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Reactions of Bis(alkyl)yttrium Complexes Supported by Bulky N,N Ligands with 2,6-Diisopropylaniline and Phenylacetylene

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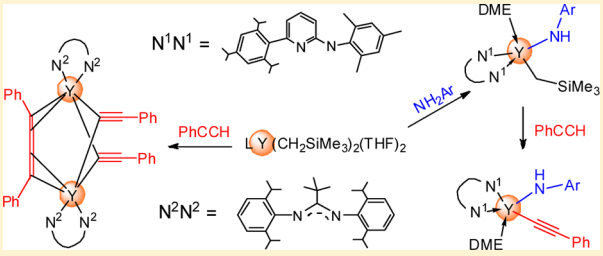
Supporting Information

ABSTRACT: The reactions of bis(trimethylsilylmethyl)yttrium complexes supported by bulky amidopyridinate (Ap) and amidinate (Amd) ligands ($LY(CH_2SiMe_3)_2(THF)_n$: L = Ap, n = 1 (**1**); L = Amd, n = 1 (**2**)) with 2,6-diisopropylaniline and phenylacetylene were performed. The reaction of **1** with an equimolar amount of 2,6-diisopropylaniline occurs with TMS elimination and affords an yttrium alkyl anilido species which was isolated as a DME adduct, $ApY(CH_2SiMe_3)(NH\text{-}2,6\text{-}^iPr_2C_6H_3)(DME)$ (**3**). The protonolysis of **3** with phenylacetylene results in the alkynyl anilido derivative $ApY(C{\equiv}CPh)(NH\text{-}2,6\text{-}^iPr_2C_6H_3)(DME)$ (**6**). The treatment of complexes **3** and **6** with 2,2′-bipy leads to the formation of the bis(anilido) derivative $ApY(NH\text{-}2,6\text{-}iPr_2C_6H_3)_2(bipy)$ (**5**). The formation of a dimeric complex containing two ApY fragments linked by two μ_2-alkynyl groups and a $\mu\text{-}\eta^2{:}\eta^2$-butatrienediyl fragment, $[\{AmdY(\mu_2\text{-}C{\equiv}CPh)\}_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}PhCCCCPh)]$ (**7**), was observed in the reaction of **2** with 2 equiv of phenylacetylene.



INTRODUCTION

Hydrocarbyl derivatives of rare-earth metals continue to attract considerable attention as highly active species that exhibit unique reactivity[1] and high potential in the activation and derivatization of unsaturated[2] and saturated[3] substrates. Due to the electrophilic nature of the metal center, rare-earth alkyl complexes engage in σ-bond metathesis reactions.[4] Bis(alkyl) rare-earth complexes have been the focus of special interest as potential precursors to cationic mono(alkyl) species that were found to be efficient catalysts of homo- and copolymerization of olefins and dienes.[5] Moreover, they were successfully employed for the synthesis of polyhydrido rare-earth clusters.[6] Another possible field of application of bis(alkyl) complexes is the preparation of rare-earth imido and alkynyl species. Complexes with multiple nitrogen−metal bonds are of significant interest, owing to the ability of the M═N functionality to undergo various reactions (metathesis of imines, aldehydes, and carbodiimides, metallacycle formation with alkynes and alkenes, and C−H bond activation).[7] Surprisingly, unlike the well-developed imido chemistry of the metals of groups 4−6,[8] that of rare-earth metals until recently remained virtually unexplored.[9] The synthesis and characterization of the sole example of a scandium complex with a terminal imido ligand was documented by Chen in 2010.[10] Obviously the difficulty of synthesis of terminal imido rare-earth complexes is related to the strongly pronounced tendency of these large metal ions to assemble more stable bi- or polymetallic complexes with μ_2-imido ligands.[9,11] Another possible path of transformation of terminal imido rare-earth complexes is C−H bond activation.[9d] Supposedly these synthetic limitations can be overcome by using bulky polydentate ligand systems able to provide kinetic stability. Bulky amidopyridinate[6h,i,12] and amidinate[13] ligands which were shown to allow for the synthesis and isolation of rather stable alkyl rare-earth complexes might provide a suitable coordination environment for stabilization of the related imido species.

Alkynyl rare-earth complexes are intriguing objects for investigating the variety of coordination modes of alkynyl ligands and the factors that drive their coupling in the metal atom coordination sphere. The chemistry of metallocene type mono(alkynyl) rare-earth complexes has been explored in detail,[14] while little is still known about bis(alkynyl) species.[15]

Herein we report on the attempted synthesis of terminal imido species via the reactions of bis(alkyl) yttrium complexes supported by bulky amidopyridinate and amidinate ligands with 2,6-diisopropylaniline. The reactions of bis(alkyl) yttrium complexes with phenylacetylene and the characterization of the obtained alkynyl derivatives will be considered.

RESULTS AND DISCUSSION

In continuation of our ongoing work on the synthesis and reactivity investigation of bis(alkyl) rare-earth complexes we focused on the reactions of bis(trimethylsilylmethyl)yttrium complexes supported by bulky amidopyridinate (Ap)[12] and

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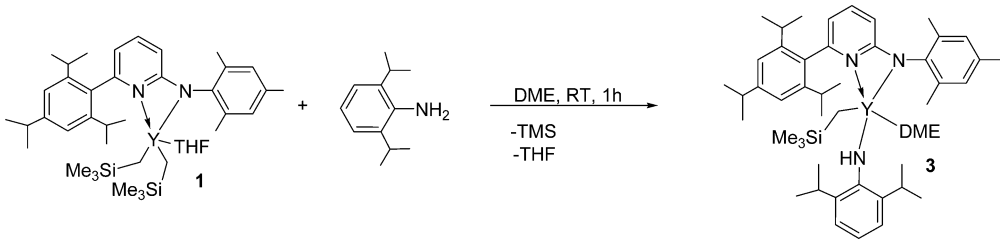
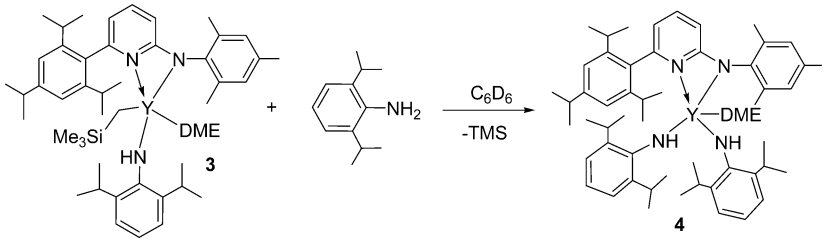
Scheme 1



Scheme 2



amidinate (Amd) ligands ($LY(CH_2SiMe_3)_2(THF)_n$: L = Ap, n = 1 (**1**); L = Amd, n = 1 (**2**)) with reagents containing acidic N−H or C−H bonds.

Recently Chen and co-workers reported[10] that the reaction of a dimethyl scandium complex coordinated by a tridentate amino-substituted nacnac ligand with 2,6-diisopropylaniline afforded a related terminal imido species. In order to prepare new imido yttrium derivatives, we attempted the reactions of **1** and **2** with 2,6-diisopropylaniline.

The NMR-tube reaction of **1** with an equimolar amount of 2,6-diisopropylaniline gave evidence for the loss of one alkyl group and concomitant formation of 1 equiv of TMS and an alkylamido species (Scheme 1).

Similarly to the scandium compound[10] the preparative-scale reaction afforded a pale yellow solution. All our attempts to isolate the reaction product in a crystalline state failed. Evaporation of the volatiles under vacuum afforded an off-white viscous oil. However, subsequent recrystallization of the oily residue from DME at −20 °C allowed the isolation of a new alkyl amido yttrium complex coordinated by an Ap ligand as a DME adduct (**3**).[16] Pale yellow crystals of **3** were obtained in 72% yield. **3** is soluble in THF and benzene and sparingly soluble in hexane. The NMR spectra of **3** clearly prove the presence of both alkyl (^{1}H, −0.42 ppm, d, $^2J_{YH}$ = 36.5 Hz, YCH_2; ^{13}C, 31.69 ppm, d, $^1J_{Y,C}$ = 43.4 Hz) and anilido (^{1}H, 4.68 ppm, NH) fragments attached to the yttrium atom. The evolution of complex **3** in benzene solution was monitored by ^{1}H and ^{13}C NMR spectroscopy. Complex **3** slowly decomposes in C_6D_6 solution at 20 °C (∼15% per day) with TMS elimination. No activation of C−H bonds of the Me or ^{i}Pr groups of the Ap ligand[17] was detected, but at the same time a broad singlet appeared in the region characteristic for anilido NH protons (4.53 ppm). In 1 week the ^{1}H NMR spectrum of **3** did not contain the signal of the alkyl CH_2 protons attached to yttrium. In order to assign the signal at 4.53 ppm, an NMR-scale reaction of **3** with 1 equiv of 2,6-diisopropylaniline was carried out (Scheme 2). This experiment unambiguously proved that the signal at 4.53 ppm corresponds to the NH protons of bis(anilido) complex **4**. Thereafter, complex **3** slowly decomposes in solution at 20 °C with formation of TMS and the bis(anilido) species **4**. Hence, complex **4** does not simply result from ligand redistribution, which is further corroborated by the absence of the putative co-redistribution product **1** in the ^{1}H NMR spectrum.

Clear pale yellow crystals of **3** suitable for X-ray analysis were obtained by slow concentration of a DME solution at −20 °C. Complex **3** crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell (one crystallographically independent molecule in the asymmetric unit). The molecular structure of complex **3** is shown in Figure 1, and the structure refinement data are given in Table 1. The X-ray study revealed that **3** is monomeric in the crystalline state. The yttrium atom is coordinated by two nitrogen atoms of the chelating amidopyridinate ligand, one nitrogen of the anilido fragment, one carbon atom of the alkyl group, and two oxygens of the DME molecule, thus resulting in a coordination number of 6. The coordination polyhedron around the yttrium atom adopts a distorted-octahedral geometry.

The Y−C bond length in **3** (2.421(4) Å) is very close to the values previously reported for six-coordinated alkyl yttrium complexes.[18] The distances between Y and the nitrogen atoms of amidopyridinate ligand in **3** are nonequivalent: the distance to the amido nitrogen (2.317(3) Å) is noticeably shorter than that to the pyridinato nitrogen (2.504(3) Å). The average Y−N bond length in **3** is similar to those observed in amidopyridinate yttrium complexes.[17a] The distance between Y and the nitrogen atom of the anilido fragment (2.250(3) Å) is significantly shorter than the Y−N distances of the amidopyridinate ligand and is similar to those observed in related compounds.[19b]

The reaction of complex **2** with 1 equiv of 2,6-diisopropylaniline under similar conditions afforded a deep violet solution. Unfortunately, all our attempts to isolate the reaction products in an individual state were unsuccessful.

Chen emphasized the crucial role of Lewis base coordination to the metal center in alkylanilido species for the formation of a terminal imido scandium complex.[10] According to the procedure described in the publication,[10] complex **3** was treated with an equimolar amount of 4-dimethylaminopyridine. At 20 °C no reaction occurred. After heating at 60 °C for 2 days, the reaction mixture turned deep brown and ^{1}H NMR spectroscopy detected release of 1 equiv of TMS. Unfortu-

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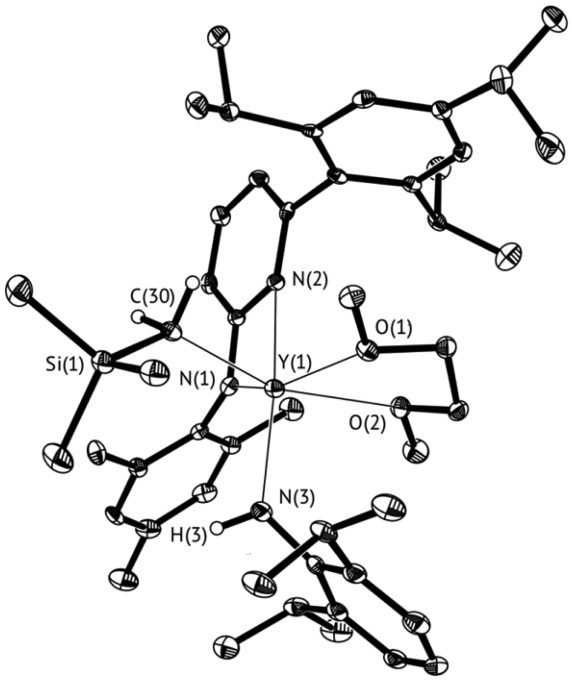
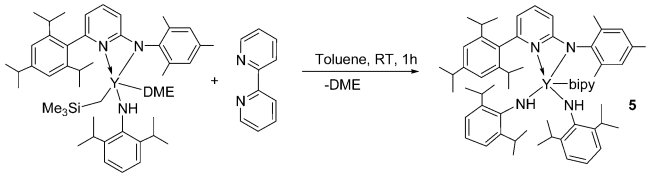


Figure 1. Crystal structure of $[ApY(CH_2SiMe_3)(NHAr)(DME)_2]$ (**3**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those of CH_2 and NH fragments) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)−N(3) = 2.250(3), Y(1)−N(1) = 2.317(3), Y(1)−O(1) = 2.409(3), Y(1)−C(30) = 2.421(4), Y(1)−O(2) = 2.459(3), Y(1)−N(2) = 2.504(3); N(1)−Y(1)−N(2) = 55.8(1), N(3)−Y(1)−C(30) = 108.1(1), N(3)−Y(1)−N(2) = 146.3(1).

nately, all attempts of isolation of the product in an individual state failed. Complex **3** was reacted with an equimolar amount of 2,2′-bipy in toluene at 20 °C (Scheme 3). The reaction

Scheme 3



mixture immediately became brownish violet. Slow concentration of the reaction mixture at ambient temperature allowed for the isolation of deep red crystals of an amidopyridinate bis(anilido) yttrium complex coordinated by 2,2′-bipy, **5**. Complex **5** was obtained in 45% yield. In order to elucidate the path of formation of **5**, the NMR-scale reaction of **3** with 2,2′-bipy was carried out in C_6D_6 and monitored by ^1H NMR. The ^1H NMR spectrum of the reaction mixture indicated a rapid substitution of DME by 2,2′-bipy in the coordination sphere of the metal. The signal at −0.42 ppm related to the YCH_2 protons of the parent complex **3** disappeared; however, no elimination of TMS was observed. The appearance of a new high-field-shifted singlet at −0.09 ppm of an integral intensity corresponding to two protons gave evidence for the formation of new alkyl species in the reaction mixture. Thus, a ligand redistribution reaction seems to be a plausible explanation for the formation of complex **5**. Attempts to isolate $ApY(CH_2SiMe_3)_2(bipy)$, the expected second product of this reaction, failed. A gradual decay of the signal at −0.09 ppm implies further transformation of this compound.

Table 1. Crystallographic Data and Structure Refinement Details for 3 and 5−7

	3	5	6	7
empirical formula	$C_{49}H_{76}N_3O_2SiY$	$C_{70}H_{89}N_6Y$	$C_{65}H_{94}N_3O_2Y$	$C_{96}H_{112}H_4Y_2$
formula wt	856.13	1103.38	1038.34	1499.72
cryst syst	orthrohombic	monoclinic	triclinic	monoclinic
space group	*Pbca*	*C*2/*c*	$P\bar{1}$	$P2_1/m$
a, Å	17.1047(13)	41.4345(11)	14.0702(14)	12.5802(4)
b, Å	19.2401(14)	15.4298(4)	14.8777(16)	27.1104(9)
c, Å	29.473(2)	26.6797(7)	16.2464(17)	24.6206(8)
α, deg	90	90	111.528(2)	90
β, deg	90	128.250(1)	94.874(2)	97.372(1)
γ, deg	90	90	105.769(2)	90
V, Å^3	9699.6(12)	13395.2(6)	2979.1(5)	8327.6(5)
Z	8	8	2	4
D_{calcd} (g/cm^3)	1.173	1.094	1.158	1.196
μ (mm^{-1})	1.266	0.912	1.022	1.434
F(000)	3680	4720	1120	3176
cryst size, mm	0.16 × 0.14 × 0.06	0.18 × 0.16 × 0.15	0.41 × 0.23 × 0.08	0.24 × 0.12 × 0.10
2*θ*, deg	52	50	55	52
index ranges	$-21 \le h \le 21$	$-49 \le h \le 49$	$-16 \le h \le 8$	$-15 \le h \le 15$
	$-23 \le k \le 23$	$-18 \le k \le 18$	$19 \le k \le 8$	$-33 \le k \le 33$
	$-36 \le l \le 36$	$-31 \le l \le 31$	$19 \le l \le 21$	$-30 \le l \le 30$
no. of rflns collected	79 809	51 618	20 126	72 470
no. of indep rflns (R_{int})	9479 (0.3095)	11 638 (0.0820)	13 511 (0.0337)	16 692 (0.1785)
GOF on F^2	0.867	0.978	1.022	0.996
final *R* indices ($I > 2\sigma(I)$)	0.0615	0.0610	0.0538	0.0704
R indices (all data)	0.1250	0.1657	0.1204	0.1462
largest diff in peak and hole, e/Å^3	0.871/−1.080	0.616/−0.461	0.787/−0.469	2.181/−0.975

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Single-crystal samples of **5** suitable for X-ray analysis were obtained by slow concentration of a toluene solution at ambient temperature. The complex crystallizes as a solvate: $5{\cdot}2C_7H_8$. Complex **5** crystallizes in the monoclinic *C2/c* space group with eight molecules in the unit cell (one crystallographically independent molecule in the asymmetric unit). The molecular structure of complex **5** is shown in Figure 2, and the structure refinement data are given in Table 1. The X-ray diffraction study of **5** revealed that the compound is monomeric in the crystalline state. The yttrium ion is coordinated by two nitrogen atoms of the chelating amidopyridinate ligand, two nitrogens of chelating 2,2′-bipy, and two nitrogens of two monoanionic anilido fragments, thus resulting in a coordination number of 6. The distances between Y and the nitrogen atoms of amidopyridinate ligand in **5** are nonequivalent: the distance to the amido nitrogen (2.326(2) Å) is noticeably shorter than that to the pyridinato nitrogen (2.497(2) Å). Both distances exceed those to the nitrogen atoms of the monodentate anilido fragments (2.228(2) and 2.269(2) Å). The values of Y−N bonds for anilido fragments in **5** are close to that in **3** (2.250(3) Å). The coordination bonds between Y and the nitrogen atoms of the 2,2′-bipy ligand (2.555(2) and 2.5428(18) Å) are slightly shorter than the distance to the pyridinato nitrogen atom of the Ap ligand. The 2,2′-bipy ligand is not planar. The value of the dihedral angle between the pyridyl rings is 14.5°. The lengths of covalent and coordination Y−N bonds determined in **5** fall into the region normally observed for six-coordinated yttrium complexes.[19,15d]

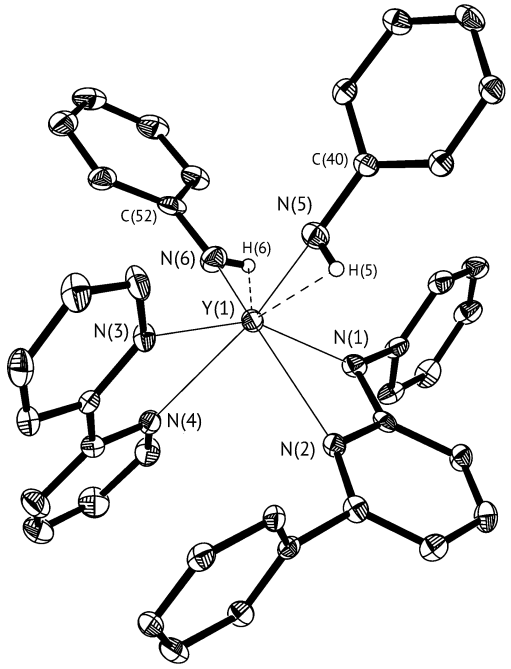


Figure 2. Crystal structure of $[ApY(NHAr)_2(bipy)]$ (**5**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, methyl and isopropyl groups of Ap, and the anilido ligand are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)−N(6) = 2.228(2), Y(1)−N(5) = 2.269(2), Y(1)−N(1) = 2.326(2), Y(1)−N(2) = 2.497(2), Y(1)−N(4) = 2.525(2), Y(1)−N(3) = 2.555(2); N(6)−Y(1)−N(5) = 111.29(7), N(1)−Y(1)−N(2) = 55.83(7), N(4)−Y(1)−N(3) = 64.07(6).

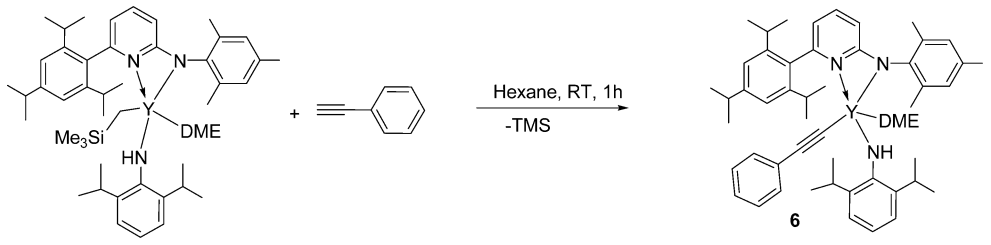
Rare-earth alkynyl complexes have attracted considerable attention, due to the variety of bonding modes and metal-mediated transformations of alkynyl ligands.[14] Some of these alkynyl complexes demonstrated high catalytic activity in the dimerization of terminal alkynes to enynes.[15d,20] In order to synthesize a bis(alkynyl) yttrium species supported by an Ap ligand, the reaction of **1** with 2 equiv of phenylacetylene was attempted in C_6D_6 at ambient temperature under ^1H and ^{13}C NMR control. When the reagents were mixed, the solution color remained pale yellow while the ^1H NMR spectrum indicated that the reaction occurred with cleavage of both Y−alkyl bonds and formation of 2 equiv of TMS. The preparative-scale reaction was carried out in toluene. Unfortunately, attempts to isolate the reaction product failed.

Rare-earth complexes proved to be excellent initiators for alkene and alkyne hydroamination reactions—a promising path for catalytic C−N bond formation.[21] This prompted us to synthesize yttrium complexes containing both alkynyl and amido fragments and to explore their behavior in the metal coordination sphere. The reaction of complex **3** with 1 equiv of phenylacetylene in hexane at ambient temperature was found to occur selectively with the protonation of the Y−alkyl bond, elimination of TMS, and formation of the yttrium alkynyl amido species **6** (Scheme 4).

Recrystallization of the reaction product from hexane afforded complex **6** as a yellow crystalline solid in 81% yield. The ^1H and ^{13}C NMR spectra of **6** present the expected sets of signals characteristic for Ap and anilido fragments. The alkynyl carbons give rise to two doublets in the ^{13}C NMR spectrum: 142.90 (d, $^1J_{YC}$ = 66.0 Hz, *C*CPh) and 103.40 (d, $^2J_{YC}$ = 13.3 Hz, CCPh). Heating complex **6** in C_6D_6 to 60 °C does not lead to an intramolecular reaction of the alkynyl and amido fragments. Complex **6** turned out to be inert in the initiation of hydroamination of phenylacetylene with aniline.

Transparent single-crystal samples of **6** suitable for an X-ray diffraction study were obtained by slow concentration of a cyclohexane solution at ambient temperature. Complex **6** crystallizes in the triclinic $P\bar{1}$ space group with two molecules in the unit cell (one crystallographically independent molecule in the asymmetric unit). The complex crystallizes as a solvate: $6{\cdot}2C_6H_{12}$. The molecular structure of complex **6** is shown in Figure 3, and the structure refinement data are given in Table 1.

Scheme 4



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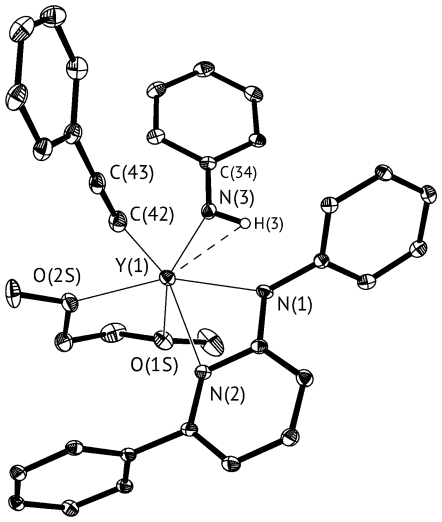


Figure 3. Crystal structure of [ApY(CCPh)(NHAr)(DME)] (**6**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, methyl and isopropyl groups of Ap, and the anilido ligand are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)−N(3) = 2.228(1), Y(1)−N(1) = 2.312(1), Y(1)−N(2) = 2.487(1), Y(1)−C(42) = 2.386(2), Y(1)−O(1S) = 2.416(2), Y(1)−O(2S) = 2.473(2), C(42)−C(43) = 1.209(3); C(43)−C(42)−Y(1) = 169.7(2), N(1)−Y(1)−N(2) = 55.92(4), N(3)−Y(1)−C(42) = 104.99(6).

The X-ray diffraction study of **6** revealed that the compound is monomeric and contains terminal alkynyl and anilido fragments. The yttrium ion in **6** is coordinated by two nitrogen atoms of the monoanionic chelating amidopyridinate ligand and two oxygens of the DME molecule. Moreover, the yttrium ion is covalently bonded to one carbon atom of the alkynyl ligand and the nitrogen atom of the anilido fragment. The formal coordination number of yttrium is 6, and its coordination environment adopts a distorted-octahedral geometry. Similarly to complexes **3** and **5**, the distances between Y and the nitrogen atoms of the amidopyridinate ligand in **6** are nonequivalent: the distance to the amido nitrogen (2.312(1) Å) is noticeably shorter than that to the pyridinato nitrogen (2.487(1) Å). The both values exceed the distance to the nitrogen atom of the anilido fragment (2.228(1) Å). The Y(1)−C(42) distance in **6** (2.386(2) Å) is slightly longer in comparison to the corresponding bond length in the related six-coordinated yttrium complex $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh(THF)$, with a terminal alkynyl ligand (2.448(4) Å),[22] but noticeably shorter than that in the parent complex **3**. The C≡C bond lengths in **6** (1.209(3) Å) and $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh(THF)$ (1.217(5) Å)[22] have similar values. In seven-coordinated complexes the distances between yttrium and carbon of terminal alkynyl fragments are expectedly longer (2.412(3) Å[23] and 2.456(4) Å[15d]) than those in **6**. The Y(1)−C(42)−C(43) moiety is slightly bent (169.74(15)°). The Y−N bond lengths (for both Ap and anilido ligands) in **6** and **3** have similar values.

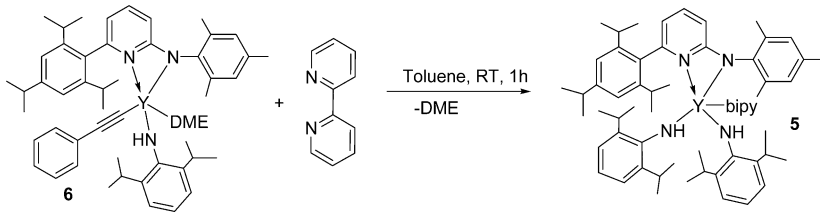
The reaction of **6** with 1 equiv of 2,2′-bipy in toluene at ambient temperature resulted in an immediate change of solution color from pale yellow to brown. Unexpectedly, similarly to the reaction of **3** with 2,2′-bipy, bis(anilido) complex **5** was isolated from the reaction mixture in 43% yield (Scheme 5). All attempts to isolate a complex containing alkynyl ligands (or the product of their evolution) which could be expected as a result of the ligand redistribution reaction were unsuccessful.

We succeeded in isolating the product of treatment of bis(alkyl) complex **2** supported by a bulky amidinate ligand with phenylacetylene (hexane, 1:2 molar ratio, 20 °C). The reaction resulted in a color change from pale yellow to brownish red. Cooling of the concentrated reaction mixture at −20 °C afforded red crystals of complex **7** (Scheme 6) in 78% yield. Complex **7** is highly air- and moisture-sensitive. It is quite soluble in THF and toluene and sparingly soluble in hexane.

Monocrystalline samples of **7** suitable for an X-ray diffraction study were obtained by slow concentration of a benzene solution at ambient temperature. Complex crystallizes as a solvate: $7{\cdot}0.5C_6H_6$. Complex **7** crystallizes in the monoclinic $P2_1/m$ space group with four molecules in the unit cell. Complex **7** contains two crystallographically independent molecules in the asymmetric unit. Both molecules have similar parameters; therefore, only one of them will be discussed. The molecular structure of complex **7** is shown in Figure 4, and the structure refinement data are given in Table 1.

The X-ray diffraction study revealed that complex **7** adopts a symmetric dimeric structure (the molecule contains a plane of symmetry) in which two AmdY fragments are linked by two symmetric μ_2-phenylacetylene ligands. Moreover, each of the yttrium ions is η^2 coordinated to the μ_2-dialkynyl unit resulting from coupling of two phenylacetylene ligands. The geometry and bonding of the Ph_2C_4 ligand are of particular interest. The C_4 core is nearly linear, and the bond angles within the coupled dialkynyl moiety are 176.4(2)°. The values of C−C bond lengths within the C_4 fragment (1.320(5), 1.281(7), and 1.320(5) Å) are typical for a double bond[24] and clearly indicate that the ligand is fully conjugated. Thus, the bonding situation within the Ph_2C_4 bridging unit is best described as butatrienediyl.[25] The Ph_2C_4 ligand adopts a *Z* conformation, with both yttrium atoms on the same side of the C_4 chain. Two carbon atoms of the phenylacetylene ligands are also in a bridging site between two yttrium centers. It is worth noting that such a geometry of a dialkynyl unit is very rare and only one example has been described so far.[26] Unlike the commonly observed asymmetric bridging structure of a $Ln_2(C{\equiv}CR)_2$ core[14b,26,27] in complex **7**, the bond lengths between the yttrium atoms and the carbons of μ_2-phenylacetylene ligands are very similar (2.467(4) and 2.490(4) Å). The distances from

Scheme 5



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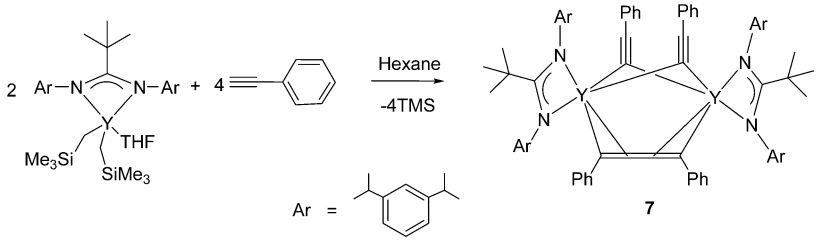
Scheme 6



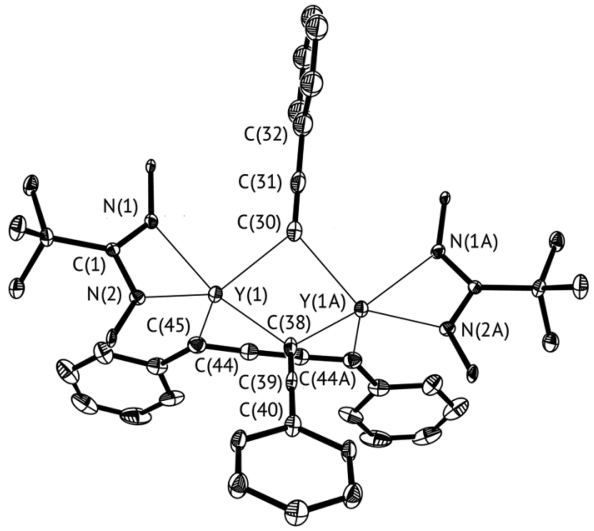


Figure 4. Crystal structure of [{AmdY(μ_2-C≡CPh)}$_2$(μ_2-η^2:η^2-PhCCCCPh)] (7). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and 2,6-diisopropylphenyl groups of the Amd ligand are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)–C(45) = 2.371(4), Y(1)–C(30) = 2.467(4), Y(1)–C(38) = 2.490(4), Y(1)–C(44) = 2.688(3), Y(1)–Y(1A) = 3.5145(7), Y(1)–N(1) = 2.308(3), Y(1)–N(2) = 2.337(3), C(44)–C(45) = 1.320(5), C(44)–C(44A) = 1.281(7); C(45)–C(44)–C(44A) = 176.4(2), C(30)–C(31)–C(32) = 176.5(6), C(38)–C(39)–C(40) = 178.8(5), Y(1A)–C(38)–Y(1) = 89.8(2), Y(1)–C(30)–Y(1A) = 90.9(2).

yttrium atoms to carbons of the Ph_2C_4 fragment (2.371(4) and 2.688(3) Å) fall into the region previously reported for yttrium complexes with coupled alkynyl ligands (2.283(4)–2.691(4) Å).[15b]

Unlike the related butatrienediyl yttrium complex described by Berg,[26] the variable-temperature NMR spectroscopic studies of 7 did not reveal any evidence for an equilibrium between phenylacetylene and butatrienediyl species. The probable mechanism of the coupling of two alkynyl ligands and the formation of a butatrienediyl fragment bridging two lanthanide centers was proposed by Marks and co-workers.[14d]

Compound 7 initiates the polymerization of phenylacetylene (40 °C, toluene, [initiator]:[monomer] = 200). The total conversion was reached in 8 h, and the PPA was isolated in 86% yield as a soluble pale yellow solid. The PPA was purified by precipitation from a toluene–hexane mixture. The obtained polymer has a number-average molecular weight of 13 500 and rather large polydispersity (2.37). In the ^{1}H NMR spectrum of PPA the vinylic (5.86 ppm) and aromatic (6.76 and 6.97 ppm) protons are presented by broad singlets; furthermore, the signals observed in the ^{13}C{^{1}H} NMR spectrum (127.4, 139.2, and 140.5 ppm) are also broadened. This indicates low regularity of the polymer. However, the chemical shift of the signal assignable to vinylic protons and the integration of this peak allows us to suggest a slightly predominant cis-transoidal structure (~70%).[28] The presence of both cis and trans contents in the polymer is supported by the IR spectrum, which displays strong absorption bands at specific wavelengths (cis, 754, 1377 cm^{-1}; trans, 1265 cm^{-1}).

CONCLUSIONS

The reactions of bis(alkyl) yttrium complexes supported by bulky NCN (amidopyridinate and amidinate) ligands with reagents containing acidic N–H or C–H bonds were investigated. The treatment of ApY(CH_2SiMe_3)$_2$(THF) with an equimolar amount of 2,6-diisopropylaniline afforded the rather stable alkyl anilido species ApY(CH_2SiMe_3)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)(DME). No further intramolecular protonolysis of the Y–C bond by NH of the anilido fragment and formation of a terminal imido complex was detected. The reaction of ApY(CH_2SiMe_3)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)(DME) with PhC≡CH (1:1 molar ratio) results in the selective protonolysis of the Y–C bond and the formation of the alkynyl anilido derivative ApY(C≡CPh)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)(DME). No intra- or intermolecular additions of NH to C≡C were observed. Ligand redistribution reactions and formation of the bis(anilido) complex ApY(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(bipy) took place when ApY(CH_2SiMe_3)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)(DME) and ApY(C≡CPh)(NH-2,6-^{i}Pr$_2$C$_6$H$_3$)(DME) were treated with bipy. A very unusual dimeric complex containing simultaneously two symmetrically bridging alkynyl ligands and a μ-η^2:η^2-butatrienediyl fragment, [{AmdY(μ_2-C≡CPh)}$_2$(μ_2-η^2:η^2-PhCCCCPh)], was obtained in the reaction of AmdY(CH_2SiMe_3)$_2$(THF) with 2 equiv of phenylacetylene.

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 and phenylacetylene were purchased from Acros and were dried over CaH_2 and molecular sieves, respectively. Anhydrous YCl_3,[29] Me_3SiCH_2Li,[30] $(Me_3SiCH_2)_3Y(THF)_2$,[31] and [ApY(CH_2SiMe_3)$_2$(THF)][12] were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purifications. NMR spectra were recorded with Bruker DPX 200 and Bruker Avance DRX-400 spectrometers in $CDCl_3$ or C_6D_6 at 25 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls with a Bruker Vertex 70 instrument. SEC analysis was provided by a Knauer Smartline chromatograph with Phenogel Phenomenex columns 5u (300 × 7.8 mm) 10^4, 10^5 and a Security Guard Phenogel column with RI and

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UV detectors (254 nm). The mobile phase was THF, and the flow rate was 2 mL/min. Columns were calibrated by Phenomenex Medium and High Molecular Weight Polystyrene Standard Kits with peak molecular weights from 2700 to 2 570 000 Da. Lanthanide metal analyses were carried out by complexometric titration. The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of AmdY(CH_2SiMe_3)$_2$(THF) (2). A solution of AmdLi (0.652 g, 1.53 mmol) in THF (10 mL) was added to a suspension of YCl_3 (0.292 g, 1.49 mmol) in THF (30 mL). The reaction mixture was stirred at 60 °C for 1 h, and THF was removed under vacuum. The solid residue was dissolved in toluene (40 mL), and a solution of Me_3SiCH_2Li (0.298 g, 3.17 mmol) in toluene (10 mL) wad added at 0 °C. The reaction mixture was stirred for 1 h, toluene was removed under vacuum, and the solid residue was extracted with hexane. LiCl was removed by filtration, and the solution was concentrated and kept overnight at −18 °C. A 0.800 g amount of colorless crystals of compound **2** was isolated (yield 71%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): −0.29 (4H, d, $^2J_{YH}$ = 3.1 Hz, YCH_2), 0.24 (18H, s, SiMe_3), 0.97 (9H, s, *t*Bu), 1.14 (4H, br s, *β*-CH_2, THF), 1.35 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.38 (12H, d, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 3.44 (4H, br s, *α*-CH_2, THF), 3.62 (4H, sept, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 6.98−7.12 (6H, m, Ar). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 4.0 (SiMe_3), 23.2 (CH(CH_3)$_2$), 24.3 (*β*-CH_2, THF), 26.6 (CH(CH_3)$_2$), 28.4 (CH(CH$_3$)$_2$), 30.5 (C(CH$_3$)$_3$), 39.0 (d, $^1J_{YC}$ = 40.7 Hz, YCH_2), 44.7 (d, $^3J_{YC}$ = 2.9 Hz, CMe_3), 70.0 (*α*-CH_2, THF), 123.7 (Ar), 124.1 (Ar), 141.7 (Ar), 144.1 (Ar), 180.4 (d, $^2J_{YC}$ = 2.4 Hz, NCN). IR (KBr): 1915 (w), 1864 (w), 1805 (w), 1617 (m), 1587 (w), 1433 (s), 1400 (s), 1366 (s), 1311 (m) 1274 (w), 1248 (m), 1235 (m), 1212 (m), 1171 (s), 1098 (m), 1057 (w), 1040 (m), 1012 (m), 952 (w), 932 (w), 864 (s), 818 (m), 803 (m), 776 (w), 763 (s), 745 (m), 671 (s), 645 (w), 605 (w), 588 (w), 543 (w), 535 (w), 521 (w) cm^{-1}. Anal. Calcd for $C_{90}H_{106}N_4Y_2$ (1421.64): C, 65.21; H, 9.74; Y, 11.77. Found: C, 64.85; H, 9.60; Y, 11.53.

Synthesis of ApY(CH_2SiMe_3)(NHAr)(DME) (3). To a solution of **1** (0.426 g, 0.57 mmol) in hexane (30 mL) was added a solution of 2,6-diisopropylaniline (0.101 g, 0.57 mmol) in hexane (10 mL) at room temperature, and the reaction mixture was stirred for 1 h. Volatiles were removed under vacuum, and the solid residue was recrystallized from DME at −20 °C to give 0.35 g (72%) of pale yellow crystals of **3**. ^{1}H NMR (400 MHz, C_6D_6, 293 K): −0.42 (2H, d, $^2J_{YH}$ = 36.5 Hz, CH_2Y), 0.37 (9H, s, SiMe_3), 1.01−1.34 (30H, complex m, CH(CH_3)$_2$, Ap and anilido), 2.19 (3H, s, Me, Ap), 2.29 (3H, s, Me, Ap), 2.30−2.38 (2H, br s, CH_2, DME), 2.60−2.84 (8H, complex m, CH(CH$_3$)$_2$, Ap; Me, Ap; CH_2, DME), 2.87 (2H, sept, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$, anilido), 3.00 (6H, s, Me, DME), 4.68 (1H, s, NH), 5.83 (1H, d, $^3J_{HH}$ = 8.6 Hz, *m*-H, Py, Ap), 6.07 (1H, d, $^3J_{HH}$ = 7.5 Hz, *m*-H, py, Ap), 6.81 (1H, t, $^3J_{HH}$ = 7.5 Hz, *p*-H, anilido), 6.85 (1H, dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.1 Hz, *p*-H, Py, Ap), 6.99 (4H, complex m, *m*-H, Ap), 7.1 (2H, d, $^3J_{HH}$ = 7.5 Hz, *m*-H, anilido). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 4.2 (Me_3Si), 18.8 (br s, Me, Ap), 20.5 (Me, Ap), 23.5 (br s, CH(CH_3)$_2$), 24.2 (CH(CH_3)$_2$), 26.0 (CH(CH_3)$_2$), 26.9 (CH(CH_3)$_2$), 28.8 (CH(CH$_3$)$_2$, anilido), 30.1 (CH(CH$_3$)$_2$, Ap), 31.7 (d, $^1J_{YC}$ = 43.4 Hz, YCH_2), 34.6 (CH(CH$_3$)$_2$, Ap), 61.8 (CH$_3$, DME), 70.2 (CH_2, DME), 105.7 (Ar), 110.4 (Ar), 114.5 (Ar), 120.2 (Ar), 122.3 (Ar), 129.8 (Ar), 132.1 (Ar), 133.4 (Ar), 137.4 (Ar), 138.3 (Ar), 144.1 (d, $^2J_{YC}$ = 1.3 Hz, Ar, Ap), 147.0 (Ar), 148.6 (Ar), 152.0 (d, $^2J_{YC}$ = 3.4 Hz, Ar, anilido), 154.9 (Ar), 168.4 (d, $^2J_{YC}$ = 2.2 Hz, NCN Ap). IR (KBr): 3385 (w), 1586 (m), 1547 (m), 1423 (m), 1361 (s), 1322 (w), 1281 (w), 1249 (s), 1154 (m), 1098 (m), 1050 (s), 994 (m), 858 (s), 798 (m), 677 (w), 660 (w), 624 (w), 565 (w), 535 (w) cm^{-1}. Anal. Calcd for $C_{49}H_{76}N_3O_2SiY$ (856.14): C, 68.74; H, 8.95; Y, 10.38. Found: C, 68.31; H, 9.51; Y, 10.62.

Synthesis of ApY(NHAr)$_2$(DME) (4). 2,6-Diisopropylaniline (0.007 g, 0.04 mmol) was added to a solution of **3** (0.034 g, 0.04 mmol) in C_6D_6 (0.6 mL) at room temperature. ^{1}H NMR (400 MHz, C_6D_6, 293 K): 1.14 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$, Ap), 1.18 (6H, d, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$, Ap), 1.23 (24H, m, CH(CH_3)$_2$, anilido), 2.24 (3H, s, Me Ap), 2.37 (6H, s, Me Ap), 2.48 (4H, br s, CH_2, DME), 2.62 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$, Ap), 2.76 (1H, sept, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$, Ap), 3.11 (6H, s, OMe, DME), 3.16 (4H, m, CH(CH$_3$)$_2$, anilido), 4.52 (2H, d, $^2J_{YH}$ = 1.6 Hz, NH, anilido), 5.87 (1H, d, $^3J_{HH}$ = 8.6 Hz, Ar, Ap), 6.09 (1H, d, $^3J_{HH}$ = 7.0 Hz, Ar, Ap), 6.80 (1H, dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.0 Hz, Ar, Ap), 6.86 (2H, t, $^3J_{HH}$ = 6.5 Hz, Ar, anilido), 6.91 (2H, s, Ar, Ap), 6.99 (2H, s, Ar, Ap), 7.14 (4H, d, $^3J_{HH}$ = 8.5 Hz, Ar, anilido). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 19.5 (Me, Ap), 20.5 (Me, Ap), 22.2 (CH(CH_3)$_2$, Ap), 23.8 (br s, CH(CH_3)$_2$, anilido), 24.1 (CH(CH_3)$_2$, Ap), 27.9 (CH(CH$_3$)$_2$, Ap), 28.6 (CH(CH$_3$)$_2$, anilido), 34.4 (CH(CH$_3$)$_2$, Ap), 61.8 (Me, DME), 70.1 (CH_2, DME), 107.1 (Ar, Ap), 110.9 (Ar, Ap), 115.3 (Ar, anilido), 120.2 (Ar, Ap), 122.5 (Ar, anilido), 129.8 (Ar, Ap), 131.9 (d, $^2J_{YC}$ = 2.2 Hz, Ar, Ap), 132.5 (Ar, Ap), 134.3 (Ar, anilido), 138.0 (Ar, Ap), 140.4 (Ar, Ap), 144.1 (Ar, Ap), 148.7 (Ar, Ap), 151.7 (d, $^2J_{YC}$ = 3.7 Hz, Ar, anilido), 155.2 (Ar, Ap), 168.3 (d, $^2J_{YC}$ = 2.2 Hz, NCN).

Synthesis of ApY(NHAr)$_2$(bipy) (5). A solution of 2,2′-bipyridine (0.098 g, 0.64 mmol) in toluene (5 mL) was added to a solution of **3** (0.548 g, 0.64 mmol) in toluene (15 mL) at room temperature. The reaction mixture was stirred at room temperature for 0.5 h, and the volatiles were removed under vacuum. The resulting solid residue was dissolved in a new portion of toluene (5 mL). Slow concentration of the solution at room temperature afforded brown crystals of **5** (0.29 g, 45%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): 0.90−1.35 (42H, complex m, CH(CH_3)$_2$ Ap and anilido), 2.32 (3H, s, Me, Ap), 2.54 (6H, s, Me, Ap), 2.63 (1H, sept, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$, Ap), 2.82 (2H, br s, CH(CH$_3$)$_2$, Ap), 3.03 (4H, br s, CH(CH$_3$)$_2$, anilido), 4.77 (2H, br s, NH), 5.95 (1H, d, $^3J_{HH}$ = 7.0 Hz, Ar, Ap), 5.98 (1H, d, $^3J_{HH}$ = 8.6 Hz, Ar, Ap), 6.45 (2H, t, $^3J_{HH}$ = 5.7 Hz, Ar, bipy), 6.53 (2H, br s, Ar, bipy), 6.74 (2H, t, $^3J_{HH}$ = 7.4 Hz, Ar, anilido), 6.79−6.82 (1H, complex m, Ar, Ap), 6.84−6.92 (4H, complex m, Ar, Ap), 6.97−7.05 (6H, complex m, Ar, Ap and anilido), 8.81 (2H, s, Ar, bipy). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 19.6 (Me, Ap), 20.6 (Me, Ap), 22.2 (CH(CH$_3$)$_2$, Ap), 23.6 (CH(CH$_3$)$_2$, anilido), 26.1 (CH(CH$_3$)$_2$, Ap), 28.8 (CH(CH$_3$)$_2$, anilido), 29.9 (CH(CH$_3$)$_2$, Ap), 33.9 (CH(CH$_3$)$_2$, Ap), 106.7 (Ar, Ap), 111.3 (Ar, Ap), 114.4 (Ar, anilido), 119.6 (Ar, bipy), 120.3 (Ar, Ap), 122.1 (Ar, anilido), 125.0 (Ar, bipy), 129.8 (Ar, Ap), 131.7 (Ar, Ap), 132.5 (Ar, Ap), 133.9 (Ar, anilido), 136.3 (Ar, bipy), 138.0 (Ar, Ap), 138.4 (Ar, bipy), 144.8 (Ar, Ap), 145.8 (Ar, Ap), 146.9 (Ar, Ap), 151.1 (Ar, bipy), 152.2 (Ar, Ap), 152.6 (d, $^2J_{YC}$ = 3.5 Hz, Ar, anilido), 155.8 (Ar, Ap), 168.6 (d, $^2J_{YC}$ = 2.2 Hz, NCN). IR (KBr): 3385 (w), 3051 (w), 1604 (m), 1585 (s), 1545 (m), 1421 (s), 1357 (m), 1317 (m), 1246 (s), 1216 (m), 1171 (w), 1156 (m), 1113 (w), 1098 (w), 1059 (w), 1041 (w), 1018 (m), 990 (m), 884 (w), 874 (w), 855 (m), 837 (m), 796 (m), 764 (m), 743 (s), 682 (w), 649 (w), 629 (w), 584 (w), 562 (w), 533 (w) cm^{-1}. Anal. Calcd for $C_{63}H_{81}N_6Y$: (1011.26): C, 74.82; H, 8.07; Y, 8.79. Found: C, 75.02; H, 8.35; Y, 8.93.

Synthesis of ApY(C≡CPh)(NHAr)(DME) (6). A solution of HC≡CPh (0.053 g, 0.52 mmol) in hexane (10 mL) was added to a solution of **3** (0.445 g, 0.52 mmol) in hexane (20 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h. Hexane was removed under vacuum, and the solid residue was recrystallized from hot cyclohexane. Complex **6** was isolated as a yellow crystalline solid in 81% yield (0.37 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): 1.10 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$, Ap), 1.13 (4H, d, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$, anilido), 1.21 (8H, d, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$, Ap), 1.23−1.32 (12H, br s, CH(CH_3)$_2$, Ap and anilido), 2.26 (3H, s, Me, Ap), 2.46−2.67 (10H, br s, Me, Ap and CH_2, DME), 2.78 (4H, sept, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$, Ap and anilido), 3.12 (1H, br s, CH(CH_3)$_2$, Ap), 3.29 (6H, s, Me, DME), 5.03 (1H, d, $^3J_{YH}$ = 1.7 Hz, NH anilido), 5.84 (1H, d, $^3J_{HH}$ = 8.5 Hz, Ar), 6.08 (1H, d, $^3J_{HH}$ = 6.9 Hz, Ar, Ap), 6.83 (1H, t, $^3J_{HH}$ = 7.5 Hz, Ar, anilido), 6.89 (1H, dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.1 Hz, Ar, Ap), 6.95 (2H, s, Ar, Ap), 6.98 (1H, d, $^3J_{HH}$ = 7.4 Hz, Ar, PhC_2), 7.04−7.10 (4H, m, Ar, Ap and PhC_2), 7.13 (2H, s, Ar, anilido), 7.54−7.59 (2H, m, Ar, PhC_2). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 19.6 (Me, Ap), 20.6 (Me Ap), 22.2 (CH(CH$_3$)$_2$, anilido), 22.5 (CH(CH$_3$)$_2$, anilido), 23.8 (CH(CH$_3$)$_2$, Ap), 24.2 (CH(CH$_3$)$_2$, Ap), 26.5 (CH(CH$_3$)$_2$, Ap), 29.7 (CH(CH$_3$)$_2$, anilido), 30.3 (CH(CH$_3$)$_2$, Ap), 34.6 (CH(CH$_3$)$_2$, Ap), 62.5 (Me, DME), 70. Five (CH_2, DME), 103.4 (d, $^2J_{YC}$ = 13.3 Hz, C≡CPh), 104.8 (Ar, Ap), 110.0 (Ar, Ap), 114.3 (Ar, anilido), 120.2 (Ar, Ap), 122.5

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(Ar, anilido), 122.8 (Ar, PhC_2), 125.7 (Ar, PhC_2), 127.9 (Ar, PhC_2), 129.5 (Ar, Ap), 131.8 (Ar, PhC_2), 132.3 (Ar), 132.65 (Ar), 137.24 (Ar), 138.9 (Ar), 142.9 (d, $^1J_{YC}$ = 66.0 Hz, CCPh), 143.5 (Ar), 148.5 (Ar), 152.5 (d, $^3J_{YC}$ = 3.7 Hz, Ar, PhC_2), 154.7 (Ar, Ap), 168.8 (d, $^2J_{YC}$ = 2.3 Hz, Ar, Ap). IR (KBr): 3390 (w), 2048 (w), 1589 (m), 1547 (m), 1364 (m), 1254 (m), 1195 (w), 1154 (m), 1100 (w), 1053 (m), 1027 (w), 991 (m), 858 (m), 796 (m), 778 (w), 757 (m), 742 (m), 692 (w), 654 (w), 627 (w), 532 (w) cm^{-1}. Anal. Calcd for $C_{53}H_{70}N_3O_2Y$: C, 73.16; H, 8.11; Y, 10.22. Found: C, 72.81; H, 8.01; Y, 10.50.

Synthesis of [{AmdY(μ_2-C≡CPh)}$_2$(μ_2-η^2:η^2-PhCCCCPh)] (7). A solution of phenylacetylene (0.052 g, 0.50 mmol) in hexane (5 mL) was added to a solution of **2** (0.203 g, 0.25 mmol) in hexane (15 mL) at room temperature. The reaction mixture was stirred for 2 h at 20 °C, concentrated, and kept overnight at −18 °C. Complex **7** was isolated as a red crystalline solid in 78% yield (0.27 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): 0.97 (12H, br s, $CH(CH_3)_2$), 1.04 (18H, s, CMe_4), 1.16 (12H, br s, $CH(CH_3)_2$), 1.37 (12H, br s, $CH(CH_3)_2$), 1.41 (12H, br s, $CH(CH_3)_2$), 3.68 (4H, br s, $CH(CH_3)_2$), 3.93 (4H, br s, $CH(CH_3)_2$), 5.80 (4H, d, $^3J_{HH}$ = 7.2 Hz, *o*-Ar, PhC_2), 6.75 (12H, complex m, *m*-Ar, PhC_2 and Am), 6.91 (6H, complex m, *p*-Ar PhC_2 and Am), 7.06 (2H, d, $^3J_{HH}$ = 7.4 Hz, *p*-Ar, PhC_4Ph), 7.31 (4H, t, $^3J_{HH}$ = 7.7 Hz, *m*-Ar, PhC_4Ph), 8.13 (4H, d, $^3J_{HH}$ = 7.1 Hz, *o*-Ar, PhC_4Ph). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293 K): 21.8 ($CH(CH_3)_2$)), 22.3 ($CH(CH_3)_2$)), 24.9 ($CH(CH_3)_2$)), 26.2 ($CH(CH_3)_2$)), 28.7 ($CH(CH_3)_2$)), 29.2 ($CH(CH_3)_2$)), 30.3 ($C(CH_3)_3$), 44.9 (CMe_3), 120.8 (Ar, PhC_2), 122.5 (*p*-Ar, Am), 123.0 (t, $^2J_{YC}$ = 3.3 Hz, PhCC), 123.9 (*m*- Ar, Am), 126.7 (*p*-Ar, PhC_4Ph), 126.9 (*m*-Ar, PhC_2), 127.8 (*p*-Ar, PhC_2), 128.4 (*m*-Ar, PhC_4Ph), 131.0 (*o*-Ar, PhC_4Ph), 132.6 (*o*-Ar, PhC_2), 137.6 (t, $^1J_{YC}$ = 27.8 Hz, PhCC), 141.0 (*i*-Ar, PhC_4Ph), 141.9 (*i*-Ar, Am), 144.0 (*o*-Ar, Am), 171.7 (d, $^2J_{YC}$ = 3.4 Hz, PhCCCCPh), 180.7 (d, $^2J_{YC}$ = 2.4 Hz, NCN), 186.7 (d, $^1J_{YC}$ = 49.0 Hz, PhCCCCPh). IR (KBr): 3060 (s), 3009 (s), 2279 (w), 2050 (m), 2038 (m), 1958 (w), 1911 (w), 1853 (w), 1815 (w), 1719 (w), 1668 (w), 1656 (w), 1619 (m), 1586 (m), 1569 (w), 1540 (s), 1486 (s), 1434 (s), 1410 (s), 1396 (s), 1365 (s), 1321 (w), 1304 (w), 1246 (m), 1212 (m), 1173 (s), 1102 (m), 1070 (w), 1059 (w), 1044 (m), 1026 (w), 998 (w), 955 (m), 932 (w), 915 (w), 883 (w), 837 (m), 800 (m), 754 (s), 719 (m), 689 (s), 640 (m), 623 (w), 609 (w), 584 (w), 549 (m), 540 (w), 500 (s), 467 (m) cm^{-1}. Anal. Calcd for $C_{90}H_{106}N_4Y_2$: C, 76.04; H, 7.52; Y, 12.51. Found: C, 75.85; H, 7.63; Y, 12.86.

Polymerization of Phenylacetylene. A Schlenk flask was charged with **7** (28.0 mg, 20.0 μmol), phenylacetylene (0.408 g, 4.00 mmol), and toluene (10.0 mL). The mixture was stirred at 40 °C for 8 h. The reaction was quenched by adding ca. 1.0 mL of a 10% H_2O solution in THF, and the polymer was precipitated from toluene/hexane (ca. 1/20 mL). The polymer was then filtered and dried in vacuo to a constant weight (0.347 g, 86.4%).

X-ray Crystallography. The X-ray data for **3** and **5**−**7** were collected on a SMART APEX diffractometer (graphite-monochromated Mo Kα radiation, ω-scan technique, λ = 0.710 73 Å, T = 100 K). The structures were solved by direct methods and were refined on F^2 using the SHELXTL[32] package. All non-hydrogen atoms and H atoms in NH groups of anilido fragments in **5** and **6** were found from Fourier syntheses of electron density and were refined anisotropically. All other hydrogen atoms were placed in calculated positions and were refined in the riding model. SADABS[33] was used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection, and refinement data are shown in Table 1, and the corresponding CIF files are available as Supporting Information. CCDC-874678 (**3**), CCDC-874679 (**5**), CCDC-874680 (**6**), and CCDC-874681 (**7**) 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.

■ 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.

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