Use of Lanthanide(III) Ions as Catalysts for the Reactions of Amines with Nitriles

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Catalytic amounts of lanthanide(III) triflates promote reactions between amines and nitriles leading to a variety of products. The Ln^{3+} ions activate weakly coordinating nitriles at large amine:Ln^{3+} mole ratios, even in the presence of amines that form thermodynamically stable complexes with Ln^{3+} ions. The reactions involving primary monoamines and diamines appear to be general and provide a viable synthetic route to N,N'-disubstituted amidines (2) and cyclic amidines (4), respectively. Symmetrically substituted triazines (8 or 9) are observed as byproducts in some of these systems when the reactions are carried out by using excess nitrile. Secondary alicyclic amines or dimethylamine reacts with acetonitrile to yield pyrimidines (6) and 2,4,6-trimethyl-*s*-triazine (8). Two routes to triazine have been proposed, one involving the reaction of ammonia with the nitrile and the second involving the reaction of an amidine (1 or 5) with the nitrile. The ability of Ln^{3+} ions to activate nitriles under conditions that oppose nitrile coordination is attributed to the lability of Ln^{3+} complexes derived from N-donors.

Previously we reported that lanthanide(III) perchlorate salts catalyze reactions between unidentate cyclic secondary amines and acetonitrile to give N-substituted acetamidines (5) or 4-substituted-2,6-dimethylpyrimidines (6).[1] It is noteworthy that the latter instance represented the first example of a Ln^{3+} ion catalyzed reaction resulting in the formation of a carbon–carbon bond. Catalytic activity of the Ln^{3+} ions in these systems was quite surprising, since acetonitrile is commonly used as a solvent to prepare N-donor complexes of the lanthanides.[2] Although coordination of a nitrile to transition metal ions or other Lewis acids has been shown to promote reactions with amines leading to amidines,[3] formation of heterocyclic compounds analogous to those we have obtained using Ln^{3+} catalysts has not been reported. Furthermore, we have found that Ln^{3+} ions effectively activate nitrile molecules at levels of 1 mol % relative to the organic reagents, whereas reactions with transition metal ions are carried out by using a stoichiometric amount of catalyst.[4]

These observations prompted us to undertake a more detailed study of the scope and limitations of Ln^{3+}-catalyzed reactions between a variety of amines with acetonitrile, benzonitrile, and propionitrile. This study was carried out by using anhydrous $Ln(CF_3SO_3)_3$ salts as catalysts, rather than perchlorates, due to the evident hazards associated with the use of $Ln(ClO_4)_3$ salts in organic systems.[5]

The ability of catalytic amounts of Ln^{3+} ions to activate weakly coordinating nitriles in the presence of strongly competetive N-donors suggests that these ions may have properties that can be exploited in organic synthesis. Indeed, Sen and co-workers[8] recently reported that the presence of weakly coordinating ligands in $[Eu(CH_3CN)_2(BF_4)_3]_x$ allowed for the direct interaction of Eu^{3+} with olefinic centers, resulting in polymerization of alkenes in nitromethane. Additional examples of the use of lanthanides in a variety of organic reactions are reported in several reviews.[9-11]

Results and Discussion

Anhydrous[12] lanthanide(III) trifluoromethanesulfonates (1–10 mol %) promote reactions of primary monoamines, primary diamines, and secondary amines with the representative organonitriles to give amidines, cyclic amidines, and pyrimidines, respectively. Catalytic activity was observed for the La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Lu triflates and it may be assumed that all Ln(III) triflates are active. Yttrium(III) triflate was also found to be active. No reactions were observed in the absence of the Ln^{3+} ion. Anhydrous lanthanide(III) nitrates and chlorides were inactive in the alicyclic amine–acetonitrile systems and were not studied further.

Primary monoamines react with organonitriles (eq 1) to give an *N*-substituted amidine (1) intermediate, which then reacts with a second molecule of amine to give **2a–i**. In

$$RNH_2 + R'CN \overset{Ln^{3+}}{\rightleftharpoons} R'C(=NH)NHR \xrightarrow{RNH_2} R'C(=NR)NHR + NH_3 \quad (1)$$

1a, R = Ph; R = cyclohexyl

2a, R' = CH_3; R = *n*-propyl
b, R' = CH_3; R = isopropyl
c, R' = CH_3; R = *n*-butyl
d, R' = CH_3; R = isobutyl
e, R' = CH_3; R = *sec*-butyl
f, R' = CH_3; R = Ph
g, R' = CH_3CH_2; R = *n*-butyl
h, R' = Ph; R = *n*-propyl
i, R' = Ph; R = *n*-butyl

general, over 90% conversion of the nitrile to the disub-

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(2) (a) Forsberg, J. H. *Coord. Chem. Rev.* **1973**, *10*, 195–226. (b) Forsberg, J. H. In *Gmelin Handbuch der Anorganischen Chemie*; Moeller, T., Schleitzer-Rust, E., Eds.; Springer-Verlag: New York, 1980, Syst. No. 39, Part D 1, Chapter 2. (c) Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2867–2870. (d) Smith, P. H.; Raymond, K. N. *Inorg. Chem.* **1985**, *24*, 3469–3477.
(3) (a) Oxley, P.; Partridge, M. W.; Short, W. F. *J. Chem. Soc.* **1947**, 1110–1116. (b) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 489–494. (c) Maresca, L.; Natile, G.; Intini, F. P.; Gasparrini, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Am. Chem. Soc.* **1986**, *108*, 1180–1185. (d) Uguagliati, P.; Belluco, U.; Michelin, R. A.; Guerriero, P. *Inorg. Chim. Acta* **1984**, *81*, 61–67.
(4) Less than a stoichiometric amount of Ca^{2+}, which has properties in common with Ln^{3+} ions,[6] has been reported to promote the addition of aromatic amines to phthalonitrile.[7]
(5) (a) Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1983**, *22*, 2972. (b) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A336–A337.
(6) Moeller, T.; Martin, D. F.; Thompson, L. C.; Ferrus, R.; Feistel, G. R.; Randall, W. J. *Chem. Rev.* **1965**, *65*, 1–50.
(7) Siegl, W. O. *J. Org. Chem.* **1977**, *42*, 1872–1878.
(8) Thomas, R. R.; Chebolu, V.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 4096–4103.
(9) Natale, N. R. *Org. Prep. Proc. Int.* **1983**, *15*, 387–424.
(10) Imamoto, T.; Tawarayama, Y.; Kusumoto, T.; Yokoyama, M. *J. Synth. Org. Chem. Jpn.* **1983**, *15*, 143–152.
(11) Long, J. R. *Handbook on the Physics and Chemistry of Rare Earths*; North Holland: Amsterdam, 1986; Chapter 57.
(12) Anhydrous conditions are required to prevent formation of insoluble lanthanide hydroxides in the presence of amines and to maximize the activity of the catalyst.

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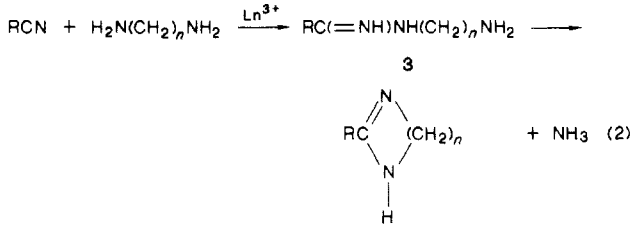
stituted amidine was obtained when the reactions were carried out using a 1:2 nitrile:amine mole ratio. This procedure thus offers an attractive, high yield alternative for the preparation of N,N′-disubstituted amidines of structure **2**.[13] The nitrile–amine mole ratio is of considerable importance in this reaction (eq 1). For example, when the reactions involving acetonitrile or benzonitrile were carried out using excess nitrile, a significant amount of a byproduct, identified as 2,4,6-trimethyl-*s*-triazine (**8**) or 2,4,6-triphenyl-*s*-triazine (**9**), respectively, was formed. Triazine formation, which stoichiometrically represents trimerization of the nitrile, is discussed in a later section of this paper.

Of the amines studied, only *tert*-butylamine revealed little tendency to react, undergoing only 10% conversion with acetonitrile to give a monosubstituted amidine as the only product. This low reactivity may be attributed to the steric bulk of the *tert*-butyl group. Steric hindrance may also account for the fact that *sec*-butylamine reacts with acetonitrile at a rate of only 5% that of *n*-butylamine under the same conditions.

Although **1** is a dectectable (NMR) intermediate in each reaction, these compounds generally decomposed to starting materials on distillation of the reaction mixtures and were not isolated. In the specific instance of cyclohexylamine with benzonitrile, however, **1a** crystallized from the reaction mixture. An NMR study revealed that reaction of **1a** with *n*-butylamine in the absence of Ln^{3+} yielded the disubstituted benzamidine, indicating that the metal ion is not required for addition of the second molecule of amine to the intermediate monoamidine.

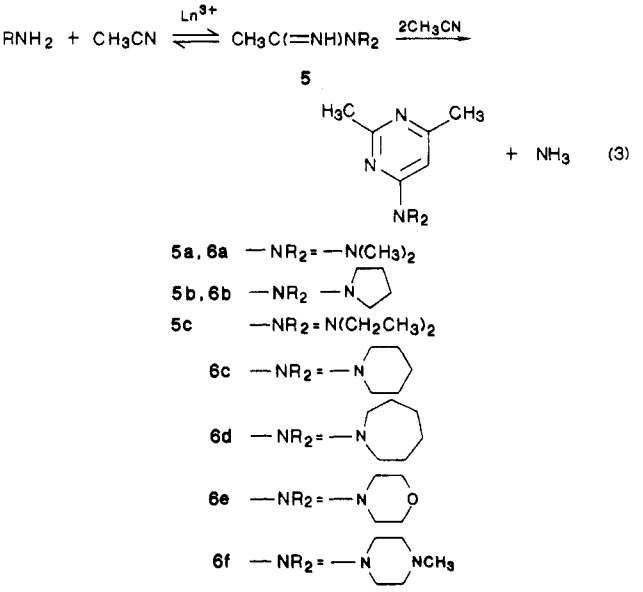
The reactions of primary diamines with nitriles result in formation of cyclic amidines **4a–i** (eq 2). These reac-



4a, R = CH_3; *n* = 2
b, R = CH_3CH_2; *n* = 2
c, R = Ph; *n* = 2
d, R = CH_3; *n* = 3
e, R = CH_3CH_2; *n* = 3
f, R = Ph; *n* = 3
g, R = CH_3; *n* = 4
h, R = CH_3CH_2; *n* = 4
i, R = Ph, *n* = 4

tions are analogous to those involving primary monoamines. However, the presumed intermediate **3**, which is not detectable by NMR, undergoes rapid intramolecular ring closure. These reactions are quite facile and essentially complete (isolated yields of 70–95%) when equimolar amounts of amine and nitrile are heated with 1 mol % Ln^{3+} for 24 h. Triazine formation was observed in some instances when the reactions were carried out with excess nitrile and the reaction time was extended to several days.

As reported previously,[1] alicyclic secondary amines react with acetonitrile (eq 3) under reflux to give 4-substitut-



ed-2,6-dimethylpyrimidines **6a–f** in 35% to 45% yield. When the reactions are carried out at room temperature only the amidines **5** are formed. We have subsequently discovered that **8** may also be obtained from these reactions when carried out under reflux. The relative amounts of **6** and **8** are variable and appear sensitive to the reaction conditions. When the reactions were carried out open to the atmosphere, the two products were generally formed in ca. equimolar quantities. However, the triazine:pyrimidine mole ratio increased to ca. 3:1 when the reactions were carried out in a sealed reaction vessel.

These reactions are quite sensitive to steric factors as revealed by the fact that 2-methylpiperidine and 2,6-dimethylpiperidine do not react with acetonitrile. Steric factors may further account for the limited reactivity observed for noncyclic secondary amines with acetonitrile. For example, whereas dimethylamine reacts to form the pyrimidine **6a**, diethylamine reacts to give the amidine **5c**, but the pyrimidine was not formed. No reaction was observed with dipropylamine. The reaction of piperidine with proprionitrile gave the monoamidine, but NMR data indicated that only a trace amount of the pyrimidine was formed.

Role of the Metal Ion. It is likely that the Ln^{3+} ions activate the nitriles through a predominantly electrostatic, ion–dipole interaction. This interaction enhances polarization of the cyano group, thereby facilitating attack by the nucleophilic amine. In a separate study,[17] we have shown that the catalytic activities of the Ln^{3+} ions are related to their effective ionic potentials, with the smaller ions (Ho^{3+}–Lu^{3+}) giving turnover rates[18] that are up to seven times those of the larger ions (La^{3+}–Sm^{3+}), vide infra. The lack of reactivity noted for the nitrate and chloride salts suggests that anion coordination in solution reduces the effective ionic potentials of the Ln^{3+} ions sufficiently to render them inactive.

An intriguing aspect of the reactions reported herein is the ability of a Ln^{3+} ion to activate a nitrile in the presence of a strongly coordinating N-donor ligand. Ethylenediamine, for example, is known to form thermodynamically stable $Ln(en)_4^{3+}$ chelates in acetonitrile. The large, exo-

(13) Other general methods for the synthesis of N,N′-disubstituted amidines include the aminolysis of nitrilium salts resulting from the N-alkylation of nitrile–Lewis acid complexes ($FeCl_3$ or $AlCl_3$)[14] and the transamination reaction between amines and monoalkylated amidines.[15] There appear to be few other general methods of synthesis of N,N′-disubstituted amidines. A review of the synthesis and chemistry of amidines has recently appeared.[16]

(14) Fuks, R. *Tetrahedron*, **1973**, *29*, 2147–2156.

(15) Reynaud, P.; Brion, J.; Menard, G. *Bull Soc. Chim. Fr.* **1978**, Part 2, 449–456.

(16) Granik, V. G. *Russ. Chem. Rev.* **1983**, *52*, 377–391.

(17) Unpublished results.

(18) Turnover rate is a measure of the number of nitrile molecules activated/mol catalyst·h.

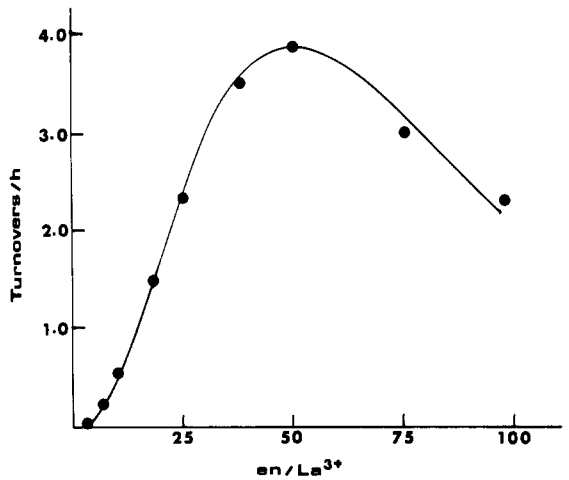


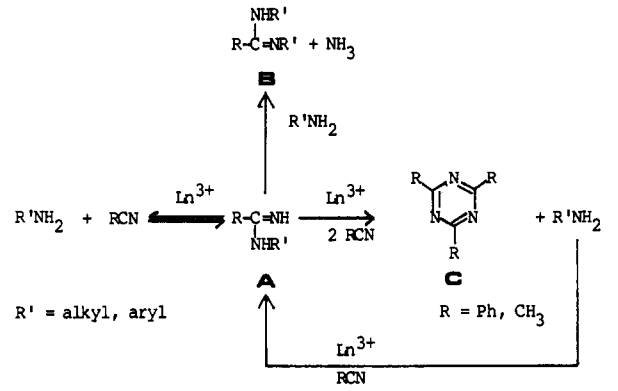
Figure 1. Dependence of turnover rate on the en:La^{3+} mole ratio (CH_3CN:La^{3+} molar ratio = 50:1) in the La^{3+}-catalyzed reaction of ethylenediamine with acetonitrile (eq 2).

thermic ligational enthalpy changes (241–277 kJ/mol)[19] that characterize formation of the tetrakis chelates from the perchlorate salts in acetonitrile demonstrate the facility of this amine to displace the solvent molecules from the coordination sphere. Yet, acetonitrile is activated even at large en:Ln^{3+} mole ratios as evidenced by the facile reactions (4 to 28 turnovers/mol Ln^{3+}·h) that occur (eq 2) when equimolar amounts of ethylenediamine and acetonitrile are heated at reflux in the presence of catalytic amounts of various Ln^{3+} ions (50:50:1 CH_3CN:en:Ln^{3+} mole ratio).

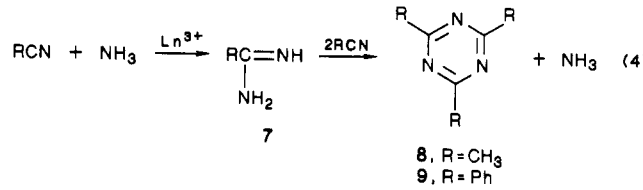
A preliminary study of the effects of the en:Ln^{3+} mole ratio on turnover rates using La^{3+} as the catalyst (Figure 1) reveals that the rate of the reaction (eq 2) is negligible when there is no free ethylenediamine in solution. For example, at a 4:1 en:La^{3+} mole ratio (2 mol % La^{3+}), there is less than 0.003 turnovers/h. Interestingly, at a 3:1 en:La^{3+} mole ratio, a ratio which allows for simultaneous ligation of both the nitrile and amine, the rate is even smaller (<0.001 turnovers/h). The latter observation reveals that a template mechanism involving a coordinated ethylenediamine molecule is not the primary route to the cyclic amidine. At mole ratios greater than 4:1, the turnover rate increases significantly (the amount of acetonitrile is kept constant) and passes through a maximum (ca. 4 turnovers/h) near a 50:50:1 CH_3CN:en:La^{3+} mole ratio. The increase in rate is consistent with a model that involves attack by free ethylenediamine on a coordinated nitrile molecule and indicates, at least initially, that increasing the amount of amine in the system does not effectively block nitrile activation. A decrease in turnover rate is not observed until the mole fraction of amine in the reaction mixture exceeds that of the nitrile.

We propose that nitrile activation under conditions that oppose nitrile coordination is due to the lability of Ln^{3+} complexes derived from N-donor ligands. The NMR spectra of the ethylenediamine–acetonitrile reaction mixtures at ambient temperatures reveal rapid exchange of amine molecules between the $Ln(en)_4^{3+}$ coordination sphere and bulk solution (mean lifetime, τ_m, of a coordinated ligand is less than 10^{-4} s[20]). During this exchange, following dissociation of a molecule of ethylenediamine from the primary coordination sphere, a nitrile molecule may slip into the inner sphere from the solvation sheath, whereupon it is activated and attacked by an incoming ethylenediamine molecule. In terms of this model, the turnover rate should depend on the availability of both the amine and nitrile in the solvation sheath of the $Ln(en)_4^{3+}$ chelate. Since increasing the availability of one reagent necessarily results in depletion of the other, it is not surprising that a maximum turnover rate is observed when the mole fractions of amine and nitrile in the bulk solution are equal.

Scheme I



Triazine Formation. As mentioned above a byproduct in reactions involving acetonitrile or benzonitrile was identified as triazine **8** or **9**, respectively. Although the yields of triazines were variable, increased yields of **8** or **9** were observed in all systems when the reactions were carried out in a closed vessel. This suggests that one route to triazine involves ammonia, which is also produced in the formation of bis amidines or pyrimidines. In the presence of the lanthanide catalyst, the ammonia may react with a nitrile to form **7**, which can react with additional nitrile ultimately leading to formation of the triazine. Indeed, we have confirmed[17] that Ln^{3+} ions catalyze a direct reaction between ammonia and nitriles in a closed reaction vessel. It is evident from eq 4 that the reaction



is autocatalytic in ammonia, thus providing a cycle for conversion of the nitrile to triazine. The variable yields of triazine observed when reactions are carried out open to the atmosphere are probably due, in part, to ammonia escaping from the reaction mixtures.

An alternative route to the triazines is shown in Scheme I. In this scheme, an initially formed amidine, A, may react sequentially with two nitrile molecules to produce triazine C and a molecule of the amine. This reaction creates a cycle autocatalytic in amine. This is the only plausible route to triazines for reactions involving benzonitrile and secondary amines, since ammonia is not a product in those reactions. Thus equimolar amounts of piperidine and benzonitrile at 105 °C using 2 mol % La^{3+} gave an equilibrium concentration (36% conversion) of intermediate A within 1 h, followed by slower conversion to **9** (40% yield after 4 days).

With primary amines, however, an additional route exists for A that leads to the N,N′-disubstituted amidine B.

(19) Forsberg, J. H.; Moeller, T. *Inorg. Chem.* **1969**, *8*, 889–892.
(20) For equal mole fractions of coordinated and free ethylenediamine (8:1 en:Ln^{3+} mole ratio), coalescence of the two resonance peaks requires that $\tau_m = 2^{1/2}/\pi\delta\nu$.[21] Values of $\delta\nu$ taken from ref 22. The upper limit of τ_m calculated for Dy^{3+}, which gave the largest isotropic shift for the methylene resonance.
(21) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228–1234.
(22) Birnbaum, E. R.; Stratton, S. *Inorg. Chem.* **1973**, *12*, 379–383.

This route competes with triazine formation. The conversion of A → B removes A from the triazine cycle, in effect quenching triazine formation. Except for the most sterically hindered amines, the conversion of A → B is rapid relative to the rate of formation of **C**. Thus triazines are generally not observed when reactions involving primary amines are carried out using stoichiometric amounts of reagents (1:2 nitrile:amine mole ratio). When reactions with primary amines are carried out using excess nitrile, however, the amount of A and B formed on depletion of the amine depends on the relative rates of formation of A vs. the conversion of A → B. Any factors which slow the conversion of A → B should increase the amount of A available for the cycle and result in increased yields of triazine. Indeed, the yields of triazine in the reactions of *n*-butylamine and *sec*-butylamine with acetonitrile using La^{3+} ion as the catalyst (100:40:1 CH_3CN:amine:La^{3+} mole ratio) were found to correlate with the steric requirements of the two amines. *n*-Butylamine, which was initially consumed at the rate of 14 mol amine/mol La^{3+}·h,[23] gave 4.7% conversion of nitrile to triazine before the amine was depleted from the system. In contrast, the reaction of the more sterically hindered *sec*-butylamine, (consumed initially at a rate less than 1 mol amine/mol La^{3+}·h[23]), gave 22% conversion of nitrile to triazine. In the case of *sec*-butylamine, the rate of conversion of A → B is significantly slower than the formation of A, thus A remains available for the triazine cycle after the amine is consumed.

For reactions involving primary diamines, A undergoes rapid intramolecular ring closure to form the cyclic amidines, effectively removing A from the triazine cycle. The fact that triazine formation may be observed in these systems after heating reaction mixtures containing excess nitrile for several days can be accounted for via the ammonia route. After 24 h, some ammonia remains in these reaction mixtures, presumably held in solution through coordination to the Ln^{3+} ion.

In the reactions of secondary amines with acetonitrile, the amidine intermediate (**5**) may react with additional acetonitrile to form either the pyrimidine (**6**) or triazine (**8**). In these instances, the rates of formation of **6** and **8** are competetive, and thus ca. equimolar amounts of the two compounds may be obtained.

Conclusions

Catalytic amounts of Ln^{3+} ions promote reactions between nitriles and amines, resulting in the formation of a variety of products. Reactions involving primary monoamines and diamines appear general and provide a viable synthetic route to amidines. The Ln^{3+} ions function as Lewis acids in these reactions, activating nitrile molecules through a primarily electrostatic interaction. We have established that Ln^{3+} ions activate nitriles even in the presence of amines that form thermodynamically stable Ln^{3+} complexes in nitrile solvents. Activation of nitriles under conditions that oppose nitrile coordination is attributed to the lability of Ln^{3+} complexes derived from N-donor ligands.

Experimental Section

Materials and Methods. Acetonitrile, benzonitrile, and propionitrile were distilled from P_4O_{10} or CaH_2 prior to use. The amines were heated at reflux over sodium for several hours and then distilled. Reagent grade trifluoromethanesulfonic acid (Aldrich) was used without further purification. NMR spectra were obtained on Varian HA 100 or EM-360 spectrometers using Me_4Si as the internal reference. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

$Ln(CF_3SO_3)_3$ (Ln = Y, La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Lu). The triflate salts were prepared by adding an excess of a lanthanide(III) oxide (99.9% purity) to an aqueous solution of trifluoromethanesulfonic acid (50% v/v) and heating at boiling for 30 min to 1 h. The mixture was filtered to remove the unreacted oxide. The water was then removed from the filtrate under reduced pressure. The resulting hydrate was dried by heating under vacuum at 180 to 200 °C for 48 h.

Syntheses. All manipulations were carried out in a glovebox under a nitrogen atmosphere to prevent contamination from atmospheric moisture.[12] The reaction vessels were removed from the glovebox and fitted with a drying tube filled with Aquasorb. Synthetic procedures, a listing of the compounds with their physical properties, and NMR spectral data are given below.

General Procedure for N,N'-Disubstituted Amidines. The *N,N'*-dialkylacetamidines **2a–f** were prepared by refluxing for 18 h a solution containing a 1:1 acetonitrile:amine mole ratio and $Ln(CF_3SO_3)_3$[24] (1 mol % relative to the nitrile or amine). *N,N'*-Dibutylproprioamidine (**2g**) and the *N,N'*-dialkylbenzamidines **2h,i** were prepared in a similar manner, except that stoichiometric amounts of nitrile and the amine (1:2 mole ratio) were used (the benzonitrile reactions were carried out at 100 °C). The liquid products were generally collected by direct vacuum distillation of the reaction mixtures (isolated yields = 50% to 70%). *N,N'*-Diphenylacetamidine (**2f**) was isolated by distilling the reaction mixture under vacuum to remove unreacted starting materials. The residue was recrystallized from benzene/hexane to give **2f** in 40% yield.

In general, attempts to isolate monoamidine intermediates by distillation of the reaction mixtures gave only starting materials. In the case of cyclohexylamine with benzonitrile, however, the *N*-cyclohexylbenzamidine (**1a**) crystallized from the reaction mixture and was purified by recrystallization from toluene/*n*-heptane.

The 2-methyl-, 2-ethyl-, and 2-phenyl-1,3-diazacycloalkenes **4a–i** derived from acetonitrile, propionitrile, and benzonitrile, respectively, were prepared by heating at reflux solutions containing 1:1 nitrile:amine mole ratios, with 1 mol % catalyst. (The benzonitrile systems were heated at 100 °C). The compounds were isolated in 70% to 95% yield by direct sublimation of the solid reaction mixtures or recrystallization of the mixture from toluene/hexanes. The compounds are very hygroscopic.

General Synthesis of 2,6-Dimethyl-4-substituted-pyrimidines. The pyrimidine derivatives **6b–f** were prepared by heating at reflux for 5 days a mixture containing acetonitrile and a secondary amine (4:1 mole ratio), with 10 mol % $La(CF_3SO_3)_3$ relative to the amine. The reaction involving dimethylamine was carried out at 80 °C in a stainless steel bomb, giving **6a**. Fractional distillation of the reaction mixtures under vacuum gave the pyrimidines in 35% to 45% yield. The monoamidines **5a–c**, which are intermediates in pyrimidine formation, can be obtained in ca. 30% yield by keeping the reaction mixtures at room temperature for 4 days, followed by vacuum distillation. Pyrimidine formation was not observed under these latter conditions.

Isolation of *s*-Triazines. Trimethyl-*s*-triazine (**8**) was isolated by sublimation of the residue obtained following distillation of several reaction mixtures (see Results and Discussion, Triazine Formation).

Trimethyl-*s*-triazine (8): white solid, mp 55–56 °C (lit.[25] mp 56 °C); NMR (100 MHz, CD_3CN) 2.48 (s). Anal. Calcd: C, 58.54; H, 7.32; N, 34.15. Found: C, 58.47; H, 7.26; N, 33.97.

Triphenyl-*s*-triazine (9) generally crystallized from reaction mixtures and was collected by filtration as a white solid, mp 231–233 °C (lit.[25] mp 235–236 °C). Anal. Calcd: C, 81.55; H, 4.85; N, 13.59. Found: C, 81.47; H, 4.94; N, 13.58.

Compounds Prepared. *N*-Cyclohexylbenzamidine (1a): white solid, mp 114–117 °C (lit.[26] mp 115–116 °C); NMR (100

(23) Rate of amine consumption, which was monitored by NMR, represents formation of a mixture of A and B.

(24) Although general catalytic activity was observed for the lanthanide series and Y^{3+}, most syntheses were carried out using the La^{3+} salt.

(25) Schaefer, F. C.; Hechenbleikner, I.; Peters, G. A.; Wystrach, V. P. *J. Am. Chem. Soc.* **1959**, *81*, 1466–1470.

(26) Cooper, F. C.; Partridge, M. W. *J. Chem. Soc.* **1953**, 255–260.

MHz, $CDCl_3$) δ 7.4 (m, 5 H), 4.34 (s, 2 H), 3.74 (br m, 1 H), 2.06–1.30 (br m, 10 H). Anal. Calcd: C, 77.18; H, 8.96; N, 13.84. Found: C, 77.18, H, 9.04; N, 13.86.

***N,N'*-Dipropylacetamidine (2a)**: colorless liquid, bp 49 °C (10 mmHg); NMR (100 MHz, CD_3CN) δ 4.43 (s, 1 H), 3.05 (t, 4 H), 1.73 (s, 3 H), 1.49 (m, 4 H), 0.88 (t, 6 H). Anal. Calcd: C, 67.60; H, 12.68; N, 19.72. Found: C, 67.60; H, 12.74; N, 19.62.

***N,N'*-Diisopropylacetamidine (2b)**: colorless liquid, bp 31–36 °C (5 mmHg); NMR (100 MHz, CD_3CN) δ 4.95 (s, 1 H), 3.75 (h, 2 H), 1.76 (s, 3 H), 1.50 (d, 12 H).

***N,N'*-Di-*n*-butylacetamidine (2c)**: colorless liquid, bp 82 °C (1 mmHg) (lit.[27] bp 117 °C (17 mmHg)); NMR (100 MHz, CD_3CN) δ 5.30 (s, 1 H), 3.15 (t, 4 H), 1.80 (s, 3 H), 1.48 (m, 4 H), 0.90 (t, 6 H). Anal. Calcd: C, 70.60; H, 12.94; N, 16.47. Found: C, 70.43, H, 13.21; N, 16.32.

***N,N'*-Diisobutylacetamidine (2d)**: colorless liquid, bp 50 °C (10 mmHg); NMR (100 MHz, CD_3CN) δ 4.50 (s, 1 H), 2.90 (d, 4 H), 1.75 (m, 2 H), 1.73 (s, 3 H), 0.87 (d, 12 H). Anal. Calcd: C, 70.60; H, 12.94; N, 16.47. Found: C, 70.76; H, 13.05; N, 16.31.

***N,N'*-Di-*sec*-butylacetamidine (2e)**: colorless liquid, bp 58 °C (5 mmHg); NMR (100 MHz, CD_3CN) δ 4.46 (s, 1 H), 3.48 (m, 2 H), 1.72 (s, 3 H), 1.36 (m, 4 H), 0.74–1.08 (m, 6 H). Anal. Calcd: C, 70.60; H, 12.94; N, 16.47. Found: C, 70.82; H, 12.94, N, 16.36.

***N,N'*-Diphenylacetamidine (2f)**: white solid, mp 131–132 °C (lit.[28] mp 131–132 °C); NMR (100 MHz, CD_3CN) δ 7.20 (m, 10 H), 5.71 (s, 1 H), 1.95 (s, 3 H). Anal. Calcd: C, 80.00; H, 6.67; N, 13.33. Found: C, 80.02; H, 6.69; N, 13.33.

***N,N'*-Di-*n*-butylpropionamidine (2g)**: colorless liquid; NMR (60 MHz, CCl_4) δ 4.13 (s, 1 H), 3.00 (t, 6 H), 1.93 (q, 4 H), 1.47–0.90 (m, 14 H). Anal. Calcd: C, 71.68; H, 13.12; N, 15.19. Found: C, 71.60; H, 13.20; N, 15.34.

***N,N'*-Di-*n*-propylbenzamidine (2h)**: colorless liquid–crystalline mixture bp 88–90 °C (1 mmHg) (lit.[29] mp 30 °C); NMR (60 MHz, CCl_4) δ 7.15 (m, 5 H), 4.30 (s, 1 H), 3.02 (t, 4 H), 1.52 (m, 4 H), 0.95 (m, 6 H).

***N,N'*-Di-*n*-butylbenzamidine (2i)**: colorless liquid (lit.[27] bp 99 °C (0.07 mmHg)); NMR (60 MHz, $CDCl_3$) δ 7.11 (m, 5 H), 4.76 (s, 1 H), 3.06 (t, 4 H), 1.40 (m, 8 H), 0.90 (m, 6 H). Anal. Calcd: C, 77.53; H, 10.41; N, 12.05. Found: C, 77.41; H, 10.26; N, 12.32.

2-Methyl-1,3-diazacyclopentene (4a): white solid, mp 102–103 °C (lit.[30] mp 103 °C); NMR (60 MHz, $CDCl_3$) δ 5.18 (s, 1 H), 3.50 (s, 4 H), 1.88 (s, 3 H). Anal. Calcd: C, 57.14; H, 9.52; N, 33.33. Found: C, 57.32; H, 9.48; N, 33.21.

2-Ethyl-1,3-diazacyclopentene (4b): white solid, mp 38–40 °C (lit.[30] mp 48 °C); NMR (60 MHz, CCl_4) δ 6.83 (s, 1 H), 3.43 (s, 4 H), 2.17 (q, 2 H), 1.10 (t, 3 H). Anal. Calcd: C, 61.18; H, 10.26; N, 28.54. Found: C, 61.45; H, 10.44; N, 28.30.

2-Phenyl-1,3-diazacyclopentene (4c): white solid, mp 98–100 °C (lit.[31] mp 101 °C); NMR (60, $CDCl_3$) δ 7.60 (m, 2 H), 7.13 (m, 3 H), 5.77 (s, 1 H), 3.48 (s, 4 H). Anal. Calcd: C, 73.97; H, 6.85; N, 19.18. Found: C, 73.98; H, 6.98; N, 19.04.

2-Methyl-1,3-diazacyclohexene (4d): white solid (lit.[32] mp 75 °C); NMR (100 MHz, CD_3CN) δ 7.91 (s, 1 H), 3.22 (t, 4 H), 1.94 (s, 3 H), 1.73 (quintet, 2 H). Anal. Calcd: C, 61.82; H, 10.27; N, 28.54. Found: C, 61.83; H, 10.36; N, 28.54.

2-Ethyl-1,3-diazacyclohexene (4e): white solid, mp 53–54 °C (lit.[31] mp 54–55 °C); NMR (60 MHz, $CD_3C(O)CD_3$) δ 3.20 (t, 4 H), 2.03 (q, 2 H), 1.67 (m, 2 H), 1.07 (t, 3 H). Anal. Calcd: C, 64.24; H, 10.78; N, 24.97. Found: C, 64.18; H, 10.81; N, 25.01.

2-Phenyl-1,3-diazacyclohexene (4f): white solid, mp 88–91 °C (lit.[32] mp 86–87 °C); NMR (60 MHz, CCl_4) 7.37 (m, 2 H), 7.07 (m, 3 H), 6.00 (s, 1 H), 3.07 (t, 4 H), 1.57 (m, 2 H). Anal. Calcd: C, 75.00; H, 7.50; N, 17.50. Found: C, 74.96; H, 7.62; N, 17.53.

2-Methyl-1,3-diazacycloheptene (4g): white solid, (lit.[33] mp 28–30 °C); NMR (100 MHz, CD_3CN) δ 7.40 (s, 1 H) 3.23 (m, 4 H), 1.91 (s, 3 H), 1.78 (m, 4 H). Anal. Calcd: C, 64.24; H, 10.97; N, 24.97. Found: C, 64.14; H, 10.84; N, 24.22.

2-Ethyl-1,3-diazacycloheptene (4h): colorless liquid, bp 115 °C (0.02 mmHg); NMR (60 MHz, $CDCl_3$) δ 7.45 (s, 1 H), 3.27 (m, 4 H), 2.17 (q, 2 H), 1.77 (m, 4 H), 1.13 (t, 3 H). Anal. Calcd: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.07; H, 11.83; N, 22.09.

2-Phenyl-1,3-diazacycloheptene (4i): white solid, mp 99–102 °C (lit.[34] mp 105 °C); NMR (60 MHz, $CDCl_3$) δ 7.57 (m, 2 H), 7.37 (m, 3 H), 4.13 (s, 1 H), 3.50 (m, 4 H), 1.83 (m, 4 H). Anal. Calcd: C, 75.86; H, 8.05; N, 16.09. Found: C, 75.58; H, 8.19; N, 15.95.

***N,N*-Dimethylacetamidine (5a)**: colorless liquid (100 MHz, neat) 6.24 (s, 1 H), 2.83 (s, 6 H), 1.98 (s, 3 H). Anal. Calcd: C, 55.77; H, 11.70; N, 32.52. Found: C, 55.53; H, 11.71; N, 32.13.

***N*-Pyrrolidinoacetamidine (5b)**: colorless liquid; NMR (100 MHz, CD_3CN) δ 6.51 (s, 1 H), 3.39 (m, 4 H), 2.13 (s, 3 H), 1.95 (m, 4 H). Anal. Calcd: C, 64.29; H, 10.71; N, 25.00. Found: C, 64.01; H, 10.76; N, 25.15.

***N,N*-Diethylacetamidine (5c)**: colorless liquid (lit.[27] bp 72 °C (25 mmHg)); NMR (100 MHz, CD_3CN) δ 6.35 (s, 1 H), 3.34 (q, 4 H), 2.16 (s, 3 H), 1.14 (t, 6 H). Anal. Calcd: C, 63.16; H, 12.28; N, 24.56. Found: C, 62.97; H, 12.50; N, 24.27.

4-(*N,N*-Dimethylamino)-2,6-dimethylpyrimidine (6a): colorless liquid (lit.[35] bp 128–130 °C (25 mmHg)); NMR (100 MHz, CCl_4) δ 5.96 (s, 1 H), 3.00 (s, 6 H), 2.36 (s, 3 H), 2.21 (s, 3 H).

4-(1-Pyrrolidinyl)-2,6-dimethylpyrimidine (6b): white solid; mp 58–59 °C; NMR (100 MHz, CD_3CN) δ 6.16 (s, 1 H), 3.54 (m, 4 H), 2.36 (s, 3 H), 2.20 (s, 3 H), 1.85 (m, 4 H). Anal. Calcd: C, 67.80; H, 8.47; N, 23.73. Found: C, 67.84; H, 8.42; N, 23.71.

4-(1-Piperidyl)-2,4-dimethylpyrimidine (6c): colorless liquid; bp 81 °C (0.2 mmHg); NMR (100 MHz, CCl_4) δ 6.03 (s, 1 H), 3.54 (m, 4 H), 2.37 (s, 3 H), 2.20 (s, 3 H), 1.60 (m, 4 H). Anal. Calcd: C, 69.08; H, 8.96; N, 21.98. Found: C, 69.08; H, 9.05; N, 21.80.

4-(1-Azacyclohept-1-yl)-2,6-dimethylpyrimidine (6d): colorless liquid; bp 110 °C (0.5 mmHg); NMR (100 MHz, CCl_4) δ 5.96 (s, 1 H), 3.58 (t, 4 H), 2.38 (s, 3 H), 2.21 (s, 3 H), 1.8–1.5 (br m, 8 H). Anal. Calcd: C, 70.20; H, 9.33; N, 20.47. Found: C, 70.24; H, 9.60; N, 20.26.

4-(4-Morpholinyl)-2,6-dimethylpyrimidine (6e): colorless liquid, bp 128–139 °C (0.2 mmHg); NMR (100 MHz, CD_3CN) δ 6.30 (s, 1 H), 3.67 (m, 4 H), 3.53 (m, 4 H), 2.36 (t, 3 H), 2.24 (s, 3 H). Anal. Calcd: C, 62.17; H, 7.77; N, 21.76. Found: C, 62.39; H, 7.88; N, 21.88.

4-(4-Methyl-1-piperazinyl)-2,6-dimethylpyrimidine (6f): colorless liquid, bp 115 °C (10 mmHg); NMR (100 MHz, CD_3CN) δ 6.27 (s, 1 H), 3.58 (t, 4 H), 2.36 (t + s, 7 H), 2.22 (s, 6 H). Anal. Calcd: C, 64.08; H, 8.74; N, 27.18. Found: C, 64.38; H, 8.86; N, 26.97.

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