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**PAPER**

# Synthesis, characterization of bridged bis(amidinate) lanthanide amides and their application as catalysts for addition of amines to nitriles for monosubstituted *N*-arylamidines†

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A series of lanthanide amide complexes supported by bridged bis(amidinate) ligand L, LLnNHAr$^1$(DME) (L = [Me$_3$SiNC(Ph)N(CH$_2$)$_3$NC(Ph)NSiMe$_3$], Ar$^1$ = 2,6-$^i$Pr$_2$C$_6$H$_3$, DME = dimethoxyethane, Ln = Y (**1**), Pr (**2**), Nd (**3**), Gd (**4**), Yb (**5**)), [Yb(μ$_2$-NHPh)]$_2$(μ$_2$-L)$_2$ (**6**) and [LYb]$_2$(μ$_2$-NHAr$^2$)$_2$ (**7**) (Ar$^2$ = (*o*-OMe)C$_6$H$_4$), were synthesized by reaction of LLnCl(THF)$_2$ with the corresponding lithium amide in good yields and structurally characterized by X-ray crystal structure analyses. All complexes were found to be precatalysts for the catalytic addition of aromatic amines to aromatic nitriles to give monosubstituted *N*-arylamidines. The catalytic activity was influenced by lanthanide metals and the amido groups with the active sequence of Y (**1**) < Gd (**4**) < Nd (**3**) < Pr (**2**) ~ Yb (**5**) for the lanthanide metals and –NHAr$^2$ < –NHPh < –NHAr$^1$ for the amido groups. The catalytic addition reaction with complex **5** showed a good scope of aromatic amines. Some key reaction intermediates were isolated and structurally characterized, including the amidinate complexes LLn[NPhCNAr$^1$](PhCN) (Ln = Y (**8**), Ln = Yb (**9**)), LYb[NAr$^2$CNAr$^1$](Ar$^2$CN) (**10**), and amide complex **5** prepared by protonation of **9** by Ar$^1$NH$_2$. Reactivity studies of these complexes suggest that the present catalytic formation of monosubstituted *N*-arylamidines proceeds through nucleophilic addition of an amido species to a nitrile, followed by amine protonolysis of the resultant amidinate species.

## Introduction

Amidinates are an important class of organic compounds, which can served as synthons for the syntheses of natural products and pharmaceuticals[1] and also as ancillary ligands for various metal complexes, including those of lanthanide and early transition metals.[2] Several synthetic strategies have been developed,[3] in which the nucleophilic addition of amines to nitriles is the most convenient and atom-economic method.[3a–e] However, the one-step synthesis of amidines from nitriles and amines requires the use of activated nitriles by electron withdrawing groups[3a] or more forcing conditions in the presence of Lewis acids[3b] or with aluminium amides.[3c] Trivalent lanthanide triflates could serve as Lewis acid catalysts to catalyze the condensation of nitriles and primary amines and diamines to give *N*,*N*′-disubstituted and cyclic amidines, but not monosubstituted amidines.[3d] The selective synthesis of monosubstituted alkylamidines by the one-step process was reported with CuCl as a reagent, but 1.2 equiv. of CuCl to amines was needed.[3f]

Lanthanide amide complexes have been disclosed to be efficient catalysts or pre-catalysts for various C–N bond formation reactions such as hydroamination/cyclization,[4] guanylation of amines,[5] homocoupling of isocyanides with terminal alkynes,[6] Mannich-type reaction of hydroxy ketones, monoaddition of terminal alkynes to carbodiimides[5c] addition of amines to nitriles,[7] Cannizzaro-type disproportionation of aromatic aldehydes.[8] Nucleophilic addition of metal amide reagents to nitriles to give the corresponding amidinate species [R′R″NC(R)NH]M″ is a well established process.[9] However, catalytic transformation of such a metal amidinate species to amidines has remained unknown, although the catalytic transformation of half-sandwich rare-earth metal amidinates by terminal alkynes was reported by Hou's group, which led to the catalytic addition of terminal alkynes to carbodiimides to give a series of propiolamidine compounds.[3h]

We have recently communicated the nucleophilic addition of amines to nitriles selectively to give monosubstituted *N*-arylamidines catalyzed by LYbNH(2,6-Me$_2$C$_6$H$_3$)(DME) under mild conditions (DME = dimethoxyethane).[7] In expanding our research we synthesized a series of bridged bis(amidinate) lanthanide amide complexes with various lanthanide metals and amido groups, LLnNHAr$^1$(DME) (Ln = Y (**1**), Pr (**2**), Nd (**3**), Gd (**4**), Yb (**5**)), [Yb(μ$_2$-NHPh)]$_2$(μ$_2$-L)$_2$ (**6**) and

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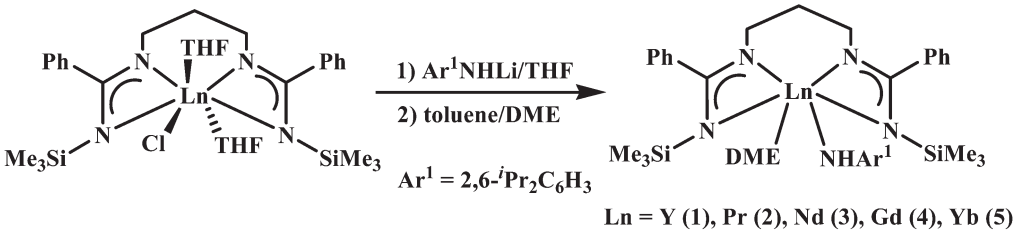



**Scheme 1** Synthesis of complexes **1–5**.

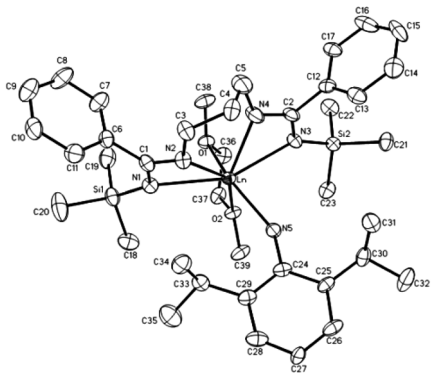


**Fig. 1** ORTEP diagram of the molecular structures of complexes **1–4**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity.

**Table 1** Selected bond distances (Å) and angles (°) for complexes **1–4**

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Ln(1)–N(1) | 2.465(4) | 2.547(4) | 2.536(7) | 2.502(5) |
| Ln(1)–N(2) | 2.358(4) | 2.451(4) | 2.427(6) | 2.387(5) |
| Ln(1)–N(3) | 2.543(4) | 2.614(4) | 2.604(7) | 2.575(5) |
| Ln(1)–N(4) | 2.332(4) | 2.429(4) | 2.413(7) | 2.364(6) |
| Ln(1)–N(5) | 2.237(4) | 2.347(5) | 2.342(7) | 2.280(5) |
| Ln(1)–C(1) | 2.780(5) | 2.879(5) | 2.868(8) | 2.804(6) |
| Ln(1)–C(2) | 2.836(5) | 2.921(5) | 2.919(8) | 2.878(6) |
| N(1)–C(1) | 1.330(7) | 1.342(7) | 1.332(10) | 1.336(8) |
| N(2)–C(1) | 1.321(6) | 1.322(6) | 1.335(10) | 1.320(8) |
| N(3)–C(2) | 1.331(6) | 1.333(6) | 1.352(10) | 1.319(8) |
| N(4)–C(2) | 1.313(7) | 1.311(7) | 1.307(11) | 1.330(9) |
| N(2)–Ln(1)–N(1) | 55.83(15) | 53.90(14) | 54.3(2) | 55.34(18) |
| N(4)–Ln(1)–N(3) | 54.95(15) | 53.12(14) | 53.3(2) | 54.17(18) |
| N(5)–Ln(1)–O(2) | 147.03(14) | 143.75(14) | 144.6(2) | 145.76(18) |
| N(1)–Ln(1)–N(3) | 156.29(15) | 151.84(14) | 152.1(2) | 155.02(17) |



$[LYb]_2(\mu_2\text{-}NHAr^2)_2$ (**7**), and further examined their catalytic activity for addition of amines to nitriles to give monosubstituted *N*-arylamidines. It was found that the lanthanide metals and the amido groups both have great influence on the reactivity and the best precatalyst was found for complex **5**, which showed a wide scope of aromatic amines. The detailed reaction mechanism was studied by the isolation and characterization of the active species of amidinate complexes and the amide complex generated by protonolysis of the amidinate species by amine. Here, we would like to report the results.

## Results and discussion

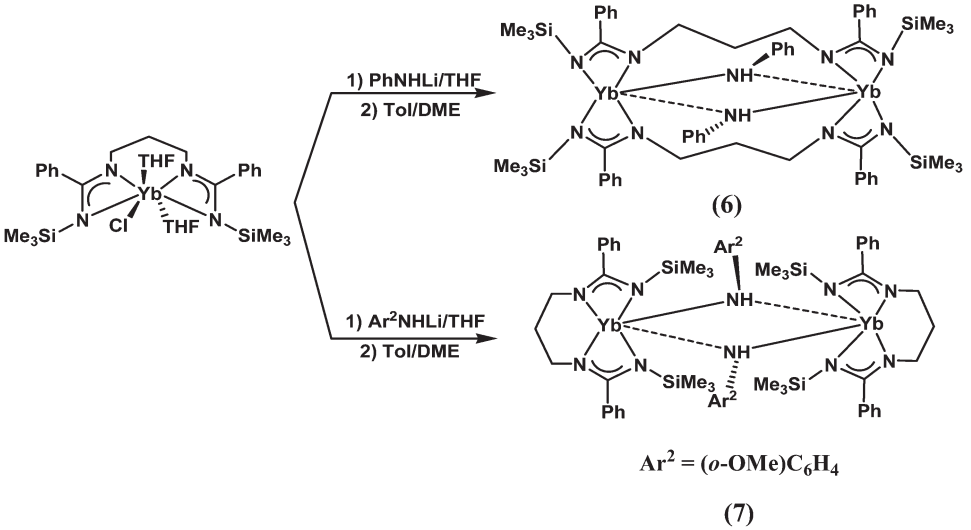
### Synthesis and molecular structures of $LLnNHAr^1(DME)$ (Ln = Y (1), Pr (2), Nd (3), Gd (4))

The ytterbium amide complex bearing the bridged bis(amidinate) ligand L $LYbNHAr^1(DME)$ (**5**) has been reported previously.[10] The analogous amide complexes $LLnNHAr^1(DME)$ (Y (**1**), Nd (**2**), Pr (**3**), Gd (**4**)) were prepared similarly in high yields by the reaction of $LLnCl(THF)_2$ with $LiNHAr^1$ in THF and then treatment with toluene and DME as shown in Scheme 1.

Complexes **1–4** were characterized by elemental analysis, IR, NMR spectroscopy in the case of complex **1** and X-ray crystal analyses. The crystal structures of complexes **1–4** are shown in Fig. 1 as they are isostructural. The selected bond distances and angles are listed in Table 1. The central metal in each complex coordinates to four nitrogen atoms from the bis(amidinate) ligand, one nitrogen atom from the amido group and two oxygen atoms from the solvated DME molecule. The coordination geometry around each central metal can be described as a distorted trigonal bipyramid, when the amidinate ligand is considered to occupy a single coordination vertex. The centers of the two amidinate groups and one of the oxygen atoms occupy equatorial positions while the nitrogen atom N(5) and the other oxygen atom O(2) are located at axial positions with a N(5)–Ln(1)–O(2) angle of 147.03(14)° for complex **1**, 143.75(14)° for complex **2**, 144.6(2)° for complex **3**, 145.76(18)° for complex **4**. The molecular structures of complexes **1–4** are quite similar to that reported for complex **5**.[10] In all complexes the amidinate groups are each unsymmetrically bound to the central metal through the nitrogen atoms in the Ln–N–C–N plane with a shorter Yb–N bond distance for the amidinate nitrogens attached to the bridge compared to the amidinate nitrogens attached to the $SiMe_3$ group. The angle between the two Yb–N–C–N planes is 36.514(145)° for complex **1**, 36.912(158)° for complex **2**, 32.393(212)° for complex **3**, 36.134(207)° for complex **4**, indicating a more open sphere around each metal in complexes **1–4** which is the same as those found in complex **5**[10] and the related complex $LY[CH(SiMe_3)_2](THF)$[2d] reported previously. The Ln–N(amido) bond distance in complexes **1–4** (2.237(4) Å for complex **1**, 2.347(5) Å for complex **2**, 2.342(7) Å for complex **3**, 2.280(5) Å for complex **4**) are a regular series in accordance with their ionic radii.

### Synthesis and molecular structures of $[Yb(\mu_2\text{-}NHPh)]_2(\mu_2\text{-}L)_2$ (6) and $[LYb]_2(\mu_2\text{-}NHAr^2)_2$ (7)

Reaction of $LYbCl(THF)_2$ with the lithium salt of the less bulky amide LiNHPh was then tried in THF. The reaction went




(6)

(7)

**Scheme 2** Synthesis of complexes **6** and **7**.

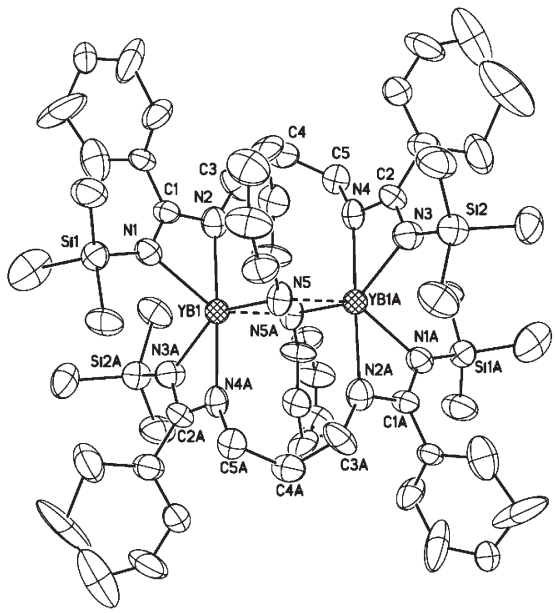


**Fig. 2** ORTEP diagram of the molecular structures of complex **6**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

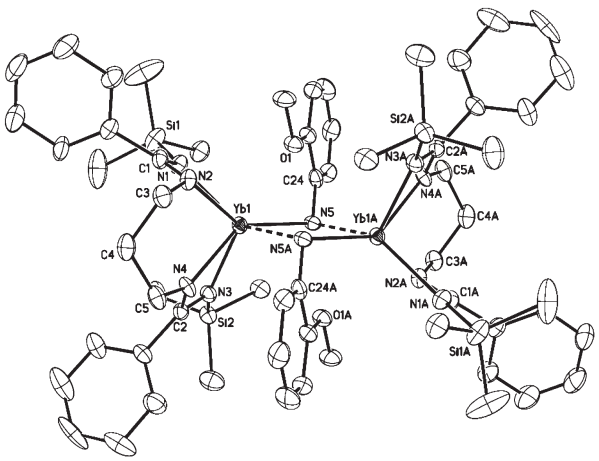


**Fig. 3** ORTEP diagram of the molecular structures of complex **7**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms and free toluene molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Yb(1)–N(1) 2.370(5), Yb(1)–N(2) 2.327 (4), Yb(1)–N(3) 2.384(5), Yb(1)–N(4) 2.267(5), Yb(1)–N(5) 2.354(4), Yb(1)–N(5A) 2.414(5), Yb(1)–C(1) 2.735(6), Yb(1)–C(2) 2.752(6), N (1)–C(1) 1.349(7), N(2)–C(1) 1.305(7), N(3)–C(2) 1.338(7), N(4)–C(2) 1.317(7), N(2)–Yb(1)–N(1) 57.45(16), N(4)–Yb(1)–N(3) 57.38(16), N (5)–Yb(1)–N(5A) 81.71(15), Yb(1)–N(5)–Yb(1A) 98.29(15).

smoothly to give light yellow crystals in desired yield upon crystallization from toluene and DME. The crystals were fully characterized, including an X-ray crystal structure analysis, to be the binuclear amide complex $[Yb(\mu_2\text{-NHPh})]_2(\mu_2\text{-L})_2$ (**6**) (Scheme 2), in which the coordination mode of both the L ligands becomes a bridging mode, not a chelating one as in the starting substrate. Obviously, the re-distribution of the ligand L occurred concomitantly during the metathesis reaction.

Although the detailed bond parameters of complex **6** could not be given due to the quality of the crystals, the structure skeleton of complex **6** is observed clearly (Fig. 2). Complex **6** has a dimetallic framework with two bridges of L and two amido bridges. Each Yb atom is ligated by two amidinate groups from two L ligands and two amido groups in a distorted tetrahedron when each bidentate amidinate ligand was considered to occupy one coordination vertex.

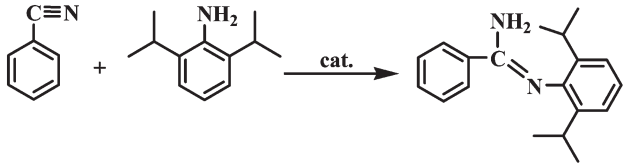
Replacing LiNHPh by the lithium amide $LiNHAr^2$ led to the isolation of another kind of binuclear amide complex **7** in reasonable yield (Scheme 2).

The dimer structure of complex **7** was confirmed by a crystal structure analysis as shown in Fig. 3.

Complex **7** is a dimer, in which the two units of LYb are linked together by two symmetric amido bridges. There are two free toluene molecules in the unit cell. Each central Yb atom is coordinated by two amidinate groups from one L ligand and two

**Table 2** The influence of lanthanide metals and amido groups on the catalytic addition reaction of $Ar^1NH_2$ to PhCN[a]




| Entry | Catalyst | Yield[b] (%) |
|---|---|---|
| 1 | **1** | 76 |
| 2 | **2** | 86 |
| 3 | **3** | 78 |
| 4 | **4** | 72 |
| 5 | **5** | 90 |
| 6 | **6** | 65 |
| 7 | **7** | 56 |
| 8 | **9** | 92 |
| 9 | **10** | Trace |

[a] All data were obtained using 1.50 mmol nitrile, under the condition of catalyst loading is 5 mol%, solvent free, 100 °C, 24 h, the mol ratio of $Ar^1NH_2$ to PhCN is 1 : 2. [b] Isolated yields.

amido groups in a distorted tetrahedron geometry. The bond parameters in the part of (YbL) is comparable to those found in complexes **1–5** and the other derivatives with the L ligand.[2d,10] The Yb(1)–N(amido) bond distance of 2.354(4) Å is longer than that found in complex **5**. The longer bond distance of Yb(1)–N (amido) found in **7**, compared to complex **5**, is normal because of the bridged Ln–N bonds which usually have longer distances in comparison with the terminal Ln–N bond distances.[11]

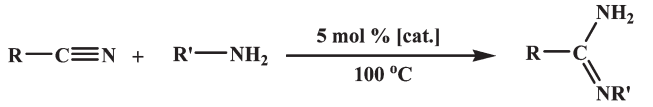
### Catalytic activity of 1–7, 9 and 10 for addition of amines to nitrile for monosubstituted *N*-arylamidinates

We screened complexes **1–7**, **9** and **10** in the reaction of $Ar^1NH_2$ with PhCN under the optimal conditions (5 mol% of catalyst, 100 °C, solvent-free, 24 h) as reported for LYbNH(2,6-$Me_2C_6H_3$)(DME).[7] All complexes were found to be efficient catalysts, however, differences in activity among them were observed. The activities of the Y, Nd and Gd complexes are slightly lower than those of Yb and Pr complexes (Table 2, entries 1–5). The amido group shows a great influence on the reactivity with the active sequence of $NHAr^2$ < NHPh < $NHAr^1$ (Table 2, entries 5–7).

The ytterbium complex **5** was then chosen as a catalyst for the catalytic addition reaction of various aromatic amines with nitriles. Representative results are summarized in Table 3.

The catalytic activity of complex **5** is almost the same as that reported for LYbNH(2,6-$Me_2C_6H_3$).[7] Also, a wide range of substituted anilines could be used for this reaction. The reaction was not influenced by either electron-withdrawing or electron-donating substituents at the phenyl ring of aromatic amines (Table 3, entries 1–11). Aromatic C–F (Table 3, entries 3, 5, 6 and 14), C–Cl (Table 3, entries 4 and 7) and C–$CH_3$ (Table 3, entries 1, 2, 8, 9 and 11) bonds survived in the present reactions. The tested aromatic nitriles with either electron-drawing or electron-donating groups at the *meta*- or *para*-position on the phenyl ring

**Table 3** Catalytic addition of aromatic amines to nitriles for monosubstituted *N*-arylamidinates by **5**: substrate scope[a]




| Entry | R | R′ | Yield[b] (%) |
|---|---|---|---|
| 1 | *p*-OMe-$C_6H_4$ | 2,6-$^iPr_2C_6H_3$ | 93 |
| 2 | *p*-Cl-$C_6H_4$ | 2,6-$^iPr_2C_6H_3$ | 86 |
| 3[b] | *p*-OMe-$C_6H_4$ | *p*-F-$C_6H_4$ | 98 |
| 4[b] | *p*-OMe-$C_6H_4$ | *p*-Cl-$C_6H_4$ | 93 |
| 5[b] | *m*-Me-$C_6H_4$ | *p*-F-$C_6H_4$ | 96 |
| 6[b] | Ph | *p*-F-$C_6H_4$ | 98 |
| 7[b] | Ph | *p*-Cl-$C_6H_4$ | 96 |
| 8 | Ph | *p*-Me-$C_6H_4$ | 94 |
| 9 | Ph | *o*-Me-$C_6H_4$ | 93 |
| 10 | Ph | Ph | 95 |
| 11 | Ph | 2,6-$Me_2C_6H_3$ | 92 |
| 12 | Ph | $PhCH_2$ | Trace |
| 13 | *o*-$CH_3O$-$C_6H_4$ | *p*-F-$C_6H_4$ | Trace |
| 14[c] | $PhCH_2$ | *p*-F-$C_6H_4$ | 89 |
| 15[c] | $CH_3$ | *p*-F-$C_6H_4$ | 76 |

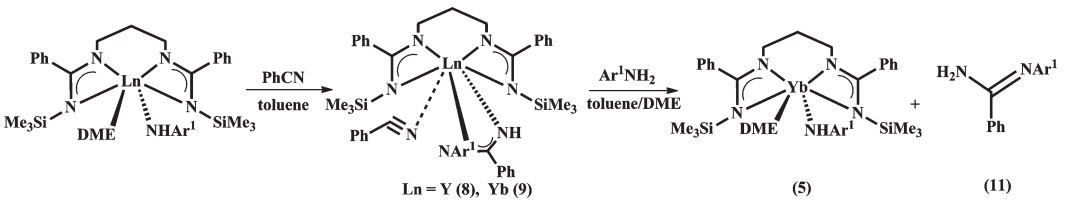
[a] All data were obtained using 1.50 mmol nitrile, the mole ratio of amine to nitrile is 1 : 2, solvent free, 24 h. [b] 12 h. [c] Catalyst loading 10 mol%, 48 h.

reacted smoothly with primary aromatic amines to give the corresponding monosubstituted aromatic amidines in 86–98% yields. The reaction with *o*-methoxybenzonitrile proceeded sluggishly (Table 3, entry 13). Aliphatic nitriles, such as $PhCH_2CN$ and $CH_3CN$, showed much less activity. They reacted with *p*-F-$C_6H_4NH_2$ to give the corresponding amidines in 89% and 76% yields, respectively (Table 3, entries 14 and 15), even in more rigorous conditions, such as extended reaction time and increased catalytic loading. Apparently, the less active cyano group of aliphatic nitriles, in comparison with that of aromatic nitriles, retarded the reaction rate. The reaction of aromatic nitriles with aliphatic amines proceeded sluggishly, and only a trace of product was isolated (Table 3, entry 12). This may be attributed to much slower protonation reaction by aliphatic amines compared to that by aromatic amines, which was one of the key steps included in catalytic cycles (discussed in the mechanism studies section).

### Mechanistic studies

To gain information on the true catalyst species, the stoichiometric reactions of complexes **1** and **5**, respectively, with PhCN in a 1 : 2 molar ratio were carried out in toluene at 100 °C for 12 h. Both reactions afforded the amidinate complexes LY(NPhCNAr[1])(PhCN) (**8**) and LYb[NPhCNAr[1]](PhCN) (**9**) in 61% and 67% yields, respectively, *via* nucleophilic addition of **1** and/or **5** to PhCN as shown in Scheme 3.

Both complexes **8** and **9** have been structurally characterized by X-ray structure analyses. Complex **9** crystallized as a toluene-solvated compound. Their molecular structures with selected bond distances and angles are shown in Fig. 4, as they are isostructural.




**Scheme 3** Formation of lanthanide anidinates (complexes **8** and **9**) and the reaction of **9** with $Ar^1NH_2$.



Each lanthanide atom in both complexes bonded to four nitrogen atoms from the L ligand, two nitrogen atoms from the newly formed mono-amidinate group and one nitrogen atom from the coordinated PhCN molecule to adopt a distorted tetrahedron if each amidinate ligand is considered to occupy a single coordination vertex. The bond parameters in the part of (LnL) for both complexes are comparable to those found in complexes **1–5** and the other derivatives.[2d,10] The angle between the two Ln–N–C–N planes (L) is 23.421(126)° for complex **8** and 26.732(94)° for complex **9** indicating a open sphere around Ln in complexes **8** and **9**. Therefore, the coordination of an additional PhCN molecule to the central metal is allowed. The Ln–N(7) bond distances of **9** and **10** are 2.514(5) Å and 2.494 (4) Å, similar to Dy–N 2.530(5) Å[12] and La–N 2.77(4) Å[13] without ionic radii effect, indicating that Ln–N are typical dative bonds. The N(5)–C(36) [1.344(5) Å (**8**), 1.338(5) Å (**9**)] and N(6)–C(36) [1.316(6) Å (**8**), 1.329(5) Å (**9**)] distances of the formed amidinate group are in the intermediate values between the C–N single- and double-bond distances, indicating that the π electrons of the C=N double bond in the present structure are partially delocalized. The bond parameters in the part of newly formed Ln–amidinate species can also be compared with those found in the lanthanide amide complexes reported.[10]

At room temperature, no reaction was observed between the amidinate complex **9** and $Ar^1NH_2$. However, when a 1 : 5 mixture of complex **9** and $Ar^1NH_2$ was heated to 100 °C in toluene, the corresponding amidine $NPhCNHAr^1$ (**11**) and the amido complex **5** were formed almost quantitatively as shown in Scheme 3.

When excess $Ar^1NH_2$ and PhCN (2 : 1) were added to complex **9** at 100 °C, catalytic formation of $NPhCNHAr^1$ was achieved and the activity of complex **9** was found to be the same as that of complex **5** (Table 2, entries 5 and 8).

On the basis of the above observations, a possible catalytic cycle for the addition of amines to nitrile could be proposed as shown in Scheme 4. The acid–base reaction between the yttrium amide complex and an amine, which is well documented,[14] should simply yield an amido species A. Nucleophilic addition of the amido species to a nitrile would afford directly the amidinate species B. Protonation of B by another molecule of amine would regenerate the amido complex A or the PhCN coordinated A and release the amidine C.

To further address the reason that **5** could not catalyze the catalytic nucleophilic addition reaction of *p*-F-$C_6H_4NH_2$ to $Ar^2CN$ (Table 3, entry 13), the reaction of complex **5** with $Ar^2CN$ was conducted under the same conditions as those used for the reaction of complex **5** with PhCN described above. The reaction went smoothly. After workup, the corresponding amidinate

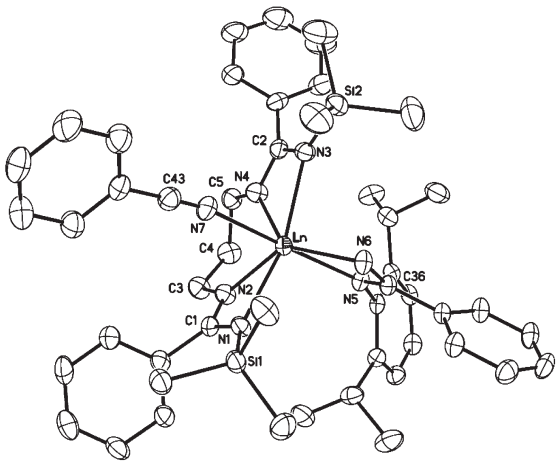


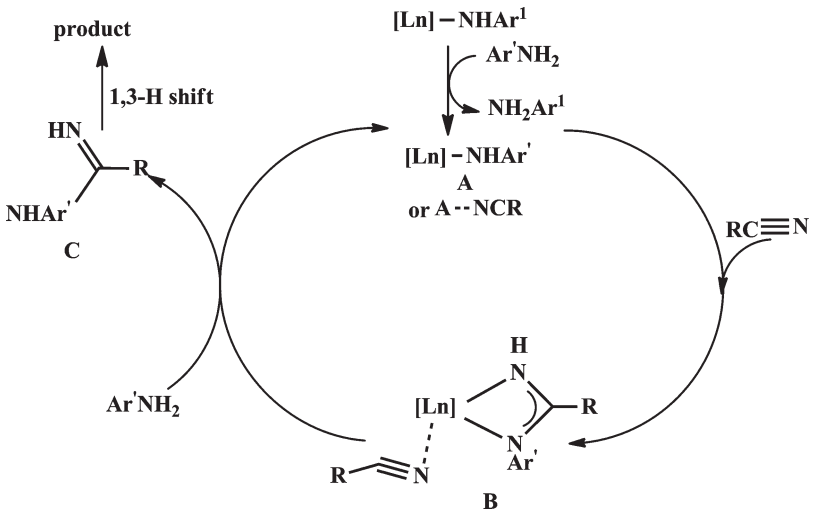

**Fig. 4** ORTEP diagram of the molecular structures of complexes **8** and **9**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms and the free toluene in **9** are omitted for clarity. Selected bond distances (Å) and angles (°): Ln(1)–N(1) 2.443(4) 2.399(3), Ln(1)–N(2) 2.339(4) 2.280(3), Ln(1)–N(3) 2.458(4) 2.407(3), Ln(1)–N(4) 2.321(4) 2.291(4), Ln(1)–N(5) 2.375(4) 2.349(3), Ln(1)–N(6) 2.372(4) 2.322(4), Ln(1)–N(7) 2.514(5) 2.494(4), N(1)–C(1) 1.342(5) 1.342(5), N(2)–C(1) 1.299(6) 1.313(5), N(3)–C(2) 1.341(6) 1.337(5), N(4)–C(2) 1.304(6) 1.320(6), N(5)–C(36) 1.344(5) 1.338(5), N(6)–C(36) 1.316(6) 1.329(5), N(2)–Ln(1)–N(1) 55.81(13) 57.45(12), N(4)–Ln(1)–N(3) 55.88(13) 56.89(13), N(6)–Ln(1)–N(5) 56.26(13) 57.25(11), N(7)–Ln(1)–N(5) 151.39(14) 168.98(12).

complex **10**, which was structurally characterized, was isolated as light yellow crystals in a reasonable yield (Scheme 5). The molecular structure of complex **10** (Fig. 5) is quite similar to those of complexes **8** and **9**.

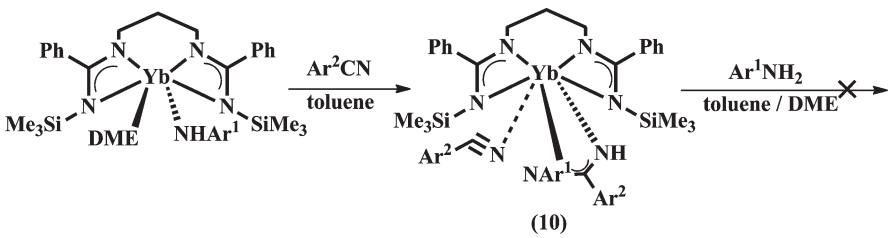
The formation of complex **10** indicates that the nucleophilic addition of **5** to $Ar^2CN$ proceeds without difficulty. However, no protonation reaction of complex **10** by amine to regenerate amide complex could occur even with excess amine at 100 °C (Scheme 5). Also, no catalytic addition reaction could be observed when excess $Ar^1NH_2$ and PhCN (in the molar ratio of 2 : 1) were added into complex **10** at 100 °C (Table 2, entry 9). This result further indicates that the formation of an amidinate species and the regeneration of an amide complex are both key steps for the catalytic nucleophilic addition of amines to nitriles.

## Conclusion

Various bridged bis(amidinate) lanthanide amide, $LLnNHAr^1$ (DME) (Ln = Y (**1**), Pr (**2**), Nd (**3**), Gd (**4**), Yb (**5**)), $[Yb(\mu_2\text{-}NHPh)]_2(\mu_2\text{-}L)_2$ (**6**) and $[LYb]_2(\mu_2\text{-}NHAr^2)_2$ (**7**), can be easily




**Scheme 4** Proposed mechanism for the addition of amines to nitriles.




**Scheme 5** Formation of complex **10** and the reaction of complex **10** with $Ar^1NH_2$.

prepared by the reaction of $LLnCl(THF)_2$ with the corresponding lithium amides in high yields. Complexes **1–5** can serve as efficient catalysts for catalytic addition of aromatic amines to aromatic nitriles selectively to give the monosubstituted amidines in excellent yields with a wide range of aromatic amines. Functional groups such as aromatic C–X (X = F, Cl, $CH_3$, $OCH_3$) bonds can survive the catalytic reaction conditions. The mechanism studies by the isolation of amidinate complexes and their activity for addition of amine to nitrile revealed that the present catalytic formation of monosubstituted aromatic amidine proceeds through nucleophilic addition of an amido species to a nitrile, followed by amine protonolysis of the resultant amidinate species.

## Experiment

### Materials and methods

All manipulations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified argon using standard Schlenk techniques. The solvents THF, DME, toluene and n-hexane were dried and distilled from sodium benzophenone ketal under argon prior to use. $LLnCl(THF)_2$ and complex **5** were prepared according to the literature procedure.[10] $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a

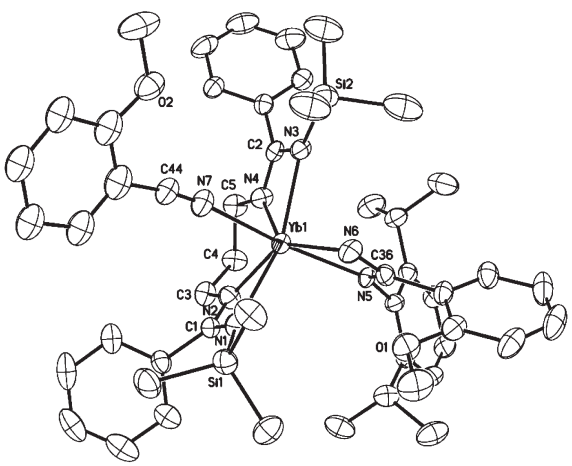



**Fig. 5** ORTEP diagram of the molecular structures of complexes **10**, Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms and free toluene molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Yb(1)–N(1) 2.425(6), Yb(1)–N(2) 2.287 (6), Yb(1)–N(3) 2.412(6), Yb(1)–N(4) 2.284(6), Yb(1)–N(5) 2.348(5), Yb(1)–N(6) 2.337(6), Yb(1)–N(7) 2.500(7), N(1)–C(1) 1.338(9), N(2)–C(1) 1.306(9), N(3)–C(2) 1.336(9), N(4)–C(2) 1.318(9), N(5)–C(36) 1.356(8), N(6)–C(36) 1.314(8), N(7)–C(43), 1.144(9), N(2)–Yb(1)–N(1) 56.8(2), N(4)–Yb(1)–N(3) 56.9(2), N(6)–Yb(1)–N(5) 57.14(18), N(7)–Yb(1)–N(5) 157.9(2).

400 MHz instrument and processed using MestReNova software. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets.

### Preparations

**LY(NHAr$^1$)(DME) (1).** A THF solution (20 mL) of LYCl(THF)$_2$ (2.07 g, 3.00 mmol) was added into a THF solution of LiNHAr$^1$ (0.55 g, 3.00 mmol) slowly under stirring. The mixture was stirred at room temperature for 12 h. After the solvent was removed under reduced pressure, the residue was extracted with hot toluene and the LiCl was removed by centrifugation. The resulting pale yellow solution was concentrated and a small amount of DME was added. Colorless crystals suitable for X-ray analysis were obtained (1.52 g, 65% yield based on Y) upon crystallization from a mixture of toluene and DME at room temperature for several days. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.32 (2 H, d, $J$ = 7.2 Hz, Ar*H*), 7.20 (4 H, d, $J$ = 7.6 Hz, Ar*H*), 7.16–7.04 (5 H, m, Ar*H*), 6.77–6.71 (1 H, m, Ar*H*), 6.59 (1 H, t, $J$ = 7.7 Hz, Ar*H*), 3.78–3.81 (4 H, m, OC$H_2$), 3.13 (6 H, s, OC$H_3$), 2.77–2.80 (6 H, m, CH$_2$C$H_2$N and C$H$(CH$_3$)$_2$), 1.16–1.21 (12 H, m, CH(C$H_3$)$_2$), 1.58–1.61 (2 H, m, C$H_2$CH$_2$N), 0.29 to −0.07 (18 H, m, Si(C$H_3$)$_3$). $^{13}$C NMR (400 MHz, $C_6D_6$) $\delta$ = 162.13 (*C*=N), 141.92 (Ar), 133.47 (Ar), 128.62 (Ar), 128.42 (Ar), 128.03 (Ar), 124.32 (Ar), 120.13 (Ar), 86.35 (OCH$_2$), 73.43 (OCH$_3$), 29.37 (*C*H$_2$CH$_2$N), 23.82 (*C*H(CH$_3$)$_2$), 4.29 (CH(*C*H$_3$)$_2$), 1.52 (Si(*C*H$_3$)$_3$). $C_{39}H_{62}N_5O_2Si_2Y$ (778.03): calcd C 60.21, H 8.03, N 9.00, Y 11.43; found C 60.29, H 8.09, N 8.74, Y 12.19. IR (KBr): 3468 (m), 3335 (m), 2959 (s), 1646 (m), 1608 (s), 1569 (m), 1490 (m), 1438 (m), 1363 (m), 1245 (s), 1158 (s), 908 (w), 835 (s), 780 (m), 746 (m), 701 (s) cm$^{-1}$.

**LPr(NHAr$^1$)(DME) (2).** The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but corresponding LPrCl(THF)$_2$ were used. Light green crystals of complex **2** were isolated (yield 1.50 g, 60% based on Pr). $C_{39}H_{62}N_5O_2Si_2Pr$ (830.03): calcd C 56.43, H 7.53, N 8.44, Pr 16.98; found C 56.62, H 7.73, N 8.31, Pr 17.02. IR (KBr): 3327 (s), 2960 (s), 2871 (m), 1647 (m), 1608 (s), 1569 (m), 1490 (m), 1439 (m), 1364 (m), 1248 (s), 1155 (s), 907 (w), 837 (s), 780 (m), 747 (s), 701 (s) cm$^{-1}$.

**LNd(NHAr$^1$)(DME) (3).** The synthesis of complex **3** was carried out in the same way as that described for complex **1**, but corresponding LNdCl(THF)$_2$ were used. The light purple crystals of complex **3** were isolated (yield 1.70 g, 68% based on Nd). $C_{39}H_{62}N_5O_2Si_2Nd$ (833.36): calcd C 56.21, H 7.50, N 8.40, Nd 17.31; found C 56.54, H 7.67, N 8.27, Nd 17.22. IR (KBr): 3406 (m), 3331 (m), 2960 (s), 2872 (m), 1609 (s), 1541 (m), 1491 (m), 1439 (s), 1365 (m), 1246 (s), 1156 (s), 908 (w), 836 (s), 780 (m), 746 (m), 701 (s) cm$^{-1}$.

**LGd(NHAr$^1$)(DME) (4).** The synthesis of complex **4** was carried out in the same way as that described for complex **1**, but corresponding LGdCl(THF)$_2$ were used. Light yellow crystals of complex **4** were isolated (yield 1.63 g, 64% based on Gd). $C_{39}H_{62}N_5O_2Si_2Gd$ (846.37): calcd C 55.34, H 7.38, N 8.27, Gd 18.58; found C 55.03, H 7.56, N 8.11, Gd 18.79. IR (KBr): 3402 (m), 3335 (m), 2960 (s), 2871 (m), 1618 (s), 1542 (m), 1468 (m), 1439 (s), 1364 (m), 1247 (s), 1155 (s), 909 (w), 836 (s), 780 (m), 746 (s), 701 (s) cm$^{-1}$.

**[Yb($\mu_2$-NHPh)]$_2$($\mu_2$-L)$_2$ (6).** The synthesis of complex **6** was carried out in the same way as that described for the synthesis of complex **1**, but LYbCl(THF)$_2$ (2.21 g, 3.00 mmol) and LiNHPh (0.29 g, 3.00 mmol) were used. Colourless single crystals suitable for X-ray analysis were obtained at −15 °C after several days (yield: 1.19 g, 51% based on Yb). $C_{58}H_{78}N_{10}Si_4Yb_2$ (1374.43): calcd C 50.71, H 5.72, N 10.20, Yb 25.19; found C 50.33, H 6.12, N 9.82, Yb 25.76. IR (KBr): 3413 (s), 2960 (m), 1646 (m), 1608 (m), 1568 (m), 1438 (m), 1384 (m), 1365 (m), 1245 (s), 1156 (s), 903 (w), 838 (m), 781 (m), 747 (m), 702 (m) cm$^{-1}$.

**[LYb]$_2$($\mu_2$-NHAr$^2$)$_2$ (7).** The synthesis of complex **7** was carried out in the same way as that described for complex **1**, but LYbCl(THF)$_2$ (2.21 g, 3.00 mmol) and LiNHAr$^2$ (0.38 g, 3.00 mmol) were used. Colourless crystals were isolated (yield: 1.41 g, 58% based on Yb). $C_{60}H_{84}N_{10}O_2Si_4Yb_2$ (1436.46): calcd C 50.19, H 5.90, N 9.76, Yb 24.10; found C 50.66, H 6.10, N 9.68, Yb 24.75. IR (KBr): 3412 (s), 3336 (m), 2960 (m), 1645 (m), 1609 (m), 1566 (m), 1466 (m), 1438 (m), 1384 (m), 1368 (m), 1246 (s), 1157 (s), 909 (w), 837 (m), 751 (m), 702 (m) cm$^{-1}$.

**LY[NPhCNAr$^1$](PhCN) (8).** LY(NHAr)(DME) (**1**) (2.33 g, 3.00 mmol) were dissolved in toluene solution (30 mL), then PhCN (0.61 mL, 6.00 mmol) was added into the solution of complex **1** quickly under stirring. The mixture was stirred at 100 °C for 12 h. After the solvent was removed under reduced pressure, the residue was extracted with toluene, centrifuged, and the centrifugal clear liquid was concentrated. Colourless crystals suitable for X-ray analysis were obtained (yield: 1.64 g, 61% based on Y) upon crystallization from toluene at room temperature for several days. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.58 (2 H, d, $J$ = 7.1 Hz, Ar*H*), 7.43 (4 H, d, $J$ = 7.3 Hz, Ar*H*), 7.34 (2 H, d, $J$ = 7.6 Hz, Ar*H*), 7.27 (7 H, t, $J$ = 8.0 Hz, Ar*H*), 7.19 (2 H, d, $J$ = 7.3 Hz, Ar*H*), 7.08–6.99 (3 H, m, Ar*H*), 6.95 (1 H, t, $J$ = 7.6 Hz, Ar*H*), 6.79 (2 H, t, $J$ = 7.7 Hz, Ar*H*), 3.05–2.99 (4 H, m, CH$_2$C$H_2$N), 2.19–2.08 (2 H, m, C$H$(CH$_3$)$_2$), 2.03–1.92 (2 H, m, C$H_2$CH$_2$N), 1.61–1.63 (6 H, m, CH(C$H_3$)$_2$), 1.30–1.32 (6 H, m, CH(C$H_3$)$_2$), 0.35 (18 H, s, Si(C$H_3$)$_3$). $^{13}$C NMR (400 MHz, $C_6D_6$) $\delta$ = 153.51 (*C*=N), 146.63 (Ar), 140.39 (Ar), 137.08 (Ar), 133.18 (Ar), 131.60 (Ar), 130.06 (Ar), 129.75 (Ar), 128.61 (Ar), 128.26 (Ar), 125.04 (Ar), 62.39 (CH$_2$*C*H$_2$N), 49.55 (*C*H$_2$CH$_2$N), 29.98 (*C*H(CH$_3$)$_2$), 25.12 (CH(*C*H$_3$)$_2$), 24.85 (CH(*C*H$_3$)$_2$), 4.30 (Si(*C*H$_3$)$_3$). $C_{49}H_{62}N_7Si_2Y$ (894.15): calcd C 65.82, H 6.99, N 10.97, Y 9.94; found C 65.31, H 7.27, N 10.99, Y 9.89. IR (KBr): 3498 (s), 3384 (m), 2960 (s), 2867 (m), 2230 (s), 1637 (s), 1600 (m), 1566 (m), 1494 (s), 1466 (s), 1368 (s), 1331 (m), 1289 (s), 1246 (s), 1157 (s), 1021 (s), 922 (m), 837 (s), 752 (s), 701 (s) cm$^{-1}$.

**LYb[NPhCNAr$^1$](PhCN) (9).** The synthesis of complex **9** was carried out in the same way as that described for the synthesis of complex **8**, but complex **5** (2.59 g, 3 mmol) was

used. Colourless crystals were isolated (yield: 2.15 g, 67% based on Yb). $C_{49}H_{62}N_7Si_2Yb$ (978.40): calcd C 60.16, H 6.39, N 10.02, Yb 17.69; found C 60.52, H 6.75, N 9.87, Yb 17.43. IR (KBr): 3499 (s), 3385 (m), 2956 (s), 2861 (m), 2229 (s), 1638 (s), 1598 (m), 1495 (s), 1466 (s), 1366 (s), 1330 (m), 1288 (s), 1245 (s), 1158 (s), 1022 (s), 915 (m), 835 (s), 746 (s), 701 (s) $cm^{-1}$.

**LYb[NAr$^2$CNAr$^1$](Ar$^2$CN) (10).** The synthesis of complex **10** was carried out in the same way as that described for the synthesis of complex **8**, but complex **5** (2.59 g, 3 mmol) and $Ar^2CN$ (0.73 ml, 6 mmol) was used. Colourless crystals were isolated (yield: 1.63 g, 48% based on Yb). $C_{51}H_{66}N_7O_2Si_2Yb$ (1038.42): calcd C 58.99, H 6.41, N 9.44, Yb 16.67; found C 59.51, H 6.72, N 9.16, Yb 15.96. IR (KBr): 3486 (s), 2962 (s), 2859 (m), 2230 (s), 1628 (s), 1583 (m), 1501 (s), 1465 (s), 1358 (s), 1285 (s), 1246 (s), 1155 (s), 1019 (s), 910 (m), 842 (s), 745 (s), 702 (s) $cm^{-1}$.

### General procedure for the reaction of 9 with $Ar^1NH_2$ ($Ar^2NH_2$)

The $Ar^1NH_2$ (2.83 mL, 15.00 mmol) was added into toluene solution (30 mL) of complex **9** (2.93 g, 3.00 mmol) quickly under stirring at 100 °C for 12 h. After the solvent was removed under reduced pressure, the residue was extracted three times with n-hexane (10 mL) and almost quantitative amidine $NPhCNHAr^1$ (**11**) was obtained from the n-hexane at 0 °C after two days. The residue after using the extraction was dissolved in toluene (15 mL) centrifuged and the amido complex **5** was formed from centrifugal clear liquid at −15 °C temperature after three days. Complexes **5** and **11** were confirmed by determination of cell parameters. The procedure for the reaction of **9** with $Ar^2NH_2$ was conducted as above (with 1.69 mL, 15.00 mmol $Ar^2NH_2$).

### General procedure for the addition of amines to nitriles for monosubstituted *N*-arylamidines catalyzed by 1–10

A 10 mL Schlenk tube under dried argon was charged with the respective catalysts (0.05 equiv.), amines (2 equiv.), and nitriles (1 equiv.). The resulting mixture was stirred at 100 °C for the desired time, as shown in Tables 2 and 3. After the reaction was completed, the product was isolated by distilling the reaction mixture under vacuum to remove unreacted starting materials. The residue was recrystallized from hexane at 0 °C for one day, dried, weighed and productivity calculated.

### X-Ray crystallographic structure determinations

Crystals suitable for X-ray diffraction of complexes **1–4** and **7–10** were sealed, respectively, in a thin-walled glass capillary filled with argon. Diffraction data were collected on a Rigaku Mercury CCD area detector in the $\omega$ scan mode using Mo $K_\alpha$ radiation ($\lambda$ = 0.71075 Å) at 223(2) K. The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Tables 4 and 5. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The structures were refined using SHELXTL-97 programs. CCDC 863200 (for complex **1**), 862443 (for complex **2**), 862444 (for complex **3**), 862445 (for complex **4**), 862449 (for complex **7**), 862446 (for complex **8**), 862447 (for complex **9**), 862448 (for complex **10**) contain the supplementary crystallographic data for this paper.†

**Table 4** Crystallographic data for complexes **1–4**

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Formula | $C_{39}H_{62}N_5O_2Si_2Y$ | $C_{39}H_{62}N_5O_2Si_2Pr$ | $C_{39}H_{62}N_5O_2Si_2Nd$ | $C_{39}H_{62}N_5O_2Si_2Gd$ |
| Mol wt | 778.03 | 830.03 | 833.36 | 846.37 |
| $\lambda$/Å | 0.71075 | 0.71075 | 0.71075 | 0.71075 |
| Cryst syst | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $C2/c$ | $C2/c$ | $P2_1/c$ |
| Cryst size/mm | 0.52 × 0.25 × 0.18 | 0.76 × 0.20 × 0.10 | 0.20 × 0.20 × 0.20 | 0.60 × 0.38 × 0.15 |
| $a$/Å | 24.757(5) | 48.194(5) | 48.267(8) | 24.7140(18) |
| $b$/Å | 8.9687(16) | 9.0139(9) | 9.0251(13) | 8.9715(5) |
| $c$/Å | 19.765(4) | 19.816(2) | 19.805(3) | 19.8141(13) |
| $\alpha$/° | 90 | 90.00 | 90 | 90 |
| $\beta$/° | 104.382(3) | 96.281(3) | 96.408(5) | 103.969(2) |
| $\gamma$/° | 90 | 90.00 | 90 | 90 |
| $V$/Å$^3$ | 4251.2(14) | 8556.6(16) | 8573(2) | 4263.3(5) |
| $Z$/Å$^3$, $D_{calcd}$/g mL$^{-1}$ | 4, 1.216 | 8, 1.289 | 8, 1.291 | 4, 1.319 |
| $M$/mm$^{-1}$ | 1.465 | 1.231 | 1.304 | 1.649 |
| $F$(000) | 1656 | 3472 | 3480 | 1756 |
| $\theta$ range/° | 3.03–25.50 | 3.10–25.50 | 3.06–25.50 | 3.02–25.50 |
| Total no. of rflns | 26 862 | 21 163 | 20 771 | 20 979 |
| No. of indep rflns | 7840 | 7915 | 7902 | 7854 |
| $R_{int}$ | 0.0823 | 0.0601 | 0.0635 | 0.0381 |
| GOF | 1.189 | 1.157 | 1.156 | 1.196 |
| $R_1$, w$R_2$ ($I > 2\sigma(I)$) | 0.0845, 0.1459 | 0.0631, 0.0989 | 0.0784, 0.1657 | 0.0547, 0.1102 |
| $R_1$, w$R_2$ (all data) | 0.1083, 0.1554 | 0.0814, 0.1064 | 0.1015, 0.1857 | 0.0634, 0.1133 |

**Table 5** Crystallographic data for complexes **7–10**

| | **7**·2toluene | **8** | **9**·toluene | **10**·toluene |
|---|---|---|---|---|
| Formula | $C_{74}H_{100}N_{10}O_2Si_4Yb_2$ | $C_{49}H_{62}N_7Si_2Y$ | $C_{56}H_{70}N_7Si_2Yb$ | $C_{58}H_{74}N_7O_2Si_2Yb$ |
| Mol wt | 1620.08 | 894.15 | 1070.41 | 1130.46 |
| $\lambda$/Å | 0.71075 | 0.71075 | 0.71075 | 0.71075 |
| Cryst syst | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ |
| Cryst size/mm | 0.30 × 0.20 × 0.18 | 0.40 × 0.20 × 0.10 | 0.35 × 0.22 × 0.20 | 0.30 × 0.18 × 0.15 |
| $a$/Å | 12.1228(6) | 13.9207(8) | 24.0074(14) | 12.8432(9) |
| $b$/Å | 12.7576(7) | 18.8194(10) | 13.3464(7) | 20.1542(13) |
| $c$/Å | 13.5956(6) | 20.0255(14) | 17.8421(11) | 22.7598(15) |
| $\alpha$/° | 80.150(5) | 76.526(5) | 90 | 90 |
| $\beta$/° | 68.709(4) | 89.145(7) | 104.8920(10) | 97.886(2) |
| $\gamma$/° | 84.206(5) | 73.163(6) | 90 | 90 |
| $V$/Å$^3$ | 1928.55(17) | 4875.4(5) | 5524.8(6) | 5835.5(7) |
| $Z$/Å$^3$, $D_{calcd}$/g mL$^{-1}$ | 1, 1.395 | 4, 1.218 | 4, 1.287 | 4, 1.287 |
| $\mu$/mm$^{-1}$ | 2.521 | 1.285 | 1.777 | 1.689 |
| $F$(000) | 826 | 1888 | 2212 | 2340 |
| $\theta$ range/° | 3.11–25.49 | 3.06–25.50 | 3.01–25.50 | 3.02–25.50 |
| Total no. of rflns | 16 590 | 42 285 | 27 958 | 29 811 |
| No. of indep rflns | 7150 | 18 054 | 10 202 | 10 830 |
| $R_{int}$ | 0.0519 | 0.0689 | 0.0428 | 0.0707 |
| GOF | 1.125 | 1.087 | 1.178 | 1.187 |
| $R_1$, w$R_2$ ($I > 2\sigma(I)$) | 0.0520, 0.0970 | 0.0749, 0.1369 | 0.0460, 0.0843 | 0.0742, 0.1404 |
| $R_1$, w$R_2$ (all data) | 0.0639, 0.1027 | 0.1164, 0.1548 | 0.0540, 0.0881 | 0.0971, 0.1505 |



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## Notes and references

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