On the Question of Site-Selective Ligand Exchange in Carboxylate-Substituted Metal Oxo Clusters

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Reaction of $[Ti_4Zr_4O_6(OBu)_4(OMc)_{16}]$ (OMc = methacrylate) with acetylacetone (acacH) resulted in dissection of the cluster and formation of $[Ti(OBu)_2(acac)_2]$ and the smaller cluster $[Ti_2Zr_4O_4(OMc)_{16}]$. In contrast, the same reaction with

$[Zr_6O_4(OH)_4(OOCR)_{12}]_2 \cdot 6RCOOH$ (R = Et, $CH_2CH=CH_2$) led to site-selective substitution of two carboxylate ligands and formation of isostructural $[Zr_6O_4(OH)_4(OOCR)_{12-x}(acac)_x]_2 \cdot 6RCOOH$ (x ≤ 1).

Introduction

Ligand-exchange reactions are an important method for modifying or functionalizing the stabilizing ligand shell of nanoparticles.[1] Details of processes involving the ligand shell (and thus the surface atoms) are difficult to investigate, because most nanoparticles have no clearly defined structures. Molecular clusters, however, can be considered model compounds, because they only have surface atoms but (in many cases) no bulk atoms. They are big molecules, which are suitable for characterization by tools of molecular chemistry. Therefore, issues associated to the ligands are better investigated with clusters.

Carboxylate-substituted metal oxo clusters are especially suitable for fundamental studies on ligand dynamics and ligand exchange, because they are easily obtained, with various functional or nonfunctional carboxylate ligands, by reaction of transition metal alkoxides and carboxylic acids.[2] Numerous post-synthesis carboxylate exchange reactions were described, that is, reactions in which cluster-bonded carboxylate ligands are exchanged by treatment with a differently substituted carboxylic acid.[3,4] Such reactions proceed also in the presence of high concentrations of carboxylic acid without degradation of the cluster.

Ligand exchange with retention of the cluster core requires a simultaneous balancing of charge and coordination sites.[5,6] When the leaving and entering ligands are different, the risk of cluster degradation or rearrangement is high, even if both have the same charge and coordination characteristics. For example, when $[Ti_7O_4(OEt)_{20}]$ was treated with benzoic acid, $[Ti_6O_4(OEt)_{14}(OOCPh)_2]$ was formed, although substitution of μ_2-OR groups in the starting complex by bridging carboxylate ligands would have been geometrically possible without disturbing the geometry of the cluster core.[7] $[Zr_4O_2(OMc)_{12}]$ (OMc = methacrylate) was degraded upon addition of eight equivalents of acetylacetone (acacH), and $[Zr(OMc)_2(acac)_2]$ was formed quantitatively, with methacrylic acid and water as byproducts.[8] In the reaction of $Ti_{16}O_{16}(OEt)_{32}$ with acetylacetone, the cluster core was retained when up to four molar equivalents of acetylacetone per cluster were added. With a higher proportion of acetylacetone, however, the formation of larger, unidentified cluster species and $[Ti(OEt)_2(acac)_2]$ was observed.[9]

In cases where ligand exchange is possible without cluster degradation or rearrangement, such as exchange of one type of carboxylate ligand against another, another issue comes up. In many (but not all) carboxylate-substituted oxo clusters, the ligands undergo dynamic site exchange at room temperature. This includes interchange between chelating and bridging ligands.[10] Exchange reactions between cluster-bonded carboxylate ligands and carboxylic acids therefore do not proceed site-specifically, and the incoming carboxylate ligands participate in the dynamic process after exchange. Site-selective ligand-exchange reactions would be interesting for either blocking specific coordination sites or creating clusters with spatially directed functionalities. The latter are required for creating ordered polymeric structures such as MOFs or other cluster-containing polymers.

Site-specific exchange reactions may have a higher chance of success, if ligands of a different kind, that is, with

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different metal–ligand bond strengths, are employed. This is, for example, indicated by the nondynamic structure of the clusters $[Ti_6O_4(OiPr)_{10}(acetate)_2(O_3PR)_2]$ with various groups R (which were, however, not prepared by ligand exchange but instead from mixtures of acetic acid and phosphonic acid).[11] Moreover, introducing "preferred coordination sites" at the cluster surface might increase the chance of site-selective substitution. This can be another metal or a cluster in which one ligand site has special characteristics.

The clusters $[Ti_4Zr_4O_6(OBu)_4(OMc)_{16}]$ (**1**)[12] and $[Zr_6O_4(OH)_4(OOCR)_{12}]_2 \cdot 6RCOOH$ (**2a**, R = Et; **2b**: R = $CH_2CH=CH_2$)[13] have these features and were therefore selected for reactions with acetylacetone. Both contain both chelating and bridging carboxylate ligands. Since acetylacetonate ligands are nearly always chelating, there was a chance that the chelating carboxylate ligands could be exchanged with retention of bridging carboxylate ligands. The preferred coordination mode of carboxylate and β-diketonate ligands in large titanium oxo clusters has previously been discussed.[14] In the heterobimetallic cluster **1**, the OMc ligands coordinated to Ti (or bridging Ti and Zr) may have a reactivity that is different from that of the same ligands coordinated to Zr atoms. Both cluster types, however, have other structural features that might affect the ligand exchange. Cluster **1** also contains terminal OBu ligands, which could be substituted (possibly with concomitant rearrangement of the cluster) by acac. Clusters **2a** and **2b** are formed from two Zr_6 subunits, which are connected through four bridging carboxylate ligands. Reaction with acacH could therefore result in the formation of monomeric Zr_6 entities if the bridging ligands were substituted.

Results and Discussion

The core of the centrosymmetric cluster $[Ti_4Zr_4O_6(OBu)_4(OMc)_{16}]$ (**1**) consists of a zig-zag chain of four central $[ZrO_8]$ or $[ZrO_7]$ polyhedra and two terminating $[TiO_6]$ octahedra sharing common edges. Two additional corner-sharing $[TiO_6]$ octahedra are condensed at both ends of the main chain (Figure 1). The OBu ligands are bonded to the terminal Ti atoms. Two OMc ligands chelate Zr atoms at the center of the cluster (Zr1), four bridge two Ti atoms, four bridge two Zr atoms, and the remaining six bridge a Ti and a Zr atom. NMR spectra show that, despite the mixed-metal composition of the cluster core of **1**, the OMc ligands are dynamic.

Colorless crystals were obtained from the reaction of 4 equiv. of acetylacetone with **1** in CH_2Cl_2 after recrystallization from CH_2Cl_2. The crystalline compound was identified as a new Ti/Zr cluster with the composition $[Ti_2Zr_4O_4(OMc)_{16}]$ (**3**) (Figure 2).

This cluster can formally be obtained by elimination of $[Ti(OBu)_2(acac)_2]$ and water [corresponding to a TiO$(OBu)_2$ unit] from **1** and reorganization of the remaining cluster core. The presence of the $Ti(OBu)_2(acac)_2$ in the reaction solution was verified by mass spectrometry and

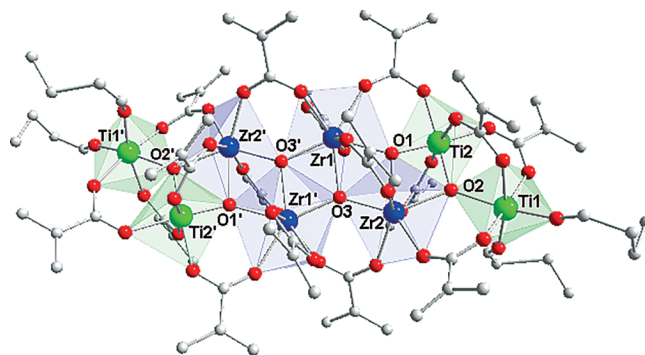Figure 1. Molecular structure of $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ (**1**).
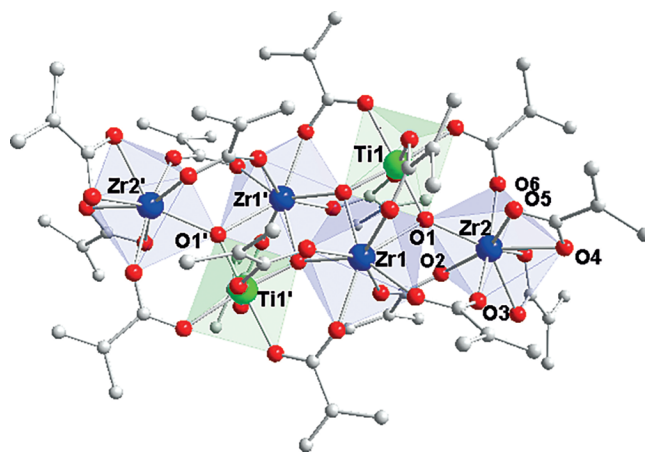

Figure 2. Molecular structure of $Ti_2Zr_4O_4(OMc)_{16}$ (**3**). Selected bond lengths [pm] and bond angles [°]: Zr2–O5 222.2(4), Zr2–O4 223.8(5), Zr2–O2 212.2(4), Zr2–O6 209.6(4), Zr2–O3 207.6(4), Zr2–O1 217.8(3), Zr1–O1 228.3(3); O4–Zr2–O5 57.34(2), O5–Zr2–O1 76.52(1), O4–Zr2–O1 133.84(2), Zr2–O1–Ti1 132.79(2), Zr1–O1–Zr2 128.56(2), Zr1–O1–Ti1 97.11(1), O1–Zr2–O3 83.87(1), O1–Zr2–O6 83.27(1).

NMR spectroscopy. The ESI mass spectrum showed the sodium adduct of the complex with highest intensity at m/z = 415.1 as well as the $[Ti(OBu)(acac)_2]^+$ fragment at m/z = 319.1. The signal at m/z = 401.1 was assigned to the sodium adduct of $Ti(OBu)(OiPr)(acac)_2$, which stems from $iPrOH$ impurities in the mass spectrometer. The $[Ti(OBu)_2(acac)_2Na_2Cl]^+$ adduct was found at m/z = 473.1.

The core of centrosymmetric **3** (Figure 2) consists of a zig-zag chain of two $[ZrO_8]$ dodecahedra (Zr1 and Zr1') and two $[TiO_6]$ octahedra (Ti1 and Ti1') sharing edges. This chain is terminated by two $[ZrO_8]$ dodecahedra (Zr2 and Zr2'), which share a corner (O1) with the $[ZrO_8]$ and $[TiO_6]$ polyhedra of the zig-zag chain. Four OMc ligands are chelating, two at each terminal $[ZrO_8]$ unit. Two OMc ligands bridge two Zr atoms, and the remaining four bridge a Ti and a Zr atom. Cluster **3** is isostructural to the previously reported cluster $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$,[12] where one of the OMc ligands bridging Zr1 and Zr2 (and Zr1'/Zr2', respectively) is replaced by a μ_2-OBu group. The NMR spectra of **3** show that the OMc ligands undergo dynamic site exchange.

When comparing the structures of **1** and **3**, it becomes evident that, upon reaction of **1** with acetylacetone, the connectivity of the remaining Ti/Zr polyhedra was considerably changed. The elimination of a (neutral) TiO(OBu)$_2$ unit vacates two coordination sites at Zr but results in three dangling OMc ligands. Despite compensation by an increase of the coordination number of the terminal Zr atoms from seven in **1** to eight in **3**, the Ti/Zr oxo framework did undergo a major rearrangement. In **3**, the two central Zr$_2$Ti(μ_3O) units of **1** are twisted relative to each other and connected in a different manner. This is accompanied by a major rearrangement of the OMc ligands. This must be a multistep process, where a distinction between an intramolecular rearrangement of the polyhedra/ligands and degradation to smaller (but not monomeric) units and their reassembly cannot be made.

Since no other clusters or degradation products were observed, compound **1** appears to be stable against further attack of acacH.

The second cluster type used for exchange experiments with acacH, centrosymmetric [Zr$_6$O$_4$(OH)$_4$(OOCR)$_{12}$]$_2$ (**2a** and **2b**), was described before with various carboxylate ligands (OOCR). Cluster **2b** is shown in Figure 3a as an example. It is built of two octahedral Zr$_6$O$_4$(OH)$_4$ ("Zr$_6$") units, which are connected by four carboxylate bridges ("Zr$_6$-bridging" ligands). Each Zr$_6$ unit comprises three chelating and seven bridging carboxylate ligands. The three chelating carboxylate ligands are bonded to the Zr atoms of the Zr$_3$ face opposite the ligands bridging the two Zr$_6$ units. Six carboxylic acid molecules are additionally bonded to the cluster through hydrogen bonds.

Reaction of 50 equiv. acetylacetone with **2a** and **2b**[13] resulted in exchange of one chelating carboxylate ligand on each Zr6 unit and [Zr$_6$O$_4$(OH)$_4$(OOCR)$_{11}$(acac)]$_2$· 6RCOOH (**2a_ac** and **2b_ac**) was formed (Figure 3b). The clusters **2b** and **2b_ac** are isostructural, thus the cluster core remains unaltered in this reaction as well as the coordination of the remaining carboxylate ligands and the six hydrogen-bonded carboxylic acid molecules. The molecular structure was completely solved for **2b_ac**. Crystals of **2a_ac** were of poor quality, and therefore the data could not be sufficiently refined. The XRD experiment nevertheless clearly showed that **2a_ac** is isostructural with **2b_ac**. The Zr–O bond lengths of the acac ligands are shorter and the bite angle is larger than those of the chelating carboxylate ligands. This affects the other bond lengths and angles only slightly, with a tendency to longer Zr–O bond lengths for the μ_3-O and μ_3-OH groups in **2b_ac** (Table 1).

Despite the large excess of acacH, substitution of a second carboxylate ligand per Zr6 unit was not observed, and substitution occurred only at Zr6. The chelating carboxylate ligand at Zr6 appears to be somewhat activated, possibly because Zr6 is *trans* to Zr3, to which two Zr$_6$-bridging carboxylate ligands are bonded (in contrast, only one is bonded to Zr1 and Zr4). In the structure of **2b**,[13] the chelating ligand that is eventually replaced by acac is more asymmetrically bonded [Zr-O 225.2(3) and 231.0(3)pm] than the other two chelating ligands in the Zr$_6$ unit.
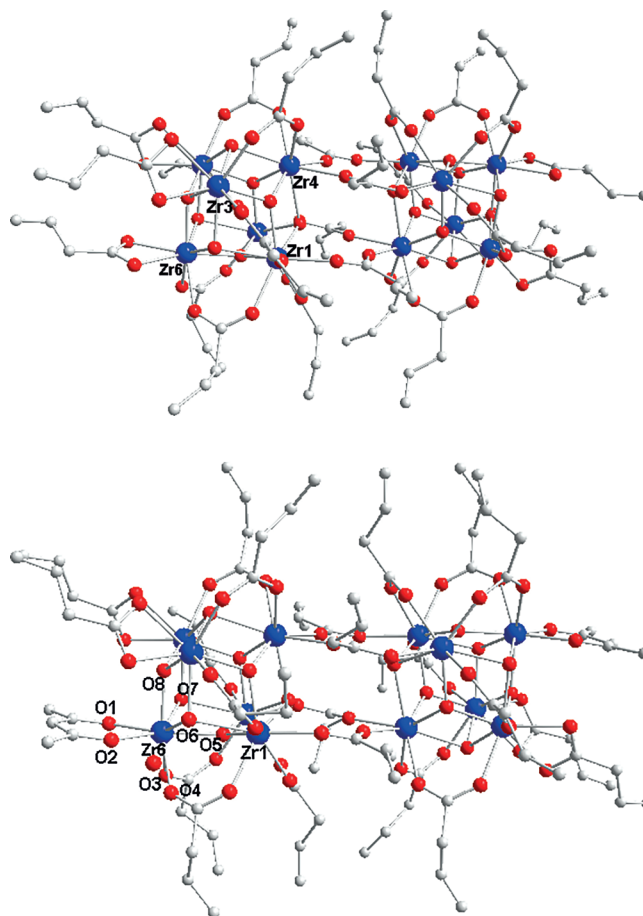

Figure 3. Molecular structure of [Zr$_6$O$_4$(OH)$_4$(OOCCH$_2$CH= CH$_2$)$_{12}$]$_2$ (**2b**)[13] (top) and [Zr$_6$O$_4$(OH)$_4$(OOCCH$_2$CH=CH$_2$)$_{11}$-(acac)]$_2$ (**2b_ac**) (bottom).

Table 1. Comparison of selected bond lengths [pm] and bond angles [°] of **2b_ac** and **2b**.

Bond lengths	2b_ac	2b	Bond angles	2b_ac	2b
Zr6–O2	217.0(6)	225.2(3)	O1–Zr6–O2	73.77(9)	56.47(9)
Zr6–O1	218.9(7)	231.0(3)	O6–Zr6–O8	69.1(2)	69.7(1)
Zr6–O6	224.5(7)	221.3(3)	O6–Zr6–O5	71.1(2)	73.4(1)
Zr6–O8	211.7(6)	209.4(3)	O8–Zr6–O7	121.3(2)	124.6(1)
Zr6–O5	207.6(5)	203.6(2)	O8–Zr6–O5	91.2(2)	94.6(1)
Zr6–O7	224.8(7)	221.0(3)	O8–Zr6–O7	68.6(2)	70.0(1)
Zr6–O4	224.7(7)	223.4(3)	O5–Zr6–O7	71.2(2)	73.54(9)
Zr6–O3	223.2(7)	219.3(3)			

Reactions of **2a** and **2b** were also performed with 2, 4, 8, 12, or 24 equiv. of acetylacetone. From those experiments crystals were grown by slow concentration of a thf solution at –11 °C; all crystals showed the same triclinic unit cell. The structures of the crystals obtained from the reaction of **2a** and **2b** with 24 equiv. of acacH were solved and showed partial displacement of the carboxylate ligand by acetylacetonate ligands (ca. 60 % acac occupation for **2a** and 70 % for **2b**). The isostructural clusters [Zr$_6$O$_4$(OH)$_4$(OOCR)$_{12}$]$_2$ and [Zr$_6$O$_4$(OH)$_4$(OOCR)$_{11}$(acac)]$_2$ (**2b** and **2b_ac**) may thus replace each other in the unit cell, resulting in the over-

all composition $[Zr_6O_4(OH)_4(OOCR)_{12-x}(acac)_x]_2$ in the range $0 \leq x \leq 1$.

The exchange reaction with acetylacetone was also monitored by NMR spectroscopy. Ligand dynamics in the clusters $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ was previously investigated in detail.[13] At room temperature, only partial site exchange was observed, and the most dynamic region was that of the chelating ligands. Cluster **2a** showed a distinct splitting of the carboxylate ligand signals in the ^{1}H NMR spectrum (Figure 4a). This same splitting was observed after ligand exchange with acacH, which indicates retention of the cluster core structure. The appearance of only one signal at $\delta = 2.05$ ppm (from the methyl group of coordinated acac ligand) and the absence of the signal at $\delta = 2.24$ ppm (from the methyl group of acacH) are typical for the coordination of the acac ligand (Figure 4b, c).
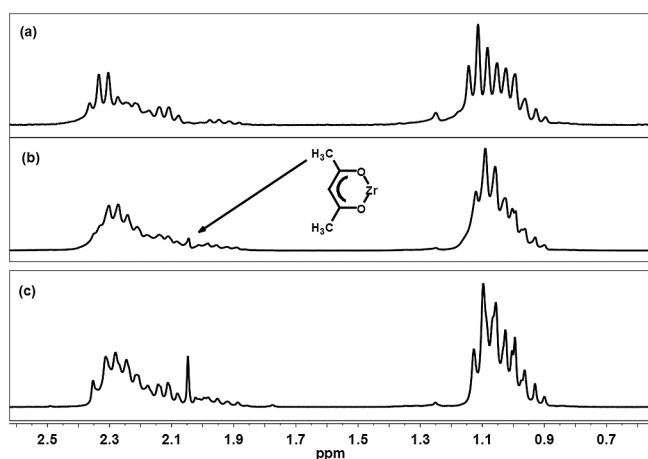

Figure 4. ^{1}H NMR spectra (CDCl$_3$, 25 °C) of $[Zr_6O_4(OH)_4$-$(OOCEt)_{12}]_2$ (**2a**) before (a) and after reaction with 4 equiv. of acetylacetone (b) and 50 equiv. of acetylacetone (c).

Conclusions

The outcome of the reactions of three different carboxylate-substituted oxo clusters with acacH, namely $[Zr_4O_2(OMc)_{12}]$,[8] $[Ti_4Zr_4O_6(OBu)_4(OMc)_{16}]$ (**1**), and $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$·6RCOOH (**2**) (this article), is very different. While $[Zr_4O_2(OMc)_{12}]$ was completely degraded to monomeric units and only two monomeric Ti units were cleaved from **1**, the cluster core of **2** was retained and one chelating carboxylate ligand per Zr$_6$ unit was substituted.

The robustness of the cluster core appears to be of uttermost importance. In **2**, *each* metal atom of the cluster is connected to the other atoms through four μ$_3$-O or μ$_3$-OH groups. It should be stated that the structure of the Zr$_6$O$_4$(OH)$_4$ core can be considered as the smallest possible section of tetragonal zirconia. Removing one or more units from such a closed structure by a chemical reaction is apparently difficult, if not impossible. This renders substitution of a chelating ligand possible, with retention of the cluster core structure, although some activation of the chelating carboxylate ligand appears to be necessary.

As discussed previously,[3] the exchange of carboxylate ligands against each other is possibly initiated by the change of coordination of a carboxylate ligand from μ$_2$ to η^1 to thus vacate a coordination site. If the metal atom is coordinated to too many carboxylate ligands, this may eventually lead to an expulsion of a monomeric unit. If the remaining fragment cannot be stabilized by re-organization, then complete degradation occurs, as in $[Zr_4O_2(OMc)_{12}]$.

In the case of **1**, elimination of Ti(OBu)$_2$(acac)$_2$ leads to a Ti/Zr fragment, which is able to stabilize itself by re-arrangement of the remaining cluster core and the ligands. Why the resulting cluster (compound **3**) is so stable against further degradation remains an open question.

Experimental Section

General: All operations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Hexane, toluene, and tetrahydrofuran were dried with Na/benzophenone prior to use. CH$_2$Cl$_2$ was distilled from CaH$_2$. CDCl$_3$ and [D$_8$]toluene were purchased from Euriso-Top and degassed by freeze-pump-thaw cycles. Methacrylic acid (99%), propionic acid (99%), 3-butenoic acid (97%), and acetylacetone (99%) were obtained from Sigma Aldrich and freshly distilled from P$_2$O$_5$ prior to use. Ti(OBu)$_4$ (97%) and Zr(OBu)$_4$ (80% in butanol) were obtained from Sigma Aldrich and used as received. $[Ti_4Zr_4O_6(OBu)_4(OMc)_{16}]$ (**1**),[12] $[Zr_6O_4(OH)_4$-$(OOCEt)_{12}]_2$·6EtCOOH (**2a**),[13] and $[Zr_6O_4(OH)_4$-$(OOCCH_2CH=CH_2)_{12}]_2$·6CH$_2$=CHCH$_2$COOH (**2b**)[13] were prepared as previously reported. **2a** and **2b** were purified by multiple precipitation from hexane. Compound **1** was purified from the free acid by multiple dissolution in toluene and removal of the solvent in vacuo.

Characterization Techniques

Solution ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE 250 (250.13 MHz {^{1}H}, 62.86 MHz {^{13}C}) instrument. Gas-tight Young tubes were used for all experiments.

Mass spectrometric measurements were performed with an Esquire 3000^{plus} 3D-quadrupole ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) in the positive-ion mode by means of electrospray ionization (ESI). Mass calibration was done with a commercial mixture of perfluorinated trialkyltriazines (ES Tuning Mix, Agilent Technologies, Santa Clara, CA, USA). The analyte was dissolved in butanol (p.a. Merck) to a concentration of ca. 1 mg/mL. Direct infusion experiments were carried out by using a Cole Parmer model 74900 syringe pump (Cole Parmer Instruments, Vernon Hills, IL, USA) at a flow rate of 2 μL/min. Full scans were measured in the range $m/z = 100$–1100 with the target mass set to $m/z = 1000$. Mass calculations are based on the most abundant Ti isotope (^{48}Ti-isotope). Mass spectra and CID spectra were averaged over the data acquisition time of 1 to 2 min; one analytical scan consisted of five successive microscans resulting in 50 and 100 analytical scans, respectively, for the final mass spectrum.

X-ray Structure Analyses

Measurements for **3** were performed at 100 K, and those for **2b_ac** were carried out at 243 K by using Mo-K_a ($\lambda = 71.073$ pm) radiation. Data were collected with a Bruker AXS SMART APEX II four-circle diffractometer with κ-geometry with ϕ and ω scans and different frame widths. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction

Table 2. Crystal data and refinement details for **3** and **2b_ac**.

	3	**2b_ac**
Emp. formula	$C_{64}H_{80}O_{36}Ti_2Zr_4$	$C_{122}H_{158}O_{76}Zr_{12}$
M_r	1885.96	3935.12
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [pm]	1079.2(5)	1409.5(1)
b [pm]	1110.3(2)	1429.4(5)
c [pm]	1656.4(2)	2012.0(9)
α [°]	101.589(2)	98.8(1)
β [°]	96.224(2)	95.5(7)
γ [°]	96.154(2)	99.8(2)
V [pm^3 10^6]	1915.9	3915.6
Z	1	1
D_x [g cm^{-3}]	1.635	1.669
μ [mm^{-1}]	0.812	0.858
Crystal size, mm	$0.6 \times 0.5 \times 0.4$	$0.4 \times 0.3 \times 0.2$
No. measured refl.	53061	100555
Measured refl. [$I > 2\sigma(I)$]	4903	10870
θ_{max} (°)	25.09	25.41
R [$F^2 > 2\sigma(F)$], wR (F^2), S	0.0457, 0.1369, 1.088	0.0731, 0.2195, 1.036
Refl./param.	6790/486	14397/903
Weighting scheme[a]	$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 4.3097P]$	$w = 1/[\sigma^2(F_o^2) + (0.0950P)^2 + 39.6146P]$
$\delta\rho_{max,min}$, [e 10^{-6} pm^{-3}]	1.607, −1.260	1.614, −1.624

[a] $P = (F_o^2 + 2F_c^2)/3$.

(SADABS) was employed. The cell dimensions were refined with all unique reflections. SAINT PLUS software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames (Table 2).

The structures were solved by the Patterson method (SHELXS-97[15]). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL-97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined as riding with the corresponding atom. Two of the acid molecules hydrogen-bonded to the cluster showed positional disorder.

CCDC-1047803 (for **3**) and -1047804 (for **2b_ac**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of [Ti$_4$Zr$_4$O$_6$(OBu)$_4$(OMc)$_{16}$] (1) with Acetylacetone: In a typical experiment, **1** (50 mg, 0.022 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL). Acetylacetone (2 or 4 molar equiv.) was added, and the reaction mixture was stirred for 30 min, during which the pale yellow solution darkened. All volatiles were then removed, and the crude product was dissolved in CH$_2$Cl$_2$ (2 mL). Crystals of **3** were grown by slow evaporation of the solvent at –11 °C. Yield 78 %. The unit cell of the obtained crystals was the same, regardless of whether 2 or 4 equiv. of acacH was used. For MS measurements, the supernatant liquid of the crystallization experiment was separated. After removal of all volatiles, the solid residue was dissolved in BuOH.

[Ti(OBu)$_2$(acac)$_2$]: ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): $\delta = 0.94$ (s, CH$_3$), 0.97 (m, CH$_3$), 1.46–1.88 (m, CH$_2$), 4.62 (m, CH$_2$O), 5.37 (s, CH) ppm. ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta = 13.59$ (CH$_3$), 19.24 (CH$_3$CH$_2$), 25.93 (CH$_3$C(O)), 35.17 (CH$_2$CH$_2$), 35.17 (CH$_2$O), 100.85 [CH$_3$C(O)CH], 188.46 [CH$_3$C(O)CH] ppm. ESI-MS (BuOH, NaCl) positive ion: $m/z = 415.1$ [M – Na]$^+$.

3: ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): $\delta = 1.18$–2.25 (CH$_3$), 5.28–5.82 and 5.97–6.35 (CH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta =$

18.31 (CH$_3$), 128.06 (CH$_2$), 138.20 [C(CH$_2$)CH$_3$], 173.68 (COO) ppm.

Reaction of [Zr$_6$O$_4$(OH)$_4$(OOCEt)$_{12}$]$_2$·6EtCOOH (2a) and [Zr$_6$O$_4$(OH)$_4$(OOCCH$_2$CH=CH$_2$)$_{12}$]$_2$·6CH$_2$=CHCH$_2$COOH (2b) with Acetylacetone: Typically, the cluster (50 mg; 0.014 mmol **2a** or 0.013 mmol **2b**) was dissolved in CH$_2$Cl$_2$ (5 mL). After addition of acetylacetone, the solution was stirred for 30 min. All volatiles were then removed in vacuo, and the residue was dissolved in THF (2 mL). Crystals were grown by slow concentration at –11 °C. The reaction was performed for 2, 4, 8, 12, 24, and 50 equiv. of acetylacetone. Crystals obtained for 2–24 equiv. of acacH showed the same unit cell. The structure was solved for experiments with 24 equiv. of acacH for **2a** and **2b**. Crystals of a different unit cell were achieved by reaction with 50 equiv. incoming ligand. Only the structure for the reaction of **2b** with 50 equiv. acac could be solved. The measurement was done at 243 K, since the crystals cracked upon cooling to 100 K. The same reaction with **2a** resulted in crystals of poor quality.

2a_ac: (Spectra from the crystalline compound): ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): $\delta = 0.98$–1.11 (CH$_3$), 1.97–2.31 (CH$_3$CH_2), 2.02 (CH$_3$), 5.45 (CH), 11.02 (COOH) ppm. ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta = 8.4$–9.8 (CH$_3$), 26.71 [CH$_3$C(O)] 28.22–30.25 (CH$_2$), 100.37 [C(O)CH], 178.51–183.85 (COOH) 183.99 [CH$_3$$C$(O)] ppm.

2b_ac: (Spectra from the crystalline compound): ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): $\delta = 2.62$–3.00 (CH$_2$), 4.90–5.09 (CH), 5.73–5.87 (=CH$_2$)1.96 (CH$_3$), 5.48 (CH), 10.95 (COOH) ppm. ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta = 8.4$–9.8 (CH$_3$), 27.48 [CH$_3$C(O)], 28.22–30.25 (CH$_2$), 101.26 [C(O)CH], 178.51–183.85 (COOH), 184.87 [CH$_3$$C$(O)] ppm.

Acknowledgments

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