Polyhedron 32 (2012) 49–53

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Mild formation of cyclic carbonates using Zn(II) complexes based on N_2S_2-chelating ligands

Daniele Anselmo [a], Vladica Bocokić [b], Antonello Decortes [a], Eduardo C. Escudero-Adán [a], Jordi Benet-Buchholz [a], Joost N.H. Reek [b,*], Arjan W. Kleij [a,c,*]

[a] Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain
[b] University of Amsterdam, van't Hoff Institute for Molecular Sciences, Science Park 904, 1098 XH, Amsterdam, The Netherlands
[c] Catalan Institute for Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

ARTICLE INFO

Article history:
Available online 2 June 2011

Keywords:
Carbon dioxide
Cyclic carbonates
Homogeneous catalysis
N,S-chelating ligands
Zinc

ABSTRACT

We have prepared a series of Zn(II) complexes (**1–3**) based on a versatile N_2S_2-chelating ligand abbreviated as btsc [btsc = bis-(thiosemicarbazonato)] derived from simple and accessible building blocks. These complexes comprise a Lewis acidic Zn(II) center useful for substrate activation, and we have investigated the potential of these compounds in the cyclo-addition reaction of carbon dioxide to various epoxides yielding cyclic carbonate structures. Initial screening studies with complexes **1–3** showed that complex **3** is most suited for this CO_2 fixation reaction under particularly mild conditions (45 °C, $pCO_2 = 10$ bar) and low catalyst loadings (1 mol%). Furthermore, upon examination of the substrate scope, complex **3** shows appreciable catalytic turnover for a range of terminal epoxides, while for the sterically more challenging epoxides almost no conversion was achieved under comparable conditions. Additional experiments indicated that higher yields of cyclic carbonates may be realized by simply increasing the (co)catalyst loading up to 3%, while maintaining mild reaction conditions. The use of a relatively non-toxic and abundant metal and an environmentally benign solvent system (MEK, methyl ethyl ketone) mark this protocol as an attractive way for organic carbonate production.

1. Introduction

The synthesis of organic carbonates is an area of research that has received a great deal of attention in the last decade [1–7]. These carbonate structures find many useful applications including new non-protic solvents, as substitutes for toxic reagents in organic synthesis and as valuable precursors for their polymeric counterparts [1,2,4]. Cyclic carbonates form a sub-family of carbonates which can be derived from epoxides; in the past these were primarily prepared by treatment of the oxiranes by phosgene followed by ring closure [8]. This protocol, however, is characterized by the use of a highly toxic and hazardous reagent and concomitantly produces large amounts of corrosive by-products, which are difficult to handle. For this reason, alternative synthetic pathways have been investigated and the cycloaddition of carbon dioxide (CO_2) to epoxides represents an attractive and green process. Such a process has a number of advantages; CO_2 is an economical, abundant, non-toxic and renewable C1 reagent and the only by-product that is formed during the formation of the cyclic carbonate target is water. However, since CO_2 has a tremendously high kinetic and thermodynamic stability, conversion into a cyclic carbonate requires catalytic activation [9]. Various research groups explored homogeneous and heterogenous catalytic solutions that are known to effectively catalyze this transformation [6]. A major drawback of most of these proposed catalysts is the need for harsh reaction conditions which either translates into elevated CO_2 pressures, high reaction temperatures or a combination of both. Obviously, such demanding process conditions compromise the degree of sustainability, the net consumption of CO_2 and the overall energy balance.

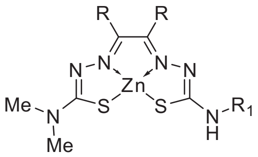
Recent breakthroughs have demonstrated the potential that metal-catalysis can have for the design of more sustainable options focusing on (nearly) ambient conversion of CO_2 [10–12]. In this respect, metallosalen structures have emerged as powerful catalysts for cyclic carbonate synthesis [6] with the Al(III) [11], Co(III) [13] and Cr(III) complexes [14] among the most active systems. We have recently designed Zn-based salen complexes that have shown great promise in cyclic carbonate synthesis under extremely mild (25 °C, $p(CO_2) = 2$ bar) and green reaction conditions [15,16]. While the salen ligands comprise typical N_2O_2 coordination environments around the complexed metal ion, other combinations of hetero-atoms within the ligand structure could give rise to new yet unexplored reactivity patterns. In our search for such ligands,

---

* Corresponding authors. Address: Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain. Tel.: +34 977920247; fax: +34 977920224 (A.W. Kleij), tel.: +31 (0) 20 5256437; fax: +31 (0) 20 5255604 (J.N.H. Reek).

E-mail addresses: J.N.H.Reek@uva.nl (J.N.H. Reek), akleij@iciq.es (A.W. Kleij).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.05.025



1. R= Me, R_1 = Ph
2. R= R_1 = Me
3. R= R_1 = Ph

Scheme 1. Schematic structures for Zn(btsc) complexes **1**–**3**.

we considered that bis-(thiosemicarbazonato) ligands (abbreviated as btsc) could be useful to construct N_2S_2-chelated complexes as these can be readily assembled from available precursors [17–20]. It should be mentioned here that the choice for btsc ligands opposing analogous salen systems having N_2S_2 donor sets can be justified from the viewpoint of their synthetic accessibility; as a testament of this postulation, only a few of these N_2S_2-salen ligands have been reported to date and their synthesis is less developed [21].

Herein we report on the use of Zn(II)–btsc complexes (Scheme 1) as effective catalysts in cyclic carbonate synthesis under mild and environmentally friendly conditions using comparably low loadings of catalyst. This protocol features an easily synthesized catalyst comprising a cheap and abundant metal. The scope of cyclic carbonate synthesis has been investigated in detail and shows that the Zn(II) based complexes are active mediators for this synthetic conversion under mild conditions.

2. Experimental

2.1. Complex synthesis

The preparation of Zn(II)–btsc complexes **1–3** is straightforward and consists of two steps. The first step involves preparation of the (pro)ligand by condensation of a dicarbonyl compound with two thiosemicarbazide molecules, followed by metallation with an appropriate metal salt. Full details on the synthesis of **1–3** are provided elsewhere, see also Supporting Information [22].

2.2. Catalytic protocol

2.2.1. Typical procedure

Catalyst **3** (2.0×10^{-5} mol, 10.4 mg) and (co-catalyst) NBu_4I (2×10^{-5} mol, 7.4 mg) were added in a two-necked round-bottomed flask under a gentle flux of argon. Then, methyl ethyl ketone (5.0 mL) and mesitylene (280 μL, 2.0×10^{-3} mol) were added and the solution stirred until complete dissolution occurred. To this mixture, propylene oxide (140 μL, 2.0×10^{-3} mol) was added and the solution transferred to a 25 mL stainless-steel reactor previously purged with argon. Three cycles of pressurization and depressurization of the reactor (with CO_2 at 5 bar) were carried out before finally stabilizing the pressure at 10 bar and the solution left stirring at 45 °C for 18 h. A sample of the solution was then analyzed by means of ^1H NMR spectroscopy (DMSO-d_6) and the yield determined using mesitylene as an internal standard.

2.3. X-ray structure determination

Crystals of compound **3** were obtained by slow evaporation in CH_3CN at 55 °C. The measured crystals were stable under atmospheric conditions; nevertheless they were prepared under inert conditions immersed in perfluoropoly-ether as protecting oil for manipulation.

Data collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4 K CCD area detector, a FR591 rotating anode with Mo Kα radiation, Montel mirrors and a Kryoflex low temperature device ($T = -173$ °C). Full-sphere data collection was used with ω and ϕ scans.

Programs used: data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint + Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008-1 (2008).

Structure solution: SHELXTL Version 6.10 (Sheldrick, 2000) was used [23].

Structure refinement: SHELXTL-97-UNIX Version.

Crystal data for **3** at 100 K: $C_{26}H_{25}N_7S_2Zn_1$, $F_w = 565.02$ g mol^{-1}, monoclinic, $P2_1/c$, $a = 7.7782(6)$ Å, $b = 32.165(2)$ Å, $c = 10.1938(8)$ Å, $V = 2549.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.472$ Mg/m^3, $R_1 = 0.0437$ (0.0705), $wR_2 = 0.1007$ (0.1200), for 3193 reflections with $I > 2\sigma(I)$ (for 4240 reflections [R_{int}: 0.0671] with a total measured of 14 756 reflections), 332 parameters, goodness-of-fit on $F^2 = 1.088$, largest difference in peak (hole) = 0.455 (−0.748) e Å^{-3}.

3. Results and discussion

In order to establish the ability of complexes **1**–**3** to act as Lewis acid activators we first examined their structural properties. As a representative example, we combined complex **3** with various epoxides to obtain crystals suitable for X-ray diffraction. Crystals were obtained from CH_3CN upon heating **3** in the presence of an epoxide and allowing the mixture to cool to ambient temperature. Small, needle-shaped crystals were obtained which were, unfortunately, not suitable for X-ray diffraction. Recrystallization at 55 °C afforded, however, better quality crystals in the case where epoxyhexane was utilized. These crystals were subjected to X-ray diffraction studies. An isolated sample of these crystals was dried *in vacuo* and then examined by ^1H NMR (DMSO-d_6); surprisingly, the spectrum did not show the expected signals for the epoxide substrate as only **3** was present.[1] The crystal structure was then determined and the result is presented in Fig. 1. In line with the ^1H NMR observation, the structure does not contain an axially ligated epoxide, but shows an unexpected self-assembled dimer mediated through μ_2-S bridging ligands [24,25–27].

Complex **3** crystallizes in the centro-symmetric space group *P*2(1)/*c*. The Zn ions in each of the two units of **3** are pentacoordinate with the chelating N_2S_2 fragment occupying the basal plane of the approximate square pyramidal geometry. Both S2 and S2a sulfur donor atoms act as anionic bridging ligands between the Zn1a and Zn1 metal centers completing the pentacoordination. The formation of the central S_2Zn_2 unit causes the Zn center to displace from the N_2S_2 coordination plane as illustrated by the difference in Zn–S bond distances (Zn1–S1 = 2.35 Å and Zn1–S2a = 2.42 Å) within each monomeric unit.

This "self-dimerization" resembles the well-known self-assembly behavior of Zn(salen) complexes (having N_2O_2 donor sets) for which exists ample literature precedent [28–30]. We recently reported extensive studies on the features that control the strength of this self-assembly process [31,32]; one key feature is the steric control when, *ortho* to the O-donor atoms, large fragments are introduced. In these cases dimer formation may be minimized and monomeric complexes prevail. Connected with the substitution pattern of these salen ligands is their ability to act as Lewis acid activators. We have reported on a series of Zn(II)salphen complexes [salphen = *N*,*N*-bis(salicylidene)imine-1,2-diaminobenzene] that were applied as efficient catalysts for the cycloaddition of carbon dioxide (CO_2) to terminal epoxides under ambient conditions [15,16]. Within these studies, those Zn-complexes comprising sterically demanding groups near the O-donor atoms showed the

---

[1] This results contrasts our previous findings for related Zn(salphen) complexes where the coordination of various epoxides was crystallographically characterized [see Ref. [15]]. Apparently, under these conditions the Zn(btsc) complex **3** preferentially crystallizes as a dimer.

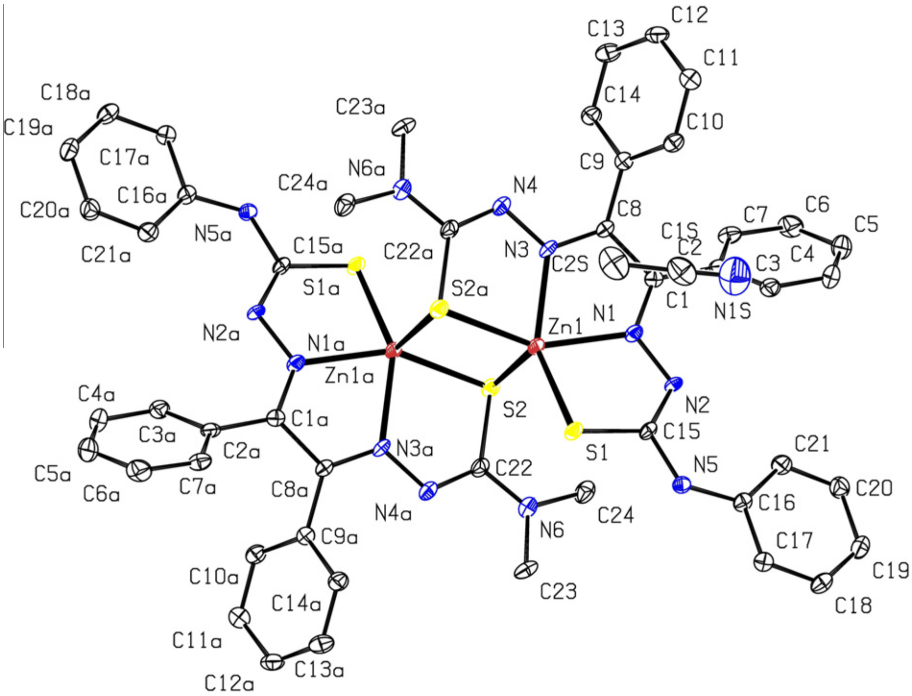
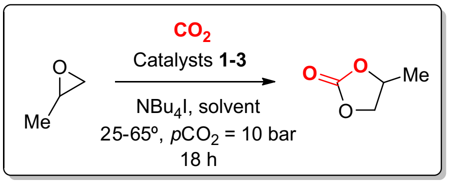


Fig. 1. X-ray molecular structure for $(\mathbf{3})_2$ with the adopted numbering scheme. Co-crystallized solvent molecules and H-atoms are omitted for clarity. Selected bond lengths/angles: Zn(1)–S(1) = 2.3546(9) Å, Zn(1)–S(2a) = 2.4236(11) Å, Zn(1)–N(3) = 2.113(3) Å, Zn(1)–N(1) = 2.107(3) Å, Zn(1)–S(2) = 2.4592(13) Å, S(2a)–Zn(1)–S(1) = 108.82(4)°, S(2a)–Zn(1)–S(2) = 96.77(4)°, S(2a)–Zn(1)–N(3) = 80.91(9)°, S(2a)–Zn(1)–N(1) = 147.16(11)°, S(1)–Zn(1)–N(3) = 142.61(9)°, S(1)–Zn(1)–S(2) = 108.57(4)°, S(1)–Zn(1)–N(1) = 79.54(8)°.

highest activities, whereas Zn(salphen) building blocks with smaller groups proved to be less efficient ascribed to their competing self-dimerization. This self-assembly behavior thus limits the effectiveness in Lewis acid mediated catalysis. The occurrence of Zn(salphen) self-assembly is easily recognized by UV–Vis spectroscopy and titration of these complexes with pyridine leads to significantly different absorption spectra [31,32]. Therefore, the possible dimer formation of Zn complex **3** was additionally studied by UV–Vis titration with a suitable titrant (epoxyhexane) in different solvents (methyl ethyl ketone) to evaluate the formation of monomeric **3** upon addition of the epoxide. The addition of epoxide did not lead to any observable changes in the UV–Vis spectrum which may be interpretated as **3** already existing as a monomer under these conditions. Alternatively, when we titrated complex **3** with pyridine (Supporting Information), clear 1:1 complexation was observed and the stability constant K_s is in the same order as for pyridine binding at Zn(salphen) structures. This further supports the preferential presence of monomeric **3** in solution.

Complexes **1**–**3** were screened as catalysts for the formation of cyclic carbonates using CO_2 and propylene oxide as reagents, under relatively mild reaction conditions (T = 45 °C, $p(CO_2)$ = 10 bar) as a starting point using tetrabutylammonium iodide as co-catalyst and methyl ethyl ketone (MEK) as medium (Table 1).

Table 1
Screening of reaction conditions and catalysts (**1**–**3**) using propylene oxide as standard substrate, a $p(CO_2)$ of 10 bar, NBu_4I as co-catalyst and a reaction time of 18 h, [Zn(btsc)] = 3.7–11.1 mM.



Entry	Complex (mol%)	Co-cat (mol%)	T (°C)	Solvent	Yield[a] (%)
1	**1** (1)	1	45	MEK	15[b]
2	**1** (1)	2.5	45	MEK	72[b]
3	**1** (1)	1	65	MEK	70[b]
4	**2** (1)	1	45	MEK	18[b]
5	**2** (1)	2.5	45	MEK	54[b]
6	**2** (1)	1	65	MEK	52[b]
7	**3** (1)		45	MEK	0
8		1	45	MEK	0
9	**3** (1)	1	25	MEK	18
10	**3** (1)	1	45	MEK	66
11	**3** (1)	1	65	MEK	89
12	**3** (2)	1	45	MEK	76
13	**3** (3)	1	45	MEK	90
14	**3** (1)	1	45	THF	16
15	**3** (1)	1	45	DCM	5[c]
16	**3** (1)	1	45	CH_3CN	19
17	**3** (1)	1	45	acetone	54

[a] Yield determined by ^1H NMR (DMSO-d_6) using mesitylene as an internal standard. No other products were observed and therefore the selectivity toward the cyclic carbonate is at least 99%.

[b] Note that in these cases only partial dissolution of the complexes is achieved before as well as after the reaction.

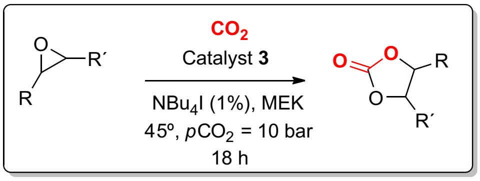
[c] After the reaction a heterogeneous mixture was observed.

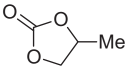
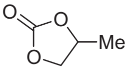
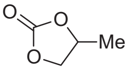
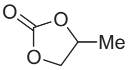
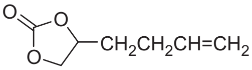
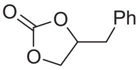
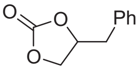
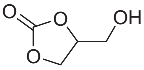
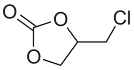
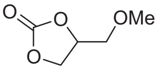
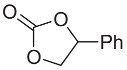
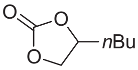
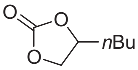
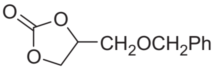
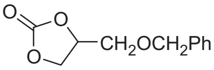
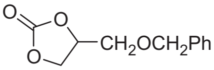
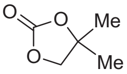
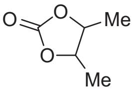
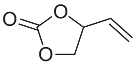
All three complexes proved to be active, although in those reactions employing either complex **1** or **2** (entries 1–6) heterogeneous mixtures were noted that may have affected catalytic turnover.[2] In all cases conversion to propylene carbonate was achieved, with the best performance noted for complex **3** (see entries 9–11). It should be noted that in the absence of either the catalyst (**3**) or co-catalyst (entries 7–8) no conversion was observed, which emphasized the need for both catalyst components for effective turnover. As may

---

[2] Attempts to solubilize complexes **1-2** at higher temperatures failed which indicates that during the reactions with these catalysts only partial dissolution is achieved. Furthermore, we analyzed these precipitates in order to identify any possible decomposition products: in these cases only the starting complexes **1-2** were identified by ^1H NMR spectroscopy.

Table 2
Screening of the substrate scope at 45 °C, pCO_2 = 10 bar, NBu_4I as co-catalyst (1 mol%), MEK as solvent and a reaction time of 18 h using catalyst **3** (1 mol%).



Entry	Substrate (R)	Substrate (R′)	Catalyst (mol%)	Product	Yield[a] (%)
1	Me	H	1		66
2	Me	H	2		76[b]
3	Me	H	3		90[c]
4	Me	H	2.5		90[d]
5	$CH_2CH_2CH{=}CH_2$	H	1		62
6	Bn	H	1		64
7	Bn	H	2		94[b,e]
8	CH_2OH	H	1		54
9	CH_2Cl	H	1		60
10	CH_2OMe	H	1		37
11	Ph	H	1		29
12	n-Bu	H	1		27[f]
13	n-Bu	H	2.5		80[d]
14	CH_2OCH_2Ph	H	1		57
15	CH_2OCH_2Ph	H	2		98[b,g]
16	CH_2OCH_2Ph	H	2.5		83[d]
17	1,1-di-Me	H	1		1
18	Me	Me	1		1
19	$CH{=}CH_2$	H	1		30

[a] Yield determined by ^1H NMR (DMSO-d_6) using mesitylene as an internal standard.
[b] 2 mol% of co-catalyst used.
[c] 3 mol% of co-catalyst used.
[d] Taken from Ref. [15]; here a Zn(salphen) complex was used.
[e] The calculated conversion using signal integration for both the remaining epoxide as well the carbonate product was 92%.
[f] The duplicate experiment gave a 29% yield of the product.
[g] The calculated conversion was 97%.

be expected, increasing co-catalyst concentration (entries 2 and 5), increasing the reaction temperature (entries 3, 6 and 11) or increasing the catalyst loading (entries 12 and 13) gives higher yield of propylene carbonate. The influence of other solvents on the product yield was also observed (entries 14–17); unlike in previous work [16], both DCM as well as CH_3CN turned out to be poor solvents, whereas acetone proved to be a rather good alternative.

The catalyst **3** was further employed to study the substrate scope in the formation of cyclic carbonates using various terminal epoxides (Table 2), MEK as solvent and using mild reaction conditions (45 °C, $p(CO_2) = 10$ bar) and a low catalyst loading. When using 1 mol% (3.7 mM) of **3**, yields of up to 66% are achieved (entry 1). These yields can simply be improved by increasing the catalyst load up to 3 mol% (11.1 mmol/l) giving, for instance, propylene carbonate in high(er) yield (entry 3, 90%). The same effect is observed for the conversion of other epoxides (entries 7 and 15). As also previously observed with Zn(salphen) based catalysts with sterically more congested epoxides [15,16], conversion of 1,1-dimethyl- and 1,2-dimethyl-oxirane (entries 17 and 18) proved to be difficult, which relates to the steric impediment in the ring-opening step of the coordinated epoxide upon using a bulky nucleophile (i.e., iodide). As may be expected for the less reactive epoxidic substrates (entries 11 and 19) lower yields under comparable conditions are achieved, while conversely, the benchmark substrate epoxyhexane unexpectedly gives only 27% yield (entry 12, 27%). This is lower than achieved with a similar substrate (entry 5) or using Zn(salphen) under similar reaction conditions [15,16].

4. Conclusions

In this work we have presented application of a new type of Zn complex based on btsc [btsc = bis-(thiosemicarbazonato)] ligands as effective catalysts for the cyclo-addition of CO_2 to various terminal expoxides under relatively mild reaction conditions. Complex **3** proved to be the most useful among the series **1**–**3** under our reaction conditions. Although X-ray diffraction revealed the formation of an unexpected dimeric assembly, the monomeric form is dominant in solution, as only the monomer is catalytically active. Also the UV–Vis experiments suggest that in solution the monomeric complex likely prevails. The use of a cheap and abundant metal in combination with an environmentally tolerable solvent such as MEK and mild reaction conditions further mark this catalytic process as a potentially sustainable way for cyclic carbonate synthesis.

Acknowledgements

This work was supported by ICIQ, ICREA, the Spanish Ministry of Science and Innovation (CTQ 2008-02050), Consolider Ingenio 2010 (CSD 2006-0003), the Marie Curie Research and Training Network “RevCat” and the Dutch National School Combination Catalysis Controlled by Chemical Design (NRSC-Catalysis).

Appendix A. Supplementary data

CCDC 817975 contains the supplementary crystallographic data for **1–3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.05.025.

References

[1] T. Sakakura, K. Kohno, Chem. Commun. (2009) 1312.
[2] T. Sakakura, J.-C. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365.
[3] M.R. Kember, A. Buchard, C.K. Williams, Chem. Commun. 47 (2011) 141.
[4] D.J. Darensbourg, Chem. Rev. 107 (2007) 2388.
[5] M. North, R. Pasquale, C. Young, Green Chem. 12 (2010) 1514.
[6] A. Decortes, A.M. Castilla, A.W. Kleij, Angew. Chem., Int. Ed. 49 (2010) 9822.
[7] M. Aresta, A. Dibenedetto, Dalton Trans. (2007) 2975.
[8] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.
[9] For an early example on direct CO_2 activation see: M. Aresta, C.F. Nobile, V.G. Albano, E. Forni, M. Manassero, J. Chem. Soc., Chem. Commun. (1975) 636.
[10] I.I.F. Boogaerts, S.P. Nolan, J. Am. Chem. Soc. 132 (2010) 8858.
[11] W. Clegg, R.W. Harrington, M. North, R. Pasquale, Chem.-Eur. J. 16 (2010) 6828.
[12] M.R. Kember, P.D. Knight, P.T.R. Reung, C.K. Williams, Angew. Chem., Int. Ed. 48 (2009) 931.
[13] R.L. Paddock, S.T. Nguyen, Chem. Commun. (2004) 1622.
[14] D.J. Darensbourg, R.M. Mackiewicz, J. Am. Chem. Soc. 127 (2005) 14026.
[15] A. Decortes, M. Martínez Belmonte, J. Benet-Buchholz, A.W. Kleij, Chem. Commun. 46 (2010) 4580.
[16] A. Decortes, A.W. Kleij, ChemCatChem 3 (2011) 831.
[17] A.R. Cowley, J.R. Dilworth, P.S. Donnelly, J.M. Heslop, S.J. Ratcliffe, Dalton Trans. (2007) 209.
[18] M. Christlieb, A.R. Cowley, J.R. Dilworth, P.S. Donnelly, B.M. Paterson, H.S.R. Struthers, J.M. White, Dalton Trans. (2007) 327.
[19] E. Hess, G. Baehr, Z. Anorg. Allg. Chem. 268 (1952) 351.
[20] E. Hess, E. Steinkopf, G. Schleitzer, G. Baehr, Z. Anorg. Allg. Chem. 273 (1953) 325.
[21] P.A. Stenson, A. Board, A. Marin-Becerra, A.J. Blake, E.S. Davies, C. Wilson, J. McMaster, M. Schroder, Chem.-Eur. J. 14 (2008) 2564.
[22] V. Bocokić, M. Lutz, A.L. Spek, J.N.H. Reek, Dalton Trans. 40, submitted for publication.
[23] G.M. Sheldrick, SHELXTL Crystallographic System Ver. 5.10, Bruker AXS, Inc., Madison, Wisconsin, 1998.
[24] For a related Cu(btsc) dimer see: A.R. Cowley, J.R. Dilworth, P.S. Donnelly, E. Labisbal, A. Sousa, J. Am. Chem. Soc. 124 (2002) 5270. Please note that in this case the S-atoms are *not* used in the formation of a dinuclear species..
[25] The chemistry of btsc ligands and their (Zn) complexes is well-documented, see: T.S. Lobana, R. Sharma, G. Bawa, S. Khanna, Coord. Chem. Rev. 253 (2009) 977.
[26] For other multinuclear Zn(btsc) systems see: D. Dayal, D. Palanimuthu, S.V. Shinde, K. Somasundaram, A.G. Samuelson, J. Biol. Inorg. Chem. 16 (2011) 621.
[27] For other multinuclear Zn(btsc) systems see: M. Christlieb, A.R. Cowley, J.R. Dilworth, P.S. Donnelly, B.M. Paterson, H.S.R. Struthers, J.M. White, Dalton Trans. (2007) 327.
[28] A.W. Kleij, Dalton Trans. (2009) 4635.
[29] J.K.-H. Hui, Z. Yu, M.J. MacLachlan, Angew. Chem., Int. Ed. 46 (2007) 7980.
[30] A.W. Kleij, M. Kuil, M. Lutz, D.M. Tooke, A.L. Spek, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, Inorg. Chim. Acta 359 (2006) 1807.
[31] M. Martínez Belmonte, S.J. Wezenberg, R.M. Haak, D. Anselmo, E.C. Escudero-Adán, J. Benet-Buchholz, A.W. Kleij, Dalton Trans. 39 (2010) 4541.
[32] J.A.A.W. Elemans, S.J. Wezenberg, E.C. Escudero-Adán, J. Benet-Buchholz, D. den Boer, M.J.J. Coenen, S. Speller, A.W. Kleij, S. De Feyter, Chem. Commun. 46 (2010) 2548.