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A Novel Type of Butadiene Coordination in $Cp_2Zr(\mu\text{-}(1,2\text{-}\eta^2\text{-}Zr):(4\text{-}\eta^1\text{-}Al)\text{-}C_4H_6)(\mu\text{-}Cl)AlCl_2$

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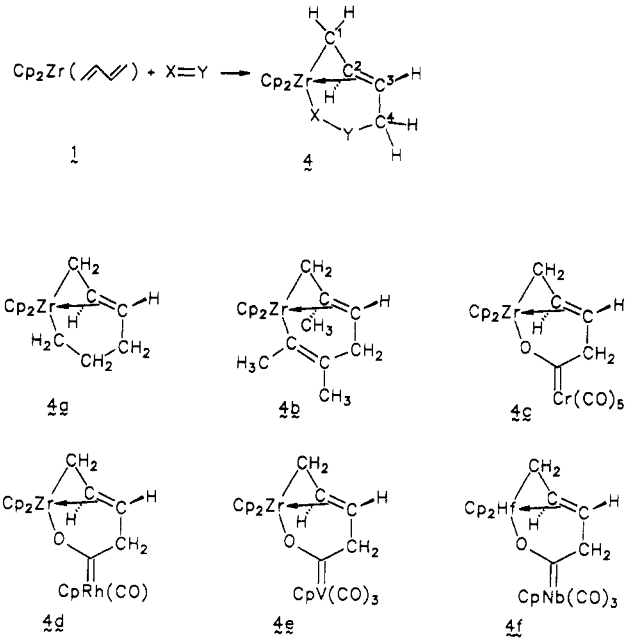
(Butadiene)zirconocene adds 1 molar equiv of aluminum trichloride to give $Cp_2Zr(\mu\text{-}C_4H_6)(\mu\text{-}Cl)AlCl_2$ (3). Complex 3 crystallizes in space group $P2_1/n$ with cell parameters a = 9.124 (1) Å, b = 15.040 (1) Å, c = 11.737 (1) Å, β = 93.60 (1)°, Z = 4, R = 0.024, and R_w = 0.032. In the crystal the butadiene carbon centers C(1) and C(2) are bonded to zirconium (Zr–C(1) = 2.348 (2) Å, Zr–C(2) = 2.525 (3) Å), whereas the Zr–C(3) separation is large at 3.04 Å. The butadiene C(4)–Al bond length is 1.966 (2) Å. A "π-agostic" interaction may serve to describe the special bonding situation observed in complex 3.

The energy surface of 1,3-butadiene contains two local minima which correspond to the planar s-cis and s-trans conformations of the conjugated diene, the latter being the energetically favored rotameric form.[1] A manifold of metal complexes ($(1,3\text{-diene})_nM_m$) is derived from these conjugated diene ligand geometries. The most often encountered ones are the (*s-cis*-η^4-butadiene)- and (*s-trans*-η^4-butadiene)metal species which contain the respective C_4H_6 rotamers bonded through all four carbon atoms either to a single metal atom or, in ligand-bridging situations, to different d- or f-block elements.[2] There are more "exotic" butadiene–metal bonding modes known from the literature, e.g. situations where only three adjacent carbon atoms are connected to a common metal center (as stable species found in a few $(\mu\text{-}C_4H_6)M_2$ complexes or calculated as reactive intermediates during isomerization reactions of mononuclear $(\eta\text{-}C_4H_6)M$ examples).[3] We have now found a stable heterodimetallic metal complex containing a related novel coordination type of the butadiene ligand. In the specific example, whose preparation and structure is

Scheme I



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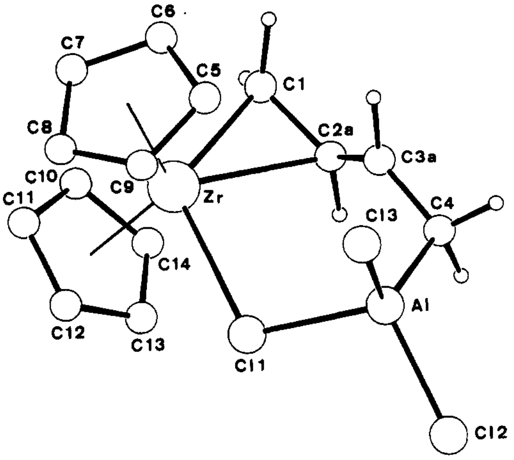
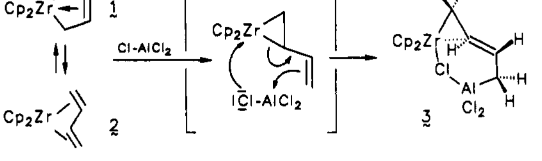


Figure 1. View of the molecular geometry of the $Cp_2Zr(\mu\text{-}CH_2CHCHCH_2)(\mu\text{-}Cl)AlCl_2$ complex **3** in the crystal form.

described and discussed below, the conjugated diene ligand is unsymmetrically bridging between two metals in such a way that it is bonded through carbon atoms C(1) and C(2) to the transition metal and carbon center C(4) to the main-group metal. To the best of our knowledge this unusual μ-(1,2-η^2):(4-η^1)-butadiene coordination mode which leaves the sp^2-hybridized carbon atom C(3) of the conjugated diene ligand untouched by the adjacent metal centers has not been observed before in an easily prepared and isolated stable metal complex.

Results and Discussion

(Butadiene)zirconocene is a reactive complex that has been shown to add a variety of organic or organometallic reagents with formation of metallacyclic reaction products.[4] We have treated the (*s-cis*/*s-trans*-η^4-butadiene)-zirconocene equilibrium mixture[2] (**1** ⇌ **2**; equilibrium ratio ~1) at ambient temperature in toluene solution with 1 molar equiv of aluminum trichloride. A single reaction product is isolated in >60% yield, which turns out to be a metallacyclic 1:1 addition product of the main-group-metal halide and the early-transition-metal complex component.



The heterodimetallic product **3** is chiral. Therefore, it exhibits two ^1H NMR singlets at δ 5.30 and 5.07, each representing five cyclopentadienyl hydrogen atoms. The methylene hydrogens at the former butadiene carbon center C(1) are diastereotopic (δ 1.79 and 1.46), as are the H atoms at C(4) (δ 1.92/1.42). The remaining methine hydrogens show resonances at δ 4.99 and 3.92. Their vicinal ^3J(2-H, 3-H) coupling constant is 15.4 Hz, which is a typical value for a trans-configurated –CH=CH– moiety in the coordination sphere of the zirconocene unit in a small- to medium-sized metallacyclic arrangement (for selected typical examples see Table III and Scheme I). The corresponding ^{13}C NMR resonances of the butadiene ligand in the $Cp_2Zr(\mu\text{-}CH_2CHCHCH_2)(\mu\text{-}Cl)AlCl_2$ complex **3** are at δ 42.8 ($^1J_{CH}$ = 147 Hz), 102.6 (149 Hz), 140.5 (149 Hz), and 25.4 (broad signal due to the adjacent Al atom) (C(1) to C(4)). Again, these NMR shift values and coupling constants are similar to those observed in many similarly structured monometallic addition products (**4**) derived from the (butadiene)zirconocene system (see Scheme I and Table III).

Table I. Selected Distances (Å) and Angles (deg) for 3

Zr–Cl(1)	2.706 (1)	Zr–C(1)	2.348 (2)
Zr–C(2a)	2.525 (3)	Zr–C(5)	2.510 (2)
Zr–C(6)	2.508 (2)	Zr–C(7)	2.489 (2)
Zr–C(8)	2.500 (2)	Zr–C(9)	2.517 (2)
Zr–C(10)	2.506 (2)	Zr–C(11)	2.491 (2)
Zr–C(12)	2.482 (2)	Zr–C(13)	2.540 (2)
Zr–C(14)	2.551 (2)	Zr–C(2b)	2.56 (1)
Cl(1)–Al	2.226 (1)	Cl(2)–Al	2.139 (1)
Cl(3)–Al	2.135 (1)	Al–C(4)	1.966 (2)
C(1)–C(2a)	1.486 (4)	C(1)–C(2b)	1.28 (1)
C(2a)–C(3a)	1.353 (4)	C(3a)–C(4)	1.434 (3)
C(4)–C(3b)	1.64 (1)	C(2b)–C(3b)	1.34 (2)
C(2a)–Zr–C(1)	35.3 (1)	C(2a)–Zr–Cl(1)	87.4 (1)
Al–Cl(1)–Zr	111.2 (1)	C(4)–Al–Cl(3)	117.5 (1)
C(4)–Al–Cl(2)	114.5 (1)	C(4)–Al–Cl(1)	102.2 (1)
Cl(3)–Al–Cl(2)	110.1 (1)	Cl(3)–Al–Cl(1)	105.9 (1)
Cl(2)–Al–Cl(1)	105.2 (1)	C(2b)–C(1)–Zr	84.1 (5)
C(2a)–C(1)–Zr	78.9 (1)	C(3a)–C(2a)–C(1)	125.8 (2)
C(3a)–C(2a)–Zr	98.7 (2)	C(1)–C(2a)–Zr	65.8 (1)
C(4)–C(3a)–C(2a)	126.1 (2)	C(3b)–C(4)–Al	110.0 (4)
C(3a)–C(4)–Al	112.0 (2)	C(3b)–C(2b)–C(1)	123 (1)
C(3b)–C(2b)–Zr	83.2 (7)	C(1)–C(2b)–Zr	66.0 (4)
C(2b)–C(3b)–C(4)	129.6 (9)		

Table II. Atomic Coordinates and Thermal Parameters (Å²) for 3

atom	*x*	*y*	*z*	U_{eq}[a]
Zr	0.2040 (1)	0.1500 (1)	0.2610 (1)	0.029 (1)
Cl(1)	0.0826 (1)	–0.0125 (1)	0.2250 (1)	0.039 (1)
Cl(2)	–0.2187 (1)	–0.1451 (1)	0.2721 (1)	0.065 (1)
Cl(3)	–0.2564 (1)	0.0377 (1)	0.0878 (1)	0.056 (1)
Al	–0.1580 (1)	–0.0095 (1)	0.2462 (1)	0.038 (1)
C(1)	0.1349 (3)	0.2453 (1)	0.4067 (2)	0.050 (1)
C(2a)	0.0423 (3)	0.1663 (2)	0.4266 (2)	0.039 (1)
C(3a)	–0.0886 (3)	0.1475 (2)	0.3713 (2)	0.038 (1)
C(4)	–0.1709 (2)	0.0670 (2)	0.3809 (2)	0.044 (1)
C(5)	0.0147 (3)	0.2154 (2)	0.1209 (2)	0.049 (1)
C(6)	0.1072 (3)	0.2855 (1)	0.1569 (2)	0.058 (1)
C(7)	0.2473 (3)	0.2684 (2)	0.1189 (2)	0.058 (1)
C(8)	0.2390 (3)	0.1879 (2)	0.0571 (2)	0.052 (1)
C(9)	0.0970 (3)	0.1561 (1)	0.0582 (2)	0.048 (1)
C(10)	0.4532 (2)	0.1819 (2)	0.3539 (2)	0.053 (1)
C(11)	0.4753 (2)	0.1425 (2)	0.2489 (2)	0.052 (1)
C(12)	0.4244 (2)	0.0542 (2)	0.2521 (2)	0.050 (1)
C(13)	0.3766 (2)	0.0386 (2)	0.3616 (2)	0.050 (1)
C(14)	0.3940 (2)	0.1168 (2)	0.4242 (2)	0.052 (1)
C(2b)	0.008 (1)	0.2096 (7)	0.3875 (9)	0.039 (2)
C(3b)	–0.018 (1)	0.1233 (7)	0.4039 (9)	0.037 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$.

Complex **3** was crystallized from toluene and characterized by X-ray diffraction. The molecule contains two metal centers (Figure 1). The zirconium atom is bonded to two η-cyclopentadienyl rings. The two metal centers are connected by means of a μ-chloro- and a μ-butadiene bridge. The chloride bridges Zr and Al unsymmetrically (Zr–Cl(1) = 2.706 (1) Å; Al–Cl(1) = 2.226 (1) Å). The

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Table III. Selected Spectroscopic Data for Complexes 3 and 4

	^{13}C NMR, δ ($^1J_{CH}$)				^1H NMR, δ				IR	
compd	C(1)	C(2)	C(3)	C(4)	1-H	2-H	3-H	^3J(2-H, 3-H)[b]	$\tilde{\nu}$(C=C)[c]	ref
3	42.8 (147)	102.6 (149)	140.5 (149)	25.4[a]	1.79, 1.46	3.92	4.99	15.4	1564	*e*
4a	36.0 (147[d])	120.1 (144)	116.2 (144)	49.9 (124)	1.78, 1.23	4.70	4.29	*f*	1585	6a
4c	44.4 (149)	129.3 (146)	112.3 (149)	68.3 (129)	1.49, 1.50	4.91	4.53	15.9	*f*	6c
4d	44.0 (150)	126.9 (144)	111.0 (142)	67.2 (131)	1.64, 1.58	4.99	4.59	16.0	*f*	6d

[a] Broad signal. [b] In Hz. [c] In cm^{-1}. [d] Averaged value. [e] This work. [f] Not reported.

Table IV. Comparison of Selected Structural Data for Complexes 3 and 4[a]

compd	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	Zr–C(1)	Zr–C(2)	Zr–C(3)	ref
3	1.486 (4)	1.353 (4)	1.434 (3)	2.348 (2)	2.525 (3)	3.04	*b*
4a	*c*	*c*	*c*	2.46 (1)	2.48 (1)	2.64 (1)	6a
4b	1.421 (11)	1.361 (11)	1.485 (11)	2.427 (8)	2.595 (8)	2.522 (7)	6b
4c	1.400 (10)	1.335 (14)	1.562 (8)	2.420 (6)	2.491 (6)	2.624 (7)	6c
4d[d]	1.414 (6)	1.332 (7)	1.497 (6)	2.435 (4)	2.515 (4)	2.640 (5)	6d
4e	1.422 (6)	1.368 (6)	1.505 (5)	2.443 (4)	2.514 (4)	2.653 (4)	6e
4f	1.435 (10)	1.319 (9)	1.507 (9)	2.392 (7)	2.483 (7)	2.711 (6)	6f

[a] Bond lengths in Å. [b] This work. [c] Data not given due to disorder. [d] Only one of two equivalent resolved disordered data sets is given.

Zr–Cl(1)–Al angle is 111.2 (1)° (Table I). The aluminum center is tetracoordinated and shows a close to tetrahedral bonding geometry (angles C(4)–Al–Cl(3) = 117.5 (1)°; C(4)–Al–Cl(2) = 114.5 (1)°; C(4)–Al–Cl(1) = 102.2 (1)°; Cl(3)–Al–Cl(1) = 105.9 (1)°; Cl(3)–Al–Cl(2) = 110.1 (1)°; Cl(2)–Al–Cl(1) = 105.2 (1)°). The Al–Cl(3) and Al–Cl(2) bonds of length 2.135 (1) and 2.139 (1) Å, respectively, are slightly shorter than the Al–Cl(1) linkage. The Al–C(4) bond between the main-group metal and one butadiene terminus is rather short at 1.966 (2) Å but falls within the typical range of an alkylaluminum Al–C(sp^3) σ bond.[5]

The structure of **3** shows an 80:20 disorder of the butadiene carbon atoms C(2) and C(3). Chemically, the resulting molecular entities correspond to the two enantiomers of the chiral complex **3**. The structural data discussed below correspond to the major molecular isomer observed.

The μ-butadiene ligand exhibits a long–short–long length sequence of the four-carbon framework.[2] The C(1)–C(2) and C(3)–C(4) bonds of 1.486 (4) and 1.434 (3) Å, respectively, are markedly longer than the C(2)–C(3) bond (1.353 (4) Å). The four butadiene carbon atoms are nearly coplanar. The bond angles about the two internal carbon atoms (C(1)–C(2)–C(3) = 125.8 (2)°; C(2)–C(3)–C(4) = 126.1 (2)°) are compatible with sp^2 hybridization, whereas the C(3)–C(4)–Al angle of 112.0 (2)° is close to that for a sp^3-hybridized carbon. The disubstituted central C(2)–C(3) multiple bond of the butadiene ligand framework is trans configurated.

The bonding situation between zirconium and the C(1)–C(2) terminus of the bridging butadiene ligand marks the extraordinary structural feature of complex **3**. To the best of our knowledge it is the first example of a dinuclear main-group-metal/transition-metal complex that contains a μ-(1,2-η^2):(4-η^1)-butadiene ligand. The Zr–C(1) bond length in **3** is 2.348 (2) Å, which is slightly longer than expected for an ordinary Cp_2Zr carbon σ bond, and the Zr–C(1)–C(2) angle is very small at 78.9 (1)°. Consequently, there is a marked interaction between zirconium and the butadiene carbon atom C(2). The Zr–C(2) distance is 2.525 (3) Å. The Zr–C(2) vector is oriented almost normal to the mean butadiene ligand plane. The C(3)–C(2)–Zr angle is near to bisected (98.7 (2)°); the C(1)–C(2)–Zr angle is 65.8 (1)°. There is thus a pronounced interaction between the electrophilic zirconium atom and only one carbon atom (C(2)) of the central carbon–carbon double bond of the bridging C_4H_6 ligand. The Zr–C(3) separation in complex **3** is 3.04 Å, which is outside the range of a strong direct coordinative interaction.

Thus, the curious situation arises that the butadiene ligand in the heterodimetallic complex **3** appears to be σ-bonded at one C_4H_6 terminus to the aluminum atom and slightly unsymmetrically η^2-coordinated to the transition-metal center through carbon atoms C(1) and C(2) at the other end of the four-carbon-containing bridging ligand.

There seems to be no simple valence-bond description for the unusual type of Zr(μ-butadiene)Al bonding situation found in complex **3**. However, a close inspection of the spectroscopic as well as the structural data for complex **3** and comparison with those for a variety of other addition products (e.g. compounds **4a–f**; see Scheme I) of the (butadiene)metallocene reagent (see Tables III and IV) reveal that the bonding situation found in this heterodimetallic compound may fit into a series of related (although differently composed) examples and may thus only represent an extreme situation in a series of overall structurally related organometallic compounds. (Butadiene)zirconocene reacts with alkenes, alkynes, or carbonyl compounds to yield the seven-membered metallacyclic products **4**.[6] Characteristically the butadiene-derived carbon atoms C(1)–C(3) in these compounds are η^3-coordinated to zirconium. The bonding features of this unit uniformly reveal, however, that the (η^3-substituted-allyl)zirconium bonding situation is very unsymmetric. The (η^3-allyl)$ZrCp_2$ moiety in complexes **4** is very much distorted and can probably be characterized by a σ,π-type ligand to metal interaction; i.e., carbon atom C(1) seems to be σ-bonded to zirconium,[7] whereas the remaining trans-configurated C(2)–C(3) multiple bond is π-bonded to the early-transition-metal center. Even the latter bonding situation in complexes **4** is very unsymmetrically oriented, with the Zr–C(3) distance usually being much

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longer than the Zr–C(2) separation in the examples looked at (see Table IV).

The distorted σ,π-allyl-type coordination found in the crystal is in accord with the typical spectroscopic data for this series of complexes **4** measured in solution. A comparison of these data between complex **3** and **4** reveals no fundamental but only gradual differences. ^{1}H and ^{13}C NMR chemical shifts of the new dimetallic complex **3** mostly fit very well into the series of complexes **4**. Typically, the $^1J_{CH}$ coupling constants at carbon atoms C(1) to C(3) do not deviate at all between **3** and the examples of the **4** series. Even the IR ν(C=C) band of **3** is typical for a metallacyclic distorted σ,π-allyl type zirconocene complex **4** (see Table III).

This may mean that complex **3** represents simply an extreme example of the general bonding situation as found in complexes **4**. In **3** the observed trend of the η^3-(σ,π)-allyl type coordination geometry toward a pronouncedly unsymmetrical distortion has reached its maximum. On formally passing from the example **4c** through complexes **4d–f** to complex **3**, one monitors an ever-increasing separation between the zirconium center and carbon atom C(3) (see Table IV). In complex **4f** this interaction already has to be regarded as rather weak. On going to complex **3**, one notices that the Zr–C(3) interaction has almost become negligible.

This unusual type of bonding as observed in the new complex **3**, where a carbon–carbon double bond (C(2)–C(3)) is only bonded through a single sp^2-hybridized carbon atom here seems to be enforced by the geometric situation encountered in the strained metallacyclic framework. Complex **3** may be described as a form of an organometallic analogue of *trans*-cycloheptene. The π-orbital at carbon center C(2) appears to be brought into the vicinity of the electron-deficient metal center sterically. This then creates a geometric situation where an energetically favorable coordinative interaction can occur which leads to a pronounced overall thermodynamic stabilization of the observed bonding situation. Similar effects have been found to lead to stable β-CH agostic interactions in a few specifically substituted (alkenyl)zirconocene complexes.[8] Since a π-orbital seems to be brought quite similarly into the vicinity of the zirconium center in **3** primarily by some steric enforcement, it is tempting to characterize the ensuing C(2) carbon atom to metal bonding situation as a "π-agostic" interaction.[9]

Experimental Section

Reactions and handling of the organometallic compounds were carried out under an inert atmosphere (argon) using Schlenk-type glassware or a glovebox. All solvents employed were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the obtained complex: NMR, Bruker AC 200 P spectrometer (^{1}H, 200 MHz; ^{13}C, 50 MHz); FT IR, Nicolet 5 DXC spectrometer; melting point, Gallenkamp apparatus (the melting point is uncorrected), elemental analysis Voss-Heraeus CHNO-Rapid instrument. (Butadiene)zirconocene was prepared according to a literature procedure.[10]

Reaction of (Butadiene)zirconocene with Aluminum Trichloride. (Butadiene)zirconocene (s-cis/s-trans equilibrium mixture; 550 mg, 2.00 mmol) is dissolved in 30 mL of toluene. Aluminum trichloride (300 mg, 2.26 mmol) is then added in 10 portions to the solution. The mixture is stirred for 2 h. The resulting precipitate is collected by filtration, washed with 20 mL of pentane, and dried in vacuo. This gives 550 mg (67%) of **3** as a yellowish powder which contains ca. 5% of zirconocene dichloride. Crystallization of this material from toluene yields analytically pure crystals of **3** suitable for the X-ray diffraction study; mp 185 °C dec. Anal. Calcd for $C_{14}H_{16}Cl_3AlZr$ (408.8): C, 41.13; H, 3.94. Found: C, 40.88; H, 3.88. ^{1}H NMR (benzene-d_6): δ 5.30, 5.07 (s, 5 H each, Cp), 4.99 (m, 1 H, 3-H), 3.92 (m, 1 H, 2-H), 1.92 (m, 1 H, 4-H), 1.79 (m, 1 H, 1-H), 1.46 (m, 1 H, 1-H′), 1.42 (m, 1 H, 4-H′), coupling constants (Hz) ^2J = 6.6 (1-H, 1-H′), 10.8 (4-H, 4-H′), ^3J = 15.4 (2-H, 3-H), 7.3 (1-H, 2-H), 12.9 (1-H′, 2-H), 6.0 (3-H, 4-H), 12.3 (3-H, 4-H′). ^{13}C NMR (toluene-d_8, 233 K, $^1J_{CH}$ coupling constants in Hz): δ 140.5 ($^1J_{CH}$ = 149, C3), 108.2, 107.7 (each 174, Cp), 102.6 (149, C2), 42.8 (147, C1), 25.4 (br s, C4). IR (KBr): $\tilde{\nu}$ 3105, 1438, 1013, 816 (Cp), 1564 (C=C) cm^{-1}. X-ray crystal structure analysis of complex **3**: yellow crystals (from toluene), 0.25 × 0.35 × 0.46 mm; $M_r = 408.8$; $Z = 4$; $D_{calcd} = 1.69$ g cm^{-3}; $F(000) = 816$ e; monoclinic space group $P2_1/n$; cell constants $a = 9.124\ (1)$ Å, $b = 15.040\ (1)$ Å, $c = 11.737\ (1)$ Å, $\beta = 93.60\ (1)°$, and $V = 1607.4$ Å^3; 25 reflections $13.24 \leq \theta \leq 18.18°$ used for determining the cell constants; $\lambda = 0.710\,69$ Å; graphite monochromator; $[(\sin\theta)/\lambda]_{max} = 0.65$ Å^{-1}; absorption coefficient $\mu = 12.14$ cm^{-1}; no absorption correction applied; 3996 reflections collected ($\pm h,+k,+l$); 3669 independent and 3300 observed reflections; 180 refined parameters; $R = 0.024$, $R_w = 0.032$; all hydrogen atoms located in a final difference map but not included in the refinement; disorder at atom positions C(2) and C(3) ratio 80:20 determined by occupancy refinement with fixed thermal parameters thereafter major component refined anisotropically (only the latter arrangement is depicted in Figure 1); final residual electron density of 0.48 e Å^{-3} at atom Zr.

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Supplementary Material Available: Detailed information on the X-ray crystal structure analysis, including complete listings of bond lengths and angles, positional parameters for the hydrogen atoms, and thermal parameters for **3** (7 pages). Ordering information is given on any current masthead page.

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