bearing potentially coordinating sulfur or oxygen atoms have been investigated,^[17] whereas those containing thienyl or furanyl groups remain much less explored.^[18]

Unexpectedly, the reaction of the thienyl-containing ligands **8** and **9** with $[Y(CH_2SiMe_3)_3(thf)_2]$ (1 equiv.) in hexane at 0 °C resulted in the unique formation of **13** and **14** by means of alkane elimination and C–H bond activation at the β position of the thienyl moiety (Scheme 4).



Scheme 4. Synthesis of yttrium(III)-alkyl-aryl complexes **13** and **14** by means of an alkyl elimination reaction.

Attempts to isolate yttrium-bis(alkyl) species by means of monoalkane elimination always resulted in the quantitative generation of the six-coordinate alkyl-heteroaryl complexes, as a result of a deprotonation of the N–H moiety followed by a rapid intramolecular sp^2 -CH bond activation at the β position of the heteroaryl fragment (Scheme 4). Further experiments conducted using different dilution conditions never allowed the isolation of dialkyl species. Finally, the reaction monitoring through 1H NMR spectroscopic experiments has revealed that the cyclometalation

step occurs immediately upon mixing of the ligands and metal precursor with no evidence for the formation of transient dialkyl intermediates.

Apparently, the presence of a coordinating thien-2-yl sulfur atom on the ligand backbone does not compete with the intramolecular sp^2 C–H bond activation for the coordination to the metal centre, which occurs rapidly, even under diluted reaction conditions, on the less acidic 3-position of the heteroaryl group.^[18] 1H NMR spectra for **13** and **14** are consistent with six-coordinate yttrium complexes, each of which contains a tridentate dianionic (L^{2-}) amidopyridinate ligand, a residual trimethylsilylmethylene fragment and two thf molecules. Both complexes contain Y–C(alkyl) and Y–C(aryl) bonds; clear doublets could be seen in the 1H NMR spectrum centred at -0.77 ppm ($^2J_{Y,H} = 3.0$ Hz) and -0.69 ppm ($^2J_{Y,H} = 3.0$ Hz), respectively, and are attributed to the hydrogen atoms of each residual methylene group attached to yttrium. The latter appears in the $^{13}C\{^1H\}$ NMR spectra as a doublet centred at 30.0 ppm ($^1J_{Y,C} = 39.6$ Hz) and 30.1 ppm ($^1J_{Y,C} = 39.6$ Hz), for complexes **13** and **14**, respectively, whereas further low-field doublets [**13**: 195.2 ppm ($^1J_{Y,C} = 38.9$ Hz); **14**: 198.6 ppm ($^1J_{Y,C} = 38.9$ Hz)] unambiguously indicate that the aryl rings are σ -bonded to the metal centre.^[18,19] Crystals of **14** suitable for X-ray analysis were grown by cooling at -20 °C a concentrated solution in *n*-hexane (Table 5). The molecular structure of **14** is shown in Figure 4.

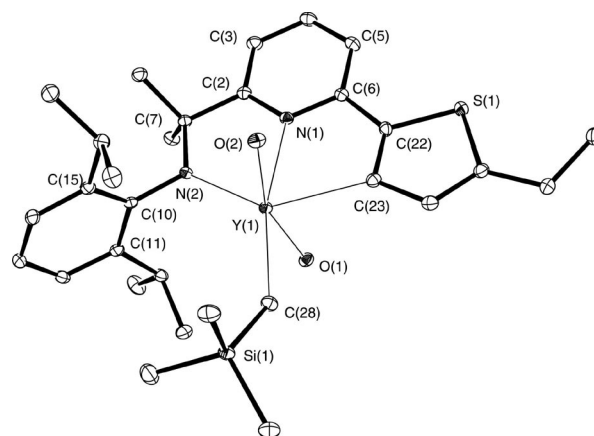


Figure 4. Crystal structure of $[N_2^{EtTh}Y(CH_2SiMe_3)(thf)_2]$ (**14**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and methylene groups of the thf molecules are omitted for clarity.

The X-ray diffraction study has shown the monomeric nature of **14**. The coordination environment at the yttrium centre is set up by two nitrogen atoms and one carbon atom from the dianionic tridentate amidopyridinate ligand, one carbon atom from the residual alkyl group and two oxygen atoms from the two thf molecules. Overall, the coordination can be considered to be a strongly distorted octahedron. The yttrium coordination number in **14** is 6. The Y–amidopyridinate fragment is planar (average deviation from the plane is 0.0156 Å) and the Y–C(alkyl) bond length [2.455(2) Å] is comparable to the values reported for related six-coordinate yttrium-monoalkyl compounds.^[18,20] The Y–

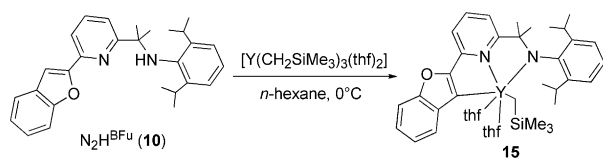
Table 2. Selected bond lengths [Å] and angles [°] for complexes **12**, **14**, and **16–18**.

	12 ^[a]	14	16 ^[a]	17	18
Y–H	–	–	2.15	2.44	2.09(2)
Y(1)–N(1)	2.42(14)	2.4616(17)	2.4252(17)	2.472(7)	2.450(2)
Y(1)–N(2)	2.2015(14)	2.2543(17)	2.2205(18)	2.198(7)	2.206(2)
Y(1)–O(1)	2.3422(13)	2.4035(14)	2.3609(15)	2.346(6)	–
Y(1)–O(2)	–	2.3816(14)	–	–	2.355(2)
Y(1)–C(23)	2.9421(17)	2.482(2)	2.469(2)	–	2.514(3)
Y(1)–C(28)	–	2.455(2)	–	–	–
Y(1)–C(29)	2.4520(18)	–	–	2.462(9)	–
Y(1)–C(30)	2.4139(17)	–	–	–	–
Y(1)–Y(1)'	–	–	3.5780(4)	3.6917(14)	3.53(11)
C(28)–Y(1)–C(23)	–	98.04(7)	–	–	–
C(29)–Y(1)–C(23)	29.47(5)	–	–	–	–
C(30)–Y(1)–C(29)	117.20(6)	–	–	–	–
N(1)–Y(1)–N(2)	70.00(5)	67.44(6)	68.24(6)	69.1(3)	66.39(8)
N(1)–Y(1)–C(29)	–	–	–	72.1(3)	–
N(1)–Y(1)–C(23)	–	–	68.43(7)	–	69.55(9)
N(2)–Y(1)–C(23)	–	–	130.34(7)	–	131.49(9)
N(2)–Y(1)–C(29)	–	–	–	111.8(3)	–
N(1)–C(6)–C(22)–C(23)	–52.57(6)	–4.13(2)	–7.52(3)	50.5(15)	8.5(4)

[a] Selected data from the literature^[20] listed here for completeness.

C(thien-2-yl) bond [2.482(2) Å] is slightly longer than that observed for related yttrium-monoalkyl thien-2-yl species featured by analogue intramolecular C–H bond activation at the β position of the thienyl moiety [2.423(3) Å].^[18] Related yttrium complexes that contain an amidopyridinate ligand with a shorter ligand backbone^[21] have shown a dramatic perturbation of the ligand coordination mode once an intramolecular C–H bond activation occurs {the Y–N covalent bond [2.431(8) Å] becomes longer than the coordinative one [2.338(7) Å]}. In contrast to this, the presence of an additional CMe₂ group between the two nitrogen atoms always results in a “classic” bonding mode (Y–N covalent bonds shorter than coordinative ones; Table 2).

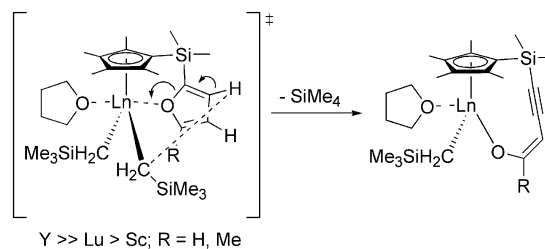
In spite of the well-known oxophilic character of lanthanide ions, the reaction of the 2-benzofuryl-substituted ligand **10** with [Y(CH₂SiMe₃)₃(thf)₂] in hexane at 0 °C yields the monoalkyl complex **15** (Scheme 5).

Scheme 5. Synthesis of the yttrium(III)-alkyl-aryl complex **15**.

As observed for the thienyl-containing systems, the 2-benzofuryl group appended to the amidopyridinate ligand **10** rapidly undergoes metalation on the 3-position irrespective of the dilution conditions used, thus affording the first example of stable cyclopentadienyl-free yttrium(III)-benzofuryl-amidopyridinate complex. Complex **15** could not be obtained in the form of single crystals. The identification as a six-coordinate yttrium complex with a tridentate dianionic (L²⁻) aminopyridinate ligand, a residual trimethylsilylmethylene fragment and two thf molecules is based on several spectroscopic features (see the Experimental Section). All the aforementioned monoalkyl complexes were

highly soluble in hydrocarbon solvents and a comparison of their ¹H and ¹³C{¹H} NMR spectra showed many similarities. The ¹H NMR spectrum of **15**, which contains both Y–C(alkyl) and Y–C(aryl) bonds, shows one clear doublet centred at –0.69 ppm (²J_{Y,H} = 3.0 Hz) attributed to the hydrogen atoms of the residual methylene group bound to yttrium. The ¹³C{¹H} NMR spectrum contains a doublet for the sp³-carbon atom centred at 30.1 ppm (¹J_{Y,C} = 37.6 Hz), whereas a further doublet at 158.6 ppm (¹J_{Y,C} = 38.9 Hz) is assigned to the sp² carbon of the benzofuryl moiety σ -bonded to the metal centre.

Recently Okuda and co-workers^[16a,16d] have shown that the introduction of a furan-2-yl group on the cyclopentadienyl ring of a half-sandwich lanthanide complex results in a rapid intramolecular C β –H bond activation, thereby triggering the formation of a thermally more stable yne-enolate yttrium product by means of furanyl ring opening^[22] (Scheme 6).



Scheme 6. Furanyl ring opening in lanthanide-cyclopentadienyl complexes.

In addition, in monitoring the intramolecular C β –H bond activation and the subsequent yne-enolate formation by ¹H NMR spectroscopy, the same authors have found first-order kinetics with respect to the complex concentration as well as an increase of the reaction rate with increasing metal size.^[16d] In our case, there is no evidence for the formation of a dialkyl intermediate with the furanyl oxygen

occupying a coordinative position at the metal centre, whereas a rapid metalation at the β position of the heteroaryl substituent takes place to give **15**. This complex is very stable, with no appreciable decomposition even in noncoordinating solvents for days. The close proximity of the Y–alkyl and the C_{β} –H bond in **15**, due to the free rotation of the pendant donor, is expected to affect the C–H bond-activation rate strongly and make it predominant over oxygen coordination.^[16d]

Synthesis and Characterization of the Yttrium-Aryl-Hydrido and -Benzyl-Hydrido Derivatives

The most common synthetic procedures for the preparation of rare-earth hydrido complexes from their M–alkyl counterparts make use of either dihydrogen^[2b,23] or phenylsilane^[8,24] as reagents. We have already reported on the treatment of **11** and **12** with an equimolecular amount of PhSiH_3 . In both cases the reaction proceeds rapidly in *n*-hexane at 0 °C, thus resulting in the formation of binuclear yttrium-aryl-hydrido and -benzyl-hydrido complexes **16** and **17** (Scheme 2). Although the crystallographic characterization of **16** has already been reported previously,^[8] orange crystals of **17** suitable for X-ray diffraction have now been prepared by the slow cooling of a benzene/*n*-hexane mixture (1:3) down to 10 °C.

Complex **17** crystallizes as a solvate with one hexane molecule per molecule of binuclear species. Its molecular structure is illustrated in Figure 5.

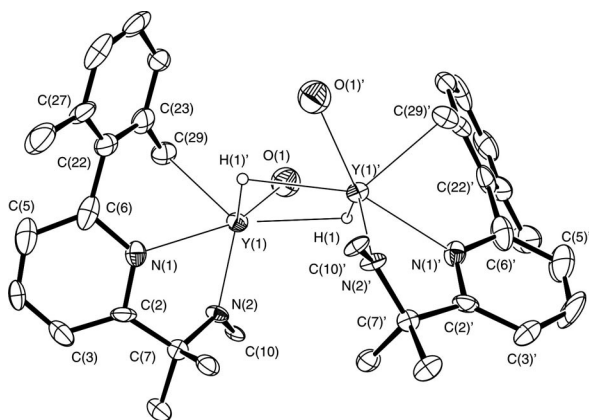


Figure 5. Crystal structure of $[\{N_2^{Xyl}Y(\mu-H)(thf)\}_2]$ (**17**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (apart from yttrium hydrides), 2,6-diisopropylphenyl fragments and methylene groups of the thf molecules and one molecule of hexane (crystallization solvent) are omitted for clarity.

By following the same chemistry, the treatment of **15** with an equimolecular amount of PhSiH_3 resulted in the formation of the binuclear heteroaryl-hydrido complex **18**. Yellow-brown crystals of complex **18** were obtained by the slow cooling of a benzene/*n*-hexane mixture (1:3) down to 10 °C. The molecular structure of the benzene solvate complex **18** is illustrated in Figure 6.

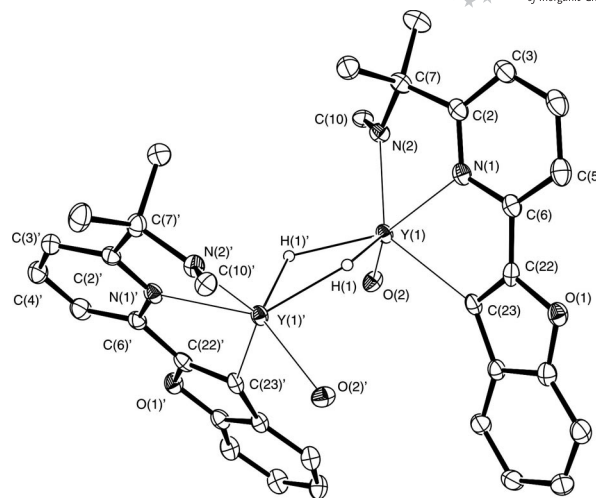


Figure 6. Crystal structure of $[\{N_2^{BFu}Y(\mu-H)(thf)\}_2]$ (**18**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (apart from yttrium hydrides), 2,6-diisopropylphenyl fragments, methylene groups of the thf molecules and two molecules of benzene (crystallization solvent) are omitted for clarity.

Unfortunately, all attempts to synthesize the hydrido complexes supported by thiophenyl-substituted amidopyridinate ligands by treating the monoalkyl complexes **13** and **14** with PhSiH_3 failed and intractable materials were invariably isolated.

The complexes adopt binuclear structures with two six-coordinate yttrium atoms. The metal coordination spheres are determined by the two nitrogen and one carbon atoms from the tridentate amidopyridinate ligand, two bridging hydrido ligands and one oxygen atom from a residual thf molecule. Unlike the majority of binuclear hydrido species, the tetranuclear Y_2H_2 cores are not planar. For complexes **16** and **18**, the dihedral angles between the $Y(1)H(1)H(1')$ and $Y(1')H(1)H(1')$ planes have close values (20.1 and 21.0°), whereas for **17** this angle is much smaller (12.4°). A similar trend is finally observed for the Y–H bonds. In complexes **16** and **18**, the Y–H bonds are significantly shorter [2.15 and 2.09(2) Å, respectively] than that measured for **17** (2.44 Å). It should be noted that the coordinated N and C atoms from the tridentate amidopyridinate ligands in **16–18** lie in the same plane, although the chelating ligand is not wholly planar. The Y–C bond lengths in **16** [2.469(2) Å], **17** [2.462(9) Å] and **18** [2.514(4) Å] match well the values previously reported for similar six-coordinate yttrium-aryl species,^[25] whereas the Y–Y distances [**16**: 3.5780(4) Å; **17**: 3.6917(14) Å; **18**: 3.53(11) Å] are noticeably shorter than those measured in related binuclear yttrium hydrides.^[11,6,26]

Notably, the Y–C(aryl) and Y–C(Bn) (Bn = benzyl) bonds do not react with PhSiH_3 even in the presence of a twofold excess amount of the reagent for prolonged reaction times. Indeed, all of the binuclear hydrido complexes can be recovered after stirring of the reagents for 24 h at room temperature in the presence of an excess amount of PhSiH_3 , with no appreciable decomposition. Unlike PhSiH_3 , the reaction of **11**, **12** and **15** with H_2 (1 bar) in

Table 3. Ethylene polymerization with yttrium(III)-alkyl and -hydride precursors.^[a]

Run	Precatalyst ^[a]	Cocatalyst (number of equiv.)	<i>T</i> [°C]	Polymer yield [g]	TOF [kg of PE (mol of Y bar h) ⁻¹]	TOF [mol of C ₂ H ₄ conv. (mol of Y bar h) ⁻¹]
1	11	MAO (300)	22	0.144	2.4	85.7
2	11	MAO (300)	50	0.096	1.6	57.1
3	12	MAO (300)	22	0.018	0.3	10.7
4	13	MAO (300)	22	0.132	2.2	78.6
5	14	MAO (300)	22	0.186	3.1	110.7
6	14	MAO (300)	50	0.162	2.7	96.4
7	11	[Me ₂ PhNH][B(C ₆ F ₅) ₄]/Al <i>i</i> Bu ₃ (1.2)/(200)	65	0.048	0.8	28.6
8	14	[Me ₂ PhNH][B(C ₆ F ₅) ₄]/Al <i>i</i> Bu ₃ (1.2)/(200)	65	0.024	0.4	14.3
9	16	MAO (300)	22	traces	–	–
10	16	[Me ₂ PhNH][B(C ₆ F ₅) ₄]/Al <i>i</i> Bu ₃ (1.2)/(200)	65	traces	–	–
11	17	MAO (300)	22	traces	–	–
12	18	[Me ₂ PhNH][B(C ₆ F ₅) ₄]/Al <i>i</i> Bu ₃ (1.2)/(200)	65	traces	–	–

[a] Reaction conditions: toluene (final volume 50 mL), precatalyst 12 μmol, 30 min.

toluene at room temperature led to their complete decomposition within a few minutes, followed by the precipitation of insoluble off-white solid materials. This result proves the effectiveness of PhSiH₃ as a reagent for the synthesis of the binuclear hydrido complexes **16–18** through a selective σ-bond metathesis of the residual Y–CH₂SiMe₃ bond.

Ethylene Polymerization Tests

The catalytic performances of the mononuclear yttrium(III)-monoalkyl complexes and of their binuclear hydride counterparts have been systematically scrutinized for ethylene polymerization under different reaction conditions. Although all these complexes turned out to be completely inert in the absence of a proper activator, some of them have shown a moderate activity upon treatment with methylaluminoxane (MAO; see the Experimental Section and Table 3). Particularly, complexes **11** and **14** have shown activities at room temperature up to 2.4 and 3.1 kg of PE [(mol of Y) bar h]⁻¹, respectively. When the sp²-coordinative carbon atom from the aryl or heteroaryl substituent of the pyridine ring is replaced by an sp³ donor, as for complex **12**, a significant decrease in the catalytic activity is observed {0.3 kg of PE [(mol of Y) bar h]⁻¹}. Finally, no polymerization activity has been observed with the more sterically crowded Y–H dimers **16–18** under similar experimental conditions. High-temperature polymerization tests (from 80 to 90 °C) have resulted in the rapid deactivation of the catalyst with the formation of traces of insoluble polyolefinic materials.

Cationic active species are also generated from catalyst precursors **11** and **14** upon treatment with [Me₂PhNH]–[B(C₆F₅)₄] in combination with Al*i*Bu₃ in toluene at 65 °C (see the Experimental Section and Table 3) and were screened in the polymerization of ethylene.^[27] Very modest activity was observed with either catalyst precursor {0.8 and 0.4 kg of PE [(mol of Y) bar h]⁻¹, respectively}, which we attribute to a rapid catalyst deactivation as indicated by the drop in ethylene consumption in the first two minutes of the reaction. The melting points (138–139 °C) of the PEs produced with catalyst precursors **11** and **14** are in the typi-

cal range of values for linear high-density polyethylene (HDPE), and the absence of any type of branches has been unambiguously confirmed by ¹³C{¹H} NMR spectroscopy. Finally, the thermogravimetric analysis (TGA) of all polyolefin materials showed comparable thermal stability within all the samples.

Conclusion

We have shown in this paper that aminopyridinate ligands bearing aryl or heteroaryl substituents at the 6-position of the pyridine ring undergo fast intramolecular sp² C–H bond activation upon treatment with an equimolecular amount of [Y(CH₂SiMe₃)₃(thf)₂], thereby leading to a novel class of yttrium complexes with unusual Y–C bonds.

Aminopyridinate systems that contain 2-thiophene or 2-benzofuryl moieties have been used to generate stable cyclopentadienyl-free yttrium(III) complexes in which the intramolecular C–H bond activation takes place at the less acidic 3-position of the heteroaryl groups. The reaction of the benzofuryl-containing ligand with the yttrium–tris(alkyl) complex gives the first example of a stable yttrium(III)-alkyl-aryl complex in which the C–H bond activation takes place at the β position of the benzofuryl group with no apparent decomposition of the heteroaromatic moiety (furan ring opening), even upon standing in solution for days.

All monoalkyl complexes undergo selective σ-bond metathesis at the residual Y–CH₂Si(CH₃)₃ bond upon treatment with phenylsilane. As a result, binuclear yttrium-heteroaryl-hydrido and -benzyl-hydrido complexes have been synthesized and characterized by spectroscopic and XRD methods. Selected complexes have been also scrutinized as catalyst precursors for ethylene polymerization and show moderate HDPE production.

Experimental Section

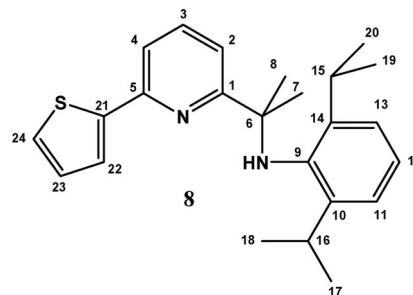
General: All air- and/or water-sensitive reactions were performed under either nitrogen or argon in flame-dried flasks using standard Schlenk-type techniques. thf was purified by distillation from sodium/benzophenone ketyl after drying with KOH. Et₂O, benzene,

n-hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or were obtained by means of a MBraun Solvent Purification Systems, whereas MeOH was distilled from Mg prior to use. C₆D₆ was dried with sodium/benzophenone ketyl and condensed in vacuo prior to use, whereas CD₂Cl₂ or CDCl₃ were dried with activated 4 Å molecular sieves. Literature methods were used to synthesize both the iminopyridine ligands N₂H^{Ph}, N₂HTh, N₂H^{EtTh},^[13] N₂H^{BFu},^[14] N₂H^{Xyl}^[8] and the aminopyridine systems N₂H^{Ph} and N₂H^{Xyl}.^[8] [Y(CH₂SiMe₃)₃(thf)₂]^[2b,23,28] [N₂H^{Ph}Y(CH₂SiMe₃)(thf)₂] (11),^[8] [N₂H^{Xyl}Y(CH₂SiMe₃)(thf)] (12),^[8] [{N₂H^{Ph}Y(μ-H)(thf)}₂] (16)^[8] and [{N₂H^{Xyl}Y(μ-H)(thf)}₂] (17)^[8] were prepared according to previously reported procedures. All the other reagents and solvents were used as purchased from commercial suppliers. ¹H and ¹³C{¹H} NMR spectra were obtained with either a Bruker ACP 200 (200.13 and 50.32 MHz, respectively) or a Bruker Avance DRX-400 (400.13 and 100.62 MHz, respectively). Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvent resonances (¹H and ¹³C). IR spectra were recorded as Nujol mulls or KBr plates with FSM 1201 and Bruker-Vertex 70 instruments. Lanthanide analyses were carried out by complexometric titration. The C, H, N elemental analyses were made in the microanalytical laboratory of IOMC or at ICCOM-CNR with a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of ±0.4 units on carbon (C), hydrogen (H) and nitrogen (N). Melting points were ensured with a Stuart Scientific Melting Point apparatus SMP3. Catalytic reactions were performed with a 250 mL stainless steel reactor constructed at ICCOM-CNR (Firenze, Italy) and equipped with a mechanical stirrer, a Parr 4842 temperature and pressure controller, a mass-flow meter equipped with a digital control for the connection to the PC and an external jacket for the temperature control. The reactor was connected to an ethylene reservoir to maintain a constant pressure throughout the catalytic runs. Ethylene was purified before use by passing it through two columns filled with activated molecular sieves (4 Å) and BASF R3-11G catalysts, respectively. The MAO solution was filtered through a D4 funnel and the solvents evaporated to dryness at 50 °C under vacuum. The resulting white residue was heated further to 50 °C under vacuum overnight. A stock solution of MAO was prepared by dissolving solid MAO in toluene (100 mg mL⁻¹). The solution was used within three weeks to avoid self-condensation effects of the MAO. Other activators/cocatalysts were used as received from the providers. Melting temperatures of the polymer materials were determined by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-7 instrument equipped with CCA-7 cooling device and calibrated with the melting transition of indium and *n*-heptane as references (156.1 and –90.61 °C, respectively). The polymer sample mass was 10 mg and aluminium pans were used. Any thermal history in the polymers was eliminated by first heating the specimen at a heating rate of 20 °C min⁻¹ to 200 °C, cooling at 20 °C min⁻¹ to –100 °C, and then recording the second scan from –100 to 200 °C. Thermogravimetric analysis (TGA) was obtained under nitrogen (60 mL min⁻¹) with a TGA Mettler Toledo instrument at a heating rate of 10 °C min⁻¹ from 50 to 700 °C.

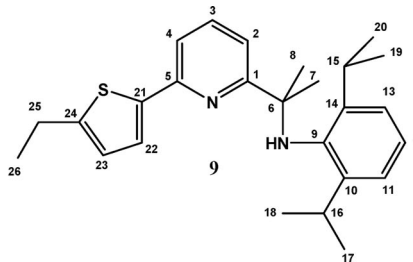
General Procedure for the Synthesis of Aminopyridinate Ligands 6–10: A solution of the appropriate iminopyridine ligand (1–5; 2 mmol) in toluene (20 mL) was cooled to 0 °C in an ice bath and treated dropwise with a 2.0 M solution of trimethylaluminium (TMA) in toluene (1.5 mL, 3 mmol). The reaction mixture was allowed to stir at room temperature for 12 h and then was quenched with water (15 mL). The aqueous phase was extracted with AcOEt (3 × 20 mL) and the combined organic layers were dried with Na₂SO₄. Removal of the solvent under reduced pressure gave the

amidopyridinate ligands (6–10) as crude off-white solids. The ligands were purified by crystallization from hot MeOH by cooling the resulting solution at either 4 °C (6, 8, 10) or –20 °C (7, 9) overnight to afford crystals. Suitable crystals for X-ray diffraction were collected after successive recrystallization from hot MeOH. N₂H^{Ph} (6): 93% yield, white crystals;^[8] N₂H^{Xyl} (7): 89% yield, white crystals;^[8] N₂HTh (8): 76% yield, pale yellow microcrystals; N₂H^{EtTh} (9): 70% yield, white needles; N₂H^{BFu} (10): 83% yield, white crystals.

N₂HTh (8): ¹H NMR (300 MHz, CD₂Cl₂, 293 K): δ = 1.10 [d, ³J_{H,H} = 6.8 Hz, 12 H, CH(CH₃), H^{17,18,19,20}], 1.48 [s, 6 H, C(CH₃)₂, H^{7,8}], 3.39 [sept, ³J_{H,H} = 6.8 Hz, 2 H, CH(CH₃), H^{15,16}], 4.52 (br. s, 1 H, NH), 7.09 (m, 3 H, CH Ar, H^{11,12,13}), 7.16 (dd, ³J = 3.7 Hz, 1 H, CH Th, H²³), 7.43 (dd, ³J = 7.7 Hz, 1 H, CH Ar, H²), 7.44 (dd, ³J = 3.7 Hz, 1 H, CCH Th, H²²), 7.60 (dd, ³J = 7.7 Hz, 1 H, CH Ar, H⁴), 7.67 (dd, ³J = 3.7 Hz, 1 H, CCH Th, H²⁴), 7.73 (t, ³J = 7.8 Hz, 1 H, CH Ar, H³) ppm. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 293 K): δ = 23.8 [CH(CH₃)₂, C^{17,18,19,20}], 28.1 [CH(CH₃)₂, C^{15,16}], 28.7 [C(CH₃)₂, C^{7,8}], 59.2 [C(CH₃)₂, C⁶], 116.1 (C⁴), 117.4 (C²), 122.9 (C^{11,13}), 124.2 (C²⁴), 124.4 (C¹²), 127.3 (C²²), 127.8 (C²³), 137.1 (C³), 140.3 (C²¹), 145.5 (C⁹), 146.9 (C^{14,10}), 150.9 (C⁵), 167.8 (C¹) ppm. M.p. 99.3 °C. C₂₄H₃₀N₂S (378.56 g mol⁻¹): calcd. C 76.14, H 7.99, N 7.40, S 8.47; found C 76.71, H 7.85, N 7.24, S 8.20.



N₂H^{EtTh} (9): ¹H NMR (300 MHz, CD₂Cl₂, 293 K): δ = 1.12 [d, ³J_{H,H} = 6.8 Hz, 12 H, CH(CH₃), H^{17,18,19,20}], 1.37 (t, ³J_{H,H} = 7.5 Hz, 3 H, CH₂CH₃, H²⁶), 1.47 [s, 6 H, C(CH₃)₂, H^{7,8}], 2.91 (q, ³J_{H,H} = 7.5 Hz, 2 H, CH₂CH₃, H²⁵), 3.42 [sept, ³J_{H,H} = 6.8 Hz, 2 H, CH(CH₃), H^{15,16}], 4.52 (br. s, 1 H, NH), 6.85–6.87 (m, 1 H, CCH Th, H²³), 7.10 (m, 3 H, CH Ar, H^{11,12,13}), 7.37 (dd, ³J = 7.8, ⁴J = 0.87 Hz, 1 H, CH Ar, H²), 7.49 (d, ³J = 3.6 Hz, 1 H, CCH Th, H²²), 7.53 (dd, ³J = 7.8, ⁴J = 0.87 Hz, 1 H, CH Ar, H⁴), 7.70 (t, ³J = 7.8 Hz, 1 H, CH Ar, H³) ppm. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 293 K): δ = 15.6 (CH₂CH₃, C²⁶), 23.8 (CH₂CH₃, C²⁵), 23.8 [CH(CH₃)₂, C^{17,18,19,20}], 28.1 [CH(CH₃)₂, C^{15,16}], 28.7 [C(CH₃)₂, C^{7,8}], 59.2 [C(CH₃)₂, C⁶], 115.6 (C²), 116.8 (C⁴), 122.9 (C^{11,13}), 124.1 (C²²), 124.3 (C²³), 124.4 (C¹²), 137.0 (C³), 140.3 (C²⁴), 142.5 (C²¹), 146.9 (C^{10,14}), 150.1 (C⁹), 151.2 (C⁵), 167.6 (C¹) ppm. M.p. 97.6 °C. C₂₆H₃₄N₂S (406.63 g mol⁻¹): calcd. C 76.80, H 8.43, N 6.89, S 7.89; found C 76.91, H 8.40, N 6.75, S 7.94.



N₂H^{BFu} (10): ¹H NMR (300 MHz, CD₂Cl₂, 293 K): δ = 1.12 [d, ³J_{H,H} = 6.8 Hz, 12 H, CH(CH₃), H^{17,18,19,20}], 1.52 [s, 6 H,

Synthesis of $[N_2^{BFu}Y(CH_2SiMe_3)(thf)_2]$ (15): A solution of $N_2^{BFu}H$ (**10**) (0.190 g, 0.46 mmol) in *n*-hexane (15 mL) was added to a solution of $[Y(Me_3SiCH_2)_3(thf)_2]$ (0.228 g, 0.46 mmol) in *n*-hexane (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The solution was concentrated in vacuo to approximately one third of its initial volume and was kept overnight at –20 °C. Complex **15** was isolated as a yellow-orange microcrystalline solid in 69% yield (0.232 g). 1H NMR (400 MHz, C_6D_6 , 293 K): δ = –0.69 (d, $^2J_{Y,H}$ = 3.0 Hz, 2 H, YCH_2), 0.20 [s, 9 H, Si(CH_3)], 0.95 (m, 8 H, β - CH_2 thf), 1.27 [s, 6 H, $C(CH_3)_2$, $H^{7,8}$], 1.30 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$; $H^{17,18,19,20}$], 1.34 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$, $H^{17,18,19,20}$], 3.65 (m, 8 H, α - CH_2 thf), 3.79 [sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, $CH(CH_3)_2$, $H^{15,16}$], 6.63 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, CH Ar, H^2), 7.17–7.26 (compl. m, together 4 H, CH Ar, $H^{3,12,25,26}$), 7.32 (m, 2 H, CH Ar, $H^{11,13}$), 7.57 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, CH Ar, H^4), 7.62 (dd, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 2.0 Hz, 1 H, CH Ar, H^{27}), 8.12 (dd, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 2.0 Hz, 1 H, CH Ar, H^{24}) ppm. $^{13}C\{H\}$ NMR (100 MHz, C_6D_6 , 293 K): δ = 4.5 [s, Si(CH_3) $_3$], 23.8 [s, $CH(CH_3)_2$, $C^{17,18,19,20}$], 24.7 (s, β - CH_2 thf), 27.7 [s, $CH(CH_3)_2$, $C^{15,16}$], 27.7 [s, $CH(CH_3)_2$, $C^{17,18,19,20}$], 30.1 (d, $^1J_{Y,C}$ = 37.6 Hz, YCH_2), 31.1 [s, $C(CH_3)_2$, $C^{7,8}$], 68.6 [d, $J_{Y,C}$ = 2.6 Hz, $C(CH_3)_2$, C^6], 70.2 (s, α - CH_2 thf), 110.5 (s, C^{27}) 113.5 (s, C^4), 117.8 (s, C^2), 122.1 (s, C^{26}) 123.8 (s, $C^{11,13}$), 124.1 (s, C^{12}), 124.5 (s, C^{25}), 126.7 (s, C^{24}), 139.0 (s, C^3), 140.0 (d, $^2J_{Y,C}$ = 2.8 Hz, C^{23}), 144.1 (s, C^9), 149.7 (s, $C^{10,14}$), 153.4 (br. s, C^5), 156.6 (s, C^{28}), 158.6 (d, $^1J_{Y,C}$ = 38.9 Hz, YC , C^{22}), 160.8 (br. s, C^{21}), 175.0 (br. s, C^1) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3075 (w), 3045 (m), 1600 (s), 1585 (w), 1570 (s), 1500 (s), 1415 (s), 1350 (m), 1335 (w), 1325 (m), 1300 (m), 1255 (s), 1235 (m), 1220 (s), 1200 (w), 1175 (s), 1145 (s), 1120 (m), 1005 (m), 1080 (s), 1045 (w), 1025 (s), 1010 (m), 970 (w), 925 (s), 895 (w), 885 (m), 865 (s), 850 (s), 820 (m), 810 (s), 795 (m), 770 (m), 715 (m), 705 (m), 675 (s), 635

(w), 620 (m) cm^{-1} . $\text{C}_{40}\text{H}_{57}\text{N}_2\text{O}_3\text{SiY}$ (730.88 g mol^{-1}): calcd. C 65.73, H 7.68, N 3.83, Y 12.16; found C 65.32, H 7.93, N 3.71, Y 12.04.

Synthesis of $[\{\text{N}_2\text{BF}_4\text{Y}(\mu\text{-H})(\text{thf})\}_2]$ (18**):** PhSiH_3 (0.047 g, 0.431 mmol) was added to a solution of **12** (0.315 g, 0.431 mmol) in *n*-hexane (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and kept overnight at room temperature. The solution was concentrated in vacuo and maintained overnight at –20 °C. Complex **18** was isolated as a yellow-brown crystalline solid in 72% yield (0.201 g). ^1H NMR (400 MHz, C_6D_6 , 293 K): δ = 0.72 [br. s, 6 H, $\text{CH}(\text{CH}_3)_2$; $\text{H}^{17,18,19,20}$], 0.79 [s, 6 H, $\text{C}(\text{CH}_3)_2$, $\text{H}^{7,8}$], 1.01 [m, 12 H, $\text{CH}(\text{CH}_3)_2$; $\text{H}^{17,18,19,20}$], 1.24 (m, 8 H, $\beta\text{-CH}_2$ thf), 1.33 [s, 6 H, $\text{CH}(\text{CH}_3)_2$; $\text{H}^{17,18,19,20}$], 2.17 (s, 6 H, $\text{H}^{7,8}$), 2.72 [m, 2 H, $\text{CH}(\text{CH}_3)_2$, $\text{H}^{15,16}$], 3.19 (m, 4 H, $\alpha\text{-CH}_2$ thf), 3.42 (m, 4 H, $\alpha\text{-CH}_2$ thf), 4.54 [m, 2 H, $\text{CH}(\text{CH}_3)_2$, $\text{H}^{15,16}$], 6.75 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 1 H, CH Ar , H^2), 6.92–7.18 (compl. m, together 8 H, CH Ar , $\text{H}^{3,11,12,13}$), 7.23 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H, CH Ar , H^{26}), 7.33 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, CH Ar , H^{25}), 7.61 (d, $^3J_{\text{H,H}} = 7.5$ Hz, 2 H, CH Ar , H^4), 7.64 (d, $^3J_{\text{H,H}} = 7.5$ Hz, 2 H, CH Ar , H^{27}), 7.71 (t, $^1J_{\text{Y,H}} = 27.0$ Hz, 2 H, YH) 7.99 (d, $^3J_{\text{H,H}} = 7.5$ Hz, 2 H, CH Ar , H^{24}) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, C_6D_6 , 293 K): δ = 23.0 [s, $\text{CH}(\text{CH}_3)_2$, $\text{C}^{17,18,19,20}$], 23.9 (s, $\beta\text{-CH}_2$, thf), 24.2 [s, $\text{CH}(\text{CH}_3)_2$, $\text{C}^{17,18,19,20}$], 25.9 [s, $\text{CH}(\text{CH}_3)_2$, $\text{C}^{17,18,19,20}$], 26.7 [s, $\text{CH}(\text{CH}_3)_2$, $\text{C}^{17,18,19,20}$], 26.8 [s, $\text{CH}(\text{CH}_3)_2$, $\text{C}^{15,16}$], 28.3 [s, $\text{C}(\text{CH}_3)_2$, $\text{C}^{7,8}$], 29.1 [s, $\text{CH}(\text{CH}_3)_2$, $\text{C}^{15,16}$], 42.9 [s, $\text{C}(\text{CH}_3)_2$, $\text{C}^{7,8}$], 66.2 [d, $J_{\text{Y,C}} = 2.6$ Hz, $\text{C}(\text{CH}_3)_2$, C^6], 70.3 (s, $\alpha\text{-CH}_2$ thf), 110.6 (s, C^{27}), 114.3 (s, C^4), 115.2 (s, C^2), 121.2 (s, C^{26}), 122.8 (s, $\text{C}^{11,13}$), 123.2 (s, $\text{C}^{11,13}$), 124.0 (s, C^{12}), 127.0 (s, C^{25}), 128.0 (s, C^{24}), 138.9 (s, C^3), 140.4 (d, $^2J_{\text{Y,C}} = 2.8$ Hz, C^{23}), 147.1 (s, C^9), 148.6 (s, $\text{C}^{10,14}$), 150.2 (s, $\text{C}^{10,14}$), 153.2 (br. s, C^5), 156.6 (s, C^{28}), 160.1 (d, $^1J_{\text{Y,C}} = 43.3$ Hz, Y-C^{22}), 162.6 (br. s, C^{21}), 175.8 (br. s, C^1) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3080 (w), 3050 (m), 1605 (s), 1580 (w), 1560 (s), 1505 (s), 1425 (s), 1340 (m), 1330 (w),

1320 (m), 1295 (m), 1230 (m), 1220 (s), 1200 (w), 1170 (s), 1140 (s), 1120 (m), 1010 (m), 1085 (s), 1040 (w), 1025 (s), 1015 (m), 975 (w), 935 (s), 895 (w), 880 (m), 820 (m), 810 (s), 790 (m), 770 (m), 710 (m), 675 (s), 635 (w), 615 (m) cm^{-1} . $\text{C}_{64}\text{H}_{76}\text{N}_4\text{O}_2\text{Y}_2$ (1145.14 g mol^{-1}): calcd. C 67.13, H 6.87, N 4.89, Y 15.53; found C 66.98, H 7.11, N 4.91, Y 15.44.

General Procedure for Ethylene Polymerization: A 200 mL stainless steel reactor was heated to 60 °C under vacuum overnight and then cooled to room temperature under a nitrogen atmosphere.

Activation with MAO: The solid precatalyst (12 μmol) was charged into the reactor, which was sealed and placed under vacuum. A solution of MAO in toluene (3600 μmol , 300 equiv.), prepared by diluting a standard solution of MAO (2.4 mL, 10 wt% in toluene) in toluene (47.6 mL), was then introduced by suction into the reactor previously evacuated by a vacuum pump. The system was heated to the desired temperature, pressurized with ethylene to the final pressure (10 bar), and stirred at 1500 rpm for 30 min.

Activation with $[\text{Me}_2\text{PhNH}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}(\text{iBu})_3$: The reactor was charged with a suspension of the cocatalyst $[\text{Me}_2\text{PhNH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (14.4 μmol) in toluene (35 mL) followed by the rapid addition of a 25 wt% solution of $\text{Al}(\text{iBu})_3$ in toluene (2.4 mL, 2.4 mmol, 200 equiv.). After sealing the reactor, the system was pressurized with ethylene at 2 bar and heated at 65 °C for 10 min so as to dissolve the activator. The ethylene pressure was then released slowly and a precatalyst solution (2.5 mL), prepared by dissolving the solid precatalyst (12 μmol) in toluene (2.5 mL), was added into the reactor with a syringe. The autoclave was then pressurized with ethylene to the final pressure (10 bar) and stirred at 1500 rpm for 30 min. Irrespective of the procedure used, catalysts and cocatalyst (activator) solutions were handled in the glove box and ethylene

Table 4. Crystal data and structure refinement for ligands **6–10**.^[a]

	6	7	8	9	10
Empirical formula	$\text{C}_{26}\text{H}_{32}\text{N}_2$	$\text{C}_{28}\text{H}_{36}\text{N}_2$	$\text{C}_{24}\text{H}_{30}\text{N}_2\text{S}$	$\text{C}_{52}\text{H}_{68}\text{N}_4\text{S}_2$	$\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}$
M_r	372.54	400.59	378.56	813.22	412.56
T [K]	293(2)	293(2)	293(2)	150(2)	293(2)
λ [Å]	1.54180	0.71069	0.71073	0.71069	0.71069
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Pc2_1n$	$Pna2_1$	$P2_1c$
a [Å]	8.9657(10)	12.087(1)	8.8099(14)	14.551(1)	15.321(17)
b [Å]	22.814(4)	13.064(1)	10.711(4)	9.164(1)	13.032(16)
c [Å]	10.8298(10)	15.807(1)	22.911(10)	35.733(2)	12.129(12)
α [°]	90	90	90	90(5)	90(5)
β [°]	95.554(10)	97.095(4)	90	90(4)	102.738(11)
γ [°]	90	90	90	90(4)	90(5)
V [Å ³]	2204.7(5)	2476.9(3)	2162.0(10)	4764.8(7)	2362(5)
D_{calcd} [g cm ^{–3}]	1.122	1.074	1.163	1.134	1.160
Absorption coefficient [mm ^{–1}]	0.491	0.062	0.160	0.150	0.070
$F(000)$	808	872	816	1760	888
Crystal size [mm]	0.52 × 0.28 × 0.15	0.1 × 0.1 × 0.2	0.33 × 0.30 × 0.20	0.25 × 0.3 × 0.3	0.01 × 0.01 × 0.01
θ range for data collection [°]	3.88–60.06	3.71–25.70	2.48–24.96	3.75–28.90	3.75–24.36
Limiting indices	–10 ≤ h ≤ 10, –5 ≤ k ≤ 25, 0 ≤ l ≤ 12	–14 ≤ h ≤ 12, –15 ≤ k ≤ 15, –19 ≤ l ≤ 19	0 ≤ h ≤ 10, 0 ≤ k ≤ 12, 0 ≤ l ≤ 27	–19 ≤ h ≤ 18, –7 ≤ k ≤ 12, –39 ≤ l ≤ 47	–17 ≤ h ≤ 12, –14 ≤ k ≤ 14, –13 ≤ l ≤ 13
Reflections collected/unique	3467/3275	13804/4654	2013/2013	15778/8366	6754/2914
GOF on F^2	1.028	0.914	1.042	0.776	0.815
Data/restraints/parameters	3275/1/252	4654/0/275	2013/1/252	8366/1/539	2914/0/283
Final R indices	$R_1 = 0.0830$, $wR_2 = 0.2039$	$R_1 = 0.0717$, $wR_2 = 0.1748$	$R_1 = 0.0699$, $wR_2 = 0.1318$	$R_1 = 0.0456$, $wR_2 = 0.0804$	$R_1 = 0.0507$, $wR_2 = 0.0749$
$[I > 2\sigma(I)]$	$R_1 = 0.1075$, $wR_2 = 0.2264$	$R_1 = 0.1809$, $wR_2 = 0.2169$	$R_1 = 0.1579$, $wR_2 = 0.1623$	$R_1 = 0.1354$, $wR_2 = 0.0987$	$R_1 = 0.1557$, $wR_2 = 0.0918$
Largest diff. peak and hole [e Å ^{–3}]	0.2063 and –0.241	0.255 and –0.192	0.250 and –0.245	0.330 and –0.303	0.151 and –0.156

[a] For all compounds, $Z = 4$.

Table 5. Crystal data and structure refinement for complexes **12**, **14**, and **16–18**.^[a]

	12 ^[b]	14	16 ^[a]	17	18
Empirical formula	C ₃₆ H ₅₃ N ₂ O ₂ SiY	C ₃₈ H ₅₉ N ₂ O ₂ SiY	C ₆₀ H ₇₈ N ₄ O ₂ Y ₂	C ₇₀ H ₁₀ N ₄ O ₂ Y ₂	C ₇₆ H ₉₀ N ₄ O ₄ Y ₂
<i>M</i> _r	646.80	724.93	1065.08	1207.36	1301.34
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71069	0.71069
Crystal system	monoclinic	monoclinic	tetragonal	tetragonal	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 4 ₁ 2 ₁ 2	<i>P</i> 4 ₁ 2	<i>P</i> b <i>cn</i>
<i>a</i> [Å]	10.0924(5)	17.5740(7)	12.9842(3)	23.7470(6)	17.666(5)
<i>b</i> [Å]	18.8418(9)	12.4289(5)	12.9842(3)	23.7470(6)	17.642(9)
<i>c</i> [Å]	18.4703(9)	18.4721(7)	33.0971(1)	12.3501(4)	21.625(7)
α [°]	90	90	90	90	90(5)
β [°]	99.8130(10)	110.97(10)	90	90	90(5)
γ [°]	90	90	90	90	90(5)
<i>V</i> [Å ³]	3460.9(3)	3767.5(3)	5579.8(3)	6964.5(3)	6740(4)
<i>D</i> _{calcd.} [g cm ^{−3}]	1.241	1.278	1.268	1.151	1.283
Absorption coefficient [mm ^{−1}]	1.749	1.669	2.113	1.701	1.765
<i>F</i> (000)	1376	1544	2240	2568	2736
Crystal size [mm]	0.30 × 0.20 × 0.15	0.35 × 0.26 × 0.13	0.15 × 0.12 × 0.06	0.2 × 0.1 × 0.1	0.05 × 0.01 × 0.1
θ range for data collection [°]	2.43–26.00	2.75–26.00	2.42–26.00	3.82–26.45	3.83–27.51
Limiting indices	−12 ≤ <i>h</i> ≤ 12, −23 ≤ <i>k</i> ≤ 23, 22 ≤ <i>l</i> ≤ 22	−21 ≤ <i>h</i> ≤ 21, −15 ≤ <i>k</i> ≤ 15, −22 ≤ <i>l</i> ≤ 22	−16 ≤ <i>h</i> ≤ 15, −16 ≤ <i>k</i> ≤ 16, −40 ≤ <i>l</i> ≤ 40	−28 ≤ <i>h</i> ≤ 14, −12 ≤ <i>k</i> ≤ 28, −15 ≤ <i>l</i> ≤ 8	−21 ≤ <i>h</i> ≤ 21, −15 ≤ <i>k</i> ≤ 20, −27 ≤ <i>l</i> ≤ 14
Reflections collected/unique	29249/6787	31546/7391	48076/5466	13954/5555	18112/6035
GOF on <i>F</i> ²	1.032	1.037	1.079	0.972	0.903
Data/restraints/parameters	6787/3/380	7391/4/419	5466/0/316	5555/22/361	6035/0/391
Final <i>R</i> indices	<i>R</i> 1 = 0.0349, <i>wR</i> 2 = 0.0761	<i>R</i> 1 = 0.0326, <i>wR</i> 2 = 0.0747	<i>R</i> 1 = 0.0257, <i>wR</i> 2 = 0.0608	<i>R</i> 1 = 0.0630, <i>wR</i> 2 = 0.1591	<i>R</i> 1 = 0.0363, <i>wR</i> 2 = 0.08
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0523, <i>wR</i> 2 = 0.0806	<i>R</i> 1 = 0.0489, <i>wR</i> 2 = 0.0792	<i>R</i> 1 = 0.0301, <i>wR</i> 2 = 0.0619	<i>R</i> 1 = 0.1205, <i>wR</i> 2 = 0.1731	<i>R</i> 1 = 0.0838, <i>wR</i> 2 = 0.0877
Largest diff. peak and hole [e Å ^{−3}]	0.439 and −0.289	0.996 and −0.367	−0.190 and 0.389	0.941 and −0.349	0.470 and −0.471

[a] For all compounds, *Z* = 4. [b] Selected data in the literature^[20] listed here for completeness.

was continuously fed to maintain the reactor pressure at the desired value throughout the catalytic run. After 30 min, the reaction was terminated by cooling the reactor to 0 °C, venting off the volatiles, and introducing acidic MeOH (1 mL, 5% HCl v/v). The solid products were filtered off, washed with cold toluene and MeOH, and dried in a vacuum oven at 50 °C. The filtrates were analyzed by GC and GC–MS for detecting the presence of short oligomers.

X-ray Diffraction Data: Crystallographic data of ligands **6–10** and complexes **12**, **14**, **16–18** are reported in Tables 4 and 5, respectively. X-ray diffraction intensity data were collected with either a SMART APEX or Oxford Diffraction CCD diffractometer with graphite monochromated Mo-*K*_α radiation (λ = 0.71073 Å) using ω scans. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS.^[29] All structure determination calculations were performed with the WINGX package^[30] with SIR-97,^[31] SHELXL-97^[32] and ORTEP-3 programs.^[33] Final refinements based on *F*² were carried out with anisotropic thermal parameters for all non-hydrogen atoms, which were included using a riding model with isotropic *U* values depending on the *U*_{eq} of the adjacent carbon atoms. In **9**, a nonmerohedral twin is present; the twin component was found to be 0.7(1). Two molecules are present in the asymmetric unit, thus generating a “pseudochiral” helical lattice packing [for this reason the space group found (*P*na2₁) is noncentrosymmetric]. The hydride ligand positions in complexes **16** and **17** were determined from the residual density map during the refinement and subsequently fixed at 2.15 and 2.44 Å from the Y atom, respectively. The accessible voids of 273 Å³ found in the lattice of **17** are probably occupied by disordered thf crystallization molecules that could not be located precisely. The coordinated thf molecules are

disordered as well, even at 100 K; this disorder was not explicitly treated since the final *R*1/*wR*2 values do not change significantly when it is included in the refinement. CCDC-740105 (**6**), -740107 (**7**), -740106 (**8**), -740104 (**9**), -740103 (**10**), -740102 (**14**), -740100 (**17**) and -740101 (**18**) 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.

Acknowledgments

The authors thank the Ministero dell'Istruzione, dell'Università e della Ricerca of Italy (NANOPACK - FIRB project no. RBNE03R78E), the Russian Foundation for Basic Research (grant no. 08-03-00391-a, 06-03-32728), FIRENZE HYDROLAB project by Ente Cassa di Risparmio di Firenze (<http://www.iccom.cnr.it/hydrolab/>) and the GDRE network “Homogeneous Catalysis for Sustainable Development” for financial support of this work. G. G. also thanks Dr. Andrea Meli and Dr. Andrea Ienco for fruitful discussions.

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Received: September 18, 2009

Published Online: December 15, 2009