

PREPARATION AND CRYSTAL STRUCTURES OF LOW-VALENT ZIRCONOCENE COMPLEXES CONTAINING TETRAMETHYL(PHENYL)CYCLOPENTADIENYL LIGANDS

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organometallic Group IVB chemistry.

Zirconocene complex $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]$ (**1**) prepared by metathesis of the appropriate lithium cyclopentadienide and ZrCl_4 was reduced with magnesium in tetrahydrofuran in the presence of excess bis(trimethylsilyl)acetylene, yielding the low-valent complex $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (**2**). However, in addition to **2**, the reduction afforded an unexpected Zr(II) complex $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2(s\text{-trans-}\eta^4\text{-buta-1,3-diene)}]$ (**3**). Compounds **1–3** were characterized by spectroscopic methods and by X-ray single-crystal diffraction.

Keywords: Metallocenes; Zirconocenes; Bis(trimethylsilyl)acetylene; Low-valent zirconium complexes; Cyclopentadienyl ligand; Alkynes; Crystal structures; X-ray diffraction.

The low-valent zirconocene(II), Cp_2Zr ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$) is the simplest fragment among the precursors of zirconium metallocene complexes^{1a}. This fragment proves to be useful for both stoichiometric and catalytic reactions of zirconocene compounds, particularly in the synthesis of small molecules, in metallocene-assisted organic syntheses and for polymerization^{1b–1e}. Under such conditions, the zirconocene fragment typically coordinates the molecules of substrate, activates them and controls the formation of products; this mechanism is common in synthetic organic reactions. Typical examples of such reactions involve the formation of metalacycles from acetylenes, alkenes, diacetylenes, dialkenes, carbonyl compounds, imines, ketimines^{1f}; as well as reaction with terminal alkynes

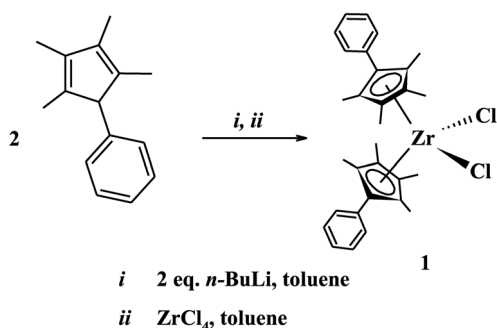
yielding linear dimers of these alkynes² and many others which are summarized in a number of reviews³. The $[\text{Cp}_2\text{Zr}^{\text{II}}]$ species is both coordinatively and electronically unsaturated and seeks stabilization by either coordinating molecules with triple or double bond having suitable orbitals to accommodate the two d electrons of Zr(II) atom or by coordinating ligands capable of electron donation. Hence, the preparation of such highly reactive species usually combines well defined precursors like Cp_2ZrCl_2 with a reducing agent – and in many cases another stabilizing molecule (PR_3 , THF, pyridine). A list of such systems can start with the reduction with *n*-BuLi forming $[\text{Cp}_2\text{Zr}(\eta^2\text{-butene})]$ (Negishi)^{4a}, reactions with EtMgCl to give $[\text{Cp}_2\text{Zr}(\eta^2\text{-ethene})]$ (Takahashi)^{4a}, continuing with examples of complexes with additional ligands like $[\text{Cp}_2\text{Zr}(\text{PR}_3)(\eta^2\text{-butene})]$ ^{4b}, $[\text{Cp}_2\text{Zr}(\eta^4\text{-buta-1,3-diene})]$ ^{4c} and, at the end of this list, the reduction of Cp_2ZrCl_2 with Mg in the presence of bis(trimethylsilyl)acetylene (BTMSA) affording $[\text{Cp}_2\text{Zr}(\eta^2\text{-btmsa})]$ complexes which require the coordination of an additional ligand like thf ^{4d}, or pyridine^{4e}.

The investigations as to which ligand or molecule is more useful for stabilizing the zirconocene fragment quite frequently has to deal also with the effect of substituents on the cyclopentadienyl ligand. It has been well established that the presence of methyl substituents at the cyclopentadienyl ring increases the electron density at the metal centre, this effect being more pronounced with increasing number of methyl groups. The chemical properties rapidly change in the range of methyl-substituted zirconocene complexes starting from the unsubstituted up to the permethylated derivative⁵. The properties of permethylated metallocene compounds can be further finely tuned by substituting one methyl group on both cyclopentadienyl rings for a different substituent^{6a}. The substituent properties are important in the case of low-valent metallocene complexes since they have an important influence on the electronic properties of the metal centre, which is active in catalytic reactions. In addition, the steric effects of bulky substituents appear to be of high importance, although a proper understanding of this influence (especially for solutions) still needs further elaboration^{6b}.

In this work we report the synthesis of a new zirconocene dichloride complex **1** with one phenyl substituent on each tetramethylcyclopentadienyl ring and its reduction with magnesium in an effort to prepare the low-valent zirconocene complex with coordinated bis(trimethylsilyl)acetylene.

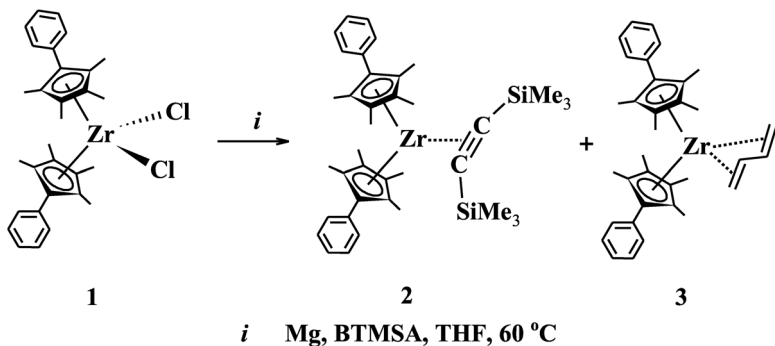
RESULTS AND DISCUSSION

Synthesis of zirconocene dichloride complex $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]$ (**1**) was carried out by a standard method.^{5b} The lithium 2,3,4,5-tetramethyl-1-phenylcyclopentadienide⁷ was prepared in situ by deprotonation of the corresponding cyclopentadiene with *n*-BuLi in toluene. Subsequent transmetalation of the lithium salt with ZrCl_4 gave the corresponding zirconocene dichloride **1** in a high yield (Scheme 1).



SCHEME 1

The reduction of **1** was conducted in hot (60 °C) THF with activated magnesium in the presence of excess BTMSA. The progress of reaction was easily followed by the color changes, as the initially yellow solution slowly turned to intense green (within 5 days). The reduction products were separated by fractional crystallization from hexane. Whereas the less soluble green fraction yielded crystals of the desired complex $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (**2**), the more soluble part after crystallization at -18 °C afforded yellow crystals, which were identified by X-ray single crystal diffraction (vide infra) as (*s*-*trans*- η^4 -buta-1,3-diene)-zirconocene complex **3** (Scheme 2).



SCHEME 2

All isolated complexes were characterized by standard spectroscopic methods. The ^1H and ^{13}C NMR spectra of complexes **1** and **2** are consistent with the AA'BB' spin system for methyl groups bonded to cyclopentadienyl rings. A notable feature in the ^{13}C NMR spectrum of **2** is the large downfield shift of the triple-bonded carbons (δ_{C} 259.83 ppm) typical of η^2 -acetylenic coordination to a zirconocene moiety^{5b,6}. The zirconocene complex **3** has C_2 symmetry in solution as expected for *s-trans*-butadiene coordination. The symmetry relation leads to the presence of only one set of signals in ^1H and ^{13}C NMR spectra for both η^5 -coordinated cyclopentadienyl rings; however, the methyl groups on each ring are mutually non-equivalent (ABCD spin system). The coupling constant between the geminal vinyl protons in the butadiene moiety was small ($^2J_{\text{HH}} = 4.5$ Hz) as a consequence of *s-trans* conformation of buta-1,3-diene⁸.

The EI-MS measurements of complex **1** showed the molecular ion with abundance around 34%, the most intense fragment species being $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{Ph})]^+$; a loss of the $(\eta^5\text{-C}_5\text{Me}_4\text{Ph})$ ligand is typical of highly substituted zirconocene dichloride complexes. On the other hand, in the case of low-valent zirconocene compounds **2** and **3**, the molecular ion was either not observed at all or had a lower abundance in comparison with the corresponding zirconocene dichloride. This is in accordance with a stronger coordination of butadiene in comparison with the BTMSA molecule to the zirconium atom. Specifically, the peak attributable to $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]^+$ had the highest abundance in the mass spectra of **2** and **3**. The IR spectra of complexes **1**, **2**, **3** show vibrations characteristic of the phenyl ring: the =C–H stretching vibrations of phenyl ring in the range 3060–3023 cm^{-1} , the C=C stretching vibration of phenyl ring in the range 1601–1599 cm^{-1} , the ring vibration of phenyl ring in the range 1507–1504 cm^{-1} , and the =C–H bending vibrations of monosubstituted phenyl at 759 and 705 cm^{-1} . The btmsa complex **2** exhibits both typical vibrations of the SiMe_3 groups at 1244 and 854 cm^{-1} , which are absent in IR spectra of **1** and **3**. The stretching vibration of the C≡C bond of 1515 cm^{-1} in complex **2** corresponds to the value found for $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (1516 cm^{-1})^{5b}. Assignment of butadiene vibrations in **3** is prevented by their overlap with those of the phenyl group.

Although in principle, there are two possible “sources” (BTMSA or THF) of the butadiene moiety in the complex **3**, the former one (which could form butadiene motif by a C–C coupling of two acetylenic units, followed by a cleavage of the trimethylsilyl groups) is strongly disfavored by steric reasons⁹. Thus we prefer the possibility of butadiene being generated from a THF molecule, since the latter already possesses the chain of four

carbon atoms. This explanation is supported by the fact that several works have already demonstrated THF as a solvent is much less inert than generally assumed. The nucleophilic cleavage of the C–O bond in THF coordinated to zirconium was observed both with phosphines and tertiary amines¹⁰. On the other hand, activated magnesium in the presence of transition metal salts is capable of slow insertion into the C–O bond to form 2-magnesapyran^{11a}. Gilman reported the cleavage of THF by the Mg/MgI₂ system to give I(CH₂)₄OMgI^{11b}. The easy C–O cleavage of THF by a wide range of metal halides giving 4-halobutyl benzoates from benzoyl chloride even under mild conditions was published^{11c}. Moreover a photo-assisted ring opening of THF and its dimerization by zirconium complex [Zr(*n*-Bu)₂(OEt)₂] was recently published^{11d}. In the light of these facts, we expect the C–O cleavage in THF by Mg and/or zirconocene species and transfer of the activated molecule to the zirconocene moiety, although the mechanism of formation of **3** is still unclear. Further investigations in this direction are already in progress.

Crystal Structure of Compound **1**

The structure of zirconocene dichloride **1** is as expected. Both cyclopentadienyl ligands are η^5 -coordinated to the zirconium atom which, being tetravalent, is completed by two chlorine ligands in its coordination sphere (Fig. 1). The molecule is symmetrical with respect to the crystallographic two-fold axis, which passes through the zirconium atom and the centre of

TABLE I
Selected bond lengths (in Å) and angles (in °) for **1**

Bond lengths			
Zr1–Cl1	2.435(1)	Zr–C(Cp)	2.544(1)–2.595(1)
C(Cp)–C(Cp)	1.411(2)–1.438(2)	C(Cp)–C(Me)	1.500(2)–1.504(2)
C(Ph)–C(Ph)	1.380(3)–1.399(2)	C5–C6	1.484(2)
Cg1 ^a –Zr1	2.258(1)		
Bond angles			
Cl1–Zr1–Cl1'	94.75(2)	Cg1–Zr–Cg2	136.34(2)
Cg1–Zr–Cl1	105.02(2)	Cg1–Zr–Cl1'	104.15(2)
ϕ^b	46.0(1)	χ^c	44.6(1)

^a Cg1 denotes the centroid of the C1–C5 cyclopentadienyl ring. ^b Dihedral angle subtended by the cyclopentadienyl least-squares planes. ^c Dihedral angle between the least-squares planes of the C(1–5) cyclopentadienyl ring and the C(6–11) phenyl ring. Symmetry ('): –x, y, 1/2 – z

the line defined by the two chlorine atoms. Thus, only one half of the molecule is located in the asymmetric unit, while its second part is generated through the crystallographic two-fold axis. The list of selected bond distances and angles is given in Table I.

The bond distance Zr1-Cl1 is 2.435(1) Å is similar to those values found for $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{HMe}_4)_2]$ ^{12a} (2.434(3) Å), $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)]$ ^{12b} (2.438(2) Å), $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{EtMe}_4)_2]$ ^{12c} (2.444(13) Å), $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H-2,3-Me}_2\text{-1,4-Ph}_2)_2]$ ^{12d} (2.432(1) Å). On the other hand, the angle between the least-squares planes of the cyclopentadienyl rings is 46.0(1)°, about 7° smaller than in complexes $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H-2,3-Me}_2\text{-1,4-Ph}_2)_2]$ ^{12d} (54.34(6)°) or $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{HMe}_4)_2]$ ^{12a} (53.7(4)°). This difference can be explained by the presence of H atoms on the cyclopentadienyl rings in the reference compounds (this phenomenon will be discussed later for **2**). The ϕ value in **1** is similar to those reported for complexes with fully substituted cyclopentadienyl rings $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)]$ ^{12b} and $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{EtMe}_4)_2]$ ^{12c}. The angles between the cyclopentadienyl ring and the plane of its phenyl substituent is 44.6(1)°.

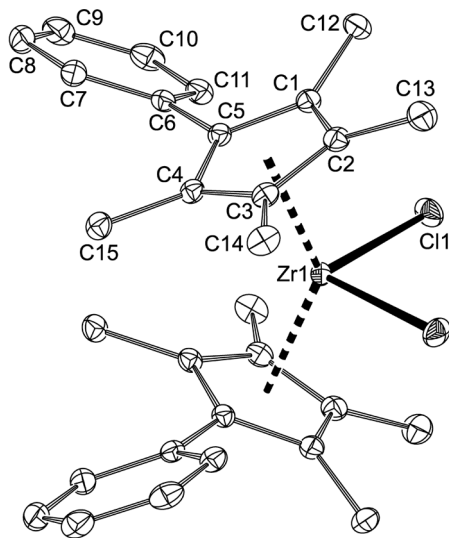


FIG. 1

PLATON drawing of compound **1** at the 30% probability level, with atom labeling scheme. Hydrogen atoms are omitted for clarity

Crystal Structure of Compound 2

Compound **2** crystallizes in the $P\bar{1}$ space group. The molecule is built up of two cyclopentadienyl ligands η^5 -coordinated to the zirconium atom, and one η^2 -coordinated molecule of BTMSA. Relevant geometric parameters (Fig. 2 and Table II) are comparable with those of similar crystal structures^{5b,6}. There are, however, some important fine differences in the present case. Both Zr–Cg distances 2.261(2) Å, 2.251(2) Å are longer than those found in the crystal structures of $[\text{Zr}(\eta^5\text{-C}_5\text{HMe}_4)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ ^{5b} (2.230(3) Å) but shorter than found in the crystal structure of $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{(SiMe}_3)_2)(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ ⁶ (2.275(3) Å). The bond distance between the acetylenic carbon atoms being 1.333(5) Å is among the largest reported for similar zirconocene complexes described, cf. 1.316(3) Å for $[\text{Zr}(\eta^5\text{-C}_5\text{HMe}_4)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$, 1.320(3) Å for $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ and 1.327(5) Å for $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{(SiMe}_3)_2)(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$. The bent zirconocene moiety having the phenyl groups oriented towards opposite sides along with the staggered conformation of the cyclopentadienyl ligands is a typical geometric feature for highly-substituted zirconocene⁶ and titanocene¹³ derivatives, since such an arrangement alleviates the steric repulsion of the coordinated BTMSA molecule. The Cg–Zr–Cg angle 139.2(1)°

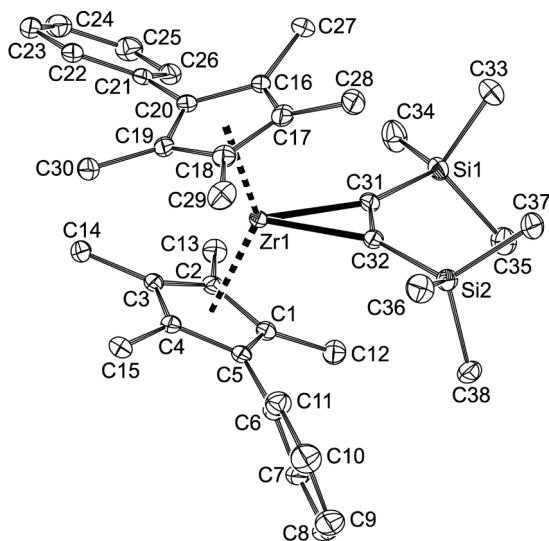


FIG. 2

PLATON drawing of compound **2** at the 30% probability level, with atom labeling scheme. Hydrogen atoms are omitted for clarity

is the same as in $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_3))_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (139.2(2)°) or $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (139.0(1)°) and about five degrees larger than in $[\text{Zr}(\eta^5\text{-C}_5\text{HMe}_4)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (134.5(1)°), which is in accordance with the position of hydrogen atoms at the hinge positions between the staggered rings in the octamethyl complex. Moreover, the angle between the least-squares planes of the cyclopentadienyl rings, ϕ , is 41.7(1)° in **2** and is close to that in $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (41.0(2)°) or $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_3))_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (41.5(2)°) but smaller than for $[\text{Zr}(\eta^5\text{-C}_5\text{HMe}_4)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (49.5(2)°). The plane constructed from the Zr and two acetylenic carbon atoms C(31), C(32) approximately bisected the ϕ angle with a small declination towards the cyclopentadienyl ring (C16–C20), where the phenyl substituent is more distant from the co-

TABLE II
Selected bond lengths (in Å) and angles (in °) for **2**

Bond lengths			
Zr1–C32	2.206(3)	Zr1–C31	2.207(3)
Zr–C(Cp)	2.534(3)–2.592(3)	C(Cp)–C(Cp)	1.406(5)–1.443(4)
C(Cp)–C(Me)	1.496(5)–1.514(5)	C(Ph)–C(Ph)	1.364(5)–1.414(5)
C5–C6	1.479(5)	C20–C21	1.477(5)
C31–C32	1.333(5)	Cg1 ^a –Zr1	2.261(2)
Cg2 ^a –Zr1	2.251(2)		
Bond angles			
C32–Zr1–C31	35.17(12)	Si1–C31–Zr1	154.11(19)
Si2–C32–Zr1	151.70(19)	C31–C32–Si2	135.8(3)
C32–C31–Si1	133.5(3)	C31–C32–Zr1	72.45(19)
C32–C31–Zr1	72.38(19)	Cg1–Zr–Cg2	139.23(6)
Cg1–Zr–C31	109.97(9)	Cg1–Zr–C32	110.12(9)
Cg2–Zr–C31	108.95(9)	Cg2–Zr–C32	108.53(9)
ϕ^b	41.7(1)	χ^c	49.6(1)
χ^d	42.5(1)		
Torsion angle			
Si1–C31–C32–Si2	1.7(5)		

^a Cg1 denotes the centroid of the C1–C5 cyclopentadienyl ring, Cg2 denotes the centroid of the C16–C20 cyclopentadienyl ring. ^b Dihedral angle subtended by the cyclopentadienyl least-squares planes. ^c Dihedral angle between the least-squares planes of the C(1–5) cyclopentadienyl ring and the C(6–11) phenyl ring. ^d Dihedral angle between the least-squares planes of the C(16–20) cyclopentadienyl ring and the C(21–26) phenyl ring.

ordinating BTMSA molecule. The angles between the least-squares of phenyl groups and their parent rings are $49.6(1)$ and $42.5(1)^\circ$. Such an arrangement is the consequence of solid-state packing, as both the Cp ligands and the Ph substituents exhibit an apparent π - π stacking between two neighboring molecules related through the crystallographic inversion centre (Fig. 3). Such a rotation of phenyl groups was observed also for titanocene complexes with this type of cyclopentadienyl substitution¹⁴. The second set of stabilizing forces in the solid state structure is due to the presence of Si-C bonds in the molecule. According to DFT studies on complexes carrying at least one SiMe₃ group¹⁵, the Si-C bonds are essentially of σ^* -character, causing the transfer of electron density away from the silicon atom towards the outer side of the methyl substituents. Consequently, the electron density around the SiMe₃ carbon atoms increases significantly, imparting an "aromatic" character to the SiMe₃ group as a whole, which thus becomes capable of secondary interactions with more distant centers. Such long-range interactions are possibly the explanation for (presumably stabilizing) interaction between two adjacent molecules (Fig. 4). Nevertheless, the interactions do not ensure the compact molecular packing as the large part of volume of unit cell (21%) is void, accessible to host small solvent molecules (see Experimental).

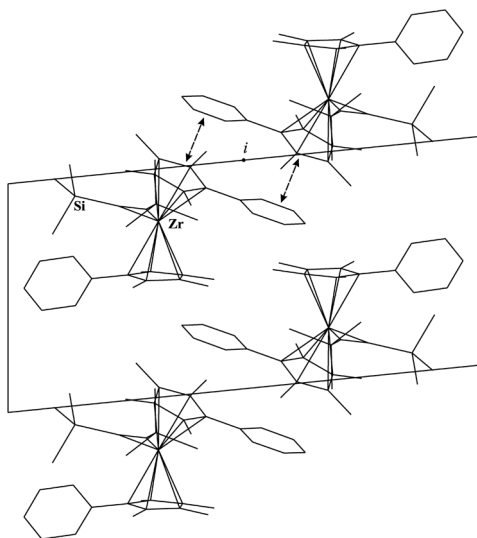


FIG. 3
Packing of **2** viewed along [010]

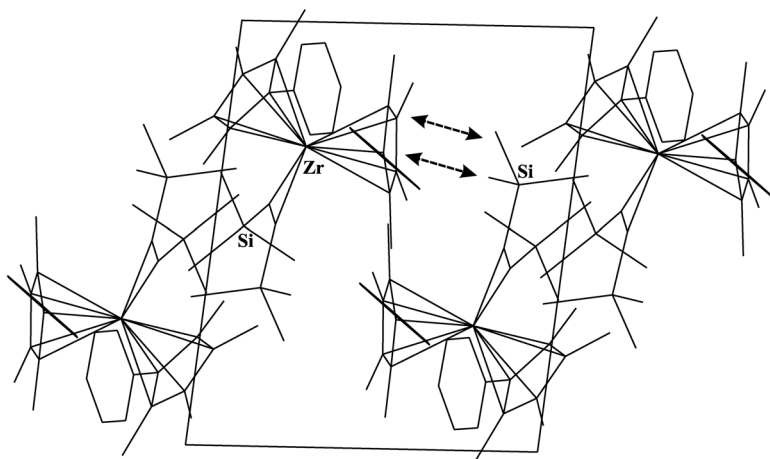


FIG. 4
Packing of **2** viewed along [001]

Crystal Structure of Compound 3

The complex with coordinated butadiene crystallizes with monoclinic lattice. Similarly to complex **1**, the molecule is symmetrical with respect to the crystallographic two-fold axis, passing through the zirconium atom and the center of the C17–C17' bond. Thus, only one half of molecule is symmetrically independent, the second part being generated by the symmetry operation $(-x, y, 1/2 - z)$. The molecule contains two η^5 -bonded cyclopentadienyl ligands and one η^4 -coordinated butadiene molecule (Fig. 5). Selected geometric parameters are listed in Table III. The angle between the cyclopentadienyl ligands in **3** ($46.9(1)^\circ$) is higher compared to **2** ($41.7(1)^\circ$) due to the larger steric requirements of the butadiene molecule, which is also reflected in more distant positions of both phenyl groups. The phenyl substituents are rotated from the plane of cyclopentadienyl ring by $48.4(1)^\circ$ as in the case of complex **2**. The butadiene molecule coordinated to zirconium atom adopts an *s-trans* conformation. In the complex **3** the internal C17–Zr1 distance ($2.372(2)$ Å) is about 0.1 Å shorter than the external C16–Zr1 ($2.461(2)$ Å) bond. The bond distances C(16)–C(17) ($1.401(3)$ Å) and C(17)–C(17') ($1.423(5)$ Å) are very similar while the torsion angle C(16)–C(17)–C(17')–C(16) is $119.9(3)^\circ$ close to the ideal value 120° . Only few examples of such type of coordination of butadiene to transition metals have been published¹⁶. On the other hand, the geometric parameters ob-

served for **3** do not differ much from those in other (*s-trans*- η^4 -butadiene)-zirconocene complexes^{16b,16c}.

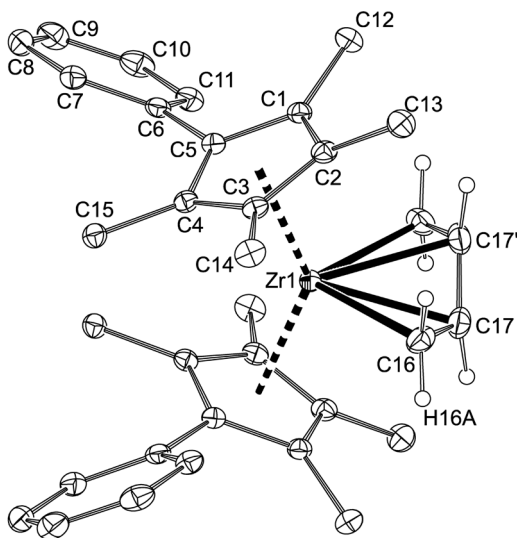


FIG. 5

PLATON drawing of compound **3** at the 30% probability level, with atom labeling scheme. Hydrogen atoms are omitted for clarity

Comparison of Crystal Structures 1–3

Despite the apparent different coordination environment and the character of the non-Cp ligands (two chlorides vs butadiene) present in **1** and **3**, the compounds are practically isostructural (Fig. 6). They crystallize in strikingly similar crystallographic lattices and with very similar distribution of the atoms forming the bent metallocene unit in them. This phenomenon is most probably due to the fact that the solid-state assembly is determined primarily by the packing of the bulky metallocene moieties while the unoccupied space can accommodate ligands with similar moderate sterical requirements. This explanation is supported by the fact that the interatomic C11–C11' distance in **1** (3.583(1) Å) compares well with the C16–C16' distance in **3** (3.596(4) Å) and by the fact that both structures are similarly stabilized through π - π stacking of adjacent aromatic systems (Cp, Ph). Clearly, the space required for the coordinated BTMSA in **2** is much larger, leading to a different distribution of the molecules and, hence, a different crystal structure.

TABLE III
Selected bond lengths (in Å) and angles (in °) for **3**

Bond lengths			
Zr1-C17	2.372(2)	Zr1-C16	2.461(2)
C16-C17	1.401(3)	C17-C17'	1.423(5)
C17-H17	1.01(2)	C16-H16A	0.96(2)
C16-H16B	0.90(3)	Zr-C(Cp)	2.559(2)–2.626(2)
C(Cp)–C(Cp)	1.413(3)–1.434(2)	C(Cp)–C(Me)	1.498(3)–1.510(3)
C5–C6	1.488(3)	C(Ph)–C(Ph)	1.375(3)–1.400(3)
Cg1 ^a	2.287(1)		
Bond angles			
C17-Zr1-C17'	34.91(11)	C17-Zr1-C16'	61.98(8)
C17-Zr1-C16	33.63(8)	C16'-Zr1-C16	93.91(11)
C17-C16-Zr1	69.72(12)	C16-C17-C17'	123.7(2)
C16-C17-Zr1	76.64(13)	C17'-C17-Zr1	72.55(6)
Cg1-Zr1-Cg1'	137.45(3)	Cg1-Zr1-C16	102.12(6)
Cg1-Zr1-C17	119.33(6)	Cg1-Zr1-C16'	106.58(6)
Cg1-Zr1-C17'	101.68(6)	ϕ^b	46.9(1)
χ^c	48.4(1)		
Torsion angle			
C16-C17-C17'-C16'	119.9(3)		

^a Cg1 denotes the centroid of the C1–C5 cyclopentadienyl ring. ^b Dihedral angle subtended by the cyclopentadienyl least-squares planes. ^c Dihedral angle between the least-squares planes of the C(1–5) cyclopentadienyl ring and the C(6–11) phenyl ring. Symmetry ('): $-x, y, 1/2 - z$

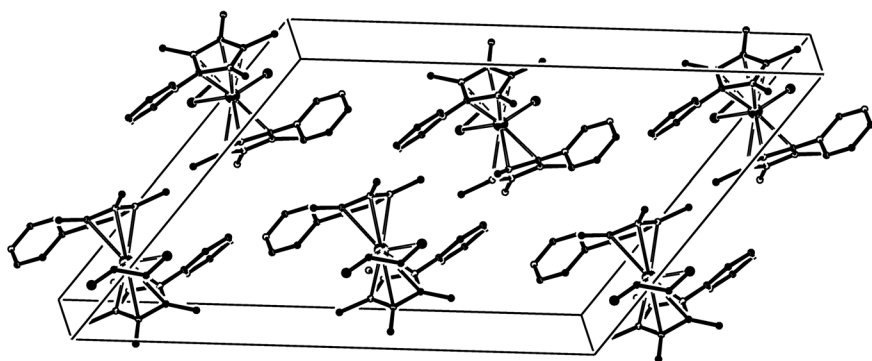


FIG. 6
View along *b*-axis on the superposition of unit cells **1** and **3**. The position of chlorine atoms in **1** overlap with the atoms C(16), C(16') in **3**. Hydrogen atoms are omitted for clarity

Conclusions

The preparation of the BTMSA complex **2** by a commonly used reaction was successful; however, the use of the bulky 1-phenyl-2,3,4,5-tetramethylcyclopentadienyl ligand instead of pentamethylcyclopentadienyl coordinated to zirconium changed both the steric and electronic properties of the resulting zirconocene moiety, which had an influence on its reactivity leading to a lower yield of **2** compared to previously reported reactions with highly methylated zirconocene complexes. The steric demands and/or the electronic properties of the BTMSA ligand had an important effect on the packing in solid state, since the complex containing this ligand, symmetrical in solution, chose a less crystallographic lattice with this symmetry removed. An unattended transformation of zirconocene dichloride **1** to (butadiene)-zirconocene complex **3** changed the general meaning of inertness of common organic solvent/substrate.

EXPERIMENTAL

General Comments and Methods

Synthesis of $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]$ (**1**) was carried out under argon atmosphere. The reduction of **1** as well as its purifications, handling and spectroscopic measurements were performed in vacuo using all-sealed glass device equipped with breakable seals. UV-near-IR measurements were performed in attached quartz cuvettes (10.0, 1.0 mm, Hellma). UV-VIS spectra (in nm) were collected on a Varian Cary 17D spectrometer in the range 300–2000 nm. EI-MS spectra were obtained on a VG-7070E double-focusing mass spectrometer at 70 eV. The crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. Spectra are represented by the peaks of relative abundance higher than 5% and by important peaks of lower intensity. The adjustment of single crystals into capillaries for X-ray analysis and preparation of KBr pellets for IR measurements were performed under purified nitrogen in a glovebox (mBraun Labmaster 130; O₂ and H₂O concentrations lower than 1.0 ppm). IR spectra of KBr pellets (in cm⁻¹) were recorded in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm⁻¹. ¹H and ¹³C NMR spectra (δ, ppm; J, Hz) were recorded on a Varian Mercury 300 (¹H at 299.98 and ¹³C at 75.44 MHz) or Varian Unity Inova 400 (¹H at 399.95 and ¹³C at 100.58 MHz) spectrometers at 298 K. Chemical shifts are given relative to the solvent signal (C₆D₆: δ_H 7.15, δ_C 128.00).

Chemicals

Tetrahydrofuran (THF), hexane and toluene were purified by conventional methods, dried by refluxing over LiAlH₄ and stored as solution of dimeric titanocene $[(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)\text{-}\{(\text{C}_5\text{H}_5)\text{Ti}(\mu\text{-H})\}_2]$ ¹⁷. Bis(trimethylsilyl)acetylene (BTMSA) (Aldrich) was degassed, stored like a solution of dimeric titanocene for 4 h, and distilled into ampoules. 1,3,4,5-Tetramethyl-2-phenylcyclopenta-1,3-diene was prepared as described recently². Butyllithium (*n*-BuLi)

(1.6 M in hexane), LiAlH_4 , Mg turnings (purum for Grignard reactions) and ZrCl_4 were obtained from Aldrich and used as received.

*Preparation of $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]$ (**1**)*

1,3,4,5-Tetramethyl-2-phenylcyclopenta-1,3-diene (9.9 g, 50 mmol) was diluted with 100 ml of toluene, vigorously stirred, and 50 mmol of *n*-BuLi were added dropwise. The pale yellow solution was stirred for another 8 more h till a white precipitate was formed. ZrCl_4 (5.8 g, 25 mmol) was added, the color of the suspension immediately turned to brown, and the mixture was refluxed about 20 h till its color turned to pale yellow. After cooling to ambient temperature, all volatiles were evaporated in vacuum at 60 °C. The residue was extracted with CH_2Cl_2 , and the concentrated extract afforded pale yellow crystals, which were crystallized from toluene. The yield was 10.4 g (75%). M.p. 230 °C. $^1\text{H NMR}$ (400 MHz, C_6D_6): 1.79, 2.00 $2 \times \text{s}$, $2 \times 6 \text{ H}$ (C_5Me_4); 6.99–7.21 m, 10 H (Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): 12.6, 13.0 (C_5Me_4); 127.0 (2 C), 128.3 (4 C), 130.5 (4 C) (CH, Ph); 121.2, 126.4, 126.6, 134.5 (C_{ipso} , C_5Me_4 and Ph). EI-MS (160 °C), *m/z* (relative abundance): 560 (12), 559 (9), 558 (26), 557 (17), 556 (37), 555 (M^{++} ; 20), 554 (34), 381 (5), 365 (14), 364 (10), 363 (60), 362 (25), 361 (94), 360 (58), 359 (99), 358 (72), 357 ($[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})\text{Cl}_2]^+$; 100), 343 (6), 341 (7), 339 (6), 337 (5), 325 (12), 324 (5), 323 (23), 322 (12), 321 (37), 320 (9), 319 (33), 318 (8), 317 (17), 315 (7), 307 (7), 306 (4), 305 (10), 304 (3), 303 (3), 293 (6), 198 (15), 197 (28), 196 (9), 183 (8), 182 (14), 181 (22), 169 (6), 167 (19), 166 (17), 165 (18), 155 (8), 141 (6), 131 (11), 119 (13), 105 (5), 92 (5), 91 (18), 69 (59), 55 (8), 41 (6). IR (KBr): 3059 (m), 3025 (m), 2910 (s), 1600 (s), 1574 (m), 1505 (s), 1477 (m), 1448 (m), 1394 (m), 1377 (m), 1214 (w), 1181 (w), 1154 (w), 1079 (m), 1025 (m), 1004 (w), 982 (w), 923 (w), 844 (w), 758 (vs), 706 (vs), 652 (w), 642 (m), 618 (w), 588 (m), 575 (w), 503 (w), 431 (w).

*Reduction of **1** in THF with magnesium in the presence of BTMSA*

2.22 g (4.0 mmol) of **1** was mixed together with excess of Mg and BTMSA in 50 ml of THF in an ampoule equipped with breakable seals. The pale yellow mixture was heated at 60 °C till its color turned from dark yellow to dark green (5 days). All volatiles (THF, BTMSA) were evaporated in vacuum at 60 °C, and the residue was extracted with hexane. The concentrated dark green hexane solution afforded after cooling to 0 °C green crystals of **2**. The yield of **2** was 1.1 g (42% based on **1**). The green crystals were removed and the dark yellow mother solution was again concentrated. After cooling to -18 °C, yellow crystals of **3** were obtained. The yield of **3** was 0.45 g (21% based on **1**).

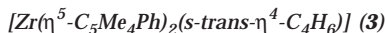
*$[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (**2**)*

M.p. 144 °C. $^1\text{H NMR}$ (400 MHz, C_6D_6): 0.13 s, 18 H (SiMe_3); 1.84, 1.93 $2 \times \text{s}$, $2 \times 12 \text{ H}$ (C_5Me_4); 6.47–7.11 m, 10 H (Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): 3.70 (SiMe_3); 12.44, 13.43 (C_5Me_4); 119.14, 122.07, 123.93 (C_5Me_4); 126.23, 128.20, 128.69 (CH, Ph); 137.13 (C_{ipso} , Ph); 259.83 ($\eta^2\text{-C}\equiv\text{C}$). EI-MS (120 °C), *m/z* (relative abundance): 489 (8), 488 (23), 487 (10), 486 (30), 485 (38), 484 ($[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]^+$; 68), 483 (9), 482 (7), 481 (8), 480 (6), 479 (7), 478 (6), 477 (6), 469 (6), 467 (9), 465 (5), 285 (7), 284 (7), 283 (15), 282 (7), 281 (9), 280 (5), 279 (11), 244 (6), 243 (9), 243 (10), 242 (20), 198 (11), 183 (9), 181 (5), 170 (btmsa; 9), 167 (6), 166 (7), 165 (10), 157 (9), 156 (19), 155 ($[\text{btmsa-Me}]^+$; 100), 141 (5), 97 (10), 91 (9), 83 (9), 74 (6), 73 (73), 70 (6), 59 (7), 45 (27), 43 (15), 41 (6). IR (KBr): 3056 (m), 2954 (s), 2902

TABLE IV
Crystal and structure refinement data for **1**, **2**, and **3**

Parameter	1	2	3
Empirical formula	C ₃₀ H ₃₄ Cl ₂ Zr	C ₃₈ H ₅₂ Si ₂ Zr	C ₃₄ H ₄₀ Zr
Formula weight	556.69	656.20	539.88
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>C2/c</i>	$P\bar{1}$	<i>C2/c</i>
<i>a</i> , Å	23.1962(6)	9.3726(2)	22.7400(5)
<i>b</i> , Å	8.4556(2)	11.4848(3)	8.8245(3)
<i>c</i> , Å	16.1035(3)	19.5777(6)	16.2379(4)
α , °	90	79.5863(8)	90
β , °	126.4968(10)	83.0503(9)	125.6851(15)
γ , °	90	82.4792(18)	90
<i>V</i> , Å ³	2539.09(10)	2044.58(9)	2646.62(13)
<i>Z</i>	4	2	4
<i>d</i> _{calc} , g cm ⁻³	1.456	1.066	1.355
μ (MoK α), mm ⁻¹	0.660	0.348	0.436
<i>F</i> (000), e	1152	696	1136
θ_{\min} , θ_{\max} , °	2.64, 27.51	3.01, 27.51	2.21, 27.47
<i>T</i> , K	150.0(1)	150.0(1)	150.0(1)
Crystal description	prism	prism	prism
Crystal color	colorless	turquoise	yellow
Crystal size, mm ³	0.4 × 0.35 × 0.25	0.45 × 0.15 × 0.08	0.3 × 0.15 × 0.12
Reflection collected	19287	37758	23664
Independent reflections	2906	9276	3033
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0239, 0.0573	0.0800, 0.1501	0.0370, 0.0725
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0221, 0.0561	0.0534, 0.1366	0.0285, 0.0683
Range of <i>hkl</i> indices	-29→30, -10→10, -20→20	-11→12, -14→14, -25→25	-29→29, -11→11, -21→21
Data/restraints/parameters	2906/0/155	9276/0/384	3033/0/175
Goodness-of-fit on <i>F</i> ²	1.069	1.067	1.059
Maximal and minimal residual density, eÅ ⁻³	0.316, -0.263	1.443, -0.445	0.423, -0.298

(s), 2858 (m), 1601 (s), 1574 (w), 1515 (s), 1507 (s), 1482 (m), 1445 (m), 1377 (m), 1244 (s), 1181 (m), 1076 (s), 1023 (s), 984 (m), 919 (m), 854 (vs), 759 (vs), 705 (vs), 655 (m), 620 (w), 589 (w), 469 (s), 446 (m). UV-VIS (hexane): 727.



^1H NMR (300 MHz, C_6D_6): 1.00 s, 6 H (C_5Me_4); 1.32–1.40 m, 2 H (H_{anti}); 1.42, 1.60, 1.87 s \times s, 3 \times 6 H (C_5Me_4); 2.25–2.34 m, 2 H (H_{meso}); 3.02 dd, 2 H, $^3J_{\text{HH}} = 6.9$, $^2J_{\text{HH}} = 4.5$ (H_{syn}); 7.10 tt, 2 H, $^3J_{\text{HH}} = 7.5$, $^4J_{\text{HH}} = 1.5$ (H_{para}); 7.21–7.28 m, 4 H (H_{meta}); 7.40–7.46 m, 4 H (H_{ortho}). ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): 11.60, 11.90, 11.97, 12.26 (C_5Me_4); 68.20 ($\text{CH}=\text{CH}_2$); 102.44 ($\text{CH}=\text{CH}_2$); 110.27, 110.42, 111.74, 112.57, 115.39 (C_5Me_4); 125.96, 128.05, 132.16 (CH, Ph); 136.60 (C_{ipso} , Ph). EI-MS (140 °C), m/z (relative abundance): 538 (7), 521 (6), 520 (5), 519 (6), 490 (8), 489 (13), 488 (34), 487 (22), 486 (52), 485 (61), 484 ($[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]^+$; 100), 483 (40), 482 (31), 481 (13), 480 (10), 479 (9), 478 (8), 477 (5), 471 (10), 469 (13), 468 (14), 467 (25), 465 (6), 283 (9), 281 (5), 279 (7), 244 (7), 243 (9), 243 (9), 242 (17), 241 (6), 57 (11), 56 (20), 55 (9), 43 (12), 42 (7), 41 (31), 39 (12), 29 (10), 28 (8), 27 (12). IR (KBr): 3065 (s), 3023 (m), 3000 (s), 2909 (s), 1599 (s), 1573 (w), 1553 (w), 1504 (s), 1478 (m), 1435 (m), 1378 (m), 1261 (w), 1195 (w), 1160 (m), 1074 (m), 1024 (m), 980 (w), 945 (m), 919 (w), 842 (w), 808 (m), 758 (vs), 705 (vs), 641 (w), 622 (w), 588 (w), 539 (w), 501 (w), 433 (w).

X-ray Structure Determination

The pale yellow crystals obtained from toluene solution of **1** were attached in air to a glass rod with grease. The green crystal fragment of **2** and the yellow crystals of **3** under nitrogen in a glovebox were fixed into Lindenmann glass capillaries, which were sealed with wax. Diffraction data for **1**, **2** and **3** were collected on a Nonius KappaCCD diffractometer and analyzed by the HKL program package¹⁸. The structure was solved by direct methods (SIR92)¹⁹ and refined by full-matrix least-squares on F^2 (SHELXL97)²⁰. Relevant crystallographic data are given in Table IV. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **2** were fixed and refined in their theoretical positions. There are large void areas in the crystals of **2** (435 Å³ each, total 21% of the unit cell volume) that accommodate the most positive residual electron density peaks on the final difference Fourier map, suggesting the presence of solvent molecules. Although the void dimensions are suitable for hosting small solvent molecules (e.g., hexane) in the unit cell, the solvent was probably lost during manipulation with the crystal in glove box. The resulting poor quality of the crystal excludes either identification of the solvent or subtraction of the residual electron density from diffraction data using the SQUEEZE²¹ procedure. Nonetheless, the structure determination of **2** itself is unambiguous. The hydrogen atoms in **3** on the butadiene ligand were located on difference Fourier maps and refined isotropically without restraints, all other hydrogens were included in ideal positions. CCDC 635586 (for **1**), 635587 (for **2**) and 635588 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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