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DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Synthesis and Single Crystal X-ray Structures of Cationic Zinc β -Diketiminato Complexes

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Dedicated to Prof. H. Nöth on the occasion of his 85th birthday

Keywords: Cations / Zinc / X-ray Analysis

The cationic zinc complex $[L^1Zn][Al(OC(CF_3)_3)_4]$ (**1**) ($L^1 = \{[(2,4,6-Me_3-C_6H_2)NC(Me)]_2CH\}$) bearing a weakly coordinating aluminate anion was obtained from reaction of L^1ZnCl with $Li[Al(OC(CF_3)_3)_4]$. In addition, base-stabilized zinc cations $[L^{1/2}Zn(base)_2][X]$ (**2** - **5**) ($L^2 = \{[(2,6-i-Pr_2-C_6H_3)NC(Me)]_2CH\}$; $X = [Al(OC(CF_3)_3)_4]$, $[B(C_6F_5)_4]$) containing weakly coordinating anions and different Lewis bases (dimethylaminopyridine (dmap), *tert*-butylpyridine (*t*-BuPy)) were synthesized and structurally

characterized. Moreover, the solid state structures of L^1ZnMe (**6**) and the neutral base-stabilized complexes *t*-BuPy- $Zn(Cl)L^1$ (**7**) and base- $Zn(Me)L^2$ (base = dmap **8**, *t*-BuPy **9**) are reported and compared with those of **2** - **5**. In addition, preliminary studies showed that **1** is catalytically active in lactide polymerization at 160 °C.

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Introduction

The ring opening polymerization of lactide has become a very active research field in the last decade,^[1,2] since polylactides have received considerable interest due to their biodegradable properties.^[3] Unfortunately, the commercially used catalyst, $SnOct_2$, causes problems in the biomedical field due to its toxicity.^[2,4] As a consequence, there is an increasing demand in the development of new catalysts, which are non-toxic and of low cost, hence leading to the synthesis of very active zinc, aluminum, magnesium or lanthanide catalysts.^[5-8]

Organozinc-based catalysts have been investigated for a long time. Early studies of Dittich and Schulz reported on the use of $ZnMe_2$, $AlMe_3$ and $SnCl_4$ in the lactide polymerization,^[9] whereas Kricheldorf et al. later on introduced more active aluminum alkoxides.^[10] However, it was the pioneering work of Coates et al., that clearly set the focus on neutral zinc alkoxide complexes based on monoanionic β -diketiminato ligands. Complexes of this type were found to show a very high activity and also stereoselectivity in lactide polymerization.^[11] Moreover, these complexes were found even to copolymerize CO_2 and epoxides.^[12] The β -diketiminato ligands of the type $[HC\{C(Me)NR\}_2]$ are almost ideal ligands for the synthesis

of tailor-made catalysts since their steric demand as well as electronic properties can be precisely controlled by variation of the organic substituents R bound to the imine centers.

Scheme 1. Catalytically active cationic zinc complexes.

Based on the experimental finding, that zwitterionic tris(pyrazolyl)borate complexes are active polymerization catalysts,^[13] Hayes et al. suggested, that the activity of metal complexes in the lactide polymerization can be increased by use of more electropositive metals.^[14] Aside from changing the metal atom, the acidity of a cationic metal complex is also higher compared to its neutral form, hence promoting facile coordination of lactide. Cationic metal complexes have been shown to be effective catalysts in the ring-

opening polymerization of lactones,^[15] whereas lactide polymerization has been studied to a lesser extent.^[16]

Structurally characterized cationic complexes containing coordinative saturated zinc atoms are well known,^[17] whereas the number of structurally characterized three-coordinated cationic zinc complexes was limited for a long time to Bochmann cationic zinc diazadiene complexes.^[15b,f] Recently, Hayes et al. synthesized three-coordinated cationic zinc complexes bearing weakly coordinating anions based on mono(phosphinimine)dibenzofuran as well as on bis(phosphinimine)dibenzofuran pincer-type ligands (type **II**).^[18,19] Unfortunately, these cationic alkyl zinc complexes of the type $[LZnR]^+$ ($R = \text{Me, Ph}$) were found to be almost inactive for the polymerization of lactide. However, the steric demand of the organic ligand bound to the imine center as well as the alkyl group bound to the Zn center were found to play a crucial role on the catalytic activity of the complex. For instance, the cationic complex **VI** containing the sterically less demanding Pipp-substituent (Pipp = *p*-isopropyl phenyl) and a zinc-lactate moiety was found to polymerize 200 equiv. of lactide within 50 min at ambient temperature.^[20] In contrast, the sterically less demanding Ph-substituted complex **IV** is unexpectedly less active than **VI**, most likely due to electronic effects.^[21] The phenyl group on the N-aryl rings reduces the electron donating capacity of the ligand, whereby the zinc center in **IV** is more electropositive and reduces its polymerization activity. The exchange of the bulky phenyl ligands at the phosphorus atoms by sterically less demanding ethyl groups yielded **V**,^[22] which showed an increased catalytic activity. 200 equiv. of lactide were polymerized within 20 min at ambient temperature, clearly demonstrating the crucial role of steric and electronic effects on the resulting catalytic activity. Very recently, cationic zinc complexes containing both three- and four-coordinated zinc atoms were successfully used in polymerization reactions.^[16f,g,19-23] Three-coordinated cationic complexes of type **VII** are active in lactide polymerization and trimethylene carbonate polymerization.^[16g] In addition, the base-stabilized complex **VIII** was found to polymerize ϵ -caprolactone without the need of additional initiators such as alcohols.^[23]

Herein, we report on the synthesis of base-free and base-stabilized cationic zinc complexes based on β -diketiminato ligands. The latter were also structurally characterized by single crystal X-ray diffraction. Furthermore, the catalytic activity of $[L^1Zn][Al\{OC(CF_3)_3\}_4]$ (**1**) in the ring opening polymerization of lactide was investigated.

Results and Discussion

L^1ZnCl ($L^1 = \{(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)\text{NC}(\text{Me})_2\text{CH}\}$ ^[24]) reacts with one equivalent of $[M\{Al\{OC(CF_3)_3\}_4\}]$ ($M = \text{Li, Ag}$), which contains a weakly coordinating perfluorinated alkoxyaluminate anion,^[25,26] with subsequent formation of $[L^1Zn][Al\{OC(CF_3)_3\}_4]$ (**1**) in high yield. **1** is soluble in CH_2Cl_2 upon warming to 40 °C and precipitates slowly as colorless crystalline solid upon cooling to ambient temperature. ¹H and ¹³C NMR spectra of **1** show two sets of resonances due to the Mesnacnac ligand, most likely indicating the coordination of one mesityl group to the electrophilic Zn cation as was observed in the solid state structure of the neutral amidinate complex $[t\text{-BuC}(\text{NDipp})_2\text{ZnMe}]$.^[27] Unfortunately, numerous attempts

to grow suitable crystals for a single crystal X-ray diffraction study failed, to date.

Since the solubility of the cationic zinc β -diketiminato complexes $[L^{1/2}Zn]^+[Anion]^-$ was expected to be increased by coordination of strong Lewis bases to the electrophilic zinc center, we reacted L^1ZnCl and L^2ZnMe with $M[Al\{OC(CF_3)_3\}_4]$ ($M = \text{Li, Ag}$) and $\text{Ph}_3\text{C}[X]$ [$X^1 = [Al\{OC(CF_3)_3\}_4]$, $X^2 = [B(C_6F_5)_4]$, respectively, in the presence of two equivalents of either 4-dimethylaminopyridine (dmap) or *t*-BuPy. The reaction progress on the reaction with $\text{Ph}_3\text{C}[X]$, which is given by the formation of Ph_3CMe , can be *in situ* monitored by ¹H NMR spectroscopy.

Scheme 2. Synthetic routes to cationic β -diketiminato zinc complexes.

Base-stabilized $[L^1Zn(\text{dmap})_2][Al\{OC(CF_3)_3\}_4]$ (**2**) and $[L^2Zn(\text{base})_2][X^{1/2}]$ ($L^2 = \{(2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)\text{NC}(\text{Me})_2\text{CH}\}$ (Dippnacnac); $X^1 = [Al\{OC(CF_3)_3\}_4]$, base = *t*-BuPy (**3**), $X^2 = [B(C_6F_5)_4]$, base = dmap (**4**), *t*-BuPy (**5**)) were obtained in high yields (> 80%). The resonances of the Lewis bases (dmap, *t*-BuPy) are shifted toward higher (CH) and lower field (CH_3) compared to those of the "free" bases. Moreover, the relative intensity of the resonances due to the anionic β -diketiminato group and the Lewis bases (dmap, *t*-BuPy) of 1:2 indicates the formation of stable bis-adducts in solution. Complexes **2** – **5**, which are soluble in organic solvents such as CH_2Cl_2 , toluene or benzene, do not show any sign of decomposition over a period of several days.

2 – **5** were structurally characterized by single crystal X-ray diffraction. The complexes, which show almost identical structural parameters (Table 1), each consist of a twofold base-stabilized zinc cation and the respective anion, which shows no interactions to the cationic zinc center. The zinc centers in the cations adopt a tetrahedral coordination sphere as was previously reported for cationic zinc complexes.^[26,32,16h] Analogous findings were observed for the corresponding neutral base-stabilized complexes *t*-BuPy-Zn(Cl) L^1 (**7**) and base-Zn(Me) L^2 (base = dmap **8**, *t*-BuPy **9**), which have been prepared by equimolar reaction of L^1ZnCl and L^2ZnMe with the corresponding Lewis base and structurally characterized in order to compare their structural

parameters with those of **2** – **5**. In contrast, L^1ZnMe **6** exhibits a threefold-coordinated Zn center.^[29c]

The bonding parameters of the β -diketiminate ligand frameworks as well as the Zn-N bond distances of the six-membered ZnN_2C_3 rings in **2** – **5** are within the typical range as reported by us and others.^[29] The C-N and C-C bond lengths within the β -diketiminate backbones are almost identical compared to those of the neutral base stabilized complexes t -BuPy-Zn(Cl) L^1 (**7**), dmap-Zn(Me) L^2 (**8**), and t -BuPy-Zn(Me) L^2 (**9**) (Table 2).

Figure 1. Crystal structure of $[L^1Zn(dmap)_2][Al\{OC(CF_3)_3\}_4]$ (**2**). All hydrogen atoms and alternative site of the disorder have been omitted for clarity. Ellipsoids are drawn at 50 % probability level.

Table 1. Central bond lengths (Å) and bond angles (°) of $[L^1Zn(dmap)_2][Al\{OC(CF_3)_3\}_4]$ (**2**), $[L^2Zn(t-BuPy)_2][Al\{OC(CF_3)_3\}_4]$ (**3**), $[L^2Zn(dmap)_2][B(C_6F_5)_4]$ (**4**), and $[L^2Zn(t-BuPy)_2][B(C_6F_5)_4]$ (**5**).

	2	3	4	5
Zn-N1/2	1.9595(18)	1.955(3)	1.9723(8)	1.9562(13)
	1.9638(17)	1.956(4)	1.9682(18)	1.9602(14)
Zn-N _{amine}	1.9947(17)	2.060(4)	1.9935(18)	2.0257(14)
	2.0488(18)	2.020(4)	2.0540(19)	2.0417(14)
N1-C1	1.328(3)	1.331(5)	1.333(3)	1.332(2)
N2-C3	1.327(3)	1.321(5)	1.318(3)	1.328(2)
C1-C2	1.404(3)	1.401(6)	1.400(3)	1.408(2)
C2-C3	1.404(3)	1.408(6)	1.422(3)	1.409(2)
N1-Zn1-N2	97.50(7)	99.19(14)	98.75(7)	99.19(6)
Zn1-N1-N1-C1	119.12(15)	118.5(3)	116.46(14)	117.83(11)
Zn1-N2-N2-C3	118.74(15)	119.2(3)	117.42(15)	119.01(11)
C1-C2-C3	128.7(2)	129.7(4)	129.6(2)	129.43(15)

Table 2. Central bond lengths (Å) and bond angles (°) of $[L^1ZnMe]$ (**6**) and base-stabilized, neutral zinc complexes t -BuPy-Zn(Cl) L^1 (**7**) as well as base-Zn(Me) L^2 (base = dmap **8**, t -BuPy **9**).

	6	7	8	9
Zn-N1/2	1.946(2)	1.9842(12)	2.023(2)	2.0423(11)
	1.9596(16)	1.9803(12)	2.028(2)	2.0251(10)
Zn-N _{amine}	–	2.0699(12)	2.097(2)	2.1464(11)
Zn-Cl	–	2.2074(4)	–	–

Zn-C	1.946(2)	–	1.995(3)	1.9825(14)
N1-C1	1.327(2)	1.3251(18)	1.331(3)	1.3178(15)
N2-C3	1.336(3)	1.3243(18)	1.327(3)	1.3279(16)
C1-C2	1.408(3)	1.410(2)	1.410(3)	1.4130(17)
C2-C3	1.399(3)	1.407(2)	1.403(4)	1.4051(18)
N1-Zn1-N2	96.02(7)	97.48(5)	94.62(9)	93.90(4)
Zn1-N1-N1-C1	123.42(13)	120.27(9)	122.30(18)	122.85(8)
Zn1-N2-N2-C3	122.69(13)	120.61(9)	122.07(17)	121.60(9)
C1-C2-C3	128.62(18)	129.12(13)	130.0(2)	128.98(11)

In contrast, the neutral complexes **7** – **9** show slightly elongated Zn-N bond lengths compared to those of the cationic complexes **2** – **5**, most likely resulting from the increased electrophilicity of the cationic zinc centers and due to higher ionic bonding contributions, as well as slightly larger Zn-N-C bond angles. L^1ZnMe (**6**), which only contains a threefold-coordinated Zn center, shows almost identical bonding parameters compared to the cationic complex **2**. Moreover, the Zn-N bond lengths compare very well with the values obtained from DFT calculations for L^1ZnMe (2.0025, 2.0018)^[29c] and L^2ZnMe (1.9480(18), 1.9429(18) Å), respectively.^[24] The Zn-N_{amine} bond lengths to the coordinating Lewis bases are significantly longer as was expected (Table 1).

Figure 2. Crystal structure of $[L^2Zn(t-BuPy)_2][B(C_6F_5)_4]$ (**5**). All hydrogen atoms as well as the solvent molecule have been omitted for clarity. Ellipsoids are drawn at 50 % probability level. The relative orientation of the ions does not resemble their orientation in the asymmetric unit.

Preliminary polymerization studies. Initial studies demonstrated the capability of complex **1** to serve as catalyst in ring opening polymerization (ROP) of lactide.

Scheme 3. Ring opening polymerization of lactide by use of bulk **1**.

Since **1** is not soluble in organic solvents at room temperature, its catalytic activity could not be investigated at ambient temperature. However, **1** is active in bulk

polymerization at 160 °C, converting 200 equivalents of lactide within 8 min into polylactide. The molecular weight (M_w ; $1.2 \cdot 10^5$ g/mol) and the polydispersity index (PDI; 1.73) of the resulting polylactide was determined by gel permeation chromatography (GPC) in hexafluoroisopropanol (HFIP) with 0.05 M potassiumtrifluoroacetate (KTFAC) at 23 °C (flow 1 mL/min) using a refractive index detector (RI).

Conclusions

The base-free cationic zinc complex $[L^1Zn][Al\{OC(CF_3)_3\}_4]$ (**1**) is accessible by reactions of $[L^1ZnCl]$ with $M[Al\{OC(CF_3)_3\}_4]$ ($M = Li, Ag$). In contrast, reactions of $[L^2ZnMe]$ with $Ph_3CX^{1/2}$ in the presence of two equivalents of a Lewis base yielded base-stabilized complexes $[L^1Zn(dmap)_2][Al\{OC(CF_3)_3\}_4]$ (**2**), $[L^2Zn(t-BuPy)_2][Al\{OC(CF_3)_3\}_4]$ (**3**), $[L^2Zn(dmap)_2][B(C_6F_5)_4]$ (**4**), and $[L^2Zn(t-BuPy)_2][B(C_6F_5)_4]$ (**5**), respectively, which were fully characterized including single crystal X-ray analyses. $[L^1Zn][Al\{OC(CF_3)_3\}_4]$ **1** is an active lactide polymerization catalyst in its bulk form at 160 °C. Detailed studies on the catalytic activity of **1** as well as of base-stabilized complexes **2** - **5** in ROP of lactide are currently under investigation.

Experimental Section

General: All manipulations involving air-sensitive materials were performed using standard vacuum techniques and inert gas atmosphere (argon, < 0.3 ppm O_2) or in a glove box (MBraun Unilab V2.0). Solvents were carefully dried (CH_2Cl_2) with CaH_2 , degassed and stored in teflon-sealed glass vessel over appropriate drying agents (molecular sieve). L^1ZnR ($R = Me$ (**6**), Cl),^[29c] L^2ZnR ($R = Me, Cl$),^[24,30] $M[Al\{OC(CF_3)_3\}_4]$ ($M = Li, Ag$),^[25] $Ph_3C[Al\{OC(CF_3)_3\}_4]$,^[31] $Li[B(C_6F_5)_4]$,^[32] and $Ph_3C[B(C_6F_5)_4]$ ^[32] were synthesized according to literature methods. 1H , ^{13}C and ^{19}F NMR spectra were collected with a Bruker Advance 300 spectrometer and are referenced to internal CD_2Cl_2 (1H : $\delta = 5.36$, ^{13}C : $\delta = 53.4$) and external CCl_3F (^{19}F : $\delta = 0.31$). Elemental analyses were performed at the Labor für Elementaranalyse of the University of Duisburg-Essen. GPC data, the average molar mass (M_n) and molar mass distribution (M_w/M_n) were obtained on a gel permeation chromatography (GPC) in hexafluoroisopropanol (HFIP) with 0.05 M potassiumtrifluoroacetate (KTFAC) at 23 °C (flow rate 1 mL/min). Three column (PSS-PFG 1000; 300; 100 Å, 7 μm) were used in combination with a refractive index and diode array detector and calibrated with polymethylmethacrylate. The polymer samples were dissolved in HFIP (3.4 mg/mL) at 23 °C.

$[L^1Zn][Al\{OC(CF_3)_3\}_4]$ (1**):** L^1ZnCl (0.43 g, 1.0 mmol) and $Li(Al(OC(CF_3)_3)_4)$ (0.97 g, 1.0 mmol) were dissolved in 50 mL of CH_2Cl_2 and heated to 60 °C for 1 h. The resulting suspension was hot filtered and the solvent of the filtrate evacuated under vacuum to give **1** as a colorless solid (1.11 g, 81 %). Elemental analysis calcd (%) for $C_{39}H_{29}N_2ZnAlO_4F_{36}$: C 34.3, H 2.1, N 2.1; found: C 37.5, H 2.8, N 2.0. 1H NMR (300 MHz, CD_2Cl_2 , 27 °C): $\delta = 1.54$ (s, 3H, $\beta-CCH_3^1$), 1.76 (s, 6H, $o-CH_3^1$), 1.86 (s, 6H, $o-CH_3^2$), 2.06 (s, 3H, $\beta-CCH_3^2$), 2.46 (s, 3H, $p-CH_3^1$), 2.47 (s, 3H, $p-CH_3^2$), 3.98 (s, 1H, $\gamma-CH$), 6.82 (s, 2H, $m-H^1$), 6.91 (s, 2H, $m-H^2$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): $\delta = 17.4$ ($o-CH_3^1$), 17.6 ($o-CH_3^2$), 20.7 ($\beta-CCH_3^1$), 20.9 ($\beta-CCH_3^2$), 22.9 ($p-CH_3^1$), 24.9 ($p-CH_3^2$), 95.1 ($\gamma-C$), 121.2 (q, $J_{C-F} = 292.3$ Hz, CF_3), 127.6 ($m-C^1$), 129.3 ($m-C^2$), 130.3 ($o-C^1$), 131.5 ($o-C^2$), 133.9 ($p-C^1$), 137.3 ($p-C^2$), 138.7 ($i-C^1$),

143.0 ($i-C^2$), 169.9 ($\beta-C^1CH_3$), 183.7 ($\beta-C^2CH_3$). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C) $\delta = -75.4$.

$[L^1Zn(dmap)_2][Al\{OC(CF_3)_3\}_4]$ (2**):** L^1ZnCl (0.22 g, 0.5 mmol) was dissolved in 40 mL of CH_2Cl_2 . $Ag(Al(OC(CF_3)_3)_4)$ (0.54 g, 0.5 mmol) and $dmap$ (0.12 g, 1.0 mmol) were added and the resulting mixture was stirred for 18 h at room temperature. The solution was filtered, concentrated to 5 mL and stored at -30 °C. Colorless crystals of **2** were formed within 24 h (0.72 g, 89 %). Elemental analysis calcd (%) for $C_{53}H_{49}N_6ZnAlO_4F_{36}$: C 39.5, H 3.1, N 5.2; found: C 39.6, H 3.3, N 5.5. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): $\delta = 1.80$ (s, 6H, $\beta-CCH_3$), 1.88 (s, 12H, $o-CH_3$), 2.31 (s, 6H, $p-CH_3$), 3.05 (s, 12H, $N(CH_3)_2$), 5.01 (s, 1H, $\gamma-CH$), 6.40 (d, $^3J_{HH} = 7.2$ Hz, 4H, $C(3)-H_{dmap}$), 6.82 (s, 4H, $m-H$), 7.11 (d, $^3J_{HH} = 7.2$ Hz, 4H, $C(2)-H_{dmap}$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) $\delta = 17.9$ ($o-CH_3$), 20.4 ($\beta-CCH_3$), 20.6 ($p-CH_3$), 39.0 ($N(CH_3)_2$), 93.8 ($\gamma-C$), 107.1 ($C(3)_{dmap}$), 121.2 (q, $J_{C-F} = 293.3$ Hz, CF_3), 129.3 ($m-C$), 131.6 ($o-C$), 134.4 ($p-C$), 144.2 ($i-C$), 147.3 ($C(2)_{dmap}$), 155.5 ($C(4)_{dmap}$), 168.6 ($\beta-CCH_3$). ^{19}F NMR (282 MHz, CD_2Cl_2 , 25 °C) $\delta = -75.7$.

$[L^2Zn(t-BuPy)_2][Al\{OC(CF_3)_3\}_4]$ (3**):** L^2ZnMe (0.25 g, 0.5 mmol) was dissolved in 40 mL of CH_2Cl_2 . $Ph_3C(Al(OC(CF_3)_3)_4)$ (0.61 g, 0.5 mmol) and $t-BuPy$ (0.14 g, 1.0 mmol) were added and the resulting mixture was stirred for 18 h at room temperature. The solvent was removed at reduced pressure and the colorless solid extracted with n -pentane (20 mL). **3** was obtained after storage at -30 °C as colorless crystals (0.68 g, 79 %). Elemental analysis calcd (%) for $C_{63}H_{67}N_4ZnAlO_4F_{36}$: C 44.0, H 3.9, N 3.3; found: C 45.6, H 4.0, N 3.0. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): $\delta = 0.52$ (d, $^3J_{HH} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 1.14 (d, $^3J_{HH} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 1.33 (s, 18H, $C(CH_3)_3$), 1.95 (s, 6H, $\beta-CCH_3$), 2.90 (sept, $^3J_{HH} = 6.8$ Hz, 4H, $CH(CH_3)_2$), 5.15 (s, 1H, $\gamma-CH$), 7.19-7.28 (6H, $m/p-H$), 7.47 (d, $^3J_{HH} = 6.4$ Hz, 4H, $C(3)-H_{Py}$), 7.52 (d, $^3J_{HH} = 6.4$ Hz, 4H, $C(2)-H_{Py}$). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) $\delta = 23.2$ ($CH(CH_3)_2$), 23.5 ($\beta-CCH_3$), 24.0 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 29.7 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 94.5 ($\gamma-C$), 121.3 (q, $J_{C-F} = 293.3$ Hz, CF_3), 123.6 ($C(3)_{Py}$), 124.4 ($m-C$), 126.5 ($p-C$), 142.2 ($o-C$), 143.0 ($i-C$), 148.2 ($C(2)_{Py}$), 167.4 ($C(4)_{Py}$), 170.5 ($\beta-CCH_3$). ^{19}F NMR (282 MHz, CD_2Cl_2 , 25 °C) $\delta = -75.7$.

$[L^2Zn(dmap)_2][B(C_6F_5)_4]$ (4**):** L^2ZnMe (0.25 g, 0.5 mmol) was dissolved in 40 mL of CH_2Cl_2 . $Ph_3C(B(C_6F_5)_4)$ (0.46 g, 0.5 mmol) and two equivalents of $dmap$ (0.12 g, 1.0 mmol) were added and the resulting mixture was stirred for 18 h at 60 °C. The solvent was removed at reduced pressure and the resulting light green powder extracted with n -pentane. **4** was obtained as colorless crystalline solid after storage at -30 °C for 24 h (0.61 g, 86 %). Elemental analysis calcd (%) for $C_{67}H_{61}N_6ZnBF_2O$: C 57.2, H 4.4, N 6.0; found: C 61.3, H 4.5, N 4.9. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): $\delta = 0.67$ (d, $^3J_{HH} = 6.78$ Hz, 12H, $CH(CH_3)_2$), 1.15 (d, $^3J_{HH} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 1.89 (s, 6H, $\beta-CCH_3$), 3.04 (s, 12H, $N(CH_3)_2$), 3.04 (sept, $^3J_{HH} = 6.8$ Hz, 4H, $CH(CH_3)_2$), 5.04 (s, 1H, $\gamma-CH$), 6.40 (d, $^3J_{HH} = 6.80$ Hz, 4H, $C(3)-H_{dmap}$), 7.10 (d, $^3J_{HH} = 6.80$ Hz, 4H, $C(2)-H_{dmap}$), 7.20-7.28 (6H, $m/p-H$); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) $\delta = 23.4$ ($CH(CH_3)_2$), 23.5 ($\beta-CCH_3$), 24.0 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 39.0 ($N(CH_3)_2$), 94.0 ($\gamma-C$), 107.2 ($C(3)_{dmap}$), 124.1 ($m-C$), 129.0 ($p-C$), 134.6 ($i-C_6F_5$), 137.9 ($m-C_6F_5$), 142.4 ($o-C$), 143.7 ($i-C$), 146.5 ($p-C_6F_5$), 147.5 ($C(2)_{dmap}$), 149.7 ($o-C_6F_5$), 155.4 ($C(4)_{dmap}$), 169.7 ($\beta-CCH_3$). ^{19}F NMR (282 MHz, CD_2Cl_2 , 25 °C) $\delta = -167.6$, -163.8, -133.1.

$[L^2Zn(t-BuPy)_2][B(C_6F_5)_4]$ (5**):** L^2ZnMe (0.25 g, 0.5 mmol) was dissolved in 40 mL of CH_2Cl_2 . $Ph_3C(B(C_6F_5)_4)$ (0.46 g, 0.5 mmol) and $t-BuPy$ (0.14 g, 1.0 mmol) were added and the resulting mixture was stirred for 18 h at room temperature. The solvent was removed at reduced pressure and the colorless solid extracted with

n-pentane (20 mL). **5** was obtained as colorless crystalline solid after storage at -30 °C for 24 h (0.67 g, 94 %). Elemental analysis calcd (%) for $C_{71}H_{67}N_4ZnBF_{20} \cdot CH_2Cl_2$: C 57.3, H 4.5, N 3.7; found: C 56.9, H 4.6, N 3.5. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 0.52 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.33 (s, 18H, $C(CH_3)_3$), 1.95 (s, 6H, β -CCH₃), 2.90 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 5.15 (s, 1H, γ -CH), 7.19–7.28 (6H, *m/p*-H), 7.47 (d, $^3J_{HH}$ = 6.4 Hz, 4H, C(3)-H_{Py}), 7.52 (d, $^3J_{HH}$ = 6.4 Hz, 4H, C(2)-H_{Py}). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C) δ = 23.2 ($CH(CH_3)_2$), 23.5 (β -CCH₃), 24.0 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 29.7 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 94.5 (γ -C), 123.6 (C(3)_{Py}), 124.4 (*m*-C), 126.5 (*p*-C), 134.6 (*i*-C₆F₅), 137.9 (*m*-C₆F₅), 142.2 (*o*-C), 143.0 (*i*-C), 146.5 (*p*-C₆F₅), 148.2 (C(2)_{Py}), 149.7 (*o*-C₆F₅), 167.4 (C(4)_{Py}), 170.5 (β -CCH₃). ^{19}F NMR (282 MHz, CD_2Cl_2 , 25 °C) δ = -167.6, -163.8, -133.1.

t-BuPy-Zn(Cl)L¹ (7): L^1ZnCl (0.43 g, 1.0 mmol) and t-BuPy (0.14 g, 1.0 mmol) were dissolved in 50 ml of THF and the resulting mixture was stirred for 18h at room temperature. The solution was concentrated to 5 mL and stored at -30 °C. Colorless crystals of **7** were formed within 24 h (0.52 g, 92 %). Elemental analysis calcd (%) for $C_{32}H_{42}ClN_3Zn$: C 67.5, H 7.4, N 7.4; found: C 66.3, H 7.3, N 7.1. 1H NMR (300 MHz, CD_2Cl_2 , -80 °C): δ = 1.23 (s, 9H, $C(CH_3)_3$), 1.41 (s, 6H, *o*-CH₃¹), 1.54 (s, 6H, *o*-CH₃²), 2.09 (s, 6H, β -CCH₃), 2.17 (s, 6H, *p*-CH₃), 4.76 (s, 1H, γ -CH), 6.70 (s, 2H, *m*-H¹), 6.83 (s, 2H, *m*-H²), 7.39 (d, $^3J_{HH}$ = 5.8 Hz, 2H, C(3)-H_{Py}), 8.38 (d, $^3J_{HH}$ = 5.8 Hz, 2H, C(2)-H_{Py}); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = 18.2 (*o*-CH₃¹), 19.1 (*o*-CH₃²), 21.1 (β -CCH₃), 23.4 (*p*-CH₃), 30.5 ($C(CH_3)_3$), 35.8 ($C(CH_3)_3$), 93.6 (γ -C), 122.6 (C(3)_{Py}), 128.9 (*m*-C¹), 129.5 (*m*-C²), 131.6 (*o*-C¹), 133.0 (*o*-C²), 134.0 (*p*-C), 143.0 (*i*-C), 149.3 (C(2)_{Py}), 165.3 (C(4)_{Py}), 168.3 (β -CCH₃).

dmap-Zn(Me)L² (8): L^2ZnMe (0.50 g, 1.0 mmol) and dmap (0.12 g, 1.0 mmol) were dissolved in 5 ml of CH_2Cl_2 and the resulting mixture was stirred for 18h at room temperature. The solution was concentrated to 2 mL and stored at -30 °C. Colorless crystals of **8** were formed within 24 h (0.56 g, 90 %). Elemental analysis calcd (%) for $C_{37}H_{54}N_4Zn \cdot CH_2Cl_2$: C 64.7, H 8.0, N 7.9; found: C 65.1, H 7.8, N 8.3. 1H NMR (300 MHz, CD_2Cl_2 , 20 °C): δ = -1.24 (s, 3H, $ZnCH_3$), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.26 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.79 (s, 6H, β -CCH₃), 3.01 (s, 6H, $N(CH_3)_2$), 3.07 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 5.07 (s, 1H, γ -CH), 6.53 (d, $^3J_{HH}$ = 6.50 Hz, 2H, C(3)-H_{dmap}), 7.19 (s, 6H, *m/p*-H), 8.20 (d, $^3J_{HH}$ = 6.50 Hz, 2H, C(2)-H_{dmap}). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = -18.5 ($ZnCH_3$), 23.3 ($CH(CH_3)_2$), 23.4 (β -CCH₃), 24.0 ($CH(CH_3)_2$), 27.9 ($CH(CH_3)_2$), 38.9 ($N(CH_3)_2$), 94.1 (γ -C), 106.4 (C(3)_{dmap}), 123.2 (*m*-C), 124.7 (*p*-C), 141.9 (*o*-C), 145.3 (*i*-C), 149.5 (C(2)_{dmap}), 154.5 (C(4)_{dmap}), 166.8 (β -CCH₃).

t-BuPy-Zn(Me)L² (9): L^2ZnMe (0.50 g, 1.0 mmol) and t-BuPy (0.14 g, 1.0 mmol) were dissolved in 5 ml of CH_2Cl_2 and the resulting mixture was stirred for 18h at room temperature. The solution was concentrated to 2 mL and stored at -30 °C. Colorless crystals of **9** were formed within 24 h (0.58 g, 91 %). Elemental analysis calcd (%) for $C_{39}H_{57}N_3Zn \cdot C_2H_4Cl_4$: C 61.3, H 7.7, N 5.2; found: C 60.7, H 8.3, N 4.5. 1H NMR (300 MHz, CD_2Cl_2 , 20 °C): δ = -1.23 (s, 3H, $ZnCH_3$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.35 (s, 9H, $C(CH_3)_3$), 1.79 (s, 6H, β -CCH₃), 3.06 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 5.08 (s, 1H, γ -CH), 7.19 (s, 6H, *m/p*-H), 7.32 (d, $^3J_{HH}$ = 6.40 Hz, 2H, C(3)-H_{Py}), 8.51 (s, $^3J_{HH}$ = 6.40 Hz, 2H, C(2)-H_{Py}). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = -17.6 ($ZnCH_3$), 23.0 ($CH(CH_3)_2$), 23.2 (β -CCH₃), 23.9 ($CH(CH_3)_2$), 27.9 ($CH(CH_3)_2$), 30.2 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 94.8 (γ -C), 122.6 (C(3)_{Py}), 123.3 (*m*-C), 125.1 (*p*-C), 141.6 (*o*-C), 144.5 (*i*-C), 149.3 (C(2)_{Py}), 165.3 (C(4)_{Py}), 167.3 (β -CCH₃).

Polymerization studies. A mixture of freshly prepared **1** (0.0683 g, 0.05 mmol) and lactide (1.4413g, 10 mmol) was heated in the absence of any solvent over the melting point of lactide to 160 °C for 8 min in a glass reactor. After cooling to room temperature the less remaining monomer lactide on the reactor wall was dissolved in CH_2Cl_2 and separated. The crude polymer was slowly dissolved in 10 mL of THF, exposed to air and 10 mL of cold methanol was added. This solution was quenched in 80 mL of *n*-hexane and the white polymer precipitation was isolated by filtration and dried in vacuo.

Single crystal X-ray analyses. X-ray crystal structures were collected using a Bruker AXS D8 Kappa diffractometer with APEX2 detector (MoK α radiation, λ = 0.71073 Å) at T = 100(1) K (**6** 180(1)K). The structures were solved by Direct Methods (SHELXS-97)^[33] and refined by full-matrix least-squares on F^2 . Semi-empirical absorption corrections from equivalent reflections on basis of multi-scans (Bruker AXS APEX2) were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model.^[34] **2:** [$C_{37}H_{49}N_6Zn$][$AlCl_6F_{36}O_4$], M = 1610.33, colorless crystal (0.32 x 0.26 x 0.18 mm); monoclinic, space group $P2_1/n$; a = 13.7265(3), b = 23.7765(5), c = 20.4753(5) Å; β = 107.2980(10)°, V = 6380.2(2) Å³; Z = 4; μ = 0.554 mm⁻¹; $\rho_{ber.}$ = 1.676 g cm⁻³; 89530 reflexes ($2\theta_{max}$ = 57°), 16119 unique (R_{int} = 0.0326); Goof 1.020; 1018 parameters; largest max./min. in the final difference Fourier synthesis 1.282 eÅ⁻³/-0.682 eÅ⁻³; max./min. transmission 0.75/0.67; R_1 = 0.044 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1237. Perfluoromethyl groups (C92 to C94) are disorder over two sites with occupancies of 0.7 and 0.3 respectively. The highest peaks of the residual electron density indicate further disorder of this group which could not be resolved. **3:** [$C_{47}H_{67}N_4Zn$][$AlCl_6F_{36}O_4$]*0.1 CH_2Cl_2 , M = 1727.56, colorless crystal (0.30 x 0.25 x 0.07 mm); orthorhombic, space group $Pbca$; a = 23.2213(7), b = 20.5324(6), c = 31.0581(9) Å; V = 14808.2(8) Å³; Z = 8; μ = 0.488 mm⁻¹; $\rho_{ber.}$ = 1.550 g cm⁻³; 111316 reflexes ($2\theta_{max}$ = 50°, >43° approx. 65% unobserved, i.e. $I < 2\sigma(I)$), unique (R_{int} = 0.0651); Goof 1.052; 1001 parameters; largest max./min. in the final difference Fourier synthesis 0.860 eÅ⁻³/-0.811 eÅ⁻³; max./min. transmission 0.75/0.60; R_1 = 0.0508 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1407. The perfluoromethyl groups connected to C300 are disordered over at least two sites. Two of them could be identified but only refined isotropically with various restraints. The position of the residual electron density peaks suggests further sites which could not be modeled. The structure contains a dichloromethane whose site is partially occupied (about 10%) which could also only be refined isotropically. Due to the poor crystal quality only the connectivity of the structure model should be regarded reliable. **4:** [$C_{43}H_{61}N_6Zn$][$C_{24}BF_{20}$]* CH_2Cl_2 , M = 1491.32, colorless crystal (0.33 x 0.18 x 0.13 mm); triclinic, space group $P-1$; a = 12.7348(3), b = 16.5546(4), c = 17.9992(4) Å; α = 65.7970(10)°, β = 75.9020(10)°, γ = 84.9610(10)°, V = 3356.48(14) Å³; Z = 2; μ = 0.548 mm⁻¹; $\rho_{ber.}$ = 1.476 g cm⁻³; 66800 reflexes ($2\theta_{max}$ = 56°), 15951 unique (R_{int} = 0.0228); Goof 1.043; 883 parameters; largest max./min. in the final difference Fourier synthesis 1.097 eÅ⁻³/-1.566 eÅ⁻³; max./min. transmission 0.75/0.68; R_1 = 0.0483 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1376. **5:** [$C_{47}H_{67}N_4Zn$][$C_{24}BF_{20}$]* CH_2Cl_2 , M = 1517.39, colorless crystal (0.38 x 0.33 x 0.25 mm); monoclinic, space group $P2_1/c$; a = 13.2455(2), b = 25.5145(5), c = 22.0286(4) Å; β = 105.598 (1)°, V = 7170.4(2) Å³; Z = 4; μ = 0.513 mm⁻¹; $\rho_{ber.}$ = 1.406 g cm⁻³; 108166 reflexes ($2\theta_{max}$ = 58°), 19351 unique (R_{int} = 0.0258); Goof 1.087; 901 parameters; largest max./min. in the final difference Fourier synthesis 1.905 eÅ⁻³ (1.05 Å from CL2)/-1.082 eÅ⁻³; max./min. transmission 0.75/0.65; R_1 = 0.0445 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1290. The refinement was performed with

solvent-free reflection data following PLATON/squeeze run. A refinement of the untreated reflection data set produces several peaks with 2.5 - 7.5 e/Å³ corresponding to highly disordered dichloromethane molecule. The peaks attributed to two chlorine and one carbon atoms over two sites with occupancies factor 0.5 result in R₁ = 0.0783. The SQUEEZE refinement revealed 4 voids corresponding to 119 Å³ each. **6**: C₂₄H₃₂N₂Zn, *M* = 413.89, colorless crystal (0.38 x 0.32 x 0.23 mm); monoclinic, space group *P* 2₁/*n*; *a* = 8.8277(10), *b* = 32.260(4), *c* = 16.7973(18) Å; β = 104.955(4)°, *V* = 4621.6(9) Å³; *Z* = 8; μ = 1.072 mm⁻¹; ρ_{ber.} = 1.190 g cm⁻³; 71621 reflexes (2θ_{max} = 55°), 11467 unique (*R*_{int} = 0.0313); Goof 1.099; 487 parameters; largest max./min. in the final difference Fourier synthesis 0.381 eÅ⁻³ / -0.541 eÅ⁻³; max./min. transmission 0.75/0.52; *R*₁ = 0.0400 (*I* > 2σ(*I*)), *wR*₂ (all data) = 0.0969. **7**: C₃₂H₄₂ClN₃Zn, *M* = 569.51, colorless crystal (0.38 x 0.12 x 0.08 mm); triclinic, space group *P*-1; *a* = 7.9599(2), *b* = 12.2162(3), *c* = 16.4476(4) Å; α = 109.169 (1), β = 93.783 (1), γ = 92.229 (1), *V* = 1504.28(6) Å³; *Z* = 2; μ = 0.929 mm⁻¹; ρ_{ber.} = 1.257 g cm⁻³; 43585 reflexes (2θ_{max} = 58°), 7808 unique (*R*_{int} = 0.0284); Goof 1.036; 334 parameters; largest max./min. in the final difference Fourier synthesis 0.430 eÅ⁻³ / -0.316 eÅ⁻³; max./min. transmission 0.75/0.65; *R*₁ = 0.0282 (*I* > 2σ(*I*)), *wR*₂ (all data) = 0.0727. **8**: C₃₇H₅₄N₄Zn * 3(CH₂Cl₂), *M* =, colorless crystal (0.37 x 0.12 x 0.10 mm); triclinic, space group *P*-1; *a* = 9.2948(3), *b* = 12.2388(4), *c* = 20.7088(7) Å; α = 104.079(2) β = 102.4820(10), γ = 95.013(2), *V* = 2206.50(13) Å³; *Z* = 2; μ = 0.952 mm⁻¹; ρ_{ber.} = 1.317 g cm⁻³; 42837 reflexes (2θ_{max} = 58°), 10961 unique (*R*_{int} = 0.0332); Goof 1.050; 460 parameters; largest max./min. in the final difference Fourier synthesis 1.675 eÅ⁻³ / -1.260 eÅ⁻³; max./min. transmission 0.75/0.57; *R*₁ = 0.0538 (*I* > 2σ(*I*)), *wR*₂ (all data) = 0.1494. **9**: C₃₉H₅₇N₃Zn * CH₂Cl₂, *M* = 718.17, colorless crystal (0.37 x 0.32 x 0.23 mm); monoclinic, space group *P* 2₁/*n*; *a* = 16.7558(10), *b* = 13.5456(8), *c* = 17.8375(10) Å; β = 101.587(2)°, *V* = 3966.0(4) Å³; *Z* = 4; μ = 0.784 mm⁻¹; ρ_{ber.} = 1.203 g cm⁻³; 50562 reflexes (2θ_{max} = 60°), 11425 unique (*R*_{int} = 0.0234); Goof 1.034; 415 parameters; largest max./min. in the final difference Fourier synthesis 0.885 eÅ⁻³ / -0.736 eÅ⁻³; max./min. transmission 0.75/0.67; *R*₁ = 0.0326 (*I* > 2σ(*I*)), *wR*₂ (all data) = 0.0928.

Supporting Information: X-ray crystallographic data of **2** - **9** are given in the electronic supplement. The crystallographic data (without structure factors) were also deposited as „supplementary publication no. CCDC 91429 (**2**), 914735 (**3**), 914731 (**4**), 914734 (**5**), 914736 (**6**) 914730 (**7**), 914733 (**8**), 914732 (**9**) at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

S. Schulz likes to thank the University of Duisburg-Essen for financial support.

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Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents

Layout 1:

((Key Topic))

Several cationic zinc complex bearing weakly coordinating anions were synthesized and structurally characterized by single crystal X-ray diffraction. Preliminary results on the ROP of lactide using base-free cation **1** as catalyst are presented.

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Synthesis and Single Crystal X-ray Structures of Cationic Zinc β -Diketiminato Complexes

Keywords: Cations / Zinc / X-ray Analysis

Single crystal X-ray analyses. X-ray crystal structures were collected using a Bruker AXS D8 Kappa diffractometer with APEX2 detector ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The structures were solved by Direct Methods (SHELXS-97)^[33] and refined by full-matrix least-squares on F^2 . Semi-empirical absorption corrections from equivalent reflections on basis of multi-scans (Bruker AXS APEX2) were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model.^[34]

Table 1: Crystallographic details for complexes **2** - **9**.

	2 ^[a]	3 ^[b]	4	5 ^[c]	6	7	8	9
Empirical formula	$[\text{C}_{37}\text{H}_{49}\text{N}_6\text{Zn}] [\text{AlCl}_6\text{F}_{36}\text{O}_4]$	$[\text{C}_{47}\text{H}_{67}\text{N}_4\text{Zn}] [\text{AlCl}_6\text{F}_{36}\text{O}_4] \cdot 0.1\text{CH}_2\text{Cl}_2$	$[\text{C}_{43}\text{H}_{61}\text{N}_6\text{Zn}] [\text{C}_{24}\text{BF}_{20}] \cdot \text{CH}_2\text{Cl}_2$	$[\text{C}_{47}\text{H}_{67}\text{N}_4\text{Zn}] [\text{C}_{24}\text{BF}_{20}] \cdot \text{CH}_2\text{Cl}_2$	$\text{C}_{24}\text{H}_{32}\text{N}_2\text{Zn}$	$\text{C}_{32}\text{H}_{42}\text{ClN}_3\text{Zn}$	$\text{C}_{37}\text{H}_{54}\text{N}_4\text{Zn} \cdot 3\text{CH}_2\text{Cl}_2$	$\text{C}_{39}\text{H}_{57}\text{N}_3\text{Zn} \cdot \text{CH}_2\text{Cl}_2$
Molecular mass	1610.33	1727.56	1491.32	1517.39	413.89	569.51	874.99	718.17
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$Pbca$	$P-1$	$P2_1/c$	$P2_1/n$	$P-1$	$P-1$	$P2_1/n$
T [K]	100(1)	100(1)	100(1)	100(1)	180(1)	100(1)	100(1)	100(1)
a [Å]	13.7265(3)	23.2213(7)	12.7348(3)	13.2455(2)	8.8277(10)	7.9599(2)	9.2948(3)	16.7558(10)
b [Å]	23.7765(5)	20.5324(6)	16.5546(4)	25.5145(5)	32.260(4)	12.2162(3)	12.2388(4)	13.5456(8)
c [Å]	20.4753(5)	31.0581(9)	17.9992(4)	22.0286(4)	16.7973(18)	16.4476(4)	20.7088(7)	17.8375(10)
α [°]	-	-	65.7970(10)	-	-	109.169 (1)	104.079(2)	-
β [°]	107.298(1)	-	75.9020(10)	105.598 (1)	104.955(4)	93.783(1)	102.482(1)	101.587(2)
γ [°]	-	-	84.9610(10)	-	-	92.229 (1)	95.013(2)	-
V [Å ³]	6380.2(2)	14808.2(8)	3356.48(14)	7170.4(2)	4621.6(9)	1504.28(6)	2206.50(13)	3966.0(4)
Z	4	8	2	4	8	2	2	4
μ [mm ⁻¹]	0.554	0.488	0.548	0.513	1.072	0.929	0.952	0.784
$D_{\text{calcd.}}$ [g cm ⁻³]	1.676	1.550	1.476	1.406	1.190	1.257	1.317	1.203
Crystal dim. [mm]	0.32 x 0.26 x 0.18	0.30 x 0.25 x 0.07	0.33 x 0.18 x 0.13	0.38 x 0.33 x 0.25	0.38 x 0.32 x 0.23	0.38 x 0.12 x 0.08	0.37 x 0.12 x 0.10	0.37 x 0.32 x 0.23
No. of reflections	89530	111316	66800	108166	71621	43585	42837	50562
No. of unique reflections	16119	12637	15951	19351	11467	7808	10961	11425
max./min. transmission	0.75/0.67	0.75/0.60	0.75/0.68	0.75/0.65	0.75/0.52	0.75/0.65	0.75/0.57	0.75/0.67
R_{merge}	0.0326	0.0651	0.0228	0.0258	0.0313	0.0284	0.0332	0.0234
No. param. ref. / restraints	1018 / 0	1001 / 1059	883 / 0	901 / 0	487 / 0	334 / 0	460 / 0	415 / 0
R_1	0.044	0.0508	0.0483	0.0445	0.0400	0.0282	0.0538	0.0326
wR_2	0.1237	0.1407	0.1376	0.1290	0.0969	0.0727	0.1494	0.0928
Goodness of fit ^[c]	1.020	1.052	1.043	1.087	1.099	1.036	1.050	1.034
Final max/min. $\Delta\rho$, e Å ⁻³	1.282/-0.682	0.860/-0.811	1.097/-1.566	1.905 (1.05 Å from Cl2)/-1.082	0.381/-0.541	0.430/-0.316	1.675/-1.260	0.885/-0.736

[a] Perfluoromethyl groups (C92 to C94) are disorder over two sites with occupancies of 0.7 and 0.3 respectively. The highest peaks of the residual electron density indicate further disorder of this group which could not be resolved.

[b] The perfluoromethyl groups connected to C300 are disordered over at least two sites. Two of them could be identified but only refined isotropically with various restraints. The position of the residual electron density peaks suggests further sites which could not be modeled. The structure contains a dichloromethane whose site is partially occupied (about 10%) which could also only be refined isotropically. Due to the poor crystal quality only the connectivity of the structure model should be regarded reliable.

[c] The refinement was performed with solvent-free reflection data following PLATON/squeeze run. A refinement of the untreated reflection data set produces several peaks with 2.5 - 7.5 e/Å³ corresponding to highly disordered dichloromethane molecule. The peaks attributed to two chlorine and one carbon atoms over two sites with occupancies factor 0.5 result in $R_1 = 0.0783$. The SQUEEZE refinement revealed 4 voids corresponding to 119 Å³ each.

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DOI: 10.1002/zaac.201300119

URN: urn:nbn:de:hbz:464-20201116-103011-2

This is the peer reviewed version of the following article: Z. Anorg. Allg. Chem. 2013, 639, 216-220, which has been published in final form at:
<https://doi.org/10.1002/zaac.201300119>

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