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Direct Carboxylation of Zincocene Cp^*_2Zn

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The reaction of zincocene Cp^*_2Zn with CO_2 proceeds with the formation of $[Zn_4(\mu_4\text{-}O)(O_2CCp^*)_6]$ (**1**), which was characterized by NMR (^1H, ^{13}C) and IR spectroscopy as well as by elemental analysis and single-crystal X-ray diffraction. The solid-state structure of **1** is comparable to that previously observed for basic zinc acetate. In contrast to many previously reported CO_2 activation reactions, the formation of **1** occurred without the use of any additional transmetalation catalyst.

Introduction

The effective utilization of CO_2 as C_1-feedstock in organic chemistry has received growing interest over the last decades since CO_2 is abundant, renewable, nontoxic, and inexpensive.[1] Unfortunately, CO_2 is thermodynamically very stable and kinetically inert, thus its use is limited in industrial syntheses. Only highly nucleophilic reagents such as organolithium and Grignard reagents readily react with CO_2 with the formation of carboxylic acids and their derivatives. However, the range of functional groups that are compatible to these reagents is somewhat limited. As a consequence, activation reactions of CO_2 by coordination to transition-metal complexes, which lower the activation energy for further reactions, have been investigated in detail.[2] Recently, carboxylation reactions of organoboronic acids, organozinc, and organotin reagents with CO_2 were found to be catalyzed by complexes containing late transition metals such as Pd, Rh, Ni, and Pd, whose presence is essential for this purpose.[3]

Organozinc reagents RZnX (X = halide) and R_2Zn, which have been established as soft nucleophiles in various organic reactions in the past, are of particular interest, since they show a much higher tolerance toward functional groups than the stronger nucleophilic organolithium and -magnesium reagents. Unfortunately, only zinc hydrides, zinc alkoxides, and zinc amides are known to react with CO_2 with insertion into the Zn–H, Zn–O, and Zn–N bond and subsequent formation of zinc formates, zinc carbonates, and zinc carbamates.[4] As a consequence, zinc amides, alkoxides, and carboxylates are very active *living single-site catalysts* for the ring-opening polymerization (ROMP) of lactide[5] and epoxide/CO_2 copolymerization.[6] Moreover, bimetallic calcium/zinc complexes effectively catalyze the terpolymerization of epoxides, cyclic anhydrides, and CO_2.[7] In remarkable contrast, insertion reactions into Zn–C bonds are less favored and typically require transition-metal complexes of electron-rich, late transition metals (Ni, Pd) as effective transmetalation catalyst.[8] In these carboxylation reactions, the presence of LiCl also plays a critical, yet not fully understood, role. In addition, nickel complexes such as $[Ni\{\eta^2\text{-}CO(PCy_3)_2\}]$ were successfully used.[9] Very recently, Kondo et al. reported on carboxylation reactions of organozinc reagents using CO_2, in which the solvent (DMF) was found to have a crucial influence on the reaction.[10] To the best of our knowledge, this is the only report on a transition-metal-free carboxylation reaction of organozinc complexes, to date.

We started recently to investigate the activation of carbon dioxide as well as heterocumulenes such as isocyanates and carbodiimides using zinc hydride and zinc alkyl complexes.[11] Herein, we report on the direct carboxylation reaction of zincocene Cp^*_2Zn with CO_2 in the absence of any transmetalation reagent. The resulting zinc oxocarboxylate $[Zn_4(\mu_4\text{-}O)(O_2CCp^*)_6]$ (**1**) contains a central $[Zn_4O]^{6+}$ tetrahedron, which is the characteristic structural motif in basic zinc acetate,[12] zinc carbonates and carbamates,[4] zinc phosphates and phosphonates,[13] as well as in microporous metal–organic frameworks (MOFs) such as MOF-5 and IRMOF-9.[14] Zinc oxocarboxylates, which are known for decades,[15] are typically prepared by solvothermal methods. Recently, Lewinski et al. reported on the synthesis of $[Zn_4(\mu_4\text{-}O)(O_2CPh)_6]$ through oxidation of the corresponding zinc carboxylate with dry oxygen,[16] whereas Redshaw et al. obtained an oxocarboxylate complex by reaction of $Zn(C_6F_5)_2$ with 3-dimethylaminobenzoic acid in the presence of trace amounts of water.[17]

Results and Discussion

The stirring of a toluene solution of Cp^*_2Zn under a CO_2 atmosphere of 6 bar for 1 h at 70 °C yielded $[Zn_4(\mu_4\text{-}$

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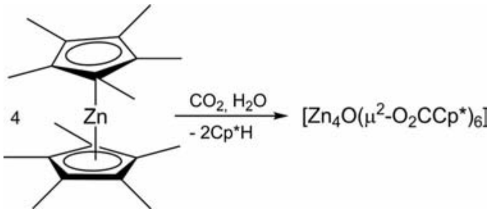
$O)(O_2CCp^*)_6]$ (**1**) in about 30% yield (Scheme 1), whereas lower yields (<10%) were obtained under milder reaction conditions (50 °C, no CO_2 pressure, 4 h). The formation of **1** occurred with the formation of Cp*H, which was unambiguously identified by in situ ^1H NMR spectroscopy. Cp*H is obviously formed because of a partial hydrolysis/condensation reaction of Cp^*_2Zn as was described previously for the formation of zinc carbamates, which are typically synthesized by reaction of zinc alkyls, primary amines, and water.[18] As a consequence, when Cp^*_2Zn was treated with CO_2 in toluene that was not dried prior to use, **1** was obtained in a higher yield of almost 80%.



Scheme 1. Synthesis of $[Zn_4(\mu_4\text{-}O)(O_2CCp^*)_6]$ (**1**).

The formation of **1** was monitored by in situ ^1H NMR spectroscopy ([D$_8$]toluene), which shows a continuously decreasing signal of the Zn-bonded Cp* group at δ = 1.88 ppm and steadily increasing new singlet bands at δ = 1.22, 1.63, and 1.82 ppm with a relative intensity of 1:2:2. This indicates the formation of a σ-bonded Cp* group. The ^{13}C NMR spectrum of **1** shows an additional signal at δ = 184.9 ppm and the IR spectrum strong absorption bands at 1580 [$\nu(CO_2)_{as}$] and 1402 cm^{-1} [$\nu(CO_2)_s$], which clearly indicate the formation of a μ^2-bonded carboxylate group. Comparable values have been reported for basic zinc pivalate (1594, 1424 cm^{-1}), benzoate (1562, 1410 cm^{-1}), and others.[19] Moreover, a very broad absorption band at 494 cm^{-1}, which most likely results from the overlapping of several absorption bands, can be assigned to the asymmetric vibration of the central Zn_4O oxygen atom. Basic zinc carboxylates of the type $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ (R = Me, Et) typically show values near 530 cm^{-1} according to experimental findings and theoretical calculations.[20]

Single crystals of **1** were obtained from a solution in toluene upon storage at –30 °C (Figure 1).[21] The central core of **1** shows an almost ideal T_d symmetry as was reported for basic zinc acetate.[12b] The central $[Zn_4O]^{6+}$ tetrahedron is also coordinated by six anionic Cp^*CO_2 carboxylate units, which adopt μ^2-bridging positions on the edges of the $[Zn_4O]^{6+}$ tetrahedron (Figure 2).

The Zn atoms are also tetrahedrally coordinated by four oxygen atoms. The Zn–O distances to the central Zn_4O oxygen atom [1.9364(9)–1.9458(10) Å] are almost identical to the Zn–O bonds of the bridging carboxylate groups [1.9271(10)–1.9622(10) Å]. The average C–O bond length of 1.26 Å clearly indicates delocalized π electrons as was expected. The Zn–O–Zn [107.55(5)–110.89(4)°] and O–C–O [125.14(13)–125.78(13)°] bond angles are within the typical range previously reported for basic zinc carboxylates. Almost identical values were observed for $[Zn_4(\mu_4\text{-}O)(O_2CMe)_6]$, $[Zn_4(\mu_4\text{-}O)(O_2CPh)_6]$, and $[Zn_4(\mu_4\text{-}O)(O_2CCMe_3)_6]$.[12,19] The C–C$_{Cp*}$ bond lengths range from 1.520(2) to 1.5317(19) Å, which is comparable to the C–C$_{Cp*}$ bond lengths reported very recently for the homoleptic zinc amidate complex $[Zn\{OC(Cp^*)NiPr\}_2]_2$ (av. 1.54 Å).[11d]

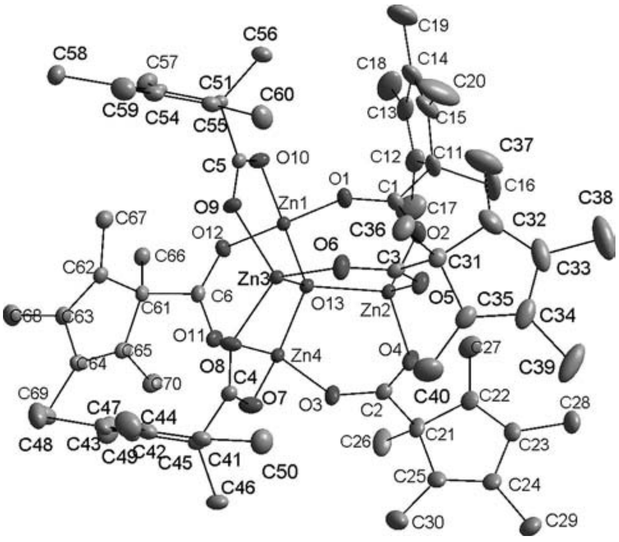


Figure 1. Molecular structure of the **1**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–O1 1.9441(10), Zn1–O10 1.9622(10), Zn1–O12 1.9517(10), Zn1–O13 1.9458(10), C1–O1 1.2624(17), C1–O2 1.2587(18), C1–C11 1.523(2); Zn1–O13–Zn2 110.37(5), Zn1–O13–Zn3 110.48(5), Zn1–O13–Zn4 109.79(4), O1–Zn1–O10 107.75(5), O1–Zn1–O12 110.52(4), O1–Zn1–O13 110.86(4), O1–C1–O2 125.27(14).

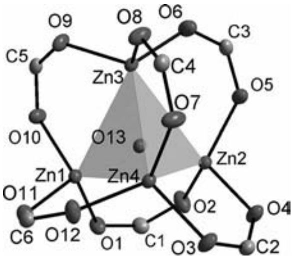


Figure 2. Projection of the tetrahedral $[Zn_4O]^{6+}$ core of **1** coordinated by six bridging carboxylate anions (Cp* groups are omitted for clarity).

Conclusions

We have reported for the first time the direct carboxylation reaction of a Zn–C bond without the use of any transmetalation catalyst. The structure of as-formed **1** is typical for basic zinc carboxylates, which consists of a central $[Zn_4O]^{6+}$ tetrahedron. This unit is well known as a structure-determining rigid SBU in microporous zinc-based metal–organic frameworks (MOFs). The $[Zn_4O]^{6+}$ nodal regions within these materials, which are of particular interest as novel hydrogen storage materials,[22] have been identified as the principal sites for the adsorption of hydrogen gas.[23] The potential capability of **1** as a molecular model for hydrogen adsorption, which seems to be generally possible according to previous findings by Redshaw et al.,[17] is currently under investigation. Moreover, the potential capability of **1** to serve as a *single source precursor* for the solution-based and gas-phase based (MOCVD) formation of ZnO, which was shown for structurally related zinc oxocarboxylates and oxocarbamates in the past,[4e,24] will be studied in detail.

Experimental Section

All manipulations were performed under an Ar atmosphere. Cp^*_2Zn was prepared according to literature methods.[25] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal C_6D_5H (^1H: δ = 7.154 ppm; ^{13}C: δ = 128.0 ppm). IR spectra were recorded on an ALPHA-T FTIR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Essen.

$[Zn_4(\mu_4\text{-}O)(O_2CCp^*)_6]$ (1): Cp^*_2Zn (0.34 g, 1 mmol) was dissolved in wet toluene (15 mL) and stirred for 1 h at 70 °C under a CO_2 atmosphere of 6 bar in a glass autoclave. Colorless crystals of **1** were formed within 24 h after storage at –30 °C. Yield: 0.28 g (78 %). Melting point: >220 °C. $C_{66}H_{90}O_{13}Zn_4{}^*C_7H_8$ (1444.99 g/mol): calcd. C 58.6, H 6.7; found C 58.6, H 6.8. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.22 (s, 3 H, C_5Me_5), 1.63 (s, 6 H, C_5Me_5), 1.82 (s, 6 H, C_5Me_5) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ = 10.5 (C_5Me_5), 11.2 (C_5Me_5), 19.2 (C_5Me_5), 66.2 (C_5Me_5), 136.3 (C_5Me_5), 136.6 (C_5Me_5), 184.9 (CO_2) ppm. IR: $\tilde{\nu}$ = 2968, 2911, 2854, 1580, 1441, 1402, 1383, 1356, 1327, 1292, 1260, 1110, 1062, 1018, 842, 809, 725, 696, 643, 626, 494, 465 cm^{-1}.

CCDC-826463 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from at the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] Bruker AXS D8 Kappa diffractometer with APEX2 detector [Mo-K_α radiation, λ = 0.71073 Å; T = 100(1) K]. The structure was solved by direct methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares on F^2. Semiempirical absorption correction from equivalent reflections on the basis of multiscans (Bruker AXS APEX2) was applied. All non-hydrogen atoms

were refined anisotropically and hydrogen atoms by a riding model. (G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, **1997**; see also: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112). **1**: $C_{66}H_{90}O_{13}Zn_2{\cdot}xC_7H_8$, M = 1444.99, colorless crystal (0.33 × 0.28 × 0.23 mm); triclinic, space group $P\bar{1}$; a = 12.5160(7), b = 15.3748(10), c = 19.6899(12) Å; α = 89.586(3), β = 76.430(3), γ = 88.709(3)°, V = 3682.2(4) Å^3; Z = 2; μ = 1.345 mm^{-1}; $\rho_{\text{ber.}}$ = 1.303 g cm^{-3}; 83967 reflections ($2\theta_{\max}$ = 61°), 21910 unique (R_{int} = 0.0235); 811 parameters; largest max./min. in the final difference Fourier synthesis 0.692 e Å^{-3}/–0.376 e Å^{-3}; max./min. transmission 0.75/0.62; R_1 = 0.0284 [$I > 2\sigma(I)$], wR_2 (all data) = 0.0747. The ADP of C20 indicates severe disorder which could not be resolved.

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