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Chiral Bis(η^5:η^1-pentafulvene)titanium Complexes

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The series of bis(pentafulvene)titanium complexes (η^6-C_5H_4=CR_2)$_2$Ti (=CR_2 = C(*p*-tol)$_2$ (**3**), adamantyl (**4**)) and their corresponding bis(benzofulvene) derivatives (η^6-C_9H_6=CR_2)$_2$Ti (=CR_2 = C(*p*-tol)$_2$ (**7**), adamantyl (**8**)) have been synthesized by reaction of $TiCl_3$·3THF with the pentafulvene ligands (2 equiv) and magnesium as reducing agent (1.5 equiv). The bis(fulvene) complexes **7** and **8** have been obtained as diastereomerically pure compounds. All complexes have been characterized by spectroscopy and by single-crystal X-ray diffraction. The bonding situation is best described as a π-η^5:σ-η^1 coordination mode. The bis(fulvene) complex **3** is approximately C_2 symmetric, whereas **7** crystallizes as a conglomerate in the monoclinic space group $P2_1$ and one of the enantiomers was identified as a (*S*,p*S*,p*R*) stereoisomer showing C_1 symmetry. The adamantyl benzofulvene complex **8** crystallizes in the monoclinic space group $P2_1/c$; both benzofulvene ligands are coordinated as optical antipodes, and a (*S*,p*S*,p*R*)/(*R*,p*R*,p*S*) configuration is found in the solid state. Reaction of **3** and **7** with HCl/Et_2O leads to the corresponding bis(cyclopentadienyl)titanium chlorides (η^5-C_5H_4−CHR_2)$_2TiCl_2$ (R = *p*-tol (**9**)) and the bis(indenyltitanium) derivative (η^5-C_9H_6−CHR_2)$_2TiCl_2$ (R = *p*-tol$_2$ (**10**)).

Introduction

Pentafulvenes can be bound to transition metals in several different modes. In unusual examples, fulvenes bind through selected double bonds of the five-membered ring as well as the exocyclic double bond. η^2 coordination to the exocyclic double bond was demonstrated for Pd(η^2-C_5Me_4=CH_2)(PMe_3)$_2$[1] and Rh(η^2-C_5H_4=CPh_2)(CO)$_2$Cl[2] or through one of the ring double bonds, as in Pt(η^2-C_5H_4=CPh_2)(PPh_3)$_2$.[3] An η^4 mode was found in Fe(η^4-C_5H_4=CPh_2)(CO)$_3$, (COD)Ni(η^4-C_5H_4=CPh_2),[4] and CpCo(η^4-C_5H_4=CPh_2).[5] More commonly, however, fulvene ligands act as six-electron donors. In the case of early transition metals, the bonding situation is best described as a π-η^5:σ-η^1 coordination mode. The majority of the known fulvene complexes of early transition metals have been generated by thermal transformations of methyl-substituted cyclopentadienyl complexes.[6] Using stronger thermal conditions, 2-fold selective C−H bond activations of one bis(alkyl)-substituted cyclopentadienyl ring are observed.[7] Alternatively, the direct use of pentafulvenes as starting materials becomes possible, as shown first for the exchange reaction of bis(η^6-toluene)titanium(0) and 6,6-diphenylfulvene.[8] Additionally, cyclopentadienyltitanium fulvene complexes of the type (η^5-C_5R_5)Ti(Cl)(η^6-C_5H_4=CR_2) are formed by reductive complexation of pentafulvenes.[9] Here, we report on an efficient route to bis(η^6-pentafulvene)titanium complexes, by reaction of pentafulvenes and titanium halides with magnesium as reducing agent. Generally, the reductive dimerization of pentafulvenes is known for various metals.[10] This procedure has been used for the syntheses of *ansa*-metallocenes of group 4 metals in a direct[11] or indirect way.[12]

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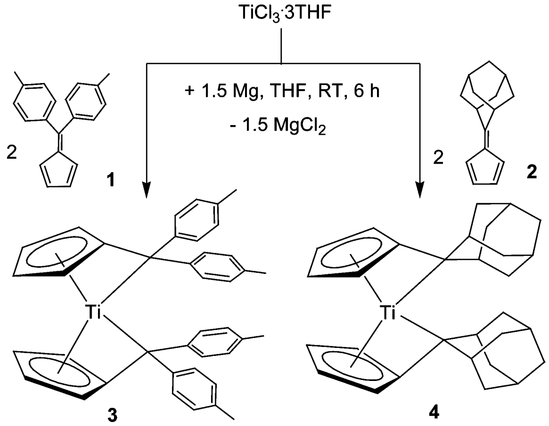
Scheme 1



However, to prevent C−C coupling reactions at the exocyclic position, bulky substituents seem to be necessary in this position. Additionally, reactions of prochiral 1,2-benzofulvenes will be presented. Benzofulvenes have also been characterized by an ambivalent coordination chemistry. Comparable to the case for fulvene complexes, coordination modes of η^2 up to η^6 are found, including the possibility to coordinate through the benzene ring instead of the five-membered ring.[13]

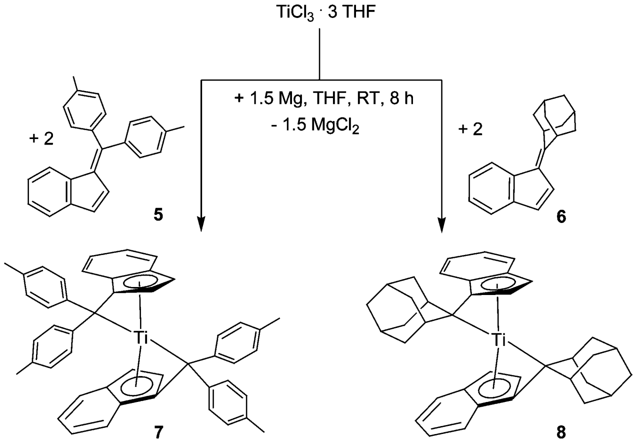
Results and Discussion

Upon reaction of $TiCl_3$·3THF with 1.5 equiv of magnesium turnings and 2 equiv of bis-*p*-tolylfulvene (**1**) in THF as solvent at room temperature over a period of 6 h, a dark green solution is formed. After separation from $MgCl_2$ the bis(fulvene)titanium complex **3** can be isolated as a dark green solid (mp 154 °C, 75% yield) (Scheme 1). In a similar procedure, using fulvene **2** as ligand, complex **4** is obtained as a turquoise-blue solid (mp 135 °C, 70% yield). Both complexes are easily soluble in ethers and aromatic solvents but less soluble in aliphatic hydrocarbons. A more satisfactory solubility is obtained in hot *n*-hexane (65 °C). On contact with air and moisture, fast decomposition occurs. The mass spectra (EI) show the peaks of the molecular ions at *m*/*z* 564 (**3**) and 444 (**4**).

Instead of $TiCl_3$·3THF, the use of $TiCl_4$·2THF as starting material is possible and similar yields are found for the formation of **3**. However, in the case of **4** only low yields are found if $TiCl_4$·2THF is used as starting material. We propose side reactions of the stronger bipolar fulvene **2**[14] and $TiCl_4$·2THF to be responsible for this drop in yield.[15] Such side reactions can be circumvented if the more weakly Lewis acidic $TiCl_3$ is used.

Using the related prochiral benzofulvenes ligands **5** and **6** in reactions with $TiCl_3$·3THF and Mg in THF as solvent, the dark brown bis(fulvene) complexes **7** and **8** are obtained as pure diastereomers in 68% and 45% yield (dec pt 139 °C (**7**), 160 °C (**8**)), respectively (Scheme 2). A lower solubility and higher sensitivity to air is found compared to the case for **3** and **4**. Again, the mass spectra (EI) show peaks of the molecular ions at *m*/*z* 664 (**7**) and 545 (**8**).

Scheme 2



X-ray Crystal Structures. Suitable crystals for X-ray structure determinations of **3**, **7**, and **8** were obtained from *n*-hexane as well as *n*-hexane/toluene solutions. Unfortunately, **4** forms very thin needle-shaped crystals, which only allowed collection of low-quality X-ray data sets. However, its connectivity was still confirmed, but no further detailed data will be discussed.[16] The Ortep plots of **3**, **7**, and **8** are given in Figures 1−4, and selected bond distances are summarized in Table 1. The bis(fulvene) complex **3** crystallizes in the orthorhombic space group *Pbca*. Compound **3** exhibits a typical bent-metallocene conformation which is approximately C_2 symmetric (Figure 2). **4** shows similar structural features and possesses, as does **3**, a noncrystallographically imposed C_2 axis.[16]

Typical features of a fulvene ligand coordinated to early transition metals are found for **3**, **7**, and **8**. The molecular struc-

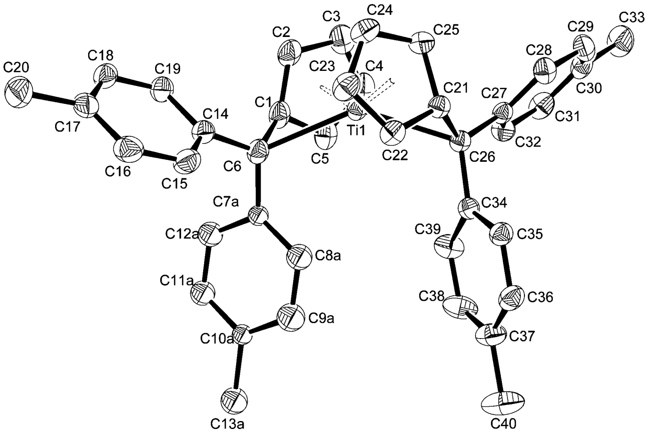


Figure 1. Molecular structure of **3** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−C1 = 2.149(3), Ti1−C2 = 2.248(2), Ti1−C3 = 2.394(2), Ti1−C4 = 2.431(3), Ti1−C5 = 2.299(3), Ti1−C6 = 2.408(2), C1−C2 = 1.438(4), C2−C3 = 1.422(4), C3−C4 = 1.399(5), C4−C5 = 1.407(4), C1−C5 = 1.448(4), C1−C6 = 1.453(3), Ti1−C21 = 2.148(2), Ti1−C22 = 2.274(2), Ti1−C23 = 2.408(3), Ti1−C24 = 2.394(3), Ti1−C25 = 2.258(3), Ti1−C26 = 2.392(2), C21−C22 = 1.448(3), C22−C23 = 1.411(3), C23−C24 = 1.411(4), C24−C25 = 1.412(4), C21−C25 = 1.448(3), C21−C26 = 1.453(3), Ti1−Ct1 = 1.964, Ti1−Ct2 = 1.953; Ct1−Ti1−Ct2 = 145.9, C6−Ti1−C26 = 139.25(8). Ct1 = centroid of C1−C5; Ct2 = centroid of C21−C25. All hydrogen atoms and one disordered tolyl ligand are omitted for clarity.

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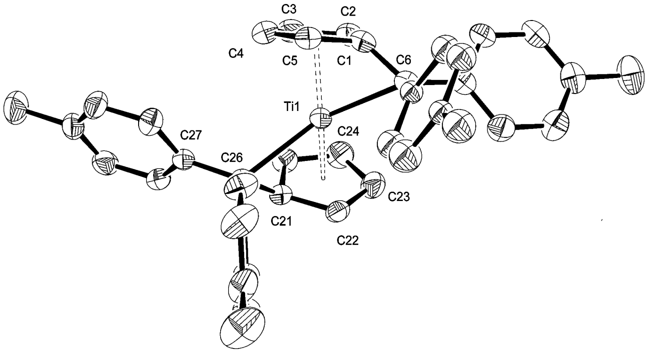


Figure 2. View along the C_2 axis of **3** (the *R* isomer is shown).

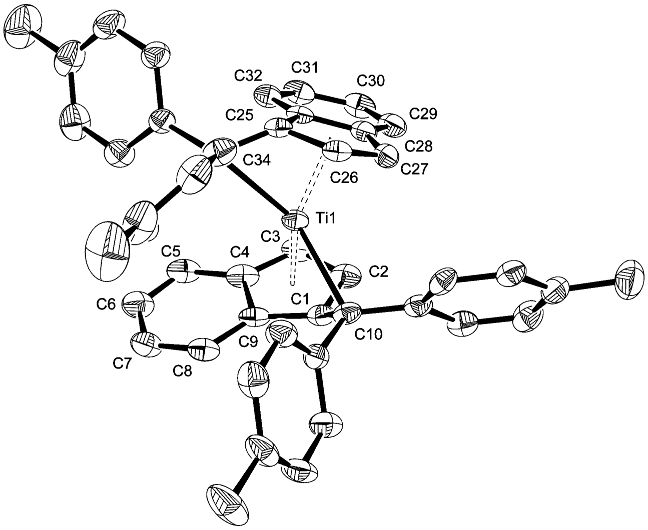


Figure 3. Molecular structure of **(***S*,p*S*,p*R*)-**7** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−C1 = 2.155(3), Ti1−C2 = 2.225(3), Ti1−C3 = 2.342(3), Ti1−C4 = 2.488(3), Ti1−C9 = 2.365(3), Ti1−C10 = 2.400(2), C1−C2 = 1.445(4), C2−C3 = 1.407(5), C3−C4 = 1.420(5), C4−C9 = 1.440(4), C4−C5 = 1.414(5), C5−C6 = 1.354(5), C6−C7 = 1.424(4), C7−C8 = 1.362(4), C1−C9 = 1.457(4), C1−C10 = 1.456(4), Ti1−C25 = 2.146(3), Ti1−C26 = 2.235(3), Ti1−C27 = 2.409(3), Ti1−C28 = 2.497(3), Ti1−C33 = 2.328(3), Ti1−C34 = 2.410(3), C25−C26 = 1.449(4), C26−C27 = 1.379(5), C27−C28 = 1.420(4), C28−C33 = 1.420(4), C28−C29 = 1.419(4), C29−C30 = 1.359(4), C30−C31 = 1.397(5), C31−C32 = 1.369(4), C32−C33 = 1.429(4), C25−C34 = 1.425(4), Ti1−Ct1 = 1.972, Ti1−Ct2 = 1.983; Ct1−Ti1−Ct2 = 142.9, C10−Ti1−C34 = 126.64(9). Ct1 = centroid of C1−C4, C9; Ct2 = centroid of C25−C28, C33.

ture of **3** is comparable with that of the bis(6,6-diphenylfulvene)titanium complex prepared from bis(toluene)titanium(0).[8] In such a way the C1−C6 and C21−C26 bonds are elongated to 1.453(3) Å, in comparison to the length in the free ligand **1** (1.359(2) Å).[17] The exocylic carbon atom of the fulvene ligand is bent toward the metal center, leading to bent angles θ of 34.1 and 35.3°, respectively. The Ti−C6 (2.408(2) Å) and Ti−C26 (2.392(2) Å) distances in **3** are found to be significantly shorter than those in the fulvene complexes (η^5-C_5Me_5)(η^6-C_5H_4=C(*p*-tol)$_2$)TiCl (2.535(5) Å)[17] and {(η^5-C_5Me_5)(η^6-C_5H_4=C(*p*-tol)$_2$)Ti}$_2$(μ_2-η^1:η^1-N_2) (2.601(3), 2.612(3) Å).[18] The Ti−Ct distances (1.964, 1.953 Å) are found to be slightly shorter than those in typical bent titanocenes (2.062 Å[19]), forming an Ct−Ti−Ct angle of 145.9°, which is in the expected range for

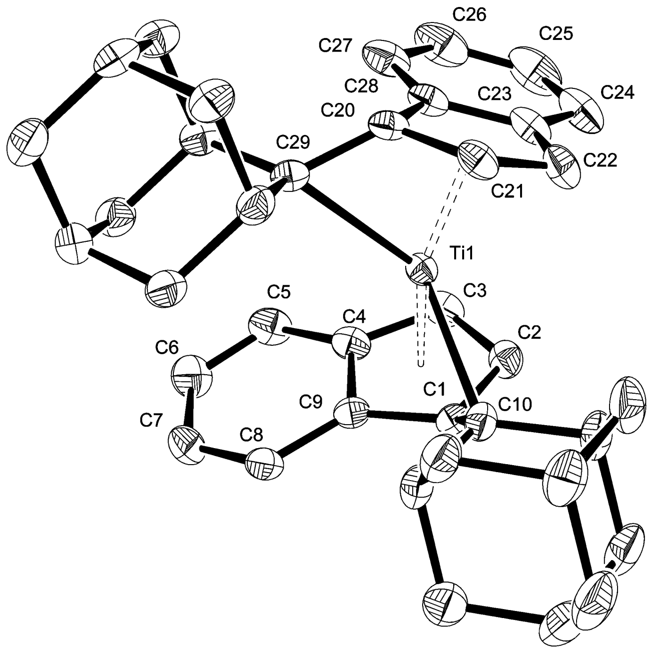
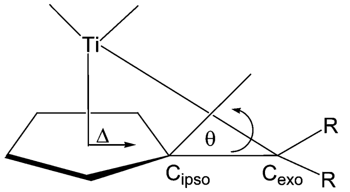


Figure 4. Molecular structure of **8** (50% probability ellipsoids, (*S*,p*S*,p*R*) enantiomer shown). Selected bond lengths (Å) and angles (deg): Ti1−C1 = 2.146(2), Ti1−C2 = 2.233(2), Ti1−C3 = 2.257(2), Ti1−C4 = 2.529(2), Ti1−C9 = 2.415(2), Ti1−C10 = 2.341(2), C1−C2 = 1.449(3), C2−C3 = 1.400(3), C3−C4 = 1.429(3), C4−C9 = 1.436(3), C4−C5 = 1.420(3), C5−C6 = 1.372(3), C6−C7 = 1.412(3), C7−C8 = 1.374(3), C1−C9 = 1.479(3), Ti1−C20 = 2.138(2), Ti1−C21 = 2.259(2), Ti1−C22 = 2.411(2), Ti1−C23 = 2.4964(18), Ti1−C28 = 2.345(2), Ti1−C29 = 2.363(2), C20−C21 = 1.440(3), C21−C22 = 1.403(3), C22−C23 = 1.426(3), C23−C28 = 1.438(3), C23−C24 = 1.429(3), C24−C25 = 1.362(4), C25−C26 = 1.406(4), C26−C27 = 1.379(4), C27−C28 = 1.423(3), Ti1−Ct1 = 1.988, Ti1−Ct2 = 1.995; Ct1−Ti1−Ct2 = 143.2, C10−Ti1−C2 =9 120.09(8). Ct1 = centroid of C1−C4, C9; Ct2 = centroid of C20−C23, C28.

Table 1. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 3, 7, and 8

	3	7	8
Ti−Ct	1.964	1.972	1.988
	1.953	1.983	1.995
Ti−C_{ipso}	2.149(3)	2.155(3)	2.146(2)
	2.148(2)	2.146(3)	2.138(2)
Ti−C_{exo}	2.408(2)	2.400(2)	2.341(2)
	2.392(2)	2.410(3)	2.363(2)
C_{ipso}−C_{exo}	1.453(3)	1.456(4)	1.447(3)
	1.453(3)	1.425(4)	1.458(3)
Ct1−Ti−Ct2	145.89	142.94	143.15
θ^a	34.1	34.6	35.4
	35.3	32.6	34.4
Δ^a	0.282	0.309	0.316
	0.267	0.346	0.375

[a] The values Δ and θ are defined as shown:



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(16) For details please see the Supporting Information.

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(19) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

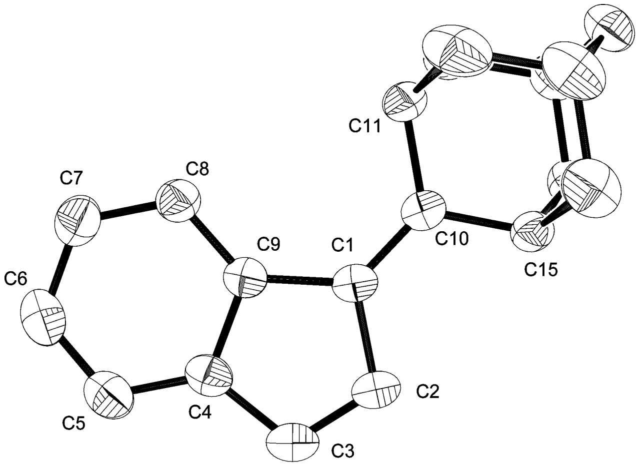

Figure 5. Molecular structure of **6** (50% probability ellipsoids). Selected bond lengths (Å): C1−C2 = 1.479(2), C2−C3 = 1.340(2), C3−C4 = 1.457(3), C4−C9 = 1.417(2), C9−C1 = 1.494(2), C4−C5 = 1.384(2), C5−C6 = 1.379(3), C6−C7 = 1.393(3), C7−C8 = 1.389(2), C8−C9 = 1.393(2), C1−C10 = 1.361(2).

low-valent Cp_2−Ti fragments.[20] A ring slippage Δ^{21} of 0.27 Å (average) toward the C_{ipso} atom of the five-membered ring is found.

To compare the structural data of the free and coordinated pentafulvenes, the structure of **6** was determined (Figure 5). The structural data of **6** are in the expected range for pentafulvenes (**1**,[17] **2**,[22] **5**[18]). The torsion angles C9−C1−C10−C11 (1.71°) and C2−C1−C10−C15 (1.49°) are found to be smaller than in the *p*-tolyl-substituted fulvenes **1** (average 9.95°)[17] and **5** (average 16.63°),[18] illustrating the nearly coplanar arrangement of the substituents at the exocyclic double bond, leading to an approximately C_s-symmetric molecule.

The exocyclic C−C bonds in **5** (1.359(2) Å)[18] and **6** (1.361(2) Å) are elongated in the benzofulvene complexes **7** (1.456(4), 1.425(4) Å) and **8** (1.447(3), 1.458(3) Å) in a typical manner. A slightly stronger elongation is found in the low-coordinated benzofulvene complex $(\eta^5\text{-}C_5Me_5)Ti(\eta^6\text{-}C_9H_6{=}C(p\text{-tol})_2)$ (1.465(3) Å).[18] Due to the increased aromatic character of the five-membered fulvene ring, the C2−C3 bond is elongated in the benzofulvene complexes **7** and **8**. On the other hand, the double bonds in the six-membered ring become more localized, leading to a shortening of the bonds comparable to those between C5−C6 and C7−C8 in **7** and **8**. The other structural parameters are in excellent agreement with those of other known titanium pentafulvene complexes. The exocyclic carbon atoms are bent out of the fulvene plane by 33.6° (**7**, average) and 34.9° (**8**, average). Ring slippage values Δ toward the C_{ipso} atom of 0.327 Å (**7**, average) and 0.345 Å (**8**, average) are found, and likewise Ti−Ct distances are also found to be shorter than in bent metallocenes. In addition, the Ti−C_{exo} distances in **8** (2.341(2), 2.363(2) Å) are found to be shorter than in **7** (2.400(2), 2.410(3) Å), which are nearly identical with the values in **3** (2.408(2), 2.392(2) Å).

Chirality. The chirality of the bis(fulvene) complexes **3** and **4** arises from the fact that they bear two bidendate fulvene ligands. Chelation via the exocyclic carbon atoms of the ligands is possible in two stereochemical arrangements, making the titanium complex become chiral. In a simplified approach the bonding situation can be regarded as an elongated tetrahedron whose corners can be assigned to the centroids and the exocyclic carbon atoms of both fulvene ligands, as schematically represented in Figure 6. This geometry is best known for suitable substituted spiranes, and the formation of similar spiro compounds exhibiting bis(cyclopentadienylalkoxide)[23] and bis(indenylphenoxide)[24] ligands as well as further 2-fold-chelated metallocene systems[25] has actually been studied before. For the stereochemical description one fulvene ligand is arbitrarily given preference and the substituents are ranked using the Cahn−Ingold−Prelog rules.[26,27] In this case, Ct is given priority 1, and the Ct on the other side is ranked 2. The C_{exo} atoms are then ranked 3 and 4, and now the chirality can be assigned as *R* or *S*, respectively.[16]

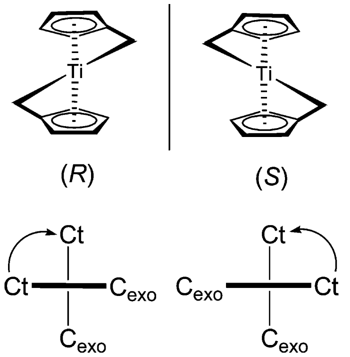

Figure 6. Chirality of the bis(fulvene) complexes. Ct = centroid of the five membered fulvene ring; C_{exo} = exocyclic carbon atom of the fulvene ligand.

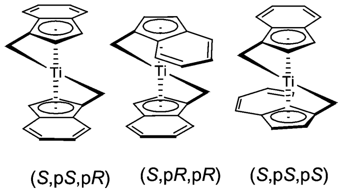

Figure 7. Diastereomers of the bis(benzofulvene) complexes (only one enantiomer given for each).[16]

The stereochemistry of the bis(benzofulvene) compounds **7** and **8** is slightly more complicated, however. The monosubstituted benzofulvenes **5** and **6** exhibit enantiopic faces, leading to the occurrence of two planar chiral elements per bis(benzofulvene) complex. Together with the chiral metal center as in the bis(fulvene) compounds, this adds up to three stereogenic elements; thus, there are 2^3 possible stereoisomers for the bis(benzofulvene) complexes. However, the (*R*,p*R*,p*S*)/(*S*,p*S*,p*R*) and (*R*,p*S*,p*R*)/(*S*,p*R*,p*S*) isomers are in a meso relationship, and therefore, only three pairs of racemic diastereomers can be formed (Figure 7). [23]

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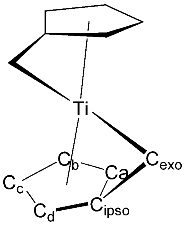
Table 2. Selected ^{1}H (ppm; C_6D_6, 500 MHz, 300 K) and ^{13}C NMR Data (ppm; C_6D_6, 125 MHz, 300 K) of 1[17] and 2,[28,18] Compared with Those of 3 and 4



	1	3	2	4
		^{1}H NMR Data		
H_a	6.57	4.96	6.66	4.63
H_b	6.65	4.20	6.61	4.84
H_c	6.65 (H_b)	5.88	6.61 (H_b)	6.06
H_d	6.57 (H_a)	6.53	6.66 (H_a)	6.55
		^{13}C NMR Data		
C_a	124.8	108.8	119.8	110.8
C_b	132.4	110.0	131.0	111.9
C_c	132.4 (C_b)	121.7	131.0 (C_b)	116.9
C_d	124.8 (C_a)	116.5	119.8 (C_a)	115.0
C_{ipso}	144.2	132.6	136.9	133.4
C_{exo}	152.2	112.0	164.8	113.3

The benzofulvene complex **7** crystallizes as a conglomerate in the monoclinic space group $P2_1$, and one of the enantiomers was identified as (*S*,p*S*,p*R*)-**7**. The central titanium atom lies in a highly distorted pseudotetrahedral coordination sphere and is π-η^5:σ-η^1-bound to each of the benzofulvene ligands. The isomers (*S*,p*S*,p*R*)-**7** and (*R*,p*R*,p*S*)- **7** have no symmetry elements and show C_1 symmetry.

The adamantyl-substituted benzofulvene complex **8** crystallizes in the monoclinic space group $P2_1/c$. The X-ray structure determination of **8** established that, similar to **7**, both benzofulvene ligands are coordinated as optical antipodes and, accordingly, **8** possesses a (*S*,p*S*,p*R*)/(*R*,p*R*,p*S*) configuration in the solid state.

NMR Investigations. ^{1}H and ^{13}C NMR spectroscopic measurements showed that the 2-fold symmetry of **3** and **4** is retained in solution; thus, for both fulvene ligands a single set of signals is found. For **3** the chemical shifts of the fulvene ring protons appear as four separated multiplets at δ 4.20 (H_b), 4.96 (H_a), 5.88 (H_c), and 6.53 ppm (H_d), all signals being shifted upfield by nearly 2.4 ppm compared to the those in the spectrum of the corresponding fulvene **1** (Table 2). The chemical shifts of the fulvene ring protons of **4** at δ 4.63 (H_a), 4.84 (H_b), 6.06 (H_c), and 6.55 ppm (H_d), respectively, exhibit very similar patterns, and an upfield shift up to 2 ppm is found. The strongest shift differences are found for H_a and H_b, comparing free and complexed ligands. Analogous to the ^{1}H NMR data, the signals of the C atoms of the fulvene ligand do also experience a significant upfield shift upon coordination to the titanium center. This is particularly true for the C_{exo} atoms, which show differences of 51.5 (**4**/**2**) and 40.2 ppm (**3**/**1**), indicating a remarkable electron transfer from the titanium center to the ligand.

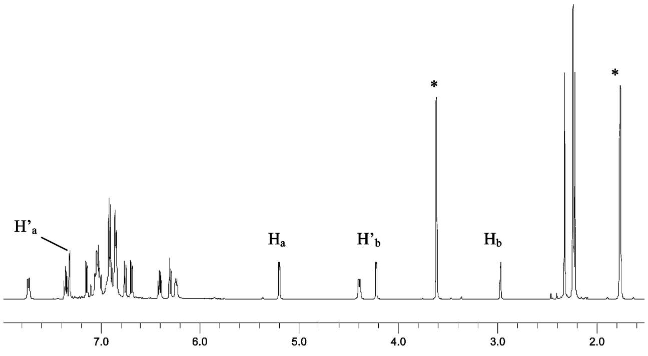
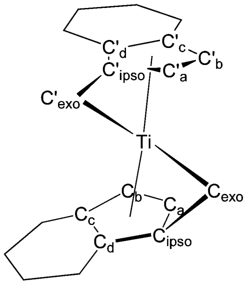


Figure 8. ^{1}H NMR spectrum of **7** in THF-d_8 (275 K, 500.1 MHz). The asterisks denote THF.

Table 3. Selected ^{1}H (ppm; 500 MHz, 300 K) and ^{13}C NMR Data (ppm; 125 MHz, 300 K) of 8 and 7 Compared with Those of 6 and 5[18]



	5^{18}	7	6	8
solvent	C_6D_6	THF-d_8	C_6D_6	C_6D_6
		^{1}H NMR Data		
H_a	6.75	5.17	6.84	4.81
H'_a		7.28		7.13
H_b	6.94	2.94	6.73	3.07
H'_b		4.19		5.37
		^{13}C NMR Data		
C_a	130.7	121.9	127.0	122.5
C'_a		116.4		116.6
C_b	130.7	109.4	128.5	107.3
C'_b		110.6		106.2
C_c	136.0	123.3	145.4	124.0
C'_c		127.9		126.6
C_d	138.2	126.6	136.6	126.5
C'_d		125.6		126.6
C_{ipso}	144.2	131.7	131.3	133.4
C'_{ipso}		125.6		127.1
C_{exo}	147.3	114.3	159.9	117.3
C'_{exo}		114.6		120.4

The lower symmetry complexes **7** and **8** exhibit the expected separated set of signals for each benzofulvene group in the ^{1}H and ^{13}C NMR spectra, diagnostic for the complexes' C_1 symmetry.[16] Due to severe signal crowding in benzene-d_6 the detailed NMR studies of **7** were performed with THF-d_8 solutions. The most characteristic features are again the chemical shifts for the nuclei of the fulvene skeleton; especially, the ^{1}H signals vary over a wide range (Figure 8). For **7** they are located at δ 5.17 (H_a), 7.28 (H'_a), 2.94 (H_b), and 4.19 (H'_b) (Table 3), each found as doublets with a coupling constant of $^3J_{HH} = 3.4$ Hz (comparable values are also found for C_6D_6 solutions at δ 5.27 (H_a), 7.52 (H'_a), 2.97 (H_b), and 4.47 (H'_b)). For **8** resonances occur at δ 4.81 (H_a), 7.13 (H'_a), 3.07 (H_b), and 5.37 (H'_b) (J_{HH} not resolved). As in the solid-state structure, compound **7** exhibits a proton (H3 (=H_b)) lying directly above the arene ring of the opposite benzofulvene ligand, which thus is strongly influenced by the arene's anisotropy cone (Figure 9). Therefore, H3 (=H_b) is most effectively shielded, and in consequence, its resonance shows an unusual upfield shift at 2.94 ppm. In **8**, H3 (=H_b) is similarly oriented and shows a comparable shift (3.07 ppm). Vice versa, the most deshielded signals at δ 7.28 (**7**) and 7.13 (**8**) ppm can be assigned to the coordinatively less affected protons H26 (**7**) and H21 (**8**), respectively.

Analysis of variable-temperature NMR data and NOE experiments revealed that three of the four phenyl rings (**A**−**C**) of **7** undergo a fast rotation on the time scale of the NMR experiment at 275 K. Thus, only averaged signals for the corresponding

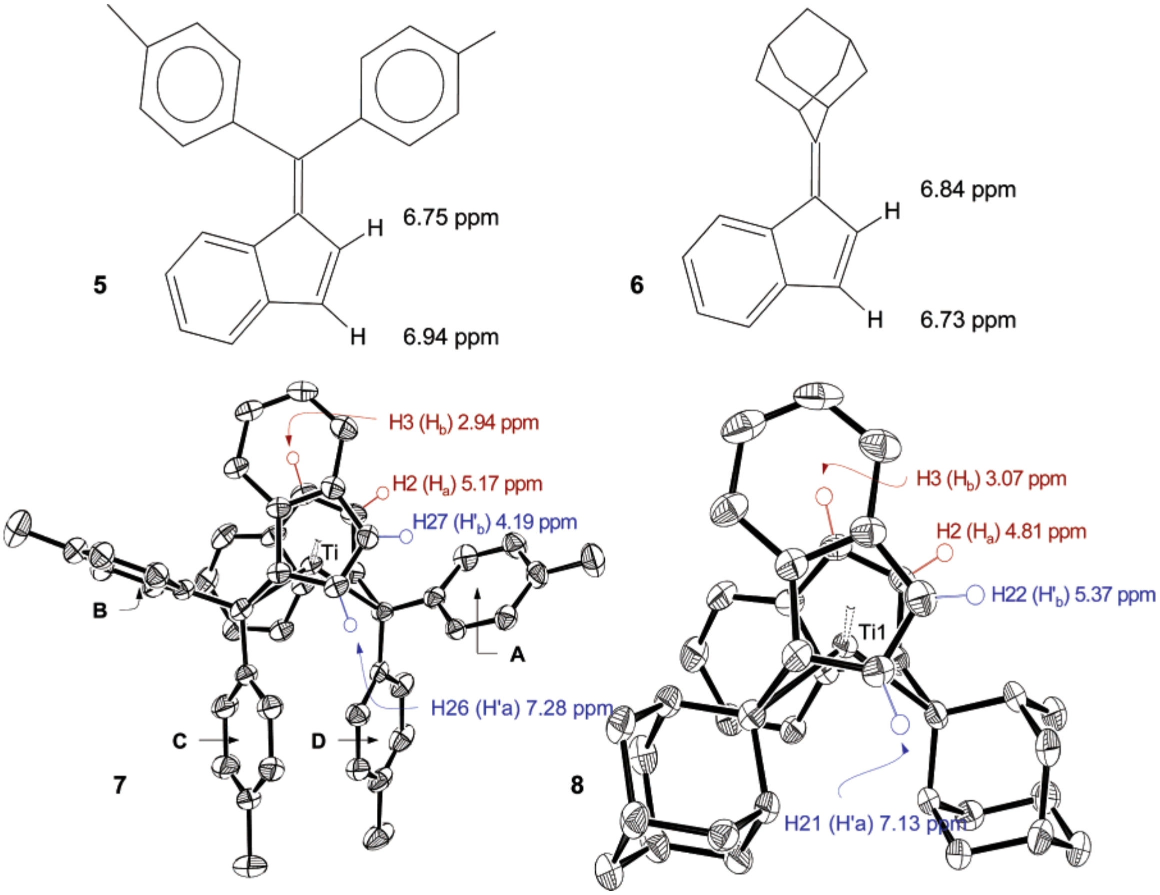


Figure 9. Assignment and chemical ^{1}H NMR shifts of selected protons in **5**−**8**.

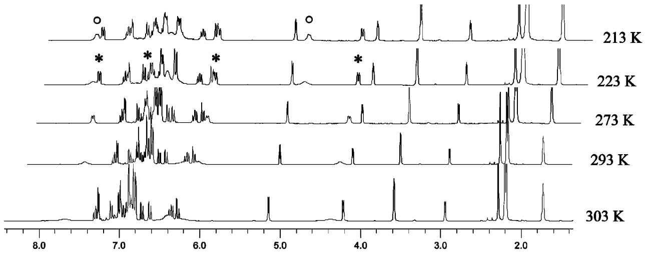


Figure 10. Variable-temperature ^{1}H NMR spectra of **7** in THF-d_8 (300.1 MHz). The asterisks mark the resonances of the protons from ring D, and the circles denote the C−H resonances of ring C (two of them are overlapped by the aromatic region).

ortho and meta nuclei are observed. However, the ring rotation of phenyl group **D** is already so restricted that it can be spectroscopically monitored and distinct signals are found (^{1}H, δ 4.36, 6.20, 6.96−7.02, and 7.69 ppm; ^{13}C, δ 134.3, 133.0, 128.6, 141.7, 128.5, and 129.1 ppm). As shown in Figure 10, these resonances are found to be broadened at 303 K but become sharpened when the temperature is lowered. Additionally, the restricted motion of a second ring (**C**) can be observed at 213 K.

Compounds **7** and **8** also feature the typical ^{13}C resonances of the nonannelated fulvene frameworks, with slight deviations of the two chelating ligands. Namely, the resonances of the tertiary carbons C_a/C'_a and C_b/C'_b occur at δ 121.9/116.4 and 109.4/110.6 ppm (**7**) and at δ 122.5/116.6 and 107.3/106.2 ppm (**8**), respectively. As observed for **3** and **4**, they show similar upfield shifts in comparison with the signals for the free ligands. The C_{ipso}/C'_{ipso} shifts are found in a comparable range (δ 131.7/125.6 (**7**) and δ 133.4/127.1 ppm (**8**)). The exocyclic carbon atoms in **7** resonate almost equally (δ 114.3/114.6 ppm) and are at slightly higher field than the C_{exo} shifts of **8** (δ 117.3/120.4 ppm). They all show considerable shift differences up to 39.5 ppm with regard to the parent fulvenes (δ 147.3 (**5**), 159.9 ppm (**6**)), indicating their increased sp^3 character.

Saturation transfer phenomena showed that the benzofulvene ligands in **7** apparently exchange their positions. Even at lower temperatures a considerable ligand exchange still occurs. For **8** a similar fluxional behavior is not observed. However, a rotation of the benzofulvene ligand comparable to the fulvene rotation around the Ti−Ct axis in Cp*{η^6-C_5H_4═C(*p*-tolyl)$_2$}TiCl is not observed.[17]

Reactions with HCl. Due to the general nucleophilic character of the exocyclic carbon of the pentafulvene complexes of early transition metals, subsequent reactions with electrophiles can be expected, as shown for monofulvene titanium derivatives.[9,29] For bis(diphenyl) pentafulvene titanium a reversible coordination of carbon monoxide is described as the first reaction of bis(fulvene)titanium complexes.[8] On treatment of a hexane solution of **3** and a toluene solution of **7** with 2 equiv of a 1 M solution of HCl/Et$_2$O an immediate color change from green (**3**) and brown (**7**) to red (**9**) and dark red (**10**), respectively, occurs (Scheme 3). Whereas the crystalline

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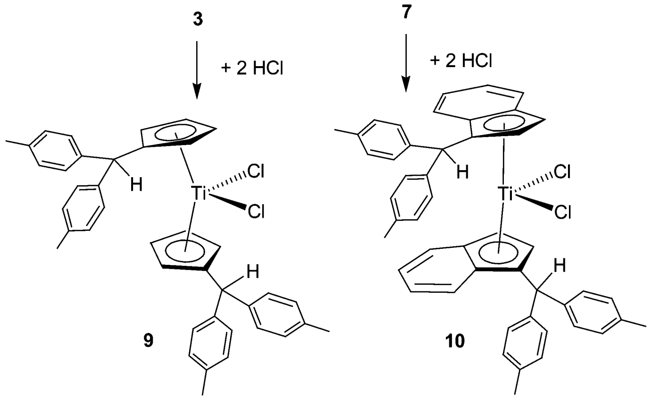
(28) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 661−666.

(29) Examples of different electrophiles used are as follows. Ketones: (a) Stroot, J.; Beckhaus, R.; Saak, W.; Haase, D.; Lützen, A. *Eur. J. Inorg. Chem.* **2002**, 1729−1737. Nitriles: (b) Stroot, J.; Saak, W.; Haase, D.; Beckhaus, R. *Z. Anorg. Allg. Chem.* **2002**, *628*, 755−761. H$_2$O: (c) Stroot, J.; Haase, D.; Saak, W.; Beckhaus, R. *Z. Kristallogr.-New Cryst. Struct.* **2002**, *217*, 47−48. HCl: (d) Stroot, J.; Haase, D.; Saak, W.; Beckhaus, R. *Z. Kristallogr.-New Cryst. Struct.* **2002**, *217*, 49−50.

Scheme 3



substituted titanocene dichloride **9** is precipitated directly from the reaction solution, the bis(indenyl) derivative **10** can be isolated after adding *n*-hexane.

The ^{1}H NMR spectrum of **9** shows, as expected, one set of signals which can be attributed to the exocyclic CH group (δ 5.98 ppm) and the typical cyclopentadienyl protons (δ 6.01, 5.65 ppm). In the case of **10** the exocyclic CH proton is located at δ 6.55 ppm, whereas the protons of the five-membered ring are found at δ 6.23 and 4.34 ppm, respectively. As for **9**, both η^5 ligands are also found to be equivalent in **10**. A consistent behavior is found in the ^{13}C NMR spectra of **9** and **10**.

The molecular structures of **9** and **10** are given in Figures 11 and 12. The substituted titanocene halide **9** crystallizes in the triclinic space group $P\bar{1}$ with 0.5 equiv of *n*-hexane per molecule, whereas **10** crystallizes in the monoclinic space group $P2_1/n$ with 1 equiv of toluene per molecule. Both substituted indenyl ligands in **10** are arranged as optical antipodes, leading to a meso-like form. The terminal Ti−Cl bond lengths (2.3506(5), 2.3397(5) Å, **9**; 2.3026(6), 2.3192(6) Å, **10**) are comparable to those of other titanocene chlorides.[30] Also, the typical pseudo-tetrahedral coordination features are found, when the Ct−Ti−Ct (132.6, 131.69(2)°) and Cl−Ti−Cl angles (95.32, 97.61(3)°) of **9** and **10** are compared with those of other titanocene derivatives.[31]

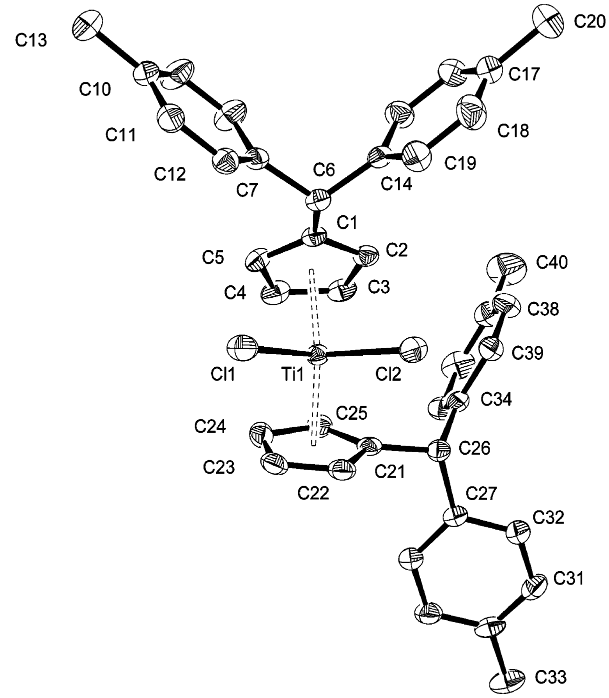


Figure 11. Molecular structure of **9** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−C1 = 2.4475(15), Ti1−C2 = 2.4149(15), Ti1−C3 = 2.3532(16), Ti1−C4 = 2.3416(15), Ti1−C5 = 2.3977(15), Ti1−C21 = 2.4117(16), Ti1−C22 = 2.4279(16), Ti1−C23 = 2.4152(16), Ti1−C24 = 2.3386(17), Ti1−C25 = 2.3632(17), Ti1−Cl1 = 2.3506(5), Ti1−Cl2 = 2.3397(5), C1−C6 = 1.507(2), C21−C26 = 1.510(2), Ti1−Ct1 = 2.070, Ti1−Ct2 = 2.070; Ct1−Ti1−Ct2 = 132.6, Cl1−Ti1−Cl2 = 95.32. Ct1 = centroid of C1−C5; Ct2 = centroid of C21−C25.

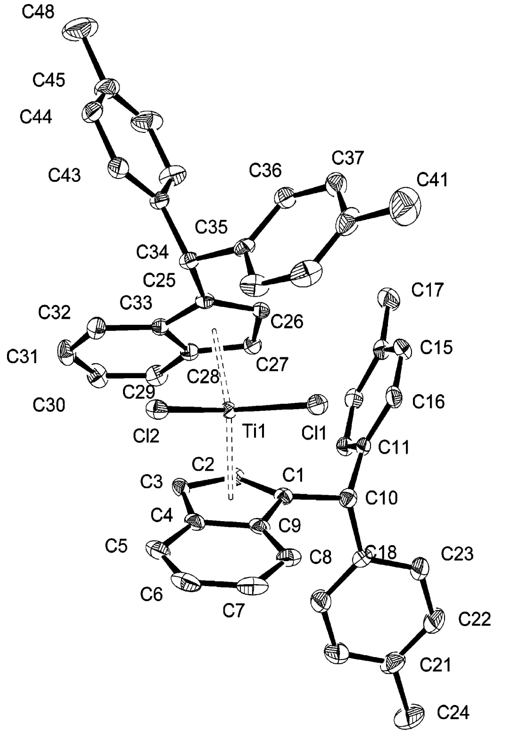


Figure 12. Molecular structure of **10** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−C1 = 2.493(2), Ti1−C2 = 2.355(2), Ti1−C3 = 2.308(2), Ti1−C4 = 2.552(2), Ti1−C9 = 2.626(2), Ti1−C25 = 2.450(2), Ti1−C26 = 2.373(2), Ti1−C28 = 2.494(2), Ti1−C33 = 2.521(2), C1−C10 = 1.512(3), C25−C34 = 1.508(3), Ti1−Cl1 = 2.3026(6), Ti1−Cl2 = 2.3192(6), Cl1−Ti−Cl2 = 97.61(3), Ct1−Ti−Ct2 = 131.69(2). Ct1 = centroid of C1−C4, C9; Ct2 = centroid of C25−C28, C33.

Using the classification of Cp_2MX_2 conformations,[32] the bis(fulvene) complexes **3** and **7** can be attributed to class I compounds, where the five-membered rings of the fulvene ligands are essentially staggered and one carbon atom of each ring lies over the C_{exo}−Ti−C_{exo} fragment. On the other hand, the bis(indenyl) complex **10** can be attributed to class II compounds (Cp rings staggered, three carbons over MX_2). Additionally, the coordination mode of indenyl ligands was classified using different parameters to explain distortions in the metal−indenyl bond.[33] A detailed discussion of comparable parameters has been given for indenylthorium complexes,[34] which seems to be useful to apply to the titanium complexes given here. The slip distortion Δ_{M-Ca} of 0.121 Å ($\Delta_{M-Ca} = 0.5[M-C_c + M-C_d] - 0.5[M-C_{ipso} + M-C_b]$)[34] and the

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(30) Ti−Cl = 2.352(1), 2.346(1) Å in $Cp^*{}_2TiCl_2$: (a) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457−466. Ti−Cl = 2.364(3) Å in Cp_2TiCl_2: (b) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622−1629.

(31) Cozak, D.; Melnik, M. *Coord. Chem. Rev.* **1986**, *14*, 53−99.

(32) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.

planar indenyl ring systems of **10** are consistent with a η^5-coordinated indenyl ligand. For a perfect η^5 coordination, the "slip parameter" $\Delta_{M-C} = 0$, while for η^3-bonded complexes Δ_{M-C} ranges from 0.69 to 0.79 Å.[35] The conformational preference of the substituted indenyl ligand in **10** can be described by the dihedral angle ($C_2-Ct-Ct'-C_{26}$) of 104.9°. This conformation allows sufficient distances between the sterically demanding substituents on adjacent indenyl rings. Similar values are found in the case of bulky substituted bis(indenyl)zirconium halides.[36]

Conclusions

An efficient procedure for the synthesis of bis(fulvene)titanium complexes based on the reaction of $TiCl_3{\cdot}3THF$, with magnesium as reducing agent and exocyclic bulky substituted pentafulvenes could be established. In comparison with the known pathway using bis(toluene)titanium(0) this reductive approach employs common starting materials and makes this protocol a very attractive way for the preparation of chiral bis(fulvene)titanium complexes. Using prochiral benzofulvene ligands, this approach also offers the possibility to prepare group 4 metal complexes in a diastereoselective manner. Due to the nucleophilic character of the exocyclic carbon of the bis(pentafulvene) complexes subsequent products can be expected in reactions with electrophiles, as shown for the formation of the corresponding titanocene chlorides.

Experimental Section

General Considerations. Unless otherwise noted, all reactions were carried out under an inert atmosphere of argon or nitrogen using standard glovebox and Schlenk techniques. Solvents were dried according to standard procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer (^1H, 500.1 MHz; ^{13}C 125.8 MHz). Variable-temperature ^1H NMR experiments were conducted on a Bruker Avance 300.1 MHz spectrometer. The ^1H NMR chemical shifts were referenced to residual protons of the solvent. The ^{13}C NMR spectra were referenced to benzene-d_6 or THF-d_8, respectively (signal assignment based upon NOE measurements). Electron impact (EI) mass spectra were taken on a Finnigan-MAT 95 spectrometer. IR spectra were recorded on a Bio-Rad FTS-7 spectrometer using KBr pellets. Elemental analyses were carried out by the Analytischen Laboratorien in Lindlar (Lindlar, Germany). $TiCl_3{\cdot}3THF$ was prepared according to the literature method.[37] The fulvenes were prepared according to literature procedures (**1**,[38] **2**,[39] **5**[18]).

Compound 3. A 0.697 g (2.698 mmol) portion of **1**, 0.5 g of $TiCl_3{\cdot}3THF$ (1.349 mmol), and 0.049 g of magnesium turnings (2.024 mmol) were placed in a Schlenk tube. A 30 mL amount of THF was added, and the reaction mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo, and the resulting residue was extracted with 75 mL of hot *n*-hexane (65 °C). Filtration and solvent removal yielded 570 mg (75%) of **3** as a green solid. X-ray-quality crystals were obtained upon slow cooling of a saturated hot *n*-hexane/toluene (50/50) solution of **3** to room temperature. Mp: 154 °C. IR (KBr): $\tilde{\nu}$ 3016 (m), 2916 (m), 2861 (w), 1504 (s), 1437 (m), 1186 (w), 1110 (m), 1019 (m), 807 (s), 760 (m), 573 (s) cm^{-1}. MS (70 eV): *m*/*z* (relative intensity) 564 (5) $[M]^+$, 258 (100) $[(p\text{-tolyl}_2)fv]^+$. Anal. Calcd for $C_{40}H_{36}Ti$: C, 85.09; H, 6.41. Found: C, 84.79; H, 6.46. ^1H NMR (benzene-d_6, 300 K): δ 2.09 (s, 6H, CH_3), 2.09 (s, 6H, CH_3), 4.20 (m, 2H, H_b), 4.96 (m, 2H, H_a), 5.88 (m, 2H, H_c), 6.53 (m, 2H, H_d), 6.53 (m, 4 H, tolyl C*H*), 6.62 (m, 4 H, tolyl C*H*), 6.84 (m, 4 H, tolyl C*H*), 7.31 (m, 4 H, tolyl C*H*). ^{13}C NMR (C_6D_6, 300 K): δ 20.9, 21.0 (CH_3), 108.8 (C_a), 110.0 (C_b), 112.0 (C_{exo}), 116.5 (C_d), 121.7 (C_c), 127.5, 128.5, 128.8, 129.8 (tolyl *C*H), 132.6 (C_{ipso}), 133.9, 134.9, 140.3, 143.0 (tolyl *C*).

Compound 4. A 0.535 g (2.698 mmol) portion of **2**, 0.5 g of $TiCl_3{\cdot}3THF$ (1.349 mmol), and 0.049 g of magnesium turnings (2.024 mmol) were placed in a Schlenk tube. A 30 mL amount of THF was added, and the reaction mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo, and the resulting residue was extracted with 75 mL of hot *n*-hexane (65 °C). Filtration and solvent removal yielded 417 mg (70%) of **4** as a turquoise-blue solid. Mp: 135 °C. IR (KBr): $\tilde{\nu}$ 2897 (s), 2842 (m), 1441 (m), 1262 (m), 1096 (s), 1044 (m), 943 (w), 799 (m), 779 (s), 690 (m), 582 (w) cm^{-1}. MS (70 eV): *m*/*z* (relative intensity) 444 (25) $[M]^+$, 198 (100) $[\text{adamantylfv}]^+$. Anal. Calcd for $C_{30}H_{36}Ti$: C, 81.07; H, 8.16. Found: C, 80.93; H, 8.32. ^1H NMR (benzene-d_6, 300 K): δ 0.57−2.52 (m, 28H, adamantyl C*H*/C*H*$_2$), 4.63 (m, 2H, H_a), 4.84 (m, 2H, H_b), 6.06 (m, 2H, H_c), 6.55 (m, 2H, H_d). ^{13}C NMR (benzene-d_6, 300 K): δ 28.42, 30.28, 32.00, 33.18, 36.98, 37.15, 38.51, 43.60, 43.89 (adamantyl *C*H/*C*H$_2$), 110.8 (C_a), 111.9 (C_b), 113.3 (C_{exo}), 115.0 (C_d), 116.9 (C_b), 133.4 (C_{ipso}).

Compound 6. A 9.5 mL (0.082 mol) portion of freshly distilled indene was dissolved in 150 mL of THF, and 51.3 mL of *n*-BuLi (1.6 M solution in *n*-hexane, 0.082 mol) was added dropwise at 0 °C. Over 0.5 h the reaction mixture was stirred at 0 °C, cooled to −78 °C, and 12.32 g (0.082 mol) of 2-adamantanone, dissolved in 120 mL of THF, was added. After the mixture was stirred for 8 days at room temperature, the resulting suspension was treated with water, followed by extraction with ether (3 × 150 mL). The combined organic layers were washed neutral with H_2O and dried over Na_2SO_4, and the solvents were removed under reduced pressure. The residue was dissolved in 200 mL of *n*-hexane, and crude **6** was precipitated by rapidly cooling with liquid nitrogen for a few seconds. Pure **6** was obtained after chromatography of the crude material on silica gel (eluent *n*-hexane) as a pale yellow microcrystalline solid (yield 9.99 g (49%)). Mp: 121 °C. IR (KBr): $\tilde{\nu}$ 3096 (w), 3059 (w), 3031 (w), 2962 (w), 2912 (s), 2847 (s), 1620 (s), 1450 (s), 1344 (m), 1182 (m), 1085 (m), 1021 (m), 951 (m), 896 (m), 744 (s), 725 (s) cm^{-1}. ^1H NMR (benzene-d_6, 300 K): δ 1.71−1.82 (m, 12H, adamantyl C*H*/C*H*$_2$), 3.15 (m, 1H, adamantyl C*H*), 3.89 (m, 1H, adamantyl C*H*), 6.73 (m, $^3J_{H,H} = 5.5$ Hz, 1H, H_b), 6.84 (m, $^3J_{H,H} = 5.5$ Hz, 1H, H_a), 7.12 (m, 2H, benzo C*H*), 7.16 (m, 1H, benzo C*H*), 7.31 (m, 1H, benzo C*H*), 7.81 (m, 1H, benzo C*H*). ^{13}C NMR (benzene-d_6, 300 K): δ 28.3, 35.1, 37.0, 37.4, 39.4, 40.2 (adamantyl *C*H/*C*H$_2$), 121.4, 124.0, 125.0, 126.2 (benzo *C*H), 127.0 (C_a), 128.5 (C_b), 131.3 (C_{ipso}), 136.6 (C_d), 145.5 (C_c), 159.9 (C_{exo}).

Compound 7. A 0.832 g (2.698 mmol) portion of **5**, 0.5 g of $TiCl_3{\cdot}3THF$ (1.349 mmol), and 0.049 g of magnesium (2.024 mmol) were placed in a Schlenk tube. A 30 mL amount of THF was added, and the reaction mixture was stirred at room temperature for 8 h. The solvent was removed in vacuo, and the resulting residue was extracted with 60 mL of toluene. After filtration and removal of

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Table 4. Crystal Structure Data for Compounds 3 and 6−10

	3	**6**	**7**	**8**	**9**	**10**
empirical formula	$C_{40}H_{36}Ti$	$C_{19}H_{20}$	$C_{48}H_{40}Ti$	$C_{38}H_{40}Ti$	$C_{43}H_{45}Cl_2Ti$	$C_{55}H_{50}Cl_2Ti$
fw	564.59	248.35	664.70	544.60	680.59	829.75
color habit	green needles	pale yellow plates	dark brown plates	dark brown prisms	red needles	red needles
cryst dimens, mm	1.00 × 0.36 × 0.11	0.45 × 0.22 × 0.03	0.40 × 0.25 × 0.25	0.40 × 0.13 × 0.09	1.10 × 0.37 × 0.21	0.83 × 0.15 × 0.09
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	*Pbca*	$C2/c$	$P2_1$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	16.7551(7)	18.9376(13)	12.1107(7)	9.9273(3)	10.8634(5)	8.1551(3)
b, Å	21.3806(5)	6.8725(3)	11.2973(6)	12.9692(5)	11.7578(5)	15.8776(7)
c, Å	16.9183(4)	21.8990(16)	14.1304(9)	21.7517(7)	16.4825(9)	34.2942(14)
α, deg	90	90	90	90	71.487(5)	90
β, deg	90	103.008(9)	109.870(7)	93.293(3)	81.618(6)	93.593(5)
γ, deg	90	90	90	90	63.231(5)	90
V, Å^3	6060.7(3)	2777.0(3)	1818.20(18)	2795.89(16)	1782.40(15)	4431.8(3)
Z	8	8	2	4	2	4
D_{calcd}, g cm^{-3}	1.238	1.188	1.214	1.294	1.268	1.244
μ, mm^{-1}	0.309	0.067	0.268	0.332	0.419	0.350
T, K	193(2)	193(2)	193(2)	193(2)	193(2)	153(2)
θ range, deg	2.25−26.00	2.21−26.04	2.54−25.96	2.45−26.00	2.20−25.91	2.20−26.02
no. of rflns collected	50 825	11 875	19 323	23 431	21 874	36 443
no. of indep rflns	5683 (R(int) = 0.0645)	2618 (R(int) = 0.0765)	6821 (R(int) = 0.0767)	5159 (R(int) = 0.0773)	6474 (R(int) = 0.0423)	8209 (R(int) = 0.0669)
no. of rflns with $I > 2\sigma(I)$	3776	1462	5215	3186	4953	5832
abs cor	numerical	none	numerical	none	none	none
max, min transmissn	0.9668 and 0.7474	0.9980 and 0.9707	0.9360 and 0.9003	0.9707 and 0.8786	0.9171 and 0.6554	0.9692 and 0.7598
final R indices ($I > 2\sigma(I)$)	R1 = 0.0454, wR2 = 0.1176	R1 = 0.0383, wR2 = 0.0762	R1 = 0.0416, wR2 = 0.0867	R1 = 0.0359, wR2 = 0.0633	R1 = 0.0285, wR2 = 0.0691	R1 = 0.0412, wR2 = 0.0891
R indices (all data)	R1 = 0.0724, wR2 = 0.1282	R1 = 0.0842, wR2 = 0.0870	R1 = 0.0591, wR2 = 0.0917	R1 = 0.0741, wR2 = 0.0706	R1 = 0.0427, wR2 = 0.0728	R1 = 0.0672, wR2 = 0.0973
absolute struct param			−0.02(2)			

the solvent crude **7** was washed with a minimum amount of *n*-hexane, leading to 610 mg (68%) of pure **7** as a dark brown solid. Single crystals suitable for X-ray diffraction were obtained upon recrystallization from *n*-hexane at room temperature. Mp: 139 °C dec. IR (KBr): $\tilde{\nu}$ 3011 (m), 2909 (m), 2857 (w), 1603 (w), 1503 (s), 1422 (m), 793 (s), 766 (s), 735 (s), 567 (s) cm^{-1}. MS (70 eV): *m/z* (relative intensity) 664 (10) [M]$^+$, 308 (100) [(*p*-tolyl)$_2$benzofv]$^+$. Anal. Calcd for $C_{48}H_{40}Ti$: C, 86.73; H, 6.07. Found: C, 85.99; H, 6.72. ^{1}H NMR (THF-d_8, 275 K): δ 2.20 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.94 (d, $^3J_{H,H}$ = 3.4 Hz, 1H, H$_b$), 4.19 (d, $^3J_{H,H}$ = 3.4 Hz, 1H, H$'_b$), 4.36 (m, 1 H, benzo CH), 5.17 (d, $^3J_{H,H}$ = 3.4 Hz, 1H, H$_a$), 6.20 (m, 1 H, benzo CH), 6.26 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, benzo CH), 6.37 (dd, $^3J_{H,H}$ = 8.7 and 6.7 Hz, 1H, benzo CH), 6.65 (d, $^3J_{H,H}$ = 8.7 Hz, benzo CH), 6.72 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, benzo CH), 6.81 (m, 4H, tolyl CH), 6.87 (m, 7H, aryl CH), 6.96−7.02 (m, 2H, aryl CH), 7.11 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, benzo CH), 7.28 (d, $^3J_{H,H}$ = 3.4 Hz, 1H, H$'_a$), 7.32 (dd, $^3J_{H,H}$ = 8.0 and 7.3 Hz, benzo CH), 7.69 (m, 1H, tolyl CH). ^{13}C NMR (THF-d_8, 275 K): δ 20.0, 20.1, 20.2, 20.2 (CH$_3$), 109.4 (C$_b$), 110.6 (C$'_b$), 114.3 (C$_{exo}$), 114.6 (C$'_{exo}$), 116.4 (C$'_a$), 120.7 (benzo CH), 121.9 (C$_a$), 123.0 (benzo CH), 123.3 (C$_c$), 124.2 (benzo CH), 125.6 (C$'_{ipso}$), 125.6 (C$'_d$), 125.7 (benzo CH), 126.6 (C$_d$), 126.6, 127.0 (benzo CH), 127.9 (C$'_c$ and 7 tolyl CH), 128.3, 128.5, 128.6, 128.9, 128.9, 128.9, 128.9, 129.1 (tolyl CH), 130.6 (benzo CH), 131.7 (C$_{ipso}$), 133.0 (tolyl CH), 133.1, (benzo CH), 133.1 (tolyl C), 133.6, 134.3, 134.6, 140.4, 141.7, 143.2, 143.8 (tolyl C).

Compound 8. A 0.670 g (2.698 mmol) portion of **6**, 0.5 g of $TiCl_3{\cdot}3THF$ (1.349 mmol), and 0.049 g of magnesium (2.024 mmol) were placed in a Schlenk tube. A 30 mL amount of THF was added, and the reaction mixture was stirred at room temperature for 8 h. The solvent was removed in vacuo, and the resulting residue was extracted with 60 mL of toluene. After filtration and removal of the solvent crude **8** was washed with a minimum amount of *n*-hexane, leading to 330 mg (45%) of pure **8** as a dark brown solid. Single crystals suitable for X-ray diffraction were obtained upon recrystallization from *n*-hexane (−20 °C). Mp: 160 °C dec. IR (KBr): $\tilde{\nu}$ 3079 (w), 3030 (w), 2898 (s), 2842 (m), 1442 (s), 1416 (m), 1338 (m), 1213 (m), 1096 (m), 1045 (m), 952 (m), 839 (m), 776 (s), 740 (m) cm^{-1}. MS (70 eV): *m/z* (relative intensity) 545 (10) [M]$^+$, 248 (100) [adamantylbenzofv]$^+$. Anal. Calcd for $C_{38}H_{40}Ti$: C, 83.81; H, 7.40. Found: C, 83.41; H, 7.59. ^{1}H NMR (benzene-d_6, 300 K): δ −0.15 to 2.79 (m, 28H, adamantyl CH/CH_2), 3.07 (m, 1H, H$_b$), 4.81 (m, 1H, H$_a$), 5.37 (m, 1H, H$'_b$), 7.13 (m, 1H, H$'_a$), 6.48−7.92 (m, 8H, benzo H). ^{13}C NMR (benzene-d_6, 300 K): 27.8, 28.1, 30.0, 30.2, 32.3, 33.2, 34.3, 34.8, 35.6, 36.2, 36.8, 37.7, 38.4, 38.5, 43.8, 44.2, 44.6, 45.2 (adamantyl CH/CH$_2$), 106.2 (C$'_b$), 107.3 (C$_b$), 116.6 (C$'_a$), 117.3 (C$_{exo}$), 120.4 (C$'_{exo}$), 121.2 (benzo CH), 122.5, 123.8 (C$_a$), 124.0 (C$_c$), 125.8 (benzo CH), 126.5 (C$_d$, C$'_c$, or C$'_d$ (assignment could be interchanged)), 126.6 (C$_d$, C$'_c$, or C$'_d$ (assignment could be interchanged)), 127.1 (C$'_{ipso}$), 124.6, 124.6, 127.1, 130.8 (benzo CH), 133.4 (C$_{ipso}$) 133.7 (benzo CH).

Compound 9. A 0.400 g (0.708 mmol) portion of **3** was dissolved in 40 mL of *n*-hexane, and while this mixture was stirred, 1.42 mL of a 1 M HCl/diethyl ether solution (1.416 mmol) was added via syringe at ambient temperature. Immediately a color change from green to red occurred and after a few minutes **9** started to precipitate as red needle-shaped crystals. After 6 h **9** (0.110 g, 24%) was filtered off, rinsed with a minimum amount of *n*-hexane, and dried in vacuo. A second crop of amorphous **9** (0.090 g, 20%) was obtained after concentrating the mother liquor to 10 mL and cooling to −20 °C for 12 h. X-ray-quality crystals were obtained from a saturated *n*-hexane solution of **9**. Mp: 123−125 °C. IR (KBr): $\tilde{\nu}$ 3021 (w), 2920 (m), 2854 (w), 1510 (s), 821 (s), 762 (s) cm^{-1}. MS (70 eV): *m/z* (relative intensity) 601 (40) [M − HCl]$^+$, 656 (5) [M − 2 HCl]$^+$, 377 (100) [M − $C_{20}H_{19}$]$^+$. Anal. Calcd for $C_{40}H_{38}Cl_2Ti$: C, 75.45; H, 6.01. Found: C, 75.65; H, 6.78. ^{1}H NMR (C_6D_6, 300 K): δ 2.07 (s, 12H, CH_3), 5.65 (m, 4H, C$_5$$H_4$), 5.98 (s, 2H, C$_{exo}$$H$), 6.01 (m, 4H, C$_5$$H_4$), 6.91 (m, 8H, tolyl C$H$), 7.09 (m, 8H, tolyl C$H$). ^{13}C NMR (benzene-$d_6$, 300 K): δ 20.9 (CH$_3$), 52.0 (C$_{exo}$), 118.6, 120.9 (C_5H$_4$), 129.3, 129.5 (tolyl CH), 136.3 (tolyl C), 140.3 (C$_{ipso}$), 141.3 (tolyl C).

Compound 10. To a solution of 0.150 g of **7** (0.226 mmol) in 15 mL of toluene was added 0.45 mL of a 1 M HCl/diethyl ether solution (0.451 mmol) at room temperature. After it was stirred for 0.5 h, the reaction mixture was concentrated to 8 mL and covered with a layer of *n*-hexane. After 3 days **10** could be isolated as dark red needle-shaped crystals (0.085 g, 51%), which were suitable for X-ray diffraction. Mp: 147−149 °C dec. IR (KBr): $\tilde{\nu}$ 3023 (w), 2915 (m), 2857 (w), 1509 (s), 1435 (w), 1261 (w), 1211 (m), 1188 (w), 1110 (m), 1201 (m), 822 (m), 800 (s), 786 (m), 765 (m), 733 (m), 574 (m), 488 (m) cm^{-1}. MS (70 eV): *m*/*z* (relative intensity) 700 (4) $[M - HCl]^+$, 392 (10) [M − HCl − (*p*-tolyl)$_2$benzofv]$^+$, 309 (100) [(*p*-tolyl)$_2$benzofv + H]$^+$, 195 (65) [(*p*-tolyl)$_2$CH]$^+$. Anal. Calcd for $C_{48}H_{42}Cl_2Ti$: C, 78,16; H, 5.74. Found: C, 77.99; H, 5.66. ^1H NMR (benzene-d_6, 300 K): δ 1.97 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 4.34 (m, 2H, H_a or H_b), 6.23 (m, 2H, H_a or H_b), 6.55 (s, 2H, $C_{exo}H$), 6.76 (m, 6H, aryl C*H*), 6.82 (m, 4H, aryl C*H*), 6.98 (m, 8H, aryl C*H*), 7.40 (m, 4H, aryl C*H*), 7.48 (m, 2H, aryl C*H*). ^{13}C NMR (benzene-d_6, 300 K): δ 20.8 (*C*H_3), 21.0 (*C*H_3), 50.9 (C_{exo}), 106.4 (C_a or C_b), 122.1 (C_a or C_b), 126.5 (aryl *C*H), 126.6 (aryl *C*H), 128.9 (aryl *C*H), 129.3 (aryl *C*H), 129.4 (aryl *C*H), 130.4 (aryl *C*H), 135.1, 135.8, 136.4, 139.4, 141.6, (all quat C).

X-ray Diffraction. Single-crystal experiments were carried out on a Stoe IPDS diffractometer with graphite -monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.[40] Crystallographic details are given in Table 4.

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Supporting Information Available: Figures and tables giving stereochemical assignments and detailed NMR data and CIF files giving crystallographic data for **3** and **6**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org. Additional crystallographic data for the structures **3** and **6**−**10** have been deposited with the Cambridge Data Centre as Supplementary Publication Nos. CCDC 284301 (**3**), CCDC 284297 (**6**), CCDC 284298 (**7**), CCDC 284299 (**8**), CCDC 284300 (**9**), and CCDC 284296 (**10**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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