JOC Article

Synthesis of Azolyl Carboximidamides as Ligands for Zn(II) and Cu(II): Application of the Zn(II) Complexes as Catalysts for the Copolymerization of Carbon Dioxide and Epoxides[1]

Martin Walther,[†] Kurt Wermann,[‡] Marion Lutsche,[‡] Wolfgang Günther,[‡] Helmar Görls,[§] and Ernst Anders*,[‡]

Institut für Bioanorganische und Radiopharmazeutische Chemie, Forschungszentrum Rossendorf e.V., PF 51 01 19, D-01314 Dresden, Germany, Institut für Organische Chemie und Makromolekulare Chemie der Friedrich-Schiller-Universität, Humboldtstrasse 10, D-07743 Jena, Germany, and Institut für Anorganische und Analytische Chemie der Friedrich-Schiller-Universität, August-Bebel-Str. 2, D-07743 Jena, Germany

Ernst.Anders@uni-jena.de

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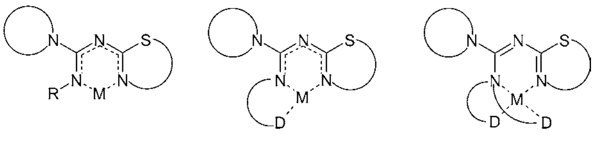

5, **6** **7** **8 - 11**

R = alkyl, D = N, S, M = Zn, Cu

A series of novel S,N-heterocyclic (thiazolyl) substituted carboximidamides **3** and **4** was synthesized in yields up to 82% from specific triazinium salts **1** and primary or secondary amines **2** which additionally bear pyridine or imidazole units. These carboximidamides are used as tailor-made ligands for the complexation of Cu(II) and Zn(II). The coordination behavior of **3** and **4** and the properties of the resulting metal complexes are affected a significant extent especially by the nature of these amine substituents. The most important structural feature of the novel complexes is that the ligation of the metal cations is achieved by a 1,3,5-triazapentadienyl anion system, compare the X-ray structure of the model complex **Cu-4d**. Analogous Zn(II) complexes **5**, **6a**, **6b**, **6c**, **7a**, and **7b** were obtained from carboximidamides **3**, **4a**, **4b**, **4c**, **4d**, and **4e** after reaction with diethylzinc. Interestingly, these Zn(II) complexes possess an intrinsic activity to catalyze the copolymerization of cyclohexene oxide and carbon dioxide to give polycarbonates **15** (TON up to 113; Turn Over Number: moles of substrate **14** consumed per moles of zinc. Molecular weights: up to 206·10^3 Da). Contaminations of **15** by polyethers are produced only in remarkably small amounts.

Introduction

The azolyl carboximidamide (commonly known as amidine) and the guanidine functionality, respectively, are frequent constituents in numerous natural compounds.[2] Structures containing such units often play an essential role because of their biological activity.[3] Recently, guanidines have been used as chiral auxiliaries in asymmetric synthesis[4] as well as superbases catalyzing ring formations from carbon dioxide and suitable amines.[5] Thus, the development of reagents which allow the syntheses of this class of compounds is in constant progress;[6] this includes some solid-phase syntheses of guanidine derivatives.[7] Despite their high importance in the field of biochemistry and their interest-attracting properties as anion receptors, the metal coordination chemistry of guanidines is barely known and appears to be

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* To whom correspondence should be addressed. Tel: +49-(0)3641 948210; fax: +49-(0)3641-948212.

[†] Institut für Bioanorganische und Radiopharmazeutische Chemie.

[‡] Institut für Organische Chemie und Makromolekulare Chemie der Friedrich-Schiller-Universität.

[§] Institut für Anorganische und Analytische Chemie der Friedrich-Schiller-Universität.

(1) Bis-(1,2,4-thiadiazolo)-1,3,5-triazinium halides. 9. For part 8, see: Wermann, K.; Walther, M.; Günther, W.; Görls, H.; Anders, E. *Tetrahedron* **2005**, *61*, 673−685.

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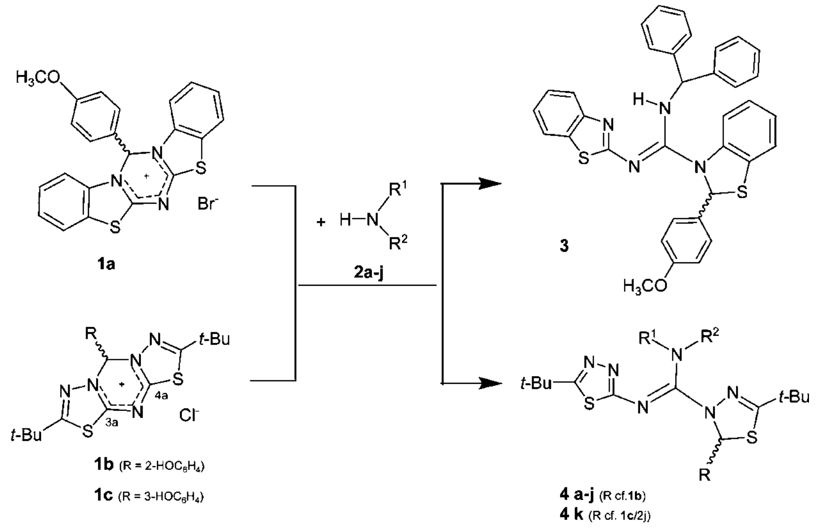
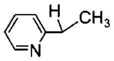
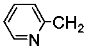
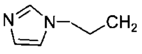
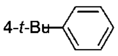
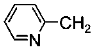
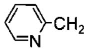
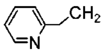
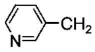
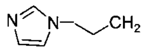
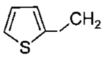
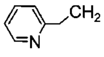
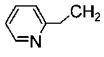
(6) See ref 13e and literature cited therein.

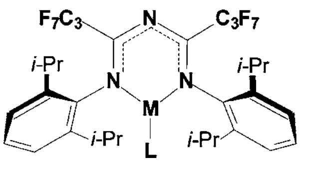
10.1021/jo052056n CCC: $33.50

SCHEME 1. Synthesis of Azolyl Carboximidamides 3 and 4a−k



2, 4	R¹	R²	2, 4	R¹	R²
a	H	$(C_6H_5)_2CH$	f	H	
b	H		g		
c	H		h		
d	H		i		
e	H		j		

surprisingly unexplored.[8] A recent communication reports the (2-guanidyl)ethyl-cyclen to be an interesting ligand capable of forming a 1:1 Zn^{2+} complex.[9] As recently demonstrated, zinc guanidinate complexes are useful catalysts in the ring-opening polymerization of lactide and further point to the clear possibility of other catalytically active metal β-diketiminates and amidinates.[10] Specific requirements are necessary for the catalytic abilities of zinc β-diketiminates in polycarbonate synthesis, described in detail in the review recently published by Coates.[11]



M = Cu, Zn, Ag,Co

L = CO, CH_3CN, PPh_3

FIGURE 1. 1,3,5-Triazapentadienylmetal complexes, cf. ref 12.

Metal complexes with sterically demanding triazapentadienyl anions[12] (Figure 1) reveal a coordination pattern similar to that of the β-diketiminate system. Furthermore, they are comparable with our new carboximidamidate complexes.

The focus of our research presented here is a strategy to synthesize azolyl carboximidamides **3** and **4** using our novel bis-(1,3,4-thiadiazolo)-1,3,5-triazinium halides **1** (so-called SNS-heterocycles, which can be understood as a shorthand to indicate the key heteroatom composition of the three fused rings; see Scheme 1) as precursors. **3** and **4** may also be viewed as guanidines because of the attached cyclic ligands. Compounds **1** are reacted with a variety of primary or secondary amines **2a−j** (aliphatic, heterocyclic, aromatic).[13a−e] Such fused tricyclic structures **1** are easily accessible in the course of a three-component reaction of an aldehyde, a thionyl halide, and a pyridine which primarily leads to *N*-(1-haloalkyl)pyridinium halides.[14a,b] These salts were reacted with 2-amino-5-alkyl-1,3,4-thiadiazoles to generate the triazinium salts **1** in excellent yields.[15]

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[9] Aoki, S.; Iweida, K.; Hanamoto, N.; Shiro, M.; Kimura, E. *J. Am. Chem. Soc.* **2002**, *124*, 5256−5257.

[10] Coles, M. P.; Hitchcock, P. B. *Eur. J. Inorg. Chem.* **2004**, 2662−2672.

[11] Coates, G. W.; Moore, D. R. *Angew. Chem.* **2004**, *116*, 6784−6806.

[12] (a) Siedle, A. R.; Webb, J. R.; Behr, F. E.; Newmark, R. A.; Weil, D. A.; Erickson, K.; Naujok, R.; Brostrom, M.; Mueller, M.; Chou, S.-H.; Young, V. G., Jr. *Inorg. Chem.* **2003**, *42*, 932−934. (b) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 5786−5788. (c) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 7396−7402.

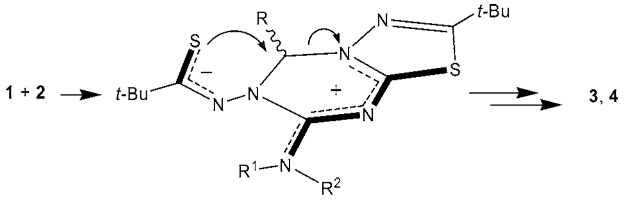
In general, the designation "guanidines" often is connected with the concept of compounds which are characterized by their highly basic properties. The observed relatively low basicity of compounds **3** and **4** is a consequence of the specific kind of heterocyclic substitution, which results in a less expressed ability to form stable delocalized guanidinium ions.

Moreover, the deprotonation of the NH function in compounds such as **3** and **4a−f** with metal organyls should result in the formation of remarkably stable 1,3,5-triazapentadienyl-anion system (vide infra).

In this paper, we describe (a) our studies on the synthesis of novel carboximidamides **3** and **4a−k**, (b) the formation of a novel Cu(II) and several Zn(II) complexes (**Cu-4d**, **5−11**) from these carboximidamides, and (c) successful attempts to use some of these Zn(II) complexes as catalysts for the copolymerization of carbon dioxide and epoxides.[16] Chemical fixation of CO_2 is of great interest in connection with the development of truly environmentally tolerable processes in which catalysis is achieved by transition-metal complexes.

Results and Discussion

The novel fused SNS-heterocycle **1c**, which was used in addition to the previously described compounds **1a** and **1b** in conjunction with the carboximidamide syntheses presented here, was generated from 1-[chloro-(3-hydroxyphenyl)methyl]pyridinium chloride and 2-amino-5-*tert*-butyl-1,3,4-thiadiazole[17] in 73% yield according to the procedure reported in the literature.[13a,b] The overall reaction of **1** with amines **2** to give the carboxamides **3** and **4a−k** (Scheme 1) can be understood in terms of an interesting example of an S_N(ANRORC) mechanism.[18] Because of their remarkable electrophilicity at the C_{3a} and C_{4a} positions of the central triazinium ring,[19] the tricyclic compounds **1** are able to react with specifically selected primary and secondary amines **2a−k**. The next steps are characterized by fast ring-opening and ring-closure steps which finally yield the products **3** and **4**.[1,13e] In more detail and as previously discussed,[13e,20] after the nucleophilic attack of the amine nitrogen of **2** at the C_{3a} position of the cations **1** and a fast deprotonation step, the consecutive ring transformations are controlled by the influence of negative hyperconjugation ($n_{N(ex.)}/\sigma_{C(3a)-S(5)}$ interaction). This effect causes the formation of the triazinium-imidothioate zwitterions **Z** (Figure 2, ring-opening step) as reactive intermediates. Accelerated by the specific reaction conditions (temperature and reaction time), compounds **Z** react to give structures **3** or **4** (ring-closure step).



Z

FIGURE 2. Imidothioate intermediate **Z**.

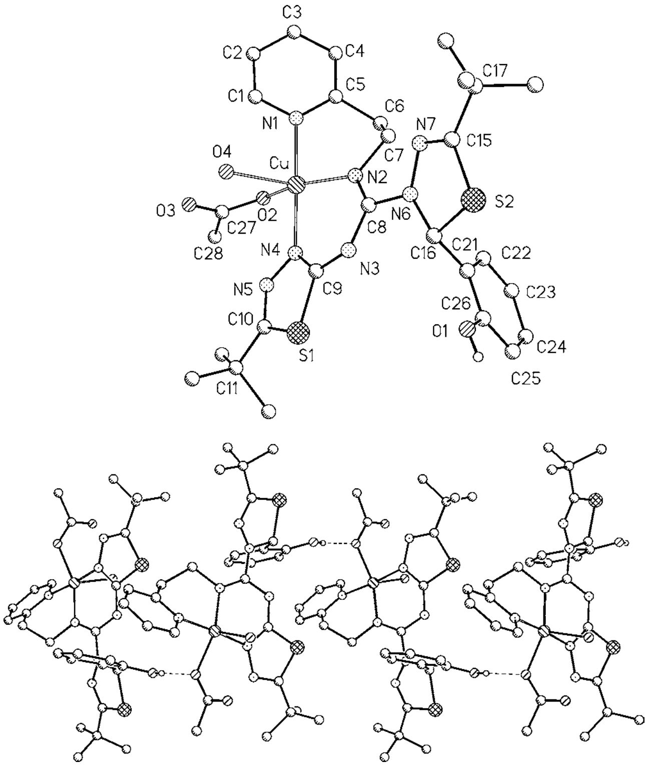


FIGURE 3. Crystal structure of the Cu(II) complex **Cu-4d**; except for H−O(1), hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angels [°]: Cu−N(1) 2.003, Cu−N(2) 1.990, Cu−N(4) 1.958 Cu−O(2) 2.002, Cu−O(4) 2.323, N(2)−C(8) 1.305, C(8)−N(3) 1.349, N(3)−C(9) 1.335, C(9)−N(4) 1.320, C(8)−N(6) 1.407, O(1)−C(26) 1.361, N(2)−Cu−O(4) 109.14, N(4)−Cu−O(4) 89.97, N(4)−Cu−N(2) 89.74, N(2)−C(8)−N(3) 127.6, N(3)−C(9)−N(4) 130.4.

The general procedure described here is quite successful as it allows the synthesis of the carboximidamides in yields up to 95%. Interestingly and fortunately, the heterocyclic nitrogen atoms in **2** which are incorporated in the substituents R^1 or R^2 do not cause any synthetic problems. In the products **4g−k**, these heteroatoms may serve as additional coordination sites for metal ions compared with the properties of our previously synthesized standard carboximidamides starting from less critical amines.[13a−e]

To prove the participation of such a pyridine nitrogen in the coordination pattern, we synthesized (from **4d** and Cu(II) acetate) and X-rayed the copper complex **Cu-4d** (Figure 3).

The Cu(II) center is surrounded by a square pyramidal coordination sphere with three different nitrogens and one

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(13) (a) Wermann, K.; Walther, M.; Günther, W.; Görls, H.; Anders, E. *J. Org. Chem.* **2001**, *66*, 720−726. (b) Walther, M.; Wermann, K.; Görls, H.; Anders, E. *Synthesis* **2001**, 1327−1330. (c) Wermann, K.; Walther, M.; Anders, E. *ARKIVOC* (Gainesville, FL) **2002**, *10*, 24−33. (d) Wermann, K.; Walther, M.; Görls, H.; Anders, E. *Synlett* **2003**, 1459−1462. (e) Wermann, K.; Walther, M.; Günther, W.; Görls, H.; Anders, E. *Eur. J. Org. Chem.* **2003**, 1389−1403.

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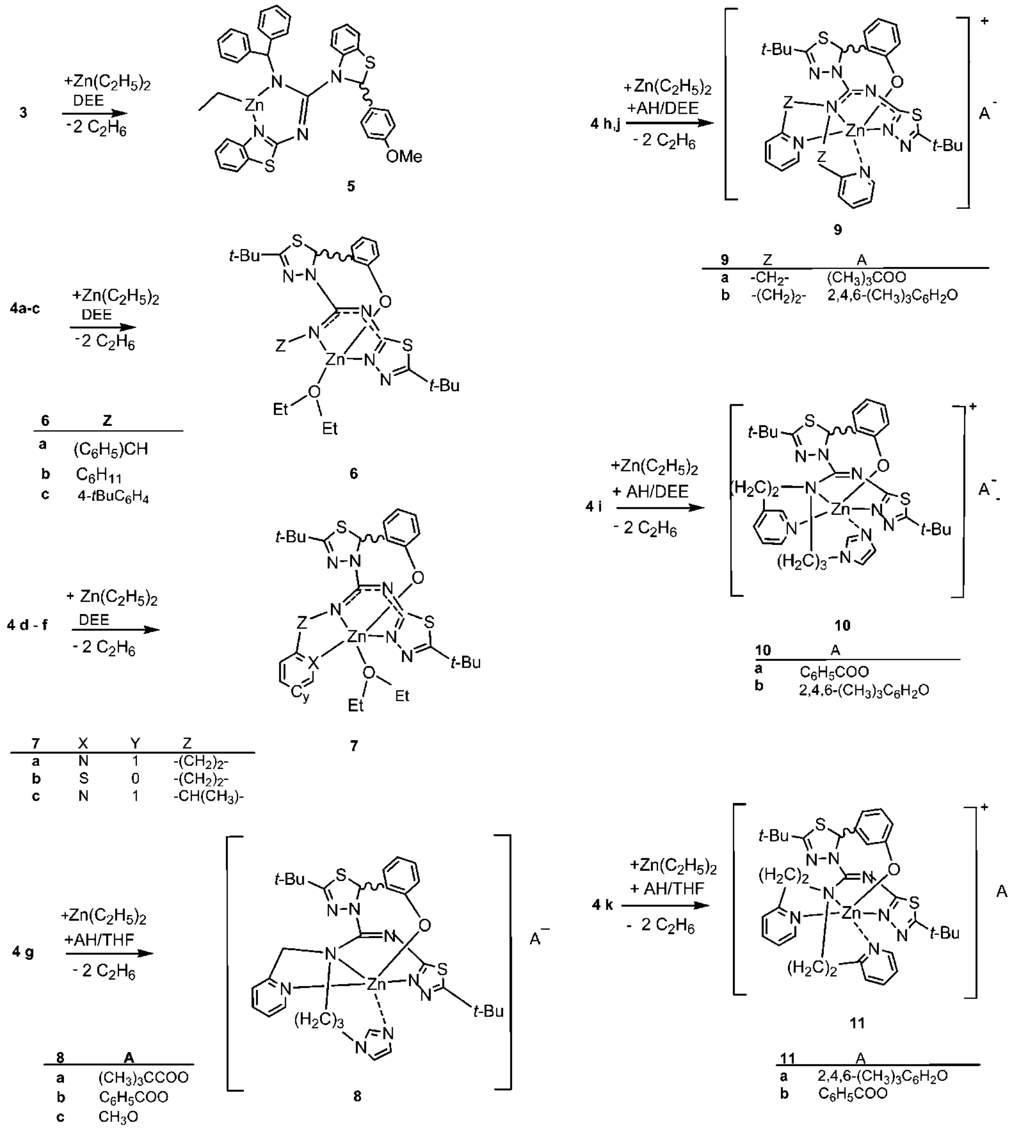
(19) Results of a natural population analysis for a model cation **1b**: R = 4-MeC_6H_4 and Me instead of *t*-Bu: $q_{C3a} = q_{C4a} = +0.30$ e B3LYP/6-311++D(d,p) opt.

(20) Nilsson Lill, S. O.; Rauhut, G.; Anders, E. *Chem. Eur. J.* **2003**, *9*, 3143−3153.

SCHEME 2. Synthesis of Zn Complexes 5−11



acetate anion in the plane and one water molecule forming the top of the pyramid. The six-membered 1,3,5-triazapentadienyl metal chelate is vitally important for structural and catalytic properties of the complex and the analogous Zn(II) compounds. The easily feasible deprotonation of the central NH-function deserves particular interest as it was performed in the presence of a hydroxyaryl function and the water molecule. Both the OH substituents survive without deprotonation. The characteristic six Cu−N and N−C distances of the copper-triazapentadienyl anion unit of **Cu-4d** (Cu−N: 1.990, 1.958 Å; N−C: 1.305, 1.349, 1.335, and 1.320 Å) are in good agreement with the reported values of a triazapentadienyl-Cu(I) complex (Cu−N: 1.939, 1.941 Å, N−C: 1.303, 1.338, 1.335, 1.301 Å).[12b] Further, the relatively large 2-ethyl-2-pyridinyl substituent (cf. R^2 **4d**) was selected with the intention to favor the formation of monomeric ligand-to-metal 1:1 complexes. This was successfully realized in this Cu(II) complex.

Structural assignments of the novel carboximidamides **3** and **4a−k** are based on ^{1}H and ^{13}C NMR data and MS and IR spectra as well as elemental analyses. As expected, the reaction of the asymmetric pyridylamine **2f**[21] and the tricyclic **1b** yielded the formation of diastereomeric carboximidamides **4f/1** and **4f/2** because these reaction paths give rise to the formation of a second chiral center in the newly formed dihydrothiadiazole ring. Both the racemic diastereomers **4f/1** and **4f/2** have been separated by means of fractional crystallization from ethyl acetate and recrystallization from MeOH and were characterized by X-ray crystal structure analyses (cf. Figure 7; Supporting Information).

The arrangement of the thiadiazole and the dihydrothiadiazole ring shows the expected E-stereochemistry with respect to the exocyclic imine double bond. Characteristic bond lengths and bond angles are in agreement with the expected properties of a guanidine subunit which has been substituted by the moieties which stem from the synthetically involved nucleophiles **2** and the SNS heterocycles **1**. The conversion of the cations **1** into the uncharged carboximidamides **4** caused a shift in the NMR signals toward higher fields (^{1}H ≈ 1 ppm; ^{13}C ≈ 10−15 ppm). All of the ^{1}H and ^{13}C NMR signals of the rearrangement products **4** have been unambiguously assigned to the newly formed dihydrothiadiazole, the aromatic thiadiazole, and the guanidine unit via HMQC, HMBC, COSY, and TOCSY

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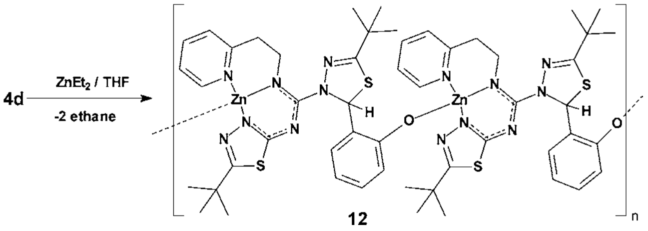
[21] Michelsen, K. *Acta Chem. Scand.* **1974**, *A28*, 428−434.

SCHEME 3. Proposed Structure of Coordination Polymer of 12



experiments. As expected, the diastereomeric carboximidamides **4f**/**1** and **4f**/**2** show slightly different NMR and IR spectra.

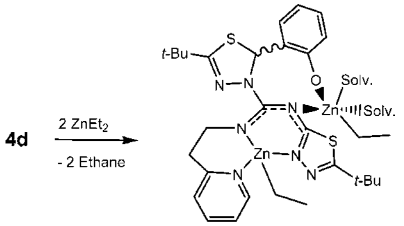
The alternating bonds of the 1,3,5-triazapentadiene system N(4)−C(1)−N(1)−C(2)−N(2) are well recognizable in the molecular structure of **4f**/**1** (cf. the bond lengths: 1.342, 1.320, 1.361, 1.314 Å) and show the expected differences to the data of the Cu(II)-complex. The bond between carboximidamide C(1) and the dihydrothiadiazole N(6) (1.369 Å) is significantly shorter than the corresponding bond in the model complex **Cu-4d** (1.407 Å).

The syntheses of the carboximidamide zinc complexes **5**−**11** (Scheme 2) are easily achieved by reaction of diethyl zinc as the appropriate zinc reagent (1 equiv) with the carboximidamides **3** or **4a**−**k** (1 equiv) according to the method described in the literature.[22] The deprotonation of **3** already starts at −30 °C (DEE as solvent) and is finished after warming to room temperature for 1 h. The Zn(II) carboximidamide complex **5** is formed in yields up to 80% as a white precipitate. Unfortunately, a complete structure characterization of **5** has not been achieved because of both the lack of suitable crystals for X-ray experiments and the insolubility of **5** in appropriate solvents for NMR measurements. Therefore, we cannot rule out the formation dimers of **5**, but because of the bulky nature of the carboximidamide ligand **3** and particularly with regard to the X-ray structure of the model Cu(II) complex **Cu-4d** synthesized for comparison (cf. Figure 3), we tend to assume the existence of intramolecular N,N six-ring chelate systems as described for metformin[23] or ethoxy guanidine zinc complexes.[24]

In comparison with **3**, the carboximidamides **4a**−**k** possess a hydroxyphenyl group at the C9 position which stems from the aldehydes used for the synthesis of the SNS heterocycles. Thus, they have a further acidic substituent which, especially after deprotonation, will increase the number of donor functions for the Zn(II) complexation. After reaction of **4a**−**f** with diethyl zinc (mole ratio 1:1) in DEE, the two protons of the OH and NH groups are split off and are replaced by the zinc coordination. The immediate formation of a precipitate together with its bad solubility in common solvents could indicate the existence of coordination polymers, for instance, compound **12** (cf. Scheme 3).

The complexes **6a**−**c** and **7a**−**c** (yields up to 87%) do not show any OH and NH bond absorptions in the IR spectra and further prove the participation of one DEE molecule in the coordination sphere. NMR investigations were not feasible because of the insolubility of these compounds. For this reason, further experiments with varying molar ratios of **4d** and ZnEt$_2$ (1:0.5 and 1:2) were performed especially to yield soluble products. From the 1:1 and the 1:0.5 ratio experiments, the same compound **12** (in the latter case together with the unaltered ligand **4d**) was obtained. In contrast, the 1:2 ratio experiment in THF or pyridine results in a clear solution of a binuclear ligand-(ZnEt)$_2$ species **13** without any precipitation (Scheme 4). In DEE as solvent, the same 1:2 experiment again results in the formation of **12** which slowly precipitated from the solution. Thus, repetition of this experiment in an NMR tube in pyridine-d_5 gains precise information regarding the zinc coordination. (e.g., on the basis of the complete ^{1}H and ^{13}C NMR spectra; see Supporting Information).

SCHEME 4. Proposed Structure of the Binuclear Species of 13 in Solution



Solv. = THF or Pyridine **13**

The ^{1}H NMR spectrum of **13** shows between 3 and 5 ppm a group of signals with various intensities and resolutions belonging to the ethylene bridge in the ligand. Two small, well-resolved multiplets in the range of 4−4.3 ppm can be assigned to a little amount of free ligand and the other signals are those of two complexed species exhibiting diastereotopic splittings of the ethylene bridge CH$_2$ protons caused by complexation. The ^{13}C NMR shows the presence of two different ethyl residues from two differently coordinated Zn-ethyl species).

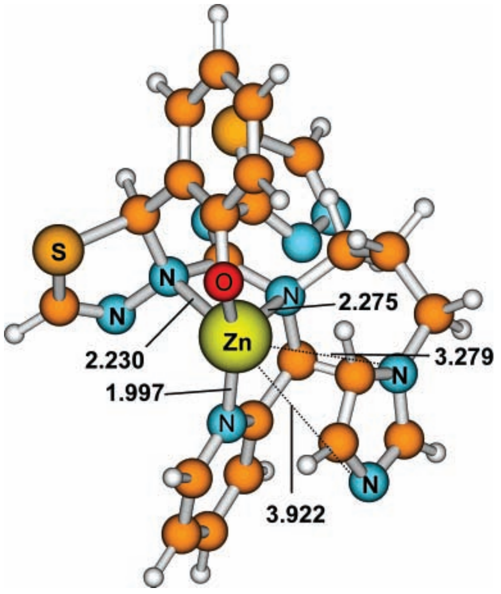


FIGURE 4. Calculated structure of **8a** (B3LYP/6-31+G(d,p)). The substituent R = *t*Bu is replaced by H. Distances in [Å]. Zn−O: 1.852 Å.

Furthermore, to study the reactivity of this kind of soluble complexes toward CO$_2$, experiments with ^{13}C labeled CO$_2$ were carried out in the NMR tube and are discussed below (cf. Figure 5). For all the isolated and insoluble Zn(II) complexes **5**, **6**, and **7**, the results of molecular weight determinations and

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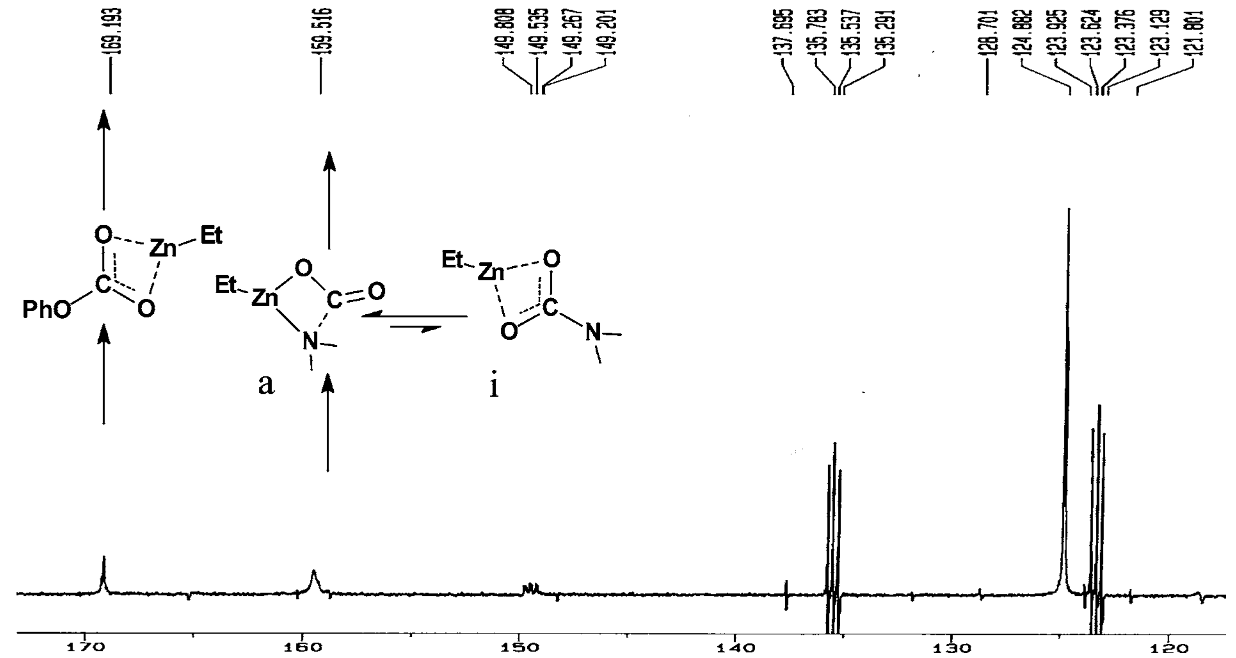

FIGURE 5. ^{13}C NMR difference spectrum of **13** and **13** + CO_2 in pyridine-d_5. (The small triplet at 149 and the two dispersion signals 135 and 123 ppm are residual resonances of the pyridine-d_5.)

elemental analyses are in agreement with the assumed structures (cf. Scheme 2 and the experimental part).

An additional type of carboximidamide/zinc complexes (structures **8**−**11**) which does not belong to the anionic 1,3,5-triazapentadienyl chelate species was synthesized by reaction of diethyl zinc and the carboximidamides **4g**−**k**. These compounds do not possess acidic NH functionalities, and just the phenolic OH groups at the C9 positions are still present. Therefore, cationic zinc carboximidamide complexes **8**−**11** are generated which finally are stabilized by the coordination of different anions which stem from external acidic compounds (alcohols, phenols, or carbonic acids) as a consequence of subsequent addition reactions. The elemental composition of these complexes was confirmed via mass spectra investigations and elemental analyses. The compounds **8a**− **c**, **10a**, and **10b** feature *m*/*z* values from 90 to 100% which is an indicator for the remarkably high complex stability. Because of improved solubility in DMSO-d_6, in some cases (**8a**, **9b**, **11a**, **b**) it was possible to achieve analyzable ^1H and ^{13}C NMR signals which are in good agreement with the designed structures **8**−**11** (cf. example Figure 8; Supporting Information).

Unfortunately, because of the lack of suitable crystals, these Zn(II) derivatives could not crystallographically be characterized. Nevertheless, a DFT calculation at the B3LYP/6-31+G-(d,p) level[25] of the complex **8a** (cf. Figure 4) shows a persuasive agreement with structural data of other zinc-phenoxide crystals.[26,27] Without consideration of the very weak interaction to imidazole ring N atom, in this model, the four zinc ligands are arranged in a slightly distorted tetrahedral configuration. Assuming that a correlation exists between the Zn−O bond lengths and the degree of nucleophility,[28] for such Zn(II) complexes a certain reactivity can be expected toward heterocumulenes such as CO_2. This is confirmed by our NMR experiments: Inspection and interpretation of our ^{13}C NMR spectra of the compounds **7a** and **8b** in DMSO-d_6 and **13** in pyridine-d_5 which are based on previous investigations[26,29] doubtless show the presence of

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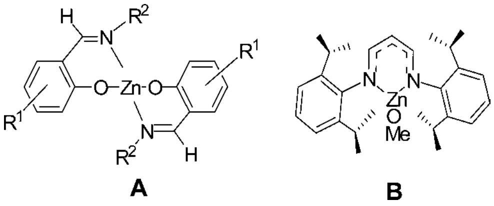
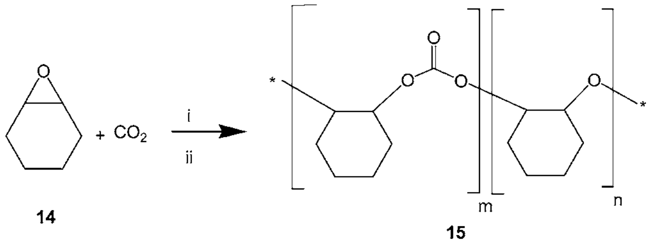


FIGURE 6. Efficient zinc catalysts **A** (four-coordinate initiator, see ref 32) and **B** (β-diimine ligand; single-site catalyst, see ref 22).

SCHEME 5. Copolymerization of Cyclohexene Oxide 14 and CO$_2$



i: Zn-catalyst: **5**, **6a**, **6b**, **7a**, **7b**, **8a**.
ii: Reaction conditions: cf. Table 1.

a zinc-phenoxide-CO$_2$ adduct (compound **13** + CO$_2$, $\delta = 169$ ppm, Figure 5) and a zinc-carbamate equilibrium (structures **a** and **i**; **13** + CO$_2$, $\delta = 159$ ppm). This is a property which necessarily must be expressed in systems which might be appropriate for catalytic CO$_2$ activation and transfer reactions.

Worldwide, there is a continuing interest in the activation and utilization of CO$_2$ as a C1 building block in organic synthesis.[30] An important application is the alternating CO$_2$ copolymerization with epoxides to produce aliphatic polycarbonates with interesting material properties. This has been extensively investigated particularly with regard to the preparation of Zn(II) complexes which finally can be used as catalysts for that reaction.[16,22,30–33]

Figure 6 shows two exemplary efficient zinc catalysts for the ring-opening copolymerization of cyclohexene oxide **14** and CO$_2$. They have been constructed on the basis of bis(phenoxide) (Darensbourg et al.)[32] and anionic β-diimine-type ligands (Coates et al.)[33] which are able to achieve turnover frequencies up to 235 (Turn Over Frequency (TOF): moles of substrate **14** consumed per moles of zinc per hour).

A typical copolymerization run (Scheme 5) was carried out in a 100-mL autoclave which was loaded with a zinc complex/**14** mixture and then was placed under 20 bar of carbon dioxide and was heated to 85 °C for 20 h (cf. the Experimental Section).

TABLE 1. Formation of the Copolymer 15 from Cyclohexene Oxide 14 and CO$_2$[a]

catalyst	time (h)	TON[b]	TOF[c]	yield (g) 15	$M_n \cdot 10^3$ (g·mol^{-1})	$M_w \cdot 10^3$ (g·mol^{-1})	ratio 15/ polyether
5	21	109.1	5.2	3.93	14.5	215.8	96.4
6a	20	104.0	5.2	5.34	21.6	241.4	95.5
6b	20	108.3	5.4	5.06	23	204.8	99.1
6c	2.5	3.5	1.4	1.10	8.0	39.9	95.5
6c	20	113.2	5.6	3.64	14.8	238.1	96.5
7a[d]	24	11.5	0.5	1.23	43.8	199.6	99.1
7a	6	7.4	1.2	0.91	16.5	43.1	99.1
7b	20	52.9	2.6	3.61	26.4	206.0	99.1
8a	20						

[a] Conditions: 85 °C, 20 bar CO$_2$, 10 mL **14**. [b] Mole **15**/mole Zn). [c] Mole **15**/(mole Zn·h). [d] 50 °C.

The catalytic properties of our zinc complexes **5**, **6a**, **6b**, **6c**, **7a**, **7b**, and **8a**, which were selected for these tests, are very different with regard to their efficiency (Table 1). For the compound **8a** which represents an example for guanidine complexes without the NH unit, no catalytic copolymerization reactivity was observed. Such carboximidamide complexes apparently do not exhibit the structural requirements for the formation of a so-called single-site catalyst (cf. ref 22, 33a and b and Figure 6). The badly soluble neutral complexes **5** and **6a**–**6c** achieved TOF values from 5.2 to 5.6; their effectiveness thus can be compared with that of some phenoxide catalysts previously published by Darensbourg.[32]

The newly synthesized polycarbonates **15** have M_w up to 206 × 10^3 Da and possess only minor amounts of polyether (1–5%, analyzed by ^{1}H NMR spectra) which indicate the high-catalyst selectivity of our complexes for such polymer insertion reactions. Further, ^{13}C NMR investigations of the polymers **15** show that our guanidine zinc complexes have a notable influence on the tacticity of the growing polymer chain because compounds **15** are substantially syndiotactic polymers.[31b,c]

These results have motivated us to design further metal complexation reactions of carboximidamides derived from novel SNS and NNS compounds and especially enantiomeric amines. These investigations are presently underway.

Conclusion

From this investigation, we conclude that the general reaction sequence which starts with the synthesis of cationic SNS heterocycles and ends with the formation of the title compounds is a very useful procedure. The products (various highly substituted carboximidamides functionalized by different electron donor moieties) can be constructed in a very efficient manner which opens paths to tailor-made novel ligands for Cu(II) and Zn(II) cations. In case of carboximidamides such as **3** and **4a**–**f**, the built-in NH function allows deprotonation and formation of negatively charged ligands which belong to the class of 1,3,5-triazapentadienylanions. This is confirmed by the X-ray crystal structure analysis of the Cu(II) complex **Cu-4d** from the ligand precursor **4d** which reveals that the phenolic OH (the R substituent in **1b** and **4d**; cf. Scheme 1) survives while the NH deprotonation yields the delocalized 1,3,5-triazapentadienyl anion. Some of their Zn(II) complexes possess promising catalytic properties for the copolymerization of CO$_2$ and **14** to give polycarbonates **15**.

Experimental Section

General methods, analytical data, and crystal structure determination of the novel compounds are assembled in the Supporting Information.[34–40]

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(40) CCDC 282561 (**Cu-4d**) and 282562 (**4f/2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, United Kingdom; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Details of experimental procedures, elemental and ^{1}H and ^{13}C NMR analytical data, MS, and crystal structure determination of the novel compounds, especially Figure 7 (crystal structures of the diastereomeric carboximidamides **4f**/**1** and **4f**/**2)** and Figure 8 (^{1}H NMR spectra of zinc complex **9b**). A general procedure for a typical copolymerization of cyclohexene oxide **14** and carbon dioxide. This material is available free of charge via the Internet at http://pubs.acs.org.

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