3856 *Organometallics* **2009,** *28,* 3856–3862
DOI: 10.1021/om900120v

ORGANOMETALLICS
Article

Trisguanidinate Lanthanide Complexes: Syntheses, Structures, and Catalytic Activity for Mild Amidation of Aldehydes with Amines

Cunwei Qian,[†] Xingmin Zhang,[†] Junmei Li,[†] Fan Xu,[†] Yong Zhang,[†] and Qi Shen*[,†,‡]

[†]*Key Laboratory of Organic Synthesis of Jiangsu Province, Department of Chemistry and Chemical Engineering, Dushu Lake Campus, Suzhou University, Suzhou 215123, People's Republic of China, and* [‡]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China*

Received February 16, 2009

A series of new trisguanidinate lanthanide complexes including the first THF-solvated trisguanidinate lanthanum complexes were synthesized and fully characterized. The complexes were found to be efficient catalysts for amidation of aldehydes with amines under mild conditions with a wide scope of substrates including pyrrolidine, piperidine, and morpholine, and one of the intermediates for this process, lanthanum amido complex $\{[(^{i}PrN)CNH^{i}Pr(NC_6H_4p\text{-}Cl)]_2La(NHC_6H_5)\}_2\cdot C_7H_8$, was isolated.

Introduction

In recent years guanidinate ligands, an alternative to cyclopentadienyl anions, have attracted increasing attention in organolanthanide chemistry, as they have the advantages of tunable steric and electronic effects by variation of the substituents on the nitrogen atoms and varied binding modes due to the third nitrogen chelating ability.[1−4] Various lanthanide guanidinate derivatives have been synthesized including hydride,[5] amide,[6] alkylide,[7] and alkoxide[8] and found to be efficient catalysts in homogeneous catalyses such as polymerization of nonpolar and polar monomers, e.g., ethylene, propylene,[5b] styrene,[7c,8] methyl methacrylate,[6a] and lactones (lactide and ε-caprolactone),[6a,6c,8] as well as hydrosilylation of alkenes.[7f] As is well known, the guanidinate anions in these transformations act as ancillary ligands to stabilize the Ln−active group bond, and themselves are "inert". Recently, guanidinate anions have proven to serve not only as an inert ligand but also an active group in some cases. For example, trisguanidinate lanthanide complexes can be used as highly active catalysts for homo-polymerization of ε-caprolactone and trimethylene carbonate, as well as their copolymerization.[9] Very recently, the insertion of phenyl isocyanate into the lanthanide−guanidinate ligand bond has also been reported using the guanidinate complexes $[(C_5H_5)_2Ln(\mu\text{-}\eta^1\text{:}\eta^2\text{-}N{=}C(NMe_2)_2)]_2$ (Ln = Gd, Er) to yield the corresponding insertion products $[(C_5H_5)_2Ln(\mu\text{-}\eta^1\text{:}\eta^2\text{-}OCN{=}C(NMe_2)_2)NPh]_2$ (Ln = Gd, Er).[10] To assess further the reactivity of the lanthanide−guanidinate

*Corresponding author. E-mail: qshen@suda.edu.cn.

(1) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91.

(2) (a) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2003**, *22*, 387. (b) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 2839. (c) Ong, T. G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1. (d) Cotton, F. A.; Daniels, L. M.; Huang, P. L.; Murillo, C. *Inorg. Chem.* **2002**, *41*, 317. (e) Bazinet, P.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2003**, *42*, 6225.

(3) (a) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808. (b) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 2809. (c) Okamoto, S.; Livinghouse, T. *Organometallics* **2000**, *19*, 1449. (d) Thiruphthi, N.; Yap, G. P. A.; Richeson, D. S. *Chem. Commun.* **1999**, 2483. (e) Thiruphthi, N.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Dalton Trans.* **1999**, 2947. (f) Bailey, P. J.; Grant, K. J.; Mitchell, L. A.; Pace, S.; Parkin, A.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **1999**, 1887.

(4) (a) Aelits, S. L.; Coles, M. P.; Swenson, D. G.; Jordan, R. F. *Organometallics* **1998**, *17*, 3265. (b) Chivers, T.; Parvez, M.; Schatte, G. *J. Organomet. Chem.* **1998**, *550*, 213. (c) Maia, J. R. da S.; Gazard, P. A.; Kilner, M.; Batsanova, A. S. *J. Chem. Soc., Dalton Trans.* **1997**, 4625. (d) Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1997**, 3349. (e) Bailey, P. J.; Bone, S. F.; Mitchell, L. A.; Parsons, S.; Taylor, K. J.; Yellowlees, L. J. *Inorg. Chem.* **1997**, *36*, 867. (f) Bailey, P. J.; Mitchell, L. A.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2389. (g) Dinger, M. B.; Henderson, W. *Chem. Commun.* **1996**, 211. (h) Bailey, P. J.; Blake, A. L.; Kryszczuk, M.; Parsons, S.; Reed, D. *Chem. Commun.* **1995**, 1647.

(5) (a) Trifonov, A. A.; Fedorova, E. A.; Fukin, G. K.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2004**, 4396. (b) Trifonov, A. A.; Skvortsov, G. G.; Lyubov, D. M.; Skorodumova, N. A.; Fukin, G. K.; Baranov, E. V.; Glushakova, V. N. *Chem.—Eur. J.* **2006**, *12*, 5320. (c) Lyubov, D. M.; Fukin, G. K.; Trifonov, A. A. *Inorg. Chem.* **2007**, *46*, 11450.

(6) (a) Yao, Y.-M.; Luo, Y.-J.; Chen, J.-L.; Zhang, Z.-Q.; Shen, Q. *J. Organomet. Chem.* **2003**, *679*, 229. (b) Milanov, A.; Bhakta, R. Baunemann, A. *Inorg. Chem.* **2006**, *45*, 11008. (c) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923.

(7) (a) Zhou, Y.; Yapp, G. P. A.; Richeson, D. S. *Organometallics* **1998**, *17*, 4387. (b) Lu, Z.; Yapp, G. P. A.; Richeson, D. S. *Organometallics* **2001**, *20*, 706. (c) Luo, Y.-J; Yao, Y.-M.; Shen, Q. *Macromolecules* **2002**, *35*, 8670. (d) Luo, Y.-J; Yao, Y.-M.; Shen, Q.; Yu, K.-B.; Weng, L.-H. *Eur. J. Inorg. Chem.* **2003**, 318. (e) Trifonov, A. A.; Lyubov, D. M.; Fedorova, E. A.; Fukin, G. K.; Schumann, H.; MXhle, S.; Hummert, M.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2006**, 747. (f) Ge, S. Z.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 3131.

(8) (a) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923. (b) Ajellal, N.; Lyubov, D. M.; Sinenkov, M. A. *Chem.—Eur. J.* **2008**, *14*, 5440.

(9) (a) Chen, J.-L.; Yao, Y.-M.; Luo, Y.; Zhou, L.-Y.; Zhang, Y.; Shen, Q. *J. Organomet. Chem.* **2004**, *689*, 1019. (b) Zhou, L.-Y.; Yao, Y.-M.; Zhang, Y.; Xue, M.-Q.; Chen, J.-L.; Shen, Q. *Eur. J. Inorg. Chem.* **2004**, *10*, 2167. (c) Zhou, L.-Y; Sun, H.-M.; Chen, J.-L.; Yao, Y.-M.; Shen, Q. *J. Polym. Sci.: Part A* **2005**, *43*, 1778.

(10) Zhang, J.; Zhou, X.-G.; Cai, R.-F.; Weng, L.-H. *Inorg. Chem.* **2005**, *44*, 716.

 Published on Web 05/20/2009

Table 1. Details of the Crystallographic Data of 1, 2, 6, and 11

	1	2	6	11
empirical formula	$C_{43}H_{65}Cl_3La$ N_9O	$C_{46}H_{75}LaN_9$ N_9O	$C_{39}H_{96}N_9Nd$ Si_6	$C_{71}H_{96}Cl_4La_2$ N_{14}
fw	969.30	909.06	1004.03	1565.24
temp (K)	223(2)	223(2)	213(2)	223(2)
λ (Å)	0.71075	0.71075	0.71075	0.71075
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P\bar{1}$
a (Å)	10.463(2)	22.072(6)	14.607(2)	10.6450(19)
b (Å)	13.118(2)	10.114(3)	23.159(3)	13.7826(19)
c (Å)	17.912(3)	44.341(12)	17.262(3)	15.599(3)
α (deg)	80.505(4)	90	90.00	66.180(6)
β (deg)	89.947(4)	94.846(3)	97.433(2)	89.372(7)
γ (deg)	86.812(5)	90	90.00	69.433(6)
V (Å^3)	2421.0(8)	9863(5)	5790.5(14)	1937.2(5)
Z	2	8	4	1
D_{calc} (g cm^{-3})	1.328	1.224	1.152	1.342
μ (mm^{-1})	1.089	0.907	1.053	1.273
$F(000)$	1002	3832	2148	802
θ range (deg)	3.00 to 25.5	3.14 to 25.5	3.00 to 27.5	3.00 to 27.5
no. of rflns	17 336	15 178	41 121	13 983
no. of unique rflns	8828	7586	10 714	7060
R_{int}	0.0384	0.0583	0.0620	0.0401
variables	531	507	527	380
$R[I > 2\sigma(I)]$	0.0409	0.0668	0.0620	0.0535
wR_2	0.0841	0.1615	0.0594	0.1130

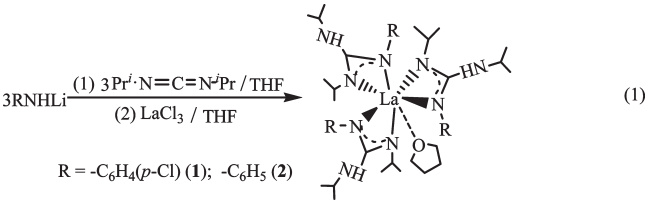
Table 2. Selected Bond Distances (Å) and Angles (deg) for 1 and 6

	1	6		1	6
Bond Distances					
Ln1−N1	2.549(3)	2.507(4)	Ln1−N8	2.592(3)	2.463(4)
Ln1−N2	2.558(3)	2.494(4)	N1−C1	1.348(4)	1.335(6)
Ln1−N4	2.532(3)	2.496(4)	N2−C1	1.330(4)	1.324(6)
Ln1−N5	2.525(3)	2.528(4)	N3−C1	1.377(4)	1.450(7)
Ln1−N7	2.547(3)	2.494(4)	La1−O1	2.585(3)	
Bond Angles					
N1−Ln1−N2	52.67(9)	53.47(13)	N7-Ln1-N8	51.66(9)	53.68(14)
N4−Ln1−N5	53.37(10)	53.54(14)			

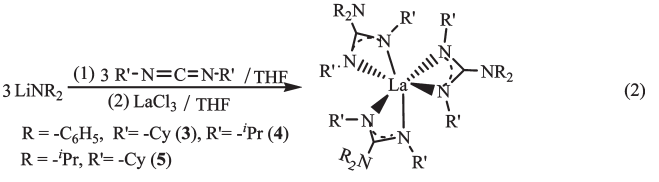
bond, we synthesized a series of guanidinate lanthanide complexes with various central metals and guanidinate anions and examined their catalytic activity for amidation of aldehydes with amines. It was found that trisguanidinate lanthanide complexes are efficient catalysts for amidation reaction of aldehydes with amines with a wide scope of amines including secondary cyclic amines. One of the intermediates in the present transformation, bisguanidinate lanthanum amido complex $\{[(^i\text{PrN})\ CNH^i\text{Pr}(NC_6H_4p\text{-Cl})]_2\text{La}(NHC_6H_5)\}_2\cdot C_7H_8$, was also isolated and fully characterized. Here we would like to report the results.

Results and Discussion

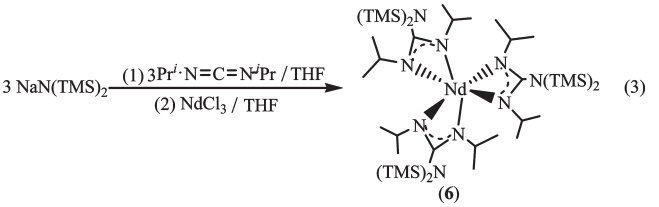
Synthesis and Characterization of Trisguanidinate Lanthanide Complexes. First, we tried to prepare a series of trisguanidinate lanthanum complexes, as this class of lanthanum complex has not been reported until now. Treatment of anhydrous $LaCl_3$ with 3 equiv of lithium salts $Li[(^i\text{PrN})CNHR(N^i\text{Pr})]$ (R = $-C_6H_4p$-Cl and $-C_6H_5$), which were freshly prepared in situ by the reaction of Li[NHAr] with *N*, *N*′-diisopropylcarbodiimide in THF, after workup, afforded the corresponding asymmetric guanidinate lanthanum complexes of **1** and **2** via a 1,3-H shift as shown in eq 1. The formation of asymmetric guanidinate complexes is expected due to the relative stability of the guanidinates complexes formed via rearrangement. The same situation has also been found in the literature.[11]



(1)



(2)



(3)

The same reaction with various lithium guanidinates yielded the trisguanidinate lanthanum complexes **3**, **4**, and **5** in good yields (eq 2).

The reaction of anhydrous $NdCl_3$ with $Na[(TMS)_2NC(N^i\text{Pr}_2)_2]$ in a 1:3 molar ratio was then conducted in THF. Upon crystallization blue crystals were isolated and characterized to be complex **6** (eq 3).

All complexes were characterized by elemental analysis and IR spectroscopy, and ^{1}H NMR for La complexes. The IR spectra of these complexes exhibit the strong absorptions in

(11) Zhang, J.; Cai, R.-F.; Weng, L.-H.; Zhou, X.-G. *Organometallics* **2004**, *23*, 3303.

the range 1600−1640 cm^{-1}, which are consistent with a partial C═N double-bond character, indicting the π-electrons being delocalized within the N−C−N linkage.

Complexes **1**−**6** are sensitive to air and moisture. They have good solubility in THF and even in toluene.

The structures of complexes **1**, **2**, and **6** were further determined by single-crystal X-ray analysis. The details for crystal data collections are given in Table 1, and selected bond lengths and angles for complexes **1** and **6** are listed in Table 2. Complex **2** has the same structure motif as that of complex **1** (see Supporting Information), but no detailed bond angles and lengths could be obtained, as the data were poor. Thus, only the crystal structures of complexes **1** and **6** are shown in Figures 1 and 2, respectively. As shown in Figure 1, complex **1** is a THF-solvated monomer, in which the central metal La ion is ligated by six nitrogen atoms of three chelating guanidinate ligands and one oxygen atom from a coordinated THF molecule to form a capped octahedron. To our best knowledge, this is the first example for a THF-solvated trisguanidinate lanthanide complex. The allowance of a coordinated THF molecule in the coordination sphere around the central metal in this complex may be attributed to the large ionic radius of La and less bulky guanidate ligand, which provides the space for the coordination of a THF molecule. Complex **6** is an unsolvated monomer (Figure 2). The central metal Nd ion is coordinated by six nitrogen atoms from three ligands to form an octahedron. The solid state structure of complex **6** is analogous to those for the known homoleptic trisguanidinate lanthanide complexes.[9] The four-membered LnNCN rings in complexes **1** and **6** are essentially planar. The average bond angle of N−Ln−N, 52.60(9)°, in complex **1** is comparable with 53.56(14)° in complex **6**. These values are also compared to the reported 54.32° in $[(^{i}Pr_2N)C(N^{i}Pr)_2]_3Nd$.[9a] The average Ln−N bond lengths, 2.550(3) Å for complex **1** and 2.497(4) Å for complex **6**, are comparable when the difference in ion radius between La and Nd metals is considered.[12] The values are also in the range for the published analogues.[9] The La−O bond length is 2.585(3) Å, which is typical.

Catalytic Activity of Trisguanidinate Lanthanide Complexes for Amidation of Aldehydes with Amines. The synthesis of aromatic and aliphatic acylamides is of significant importance in organic synthesis, as acylamides are an essential motif in polymers, natural products, and pharmaceuticals.[13] A direct amidation of aldehydes with amines is the most desired approach to acylamides due to economical and available starting materials. Very recently, pioneering work by Seo and Marks showed that homoleptic lanthanide amides $Ln[N(SiMe_3)_2]_3$ are efficient catalysts for amidation of aldehydes with amines under mild conditions without the use of a peroxide.[14] To explore the reactivity of trisguanidinate lanthanide complexes, amidation of aldehydes with amines was tried using these guanidinate complexes.

To address the influence of lanthanide metals and guanidinate ligands on the activity of trisguanidinate lanthanide complexes, the following known complexes (Scheme 1) were also synthesized according to the literature.[6a9a,9b,]

With the complexes in hand, the catalytic activity of complexes **1**−**10** for the reaction of benzaldehyde **1a** with

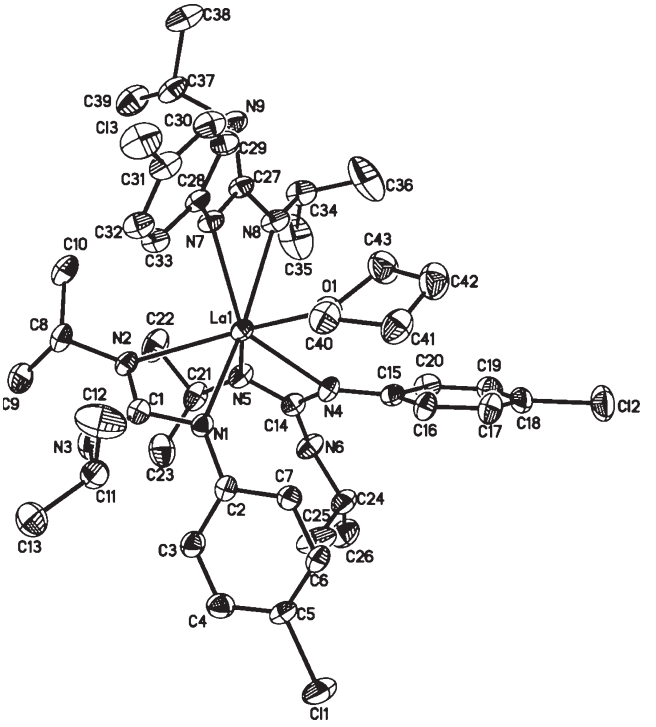


Figure 1. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level.

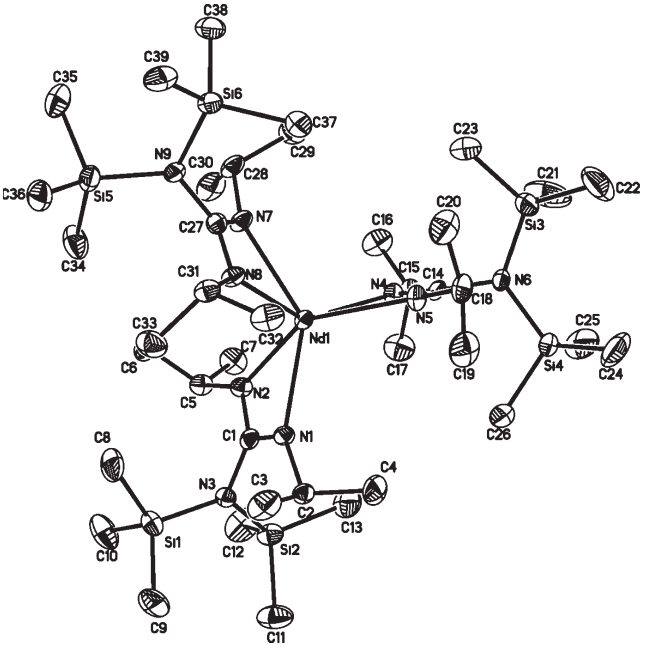
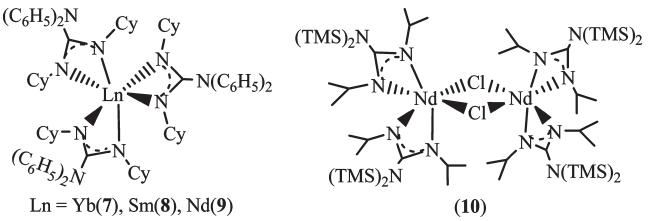


Figure 2. Molecular structure of complex **6**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level.

Scheme 1



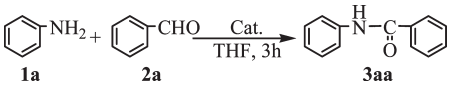
Ln = Yb(**7**), Sm(**8**), Nd(**9**) (**10**)

(12) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(13) Humphrey, J. M.; Chanberlin, A. R. *Chem. Rev.* **1997**, *97*, 2243.
(14) Seo, S.; Marks, T. J. *Org. Lett.* **2008**, *10*, 317.

aniline **2a** was examined at 25 °C. As shown in Table 3, complexes **1**−**9** can serve as the catalysts for this transformation, yielding the desired product **3aa** in moderate to excellent yields after 3 h. However, bisguanidinate neodymium chloride **10** is not so activel; the same reaction with **10** afforded **3aa** in only 10% yield. The much higher yield obtained with the corresponding homoleptic complex **6** compared to that obtained with **10** (Table 3, entries 11 and 12) may be attributed to the third Nd−guanidate bond being activated by the other two guanidinate ligands around the Nd metal. The substituents on the guanidinate anions exert an influence on the activity. For the same La complexes the active sequence for guanidinate anions is N^iPr_2 < NHC_6H_5 < $N(C_6H_5)_2$ < NHC_6H_{4p}-Clπ (Table 3, entries 6−10) and Cy < ^{i}Pr (Table 3, entries 6 and 8). The activity of the central metals follows the trend Yb < Sm < Nd < La (Table 3, entries 3−6). The same activity trend is also found for the Tishchenko reaction with homoleptic lanthanide amides.[15]

With optimized reaction conditions (Table 3, entry 10), we then screened the scope of amidation with selected aldehydes and amines. The results are listed in Table 4. All the reactions proceeded smoothly to afford the corresponding acylamides in good to excellent yields. The aromatic aldehydes with an electron-withdrawing group at the *p*-position on the phenyl

Table 3. Amidation of a Benzaldehyde 1a with an Aniline 2a Catalyzed by Complexes 1−10[a]

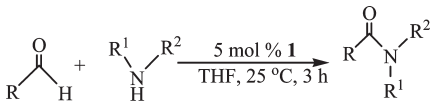


1a **2a** **3aa**

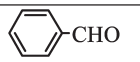
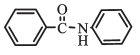
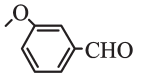
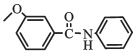
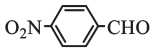
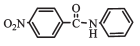
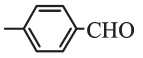
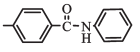
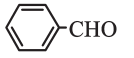
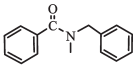
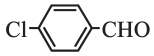
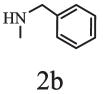
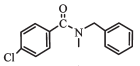
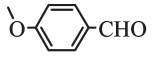
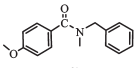
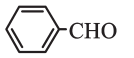
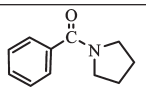
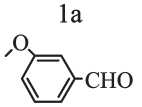
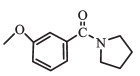
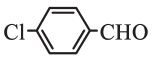
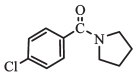
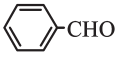
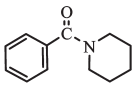
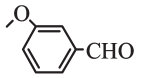
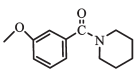
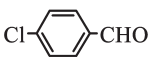
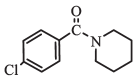
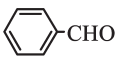
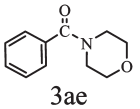
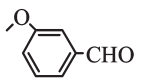
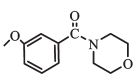
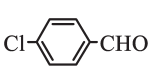
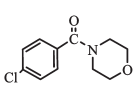
entry	cat. (amt (mol %))	yield (%)[b]	entry	cat. (amt (mol %))	yield (%)[b]
1	**8** (1%)	28	8	**4** (5%)	85
2	**8** (2%)	42	9	**2** (5%)	77
3	**8** (5%)	70	10	**1** (5%)	89
4	**7** (5%)	60	11	**6** (5%)	50
5	**9** (5%)	76	12	**10** (5%)	10
6	**3** (5%)	81	13	**11** (2.5%)	90
7	**5** (5%)	72			

[a] Starting amine, aldehyde, and catalyst concentrations are 0.02 mmol/mL in each experiment; amine/aldehyde = 1:3. [b] Isolated yields based on aniline.

Table 4. Catalytic Amidation of Various Aldehydes with Amines[a]

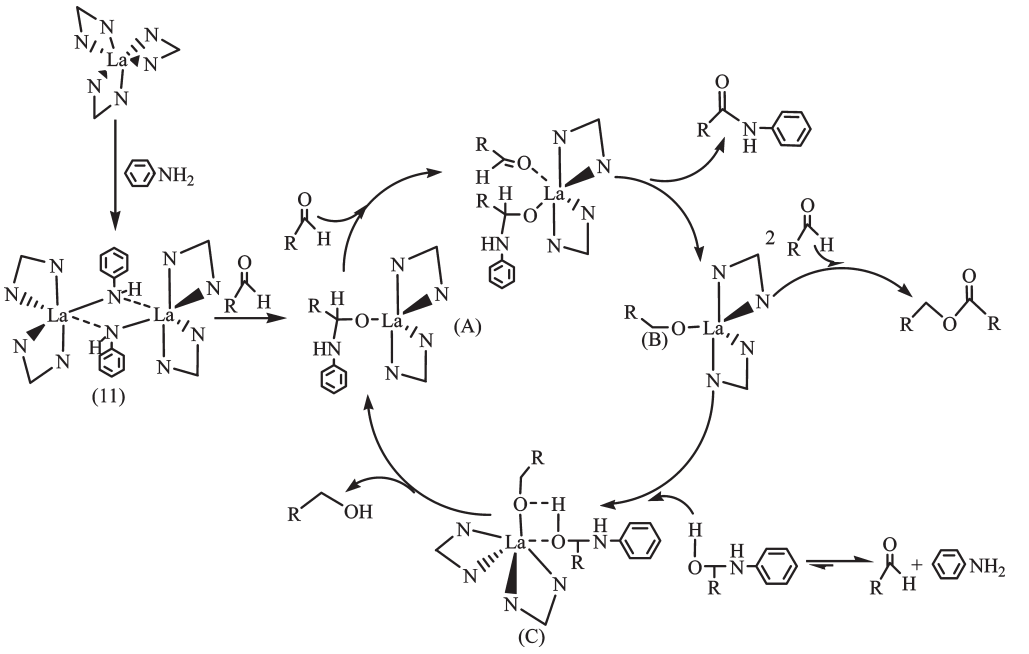


1 **2** **3**

entry	aldehyde	amine	acylamide	yield(%)[b]
1	 **1a**	 **2a**	 **3aa**	88
2	 **1b**		 **3ba**	90
3	 **1c**		 **3ca**	86
4	 **1d**		 **3da**	61
5	 **1a**		 **3ab**	93
6	 **1e**	 **2b**	 **3eb**	93
7	 **1f**		 **3fb**	75
8	 **1a**	 **2c**	 **3ac**	62
9	 **1b**		 **3bc**	81
10	 **1e**		 **3ec**	79
11	 **1a**		 **3ad**	92
12	 **1b**	 **2d**	 **3bd**	95
13	 **1e**		 **3ed**	93
14	 **1a**		 **3ae**	83
15	 **1b**	 **2e**	 **3be**	91
16	 **1e**		 **3ee**	91

[a] Starting amine, aldehyde, and catalyst concentrations are identical in each experiment; amine/aldehyde = 1:3. [b] Isolated yields based on amine.

Scheme 2. Proposed Catalytic Cycle for Amidation of Aldehydes with Amines Catalyzed by Trisguanidine Lanthanide



ring give higher yields relative to the aldehydes with an electron-donating group. The reaction with a primary aromatic amine (aniline) proceeded smoothly to give the acylamide in good yields (Table 4, entries 1−4). It is worth noting that the amidation of aldehydes with secondary cyclic amines such as pyrrolidine, piperidine, and morpholine proceeded well with the present catalyst to afford the corresponding acylamides in good to excellent yields (Table 4, entries 8−16). The reactions of aldehydes with a pyrrolidine give the products in 62−81% yields. The value (62%) for the reaction of **1a** with pyrrolidine is much higher than that obtained by homoleptic lanthanide amides.[14]

According to the catalytic cycle proposed by Seo and Marks,[13] the two byproducts, alcohol and ester, should be produced in this process. We have detected the two byproducts by ^{1}H NMR (Supporting Information). The Tishchenko reaction of benzaldehyde was further examined by use of complex **1** as the catalyst. The reaction at room temperature using 1.7 mol % of **1** afforded the ester in 73% yield after 3 h, indicating triguanidinate lanthanide complexes can also serve as catalysts for the Tishchenko reaction. Therefore, it is reasonable to propose a mechanism similar to that suggested by Seo and Marks for the amidation of aldehydes with amines by trisguanidinate lanthanide complexes. In our case the triguanidinate lanthanide complex reacts first with an amine to afford the guanidinate amido complex **11**, which then reacts with an aldehyde to yield the active species **A**. **A** reacts further with a second aldehyde to produce an acylamide and to release **B** (Scheme 2).

To further confirm the suggestion, the isolation of amido complex **11** was tried. Treatment of complex **1** with aniline in a 1:20 molar ratio, which is the same molar ratio for the catalytic reaction, in THF, after workup, afforded white crystals suitable for X-ray analysis in 40% yield. The crystals were further characterized to be the expected amido complex

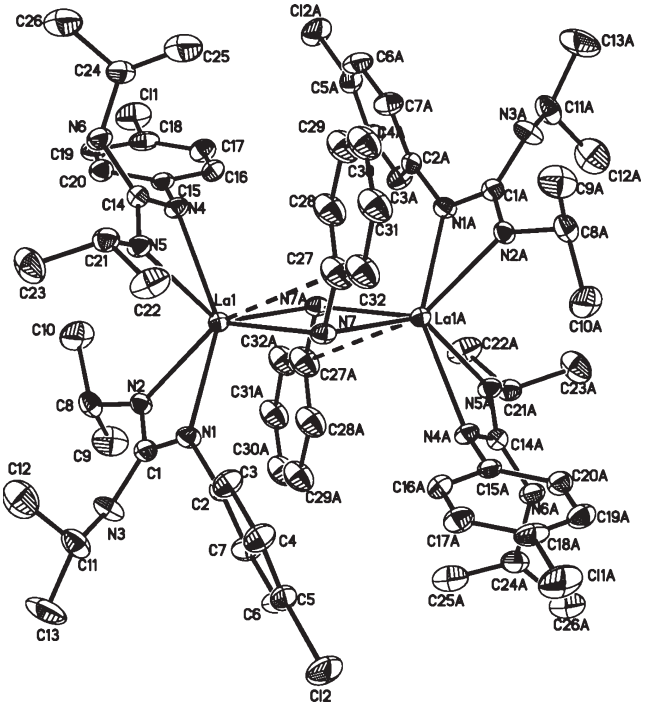


Figure 3. Molecular structure of complex **11**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level.

11. The molecular structure of **11** is shown in Figure 3. The details for crystal data collection are shown in Table 1, and selected bond lengths and angles for complex **11** are listed in Table 5. Complex **11** is a central symmetric dimer linked by two symmetric nitrogen bridges. Each La metal ion is ligated by four nitrogen atoms from two guanidinate ligands and two bridging-nitrogen atoms in an octahedral arrangement. The two four-membered LaNCN rings are essentially planar. The average La−N (guanidinate ligand) bond length is 2.527(4) Å, which is comparable with that in **1** when the difference in ionic radius for the La ions with different

(15) (a) Berberich, H.; Roesky, P. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 1569. (b) Zuyls, A.; Roesky, P. W.; Deacon, G. B.; Konstas, K.; Junk, P. C. *Eur. J. Org. Chem.* **2008**, 693.

Table 5. Selected Bond Distances (Å) and Angles (deg) for 11

Bond Distance			
La1−N1	2.553(4)	La1−N2	2.478(4)
La1−N4	2.580(4)	La1−N5	2.488(4)
La1−N7	2.538(4)	N7−La1#1	2.587(4)
N1−C1	1.353(6)	N2−C1	1.311(6)
N3−C1	1.376(6)	La1−C27	3.035(7)
Bond Angles			
N1−La1−N2	53.05(13)	N4−La1−N5	52.61(13)
C14−N5−La1	99.0(3)	La1 − N7 − C27	94.5(3)

coordination number is considered.[12] The length of La−μ^2-N bond is 2.538(4) Å, which is longer than 2.458(9) Å in $Cp_2La(NPh_2)_2Li$.[16] This is reasonable, because a bridging Ln−N bond length is normally longer than that of a terminal Ln−N bond. It was noticed that the distance of La to C_{ipso} (an aromatic carbon atom on the aniline group), La1−C27, is 3.035(7) Å. Such a short distance and the small angle La−N7−C27 (94.5°) indicate the presence of a weak bonding of the La−C (aromatic carbon) bond. The bond distance is in the same range as those found in the other known complexes with a lanthanide metal−π-arene interaction. The value can also be compared to 2.75 Å of Y−C_{ipso} in $\{[6,6'\text{-}Me_2\text{-}(C_6H_3)_2](2,2'\text{-}NSiMe_3^tBu)_2\}YCl(THF)_2$[17a] and 2.841 Å of Nd−$C_{ipso}$ in $[\mu^2\text{-}p\text{-}(Me_2SiN)_2C_6H_4]Nd(\mu^2\text{-}Cl)(THF)_4\cdot 2PhMe$[17b] when the differences in ionic radius between La and Y, and La and Nd were considered, respectively. The amido complex **11** can also serve as the precatalyst for amidation of aldehydes with amines. The reaction of **1a** with **2a** using 2.5 mol % **11** afforded the acylamide **3aa** in 90% yield, which is almost the same as that obtained by complex **1** (Table 2, entry 10). The result demonstrates that amido complex **11** formed in situ is one of the intermediates in the amidation catalyzed by a trisguanidinate lanthanide complex.

Conclusion

A series of asymmetric and symmetric trisguanidinate lanthanide complexes were synthesized, and the first THF-solvated trisguanidinate lanthanum complex was structurally characterized. All these trisguanidinate complexes serve as efficient catalysts for amidation of aldehydes with amines including secondary cyclic amines. The isolation of a bisguanidinate lanthanum amido complex demonstrates that the reaction of a trisguanidinate lanthanum complex with an amine is the first step in the present process. Further study on the reactivity of the Ln−guanidinate ligand bond is ongoing in our laboratory.

Experimental Section

All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry argon atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl prior to use. C_6D_6 was distilled under argon from Na/K alloy. *N*,*N*′-Diisopropylcarbodiimide was used without further purification. All aldehydes and amines were predried, recrystallized, or distilled before use. Complexes **7**−**10** was synthesized according to the literature.[6a,9] Melting points were determined in sealed Ar-filled capillary tube and are uncorrected. ^{1}H NMR spectra were recorded on a Unity Inova-400 spectrometer. Chemical shifts (δ) are reported in ppm.

(16) Guan, J.-W.; Jin, S.-C.; Lin, Y.-H.; Shen, Q. *Organometallics* **1992**, *11*, 2483.

Synthesis of $[^i\text{PrNHCN}^i\text{Pr}(NC_6H_4p\text{-}Cl)]_3La\cdot THF$ (1). A Schlenk flask was charged with *p*-$ClC_6H_4NH_2$ (1.905 g, 15.0 mmol), THF (30 mL), and a stir bar. The solution was cooled to 0 °C, and *n*-BuLi (8.6 mL, 15.0 mmol, 1.75 M in hexane) was added. The solution was then slowly warmed to room temperature and stirred for 1 h. To this solution was added *N*,*N*′-diisopropylcarbodiimide (2.4 mL, 15.3 mmol) at 0 °C. The resulting solution was slowly warmed to room temperature, stirred for 1 h, and then added slowly to a pale gray slurry of $LaCl_3$ (1.22 g, 5.0 mmol) in 20 mL of THF. The color of the solution immediately changed to yellow. The resulting solution was then stirred for another 24 h and evaporated to dryness in vacuo. The residue was extracted with Et_2O, and LiCl was removed by centrifugation. The extracts were concentrated and cooled to 0 °C for crystallization, to afford colorless crystals. Yield: 2.47 g (51%) Mp: 185−186 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.23−7.21 (d, 6H, *m*-H-Ph), 6.93−6.91 (m, 6H, *o*-H-Ph), 3.66−3.58 (m, 7H, α-H-THF and N-H) 3.35−3.33 (m, 6H, H-C(N)Me_2), 1.43−1.46 (m, 4H, β-H, THF), 0.90−0.88 (d, 36H, CH_3) ppm. Anal. Calcd for $C_{43}H_{65}Cl_3LaN_9O$ (969.30): C, 53.28; H, 6.76; N, 13.01; La, 14.33. Found: C, 53.05; H,6.08; N, 13.51; La, 15.00. IR (KBr pellet): 3316 (s), 3076 (s), 2973 (s), 2925 (s), 2870 (s), 1640 (s), 1580 (s), 1520 (s), 1416 (s), 1365 (s), 1327 (s), 1162 (m), 1123 (m), 1034 (m), 939 (m) cm^{-1}.

Synthesis of $[^i\text{PrNHCN}^i\text{Pr}(NC_6H_5)]_3La\cdot THF\cdot 1/2C_6H_{14}$ (2). Following the procedure similar to that for the synthesis of **1**, complex $Li[^i\text{PrNHCN}^i\text{Pr}(NC_6H_5)]$ (15.0 mmol), which was formed in situ by the reaction of $LiNHC_6H_5$ with ^{i}PrN=C=N^{i}Pr, reacted with $LaCl_3$ (1.22 g, 5.0 mmol) in THF (60 mL) to yield colorless crystals (**2**) upon crystallization from a mixture of ether and *n*-hexane. Yield: 2.45 g (54%). Mp: 138−139 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.33−7.29 (t, 6H, *m*-H-C_6H_5−), 7.24−7.21 (m, 6H, *o*-H, −C_6H_5), 6.88−6.84 (t, 3H, *p*-H-C_6H_5−), 3.57−3.37 (brm, 7H, α-H-THF and H-N), 3.35−3.33 (m, 6H, H-C(N)Me_2), 1.28−0.88 (d, 47H, CH_3, −CH_2−, overlap) ppm. Anal. Calcd for $C_{46}H_{75}LaN_9O$ (909.06): C, 60.71; N, 13.85; H, 8.42; La,15.26. Found: C, 59.98; N, 14.99; H, 7.94; La, 15.84. IR (KBr pellet): 3298 (s), 3072 (s), 2967 (s), 2930 (s), 2868 (s), 1646(s), 1619 (s), 1591 (s), 1511 (s), 1441 (s), 1363 (s), 1326 (s), 1164 (m), 1123 (m), 1067 (m), 952 (m), 865 (m), 694 (m) cm^{-1}.

Synthesis of $[(CyN)_2CN(C_6H_5)_2]_3La\cdot 2C_7H_8$ (3). Following the procedure for the synthesis of **2**, the reaction of $Li[(CyN)_2C(N(C_6H_5)_2)]$ (15.0 mmol) in THF (20 mL) with $LaCl_3$ (1.22 g, 5.0 mmol) in THF (60 mL) afforded **3** as colorless crystals after crystallization in toluene. Yield: 4.41 g (61%). Mp: 156−158 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.28−6.86 (m, 40H, Ph), 3.63−3.33 (m, 6H, unique H-Cy), 2.11 (s, 6H, CH_3), 1.69−0.84 (m, 60H, C_6H_{10}) ppm. Anal. Calcd for $C_{89}H_{112}N_9La$(1445.81): C, 73.88; N, 8.71; H, 7.80; La, 9.60. Found: C, 73.25; H, 7.66; La, 9.55; N, 8.92. IR (KBr pellet): 3440 (s), 3240 (m), 3230 (m), 2944 (m), 1628 (m), 1400 (w), 1267 (m), 1017 (s), 1072 (s), 908 (w), 870 (w), 800 (s) cm^{-1}.

Synthesis of $[(^i\text{PrN})_2CN(C_6H_5)_2]_3La$ (4). Following the procedure for the synthesis of **2**, the reaction of $Li[(^i\text{PrN})_2C(N(C_6H_5)_2)]$ (15.0 mmol) in THF (20 mL) with $LaCl_3$ (1.22 g, 5.0 mmol) in THF (60 mL) afforded **4** as colorless crystals upon crystallization from toluene. Yield: 2.60 g (51%). Mp: 142−143 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.39−6.89 (m, 30H, Ph-H), 3. 97−3.91 (m, 6H, $CHMe_2$), 1.44−1.18 (m, 36H, CH_3) ppm. Anal. Calcd for $C_{57}H_{72}N_9La$ (1021.5): C, 66.98; H, 7.10; La, 13.59; N, 12.33. Found: C, 66.02; H, 7.24; La, 14.05; N, 12.04. IR (KBr pellet): 3056 (m), 2983 (m), 1640 (s), 1577 (m), 1498 (s), 1452 (m), 1384 (m), 1311 (m), 1243 (m), 1177 (m), 1056 (w), 753 (m) cm^{-1}.

Synthesis of $[(CyN)_2CN^i\text{Pr}_2]_3La$ (5). Following the procedure for the synthesis of **2**, the reaction of $Li[(CyN)_2CN^i\text{Pr}_2]$ (15.0 mmol) in THF (20 mL) with $LaCl_3$ (1.22 g, 5.0 mmol) in THF (60 mL) afforded **5** as colorless crystals. Yield: 2.96 g (56%). Mp: 218−219 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 3.60−3.44

(m, 12H, CH, overlap), 2.13−1.28 (m, 60H, C_6H_{10}), 1.16−0.93 (m, 36H, CH_3) ppm. Anal. Calcd for $C_{57}H_{108}N_9La$ (1058.43): C, 64.68; N, 11.91; H, 10.28; La, 13.12. Found: C, 64.47; H, 10.01; N, 10.62; La, 13.01. IR (KBr pellet): 3185 (m), 2928 (s), 2851 (s), 1631 (s), 1550 (s), 1450 (s),1338 (m), 1246 (m), 1149 (m), 1099 (m), 885 (m) cm^{-1}.

Synthesis of $[(^iPrN)_2CN(TMS)_2]_3Nd$ (6). As described for **2**, a solution of $Na[(^iPrN)_2CN(TMS)_2]$ (15.0 mmol) was added to a suspension of $NdCl_3$ (1.30 g, 5.0 mmol) in 60 mL of THF. Blue-purple crystals (**6**) were isolated from dimethoxyethane. Yield: 3.3 g (66%). Mp: 231−232 °C. Anal. Calcd for $C_{39}H_{96}N_9NdSi_6$ (1004.03): C, 46.66; N, 12.56; H, 9.64; Nd, 14.37. Found: C, 45.74; H, 8.94; N, 11.99; Nd, 14.34. IR (KBr pellet): 2969 (s), 2870 (s), 1622 (s), 1455 (s), 1387 (s), 1327 (s), 1162 (m), 1123 (m), 1034 (m), 939 (m), 860 (m), 698 (m), 575 (m) cm^{-1}.

Synthesis of $\{[^iPrNHCN^iPr(NC_6H_4p\text{-}Cl)]_2La(C_6H_5NH)\}_2 \cdot C_7H_8$ (11). A Schlenk flask was charged with $[^iPrNHCN^iPr(NC_6H_4p\text{-}Cl)]_3La \cdot THF$ (2.9 g, 3.0 mmol), $C_6H_4NH_2$ (6 mL, 60 mmol), THF (30 mL), and a stir bar. The solution was stirred for 3 h at room temperature and evaporated to dryness in vacuo. Toluene (20 mL) was added to the residue and then heated until the solution became clear. The solution was cooled to room temperature for crystallization, and colorless crystals (**11**) were isolated. Yield: 0.94 g (40%). Mp: 206−207 °C. ^1H NMR (400 MHz, C_6D_6): δ 7.27−6.36 (m, 31H, H-Ph, overlap), 4.11−4.06 (s, 2H, HN-Ph); 3.46−3.19 (br m, 12H, $CHMe_2$ and H-N); 2.13 (S, 3H, CH_3-Ph); 1.13−0.86 (m, 48H, CH_3) ppm. Anal. Calcd for $C_{71}H_{96}Cl_4La_2N_{14}$ (1565.24): C, 54.48; N, 12.53; H, 6.18; La, 17.75. Found: C, 54.98; N, 12.40; H, 6.00; La, 18.25. IR (KBr pellet): 3489(s), 3072 (s), 2967 (s), 2974 (s), 1636 (s), 1609 (s), 1585 (s), 1497 (s), 1462 (s), 1377 (s), 1327 (s), 1164 (m), 1125 (m), 1091 (m), 859 (m), 807 (m), 698 (m), 597 (m) cm^{-1}.

Typical Procedure for the Amidation Reaction. A 30 mL Schlenk flask was charged with a solution of complex **1** (0.05 mmol), aniline (0.09 mL, 1.00 mmol), and THF (2.1 mL) and a stir bar. The solution was stirred for 0.5 h; then benzaldehyde was added (0.30 mL, 3.00 mmol). The resulting mixture was stirred at 25 °C for 3 h and filtered through a small plug of silica gel to remove the catalyst. The crude product was purified by column chromatography (ethyl acetate/petroleum ether, 1:8), yielding acylamide, 175.3 mg (89%).

Procedure for the Tishchenko Reaction of Benzaldehyde. A 30 mL Schlenk flask was charged with a solution of complex **1** (0.05 mmol), THF (2.2 mL), and benzaldehyde (0.30 mL, 3.00 mmol) and a stir bar. The resulting mixture was stirred at 25 °C for 3 h and filtered through a small plug of silica gel to remove the catalyst. The crude product was purified by column chromatography (ethyl acetate/petroleum ether, 1:20), yielding benzyl benzoate, 232 mg (73%).

X-ray Structural Determination of 1, 2, 3, and 11. A suitable crystal was mounted in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD equipped with graphite-monochromated Mo Kα (λ = 0.71070 Å) radiation. The structures were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using the SHELXL-97 programs.

Acknowledgment. Financial support by the National Natural Science Foundation of China (grant no. 20632040) and the Department of National Education Doctoral Foundation is gratefully acknowledged.

Supporting Information Available: Experimental details and characterization data for complexes and all acylamides. This material is available free of charge via the Internet at http://pubs.acs.org.