Substituent-Dependent Formation of Supramolecular Aggregates of 6-Hydroxy-*trans*-3-hexenoic Acids in the Solid State

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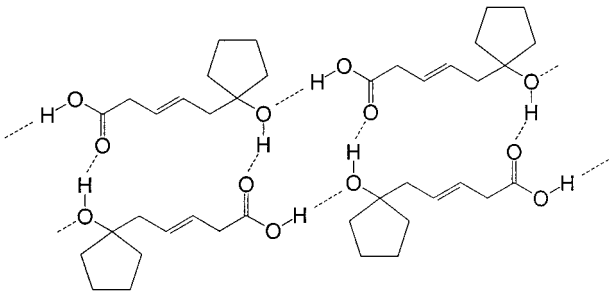
The substituted 6-hydroxy-*trans*-3-hexenoic acids **2–4** have been prepared by a template coupling reaction between (butadiene)zirconocene, $W(CO)_6$, and cyclobutanone, cyclodecanone, or cyclododecanone, respectively, followed by hydrolytic/oxidative demetallation of the resulting metallacyclic zirconoxycarbene tungsten complexes. The hydroxyalkenoic acids **2–4** have been found to form two novel fundamental types of associated supramolecular structural arrays in the solid state through intermolecular hydrogen bonding, which have been characterized by X-ray diffraction analysis. The cyclobutanone-derived compound **2** exhibits an infinitely extending sheet-like structure, which is composed of symmetrically alternating interconnected 12- and 36-membered rings, each being constructed from the functional groups or frameworks of four individual molecules of **2**. In contrast, the cyclodecanone-derived compound **3** adopts a ribbon-type structure composed of C_2-symmetrically arranged symmetry-equivalent 15-membered rings, each containing the functionalities from three individual molecules of **2**. On the basis of scanning force microscopy studies, the cyclododecanone-derived compound **4** would appear to have a similar structure in the solid state. The structural features of the molecular assemblies that are formed by intermolecular hydrogen bonding of compounds **2–4** in the solid state are selectively controlled by the size and favoured conformations of the spiro-anellated carbocyclic rings at C6 of the 6-hydroxy-*trans*-3-hexenoic acid carbon chain.

Introduction

Molecular organic compounds bearing spatially separated hydrogen-bond donor and acceptor functionalities exhibit a pronounced tendency to form μ-H connected three-dimensional supramolecular arrays.[1] Therefore, compounds such as hydroxycarboxylic acids or amino acids[2] often serve as molecular building blocks in crystal engineering and supramolecular architecture.[3] Substituted 6-hydroxy-*trans*-3-hexenoic acids undergo specific aggregations in the solid state as a result of hydrogen bonding. Owing to the rigid framework, the two functional groups cannot interact intramolecularly, but are forced to function independently at a given distance from one another in building up a supramolecular framework in the solid state. This leads to unique molecular arrangements, the characteristic structural features of which are determined primarily by the size of the substituents at the 6-position, as has been revealed by the solid-state structures of the representative examples described in this account (for previous examples, see refs.[4−6]).

We have recently reported the structure of the 6,6-tetramethylene-anellated 6-hydroxy-*trans*-3-hexenoic acid **5**. It was prepared by coupling of butadiene with $W(CO)_6$ and cyclopentanone at a Cp_2Zr template, followed by hydrolysis and oxidation (see Scheme 1).[4a,5] Compound **5** was found to form a ribbon-like supramolecular structure in the solid state, in which μ-H bonding between two CO_2H[3][7] and two OH groups[8] from four different molecules of **5** leads to the formation of a loop comprising a total of 12 atoms (i.e. four hydrogen, six oxygen, and two carbon atoms). The 12-membered ring is flanked by two symmetry-equivalent 18-membered rings, and the ribbon structure is built up of the alternating anellated 12- and 18-membered ring structures.[6] The solid-state structure of compound **5** (and of several related examples[4−6]) is thus characterized by an infinite *C_2-parallel* arrangement of the individual 6-hydroxy-*trans*-3-hexenoic building blocks, as denoted by **A** in Scheme 2.



Scheme 1. Ribbon-type aggregate structure of **5**

Two further fundamental types of aggregate structures of such rigid bifunctional substrates can be expected to be feasible, namely the *anti-parallel* type **B** and the *cyclic* arrangement (type **C** in Scheme 2). We have found that their

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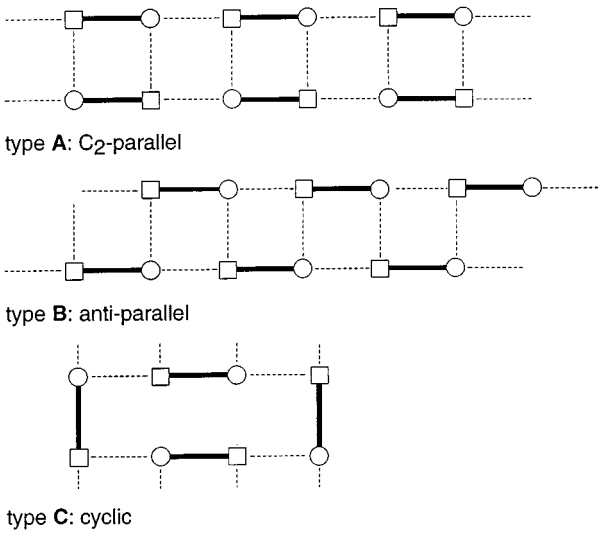
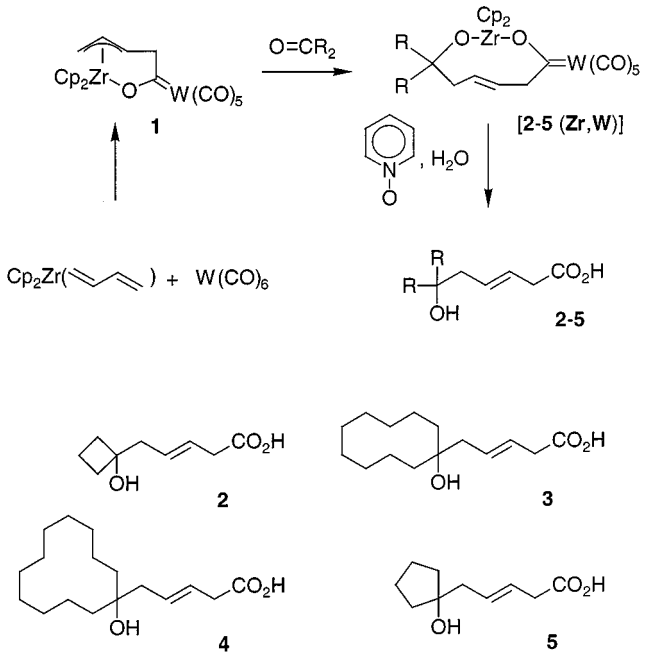


Scheme 2. Fundamental structural aggregate types of substituted 6-hydroxy-*trans*-3-hexenoic acids (open square: CO_2H; open circle: OH)



Scheme 3. General synthesis and examples of substituted 6-hydroxy-*trans*-3-hexenoic acids used in this study

selective formation is determined by the size of the 6,6-anellated ring system at the 6-hydroxy-*trans*-3-hexenoic acid framework. The first examples of each of these new aggregate structural types have now been characterized, which are described herein.

Results and Discussion

The synthesis of the substituted hydroxyhexenoic acids **2**–**4** used in this study was accomplished by employing an established organometallic template reaction.[4][9] (Butadiene)zirconocene was reacted with hexacarbonyltungsten in a 1:1 ratio to yield the metallacyclic (π-allyl)zirconoxycarbene tungsten complex **1**, which was then treated with one molar equivalent of cyclobutanone, cyclodecanone, or cyclododecanone to selectively yield nine-membered metallacyclic coupling products with an endocyclic *trans*-configurated C(4)=C(5) double bond (for details, see the Experimental Section).

Subsequent hydrolysis and oxidation of the zirconoxycarbene complexes removed the Group 4 metallocene and converted the in situ generated [W]=C(R)OH functionality to the carboxylic acid.[10] The hydroxyalkenoic acids **2**–**4** were isolated in ca. 40% yield after recrystallization.

The hydroxycyclobutylpentenoic acid **2** and the hydroxycyclodecylpentenoic acid **3** were characterized by X-ray diffraction analysis. Both systems were found to exhibit associated structures in the solid state. Figure 1 shows the molecular structures of the monomeric subunits of **2** and **3** found in these structural assemblies. Each of the compounds contains a *trans*-configurated C3–C4 carbon–carbon double bond in the central position of the C_6-carbon chain. The molecules contain conformationally extended linear central chains, resulting in a large spatial separation between the two functional groups. In the four-membered ring derivative **2**, this intramolecular separation of the CO_2H and OH groups is maximized [distance C1···C6 6.055(2) Å, O1···O3 7.369(2) Å, torsional angles θ_1(C1–C2–C3–C4) 119.0(2)°, θ_2(C3–C4–C5–C6) −129.6(2)°]. Due to slightly different conformational arrangements of the C_6 chain, this separation is marginally reduced in compound **3** [C1···C6 5.582(2) Å, O1···O3 6.591(2) Å, O2···O3 6.212(2) Å; θ_1 114.1(2)°, θ_2 129.3(2)°].

The carbocyclic four-membered ring in **2** shows a puckered conformation (puckering angle 26°) with the OH group at C6 in a pseudo-equatorial position. The ten-membered carbocycle in **3** adopts a boat-chair-boat conformational arrangement, as is often found for such medium-sized ring systems.[11]

The organized suprastructure of **2** is constructed in the following way: Four individual molecules of **2** are connected through the formation of alternating hydrogen bonds between their CO_2H and OH groups. The carboxylate C=O group serves as a monofunctional hydrogen-bond acceptor and the carboxylate C–OH group as a monofunctional μ-H donor, whereas the alcohol OH functionality is bifunctional, serving as both a H donor and acceptor. The alternating arrangement of the two CO_2H and two OH groups thus results in the formation of 12-membered ring arrangements, four of which are arranged approximately C_2-symmetrically at the corners of a supramolecular square (see Figure 2).[12] The interior of this square is constructed from the remaining framework atoms of the four individual monomers of **2**, which are arranged exactly according to the cyclic suprastructural type **C**, as is schematically visualized in Scheme 2 (see above). Thus, the supramolecular structure of **2** is composed of interlinking perpendicular pairs of 12-membered and 36-membered ring structures. These add up to form a pleated sheet-type structure. Three-

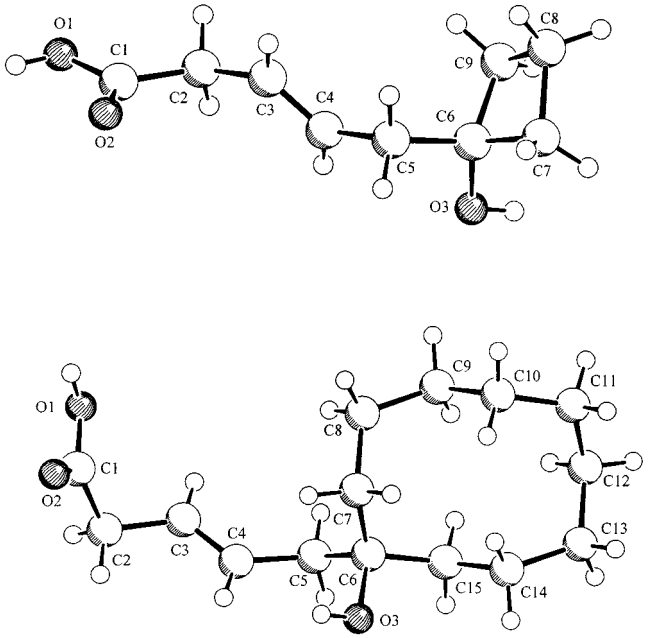


Figure 1. Structures of the molecular units of **2** and **3** in the crystal (with nonsystematic atom numbering scheme); selected bond lengths [Å] and angles [°]: **2**: C1−O1 1.309(2), C1−O2 1.204(2), C3−C4 1.314(2), C6−O3 1.430(2); O1−C1−O2 123.1(1), C3−C4−C5 125.3(1), C4−C5−C6 113.1(1), C7−C6−C9 88.7(1); **3**: C1−O1 1.318(2), C1−O2 1.196(2), C3−C4 1.312(3), C6−O3 1.457(2); O1−C1−O2 122.8(2), C2−C3−C4 123.0(2), C3−C4−C5 125.9(2), C7−C6−C15 115.8(1)

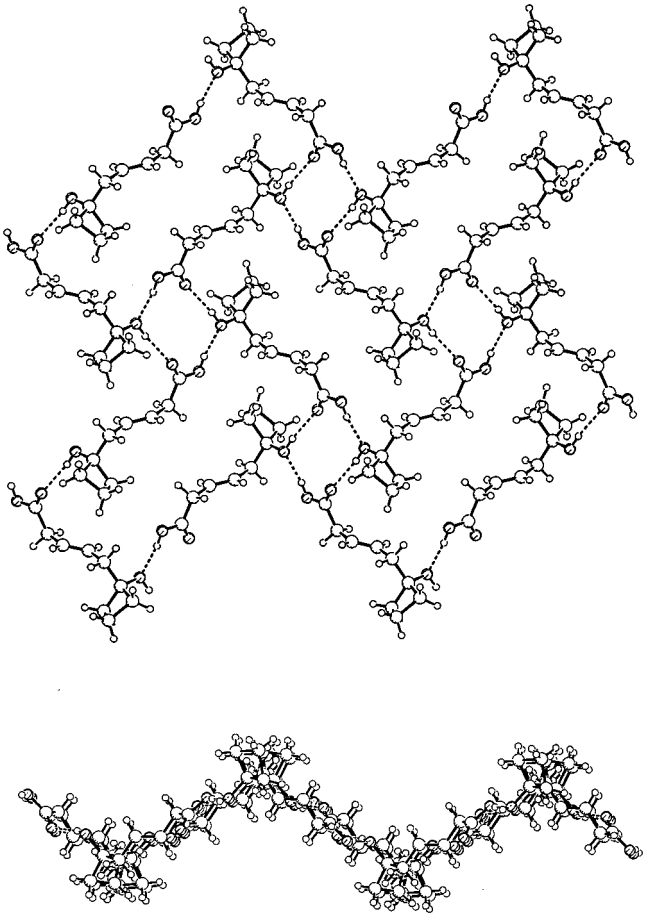


Figure 2. Two views of the pleated sheet-type structural arrangement of **2** in the solid state; rotation of the top projection by 80° gives the picture shown below

dimensional stacking of the individual sheet structures leads to the overall observed arrangement of **2** in the crystal. This supramolecular arrangement of **2** would seem to represent the first example of macrocyclic ring formation from individual bifunctional hydroxycarboxylic acids giving a structure of type **C**, as depicted in Scheme 2.

The cyclodecyl-substituted hydroxyalkenoic acid **3** also shows a novel type of associated hydrogen-bridged structure in the crystal. The compound forms a ribbon-like arrangement constructed of a sequential array of anellated loops, each of which is formed by connection of a CO_2H group of one monomeric unit with the OH group of a second molecule of **3** and further connection of both with a third bifunctional **3** unit. This closes the cycle, thus forming a 15-membered ring. The overall (nonplanar) ribbon-like structure contains an infinite array of these interconnected 15-membered rings, each being C_2-symmetrically oriented in relation to its adjacent symmetry-equivalent neighbours (see Figure 3). The supramolecular assembly of compound **3** thus represents an example of the novel *anti*-parallel structural type **B**, which is depicted schematically in Scheme 2. The ten-membered carbocyclic rings of **3** are found to be spiro-anellated at the individual loops of the central hydrogen-bonded framework, and are oriented towards the exterior of the band-like arrangement.

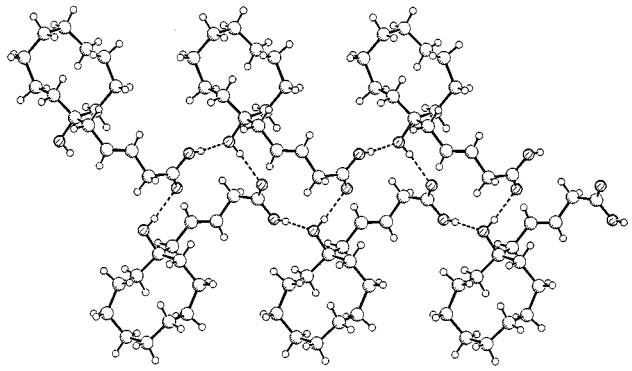


Figure 3. The ribbon-like structure of **3** formed by an *anti*-parallel assembly of monomeric units in the solid state

The cyclododecanone-derived hydroxyalkenoic acid **4** crystallizes in the form of extremely thin plates, which prohibited its structural characterization by X-ray diffraction analysis. However, it was possible to obtain a well-resolved image of the surface structure of these plates by atomic force microscopy.[13] The obtained SFM micrograph (Figure 4, top) shows a regular array of features with a recurring size of ca. 7 Å. It could be that the positive features in this array (shown in light colour in Figure 4) might each represent individual strings of $CO_2H\cdots HO$ H-bonded assemblies of **4** (two of which are combined to give the *anti*-

parallel ribbon in analogy to the solid-state structure of **3**). It seems that these ribbons are arranged in such a way that at the crystallographically favoured surface of the crystal only a single string of **4** is present at the interface and thus this is all that is observed by contact SFM under low force loading. This interpretation originates from and is supported by a comparitive inspection of a crystallographic cut through the bulk structural arrangement of the related compound **3**, the structure of which was described above, along the 001 crystallographic plane. A view of this projection of the cell is shown in Figure 4 (bottom), which probably indicates a close relationship between the crystallographic orientations of **3** and **4** in the solid state.

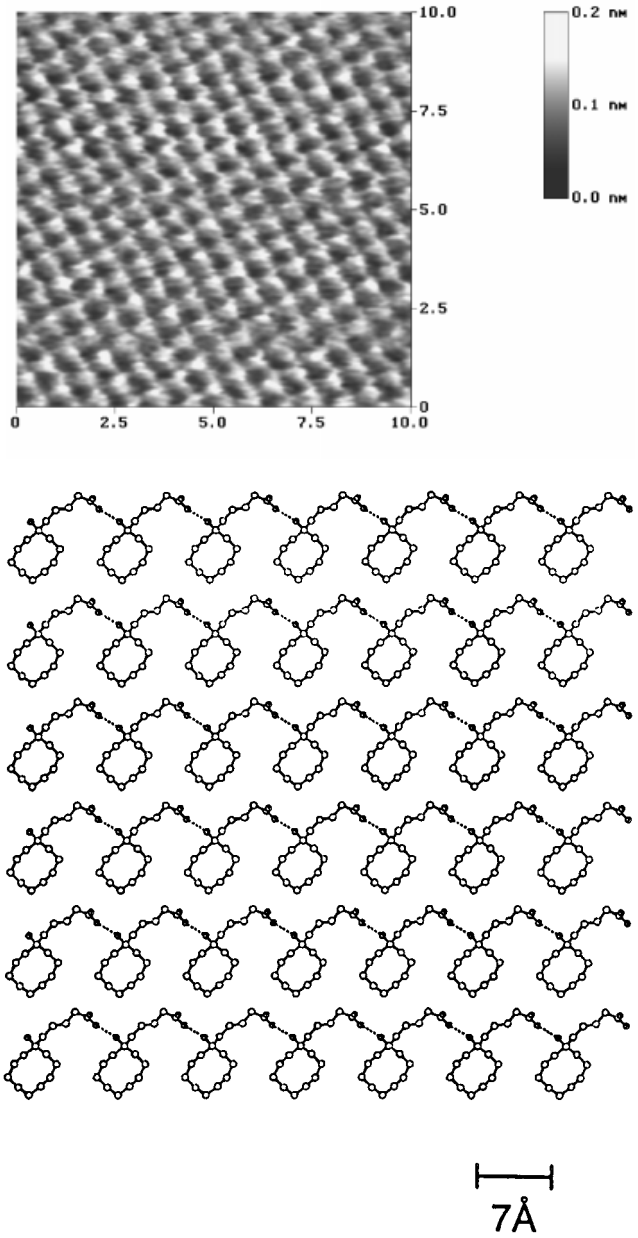


Figure 4. SFM micrograph of crystalline **4** (top) and a comparison with the structural arrangement of **3** in the crystal (bottom)

Conclusions

The hydroxyalkenoic acids **2**−**5** show a pronounced tendency to form supramolecular organic structures in the solid state that are held together by selective hydrogen bonding. Most favourable seem to be structural types that exhibit a sequential array of the CO_2H and OH functionalities of individual entities of the respective monomeric building blocks. The specific structure is then determined and its formation controlled by the specific cycloalkylidene moiety that forms part of the respective 6-hydroxy-*trans*-3-hexenoic acid.

In the cyclobutylidene example **2**, the relatively small four-membered rings adopt a conformational position oriented towards the interior of the 36-membered ring, thereby effectively inhibiting transannular hydrogen bonding. This results in the formation of an ordered patchwork of alternating 12- and 36-membered ring ″tiles″, that eventually make up the layered sheet-like structure found in the crystal. Increasing the size of the cycloalkylidene building blocks leads to a turning and an increased orientation of the attached ring systems toward the exterior of the core framework, resulting in the favoured formation of infinitely extending ribbon-like structural arrays. The *C_2-parallel* arrangement type **A**[5] (and derivatives thereof[6], see Scheme 2) is favoured for examples containing a spiro-anellated five-membered ring, but the attachment of larger rings leads to a pronounced tendency to further open the structure and eventually leads to the novel *anti-parallel* type **B** structure, observed here for the first time (**3**). Compound **4** is likely to be of the same suprastructural type. These observations demonstrate that the hydroxyalkenoic acids **2**−**5** show considerable potential for serving as building blocks in the selective construction of supramolecular arrays in organic crystals, with the fundamental structural type being controlled by the nature of the incorporated cyclic substituent at the OH end of the rigid chain. It may well be that this type of control can also be used for the selective construction of a variety of other molecular architectures. Such studies are currently being pursued in our laboratory.

Experimental Section

Reactions involving organometallic reagents were carried out under argon by using Schlenk-type glassware or in a glove box. Solvents were dried and distilled under argon prior to use. For further general information, including a listing of the instrumentation used for physical characterization of the prepared compounds, see ref.[9] The (π-allyl)(zirconoxycarbene)tungsten reagent **1**[4][9] and the 6-hydroxy-*trans*-3-hexenoic acid **5**[4a] were prepared according to literature procedures.

Reaction of 1 with Cyclic Ketones. − General Procedure: Synthesis of 2[Zr,W]: Cyclobutanone (0.12 mL, 1.59 mmol) was added dropwise by means of a syringe to a suspension of the (π-allyl)(zirconoxycarbene)tungsten complex **1** (1.00 g, 1.59 mmol) in toluene (30 mL) at ambient temperature. The mixture slowly became clear and after 5 h at room temperature a small amount of a residual solid was removed by filtration. The filtrate was then concentrated to dryness in vacuo, the residue was suspended in pentane, and

collected by filtration. The resulting yellow solid was washed twice with pentane (10 mL) and dried in vacuo to give 1.01 g (91%) of **2**[Zr,W]; m.p. 175°C. − $C_{24}H_{22}O_7ZrW$ (697.5): calcd. C 41.33, H 3.18; found C 41.61, H 3.17. − IR (KBr): $\tilde{\nu}$ = 1983, 1960, 1901, 1891 cm^{-1}. − ^1H NMR ([D$_8$]THF, 599.8 MHz): δ = 6.40/6.33 (s, each 5 H, Cp-H), 5.11−5.06 (m, 1 H, 4-H), 5.01−4.97 (m, 1 H, 5-H), 4.55 (dd, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 3.6 Hz, 1 H, 6-H′), 3.05 (dd, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 10.1 Hz, 1 H, 6-H), 2.58 (ddd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 3.1 Hz, $^4J_{HH}$ = 1.55 Hz, 1 H, 3-H′), 2.25−2.20, 2.17−2.12 (m, 2 H, 1′-H′, 3′-H′), 2.06−2.01 (m, 2 H, 1′-H, 3′-H), 1.89 (ptd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 11.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, 3-H), 1.72−1.70 (m, 1 H, 2′-H′), 1.59−1.52 (m, 1 H, 2′-H). − ^{13}C NMR ([D$_8$]THF, 150.8 MHz): δ = 332.4 (C7), 205.1 (C−CO_{trans}), 200.4 (C−CO_{cis}), 132.9 (C4), 128.2 (C5), 114.6, 113.8 (C−Cp), 87.1 (C2), 72.6 (C6), 45.9 (C3), 39.6, 35.8 (C1′, C3′), 12.9 (C2′).

Synthesis of 3[Zr,W]: According to the general procedure, reaction of the (π-allyl)(zirconoxycarbene)tungsten complex **1** (1.00 g, 1.59 mmol) and cyclodecanone (258 mg, 1.67 mmol) gave, after filtration of the reaction mixture and storage of the filtrate at −18°C, **3**[Zr,W] (0.45 g, 36%) as yellow crystals, which proved suitable for X-ray analysis; m.p. 176°C. − $C_{30}H_{34}O_7ZrW$ (781.7): calcd. C 46.09, H 4.38; found C 45.64, H 4.34. − IR (KBr): $\tilde{\nu}$ = 1957, 1917, 1891 cm^{-1}. − ^1H NMR ([D$_8$]THF, 599.8 MHz): δ = 6.41/6.34 (s, each 5 H, Cp-H), 5.18−5.13 (m, 1 H, 4-H), 5.05−5.00 (m, 1 H, 5-H), 4.52 (d, $^2J_{HH}$ = 18.3 Hz, 1 H, 6-H′), 3.13 (dd, $^2J_{HH}$ = 18.3 Hz, $^3J_{HH}$ = 10.1 Hz, 1 H, 6-H), 2.37 (pd, J_{HH} = 12.6 Hz, 1 H, 3-H′), 1.92−1.42 (m, 19 H, 3-H, 1′−9′-H). − ^{13}C NMR ([D$_8$]THF, 150.8 MHz): δ = 332.3 (C7), 205.2 (C−CO_{trans}), 200.6 (C−CO_{cis}), 132.9 (C4), 128.4 (C5), 114.6, 114.2 (C−Cp), 90.8 (C2), 72.7 (C6), 45.9 (C3), 37.1, 32.6, 27.8, 27.6, 27.3, 25.1, 24.6, 23.3, 21.7 (C1′−C9′). − Complex **3**[Zr,W] was characterized by an X-ray crystal structure analysis: formula $C_{30}H_{34}O_7WZr$, M_r = 781.64, a yellow crystal of dimensions 0.30 × 0.30 × 0.20 mm was selected, a = 10.835(2), b = 14.248(4), c = 19.290(4) Å, β = 96.25(2)°, V = 2960.2(12) Å^3, ρ_{calcd} = 1.754 g cm^{-3}, F(000) = 1536 e, μ = 42.79 cm^{-1}, empirical absorption correction using φ scan data (0.904 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 223 K, ω/2 θ scans, 6316 reflections collected (−h, −k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 5997 independent and 4569 observed reflections [$I \geq 2\,\sigma(I)$], 353 refined parameters, R = 0.055, wR^2 = 0.159, max. residual electron density 2.76 (−3.63) e Å^{-3} close to W, hydrogens calculated and refined as riding atoms. Data sets were collected with an Enraf−Nonius CAD4 diffractometer.[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127452−127455. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033, E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of 4[Zr,W]: According to the general procedure, reaction of the (π-allyl)(zirconoxycarbene)tungsten complex **1** (1.00 g, 1.59 mmol) and cyclododecanone (247 mg, 1.35 mmol) gave **4**[Zr,W] (1.15 g, 89%) as a yellow solid; m.p. 175°C. − $C_{32}H_{38}O_7ZrW$ (809.7): calcd. C 47.48, H 4.73; found C 47.53, H 4.80. − IR (KBr): $\tilde{\nu}$ = 1970, 1923, 1895, 1889 cm^{-1}. − ^1H NMR ([D$_8$]THF, 599.8 MHz): δ = 6.41/6.34 (s, each 5 H, Cp-H), 5.18−5.13 (m, 1 H, 4-H), 5.02−4.97 (m, 1 H, 5-H), 4.54 (dd, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 3.5 Hz, 1 H, 6-H′), 3.09 (dd, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 10.1 Hz, 1 H, 6-H), 2.37 (dpt, $^2J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 1.56 Hz, 1 H, 3-H′), 1.87−1.46 (m, 23 H, 3-H, 1′−11′-H). − ^{13}C NMR ([D$_8$]THF, 150.8 MHz): δ = 331.9 (C7), 205.1 (C−CO_{trans}), 200.5 (C−CO_{cis}), 133.4 (C4), 128.0 (C5), 114.4, 114.1 (C−Cp), 89.7 (C2), 72.7 (C6), 46.1 (C3), 39.6, 34.8, 29.4, 29.0, 26.0, 24.0, 23.3 (C1′−C11′).

Synthesis of the 6-Hydroxy-*trans*-3-hexenoic Acids. − General Procedure: Synthesis of 2: Complex **2**[Zr,W] (6.63 g, 9.50 mmol) was dissolved in tetrahydrofuran (100 mL). To this was added 10.5 mL of a 1.15 M solution of pyridine *N*-oxide (12.08 mmol) in THF, followed by water (1.00 mL, 55.5 mmol). The mixture was stirred for 4 h at ambient temperature. The solvent was then removed in vacuo and the residue was taken up in diethyl ether (100 mL). The organic phase was extracted with five 50-mL portions of a saturated sodium hydrogen carbonate solution. The combined aqueous phases were washed with diethyl ether until the washings were colourless and then acidified to pH 1 with ca. 6 M aqueous HCl. The resulting turbid mixture was extracted with five 60-mL portions of diethyl ether, and the combined organic phases were washed with water (2 × 60 mL). Drying with magnesium sulfate and evaporation of the solvent in vacuo gave 620 mg of **2** as a yellow oil. Storage of a solution of 620 mg of **2** in diethyl ether (5 mL) at −18°C resulted in the deposition of 510 mg (32%) of **2** as colourless crystals, which proved suitable for X-ray analysis; m.p. 52°C. − $C_9H_{14}O_3$ (170.2): calcd. C 63.51, H 8.29; found C 63.69, H 8.49. − IR (KBr): $\tilde{\nu}$ = 3428, 1710 cm^{-1}. − ^1H NMR ($CDCl_3$, 599.8 MHz): δ = 7.2−6.0 (br. s, 2 H, OH, COOH), 5.67−5.59 (m, 2 H, 3-H and 4-H), 3.09 (d, 2 H, $^3J_{HH}$ = 5.6 Hz, 2-H), 2.33 (d, 2 H, $^3J_{HH}$ = 5.6 Hz, 5-H), 2.04−2.01 (m, 4 H, 2′-H, 4′-H), 1.75−1.68 (m, 1 H, 3′-H′), 1.53−1.47 (m, 1 H, 3′-H). − ^{13}C NMR ($CDCl_3$, 150.8 MHz): δ = 177.2 (C1), 129.8 (C3), 125.5 (C4), 74.3 (C1′), 42.4 (C5), 37.7 (C2), 35.3 (C2′, C4′), 11.9 (C3′). − GHSQC NMR ($CDCl_3$, 150.8 MHz/599.8 MHz): δ = 129.8/5.63 (C3/3-H), 125.5/5.63 (C4/4-H), 42.4/2.33 (C5/5-H), 37.7/3.09 (C2/2-H), 35.3/2.04−2.01 (C2′, C4′/2′-H, 4′-H), 11.9/1.70 (C3′/3′-H′), 11.9/1.53 (C3′/3′-H). − X-ray crystal structure analysis of **2**: formula $C_9H_{14}O_3$, M_r = 170.20, a colourless crystal of dimensions 0.50 × 0.40 × 0.10 mm was selected, a = 7.822(1), b = 14.450(2), c = 8.699(1) Å, β = 103.30(1)°, V = 956.9(2) Å^3, ρ_{calcd} = 1.181 g cm^{-3}, F(000) = 368 e, μ = 7.23 cm^{-1}, empirical absorption correction using φ scan data (0.937 ≤ C ≤ 0.998), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 1.54178 Å, T = 223 K, ω/2 θ scans, 2086 reflections collected (+h,−k,±l), [(sinθ)/λ] = 0.62 Å^{-1}, 1947 independent and 1766 observed reflections [$I \geq 2\,\sigma(I)$], 111 refined parameters, R = 0.046, wR^2 = 0.130, max. residual electron density 0.28 (−0.17) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Synthesis of 3: According to the general procedure, reaction of **3**[Zr,W] (6.00 g, 9.56 mmol), 9.20 mL of a 1.15 M solution of pyridine *N*-oxide (10.5 mmol) in THF, and water (1.00 mL, 55.5 mmol) gave **3** as a yellow oil. Storage of a solution of this oil in diethyl ether (10 mL) at −18°C resulted in the deposition of 1.12 g (46%) of **3** as colourless crystals, which proved suitable for X-ray analysis; m.p. 96°C. − $C_{15}H_{26}O_3$ (254.4): calcd. C 70.83, H 10.30; found C 70.86, H 10.45. − IR (KBr): $\tilde{\nu}$ = 3336, 1705 cm^{-1}. − ^1H NMR ($CDCl_3$, 599.8 MHz): δ = 7.10−6.15 (br. s, 2 H, OH, COOH), 5.67−5.55 (m, 2 H, 3-H, 4-H), 3.08 (pd, $^3J_{HH}$ = 6.5 Hz, 2 H, 2-H), 2.48 (pd, $^3J_{HH}$ = 7.0 Hz, 2 H, 5-H), 1.70−1.40 (m, 18 H, 2-H′, 3-H′, 4-H′, 5-H′, 6-H′). − ^{13}C NMR ($CDCl_3$, 150.8 MHz): δ = 177.2 (C1), 130.1 (C3), 125.2 (C2), 76.2 (C1′), 44.0 (C5), 37.8 (C2), 33.9, 26.8, 26.3, 23.7, 21.1 (C2′, C3′, C4′, C5′, C6′). − GHSQC NMR ($CDCl_3$, 150.8 MHz/599.8 MHz): δ = 130.1/5.67−5.55 (C3/3-H), 125.2/5.69−5.57 (C4/4-H), 44.0/1.48 (C5/5-H), 37.8/3.08 (C2/2-H), 33.9, 26.8, 26.3, 23.7, 21.1/1.70−1.40 (cyclodecyl fragment). − X-ray crystal structure analysis of **3**: formula $C_{15}H_{26}O_3$, M_r = 254.36, a colourless crystal of dimensions 0.30 × 0.20 × 0.10 mm was selected, a = 9.730(2), b = 8.316(1),

c = 17.987(3) Å, β = 90.94(1)°, V = 1455.2(4) Å^3, ρ_{calcd} = 1.161 g cm^{-3}, F(000) = 560 e, μ = 6.26 cm^{-1}, empirical absorption correction using φ scan data (0.968 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 1.54178 Å, T = 223 K, ω/2 θ scans, 5904 reflections collected (±h, ±k, +l), [(sinθ)/λ] = 0.62 Å^{-1}, 2966 independent and 1841 observed reflections [$I \geq 2\,\sigma(I)$], 166 refined parameters, R = 0.046, wR^2 = 0.121, max. residual electron density 0.21 (−0.16) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Synthesis of 4: According to the general procedure, reaction of **4**[Zr,W] (7.47 g, 9.23 mmol), 10.5 mL of a 1.15 M solution of pyridine *N*-oxide (12.0 mmol) in THF, and water (1.00 mL, 55.5 mmol) gave **4** as a white solid. Storage of a solution of this solid in diethyl ether (10 mL) at −18 °C resulted in the deposition of 890 mg (34%) of **4** as colourless crystals, which were not suitable for X-ray analysis (thin plates), but could be characterized by SFM. **4**: m.p. 113 °C. − $C_{17}H_{30}O_3$ (282.4): calcd. C 72.30, H 10.71; found C 71.79, H 10.75. − IR (KBr): $\tilde{\nu}$ = 3409, 1700 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 599.8 MHz): δ = 6.3−6.22 (br. s, 2 H, OH, COOH), 5.69−5.57 (m, 2 H, 3-H and 4-H), 3.09 (d, 2 H, $^3J_{HH}$ = 6.6 Hz, 2-H), 2.14 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, 5-H), 1.53−1.49 (m, 2 H, 2′-H′), 1.41−1.22 (m, 20 H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H). − ^{13}C NMR ($CDCl_3$, 150.8 MHz): δ = 177.2 (C1), 130.1 (C3), 125.3 (C4), 75.2 (C1′), 43.6 (C5), 37.7 (C2), 34.2 (C2′), 26.0 (C7′), 26.4, 22.5, 22.0, 19.4 (C3′, C4′, C5′, C6′). − GHSQC NMR ($CDCl_3$, 150.8 MHz/599.8 MHz): δ = 130.1/5.69−5.57 (C3, 3-H), 125.3/5.69−5.57 (C4/4-H), 43.6/2.14 (C5/5-H), 37.7/3.09 (C2/2-H), 34.2/1.53−1.49 (C2′/2′-H′), 34.2, 26.0, 26.4, 22.5, 22.0, 19.4/1.41−1.22 (C2′, C3′, C4′, C5′, C6′, C7′/2′-H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H). − Scanning force microscopy of **4:** Crystals of **4** were investigated using a commercially available scanning force microscope (NanoScope, MultiMode, Digital Instruments) under ambient conditions. The SFM was operated in the contact mode using Si cantilevers. The pyramidal shaped Si tips had a spring constant of 0.032 N/m. The images were captured at low loading forces to avoid tip-induced damage to the crystal surface.

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