# Novel Nine-Membered Titanaheterocycles – Structure, ab initio Calculations, and Preparative Use towards the Selective Synthesis of Substituted Cyclopentanols

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Received March 24, 1998

**Keywords:** Cyclizations / Cross-coupling / Ab initio calculations / Titanium / Metallacycles

Reactions of $Cp_2Ti(CO)_2$ (**3**) with two equivalents of α,β-unsaturated ketones **4** yield the novel titana-2,9-dioxacyclonona-3,7-dienes **5**. Cross-coupling of **3** with two different ketones **4** and **6** to give **7** can be achieved under certain reaction conditions. Hydrolysis of **5** or **7** may generate diketones **9**, cyclopentanols **10/11**, or cyclopentenes **12/13**, depending on substituents and conditions. The X-ray crystal structure of **5a**, the first nine-membered bis($\eta^5$-cyclopentadienyl)-substituted titanaheterocycle containing carbon, is presented. Ab initio calculations were performed for **5a** and for titana-2-oxacyclopentene **1**, a conceivable intermediate in the coupling reaction.

## Introduction

Titanaheterocycles are known with ring sizes ranging from three to ten and with different degrees of "unsaturation". Whereas most of the publications focussed on systems featuring four-[1], six-[2][3][4], eight-[4][5] or ten-membered[5] rings, we were interested in the chemistry of the odd-numbered chelate complexes, like titanaheterocyclopropanes,[3] titanaheterocyclopentanes and -pentenes,[4][5][6][7][8][9][10][11] or titana-2,7-dioxacyclohepta-3,5-dienes.[6][11][12] Structurally characterized nine-membered titanacycles are known as well, but most of them lack carbon in their metallacycle, as for instance $TiS_8$ systems.[4][13] We reported[14] on the synthesis of "carbon-rich" bis($\eta^5$-cyclopentadienyl)titanadioxacyclononadienes **5** by a novel coupling of two α,β-unsaturated ketones with $Cp_2Ti(CO)_2$, and recently Okuda[15] published the X-ray structures of nine-membered titanacycles built up from a 2,2′-ethylenebisphenol and simple $TiR_4$ precursors. We now present the structure and preparative use of the titanacycles **5**, as well as cross-coupling variants of our reaction with two different ketones. We also took a closer look at the mechanism of the coupling process and performed ab initio calculations on the title complexes **5** and on conceivable intermediates like titana-2-oxacyclopent-3-enes **1**, which are hitherto unknown[16] in contrast to their zirconium analogues[17] and their isomers, the titanacyclopent-4-enes **2**.[9][10]

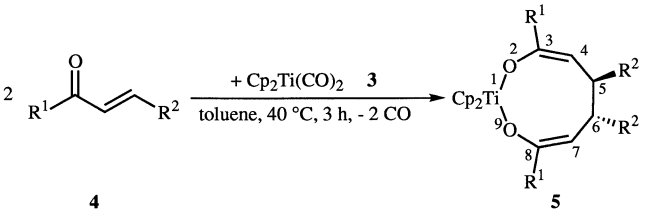
Figure 1. Unknown (**1**) and stable (**2**) 1-titana-2-oxacyclopentenes


## Results and Discussion

### Synthesis of "Symmetric" Titana-2,9-dioxacyclonona-3,7-dienes 5; Scope and Limits

We have recently shown that α,β-unsaturated arylketones (e.g. **4a**) readily react under mild, non-basic conditions with dicarbonyltitanocenes **3**[18] to furnish the corresponding nine-membered bis-unsaturated metallacycles **5** right away without five-membered species of type **1** being detectable intermediates[14]. Oxidative addition of two ketone units, loss of two equivalents of CO and exclusive *trans*-β,β coupling are the features of this reaction, which at first seemed to be restricted to bis(aryl)-substituted ketones, though.

Scheme 1




4 5

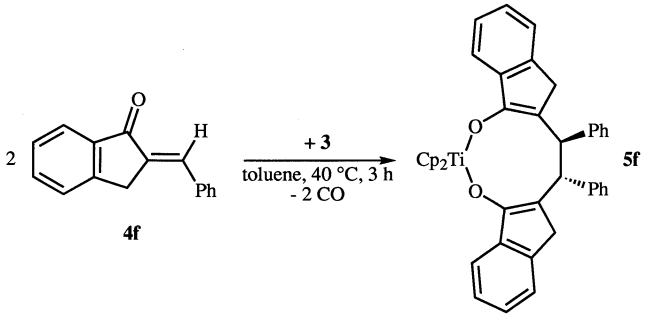
| 4/5 | a | b | c | d | e |
|---|---|---|---|---|---|
| $R^1$ | Ph | Ph | $^t$Bu | Ph | PhCH=CHCH=CH |
| $R^2$ | Ph | Me | Ph | PhCH=CH | Ph |

  1434–1948/98/0909–1253 $ 17.50+.50/0 

We now found, that the residues $R^2$ may also be aliphatic to give equally high yields of **5** (**5b**), whereas $R^1$ adjacent to the carbonyl function is more crucial to the course of the reaction. Aryl groups, alkyl systems not bearing an α-hydrogen atom, like *tert*-butyl (**5c**), or vinyl units are compatible as $R^1$. Ketones **4** with methyl or saturated primary or secondary alkyl groups next to the carbonyl function do usually not give any metallacycles **5** on reaction with **3** in isolable yields.

α,β;γ,δ-Bis(unsaturated) ketones (**4d**) do not give metallacycles with larger rings but merely the corresponding vinyl-substituted cyclononadienes (**5d**). Remarkably, reaction of **3** with the tris(unsaturated) ketone **4e** yields exclusively the symmetric 5,6-diphenyl-substituted derivative **5e** by a β,β-C−C coupling at the "short ends" of the trienones. This pathway may be preferred due to kinetic reasons or due to the highest degree of olefinic conjugation of the product compared with 11- or 13-membered metallacycles, which would result from β,δ-C−C and δ,δ-C−C coupling reactions, respectively. Reactions of **3** with carbocyclic ketones like **4f** also give rise to the corresponding metallacycles like **5f** without providing evidence for the intermediacy of − now bicyclic and thus in principle more stable − species of type **1**. **5f** is also the first derivative carrying substituents at each ring carbon atom.

Scheme 2




The most attractive extension of this basic reaction would be cross-coupling variants of **3** with two different unsaturated carbonyl moieties. *Intra*molecular cross-coupling does not take place, however, with ketones bearing a second unsaturated keto or ester group at an appropriate distance. Reaction of **3** with the keto ester **4g**, for instance, proceeds with 1:2 stoichiometry and with formation of titanacycle **5g** in low yield. Although bearing an α-hydrogen atom at a saturated residue $R^1$, complex **5g** is as stable as more typical derivatives of **5** bearing vinyl, aryl or *tert*-butyl residues at C3 and C8. **5g** is the only example of a titanacycle with this structural feature.

Table 1 shows a representative collection of new "symmetric" titanadioxacyclononadienes prepared from **4** and **3** in a 2:1 stoichiometry.

### X-ray Crystal Structure of Complex 5a

So far, only a few titanaheterocycles with ring sizes larger than six have been characterized by X-ray analysis[5][13]. Single crystals of **5a** suitable for an X-ray crystal structure analysis could be obtained from a solution in toluene kept in the dark at room temperature for twenty days. To our knowledge, the structure obtained from these crystals is the first one of an unsaturated nine-membered titanacycle except for the non-cyclopentadienyl systems Ti[2,2′-ethylenebis(6-*tert*-butyl-4-methylphenolato)]$X_2$[15] [X = Br, O*i*Pr, $CH_2(SiMe_3)_2$].

Scheme 3

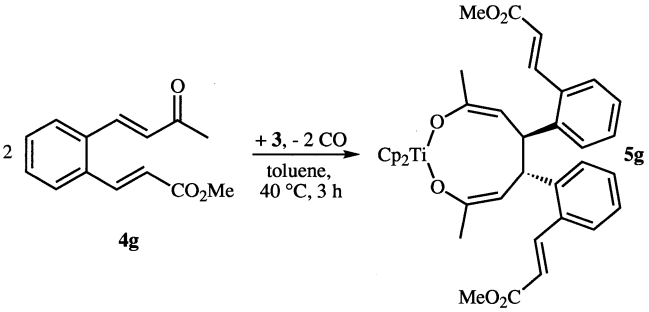
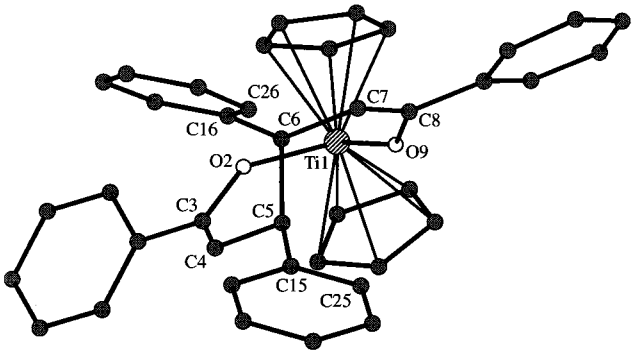



Table 1. Symmetric titanadioxacyclononadienes **5** from **3** and ketones **4**[a]

| **5** | $R^1$ | $R^2$ | Yield[b] | m.p.[c] |
|---|---|---|---|---|
| **a** | Ph | Ph | 52 | 204 |
| **b** | Ph | Me | 63 | 170 |
| **c** | *t*Bu | Ph | 70 | 181 |
| **d** | Ph | PhCH=CH | 85 | 125 |
| **e** | PhCH=CHCH=CH | Ph | 55 | 135 |
| **f** | *see Scheme 2* | Ph | 93 | 125 |
| **g** | Me | *see Scheme 3* | 12 | 170 |

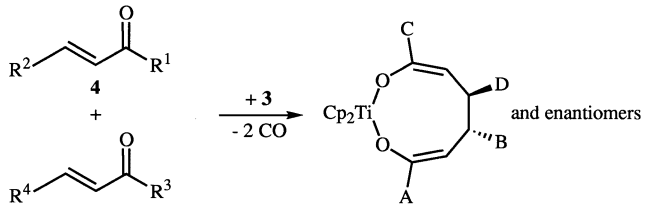
[a] Conditions: 24 h, room temperature, 1 mmol of **3**, 2 mmol of **4**. − [b] Isolated yield in [%] based on **4**. − [c] M. p. in [°C].

Figure 2. Molecular structure of **5a**; hydrogen atoms are omitted[a]




[a] Selected bond lengths [Å], angles [°] and dihedral angles [°]: Ti1−O2 1.885, Ti1−O9 1.892, O2−C3 1.359, O9−C8 1.356, C3−C4 1.344, C4−C5 1.494, C5−C6 1.587, C6−C7 1.506, C7−C8 1.346; Ti1−O2−C3 144.7, Ti1−O9−C8 143.1, O2−Ti1−O9 101.8, O2−C3−C4 121.0, O9−C8−C7 121.7, C3−C4−C5 124.3, C4−C5−C6 110.8, C5−C6−C7 111.5, C6−C7−C8 123.1; Ti1−O2−C3−C4 −67.9, Ti1−O9−C8−C7 −63.6, O2−Ti1−O9−C8 68.6, O2−C3−C4−C5 5.0, O9−Ti1−O2−C3 68.0, C3−C4−C5−C6 −58.1, C3−C4−C5−C15 174.2, C4−C5−C6−C7 150.8, C4−C5−C6−C16 −78.6, C5−C6−C7−C8 −62.0, C5−C6−C16−C26 −90.9, C6−C5−C15−C25 93.4, C6−C7−C8−O9 2.9, C15−C5−C6−C7 −79.3, C15−C5−C6−C16 51.3, C16−C6−C7−C8 167.9.

Scheme 4




| 6 | $R^3$ | $R^4$ |
|---|---|---|
| a | Ph | Ph |
| b | *o,p*-$(MeO)_2C_6H_3$ | Ph |
| c | *p*-$(MeO)C_6H_4$ | Ph |
| d | *p*-$(MeO)C_6H_4$ | *p*-$(MeO)C_6H_4$ |

**5**: A = C = $R^1$, B = D = $R^2$
**7**: A = $R^1$, B = $R^2$, C = $R^3$, D = $R^4$
**8**: A = C = $R^3$, B = D = $R^4$

**5a** features roughly $C_2$ symmetry about an axis through the titanium atom and the opposite ring bond between C5 and C6. All bonds of the chelate have lengths as expected, with only small differences for the pairs of corresponding bonds. Only the C5−C6 bond (1.59 Å) is slightly longer than an average carbon−carbon single bond (1.55 Å).The adjoining bonds (C4−C5 and C6−C7) are both roughly 1.50 Å long. The C=C bonds C3−C4 and C7−C8 have lengths of 1.34 and 1.35 Å. Both C−O bonds have very similar lengths (1.36 Å), as have the Ti−O bonds (1.89 Å). The cyclopentadienyl rings in **5a** are staggered by an angle of 132°. In contrast, the few other published nine-membered $Cp_2Ti$-chelates all show eclipsed Cp ligands.[13] The titanium atom is coordinated pseudo-tetrahedrally, with the angle O−Ti−O being 102°, which is in the typical range. The metallacyclic system is puckered about the $C_2$ axis, the angle between the O−Ti−O plane and the opposite C5−C6 bond is roughly 90°, both C=C bonds are *cis* configured. In **5a**, the angles Ti−O−C are 143° and 145°, which are common values for unstrained cycles. All four dihedral angles including Ti−O segments are close to 70°, the dihedral angles C3−C4−C5−C6 and C5−C6−C7−C8 are ca. 60°, and the angle C4−C5−C6−C7 is 151°. This results in coplanarity of the phenyl groups at C5 and C6, which are oriented formally *trans* to each other. Crystals of **5a** pertinaciously contain half an equivalent of toluene per molecule.

### Synthesis of Cross-Coupled Nine-Membered Metallacycles 7

"Unsymmetric" cross-coupled titanacycles **7** can be prepared in special cases from two unsaturated ketones **4** and **6** of sufficiently different reactivity towards **3**. In principle, three distinct products could result from reactions of a mixture of **3**, **4**, and **6**. Formation of complex **8** from **3** and two equivalents of the more reactive ketone **6** can be supressed by dropwise addition of **6** to a mixture of **4** (lower reactivity) and **3**. The ratio of chelate complexes **5** and **7** is strongly influenced by the reaction temperature. The yields of the cross-coupled products **7** increase markedly with increasing temperature. Best results are obtained by preparing a mixture of **3** and **4** at 50°C, followed immediately by dropwise addition of **6**. Only cases where **7** is formed exclusively are of synthetic interest, as separation of mixtures of **5**, **7**, and **8** is cumbersome due to their lack of air-stability and to similar chromatographic behaviour. Table 2 shows a couple of such well-defined examples.

### Hydrolysis of Titanadioxacyclononadienes 5 and 7

Acidic hydrolysis of the "symmetric" titanacycles **5** leads to only one racemic pair of highly substituted cyclopentanols **10**, bearing four stereocentres, by a selective aldol reaction.[14] In most cases some diketone **9** and/or cyclopentene **12** is formed as well but can be easily removed by column chromatography. The *trans* orientation of the substituents at C3 (B) and C4 (D) is defined in the course of the β-β coupling leading to **5**. The keto function at C2 then is oriented *trans* to B and the hydroxy group at C1 is finally formed *cis* to this keto group due to favourable hydrogen bond interactions. The unambiguous assignment of the relative stereochemistry of **10** and proof of the absence of further diastereomers (or epimers) is based on NMR spectra. Table 3 shows some new examples for the formation of cyclopentanols **10** from titanacycles **5** to illustrate the widened scope and the limits of the method and the influence of the solvent used for hydrolysis. As a rule of thumb, low temperatures and the use of ethereal instead of aqueous solutions of hydrogen chloride favour the formation of cyclopentanols **10** over that of diketones **9**. Hydrolysis of the unusual titanacycle **5f** gives rise to the interesting spiro compound **10b** (besides minor amounts of diketone **9b**) featuring five stereocentres about the central cyclopentane core, although rather unselectively. All possible eight isomers (plus enantiomers), when a *trans* orientation of the phenyl groups is assumed, are found in rather arbitrary ratios and can be separated by HPLC. Hydrolyses of the "un-

Table 2. Titanadioxacyclononadienes **7** from two different ketones **4/6**[a]

| 7 | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield[b] | m.p.[c] | starting compounds |
|---|---|---|---|---|---|---|---|
| **a** | *p*-$(MeO)C_6H_4$ | CH=CHPh | Ph | Ph | 69 | 101 | **4h**, **6a**[e] |
| **b** | *p*-$(MeO)C_6H_4$ | CH=CHPh | *o,p*-$(MeO)_2C_6H_3$ | Ph | 60 | 115 | **4h**, **6b** |
| **c** | *p*-$(MeO)C_6H_4$ | CH=CHPh | *p*-$(MeO)C_6H_4$ | Ph | 65 | 114 | **4h**, **6c** |
| **d** | Ph | CH=CHPh | *p*-$(MeO)C_6H_4$ | *p*-$(MeO)C_6H_4$ | 68 | – | **4e**, **6d** |
| **e**[d] | Ph | CH=CHPh | *o,p*-$(MeO)_2C_6H_3$ | Ph | 66 | 160 | **4e**, **6b** |
| **f** | Ph | CH=CHPh | *p*-$(MeO)C_6H_4$ | Ph | 81 | 152 | **4e**, **6c** |
| **g** | Ph | CH=CHPh | Ph | Ph | 65 | 79 | **4e**, **6a**[e] |

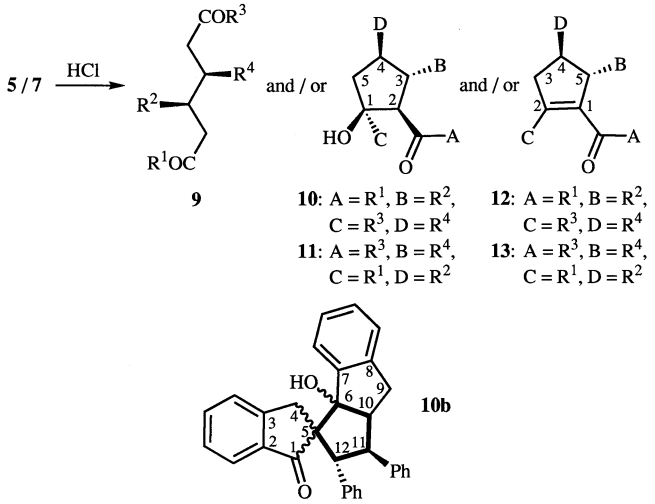
[a] Conditions: 1 h, 50°C, 1 mmol of **3**, 1 mmol of **4**, 1 mmol of **6**, dropwise addition of **6**. – [b] Isolated yield in [%] based on **4** and **6**. – [c] M.p. in [°C]. – [d] Additionally, 7% of **5d** was obtained. – [e] Identical to **4a**.

Table 3. Hydrolysis of titanacycles **5** and **7** with ethereal (C) and aqueous (D) hydrogen chloride

| **9–13** | method[a] | **9** yield[b] | **10** yield[b] | **11** yield[b] | **12** yield[b] | **13** yield[b] | starting compound |
|---|---|---|---|---|---|---|---|
| **a** | D | 89 | 9 | [c] | | | **5d** |
| **a** | C | 35 | 42 | [c] | | | **5d** |
| **b** | C | 13 | 80 | [c] | | | **5f** |
| **c** | D | | 45 | [c] | | | **5g** |
| **d** | D | 56 | 10 | 7 | | | **7d** |
| **e** | D | 55 | 11 | 8 | | | **7e** |
| **e** | C | | | | 35 | 25 | **7e** |
| **f** | C | | | | 38 | 27 | **7f** |

[a] Method C: excess HCl in $Et_2O$, 3 h, −10°C; method D: excess HCl in $H_2O$, 3 h, room temperature. – [b] Isolated yield in [%] based on **4** and **6**. – [c] **11** identical to **10**.

Scheme 5. Hydrolysis of titanadioxacyclononadienes **5**[a] and **7**




[a] If **5** is involved instead of **7**, for all compounds applies $R^1 = R^3$ and $R^2 = R^4$; only one regioisomer of cyclopentanol (designated **10** in Table 3) or cyclopentene is possible.

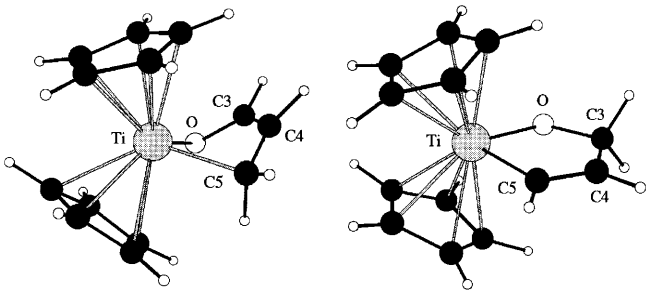
symmetric" titanacycles **7** are of little synthetic use, as leading merely to mixtures of alcohols **10/11** and of cyclopentenes **12/13**. Two typical examples are enclosed in Table 3.

### Ab Initio Calculations on Five- and Nine-Membered Metallacycles

As mentioned above, all our attempts to obtain even trace amounts of the expected intermediate titana-2-oxacyclopent-3-enes **1** instead of the exclusively formed corresponding nine-membered titanacycles **5** were unsuccessful. On the other hand, stable examples of the isomeric titana-2-oxacyclopent-4-ene **2** have been reported by several research groups. In order to understand this difference, we performed ab initio (MP2) and hybrid density functional (B3LYP) calculations on **1**, **2**, **5**, and some related species.[19][20][21][22][23] With one exception (see below), both methods yield essentially the same results. The calculated geometries are in good agreement with available experimental data. Figure 3 shows the MP2-optimized structures of **1** and **2**.

Titana-2-oxacyclopent-3-ene **1** is computed to be 10 kcal/mol more stable than its isomer **2**. The five-membered ring in **2** is planar, with bond lengths and angles indicating regular C–C single and double bonds (bond lengths are 1.506 and 1.343 Å, respectively). The computed values agree well with those obtained in the crystal structure determination of the diphenyl derivative, the main difference being a slight folding of the five-membered ring in the experimental structure.[9][10] In the computed structure of **1**, however, the ring is strongly folded, with significant delocalization (C–C bond lengths are 1.446 and 1.394 Å for the formal single and double bonds, respectively). As far as we know, no bis(cyclopentadienyl)-substituted five-membered titanacycles with structures deviating significantly from planarity are published. Thus, instead of a titanacyclopentene with a Ti–C σ bond, our calculations predict a strong interaction of the titanium centre with the $CH_2$ moiety and the C–C double bond in a π-allylic fashion. While unusual in organotitanium compounds, π-allylic bonding is common for the later transition metals. With 2.267 Å, the computed Ti–$CH_2$ distance is roughly 0.1 Å longer than a regular Ti–C single bond. The distances to the double bond carbon atoms are 2.451 and 2.520 Å. Due to the short distance between the metal centre and the double bond, an exceptionally small value of 94° results for the Ti–O–C angle. Analysis of the electronic structure reveals a strong donation from the π-bond to the metal centre and an increased polarity of the Ti–$CH_2$ σ bond. Thus, **1** is best described as a C-nucleophilic electron-rich (18 valence electrons) allyl complex.

Figure 3. MP2-optimized structures of titana-2-oxacyclopentenes **1** ($R^{1,2}$ = H), left, and **2** ($R^{1,2}$ = H), right[a]




[a] Selected bond lengths [Å] and angles [°]: **1**: Ti–O 1.9734, Ti–C3 2.4512, Ti–C4 2.5199, Ti–C5 2.2670, C3–C4 1.3942, C4–C5 1.4461; Ti–O–C3 93.8; **2**: Ti–O 1.8280, Ti–C5 2.1638, C3–C4 1.5031, C4–C5 1.3524; Ti–O–C3 125.2.

Two conformations are possible for **5**, which differ in the orientation of the organic fragment with respect to the $Cp_2TiO_2$ moiety. The geometric data of the experimental conformer are in good agreement with the X-ray structure. The relative stability of the two conformers is predicted differently by the MP2 and B3LYP methods, although the actual difference is small. At MP2/TZ2p, the experimental conformer is 1.2 kcal/mol more stable, whereas B3LYP/TZ2p predicts it to be less stable by 1.1 kcal/mol.

A possible route to **5** involves addition of **1** to propenal. This reaction is calculated to be 49 kcal/mol exothermic. The activation barrier appears to be very low: several attempts, with different starting geometries, were made to compute the structure of the initial complex for the addition but in all cases, the structure collapsed to **5** during the optimization. We believe the combination of the unusual bonding features in **1**, in particular the lengthening and corresponding weakening of the $Ti-CH_2$ bond, and the significant exothermicity of the reaction to be responsible for this behaviour.

We probed alternative mechanisms via complexes of titanocene and two propenal moieties. These gave the same result as above (optimization leads to **5** without activation barrier), but in all cases, high-energy intermediates must be involved. Hence, we consider these alternatives less probable than reaction via **1**.

## Conclusions

By careful choice of conditions, novel nine-membered titanadioxacycles **5** and **7** can be prepared from α,β-unsaturated ketones with a broad variety of substituents. The X-ray analysis of the tetraphenyl derivative **5a** revealed a $C_2$-symmetric puckered structure with two *Z*-configured C=C bonds and a *trans* orientation of residues about the newly formed C−C bond. Acidic hydrolysis of these chelate complexes is synthetically useful in case of "symmetrically" substituted derivatives **5**, where highly substituted cyclopentanes **10** are obtained as one racemic pair of stereoisomers out of eight possible ones, due to selectivity in the C−C bond formation process and to steric restraints and preferences. Ab initio calculations on the nine-membered rings **5** and on conceivable five-membered intermediates were performed. For the expected intermediate complex **1** of our coupling reaction, an unusual structure of high reactivity of the Ti−C σ bond due to an interaction of the titanium centre with the $CH_2$ moiety and the C−C double bond in a π-allylic fashion was calculated, thus providing an explanation for its elusive character. Further work is in progress now to prepare titanacycles with even larger rings by similar C−C coupling reactions or by Cope rearrangement of aptly substituted nine-membered systems like **5d**.

Financial support from the *Volkswagen-Stiftung* and the *Fonds der Chemischen Industrie e. V.* is gratefully acknowledged.

## Experimental Section

*General Information:* All reactions involving organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk-type glassware. Solvents were dried and distilled under argon prior to use according to standard procedures. The starting complex **3**[18] as well as most of the unsaturated ketones were prepared as published [**4b**[24] by Wittig reaction, **4c−e**[25], **4f**[26], **4h** [1-(*p*-methoxyphenyl)-5-phenylpentadien-1-one][25], **6b−d**[25] by aldol condensation]. Compound **4a** (= **6a**) is commercially available (Fluka). − Melting points are not corrected, boiling points quoted for Kugelrohr distillations refer to the temperature of the air bath. − NMR: Jeol JNMX GX-400 and PMX-60; δ given in ppm; TMS as internal standard. − IR: Bruker IFS 48, Beckmann Acculab A1, A3. − MS: Varian MAT CH-4B (EFO-4B-source), Varian MAT 311A (EI/FD source). − MA: Heraeus Mikromat C-H-N. − HPLC: Shimadzu LC-10 AT, SIL-10 A, CBM 10 A, SPD-10 M A, FCV-10 AL; column: Macherey-Nagel Nucleosil ET 200/4. − Isomeric ratios were determined from the relative intensities of the pertaining $^1$H-NMR signals or by analytic HPLC.

1. *Synthesis of Ketone* **4g**. − *Synthesis of Methyl (o-Formyl-trans-cinnamate):* 2.24 g (16.7 mmol) of phthaldialdehyde were dissolved in 40 ml of THF and stirred at 60°C. A solution of 4.95 g (16.7 mmol) of (methoxycarbonylmethylene)triphenylphosphorane[27] in 100 ml of THF was added dropwise over a period of 1 h and the mixture was then stirred overnight. The solvent was then removed in vacuo and most of the $PPh_3O$ by repeated chromatography over silica gel using neat $CH_2Cl_2$ as the eluent. GC analysis of the eluate showed 58% of product, 17% of starting dialdehyde, 10% of double-olefination product, and 8% of $PPh_3O$. Final purification by Kugelrohr distillation (110−120°C, 0.5 mbar) gave 1.54 g (8.0 mmol; 48%) of the cinnamate as a bright yellow viscous oil. − $^1$H NMR (60 MHz, $CDCl_3$): δ = 3.8 (s, 3 H, $CH_3$), 6.3 (d, $^3J$ = 16 Hz, 1 H, CH=C*H*C=O), 7.4−7.9 (m, 4 H, $H^{ar}$), 8.5 (d, $^3J$ = 16 Hz, 1 H, C*H*=CHC=O), 10.2 (s, 1 H, CHO). − $C_{11}H_{10}O_3$ (190.20): calcd. C 69.47, H 5.30; found C 69.11, H 5.63. − *Synthesis of Methyl [(o-3′-Oxobutenyl)-trans-cinnamate]* (**4g**): 1.54 g (8.08 mmol) of methyl (*o*-formyl-*trans*-cinnamate) was dissolved in 30 ml of THF and stirred at 40°C. A solution of 2.37 g (8.08 mmol) of (2-oxopropylene)triphenylphosphorane[28] in 50 ml of THF was added dropwise and the resulting mixture was stirred at 50°C overnight. The solvent was then removed to leave a crude product which was purified by CC (silica gel; $CH_2Cl_2$): 1.15 g (4.99 mmol; 62%); pale solid; m.p. 46°C. − $^1$H NMR (60 MHz, $CDCl_3$): δ = 2.4 (s, 3 H, $CH_3CO$), 3.8 (s, 3 H, $OCH_3$), 6.30 (d, $^3J$ = 16 Hz, 1 H, CH=C*H*$CO_2CH_3$), 6.55 (d, $^3J$ = 16 Hz, 1 H, CH=C*H*$COCH_3$), 7.2−7.65 (m, 4 H, $H^{ar}$), 7.85 (d, $^3J$ = 16 Hz, 1 H, C*H*=CHCO$CH_3$), 8.0 (d, $^3J$ = 16 Hz, 1 H, C*H*=CHCOO$CH_3$) .− $C_{14}H_{14}O_3$ (230.27): calcd. C 73.03, H 6.13; found C 73.14, H 5.90.

2. *Synthesis of* **5**. − *General Procedure (A):* The respective α,β-unsaturated ketone **4** (2 mmol) was added to a solution of **3** (234 mg; 1 mmol) in toluene (15 ml) and the resulting mixture stirred at 40°C for 3 h. Once the starting materials were completely consumed, 5 ml of hexane was added to give a precipitate which was collected on a sinter funnel, washed twice with hexane and dried in vacuo. For analytical purposes samples of **5** were recrystallized from $CH_2Cl_2$/hexane (2:1).

*(±)-(5,6-threo-3Z,7Z)-1,1-Bis(η$^5$-cyclopentadienyl)-3,5,6,8-tetraphenyl-1-titana-2,9-dioxacyclonona-3,7-diene* (**5a**)[29]: 3.50 g (5.89 mmol; 52%) from 2.65 g of **3** and 4.71 g of **4a**; dark red air-sensitive crystals from toluene; m.p. 204°C. − IR (KBr): $\tilde{\nu}$ = 3040 $cm^{-1}$, 3030, 3020, 1600, 1490, 1450, 1330, 810, 750, 700. − $^1$H NMR (400 MHz, $C_6D_6$)[30]: δ = 5.03 (d, $^3J$ = 5.50 Hz, 2 H, 5-H, 6-H), 5.89 (d, $^3J$ = 5.50 Hz, 2 H, 4-H, 7-H), 5.95 (s, 10 H, Cp), 7.07 (m, 10 H, $H^{ar}$), 7.21 (t, $^3J$ = 7.15 Hz, 2 H, $H^{ar}$), 7.31 (t, $^3J$ = 7.15 Hz, 4 H, $H^{ar}$), 7.59 (d, $^3J$ = 7.15 Hz, 4 H, $H^{ar}$). − $^{13}$C NMR

(100.4 MHz, $C_6D_6$): δ = 48.1 (C-5, C-6), 106.8 (C-4, C-7), 116.2 (Cp), 125.0, 126.1, 127.4, 128.1, 128.7, 129.9 ($CH^{ar}$), 140.6, 143.2 (*ipso*-C), 163.8 (C-3, C-8). − MS (70 eV); *m/z* (%): 386 (6) [$M^+$ − PhCH=CHCOPh], 207 (96) [PhCOCH=$CPh^+$], 178 (49) [$Cp_2Ti^+$], 105 (61) [$PhCO^+$], 77 (100) [$Ph^+$]. − $C_{40}H_{34}O_2Ti$ (594.34): calcd. C 80.83, H 5.72; found C 80.68, H 5.78.

*X-ray Crystal Structure Analysis of* **5a**[31][32]: Clear, dark red single crystals of **5a** × toluene were obtained directly from the reaction mixture upon standing 2 d in the dark. Formula $C_{44}H_{34}O_2Ti$, molar mass 642.61 g $mol^{-1}$, crystal size 0.5 × 0.3 × 0.1 mm, $a$ = 15.924(3), $b$ = 8.347(2), $c$ = 24.558(5) Å, β = 99.34(3)°, $V$ = 3221.1(11) $Å^3$, $T$ = 173(2) K; $d_{calcd.}$ = 1.325 g $cm^{-3}$, μ = 3.05 $cm^{-1}$, $Z$ = 4, monoclinic, space group $P2(1)/c$, Nonius MACH3 diffractometer, λ = 0.71037 Å, Θ range 2.58−24.98°; ω/Θ scans, index ranges $-18 \le h \le 18$, $-9 \le k \le 0$, $-29 \le l \le 0$, 5794 collected reflections, 2625 reflections [$I > 2\sigma(I)$], 428 refined parameters, absorption correction with Ψ scans. Structure solution: direct methods (SHELXS86); structure refinement: full-matrix least squares on $F^2$ (SHELXL93), H atoms calculated and not included into least-squares refinement. In the unit cell two additional strongly disordered toluene molecules were found. $R1$ = 0.0746, $wR2$ = 0.2265 (all data), largest diff. peak and hole 0.552 and −0.747 $eÅ^{-3}$ with $R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2\}^{0.5}$.

*(±)-(5,6-threo-3Z,7Z)-1,1-Bis(η⁵-cyclopentadienyl)-5,6-dimethyl-1-titana-2,9-dioxa-3,8-diphenylcyclonona-3,7-diene* (**5b**): 296 mg (0.63 mmol; 63%) from 234 mg of **3** and 444 mg of **4b**; dark red air-sensitive needles from toluene; m.p. 170°C. − IR (KBr): $\tilde{\nu}$ = 3058 $cm^{-1}$, 2961, 1680, 1447, 1271, 803. − $^1$H NMR (400 MHz, $C_6D_6$)[30]: δ = 1.18 (d, $^3J$ = 7.14 Hz, 6 H, $CH_3$), 3.36 (m, 2 H, 5-H, 6-H), 5.49 (d, $^3J$ = 5.50 Hz, 2 H, 4-H, 7-H), 5.90 (s, 10 H, Cp), 7.16−7.57 (m, 10 H, $H^{ar}$). − $^{13}$C NMR (100.4 MHz, $C_6D_6$): δ = 15.7 (5-C, 6-C), 33.5 (C-5, C-6), 109.8 (C-4, C-7), 115.8 (Cp), 125.3, 126.1, 127.1 ($CH^{ar}$), 140.1 (3-C, 8-C), 163.8 (C-3, C-8). − MS (70 eV); *m/z* (%): 276 (10), 178 (65) [$Cp_2Ti$], 171 (25), 105 (100) [$C_6H_5CO^+$]. − $C_{30}H_{30}O_2Ti$ (470.47): calcd. C 76.59, H 6.38; found C 76.20, H 5.97.

*(±)-(5,6-threo-3Z,7Z)-1,1-Bis(η⁵-cyclopentadienyl)-3,8-di-tert-butyl-1-titana-2,9-dioxa-5,6-diphenylcyclonona-3,7-diene* (**5c**): 390 mg (0.7 mmol; 70%) from 234 mg of **3** and 528 mg of **4c**; dark red air-sensitive needles from toluene; m.p. 181°C. − IR (KBr): $\tilde{\nu}$ = 3058 $cm^{-1}$, 2952, 1604, 1452, 1306, 1079, 806. − $^1$H NMR (400 MHz, $C_6D_6$)[30]: δ = 1.21 (s, 18 H, $CH_3$), 4.22 (d, $^3J$ = 6.05 Hz, 2 H, 5-H, 6-H), 5.00 (d, $^3J$ = 6.05 Hz, 2 H, 4-H, 7-H), 6.01 (s, 10 H, Cp), 7.89−7.93 (m, 10 H, $H^{ar}$). − $^{13}$C NMR (100.4 MHz, $C_6D_6$): δ = 29.5 ($CH_3$), 37.6 (3-C, 8-C), 47.8 (C-5, C-6), 101.7 (C-4, C-7), 116.3 (Cp), 127.8, 128.4, 128.9 ($CH^{ar}$), 145.2 (5-C, 6-C), 173.2 (C-3, C-8). − MS (70 eV); *m/z* (%): 378 (10), 321 (90), 278 (60), 189 (50), 131 (100). − $C_{36}H_{42}O_2Ti$ (554.63): calcd. C 77.97, H 7.58; found C 78.22, H 7.40.

*(±)-(5,6-threo-3Z,7Z)-1,1-Bis(η⁵-cyclopentadienyl)-5,6-bis-β-(trans-phenylethenyl)-1-titana-2,9-dioxa-3,8-diphenylcyclonona-3,7-diene* (**5d**): 549 mg (0.85 mmol; 85%) from 234 mg of **3** and 468 mg of **4d**; dark red air-sensitive needles from toluene; m.p. 125°C. − IR (KBr): $\tilde{\nu}$ = 2850 $cm^{-1}$, 1600, 1100, 800. − $^1$H NMR (400MHz, $C_6D_6$)[30]: δ = 4.46 (dd, $^3J$ = 4.94, 5.50 Hz, 2 H, 5-H, 6-H), 5.98 (d, $^3J$ = 5.50 Hz, 2 H, 4-H, 7-H), 6.06 (s, 10 H, Cp), 6.80 (dd, $^3J$ = 4.98, 15.95 Hz, 2 H, C*H*=CHPh), 6.98 (d, $^3J$ = 15.95 Hz, 2 H, CHPh), 7.11−8.07 (m, 20 H, $H^{ar}$). − $^{13}$C NMR (100.4 MHz, $C_6D_6$): δ = 45.1 (C-5, C-6), 92.1, 92.7 (*C*H=*C*HPh), 102.2 (C-4, C-7), 116.2 (Cp), 126.4, 126.7, 127.9, 128.6, 129.7, 130.1 ($CH^{ar}$), 145.2, 146.4 (*ipso*-C), 163.5 (C-3, C-8). − MS (70 eV); *m/z* (%): 542 (7), 348 (7), 382 (38), 234 (45), 105 (100). − $C_{44}H_{38}O_2Ti$ (646.69): calcd. C 81.73, H 5.88; found C 81.87, H 6.02.

*(±)-(5,6-threo-3Z,7Z)-1,1-Bis(η⁵-cyclopentadienyl)-3,8-bis-δ-(phenyl-trans,trans-butadienyl)-1-titana-2,9-dioxa-5,6-diphenylcyclonona-3,7-diene* (**5e**): 384 mg (0.55 mmol; 55%) from 234 mg of **3** and 520 mg of **4e**; dark red air-sensitive needles from toluene; m.p. 135°C. − IR (KBr): $\tilde{\nu}$ = 3065−3024 $cm^{-1}$, 1580, 1565, 1490, 785, 750. − $^1$H NMR (400 MHz, $C_6D_6$)[30]: δ = 4.92 (d, $^3J$ = 5.61 Hz, 2 H, 5-H, 6-H), 5.35 (d, $^3J$ = 5.61 Hz, 2 H, 4-H, 7-H), 5.98 (s, 10 H, Cp), 6.22−7.52 (m, 28 H, CH=CH-CH=CH and $H^{ar}$). − $^{13}$C NMR (100.4 MHz, $C_6D_6$), δ = 48.6 (C-5, C-6), 114.9 (C-4, C-7), 115.8 (Cp), 125.6, 126.1, 126.6, 126.7 (CH=CHCH=CH), 129.1, 129.7, 129.8 ($CH^{ar}$), 138.2, 144.2 (*ipso*-C), 163.6 (C-3, C-8). − MS (70 eV); *m/z* (%): 488 (15), 448 (35), 460 (65), 260 (100), 178 (76) [$Cp_2Ti^+$]. − $C_{48}H_{42}O_2Ti$ (698.77): calcd. C 82.52, H 6.01; found C 82.71, H 6.16.

*(±)-(5,6-threo)-1,1-Bis(η⁵-cyclopentadienyl)-5,6-diphenylbis-indeno[3,2-c;2′,3′-g]-1-titana-2,9-dioxa-cyclonona-3,7-diene* (**5f**): 380 mg (0.6 mmol; 93%) from 154 mg of **3** and 440 mg of **4f**; dark red air-sensitive needles from toluene; m.p. 125°C (decomp.). − IR ($CDCl_3$): $\tilde{\nu}$ = 3068 $cm^{-1}$, 2961, 2878,1572, 1559. − $^1$H NMR (400 MHz, $CDCl_3$)[30]: δ = 3.11 (d, $^2J$ = 22.10 Hz, 2 H, C*H*H′), 3.24 (d, $^2J$ = 22.10 Hz, 2 H, CH*H*′), 5.10 (s, 2 H, 5-H, 6-H), 6.47 (s, 10 H, Cp), 7.01 (m, 4 H, $H^{ar}$ of $C_6H_5$), 7.04 (m, 2 H, $H^{ar}$ of $C_6H_5$), 7.04 (dd, $^3J$ = 7.44, 7.44 Hz, 2 H, $H^{ar}$ of $C_6H_4$), 7.08 (m, 4 H, $H^{ar}$ of $C_6H_5$), 7.16 (d, $^3J$ = 7.44 Hz, 2 H, $H^{ar}$ of $C_6H_4$), 7.23 (d, $^3J$ = 7.44 Hz, 2 H, $H^{ar}$ of $C_6H_4$), 7.26 (dd, $^3J$ = 7.44, 7.44 Hz, 2 H, $H^{ar}$ of $C_6H_4$). − $^{13}$C NMR (100.4 MHz, $CDCl_3$): δ = 36.2 (4-C, 7-C), 49.7 (C-5, C-6), 116.7 (Cp), 117.0 ($CH^{ar}$), 119.7 (C-4, C-7), 123.7, 123.8, 125.5, 125.7, 127.4, 129.8 ($CH^{ar}$), 142.0, 143.2, 143.7 (*ipso*-C), 162.0 (C-3, C-8). − MS (70 eV); *m/z* (%): 406 (60) [$M^+$ − $Cp_2Ti(OH)_2$], 333 (93), 219 (40), 66 (100) [$CpH^+$]. − $C_{42}H_{34}O_2Ti$ (618.64): calcd. C 81.55, H 5.50; found C 81.63, H 5.44.

*(±)-(5,6-threo-3Z,7Z)-1,1-Bis(η⁵-cyclopentadienyl)-3,8-dimethyl-5,6-bis(o-methyl-trans-cinnamoyl)-1-titana-2,9-dioxa-cyclonona-3,7-diene* (**5g**): 95 mg (0.15 mmol; 12%) from 567 mg **3** and 460 mg **4g**; dark red air-sensitive needles from toluene; m.p. 170°C (decomp.). − IR ($CH_2Cl_2$): $\tilde{\nu}$ = 1710 $cm^{-1}$, 1625, 1310, 1165. − $^1$H NMR (400 MHz, $CDCl_3$)[30]: δ = 1.82 (s, 6 H, $CCH_3$), 3.82 (s, 6 H, $OCH_3$), 4.31 (d, $^3J$ = 5.70 Hz, 2 H, 5-H, 6-H), 4.92 (d, $^3J$ = 5.70 Hz, 2 H, 4-H, 7-H), 6.07 (d, $^3J$ = 8.10 Hz, 2 H, $H^{ar}$), 6.35 (d, $^3J$ = 15.70 Hz, 2 H, CH=C*H*CO), 6.40 (s, 10 H, Cp), 6.88 (dd, $^3J$ = 7.10, 8.10 Hz, 2 H, $H^{ar}$), 7.09 (dd, $^3J$ = 7.10, 8.10 Hz, 2 H, $H^{ar}$), 7.56 (d, $^3J$ = 8.10 Hz, 2 H, $H^{ar}$), 8.32 (d, $^3J$ = 15.70 Hz, 2 H, C*H*=CHCO). − $^{13}$C NMR (100.4 MHz, $CDCl_3$): δ = 23.0 (3-C, 8-C), 42.2 (C-5, C-6), 51.4 ($OCH_3$), 103.9 (C-4, C-7), 115.7 (Cp), 117.9 (CH=*C*HCO), 125.8, 125.8, 128.4, 131.7 ($CH^{ar}$), 133.9 (*C*CH=CHCO), 143.0 (5-C, 6-C), 145.3 (*C*H=CHCO), 164.4 (C-3, C-8), 167.7 ($CO_2CH_3$). − MS (70 eV); *m/z* (%): 638 (2) [$M^+$], 408 (11) [$M^+ - C_{14}H_{14}O_3$], 278 (16) [408 − 2 Cp], 219 (35) [$Cp_2TiOCCH^+$], 178 (87) [$Cp_2Ti^+$], 128 (99), 43 (100). − $C_{38}H_{38}O_6Ti$ (638.62): calcd. C 71.47, H 6.00; found C 71.42, H 5.81.

3. *Synthesis of* **7**. − *General Procedure (B):* The respective α,β-unsaturated ketone **4** (1 mmol) was added at once to a solution of **3** (234 mg; 1 mmol) in toluene (15 ml) at 50°C. Immediately thereafter, a solution of 1 mmol of the second ketone **6** in toluene (20 ml) was added dropwise over a period of 30 min. Once the starting materials were completely consumed (NMR monitoring, typically 1 h), the solution was filtered at ambient temperature, 5 ml of hexane was added and the resulting precipitate was collected on a sinter funnel, washed twice with hexane and dried in vacuo. For ana-

lytical purposes samples of **7** were recrystallized from $CH_2Cl_2$/hexane (2:1).

*(5,6-threo-3Z,7Z)-3-(p-Anisyl)-1,1-bis($\eta^5$-cyclopentadienyl)-6,8-diphenyl-5-(β-trans-phenylethenyl)-1-titana-2,9-dioxacyclonona-3,7-diene* (**7a**): 448 mg (0.69 mmol; 69%) from 234 mg of **3**, 264 mg of **4h** and 208 mg of **4a** (as the more reactive component); dark red air-sensitive needles from toluene; m.p. 101°C. − IR (KBr): $\tilde{\nu}$ = 3025 $cm^{-1}$, 2834, 1598, 1506, 1284, 811. − $^1H$ NMR (400 MHz, $C_6D_6$)[30][33]: δ = 3.42 (s, 3 H, $CH_3$), 4.46 (dd, $^3J$ = 5.62, 5.86 Hz, 1 H, 5-H), 4.84 (d, $^3J$ = 5.86 Hz, 1 H, 6-H), 5.49 (d, $^3J$ = 5.62 Hz, 1 H, 4-H), 5.97 (s, 5 H, Cp), 6.02 (s, 5 H, Cp), 6.04 (d, $^3J$ = 5.86 Hz, 1 H, 7-H), 6.15 (dd, $^3J$ = 5.86, 15.63 Hz, 1 H, C*H*=CHPh), 6.63 (d, $^3J$ = 15.63 Hz, 1 H, CH=C*H*Ph), 6.92−7.62 (m, 19 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $C_6D_6$): δ = 45.2, 47.5 (C-5, C-6), 55.1 ($CH_3$), 110.2, 112.9 (C-4, C-7), 116.1 (Cp), 125.1, 126.9 (*C*H=*C*HPh), 129.1, 129.7, 130.1, 130.7, 130.9, 134.1, 135.7, 137.2, 138.5, 138.9 ($CH^{ar}$), 141.2, 143.8, 144.3, 144.8 (*ipso*-C), 159.1 (*C*$OCH_3$), 163.1, 163.9 (C-3, C-8). − MS (70 eV); *m/z* (%): 512 (10), 456 (60), 365 (22), 295 (25), 208 (18) [PhCH=CHCOPh$^+$], 105 (100). − $C_{43}H_{38}O_3Ti$ (650.68): calcd. C 79.38, H 5.38; found C 79.52, H 5.48.

*(5,6-threo-3Z,7Z)-8-(p-Anisyl)-1,1-bis($\eta^5$-cyclopentadienyl)-3-(o,p-dimethoxyphenyl)-5-phenyl-6-β-(trans-phenylethenyl)-1-titana-2,9-dioxacyclonona-3,7-diene* (**7b**): 426 mg (0.6 mmol; 60%) from 234 mg of **3**, 264 mg of **4h** and 268 mg of **6b**; dark red air-sensitive needles from toluene; m.p. 115°C. − IR (KBr): $\tilde{\nu}$ = 3025 $cm^{-1}$, 2934, 2836, 1600, 1254, 808. − $^1H$ NMR (400 MHz, $C_6D_6$)[30][33]: δ = 3.35 (s, 3 H, $CH_3$), 3.43 (s, 6 H, $CH_3$), 4.58 (dd, $^3J$ = 5.86, 5.86 Hz, 1 H, 6-H), 4.89 (d, $^3J$ = 5.86 Hz, 1 H, 5-H), 5.53 (d, $^3J$ = 5.86 Hz, 1 H, 7-H), 6.03 (d, $^3J$ = 5.86 Hz, 1 H, 4-H), 6.07 (s, 5 H, Cp), 6.08 (s, 5 H, Cp), 6.18 (dd, $^3J$ = 5.86, 15.86 Hz, 1 H, C*H*=CHPh), 6.76 (d, $^3J$ = 15.86 Hz, 1 H, CH=C*H*Ph), 6.90−7.68 (m, 17 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $C_6D_6$): δ = 46.0, 48.1 (C-5, C-6), 54.7, 54.8, 54.9 ($CH_3$), 113.9, 114.2 (C-4, C-7), 116.1 (Cp), 124.2, 126.7 (*C*H=*C*HPh), 126.2, 126.9, 127.3, 127.8, 129.4, 132.3, 133.7, 134.5, 136.1, 137.8, 138.2 ($CH^{ar}$), 142.2, 142.9, 144.1, 144.8 (*ipso*-C), 158.5, 159.6, 160.6 (*C*$OCH_3$), 162.2, 162.9 (C-3, C-8). − MS (70 eV); *m/z* (%): 486 (42), 460 (10), 395 (15), 351 (30), 264 (17) [$C_{18}H_{16}O_2^+$], 238 (20). − $C_{45}H_{42}O_5Ti$ (710.73): calcd. C 76.05, H 5.92; found C 75.94, H 5.88.

*(5,6-threo-3Z,7Z)-3,8-Bis(p-anisyl)-1,1-bis($\eta^5$-cyclopentadienyl)-5-phenyl-6-β-(trans-phenylethenyl)-1-titana-2,9-dioxacyclonona-3,7-diene* (**7c**): 442 mg (0.65 mmol; 65%) from 234 mg of **3**, 264 mg of **4h** and 238 mg of **6c**; dark red air-sensitive needles from toluene; m.p. 114°C.− IR (KBr): $\tilde{\nu}$ = 3026 $cm^{-1}$, 2960, 1600, 1251, 810. − $^1H$ NMR (400 MHz, $C_6D_6$)[30][33]: δ = 3.21 (s, 3 H, $CH_3$), 3.23 (s, 3 H, $CH_3$), 4.50 (dd, $^3J$ = 5.71, 5.71 Hz, 1 H, 6-H), 4.86 (d, $^3J$ = 5.86 Hz, 1 H, 5-H), 5.51 (d, $^3J$ = 5.71 Hz, 1 H, 7-H), 5.96 (d, $^3J$ = 5.86 Hz, 1 H, 4-H), 6.02 (s, 5 H, Cp), 6.04 (s, 5 H, Cp), 6.18 (dd, $^3J$ = 5.71, 15.86 Hz, 1 H, C*H*=CHPh), 6.53 (d, $^3J$ = 15.86 Hz, 1 H, CH=C*H*Ph), 6.71−7.85 (m, 18 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $C_6D_6$): δ = 46.5, 48.3 (C-5, C-6), 54.5, 54.8 ($CH_3$), 113.5, 114.0 (C-4, C-7), 115.7 (Cp), 124.5, 127.2 (*C*H=*C*H), 126.4, 126.7, 127.3, 127.7, 129.5, 132.7, 134.7, 135.5, 136.5, 137.5, 138.1, 138.9 ($CH^{ar}$), 142.2, 142.5, 144.4, 145.2 (*ipso*-C), 156.5, 156.9 (*C*$OCH_3$), 163.1, 163.5 (C-3, C-8). − MS (70 eV); *m/z* (%): 516 (20), 381 (25), 264 (22) [$C_{18}H_{16}O_2^+$], 165 (100). − $C_{44}H_{40}O_4Ti$ (680.71): calcd. C 77.67, H 5.88; found C 76.50, H 5.75.

*(5,6-threo-3Z,7Z)-3,5-Bis(p-anisyl)-1,1-bis($\eta^5$-cyclopentadienyl)-8-phenyl-6-β-(trans-phenylethenyl)-1-titana-2,9-dioxacyclonona-3,7-diene* (**7d**): 462 mg (0.68 mmol; 68%) from 234 mg of **3**, 234 mg of **4d** and 268 mg of **6d**; dark red air-sensitive needles from toluene. − IR (KBr): $\tilde{\nu}$ = 3008−2800 $cm^{-1}$, 1595, 1480, 1245, 1070, 805. − $^1H$ NMR (400 MHz, $C_6D_6$)[30][33]: δ = 3.03 (s, 3 H, $CH_3$), 3.12 (s, 3 H, $CH_3$), 4.16 (dd, $^3J$ = 5.62, 5.86 Hz, 1 H, 6-H), 4.70 (d, $^3J$ = 5.62 Hz, 1 H, 5-H), 5.33 (d, $^3J$ = 5.62 Hz, 1 H, 7-H), 5.67 (s, 5 H, Cp), 5.70 (s, 5 H, Cp), 5.80 (d, $^3J$ = 5.62 Hz, 1 H, 4-H), 5.90 (dd, $^3J$ = 5.86, 15.62 Hz, 1 H, C*H*=CHPh), 6.34 (d, $^3J$ = 15.62 Hz, 1 H, CH=C*H*Ph), 6.35−7.82 (m, 18 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $C_6D_6$): δ = 45.2, 47.2 (C-5, C-6), 54.61, 54.67 ($CH_3$), 112.2, 112.4 (C-4, C-7), 116.2 (Cp), 122.2, 123.1 (*C*H=*C*HPh), 125.8, 126.3, 127.1, 127.9, 132.8, 134.5, 135.3, 136.8, 139.1, 139.9 ($CH^{ar}$), 142.1, 142.7 (*ipso*-C of $C_6H_5$), 150.2, 150.8 (*ipso*-C of $C_6H_4OCH_3$), 159.4, 159.9 (*C*$OCH_3$), 163.0, 163.8 (C-3, C-8). − MS (70 eV); *m/z* (%): 444 (20), 324 (18), 178 (65) [Cp2Ti$^+$],105 (100) [PhCO$^+$]. − $C_{44}H_{40}O_4Ti$ (680.7): calcd. C 77.64, H 6.15; found C 77.62, H 5.98.

*(5,6-threo-3Z,7Z)-1,1-Bis($\eta^5$-cyclopentadienyl)-3-(o,p-dimethoxyphenyl)-5,8-diphenyl-6-β-(trans-phenylethenyl)-1-titana-2,9-dioxacyclonona-3,7-diene* (**7e**): A mixture of 449 mg of **7e** (0.66 mmol; 66%) and **5d** (0.07 mmol; 7%) from 234 mg of **3**, 234 mg of **4d**, and 268 mg of **6b**; ratio **7e/5d** determined by NMR; **7e** purified by crystallization from $CH_2Cl_2$/hexane (2:1); dark red air-sensitive needles from toluene, m.p. 160°C. − IR (KBr): $\tilde{\nu}$ = 3030−2820 $cm^{-1}$, 1600, 1430, 1240, 1020, 810. − $^1H$ NMR (400 MHz, $C_6D_6$)[30][33]: δ = 3.36 (s, 3 H, $CH_3$), 3.44 (s, 3 H, $CH_3$), 4.56 (dd, $^3J$ = 5.71, 5.86 Hz, 1 H, 6-H), 4.86 (d, $^3J$ = 5.86 Hz, 1 H, 5-H), 5.51 (d, $^3J$ = 5.71 Hz, 1 H, 7-H), 5.96 (d, $^3J$ = 5.86 Hz, 1 H, 4-H), 6.05 (s, 5 H, Cp), 6.06 (s, 5 H, Cp), 6.19 (dd, $^3J$ = 5.86, 15.62 Hz, 1 H, C*H*=CHPh), 6.67 (d, $^3J$ = 15.62 Hz, 1 H, CH=C*H*Ph), 6.70−7.92 (m, 18 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $C_6D_6$): δ = 46.4, 48.1 (C-5, C-6), 55.3, 57.1 ($CH_3$), 105.7, 107,2 (C-4, C-7), 117.1 (Cp),122.2, 122.9 (*C*H=*C*HPh), 126.1, 128.4, 128.9, 129.2, 130.1, 132.2, 133.1, 133.7, 134.1, 135.8, 137.1, 141.9 ($CH^{ar}$), 142.5, 143.1, 143.9, 145.2 (*ipso*-C), 159.1, 160.1 (*C*$OCH_3$), 163.2, 165.1 (C-3, C-8). − MS (70 eV); *m/z* (%): 405 (20), 377 (35), 342 (30), 178 (55), 77 (100). − $C_{44}H_{40}O_4Ti$ (680.71): calcd. C 77.64, H 5.88; found C 76.47, H 5.78.

*(5,6-threo-3Z,7Z)-3-(p-Anisyl)-1,1-bis($\eta^5$-cyclopentadienyl)-5,8-diphenyl-6-β-(trans-phenylethenyl)-1-titana-2,9-dioxacyclonona-3,7-diene* (**7f**): 527 mg (0.81 mmol; 81%) from 234 mg of **3**, 234 mg of **4d** and 238 mg of **6c**; dark red air-sensitive needles from toluene; m.p. 152°C. − IR (KBr): $\tilde{\nu}$ = 3040−2800 $cm^{-1}$, 1610, 1450, 1250, 1100, 1030, 800. − $^1H$ NMR (400 MHz, $C_6D_6$)[30][33]: δ = 3.42 (s, 3 H, $CH_3$), 4.48 (dd, $^3J$ = 5.62, 5.87 Hz, 1 H, 6-H), 4.84 (d, $^3J$ = 5.62 Hz, 1 H, 5-H), 5.60 (d, $^3J$ = 5.62 Hz, 1 H, 7-H), 5.95 (d, $^3J$ = 5.62 Hz, 1 H, 4-H), 6.01 (s, 5 H, Cp), 6.03 (s, 5 H, Cp), 6.17 (dd, $^3J$ = 5.87, 15.62 Hz, 1 H, C*H*=CHPh), 6.64 (d, $^3J$ = 15.62 Hz, 1 H, CH=C*H*Ph), 6.68−7.82 (m, 19 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $C_6D_6$): δ = 46.7, 48.1 (C-5, C-6), 55.2 ($CH_3$), 105.7, 107.1 (C-4, C-7), 117.2 (Cp), 120.1, 122.2 (*C*H=*C*HPh), 125.1, 125.7, 126.4, 126.2, 131.6, 132.6, 134.1, 135.1, 135.8, 137.2, 138.1 ($CH^{ar}$), 141.1, 142.1, 142.9, 145.4 (*ipso*-C), 159.7 (*C*$OCH_3$), 163.2, 163.3 (C-3, C-8). − MS (70 eV); *m/z* (%): 412 (9), 349 (22), 131 (55), 66 (100). − $C_{43}H_{38}O_3Ti$ (650.68): calcd. C 79.38, H 5.84; found C 78.49, H 6.05.

*(5,6-threo-3Z,7Z)-1,1-Bis($\eta^5$-cyclopentadienyl)-3,5,8-triphenyl-6-β-(trans-phenylethenyl)-1-titana-2,9-dioxacyclonona-3,7-diene* (**7g**): 403 mg (0.65 mmol; 65%) from 234 mg of **3**, 234 mg of **4d** and 208 mg of **4a** (as the more reactive component); dark red air-sensitive needles from toluene; m.p. 79°C. − IR (KBr): $\tilde{\nu}$ = 3060−2800 $cm^{-1}$, 1579, 1448, 1261, 1020, 807. − $^1H$ NMR (400 MHz, $C_6D_6$)[30][33]: δ = 4.46 (dd, $^3J$ = 5.50, 5.50 Hz, 1 H, 6-H), 4.84 (d, $^3J$ = 5.50 Hz, 1 H, 5-H), 5.59 (d, $^3J$ = 5.50 Hz, 1 H, 7-

H), 5.94 (s, 5 H, Cp), 5.98 (s, 5 H, Cp), 6.03 (d, $^3J$ = 5.50 Hz, 1 H, 4-H), 6.16 (dd, $^3J$ = 5.50, 15.40 Hz, 1 H, C*H*=CHPh), 6.50 (d, $^3J$ = 15.40 Hz, 1 H, CH=C*H*Ph), 6.81−7.98 (m, 20 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $C_6D_6$): δ = 45.5, 45.6 (C-5, C-6), 106.1, 106.7 (C-4, C-7), 116.1, 116.2 (Cp), 125.2, 125,9 (*C*H=*C*HPh), 127.0, 127.9, 128.2, 128.9, 129.3, 130.1, 130.9, 132.1, 134.1, 137.2, 138.1, 139.1 ($CH^{ar}$), 141.1, 141.9, 143.9, 145.1 (*ipso*-C), 163.2, 164.0 (C-3, C-8). − MS (70 eV); *m/z* (%): 450 (10), 386 (15) [$Cp_2Ti$-OCPhCH=CHPh$^+$], 221 (45), 178 (55) [$Cp_2Ti^+$], 77 (100). − $C_{42}H_{36}O_2Ti$ (620.65): calcd. C 81.28, H 5.80; found C 81.12, H 5.69.

4. *Synthesis of* **9**, **10**, **11**, **12**, *and* **13**. − *General Procedure (C):* Complex **5** or **7** (1 mmol) was dissolved in $CH_2Cl_2$ (10 ml). 5 mmol of HCl in 5 ml of diethyl ether was added at −10°C and the mixture was then stirred for 5 h, whereupon the colour turned from dark red to bright red. The solvent and excess HCl were removed at reduced pressure, $Cp_2TiCl_2$ was removed by CC on silica gel ($CH_2Cl_2$). The eluate was concentrated and the products **9**−**13** were separated by using preparative TLC (silica gel, $CH_2Cl_2$). Separation of the respective diastereomers was done by TLC (silica gel 60, diethyl ether/petroleum ether, 1:2) or by HPLC (silica gel 60, heptane/ethyl acetate, 9:1). For analytical purposes samples were recrystallized from chloroform or $CH_2Cl_2$/hexane, 3:1. − *General Procedure (D):* Complex **7** or **5** (1 mmol) was dissolved in $CH_2Cl_2$ (10 ml). At ambient temperature 5 ml of aqueous HCl (6%) was added. After stirring this mixture for 3 h, the layers were separated, the aqueous one was washed twice with 5 ml of $CH_2Cl_2$ and the combined organic extracts thus obtained were dried with sodium sulphate. Separation of the products **9**−**13** and $Cp_2TiCl_2$ was accomplished as described in General Procedure (C).

*1,6-Diphenyl-3,4-bis-β-(trans-phenylethenyl)hexan-1,6-dione* (**9a**): According to general procedure D: 418 mg (0.89 mmol; 89%) from 646 mg of **5d**; yellow needles from chloroform; m.p. 140°C. − IR (film): $\tilde{\nu}$ = 3050 $cm^{-1}$, 2980, 2960, 1680, 1650, 1490. − $^1H$ NMR (400 HMz, $CDCl_3$): δ = 3.09−3.27 (m, 6 H, 2-H, 3-H, 4-H, 5-H), 6.16 (dd, $^3J$ = 15.62/8.97 Hz, 2 H, C*H*=CHPh), 6.42 (d, $^3J$ = 15.62 Hz, 2 H, CH=C*H*Ph), 7.21−7.93 (m, 20 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $CDCl_3$): δ = 42.2 (C-2, C-5), 43.0 (C-3, C-4), 124.0, 126.2 (*C*H=*C*HPh), 128.5, 128.9, 132.9, 132.1, 137.0, 137.2 ($CH^{ar}$), 137.8, 138.2 (*ipso*-C), 198.8 (C-1, C-6). − MS (70 eV); *m/z* (%): 470 (7) [$M^+$], 350 (80), 235 (92), 105 (100). − $C_{34}H_{30}O_2$ (470.62): calcd. C 86.80, H 6.38; found C 86.72, H 6.47.

*1,2-Bis[2′-(1′-oxoindanyl)]-1,2-diphenylethane* (**9b**): According to general procedure C: 90 mg (0.2 mmol; 13%) from 944 mg of **5f** as a separable 22:55:24 mixture of diastereomers; yellow needles from chloroform; a sample of the major isomer was separated by TLC; m.p. 200°C. − IR (film): $\tilde{\nu}$ = 1963 $cm^{-1}$, 1714, 1694. − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.82 (dd, $^2J$ = 17.00, $^3J$ = 4.40 Hz, 2 H, C*H*H′), 3.45 (dd, $^2J$ = 17.00, $^3J$ = 8.00 Hz, 2 H, CH*H*′), 4.07 (m, 2 H, CHC=O), 4.28 (m, 2 H, 1-H, 2-H), 6.85 (t, $^3J$ = 7.70 Hz, 4 H, $H^{ar}$), 6.86 (t, $^3J$ = 7.70 Hz, 2 H, $H^{ar}$), 6.92 (d, $^3J$ = 7.70 Hz, 4 H, $H^{ar}$), 7.24 (d, $^3J$ = 7.70 Hz, 2 H, $H^{ar}$), 7.28 (t, $^3J$ = 7.70 Hz, 2 H, $H^{ar}$), 7.44 (t, $^3J$ = 7.70 Hz, 2 H, $H^{ar}$), 7.73 (d, $^3J$ = 7.70 Hz, 2 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $CDCl_3$): δ = 31.7 ($CH_2$), 48.3 (*C*HC=O), 51.0 (C-1, C-2), 123.2, 126.1, 126.3, 127.0, 127.7, 129.2, 134.5 ($CH^{ar}$), 138.1, 140.5 (*ipso*-C), 154.3 [*C*(C=O)CH], 209.8 (C=O). − MS (70 eV); *m/z* (%): 442 (6) [$M^+$], 310 (68) [$M^+ - C_9H_8O$], 221 (100) [$M/2^+$], 132 (20) [$C_9H_8O^+$], 91 (48) [$PhCH_2^+$]. − $C_{32}H_{26}O_2$ (442.56): calcd. C 86.85, H 5.92; found C 86.77, H 5.82.

*1,3-Bis(p-anisyl)-6-phenyl-4-β-(trans-phenylethenyl)hexan-1,6-dione* (**9d**): According to general procedure D: 281 mg (0.56 mmol; 56%) from 680 mg **7d**; yellow needles from chloroform; m.p. 149°C. − IR (film): $\tilde{\nu}$ = 3095−2790 $cm^{-1}$, 1680, 1590, 1510, 1250. − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.90 (m, 1 H, 5-H), 3.12 (m, 1 H, 5-H′), 3.25 (m, 1 H, 4-H), 3.30 (m, 1 H, 2-H), 3.33 (m, 1 H, 2-H′), 3.67 (m, 1 H, 3-H), 3.79 (s, 3 H, $CH_3$), 3.80 (s, 3 H, $CH_3$), 5.93 (dd, $^3J$ = 9.35, 15.40 Hz, 1 H, C*H*=CHPh), 6.36 (d, $^3J$ = 15.40 Hz, 1 H, C*H*Ph), 6.82−7.82 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 504 (30) [$M^+$], 359 (45), 331 (55), 281 (100), 145 (70). − $C_{34}H_{32}O_4$ (504.63): calcd. C 80.95, H 6.35; found C 80.75, H 6.47.

*1-(o,p-Dimethoxyphenyl)-3,6-diphenyl-4-β-(trans-phenylethenyl)hexan-1,6-dione* (**9e**): According to general procedure D: 282 mg (0.56 mmol; 55%) from 680 mg of **7e**; yellow needles from cloroform; m.p. 145°C. − IR (film): $\tilde{\nu}$ = 3150−2800 $cm^{-1}$, 1680, 1600, 1255. − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.92 (m, 1 H, 5-H), 3.14 (m, 1 H, 5-H′), 3.25 (m, 1 H, 4-H), 3.30 (m, 1 H, 2-H), 3.33 (m, 1 H, 2-H′), 3.68 (m, 1 H, 3-H), 3.78 (s, 3 H, $CH_3$), 3.79 (s, 3 H, $CH_3$), 5.93 (dd, $^3J$ = 9.35, 15.40 Hz, 1 H, C*H*=CHPh), 6.36 (d, $^3J$ = 15.40 Hz, 1 H, CH=C*H*Ph), 6.82−7.82 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 504 (40) [$M^+$], 390 (53), 354 (45), 135 (100). − $C_{34}H_{32}O_4$ (504.63): calcd. C 80.95, H 6.34; found C 80.90, H 6.40.

*(±)-2-Benzoyl-1-hydroxy-1-phenyl-3,4-bis-β-(trans-phenylethenyl)cyclopentane* (**10a**)[34]: According to general procedure C: 197 mg (0.42 mmol: 42%) from 646 mg of **5d**; white needles from chloroform; m.p. 140°C. − IR (film): $\tilde{\nu}$ = 3090 $cm^{-1}$, 2780, 1675, 1590, 1515, 1250. − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.17 (dd, $^3J$ = 5.50, $^2J$ = 14.30 Hz, 1 H, 5-H), 2.59 (dd, $^3J$ = 10.45 Hz, $^2J$ = 14.30 Hz, 1 H, 5-H′), 2.92 (m, 1 H, 3-H or 4-H), 3.39 (m, 1 H, 4-H or 3-H), 4.18 (d, $^3J$ = 11.55 Hz, 1 H, 2-H), 5.04 (s, 1 H, OH), 6.02 (dd, $^3J$ = 15.94 Hz and 8.79 Hz, 2 H, C*H*=CHPh), 6.48 (d, $^3J$ = 15.94 Hz, 2 H, CH=C*H*Ph), 6.91−7.68 (m, 20 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 470 (10) [$M^+$], 452 (20) [$M^+ - H_2O$], 345 (20) [$M^+ -$ PhCO], 105 (100) [$PhCO^+$]. − $C_{34}H_{30}O_2$ (470.62): calcd. C 86.80, H 6.38; found C 86.81, H 6.35.

*Spiroketone* **10b**: According to general procedure C: 538 mg (1.22 mmol; 80%) from 944 mg of **5f** as a 8:7:3:26:5:14:17:21 mixture of 8 stereoisomers; white needles from chloroform; separation of a sample of the major diastereomer (26%) for analytical purposes by TLC; m.p. 199°C. − IR (KBr): $\tilde{\nu}$ = 3429 $cm^{-1}$, 1705, 1682, 1605. − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 1 H, OH), 2.74 (d, $^3J$ = 8.0 Hz, $^2J$ not observed, 2 H, 9-H), 2.80 (d, $^2J$ = 16.5 Hz, 1 H, 4-H), 3.26 (ddd, $^3J$ = 8.0, 8.0, 8.0 Hz, 1 H, 10-H), 3.98 (d, $^2J$ = 16.5 Hz, 1 H, 4-H′), 4.27 (d, $^3J$ = 13.5 Hz, 1 H, 12-H), 4.38 (dd, $^3J$ = 8.0, 13.5 Hz, 1 H, 11-H), 6.64 (m, 1 H, $H^{ar}$), 7.03 (m, 2 H, $H^{ar}$), 7.07 (m, 2 H, $H^{ar}$), 7.11 (m, 2 H, $H^{ar}$), 7.14 (m, 1 H, $H^{ar}$), 7.16 (m, 2 H, $H^{ar}$), 7.22 (m, 2 H, $H^{ar}$), 7.32 (m, 2 H, $H^{ar}$), 7.39 (m, 1 H, $H^{ar}$), 7.50 (m, 1 H, $H^{ar}$), 7.52 (m, 1 H, $H^{ar}$), 7.68 (m, 1 H, $H^{ar}$). − $^{13}C$ NMR (100.4 MHz, $CDCl_3$): δ = 31.4, 33.4 (C-4, C-9), 46.7 (C-11), 49.3 (C-10), 57.4 (C-12), 71.1 (C-5), 94.6 (C-6), 123.5, 124.4, 124.7, 125.9, 126.1, 126.4, 126.6, 127.0, 128.1, 128.2, 128.8, 129.0, 129.3, 134.7 ($CH^{ar}$), 137.8, 138.0, 139.6, 143.5, 144.7, 154.3 (C-2, C-3, C-7, C-8, 11-C, 12-C), 207.0 (C-1). − MS (70 eV); *m/z* (%): 442 (10) [$M^+$], 424 (2) [$M^+ - H_2O$], 310 (15) [$M^+ - C_9H_8O$], 221 (100) [$M/2^+$]. − $C_{32}H_{26}O_2$ (442.56): calcd. C 86.85, H 5.92; found C 86.77, H 5.87.

*(±)-(3,4-threo)-2-Acetyl-1-hydroxy-1-methyl-3,4-bis-o-(methyl-trans-cinnamoyl)cyclopentane* (**10c**)[34]: According to general procedure D: 31 mg (0.07 mmol; 45%) from 95 mg of **5g**; white needles from chloroform; m.p. 101°C. − IR ($CH_2Cl_2$): $\tilde{\nu}$ = 1697 $cm^{-1}$, 1660, 1618, 1342, 1300, 1178, 1155. − $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.58 (s, 3 H, 1-$CH_3$), 1.76 (s, 1 H, OH), 1.93 [s, 3 H, (CO)$CH_3$], 2.27 (dd, $^2J$ = 14.3, $^3J$ = 6.5 Hz, 1 H, 5-H), 2.43 (dd, $^2J$ = 14.3, $^3J$ = 11.0 Hz, 1 H, 5-H′), 3.59 (m, 1 H, 4-H), 3.71 (s, 3

H, $OCH_3$), 3.72 (s, 3 H, $OCH_3$), 3.72 (hidden, 1 H, 3-H), 4.00 (d, $^3J$ = 11.50 Hz, 1 H, 2-H), 5.74 (d, $^3J$ = 15.00 Hz, 2 H, CH=C*H*CO), 7.11 (m, 1 H, $H^{ar}$), 7.15 (m, 1 H, $H^{ar}$), 7.18 (m, 1 H, $H^{ar}$), 7.35 (m, 1 H, $H^{ar}$), 7.38 (m, 1 H, $H^{ar}$), 7.43 (m, 1 H, $H^{ar}$), 7.55 (m, 1 H, $H^{ar}$), 7.60 (m, 1 H, $H^{ar}$), 7.87 (d, $^3J$ = 15.00 Hz, 1 H, C*H*=CHCO), 7.88 (d, $^3J$ = 15.00 Hz, 1 H, C*H*=CHCO). − $^{13}$C NMR (100.4 MHz, $CDCl_3$): 28.1 [(CO)*C*$H_3$], 33.1 (1-C), 47.8 (C-4), 48.2 (C-5), 51.4, 51.5 ($OCH_3$), 53.5 (C-3), 66.0 (C-2), 80.1 (C-1), 118.9, 119.9 (CH=*C*HCO), 126.2, 126.7, 127.3, 127.4, 127.8, 128.1, 130.3, 130.7 (8 C, $CH^{ar}$), 133.5, 134.5 (*C*CH=CHC=O), 134.9, 138.9 (3-C, 4-C), 141.3, 142.1 (*C*H=CHCO), 166.5, 166.9 (COO), 212.1 (2-C). − MS (70 eV); *m/z* (%): 462 (9) [$M^+$], 369 (9), 337 (6), 277 (51), 232 (19) [$C_{14}H_{16}O_3^+$], 199 (68), 171 (75), 157 (99), 129 (94), 115 (70), 43 (100). − $C_{28}H_{30}O_6$ (462.54): calcd. C 72.71, H 6.54; found C 72.82, H 6.59.

*(±)-1,4-Bis(p-anisyl)-2-benzoyl-1-hydroxy-3-β-(trans-phenylethenyl)cyclopentane* (**10d**)[34]: According to general procedure D: 52 mg (0.1 mmol; 10%) from 680 mg of **7d**; white needles from chloroform. − IR (film): $\tilde{\nu}$ = 3059−2805 $cm^{-1}$, 1675, 1600, 1510, 1450, 1260. − $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.33 (dd, $^3J$ = 5.50 Hz, $^2J$ = 14.30 Hz, 1 H, 5-H), 2.77 (dd, $^3J$ = 11.00 Hz, $^2J$ = 14.30 Hz, 1 H, 5-H′), 3.25 (m, 1 H, 3-H), 3.60 (m, 1 H, 4-H), 3.76 (s, 3 H, $CH_3$), 3.80 (s, 3 H, $CH_3$), 4.37 (d, $^3J$ = 12.09 Hz, 1 H, 2-H), 4.93 (s, 1 H, OH), 5.96 (dd, $^3J$ = 9.35, 15.95 Hz, 1 H, C*H*=CHPh), 6.20 (d, $^3J$ = 15.95 Hz, 1 H, C*H*Ph), 6.45−7.82 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 504 (4) [$M^+$], 486 (10) [$M^+ - H_2O$], 389 (40), 269 (100), 135 (20). − $C_{34}H_{32}O_4$ (504.63): calcd. C 80.93, H 6.39; found C 80.85, H 6.44.

*(±)-2-Benzoyl-1-(o,p-dimethoxyphenyl)-1-hydroxy-4-phenyl-3-β-(trans-phenylethenyl)cyclopentane* (**10e**)[34]: According to general procedure D: 57 mg (0.11 mmol; 11%) from 680 mg of **7e**; white needles from chloroform. − IR (film): $\tilde{\nu}$ = 3059−2850 $cm^{-1}$, 1676, 1598, 1512, 1450, 1260, 1027. − $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.30 (dd, $^3J$ = 5.50, $^2J$ = 14.30 Hz, 1 H, 5-H), 2.75 (dd, $^3J$ = 11.10, $^2J$ = 14.30 Hz, 1 H, 5-H′), 3.26 (m, 1 H, 3-H), 3.52 (m, 1 H, 4-H), 3.78 (s, 3 H, $CH_3$), 3.80 (s, 3 H, $CH_3$), 4.39 (d, $^3J$ = 12.11 Hz, 1 H, 2-H), 4.90 (s, 1 H, OH), 6.04 (dd, $^3J$ = 9.35, 15.95 Hz,1 H, C*H*=CHPh), 6.44 (d, $^3J$ = 15.95 Hz, 1 H, CH=C*H*Ph), 6.90−7.80 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 504 (6) [$M^+$], 486 (10) [$M^+ - H_2O$], 381 (100), 135 (70). − $C_{34}H_{32}O_4$ (504.63): calcd. C 80.93, H 6.39; found C 80.87, H 6.40.

*3-(p-Anisyl)-1-hydroxy-2-(p-methoxybenzoyl)-1-phenyl-4-β-(trans-phenylethenyl)cyclopentane* (**11d**)[34]: According to general procedure D: 35 mg (0.07 mmol; 7%) from 680 mg of **7d**; white needles from chloroform. − IR (film): $\tilde{\nu}$ = 3060−2800 $cm^{-1}$, 1690, 1510, 1500, 1450, 1260, 1100. − $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.30 (dd, $^3J$ = 5.50, $^2J$ = 14.30 Hz, 1 H, 5-H), 2.78 (dd, $^3J$ = 11.00, $^2J$ = 14.30 Hz, 1 H, 5-H′), 2.96 (m, 1 H, 4-H), 3.63 (s, 3 H, $CH_3$), 3.67 (s, 3 H, $CH_3$), 3.80 (m, 1 H, 3-H), 4.32 (d, $^3J$ = 11.60 Hz, 1 H, 2-H), 4.95 (s, 1 H, OH), 5.96 (dd, $^3J$ = 9.35, 15.95 Hz, 1 H, C*H*=CHPh), 6.20 (d, $^3J$ = 15.95 Hz, 1 H, C*H*Ph), 6.45−7.82 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 504 (5) [$M^+$], 486 (9) [$M^+ - H_2O$], 360 (35), 269 (100). − $C_{34}H_{32}O_4$ (504.63): calcd. C 80.93, H 6.39; found C 80.85, H 6.34.

*2-(o,p-Dimethoxybenzoyl)-1-hydroxy-1,3-diphenyl-4-β-(trans-phenylethenyl)cyclopentane* (**11e**)[34]: According to general procedure D: 40 mg (0.08 mmol; 8%) from 680 mg of **7e**; white needles from chloroform. − IR (film): $\tilde{\nu}$ = 3059−2850 $cm^{-1}$, 2850, 1679, 1598, 1512, 1450, 1260, 1027. − $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.27 (dd, $^3J$ = 5.50, $^2J$ = 14.30 Hz, 1 H, 5-H), 2.75 (dd, $^3J$ = 11.01, $^2J$ = 14.30 Hz, 1 H, 5-H′), 3.02 (m, 1 H, 4-H), 3.76 (s, 3 H, $CH_3$), 3.78 (s, 3 H, $CH_3$), 3.82 (m, 1 H, 3-H), 4.37 (d, $^3J$ = 12.11 Hz, 1 H, 2-H), 4.91 (s, 1 H, OH), 6.04 (dd, $^3J$ = 9.35, 15.95 Hz, 1 H, C*H*=CHPh), 6.44 (d, $^3J$ = 15.95 Hz, 1 H, CH=C*H*Ph), 6.90−7.80 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 504 (6) [$M^+$], 486 (10) [$M^+ - H_2O$]. − $C_{34}H_{32}O_4$ (504.63): calcld. C 80.93, H 6.39; found C 80.78, H 6.29.

*1-Benzoyl-2-(o,p-dimethoxyphenyl)-4-phenyl-5-β-(trans-phenylethenyl)cyclopent-1-ene* (**12e**): According to general procedure C: 170 mg (0.35 mmol; 35%) from 681 mg of **7e**; white needles from chloroform. − IR (film): $\tilde{\nu}$ = 2962 $cm^{-1}$, 1721, 1677, 1604, 1450, 1261. − $^1$H NMR (400 MHz, $C_6D_6$): δ = 3.00 (m, 1 H, 4-H), 3.62 (m, 2 H, 3-H), 3.63 (s, 3 H, $CH_3$), 3.72 (s, 3 H, $CH_3$), 4.26 (dd, $^3J$ = 6.10, 9.36 Hz, 1 H, 5-H), 6.12 (dd, $^3J$ = 9.36, 15.95 Hz, 1 H, C*H*=CHPh), 6.42 (d, $^3J$ = 15.95 Hz, 1 H, CH=C*H*Ph), 7.02−7.92 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 486 (28) [$M^+$], 455 (15) [$M^+ - OCH_3$], 381 (28) [$M^+ -$ PhCO], 149 (100). − $C_{34}H_{30}O_3$ (486.62): calcd. C 83.92, H 6.21; found C 83.83, H 6.18.

*2-(p-Anisyl)-1-benzoyl-4-phenyl-5-β-(trans-phenylethenyl)-cyclopent-1-ene* (**12f**): According to general procedure C: 173 mg (0.38 mmol; 38%) from 650 mg of **7f**; white needles from cloroform. − IR (film): $\tilde{\nu}$ = 3090−2800 $cm^{-1}$, 1660, 1600, 1510, 1450, 1260. − $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.01 (m, 1 H, 4-H), 3.45 (s, 3 H, $CH_3$), 3.63 (m, 2 H, 3-H), 4.24 (dd, $^3J$ = 6.05, 9.35 Hz, 1 H, 5-H), 6.03 (dd, $^3J$ = 9.35, 15.95 Hz, 1 H, C*H*=CHPh), 6.33 (d, $^3J$ = 15.95 Hz, 1 H, CH=C*H*Ph), 6.91−7.79 (m, 19 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 456 (72) [$M^+$], 365 (20), 351 (100) [$M - C_6H_5CO$], 105 (75). − $C_{33}H_{28}O_2$ (456.59): calcd. C 86.40, H 6.14; found C 86.47, H 6.11.

*1-(o,p-Dimethoxybenzoyl)-2,5-diphenyl-4-β-(trans-phenylethenyl)cyclopent-1-ene* (**13e**): According to general procedure C: 122 mg (0.25 mmol; 25%) from 681 mg of **7e**; white needles from chloroform. − IR (film): $\tilde{\nu}$ = 2925 $cm^{-1}$, 2854, 1736, 1677, 1601, 1450, 1261. − $^1$H NMR (400 MHz, $C_6D_6$): δ = 2.91 (m, 1 H, 4-H), 3.39 (s, 3 H, $CH_3$), 3.47 (m, 2 H, 3-H), 3.75 (s, 3 H, $CH_3$), 4.45 (d, $^3J$ = 7.82 Hz, 1 H, 5-H), 6.14 (dd, $^3J$ = 9.35, 15.95 Hz, 1 H, C*H*=CHPh), 6.45 (d, $^3J$ = 15.95 Hz, 1 H, CH=C*H*Ph), 7.05−7.92 (m, 18 H, $H^{ar}$). − MS (70 eV); *m/z* (%): 486 (16) [$M^+$], 322 (16) [$M^+ - C_6H_3(OCH_3)_2CO$], 280 (45), 149 (100).− $C_{34}H_{30}O_3$ (486.62): calcd. C 83.92, H 6.21; found C 83.81, H 6.30.

*Ab initio Calculations:* The ab initio and density functional calculations were performed with the Gaussian 94 suite of programs.[19] Structures were optimzed with no constraints other than symmetry at the B3LYP/SVp level, i.e. using the B3LYP[20] density functional and a split valence basis set[21], augmented with standard polarization functions on the non-hydrogen atoms.[22] Vibrational frequencies and zero-point energy corrections, scaled by 0.98[23], were computed at this level. Refinement of the structures was performed at the MP2/SVp level. Energy calculations were done at MP2/TZ2p level (i.e., using a triple-zeta basis set[21] and split polarization functions).

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[30] $^3J$ coupling constants between 5-H und 6-H in compounds **5** und **7** are below 1 Hz and not clearly determinable (broad signals for 5-H and 6-H).

[31] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC-100857). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

[32] The moderate *R* value is due to the fact, that **5a** is a poorly reflecting compound. Unfortunately, it was only possible to solve the strong disorder of the toluene solvent molecules in a very rough way.

[33] Assignment of NMR signals by comparison with spectra of similarly substituted "symmetric" derivatives of type **5**.

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