One-pot synthesis of ultrastable pentanuclear alkylzinc complexes†

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Two organometallic pentanuclear zinc complexes, namely $[Zn_5Et_4(Me_2bta)_6]$ and $[Zn_5Me_4(Me_2bta)_6]$, containing tridentate N-donor ligands (5,6-dimethylbenzotriazolate, Me_2bta) were prepared by a one-pot synthesis. These compounds represent the first examples of organometallic complexes featuring a Kuratowski-type bond topology. Zinc ions were introduced as organometallic precursors (either diethylzinc or dimethylzinc was used), which upon mixing with the ligand yielded the desired complexes spontaneously. The organometallic complexes were characterized by a range of analytical techniques including NMR- and FT-IR spectroscopy, mass spectrometry, and elemental analysis. In addition, the structure of $[Zn_5Et_4(Me_2bta)_6]$ could be solved by single-crystal X-ray analysis. The thermal and chemical stability of the complexes was studied by TGA, VT-XRPD and DRIFT, in addition to NMR and mass spectrometric investigations. The compounds were found to be unexpectedly stable under various conditions and to lack any reactivity with electrophilic reactants such as aldehydes, which commonly react easily with organozinc compounds. However, the basic alkyl groups could be reacted with strongly acidic compounds such as trifluoroacetic acid.

Introduction

Although pentameric zinc complexes have been reported previously, largely as motifs in extended metal–organic frameworks,[1] there are only very few pentanuclear organometallic alkylzinc complexes known in the literature.[2] Herein we report on alkylzinc complexes of the so-called Kuratowski type, which are pentanuclear coordination compounds of the general formula $[M^oM^t_4L_4L'_6]$.[3] They display a rare nonplanar $K_{3,3}$ bond topology in conjunction with a T_d-point group symmetry (Fig. 1) and were named after the Polish mathematician Kazimierz Kuratowski who introduced in the 1930s the nonplanar $K_{3,3}$ graph into graph theory.[4] The compounds contain μ_3-bridging N-donor ligands (L′), as a rule 1,2,3-benzotriazolates. There are two different coordination sites: one central octahedral site (M^o) and four tetrahedral sites at the peripheral positions (M^t). The central metal ion (M^o) is coordinated to six benzotriazolate ligands, whereas the peripheral metal ions

(M^t) are coordinated to three N-donor atoms stemming from different benzotriazolate ligands and the last coordination site of each M^t is occupied by an additional ligand (L), often a halide anion. It is possible to prepare these compounds as either homonuclear ($M^{o,t} = Zn^{2+}$ or Co^{2+})[3a–c] or heteronuclear
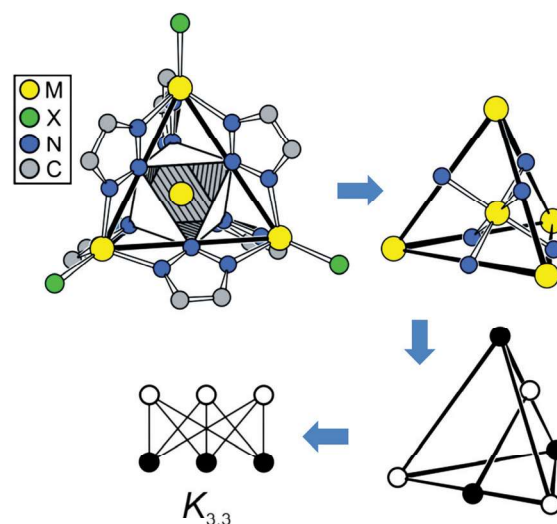

Fig. 1 Structure and bonding scheme of Kuratowski-type coordination compounds: formal derivation of the $K_{3,3}$ graph which can be used to represent the connectivity in Kuratowski-type coordination compounds.[5c]

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coordination compounds (M^o = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Ru^{2+}, and M^t = Zn^{2+}).[3d,e] Also an exchange of the ligand L is possible. For instance, we showed recently that chloride ions in the complex [$Co_5Cl_4(Me_2bta)_6$] (Me_2bta stands for 5,6-dimethyl-benzo-triazolate) could be successfully replaced by Tp* ions (Tp* stands for tris(3,5-dimethyl-1-pyrazolyl)borate).[3a] In addition, the coordination motif of Kuratowski units found recent applications as secondary building units for coordination polymers including metal–organic frameworks (MOFs).[5] Regardless of the existence of many different Kuratowski complexes, there has been no organometallic compound featuring alkyl–metal bonds as a part of the Kuratowski unit reported so far. In this work, we introduce a facile one-pot synthesis of two pentanuclear compounds (**1** and **2**) containing alkylzinc bonds.

Kuratowski complexes are usually prepared by slow addition of a metal salt (or a suitable stoichiometric ratio of different metal salts when a heteronuclear complex shall be prepared) to a solution of a benzotriazole ligand in a suitable solvent (often methanol or DMF) in the presence of a base (*e.g.* 2,6-di-methylpyridine),[3e] which is added to deprotonate the ligand molecules in order to enable their coordination. Kuratowski complexes can also be prepared by a diffusion crystallization technique.[3e] A base (*e.g.* 2,6-dimethylpyridine) is placed in a closed outer container to slowly diffuse *via* the gas phase into an opened inner container in which the ligand molecules and metal salt are dissolved in a suitable solvent (often DMF). In this work, however, we introduce another synthesis route to Kuratowski complexes, in which organozinc compounds are utilized as a source of zinc ions instead of commonly used inorganic zinc salts. Upon mixing the organozinc compound and the ligand, the organometallic complex is produced spontaneously and there is no need to use any base.

Organometallic zinc compounds are generally known as very reactive and useful species. Since their early discovery in 1848 when Edward Frankland prepared the first organozinc compound, diethylzinc,[6] organozinc compounds and their derivatives have been explored as reagents and catalysts in numerous organometallic and organic transformations.[7] Due to their high reactivity (owing to the polarized organometallic bond between zinc and carbon) many organozinc compounds are difficult to handle. For instance, diethylzinc is highly pyrophoric, reacts violently with water and ignites easily upon contact with air. On the contrary, the organozinc complexes [$Zn_5Et_4(Me_2bta)_6$] (**1**) and [$Zn_5Me_4(Me_2bta)_6$] (**2**) prepared here act differently and show exceptionally high chemical and thermal stability.

Several thermally and chemically stable complexes featuring similar coordination environments to the peripheral Zn(II) centres in compounds **1** and **2** were reported previously.[8] Tris (triazolyl)borates (Ttz) alkyl zinc complexes substituted with bulk *tert*-butyl groups were found to be stable in air and water,[8a] and their reactivity with O- and S-donors was studied.[8b] The influence of the presence of hydrogen bonding interactions, and steric and electron donor ability of the ligands on the reaction result was investigated. In another

work, thermally stable tris(oxazolinyl)boratozinc alkyl complexes were reported and their reaction with oxygen to alkylper-oxyzinc compounds was studied.[8c] It was shown that the reaction rate was influenced by the different alkyl substitution and was in agreement with the zinc–carbon bond dissociation energies estimated for different Zn–alkyl compounds.

Results and discussion

Synthesis and characterization

As a ligand, 5,6-dimethylbenzotriazole (Me_2btaH) was used. The dialkylzinc, here diethylzinc or dimethylzinc, was added dropwise under a nitrogen atmosphere to a stirred solution of the ligand in dry tetrahydrofuran at room temperature. This led to the formation of Kuratowski complexes with zinc ethyl or zinc methyl moieties in a one-step reaction without the need of adding any base. Following the reaction procedure (Scheme 1), the organometallic Kuratowski complexes [$Zn_5Et_4(Me_2bta)_6$] (**1**) and [$Zn_5Me_4(Me_2bta)_6$] (**2**) could be successfully prepared – the first two examples of this kind.

Complexes **1** and **2** were fully characterized by conventional analytical techniques including ^1H and ^{13}C NMR, and IR (Fig. S1–S4 in the ESI†), and their purity was checked by elemental analysis. In addition, due to their high stability, it was possible to analyse both complexes with mass spectrometry (Fig. S5 and S6 in the ESI†). It was also possible to recrystallize the ethylzinc Kuratowski complex (**1**) from benzene and thus to obtain colourless block single crystals suitable for X-ray analysis (Fig. S26 in the ESI†). Unfortunately, despite considerable efforts put into the crystallization of the methylzinc complex (**2**), no crystals suitable for X-ray analysis could be obtained. However, it was possible to show by an XRPD measurement (Fig. S7 and S8 in the ESI†) that both compounds are crystalline in nature.

Single X-ray analysis. Complex **1** crystallizes from a benzene solution as a solvate (**1**·C_6H_6) in the monoclinic space group $P2_1/c$ (no. 14; Table S1 in the ESI†). The pentanuclear cluster features a typical Kuratowski unit (Fig. 2), where six ligands 5,6-dimethylbenzotriazole coordinate to five zinc ions by 18 Zn–N coordination bonds. Each of the six ligands coordinates to the central Zn(II) ion (in an octahedral geometry; Zn1) and two periplanar Zn(II) ions (in a tetrahedral geometry; Zn2–Zn5). The coordination environment of each peripheral zinc ion (Zn2–Zn5) is completed by an ethyl group. The Zn–N
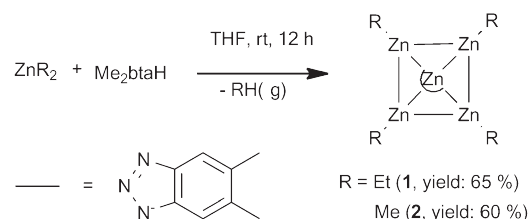
Scheme 1 Synthesis of organometallic Kuratowski complexes [$Zn_5Et_4(Me_2bta)_6$] (**1**) and [$Zn_5Me_4(Me_2bta)_6$] (**2**).
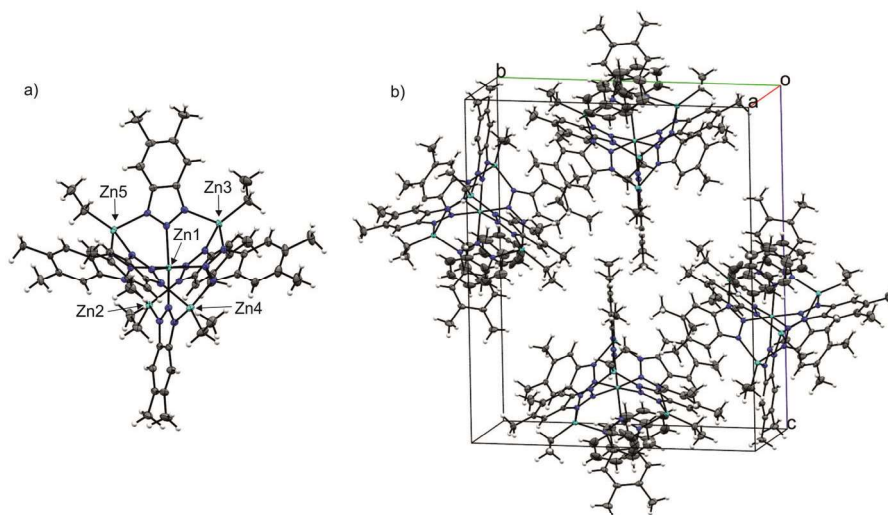
Fig. 2 ORTEP[9] style-plot of the molecular structure (a) and packing diagram of **1** (b). Thermal ellipsoid probability: 50%. Occluded benzene molecules are omitted for clarity.

bond lengths are in the range of 2.15(2)–2.26(2) Å for the Zn1 ion in the octahedral coordination geometry and in the range of 2.04(2)–2.09(2) Å for the Zn2–Zn5 ions in the tetrahedral geometry. These values are in good agreement with the data reported previously for other Zn–triazolate complexes (2.14–2.22 Å for octahedral coordination and 1.98–2.05 Å for tetrahedral coordination).[5e] Analysis of dihedral angles reveals a slightly distorted octahedral coordination of the central Zn(II) ion, as the angles deviate from the 90° angles presented in the perfectly octahedral symmetry (see Table S3 in the ESI†). The presence of the ethyl groups leads to lowering of the highest possible point group symmetry from T_d, which is typical for Kuratowski complexes,[5c] to S_4. In addition, due to the different orientation of the ethyl groups in the solid state (revealed by the single crystal X-ray analysis), the symmetry of complex **1** is further lowered to C_S.

The crystal packing motif exhibits a layered structure created by Kuratowski molecules expanding in the *a*- and *b*-directions, whereas the layers are perpendicular to the (001) plane (see Fig. S27 in the ESI†). The crystal structure of **1** contains benzene as occluded solvent molecules located between the Kuratowski units. The benzene molecules, whose positions were unequivocally determined from single-crystal data, are placed either parallel to the plane (100) or are disordered and twisted towards the plane (100) with an angle of 31.31(3)°. The whole structure is stabilized by π–π stacking of the parallel-displaced benzene rings of Me₂bta ligands and benzene solvent molecules. The non-bonding distances between the centroids of the aromatic rings from the solvent molecules and benzotriazolate ligands, and of the aromatic rings from the adjacent benzotriazolate ligands are 3.548(2) and 3.609(1) Å, respectively.

Thermal stability. In order to examine the thermal stability of **1** and **2**, variable temperature X-ray powder diffraction (VT-XRPD) analysis, variable temperature diffuse reflectance infrared Fourier transform (VT-DRIFT) spectroscopy and thermogravimetric analysis (TGA) were carried out.

Thermal stability of complex 1. VT-XRPD studies were performed in a capillary tube exposed to air. The analysis revealed that complex **1** is stable up to about 150 °C (Fig. 3a). Upon removing the solvent molecules (benzene), a new crystalline phase is formed. This second phase is stable up to 300 °C and above 350 °C, yet another crystalline phase is formed. Above 450 °C, the complex decomposes leading to the formation of ZnO. These observations are in good agreement with the results from TGA (Fig. 3b). The first weight loss step of 5.95% from 100 to 240 °C can be assigned to the evaporation of one benzene molecule per complex molecule (calc. 5.59%). The second weight loss step of 8.09% from 275 to 410 °C can be assigned to the loss of four ethyl moieties per complex molecule (8.02% calc. for four molecules of ethylene per complex molecule). These ethyl groups are cleaved from the zinc complex *via* β-hydride elimination, which is common for an unbranched alkyl group bonded to a metal center.[10] Above 420 °C, the organic part of the complex decomposes and compound **1** disintegrates. The presence of benzene and ethylene in the gas phase was confirmed by IR-TG analysis (Fig. S10 in the ESI†). In addition, the formation of the zinc hydride Kuratowski complex (**3**) as a product of the β-hydride elimination was observed by a VT-DRIFT measurement (Fig. S12 in the ESI†), where the signal at 1768 cm⁻¹ was detected (Fig. S14 in the ESI†). This band is characteristic for the valence vibration of the Zn–H bond and similar values were previously reported for structurally related zinc complexes containing terminal hydrides.[11] Such a hydride complex could find potential applications as a hydride-transfer and reducing agent as we demonstrated recently employing a metal–organic framework featuring a Kuratowski unit with Zn–H groups.[11a]

Thermal stability of complex 2. According to VT-XRPD analysis carried out under an air atmosphere, complex **2** is
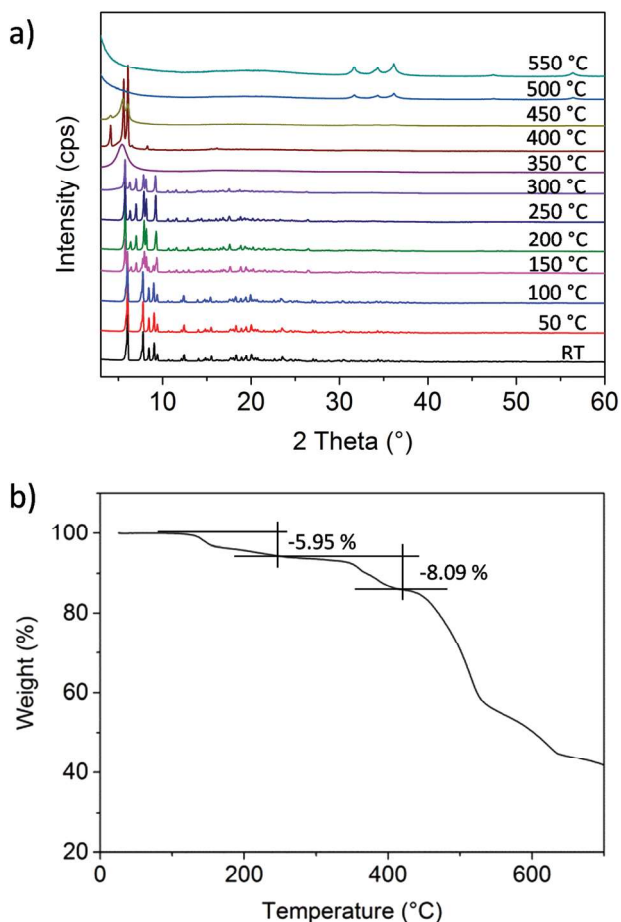
Fig. 3 Thermal stability of complex **1** studied by VT-XRPD in a capillary tube exposed to air (a) and TG analysis under a nitrogen atmosphere (b).
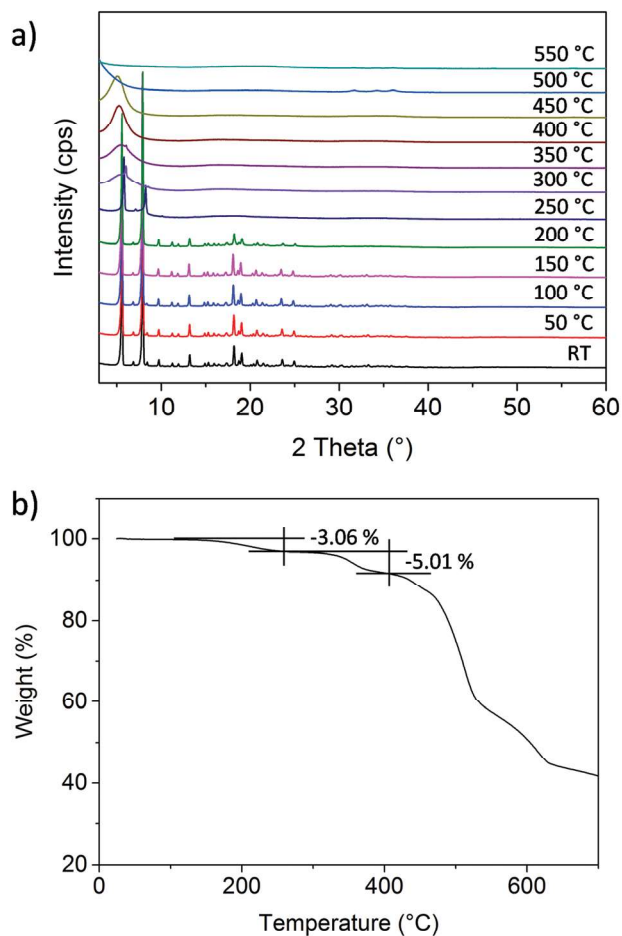
Fig. 4 Thermal stability of complex **2** studied by VT-XRPD in a capillary tube exposed to air (a) and TG analysis under a nitrogen atmosphere (b).

stable up to 250 °C (Fig. 4a). After that the compound starts to decompose giving rise to an amorphous phase which persists up to 500 °C, when the first signs of the formation of crystalline ZnO appear. In the TG curve of **2** (Fig. 4b), the gradual weight loss of 3.06% in the range of 60–200 °C can be attributed to the removal of non-coordinated solvent molecules. In the range of 265–380 °C, a second weight loss of 5.01% can be observed. Following similarities to compound **1**, this can be attributed to the loss of four methyl moieties attached to Zn(II) ions. Above 420 °C, the organic part of the complex decomposes and compound **2** disintegrates in a similar way to compound **1** (Fig. S9 in the ESI†). The IR-TG analysis carried out under a nitrogen atmosphere revealed the presence of methane in the gas phase between 250 and 400 °C (Fig. S11 in the ESI†) and the VT-DRIFT measurement under a nitrogen atmosphere (Fig. S13 in the ESI†) indicates the formation of the zinc hydride Kuratowski complex (*i.e.* the same compound which was formed by the thermal decomposition of complex **1**) with the characteristic vibration of the Zn–H bond at 1767 cm^{-1} (Fig. S15 in the ESI†).[11]

Since the coordinated methanide ligands cannot undergo β-hydride elimination, the formation of Zn–H species is an unexpected finding, which deserves further investigations in the future.

Chemical stability. Firstly, the solubility of both complexes at room temperature was tested. Both compounds showed rather uncommon selective solubility towards chlorinated solvents. They are very well soluble in dichloromethane, chloroform and carbon tetrachloride, but insoluble in all other tested organic solvents including methanol, ethanol, acetone, acetonitrile, diethylether, ethylacetate, benzene, toluene, bromobenzene, 1,1,2,2-tetrachloroethane, DMF and DMSO, and in water.

Secondly, the chemical reactivity of both complexes was investigated and is summarized in Scheme 2. Many organometallic alkylzinc compounds are known to be highly reactive and unstable in air or upon contact with water. Contrary to this, complexes **1** and **2** show high stability in air and could be stored on a bench in a container exposed to ambient conditions for at least four months without any changes detectable by XRPD or NMR.

Moreover, the complexes are resistant to humidity. They are not soluble in water, and show no reactivity when dispersed in it (proven by XRPD and MS measurements, Fig. S16–S18 in the
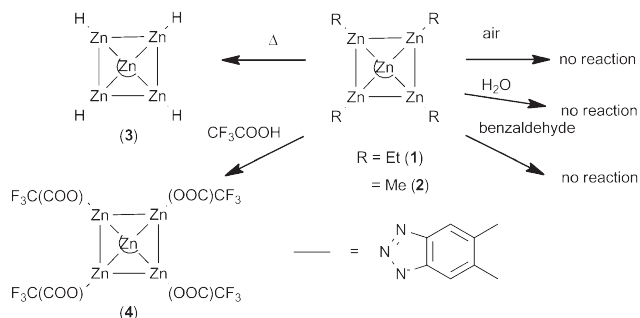
Scheme 2 Overview on the possible chemical and thermal transformations of [Zn$_5$Et$_4$(Me$_2$bta)$_6$] (**1**) and [Zn$_5$Me$_4$(Me$_2$bta)$_6$] (**2**).

Fig. 6 ^{1}H NMR spectra of **1** (a) and **2** (b) upon mixing with one and four molar equivalents of trifluoroacetic acid in CDCl$_3$.

ESI†). Alkyl zinc complexes are also known to undergo reactions with compounds containing carbonyl moieties. However, complex **1** showed no reaction upon mixing with benzaldehyde. In the experiment, compound **1** was dissolved in deuterated chloroform containing a stoichiometric amount (*i.e.* 1 : 1 molar ratio) of freshly distilled benzaldehyde, and the possible reaction was followed by an NMR measurement. There was no reaction observed, not even after three days of mixing the components (Fig. 5 and S19 in the ESI†).

The reactivity of the complexes with strong organic acids was investigated. When complexes **1** and **2** were mixed with trifluoroacetic acid in deuterated chloroform, the exchange of an alkyl group to trifluoroacetate was observed. The reaction was followed by ^{1}H and ^{19}F NMR measurements (Fig. 6 and S20 in the ESI†). Upon mixing with one equivalent of trifluoroacetic acid, the formation of the corresponding gas (either ethane: $\delta = 0.86$ or methane: $\delta = 0.22$)[12] was detected along with the splitting of the signals in the ^{1}H and ^{19}F NMR spectra (referring to the presence of several different complexes with a different degree of substitution). Upon adding three more equivalents of trifluoroacetic acid (*i.e.* four equivalents in total), well resolved signals in the ^{1}H and ^{19}F NMR spectra

were observed which were shifted compared to the spectra of the starting complexes. In both cases, the same product was obtained. The new species was identified by NMR, IR and MS analyses (Fig. S21–S25 in the ESI†) as a zinc Kuratowski complex (**4**) with all four alkyl chains substituted by trifluoroacetate moieties.

Experimental

General

All chemicals were purchased from commercial suppliers in a reagent grade and used as received except for 5,6-dimethylbenzotirazole (sublimated prior to usage), deuterated chloroform for the NMR measurements (dried passing through a pad of anhydrous magnesium sulfate) and benzaldehyde (distilled prior to usage). For the synthesis of the organometallic complexes Schlenk techniques were employed. **Caution:** Diethylzinc and dimethylzinc are highly pyrophoric. Extreme care and proper safety precautions should be taken while handling such reagents.

Fourier transform infrared (FT-IR) spectra were recorded with an ATR unit in the range 4000–400 cm^{-1} on a Bruker
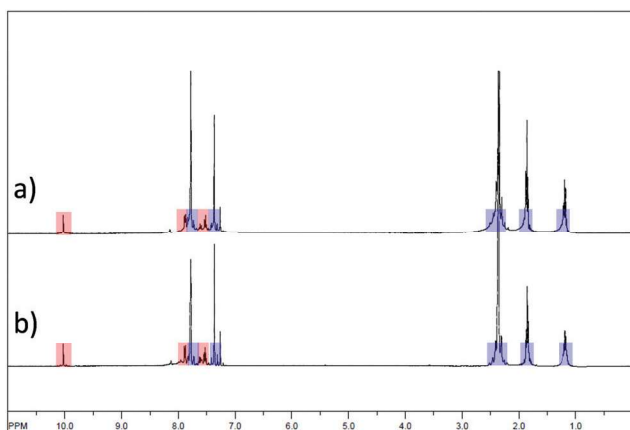

Fig. 5 NMR spectra of complex **1** with 1 molar equivalent of benzaldehyde in CDCl$_3$ after 1 h (a) and 3 days (b) after mixing the components. Signals corresponding to benzaldehyde are marked in red color and signals corresponding to complex **1** are marked in blue color.
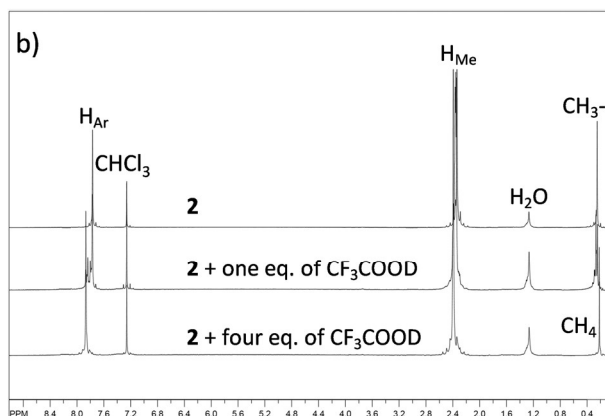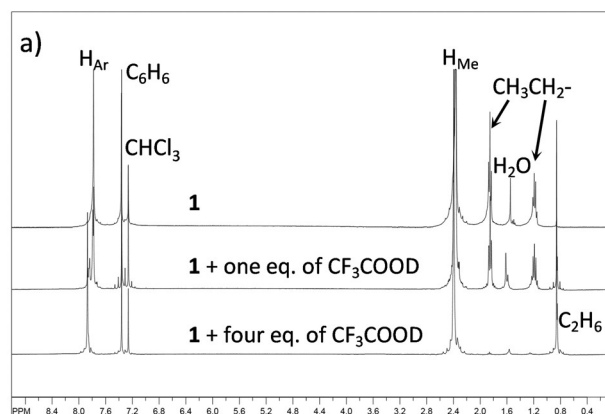
Equinox 55 FT-IR spectrometer (s, m, and w were used to assign signal intensities). Variable temperature diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected between 4000 and 400 cm^{-1} on a Bruker Equinox 55 FT-IR spectrometer equipped with a praying mantis diffuse reflectance accessory and an environmental chamber (Harrick Scientific Products) and referenced to KBr. The spectra were recorded in a temperature range of 25 to 350 °C under a nitrogen atmosphere. Molecular masses were measured with a Q-Tof Ultima mass spectrometer (Micromass) equipped with an ESI source. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Mercury plus 400 high-resolution system (Variant Deutschland GmbH). Elemental analysis was performed with a Vario EL III (Elementar-Analysensysteme GmbH). Thermogravimetric analysis (TGA) was performed with a Netzsch STA 409 PC analyser in a temperature range of 25–800 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction data were collected in the 5–50° 2θ range using a Seifert XRD 3003 TT powder diffractometer with a Meteor 1D detector operating at room temperature using Cu Kα_1 radiation (λ = 1.54187). VT-XRPD data were collected on a Bruker D8 Advance θ–2θ diffractometer in transmittance Bragg–Brentano geometry employing a Göbel mirror, Cu-radiation and equipped with a LYNXEYE 1-D detector. The samples were ground and loaded into quartz capillaries (Hilgenberg) with 0.5 mm diameter and 0.01 mm wall thickness. The patterns were recorded in a temperature range of 30 to 550 °C, in the 3–60° 2θ range with a step time of 1 s and a step width of 0.02° 2θ. The temperature program between measurements: 0.5 °C s^{-1} heating rate, followed by 10 min isothermal steps required for recording diffraction data sets. The sample was exposed to air during the whole measurement. For the X-ray single-crystal analysis the crystal of **1** was taken from the mother liquor and mounted on MiTeGen MicroMounts. The X-ray data for the single crystal structure determination were collected on a Bruker D8 Venture diffractometer. Intensity measurements were performed using monochromated (doubly curved silicon crystal) MoKα radiation (0.71073 Å) from a sealed microfocus tube. Generator settings were 50 kV, 1 mA. Data collection temperature was −173 °C. APEX2 software was used for preliminary determination of the unit cell.[13] Determination of integrated intensities and unit cell refinement were performed using SAINT.[14] The structure was solved and refined using the Bruker SHELXTL software package.[15] Selected crystal data and details of structure refinement for **1** are provided in Table S1.† Complete crystallographic data for structure **1** reported in this paper have been deposited in the CIF format with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1511903.

Synthesis

Synthesis of [Zn$_5$Et$_4$(Me$_2$bta)$_6$] (1). 5,6-Dimethylbenzotriazole (Me$_2$btaH, 177 mg, 1.2 mmol) was dissolved in 5 mL of dry tetrahydrofuran under a nitrogen atmosphere. Then 1 mL of 1 M solution of diethylzinc in hexane (1.0 mmol) was added.

The mixture was stirred at room temperature under a nitrogen atmosphere for 12 h. After the reaction time the solvents were evaporated to dryness and the crude product was recrystallized from benzene. Colourless crystals of [Zn$_5$Et$_4$(Me$_2$bta)$_6$]·C$_6$H$_6$ (183 mg, yield: 65%) were isolated *via* filtration and washed with a small amount of cold benzene. The crystals were also used to perform the single crystal X-ray analysis. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 7.78 (s, 12H, H$_{arom}$), 7.37 (s, 6H, H$_{benzene}$), 2.35 (s, 36H, H$_{Me}$), 1.86 (t, 12H, J = 8.1 Hz, H$_{Zn–Et}$), 1.19 (q, 8H, J = 8.1 Hz, H$_{Zn–Et}$); ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 141.76 (C$_{arom}$), 136.07 (C$_{arom}$), 128.32 (C$_{benzene}$), 115.04 + 114.94 (C$_{arom}$), 20.84 + 20.77 (C$_{Me}$), 13.29 (C$_{Zn–Et}$), −1.95 (C$_{Zn–Et}$); ATR-IR: 2973 (CH$_3$, m), 2929 (CH$_3$, m), 2852 (CH$_2$, m), 1575 (w), 1465 (m), 1450 (m), 1375 (w), 1294 (w), 1197 (s), 1170 (s), 1025 (w), 1001 (s), 850 (s), 826 (m), 688 (m), 674 (s), 598 (s), 495 (s), 465 (m), 436 (m) cm^{-1}; ESI-MS (*m/z*): 1343.22 [M + Na]$^+$; elemental analysis: found 52.89% C, 5.48% H, 17.70% N; calc. for C$_{56}$H$_{68}$N$_{18}$Zn$_5$·C$_6$H$_6$ 53.25% C, 5.33% H, 18.03% N.

Synthesis of [Zn$_5$Me$_4$(Me$_2$bta)$_6$] (2). 5,6-Dimethylbenzotriazole (Me$_2$btaH, 177 mg, 1.2 mmol) was dissolved in 5 mL of dry tetrahydrofuran under a nitrogen atmosphere. Then 1 mL of a 1 M solution of dimethylzinc in heptane (1.0 mmol) was added. The mixture was stirred at room temperature under a nitrogen atmosphere for 12 h. After the reaction time a precipitate was isolated *via* filtration, washed with cold THF and dried in air giving 152 mg (yield: 60%) of [Zn$_5$Me$_4$(Me$_2$bta)$_6$] (2) as a white solid. Despite many efforts, no single crystals of complex **2** could be obtained. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 7.76 (s, 12H, H$_{arom}$), 2.32 (s, 36H, H$_{Me}$), 0.26 (s, 12H, H$_{Zn–Me}$); ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 141.82 (C$_{arom}$), 136.00 (C$_{arom}$), 115.01 + 114.91 (C$_{arom}$), 20.76 + 20.69 (C$_{Me}$), −14.70 + (−14.74) (C$_{Zn–Me}$); ATR-IR: 2931 (CH$_3$, m), 2906 (CH$_3$, m), 1574 (w), 1464 (m), 1452 (m), 1376 (w), 1294 (w), 1198 (s), 1165 (s), 1025 (w), 1001 (s), 852 (s), 827 (m), 658 (s), 531 (m), 497 (s), 466 (m), 437 (m) cm^{-1}; ESI-MS (*m/z*): 1287.16 [M + Na]$^+$; elemental analysis: found 49.59% C, 4.57% H, 19.15% N; calc. for C$_{52}$H$_{60}$N$_{18}$Zn$_5$ 49.40% C, 4.78% H, 19.94% N.

Reaction of 1 with benzaldehyde. Complex **1** (14.0 mg, 0.01 mmol) was dissolved in 0.6 mL of CDCl$_3$ containing 0.01 mmol freshly distilled benzaldehyde. The possible reaction was followed by a ^{1}H NMR measurement (directly upon mixing, after 1 hour, 1 day and 3 days).

Reaction of 1 with trifluoroacetic acid. Complex **1** (14.0 mg, 0.01 mmol) was dissolved in 0.6 mL of CDCl$_3$ containing one or four molar equivalents of CF$_3$COOD. The possible reaction was followed by ^{1}H and ^{19}F NMR measurements directly upon mixing the components.

Analytical data for the sample containing four molar equivalents of trifluoroacetic acid (**4**): ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 7.87 (s, 12H, H$_{arom}$), 7.36 (s, 6H, H$_{benzene}$), 2.40 (s, 36H, H$_{Me}$), 0.86 (s, C$_2$H$_6$); ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 164.00 + 163.62 (C$_{COO}$), 141.04 (C$_{arom}$), 139.22 (C$_{arom}$), 128.32 (C$_{benzene}$), 118.07 (C$_{CF_3}$), 114.84 + 114.75 (C$_{arom}$), 21.00 + 20.92 (C$_{Me}$); ^{19}F NMR (376 MHz, CDCl$_3$, 20 °C):

$\delta = -74.40$; ATR-IR: 2928 (CH$_3$, w), 1688 (COO asym. stretch, bs), 1573 (w), 1490 (w), 1462 (m), 1431 (COO sym. stretch), 1376 (w), 1296 (w), 1195 (s), 1170 (s), 1145 (CF asym. stretch, s), 1025 (w), 1002 (m), 851 (s), 832 (m), 795 (m), 728 (m), 498 (s), 469 (m), 435 (m) cm^{-1}; ESI-MS (m/z): 1612.00 [M − CO$_2$]$^+$.

Reaction of 2 with trifluoroacetic acid. Complex **2** (12.6 mg, 0.01 mmol) was dissolved in 0.6 mL of CDCl$_3$ containing one or four molar equivalents of CF$_3$COOD. The possible reaction was followed by ^{1}H and ^{19}F NMR measurements directly upon mixing the components.

Analytical data for the sample containing four molar equivalents of trifluoroacetic acid (**4**): ^{1}H NMR (376 MHz, CDCl$_3$, 20 °C): δ = 7.87 (s, 12H, H$_{arom}$), 2.39 (s, 36H, H$_{Me}$), 0.22 (s, CH$_4$); ^{19}F NMR (100 MHz, CDCl$_3$, 20 °C): δ = −74.40; ESI-MS (m/z): 1612.00 [M − CO$_2$]$^+$.

Conclusions

In this article we report on the first organometallic compounds of a Kuratowski type featuring alkyl–metal bonds: [Zn$_5$Et$_4$(Me$_2$bta)$_6$] and [Zn$_5$Me$_4$(Me$_2$bta)$_6$]. These complexes can be easily obtained by directly mixing dialkylzinc and 5,6-dimethylbenzotriazole at room temperature. Very special are some properties exhibited by these complexes. We were able to show that in contrast to common alkylzinc compounds, these complexes stand out for their high stability under ambient conditions (for longer than four months) and do not react with electrophilic reagents such as benzaldehyde. However, they undergo a reaction with strong acids such as trifluoroacetic acid to exchange all four alkyl chains to trifluoroacetate moieties. Last but not least, these complexes show very selective solubility properties: they readily dissolve in dichloromethane, chloroform and carbon tetrachloride but literally in no other common solvents.

We think that this new class of complexes is highly interesting showing a combination of properties different from those of any other known zinc organyls. Their exceptional stability suggests their usage as long-term stable nucleophilic or basic reagents, whose reactivity could be switched on under harsh conditions (e.g. high temperature). The lack of reactivity against strong electrophiles such as benzaldehyde points to a potential usage as highly regioselective alkylation reagents. Moreover, the construction of thermally stable organometallic frameworks (as opposed to metal–organic frameworks) based on Kuratowski units and bi-functional organometallic linkers seem to offer a novel paradigm in the area of (crystalline) coordination polymers.

Acknowledgements

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