Interaction of the Negishi reagent $Cp_2ZrBu^n{}_2$ with 1,4-bis(*tert*-butyl)butadiyne

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The interaction of the Negishi reagent $Cp_2ZrBu^n{}_2$ with 1,4-bis(*tert*-butyl)butadiyne $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ leads to four products: a five-membered zirconacyclocumulene complex $Cp_2Zr(\eta^4\text{-}Bu^tC_4Bu^t)$ (**2**) synthesized earlier by another method, the previously unknown seven-membered zirconacyclocumulene $Cp_2Zr[\eta^4\text{-}Bu^tC_4(Bu^t){-}C(C_2Bu^t){=}CBu^t]$ (**3**) as well as small amounts of the zirconocene binuclear butatrienyl complex $Cp_2(Bu^n)Zr(Bu^tC_4Bu^t)Zr(Bu^n)Cp_2$ (**4**), and the dimeric acetylide $[Cp_2ZrC{\equiv}CBu^t]_2$ (**5**). The structure of complexes **2**—**5** was established by X-ray diffraction studies.

Key words: conjugated diacetylenes, dialkylmetallocenes, metallacyclocumulenes, acetylide complexes, butatrienyl complexes, zirconium, X-ray diffraction studies.

One of the most efficient methods for the introduction of the zirconocene fragment into organic molecules consists in the use of di-*n*-butylzirconocene $Cp_2ZrBu^n{}_2$ (the Negishi reagent) as a source of "Cp_2Zr" (see, for example, Refs 1—3). This method is based on the ability of extremely unstable $Cp_2ZrBu^n{}_2$ to decompose at low temperatures to form a butene complex $Cp_2Zr(EtCH{=}CH_2)$ effecting the function of zirconocene synthon in the reactions with unsaturated organic substrates.

Recently, we have reported[4,5] on the synthesis of di-*n*-butylhafnocene $Cp_2HfBu^n{}_2$, a hafnium analog of the Negishi reagent. The compound obtained turned out to be much more stable than $Cp_2ZrBu^n{}_2$: it decomposes, generating "Cp_2Hf", only at 100 °C. It was also shown that under these conditions $Cp_2HfBu^n{}_2$ readily reacts with 1,4-disubstituted butadiynes $RC{\equiv}C{-}C{\equiv}CR$ ($R = Bu^t$, $SiMe_3$, Ph) to form product whose structure strongly depends on the nature of the R moiety in the starting diyne.[4,5] Thus, the reaction of $Cp_2HfBu^n{}_2$ with $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ at 100 °C under argon gives a five-membered hafnacyclocumulene complex $Cp_2Hf(\eta^4\text{-}Bu^tC_4Bu^t)$, heating $Cp_2HfBu^n{}_2$ with $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ leads to a hafnacyclopentadiene derivative of hafnocene $Cp_2Hf[\eta^2\text{-}C(SiMe_3){=}C(C_2SiMe_3){-}C(SiMe_3){=}C(C_2SiMe_3)]$, whereas a tricyclic organohafnium [4]radialene was obtained in the reaction of $Cp_2HfBu^n{}_2$ with $PhC{\equiv}C{-}C{\equiv}CPh$.

Proceeding from these data, we decided to study the interaction of the Negishi reagent with various 1,4-disubstituted butadiynes. Earlier, it has been shown[6] that involvement of 1,4-bis(trimethylsilyl)butadiyne $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ into the reaction with $Cp_2ZrBu^n{}_2$ gives rise to a seven-membered zirconacyclocumulene complex (**1**) in 66% yield and a dimeric zirconocene acetylide $[Cp_2ZrC{\equiv}CSiMe_3]_2$ (Scheme 1). The structure of both compounds was established[6] by X-ray diffraction analysis.

In the present work, we studied the reaction of $Cp_2ZrBu^n{}_2$ with 1,4-bis(*tert*-butyl)butadiyne $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ and showed that a replacement of the trimethylsilyl groups in the molecule of butadiyne with the *tert*-butyl ones leads to essential changes in the character of the products obtained (for the preliminary communication, see Ref. 7).

Results and Discussion

Experiments were performed by mixing Cp_2ZrCl_2 and $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ with *n*-butyllithium in hexane at −78 °C under Ar ($Bu^nLi : Cp_2ZrCl_2 = 2 : 1$) with subsequent gradual warming-up the mixture to 20 °C (2—2.5 h) with stirring and keeping it at this temperature for another 2.5—3 h. The reaction resulted in obtaining a reddish brown solution containing, according to the NMR spectroscopic data, a complex mixture of products, from which four compounds were isolated and identified.

The major reaction product (relative content in the mixture 72%) is the known[8] five-membered zirconacyclo-

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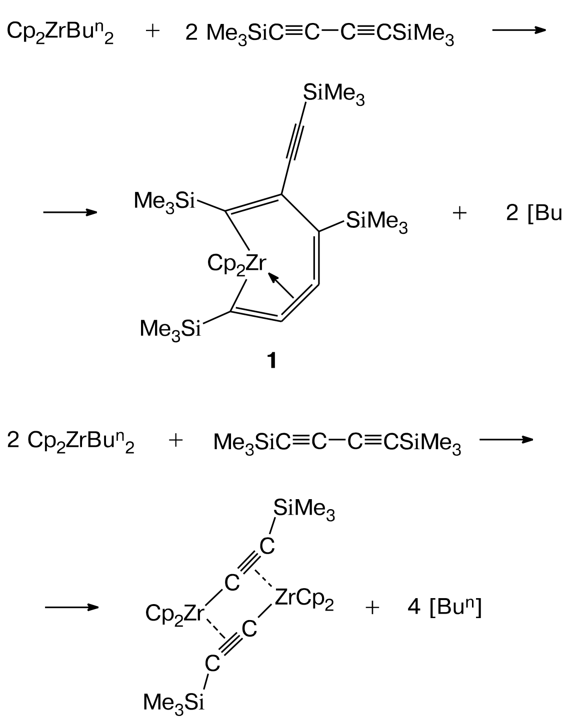
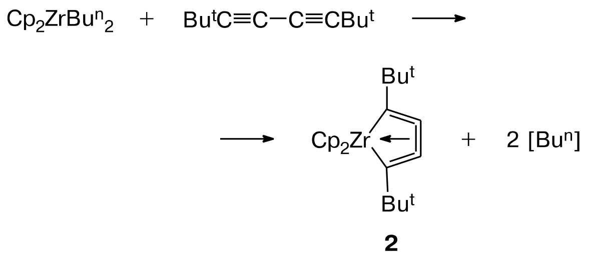
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 163—170, January, 2012.

Scheme 1



cumulene complex $Cp_2Zr(\eta^4\text{-}Bu^tC_4Bu^t)$ (**2**) (Scheme 2) representing light yellow crystals stable in air. The complex was isolated from the solution in the pure form in 30% yield based on Cp_2ZrCl_2. The structure of compound **2** was established by ^1H and ^{13}C NMR spectroscopy and confirmed by X-ray diffraction studies. The geometric parameters found by us for the complex obtained are close to the corresponding literature data.[8]

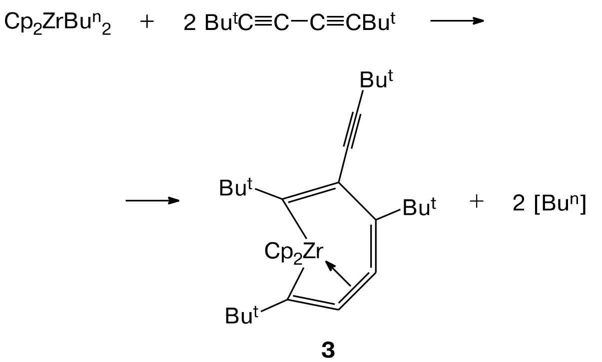
Scheme 2



Complex **2** has been synthesized earlier[8—10] starting from Cp_2ZrCl_2 in about the same yield (33%) but using three synthetic steps. Thus, the above-described one-step method for the synthesis of complex **2** which uses the Negishi reagent as a source of "Cp_2Zr" is significantly more convenient in the preparative respect.

Another product of the reaction of $Cp_2ZrBu^n{}_2$ with $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ (a yellow crystalline compound stable in air; relative content in the mixture 19%) was a seven-membered zirconacyclocumulene $Cp_2Zr[\eta^4\text{-}Bu^tC_4(Bu^t){-}C(C_2Bu^t){=}CBu^t]$ (**3**) which was isolated from the solution in the analytically pure state in 5.6% yield (Scheme 3). The structure of the complex was established by NMR spectroscopy, mass spectrometry, and X-ray diffraction.

Scheme 3



The structure of complex **3** is shown in Figure 1. The complex contains a wedge-shaped $(\eta^5\text{-}C_5H_5)_2Zr$-sandwich and a virtually planar seven-membered metallacycle located in the bisector plane of the dihedral angle (46.1°) between the Cp-rings. The presence of the butatrienyl group in the seven-membered ring of the complex is indicated by the distances C(1)—C(2) (1.2697(17) Å), C(2)—C(3) (1.3219(17) Å), and C(3)—C(4) (1.3317(17) Å), comparable with the length of an ordinary C=C double bond (1.331 Å). The elongation of the terminal double bond C(3)=C(4) of the butatrienyl fragment as compared to the terminal double bond C(1)=C(2) can be apparently attributed to its conjugation with the double bond C(5)=C(6) (1.3780(17) Å; C(4)—C(5) 1.4884(16) Å). As a result, the distance C(3)—C(4) becomes close to the length of the central bond C(2)—C(3) of the butatrienyl group. However, this central bond C(2)—C(3) is essentially elongated in comparison with the terminal bond C(1)—C(2), which can indicate its coordination to the zirconium atom. Note that in noncoordinated butatrienes, the central C=C bond, on the contrary, is essentially shorter than the terminal C=C bonds (see, for example, Refs 11—13). In the seven-membered zirconacyclocumulene **1**, the distances C=C in the butatrienyl group are equal to 1.279(6), 1.298(6), and 1.337(6) Å,[6] but the authors of this work give no structural accounting for the coordination of the central C=C bond with the zirconium atom. In the five-membered zirconacyclocumulene **2**, the lengths of the terminal C=C bonds are 1.28(1) and 1.29(1) Å, whereas the length of the central C=C bond is 1.31(1) Å.[8]

The interaction of the double bond C(2)=C(3) with the zirconium atom in complex **3** is favored by the loca-

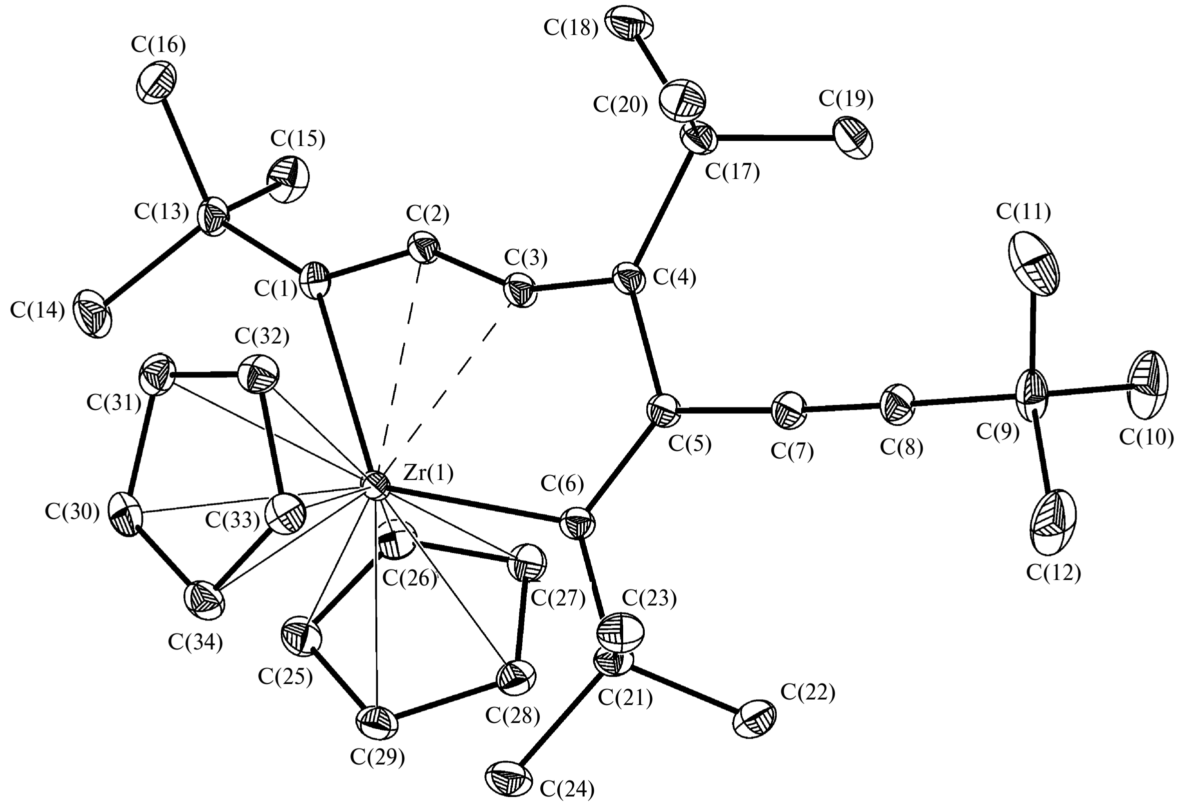


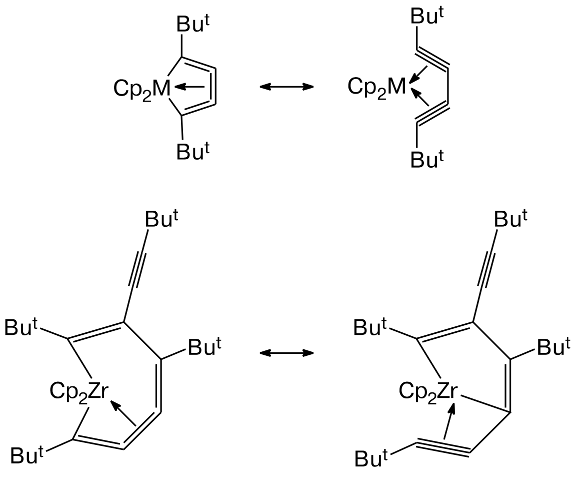
Fig. 1. Molecular structure of complex **3**. The hydrogen atoms of the Cp-rings and the *tert*-butyl groups are not shown. All the nonhydrogen atoms are shown as ellipsoids of thermal vibrations (probability 50%).

tion of one of the p-orbital pairs of the sp-hybridized carbon atoms of this bond in the plane of zirconacycle. Since the distance Zr(1)—C(3) (2.3553(12) Å) is much shorter than the distance Zr(1)—C(2) (2.4283(11) Å), one can conclude that the main contribution to this interaction is made by the carbon atom C(3). The bond distances Zr(1)—C(1) and Zr(1)—C(6) are 2.4439(12) and 2.4963(12) Å, respectively.

The butatrienyl group in compound **3** strongly deviates from linearity (the endocyclic bond angles C(1)—C(2)—C(3) and C(2)—C(3)—C(4) are 146.48(12) and 156.93(12)°, respectively), adopting a transoid configuration. The distance C(7)—C(8), equal to 1.1927(18) Å, corresponds to the C≡C triple bond distance. The angles C(5)—C(7)—C(8) and C(7)—C(8)—C(9) are close to 180° (176.76(14) and 177.62(15)°, respectively).

It should be noted, however, that though the X-ray diffraction data for complex **3** given above generally are in good agreement with its zirconacyclocumulene structure, the terminal bond C(1)=C(2) in the butatrienyl fragment of this complex (1.2697(17) Å) is nevertheless noticeably shorter than a typical C=C double bond. Analogous shortening of the terminal C=C bonds is also characteristic of five-membered titana-, zircona-, and hafnacyclocumulenes $Cp_2M(\eta^4\text{-}Bu^tC_4Bu^t)$ (the above-mentioned C=C distances are equal to 1.243(13) and 1.276(11) Å for M = Ti, 1.28(1) and 1.29(1) Å for M = Zr, 1.288(5) and 1.298(5) Å for M = Hf),[4,5,8,14] which is apparently due to a certain contribution of the resonance structure of the corresponding bis-acetylene complex to the electron structure of the metallacycle (Scheme 4, see Refs 15 and 16). Similar reasoning can also explain the shortening of the C(1)=C(2) bond observed in complex **3** if one assumes that the electron

Scheme 4



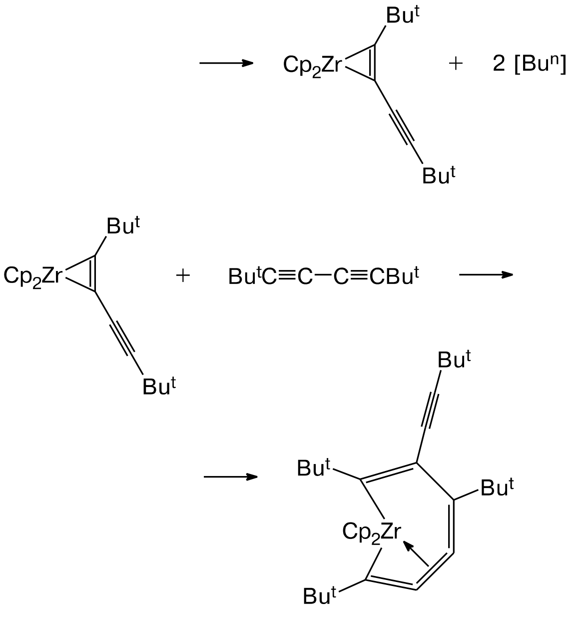
structure of this compound is significantly contributed by a resonance form of the five-membered zirconacyclopentadiene (see Scheme 4) in which the α-alkynyl group deviates toward the zirconium atom and forms a coordination bond with it. The fact that the distance Zr(1)—C(3) in complex **3** is much shorter than the distance Zr(1)—C(2) (see above) agrees with this assumption.

Similar zirconacyclopentadiene resonance form can be suggested to describe the structure of complex **1** in which the terminal bond C(1)=C(2) of the butatrienyl fragment (1.279(6) Å) is also considerably shortened as compared to a normal C=C bond.

The mechanism of the complex **3** formation apparently includes two main steps. First, the reaction of $Cp_2ZrBu^n_2$ with 1,4-bis(*tert*-butyl)butadiyne leads to the intermediate zirconocene acetylene complex (having a metallacyclopropene structure), which then reacts with the second molecule of butadiyne, giving the final seven-membered zirconacyclocumulene (Scheme 5).

Scheme 5

$$Cp_2ZrBu^n_2 + Bu^tC{\equiv}C{-}C{\equiv}CBu^t \longrightarrow$$



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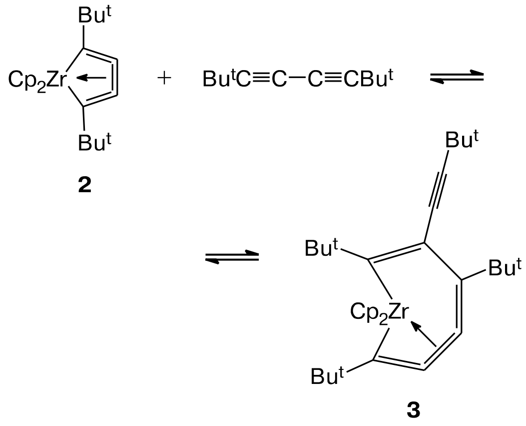
Compound **3** could be also obtained as a result of the reaction of the starting butadiyne with the five-membered zirconacyclocumulene **2** formed but this mechanism is contradicted by the fact that complex **2** does not react with $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ at room temperature even within 30 days (^1H NMR spectroscopic data). However, note that at 100 °C the reaction of compound **2** with $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ slowly does proceed, leading to a mixture of complexes **2** and **3** in the ratio ~3 : 1 within 24 h (Scheme 6). An increase in the reaction time to 11 days virtually does not change this ratio despite the presence of a free diyne in the solution, thus indicating a reversible character of this transformation.

Scheme 6

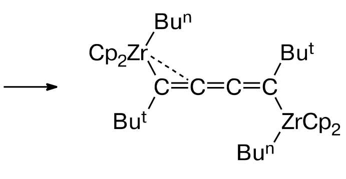


Besides compounds **2** and **3**, the reaction of $Cp_2ZrBu^n_2$ with $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ also gives a small amount (2.4%) of an unusual binuclear butatrienyl complex of zirconocene $Cp_2(Bu^n)Zr(Bu^tC_4Bu^t)Zr(Bu^n)Cp_2$ (**4**). Its reddish brown crystals are also stable in air despite the presence of two Zr—Bu σ-bonds in this compound. One can assume that the decomposition of $Cp_2ZrBu^n_2$ yields, together with "Cp_2Zr", a small amount of monobutylzirconocene Cp_2ZrBu^n whose subsequent reaction with butadiyne gives the final complex **4** (Scheme 7).

Scheme 7

$$Cp_2ZrBu^n_2 \longrightarrow Cp_2ZrBu^n + [Bu^n]$$

$$2\ Cp_2ZrBu^n + Bu^tC{\equiv}C{-}C{\equiv}CBu^t \longrightarrow$$



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An X-ray diffraction study of complex **4** (Fig. 2) showed that it in fact contains two $(\eta^5\text{-}C_5H_5)_2ZrBu^n$ groups bound *via* a butatrienyl bridge and located in the *trans*-position with respect to each other. The distances C(1)—C(2), C(2)—C(3), and C(3)—C(4) in the butatrienyl fragment are 1.312(3), 1.305(3), and 1.316(3) Å, respectively, which is close to the length of a normal C=C double bond. An important structural distinction of complex **4** is coordina-

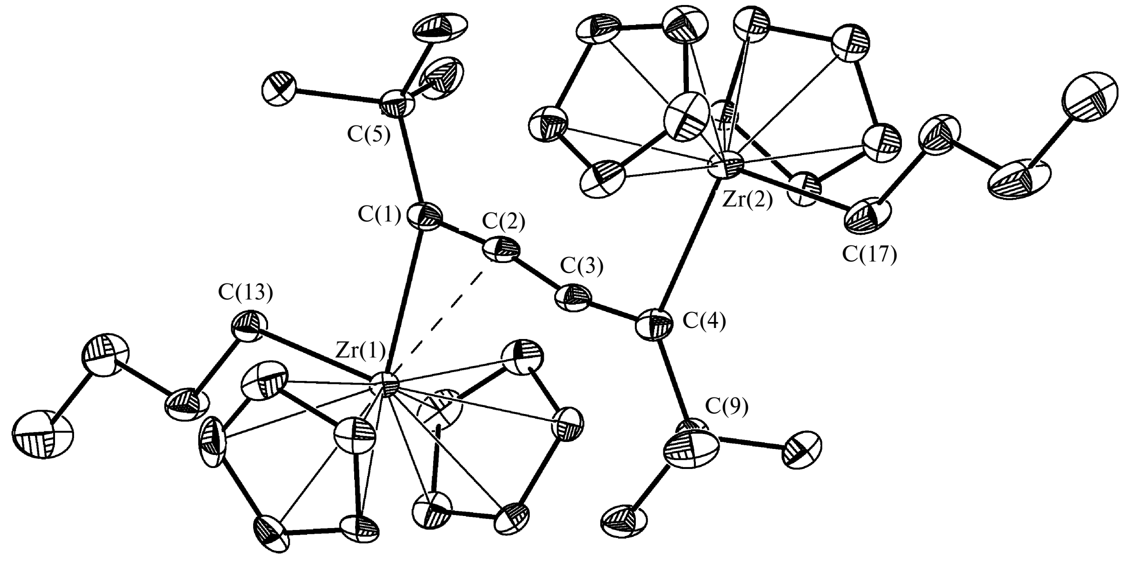


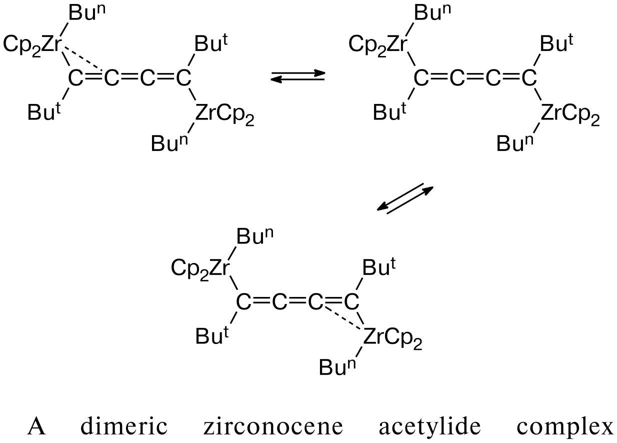
Fig. 2. Molecular structure of complex **4**. The hydrogen atoms of the Cp-rings and the butyl groups are not shown. All the nonhydrogen atoms are shown as ellipsoids of thermal vibrations (probability 50%).

tion of the atom C(2) of the butatrienyl ligand to the atom Zr(1), which is indicated by a significant shortening of the distance Zr(1)···C(2) (2.660(2) Å) as compared to the distance Zr(2)···C(3) (2.917(2) Å). As a result of the formation of the coordination bond Zr(1)···C(2), the bond angle Zr(1)—C(1)—C(5) at the sp^2-hybridized carbon atom C(1) increases 141.91(14)° and becomes by ~13° larger than the angle Zr(2)—C(4)—C(9) (129.13(14)°), whereas the butatrienyl fragment considerably deviates from linearity (the bond angles C(1)—C(2)—C(3) and C(2)—C(3)—C(4) are 170.36(18) and 166.75(19)°, respectively). In addition, the distance Zr(1)—C(1) (2.297(2) Å) proves significantly shorter than the distance Zr(2)—C(4) (2.326(2) Å) whereas the bond Zr(1)—C(13) (2.339(2) Å) somewhat elongates as compared to the bond Zr(2)—C(17) (2.311(2) Å).

The formation of the coordination bond Zr(1)···C(2) is apparently due to the interaction of electrons on one of the p-orbitals of the sp-hybridized carbon atom C(2) with the vacant d-orbital of the zirconium atom. Such an interaction is favored by the arrangement of this p-orbital and the atom Zr(1) in the bisector plane of the dihedral angle (49°) between the Cp-rings. The atoms C(1), C(5), and C(13) are located in the same bisector plane. The atom Zr(2) and one of the p-orbitals of the atom C(3) are also disposed in the bisector plane of the corresponding dihedral angle (52.5°) but they either do not interact with each other or their interaction is much more weaker than that between the atoms C(2) and Zr(1).

Note that, despite the structural nonequivalence of the two (η^5-C_5H_5)$_2$ZrBu$^n{}_2$ groups and *tert*-butyl substituents in the crystal of compound **4**, the ^{1}H NMR spectrum of the complex in C_6D_6 contains the only singlet for the η^5-cyclopentadienyl protons (δ 5.91) and, correspondingly, the only singlet for the methyl protons of the *tert*-butyl groups (δ 1.28). This fact can be accounted for by either the absence of the coordination bond Zr(1)···C(2) in the benzene solution of the complex or the existence in the solution of rapidly establishing equilibrium (Scheme 8).

Scheme 8



A dimeric zirconocene acetylide complex [$Cp_2ZrC{\equiv}CBu^t$]$_2$ (**5**), representing yellowish brown crystals stable in air, is yet another compound formed in small amounts (0.9%) in the reaction of $Cp_2ZrBu^n{}_2$ with $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ (Scheme 9).

Complex **5** was characterized by ^{1}H and ^{13}C NMR spectra, and its structure was determined by X-ray diffraction analysis (Fig. 3).

A unit cell of complex **5** contains two independent molecules differing from each other only by the mutual turn of the *tert*-butyl substituents with respect to the acetylene group. Each of these molecules is situated in the

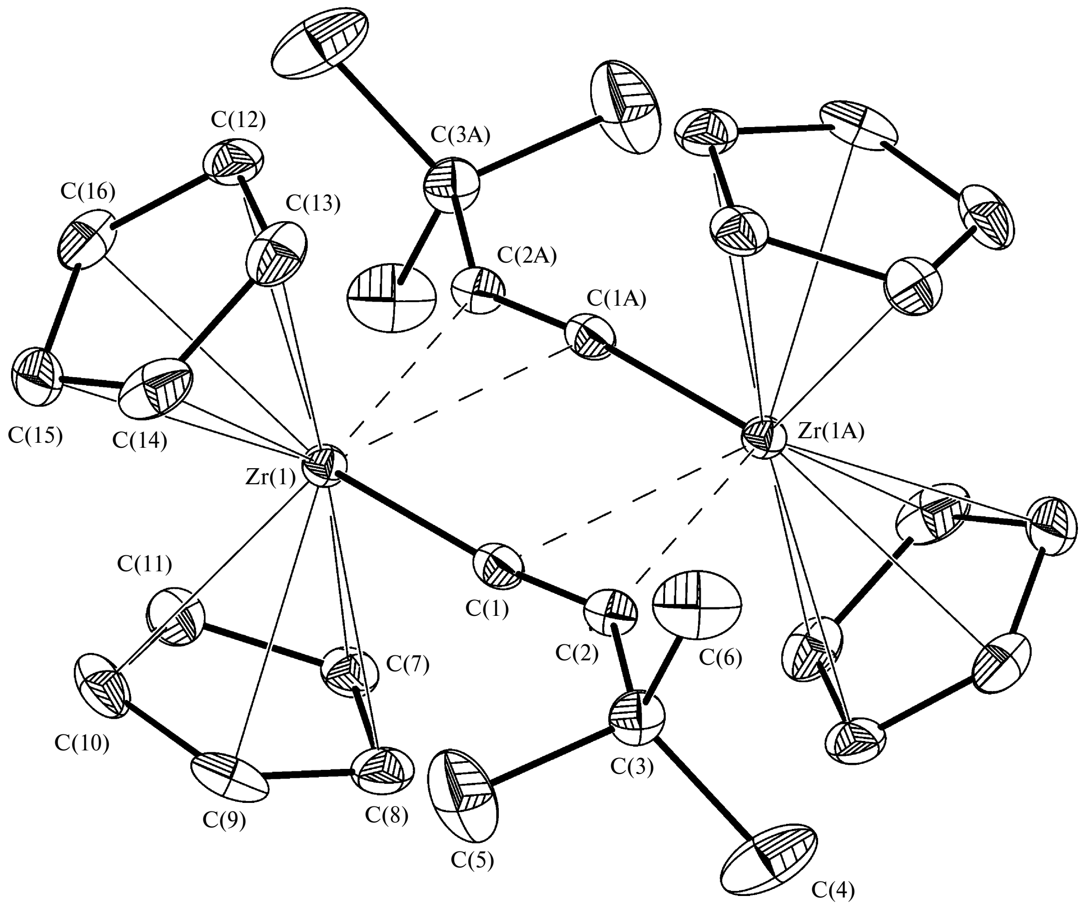
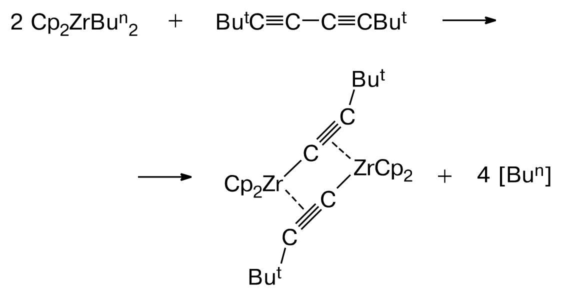


Fig. 3. Molecular structure of complex **5**. The hydrogen atoms of the Cp-rings and the *tert*-butyl groups are not shown. All the nonhydrogen atoms are shown as ellipsoids of thermal vibrations (probability 50%).

Scheme 9



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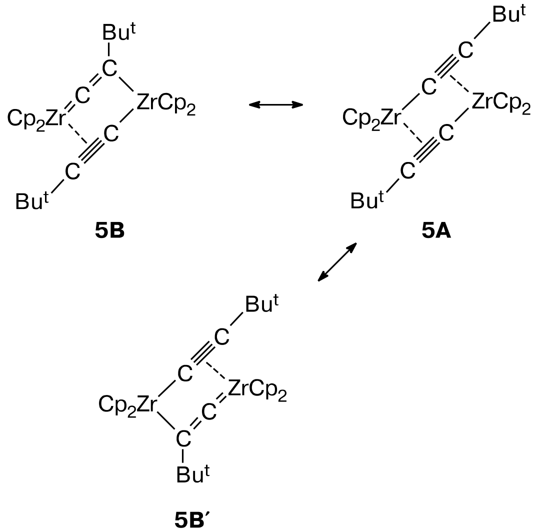
center of inversion, which coincides with the center of the $Zr_2C(1)C(2)C(1A)C(2A)$ fragment formed by two monomeric acetylides $Cp_2ZrC{\equiv}CBu^t$ due to the coordination of the C≡C triple bond of one of its molecules with the zirconium atom of the other. The indicated Zr_2C_4 fragment is ideally planar and located in the bisector plane of the dihedral angle (51.1°) between the Cp-rings.

The distance Zr(1)···Zr(1A) in compound **5** (3.504(1) Å) is significantly larger than a double van der Waals radius of a zirconium atom (3.10 Å),[17] which indicates the absence of the Zr—Zr bond in the complex. Nevertheless, despite the presence of one unpaired electron on each of the zirconium atoms, the synthesized compound, as well as all the dimeric zirconocene acetylides described earlier (see, for example, Refs 18—20), is diamagnetic. This is presumably caused by the electron spin coupling through the unsaturated bridging acetylide ligands.[18,20]

Coordination with zirconium causes elongation of the bonds C(1)—C(2) and C(1A)—C(2A) in complex **5** to 1.256(2) Å (the length of a normal noncoorditated C≡C bond is ~1.20 Å), whereas the bond angles C(1)—C(2)—C(3) and C(1A)—C(2A)—C(3A) decrease to 142.96(17)°. However, the atoms C(1) and C(1A) retain their sp-hybridization (the bond angles Zr(1)—C(1)—C(2) and Zr(1A)—C(1A)—C(2A) are equal to 173.7(1)°). The distances Zr(1)—C(1) and Zr(1A)—C(1A) in the complex are shortened (2.1819(18) Å) and close to the length of the Zr—C(sp) bond in zirconocene dicarbonyl $Cp_2Zr(CO)_2$ (2.187(4) Å),[18,21] in which a back-donation of d-electrons from the zirconium atom to the carbonyl ligands is supposedly effected.[18] The distances Zr(1)—C(1A) and Zr(1)—C(2A), as well as Zr(1A)—C(1) and Zr(1A)—C(2), are much longer: 2.4146(17) and 2.4090(17) Å, respectively. Similar shortening of the Zr—C(sp) bonds together with the strong deviation of the R—C≡C-fragments from linearity and retainment of the Zr—C≡C-fragments geometry close to linear are also characteristic of other known dimeric zirconocene acetylides.[18—20] These distinctions of coordination geometry of this type of acetylides are accounted for by significant contribution of the zirconaallene resonance forms **5B** and **5B´** to the electron structure of the complexes (Scheme 10).[18]

Scheme 10



In conclusion, the data presented above show that the reactions of the Negishi reagent with 1,4-bis(trimethylsilyl)- and 1,4-bis(*tert*-butyl)butadiynes essentially differ from each other in the character of the products formed. In fact, while the reaction of $Cp_2ZrBu^n_2$ with 1,4-bis(trimethylsilyl)butadiyne $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ leads to a seven-membered zirconacyclocumulene complex **1** and a dimeric zirconocene acetylide $[Cp_2ZrC{\equiv}CSiMe_3]_2$,[6] the use of $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ gives, besides the corresponding seven-membered zirconacyclocumulene **3** and dimeric acetylide **5**, a five-membered zirconacyclocumulene **2** (as a major product) and an unusual binuclear butatrienyl complex **4**.

Experimental

Experiments were carried out under Ar thoroughly avoiding the contact with atmospheric oxygen and moisture. The starting Cp_2ZrCl_2 was recrystallized from benzene. Hexane and benzene were purified from impurities by usual methods and before use were distilled twice over sodium under Ar. ^1H and ^{13}C NMR spectra were recorded on Bruker AMX-400 and Bruker AV-400 spectrometers, mass spectra were registered on a MAT 95-XP instrument.

Reaction of $Cp_2ZrBu^n_2$ with $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$. A 1.6 *M* solution of Bu^nLi in hexane (10.7 mL, Aldrich) was added to a mixture of Cp_2ZrCl_2 (2.50 g, 8.55 mmol) and $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ (1.387 g, 8.55 mmol) in hexane (20 mL) at −75 °C with stirring and a white suspension formed was left with stirring to gradually warm-up to ~20 °C. After 5 h, the obtained dark reddish brown solution containing a precipitate of LiCl was concentrated *in vacuo* to dryness. A small sample was collected from the solid residue, dissolved in anhydrous C_6D_6 and analyzed by NMR. The analysis showed the presence of complexes **2**, **3**, **4**, and **5** in the mixture in the ratio 72 : 19 : 2.4 : 0.9 and two unidentified side products. After the analysis was performed, the main part of the mixture of solid reaction products was dissolved in hexane (20 mL) at 50 °C, the solution was filtered and cooled to −40 °C. A light yellow crystalline precipitate was formed from the reddish brown solution within 24 h. The precipitate was separated from the mother liquor by decantation, washed with cold hexane, and dried *in vacuo*. The ^1H and ^{13}C NMR spectroscopic data as well as X-ray diffraction studies showed that the obtained crystalline precipitate virtually is a pure complex **2**. The yield was 0.984 g (30%), m.p. 191—193 °C (under Ar) (*cf.* Ref. 8: m.p. 190—192 °C). ^1H NMR (C_6D_6), δ: 1.52 (s, 18 H, Me); 5.22 (s, 10 H, Cp). ^{13}C NMR (C_6D_6), δ: 33.3 ($C\underline{C}H_3$); 37.4 ($\underline{C}CH_3$, $^2J_{C,H}$ = 3.4 Hz); 103.7 (Cp); 105.4($C(Bu^t){=}\underline{C}$); 186.4 ($\underline{C}(Bu^t){=}C$, $^3J_{C,H}$ = 4.3 Hz). The decanted brown solution was concentrated to the volume of 10—15 mL, filtered, and allowed to stand at −78 °C under Ar. A crystalline precipitate formed within 24 h was separated from the mother liquor, washed with cold hexane, and dried *in vacuo* to obtain a yellow crystalline compound (0.818 g) which was a mixture of compounds **2** and **3** with interspersion of a small amount of reddish brown and yellowish brown crystals of complexes **4** and **5**, respectively. These crystals were separated with tweezers and studied by X-ray diffraction. Compounds **4** and **5** were also identified by NMR spectroscopy.

Complex **4**. ^1H NMR (C_6D_6), δ: 1.09 (s, 6 H, Me, Bu^n); 1.28 (s, 18 H, Me, Bu^t); 5.91 (s, 20 H, Cp). The spectrum was obtained upon analysis of the concentrated to dryness final reaction mixture (see above). Chemical shifts for the methylene protons of the *n*-butyl groups cannot be determined because the signals of these protons overlap with the signals of unidentified side products.

Complex **5**. ^1H NMR (C_6D_6), δ: 1.45 (s, 18 H, Me); 5.22 (s, 20 H, Cp). ^{13}C NMR (C_6D_6), δ: 33.5 ($C\underline{C}H_3$); 37.4 ($\underline{C}Me$); 102.1 (Cp); 167.2 ($C{\equiv}\underline{C}Bu^t$); 218.1 ($\underline{C}{\equiv}CBu^t$). Repeated recrystallization of the above-mentioned yellow crystalline compound from hexane yielded an analytically pure crystalline complex **3** (0.26 g, 5.6%). M.p. 145—147 °C (under Ar). Found (%): C, 74.76; H, 8.34. $C_{34}H_{46}Zr$. Calculated (%): C, 74.80; H, 8.49. ^1H NMR (C_6D_6), δ: 1.29 (s, 9 H, C(14)—C(16)); 1.37 (s, 9 H, C(10)—C(12)); 1.73 (s, 9 H, C(18)—C(20)); 1.76 (s, 9 H, C(22)—C(24)); 5.60 (s, 10 H, Cp). ^{13}C NMR (C_6D_6), δ: 28.6 (C(9), $^2J_{C,H}$ = 3.5 Hz); 30.5 (C(10)—C(12)); 31.1 (C(18)—C(20)); 33.1 (C(14)—C(16)); 33.2 (C(22)—C(24)); 35.1 (C(13)); 38.5 (C(17), $^2J_{C,H}$ = 3.4 Hz); 43.5 (C(21), $^2J_{C,H}$ = 3.1 Hz); 77.9 (C(2)); 85.9 (C(7)); 101.8 (C(8), $^3J_{C,H}$ = 4.4 Hz); 105.2 (Cp); 137.4 (C(5)); 146.5 (C(1), $^3J_{C,H}$ = 4.3 Hz); 157.6 (C(3)); 158.3 (C(4), $^3J_{C,H}$ = = 3.4 Hz); 227.1 (C(6), $^3J_{C,H}$ = 3.0 Hz) (for the atom numeration, see Fig. 1). MS (70 eV), *m/z* (I_{rel} (%)): 544 $[M]^+$ (11.5), 487 $[M - Bu^t]^+$ (5.3), 406 $[M - Bu^tC_2Bu^t]^+$ (8.2), 382 $[M - Bu^tC_4Bu^t]^+$ (12.6), 325 $[Cp_2ZrC_4Bu^t]^+$ (8.0), 301 $[Cp_2ZrC_2Bu^t]^+$ (7.8), 220 $[Cp_2Zr]^+$ (100).

Table 1. Principal crystallographic data and parameters of refinement for compounds **3—5**

Parameter	**3**	**4**	**5**
Molecular formula	$C_{34}H_{46}Zr$	$C_{40}H_{56}Zr_2$	$C_{32}H_{38}Zr_2$
Molecular weight	545.93	719.29	605.06
T/K	100	90	100
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1$	P-1
Z	4	2	2
a/Å	14.3856(3)	11.4581(10)	8.4351(4)
b/Å	10.9385(2)	7.9044(7)	10.5748(5)
c/Å	18.5205(4)	20.6236(16)	15.6049(7)
α/deg	90.00	90.00	74.2008(8)
β/deg	91.5822(10)	101.9730(17)	83.6322(8)
γ/deg	90.00	90.00	87.9300(8)
V/Å^3	2913.22(10)	1827.2(3)	1331.08(11)
d_{calc}/g cm^{-3}	1.245	1.307	1.510
μ/cm^{-1}	3.97	5.95	8.01
F(000)	1160	752	620
$2\theta_{max}$/deg	110	60	58
Number of measured reflections	493271	31667	13654
Number of independent reflections	37340	10613	6993
Number of reflections with $I > 2\sigma(I)$	28590	10022	6119
Number of refined parameters	500	384	326
R_1	0.0277	0.0242	0.0254
wR_2	0.0734	0.0574	0.0636
GOF	0.961	0.994	1.037
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	0.749/−0.555	0.532/−0.327	0.575/−0.545

X-ray diffraction studies of complexes 3—5. X-ray diffraction studies of compounds **3**—**5** were performed on a Smart APEX diffractometer (Mo-Kα irradiation, graphite monochromator, ω-scan technique). The structures were solved by direct method and refined by least squares method in anisotropic full-matrix approximation on F^2_{hkl}. Hydrogen atoms were localized from the differential Fourier-syntheses of electron density and refined using the riding model in the structures **4** and **5** and in isotropic approximation in the structure **3**. Refinement of the Flack parameter in the structure **4** gave the value 0.48(3) which results from the presence of a pseudocenter of symmetry between the zirconium atoms, making the major contribution into the abnormal scattering of the crystal. The main crystallographic data and parameters of refinement for complexes **3**—**5** are given in Table 1. All the calculations were performed using the SHELXTL PLUS program package.[22]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 09-03-00503) and German Scientific Society (Grant GRK 1213).

References

1. E. Negishi, F. E. Cederbaum, T. Takahashi, *Tetrahedron Lett.*, 1986, **27**, 2829.
2. E. Negishi, T. Takahashi, *Bull. Chem. Soc. Jpn*, 1988, **71**, 755.
3. E. Negishi, S. Huo, in *Titanium and Zirconium in Organic Synthesis*, Ed. I. Marek, Wiley-VCH, Weinheim, Germany, 2002, 1.
4. V. V. Burlakov, V. S. Bogdanov, K. A. Lyssenko, P. V. Petrovskii, T. Beweries, P. Arndt, U. Rosenthal, V. B. Shur, *Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 1294 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 1319].
5. V. V. Burlakov, T. Beweries, V. S. Bogdanov, P. Arndt, W. Baumann, P. V. Petrovskii, A. Spannenberg, K. A. Lyssenko, V. B. Shur, U. Rosenthal, *Organometallics*, 2009, **28**, 2864.
6. D. P. Hsy, W. M. Davis, S. L. Buchwald, *J. Am. Chem. Soc.*, 1993, **115**, 10394.
7. V. V. Burlakov, V. S. Bogdanov, K. A. Lyssenko, L. I. Strunkina, M. Kh. Minacheva, B. N. Strunin, U. Rosenthal, V. B. Shur, *Izv. Akad. Nauk, Ser. Khim.*, 2010, 653 [*Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 668].
8. U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V. V. Burlakov, *Angew. Chem., Int. Ed.*, 1994, **33**, 1605.
9. U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V. V. Burlakov, V. B. Shur, *Angew. Chem., Int. Ed.*, 1993, **32**, 1193.
10. U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, H. Görls, V. V. Burlakov, V. B. Shur, *Z. Anorg. Allg. Chem.*, 1995, **621**, 77.
11. R. E. Bachman, A. Fiseha, S. K. Pollack, *J. Chem. Cryst.*, 1999, **29**, 457.
12. P. A. Morken, N. C. Baenziger, D. J. Burton, P. C. Bachand, C. R. Davies, S. D. Pedersen, S. W. Hansen, *Chem. Commun.*, 1991, 566.

13. Y. Morimoto, Y. Higuchi, K. Wakamatsu, K. Oshima, K. Utimoto, N. Yasuoka, *Bull. Chem. Soc. Jpn*, 1989, **62**, 639.
14. V. V. Burlakov, A. Ohff, C. Lefeber, A. Tillack, W. Baumann, R. Kempe, U. Rosenthal, *Chem. Ber.*, 1995, **128**, 967.
15. K. C. Lam, Z. Lin, *Organometallics*, 2003, **22**, 3466.
16. S. Roy, E. D. Jemmis, M. Ruhmann, A. Schulz, K. Kaleta, T. Beweries, U. Rosenthal, *Organometallics*, 2011, **30**, 2670.
17. J. Slater, *J. Chem. Phys.*, 1964, **41**, 3199.
18. G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund, C. Krüger, *Organometallics*, 1989, **8**, 911.
19. N. Metzler, H. Nöth, *J. Organomet. Chem.*, 1993, **454**, C5.
20. U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V. V. Burlakov, *Organometallics*, 1994, **13**, 2903.
21. J. L. Atwood, R. D. Rogers, W. E. Hunter, C. Floriani, G. Fachinetti, A. Chiesi-Villa, *Inorg. Chem.*, 1980, **19**, 3812.
22. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

Received December 3, 2010;
in revised form October 20, 2011