Zirconocene Derivatives

Formation of a Unique *ansa*-Metallocene Framework by Intramolecular Photochemical [2+2] Cycloaddition of Bis(2-alkenylindenyl)zirconium Complexes**

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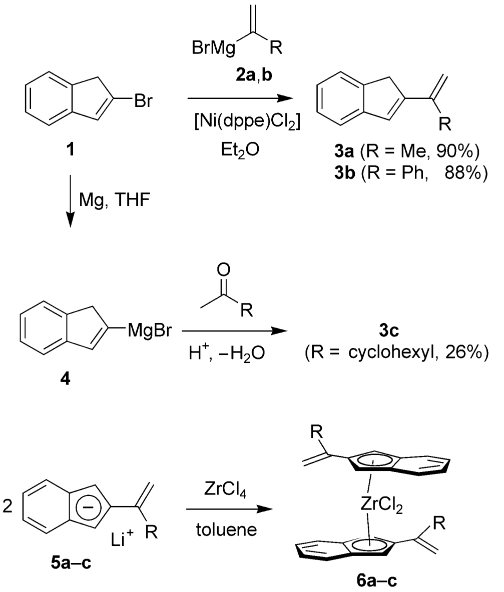
Developing the chemistry of organic functional groups on bent Group 4 metallocene frameworks and related systems has been notoriously difficult due to the high sensitivity of such organometallic compounds toward the typical reaction conditions used.[1] Noteworthy examples include a Mannich-type carbon–carbon coupling reaction[2] and selective transformations of olefinic substituents attached to the metallocene cyclopentadienyl rings, such as metallacyclic olefin coupling[3] and olefin metathesis reactions.[4] Some time ago we had shown that several bis(alkenylcyclopentadienyl)–$ZrCl_2$ complexes undergo a photochemical [2+2] cycloaddition reaction to yield novel *ansa*-metallocenes. However, many of these systems displayed unfavorable photostationary equilibria.[5] We have now found that bis(2-alkenylindenyl)–$ZrCl_2$ complexes undergo a rapid photochemical olefin [2+2] cycloaddition to produce cyclobutylene-bridged *ansa*-metallocenes in which the annelated indenyl-arene rings are located at the front side of the bent metallocene wedge in a symmetrical fashion above and below the σ-ligand system. A series of typical examples will be described herein.

Two synthetic routes were employed to prepare the ligands.[6] Cross-coupling of 2-bromoindene (**1**) with the alkenyl Grignard reagents **2a** (R = Me) and **2b** (R = Ph) gave the corresponding 2-alkenylindenes **3a**,**b** in about 90% yield each (Scheme 1). The cyclohexyl-substituted 2-alkenylindene was prepared by a complementary route starting from 2-indenyl magnesium bromide (**4**). Addition to cyclohexyl methyl ketone followed by acid-catalyzed dehydration provided both alkene isomers. Chromatographic separation furnished the required compound **3c** in 26% yield. Deprotonation of 2-alkenylindenes **3** was achieved by treatment with *n*-butyl lithium (**3a**,**c**) or LDA (**3b**) in Et_2O at 0 °C. Subsequent reaction of the resulting alkenylindenyl lithium reagents (**5a–c**) in toluene with $ZrCl_4$ then yielded the bis(2-alkenylindenyl)–$ZrCl_2$ complexes **6a** (R = Me, 60%), **6b** (R = Ph, 51%), and **6c** (R = cyclohexyl, 27%), respectively.



Scheme 1. Synthesis of bis(2-alkenylindenyl)–$ZrCl_2$ complexes **6a–c**.

In solution, complexes **6a–c** exhibit typical NMR spectra for open, nonbridged metallocenes in rapid conformational equilibrium, even at very low temperatures: complex **6a** (R = Me) displays ^{1}H NMR resonances of symmetry-equivalent $CH_2{=}C(CH_3)$ substituents at $\delta = 5.41$, 5.17 ppm (=CH_2) and $\delta = 1.94$ ppm (CH_3) [^{13}C NMR: $\delta = 137.8$, 115.3 ppm (C=CH_2), $\delta = 21.2$ ppm (CH_3)]. As expected, only a single indenyl 1-H/3-H signal ($\delta = 6.25$) is observed in addition to a simple AA′XX′ pattern for the 4-H/7-H and 5-H/6-H indene hydrogen resonances ($\delta = 7.56$, 7.22 ppm).

Single crystals for X-ray structure analysis were obtained from the complexes **6a** (R = Me) and **6c** (R = cyclohexyl), in both cases from solutions in toluene/pentane at −20 °C. In the crystal **6a** features a "*meso*-like" rotational structure[7] in which the annelated phenylene rings of the two indenyl ligands are oriented toward the same side of the bent metallocene wedge (Figure 1, left). The $CH_2{=}C(CH_3)$ substituents at the indenyl 2-positions point to the other lateral sector. The $CH_2{=}C(CH_3)$ substituents are both oriented in the indenyl ligand plane (θ(C9-C1,C10,C11) = −170.6(6)°) with the =CH_2 groups pointing toward the back side of the bent metallocene wedge.

In contrast, the cyclohexyl-substituted complex **6c** attains an approximately C_2-symmetric "*rac*-like" conformation[7,8] in the solid state, with the $CH_2{=}C$(cyclohexyl) substituents oriented toward opposite lateral metallocene sectors (Figure 1, right). Again, the alkenyl groups are almost coplanar with the adjacent indenyl rings (θ(C2-C1,C10,C11) = 13.7(5)°). In this case, the =CH_2 moieties point toward the open front side of the bent metallocene wedge.

Complexes **6a–c** provide active homogeneous Ziegler–Natta catalysts when activated with a large excess of methylalumoxane (MAO). They yield atactic polypropylene with typical activities (e.g. 100 g PP mmol^{-1}[Zr] h^{-1} bar^{-1} at

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[**] Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. W.-L. Nie thanks the Alexander-von-Humboldt-Foundation for a fellowship.

DOI: 10.1002/anie.200351886

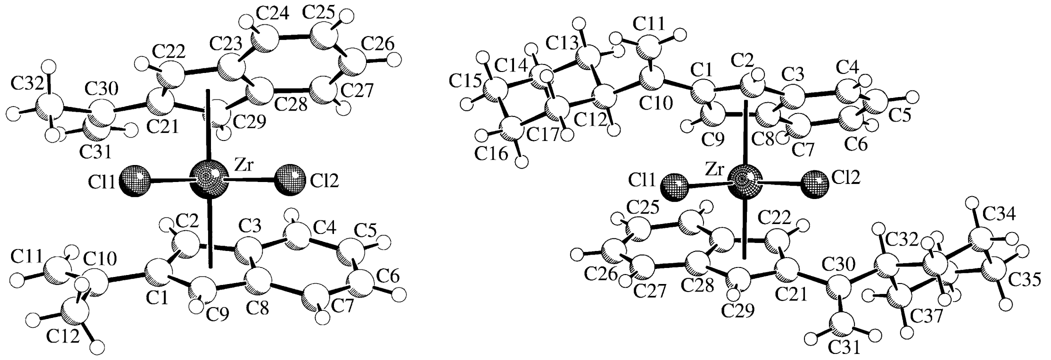
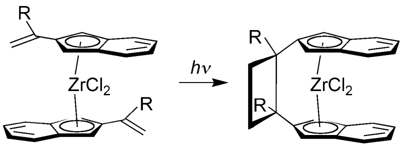


Figure 1. The molecular structure of **6a** (left) and **6c** (right). Selected bond lengths [Å] and angles [°]: **6a**: Zr–Cl1 2.438(2), Zr–Cl2 2.417(2), C1–C10 1.488(8), C21–C30 1.488(8), C10–C11 1.336(9), C30–C31 1.317(8), C10–C12 1.483(8), C30–C32 1.503(9); Cl1-Zr-Cl2 93.6(1), C1-C10-C11 120.1(6), C21-C30-C31 120.9(6), C1-C10-C12 117.1(6), C21-C30-C32 116.6(6), C11-C10-C12 122.5(6), C31-C30-C32 122.6(6). **6c**: Zr–Cl1 2.411(1), Zr–Cl2 2.402(1), C1–C10 1.467(4), C21–C30 1.472(4), C10–C11 1.325(5), C30–C31 1.329(4), C10–C12 1.507(5), C30–C32 1.514(4); Cl1-Zr-Cl2 96.30(3), C1-C10-C11 119.4(3), C21-C30-C31 119.3(3), C1-C10-C12 117.8(3), C21-C30-C32 118.5(3), C11-C10-C12 122.7(3), C31-C30-C32 122.0(3).

0 °C, $M_w = 114\,000$, $M_w/M_n = 2.1$, mmmm = 11 % for **6a**/MAO, Al:Zr ≈ 2000).

The most remarkable feature of complexes **6** is their behavior upon photolysis. Irradiation of **6a–c** in toluene results in rapid and practically complete conversion into the corresponding 1,2-disubstituted 1,2-cyclobutylene-bridged *ansa*-zirconocenes **7a–c** [Eq. (1)] The [2+2] cycloadditions are complete within 2–3 h, and the conversion **6**→**7** was nearly quantitative, as judged from NMR spectra. The photochemical ring closure takes place stereoselectively to yield **7a–c**, in which the substituents R are in 1,2-*cis* positions at the newly formed four-membered ring. This is evident from the NMR spectra of **7**, which exhibit a right/left differentiation of the indenyl signals (in contrast to the symmetry-equivalent signals of the open, conformationally equilibrated starting materials **6**). The ^{1}H NMR spectrum of **7a** (R = Me) shows equal-intensity pairs of signals for the indenyl protons 1-H/3-H ($\delta = 6.60/6.56$ ppm; ^{13}C NMR: $\delta = 102.7/99.4$ ppm), 4-H/7-H ($\delta = 7.61/7.46$ ppm), and 5-H/6-H ($\delta = 7.21/7.15$ ppm). It also features an AA′XX′ pattern of cyclobutylene proton signals at $\delta = 2.77$ and 2.23 ppm (^{13}C NMR: $\delta = 31.1$ ppm) and a single resonance for the methyl group at $\delta = 1.64$ ppm (^{13}C NMR: $\delta = 25.8$ ppm).



6 **7** (1)

Complex **7c** (R = cyclohexyl) was characterized by X-ray structure analysis (Figure 2).[9] The complex contains a pair of 2-substituted η^5-indenyl ligands with uniformly coordinated annelated five-membered rings (the Zr–C_{Cp} distances range from 2.458(4) Å to 2.608(4) Å). The cyclobutylene bridge that was formed by the photochemical [2+2] cycloaddition is located at the narrow back side of the bent metallocene wedge. Three of the cyclobutane bond lengths are in the typical range [1.548(5) Å (C10–C11), 1.527(5) Å (C11–C31), 1.556(5) Å (C31–C30)] whereas the internal C–C connection is slightly longer [1.628(5) Å (C10-C30)]. This probably indicates a slight strain within the *ansa*-metallocene framework. The four-membered carbocycle in **7c** is slightly puckered (sum of the internal bonding angles: 355.5°; angle between the C11-C10-C30 and C11-C31-C30 planes: 23.0°).

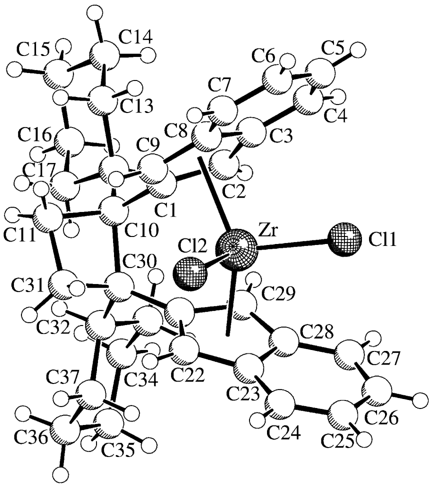


Figure 2. Molecular structure of **7c**. Selected bond lengths [Å] and angles [°]: Zr–Cl1 2.401(1), Zr–Cl2 2.469(1), C1–C10 1.532(5), C21–C30 1.507(5), C10–C30 1.628(5), C10–C11 1.548(5), C30–C31 1.556(5), C10–C12 1.553(5), C30–C32 1.562(5), C11–C31 1.527(5); Cl1-Zr-Cl2 98.19(4), C1-C10-C11 111.2(3), C21-C30-C31 114.3(3), C1-C10-C12 107.8(3), C21-C30-C32 109.1(3), C11-C10-C12 114.3(3), C31-C30-C32 111.0(3), C1-C10-C30 108.2(3), C21-C30-C10 116.0(3), C30-C10-C11 87.4(3), C10-C30-C31 86.7(2), C10-C11-C31 90.6(3), C30-C31-C11 90.8(3).

Upon activation with MAO the *ansa*-metallocenes **7** provide interesting catalysts for ethene/1-octene copolymerization at elevated temperatures.[10] At 60 °C the **7a**/MAO system (Al:Zr ≈ 1150) yields a random ethene/1-octene copolymer. The catalyst activity (ca. 2300 g copolymer mmol^{-1} [Zr] h^{-1} bar^{-1}) and the 1-octene incorporation (ethene:1-

octene ≈ 5:1) approaches values comparable with those of some "constrained geometry" catalysts;[11] however, the molecular weight of the copolymer obtained with **7a**/MAO is rather low ($M_w = 3800$; $M_w/M_n = 2.0$). Figure 3 shows a ^{13}C NMR spectrum of a typical example.

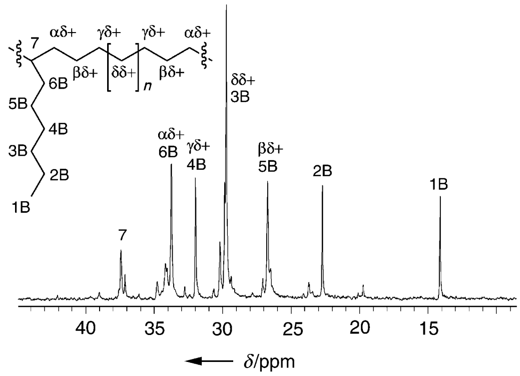
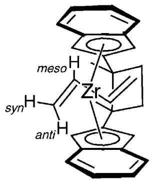


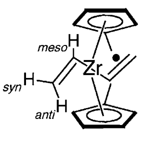
Figure 3. $^{13}C\{^1H\}$ NMR spectrum of an ethene/1-octene copolymer (ca. 5:1) obtained with the **7a**/MAO catalyst at 60 °C (1 bar C_2H_4, Al:Zr ≈ 1150, $M_w \approx 3800$)

The **7a**/MAO catalyst system is still active at 90 °C. However, at this temperature rapid decomposition occurs, which results in darkly colored polymer mixtures as well as lower activities and molecular weights of the ethene/1-octene copolymers (**7a**/MAO, Al:Zr ≈ 1150, 90 °C, activity: ca. 1400, 4.5:1 ethene/1-octene ratio in the copolymer, $M_w \approx 1500$ (bimodal distribution)).

Treatment of many *ansa*-zirconocene dichlorides with butadiene magnesium reagents predominantly (or exclusively) yields the (s-*cis*-η^4-butadiene)zirconocene isomers.[12] In contrast, the reaction of **7a** with $C_4H_6Mg{\cdot}2\,THF$ gives only



s-*trans*-**8**



s-*trans*-**9**

s-*trans*-**8**. A comparison of the ^{1}H NMR spectrum of s-*trans*-**8** (Figure 4) with that of a typical example (e.g. s-*trans*-**9**)[12] reveals a large shift of the butadiene *meso*-H resonances to negative δ values [s-*trans*-**8**: $\delta = -1.45$ (dt, $^3J_{HH(meso,anti)} = {}^3J_{HH(meso,meso)} = 16.2$ Hz, $^3J_{HH(meso,syn)} = 7.2$ Hz), $\delta = -1.55$ (dt, $^3J_{HH} = 16.2$ Hz and 7.1 Hz); s-*trans*-**9**: $\delta = +1.34$]. This indicates that the C–H$_{meso}$ bonds in s-*trans*-**8** are oriented toward the π system of the annelated arene rings. It is likely that the ensuing σ-C–H/π-arene interaction[13] stabilizes s-*trans*-**8** to such an extent that the corresponding s-*cis* isomer can no longer energetically compete under the equilibrium conditions.

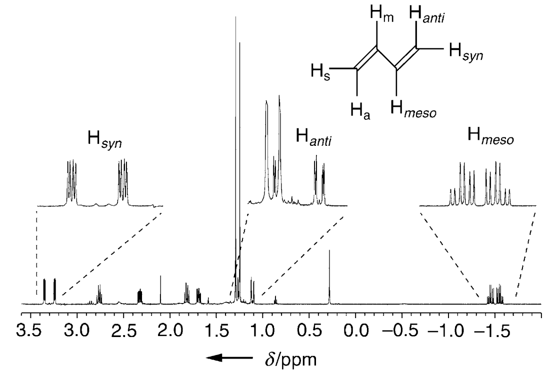


Figure 4. Portion of the ^{1}H NMR spectrum of s-*trans*-**8** (C_6D_6, 298 K, 600 MHz).

The *ansa*-zirconocene **7** was readily prepared by [2+2] cycloaddition. The remarkable spectroscopic, structural, and chemical features of *ansa*-metallocenes derived from **7** may be regarded as first indications for a unique stereoelectronic environment at the metal center inside the "phenylene π-electron box". We expect that the introduction of reactive ligands into this specific electronic environment will lead to the discovery of additional unusual chemical properties.

Experimental Section

7a: A solution of **6a** (90 mg, 0.19 mmol) in toluene (5 mL) was irradiated for 3 h at ambient temperature in a Schlenk flask with an external Philips HPK 125 UV lamp with a pyrex filter. The solvent was removed in vacuo. The residue was washed with pentane, and the product was collected by filtration to yield **7a** (45 mg, 50 %). Elemental analysis (%) calcd for $C_{24}H_{22}Cl_2Zr$ (472.6): C 61.00, H 4.69; found: C 60.32, H 4.56; ^{1}H NMR (CD_2Cl_2, 298 K, 599.0 MHz): $\delta = 7.61, 7.46$ (m, each 2H, indenyl 4-H, 7-H), 7.21, 7.15 (m, each 2H, indenyl 5-H, 6-H), 6.60, 6.56 (dd, each 2H, indenyl 1-H, 3-H), 2.77, 2.23 (m, each 2H, cyclobutylene CH_2), 1.64 ppm (s, 6H, CH_3); ^{13}C NMR (CD_2Cl_2, 298 K, 150.6 MHz): $\delta = 147.4$ (indenyl C2), 131.4, 126.8 (indenyl C3a, C7a), 126.5, 125.6 (indenyl C5, C6), 125.7, 125.4 (indenyl C4, C7), 102.7, 99.4 (indenyl C1, C3), 50.3 (cyclobutylene C), 31.1 (cyclobutylene CH_2), 25.8 ppm (CH_3).

7c: The photolysis of **6c** (90 mg, 0.15 mmol) was carried out analogously to yield **7c** (50 mg, 55 %). Single crystals of **7c** were obtained from dichloromethane. Elemental analysis (%) calcd for $C_{34}H_{38}Cl_2Zr{\cdot}0.5\,CH_2Cl_2$ (651.3): C 63.63, H 6.04; found: C 64.39, H 5.94; ^{1}H NMR (CD_2Cl_2, 298 K, 599.0 MHz): $\delta = 7.64, 7.41$ (m, each 2H, indenyl 4-H, 7-H), 7.24, 7.12 (m, each 2H, indenyl 6-H, 5-H), 6.87, 6.37 (dd, each 2H, indenyl 1-H, 3-H), 2.54, 2.42 (m, each 2H, cyclobutylene CH_2), 2.05 (m, 2H, cyclohexyl CH), 1.90–1.05 ppm (several m, 20H, cyclohexyl CH_2); ^{13}C NMR (CD_2Cl_2, 298 K, 150.6 MHz): $\delta = 144.1$ (indenyl C2), 132.4, 124.0 (indenyl C3a, C7a), 127.0, 125.5 (indenyl C6, C5), 125.31, 125.29 (indenyl C7, C4), 107.3, 99.9 (indenyl C1, C3), 61.2 (butylene C), 47.0 (cyclohexyl CH), 31.4, 29.2, 28.9, 27.5, 27.4, 27.0 ppm (CH_2).

***s-trans* 8:** Toluene (30 mL) was added to **7a** (240 mg, 0.51 mmol) and the butadiene magnesium reagent ($C_4H_6Mg{\cdot}2\,THF$, 120 mg, 0.54 mmol) at −78 °C. The mixture was allowed to reach room temperature slowly and stirred overnight. The solvent was removed in vacuo, and the residue was washed with pentane and dried in vacuo to give of **8** (120 mg, 52 %) as a dark red solid. ^{1}H NMR (C_6D_6, 298 K, 599.0 MHz): $\delta = 6.85, 6.53, 6.49, 6.27, 6.26, 6.13$ (each 1H, indenyl$_A$), 6.84, 6.58, 6.54, 6.47, 6.28, 6.21 (each 1H, indenyl$_B$), 3.35 (dd, $^3J_{HH} =$

7.2 Hz, $^{2}J_{HH}=3.2$ Hz) and 3.24 (dd, $^{3}J_{HH}=7.1$ Hz, $^{2}J_{HH}=3.1$ Hz) (each 1 H_{syn}, butadiene), 1.28 (dd, $^{3}J_{HH}=16.2$ Hz, $^{2}J_{HH}=3.2$ Hz) and 1.11 (dd, $^{3}J_{HH}=16.2$ Hz, $^{2}J_{HH}=3.1$ Hz) (each 1 H_{anti}, butadiene), −1.45 (dt, $^{3}J_{HH}=16.2$ Hz, $^{3}J_{HH}=7.2$ Hz) and −1.55 (dt, $^{3}J_{HH}=16.2$ Hz, $^{3}J_{HH}=7.1$ Hz) (each 1 H_{meso}, butadiene), 2.76/1.69 and 2.32/1.82 (each 1 H, cyclobutylene CH_2), 1.29, 1.25 ppm (each s, each 3 H, CH_3). ^{13}C NMR (C_6D_6, 298 K, 150.6 MHz): $\delta=137.8$, 123.1, 123.5, 122.6, 121.9, 121.6, 119.7, 83.2, 82.8 (indenyl$_B$), 137.2, 123.7, 123.6, 123.3, 122.7, 121.5, 118.0, 83.7, 81.2 (indenyl$_A$), 114.1, 113.5, 73.5, 71.0 (butadiene), 49.1, 48.9, 31.9, 29.9 (cyclobutylene), 27.2, 23.8 ppm (CH_3).

Received: May 13, 2003
Revised: September 8, 2003 [Z51886]

Keywords: indenyl ligands · metallocenes · photolysis · polymerization · zirconium

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[8] For the general conformational properties of substituted bis(indenyl)$ZrCl_2$ complexes see, for example: M. Knickmeier, G. Erker, T. Fox, *J. Am. Chem. Soc.* **1996**, *118*, 9623–9630; T. Jödicke, F. Menges, G. Kehr, G. Erker, U. Höweler, R. Fröhlich, *Eur. J. Inorg. Chem.* **2001**, 2097–2106, and references therein.

[9] CCDC 210084–210086 contains 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) 1223-336-033; or deposit@ccdc.cam.ac.uk). **6a**: $C_{24}H_{22}Cl_2Zr$, monoclinic, space group $P2_1/n$, $a=10.862(1)$, $b=13.507(1)$, $c=14.264(1)$ Å, $\beta=93.23(1)°$, $V=2089.4(3)$ Å^3, $\rho_{calcd}=1.502$ g cm^{-3}, $\mu=7.88$ cm^{-1}, $Z=4$, $T=198$ K, 5775 reflections collected, 3498 independent and 2383 observed, 246 refined parameters, $R=0.056$, $wR^2=0.127$. Due to the small size, the crystal diffracted very weakly. **6c**: $C_{34}H_{38}Cl_2Zr$, orthorhombic, space group $P2_12_12_1$, $a=9.391(1)$, $b=11.494(1)$, $c=26.995(1)$ Å, $V=2913.8(4)$ Å^3, $\rho_{calcd}=1.388$ g cm^{-3}, $\mu=5.82$ cm^{-1}, $Z=4$, $T=198$ K, 20454 reflections collected, 7080 independent and 5824 observed, 334 refined parameters, $R=0.037$, $wR^2=0.067$, Flack parameter −0.06(4). **7c**: $C_{34}H_{38}Cl_2Zr\cdot CH_2Cl_2$, monoclinic, space group $P2_1/n$, $a=10.694(1)$, $b=7.880(1)$, $c=37.258(1)$ Å, $\beta=94.11(1)°$, $V=3131.6(3)$ Å^3, $\rho_{calcd}=1.471$ g cm^{-3}, $\mu=7.16$ cm^{-1}, $Z=4$, $T=198$ K, 11911 reflections collected, 7160 independent, 4785 observed reflections, 362 refined parameters, $R=0.054$, $wR^2=0.156$.

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