A New Approach for the Synthesis of Neutral and Anionic Zirconocene Aldehyde Complexes

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To expand the availability of transition-metal aldehyde complexes for study, a new method for their synthesis has been developed. Our first application of this method has been to the synthesis of zirconocene η^2-aldehyde complexes. Proceeding through α-stannylalkoxide intermediates (M–OCHR–SnMe$_3$), this route provides ready access to both neutral and anionic complexes under mild conditions. The first X-ray structure of an anionic aldehyde complex is reported. The neutral complexes dimerize producing meso and racemic diastereomers. Monomeric zirconaoxiranes are shown to be excluded from the reaction coordinate during insertion and isomerization reactions of these neutral complexes. (R,S)-[Cp$_2$Zr(η^2-OCHCH$_2$CHMe$_2$)]$_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 9.7293(19) Å, b = 18.733(4) Å, c = 8.0984(13) Å, β = 109.838(13)°, and Z = 2. The refinement was carried out with 2496 observed room temperature reflections to give $R(F)$ = 2.78% and $R_w(F)$ = 3.00%. {Cp$_2$Zr(Me)(η^2-OCHCH$_2$CHMe$_2$)Li}$_2$(C$_4$H$_8$O) crystallizes in the orthorhombic space group $C2cb$ with a = 11.923(4) Å, b = 20.307(4) Å, c = 14.768(4) Å, and Z = 4. The refinement was carried out with 1439 observed room temperature reflections to give $R(F)$ = 3.56% and $R_w(F)$ = 3.51%.

Introduction

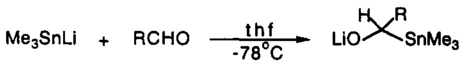
Transition-metal aldehyde complexes have been implicated as critical intermediates during homogeneously catalyzed carbon monoxide hydrogenations[1] and hold promise as new reagents for organic synthesis.[2] When bound in an η^2-fashion, the aldehyde is a π-accepting ligand and a chiral center exists at the aldehydic carbon. These features promise a diverse and asymmetric reaction chemistry tunable through the particular choice of organometallic fragment to which the aldehyde is bound.

To develop the chemistry of this under-represented class of compounds more fully, we have designed a flexible new method for their synthesis. Our first application of this method has provided us with general and efficient access to both neutral and anionic zirconocene(η^2-aldehyde) complexes (zirconaoxiranes).

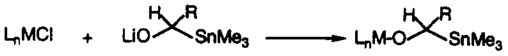
Results and Discussion

I. Synthetic Method. In order to allow for maximum convenience and generality, our synthesis starts with the free organic aldehyde. Complexation to the metal fragment is accomplished in a stepwise fashion.

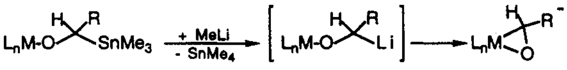
To facilitate introduction of the aldehyde fragment into the metal's coordination sphere, it is first converted to an α-stannylalkoxide by a procedure adapted from the work of Still.[3] Reactions of this type have been shown to be quite general proceeding rapidly and quantitatively under mild conditions.



The anionic handle this provides allows the metal–oxgen bond to be established using a simple metathesis reaction.



Once the α-stannylalkoxide is incorporated into the metal's coordination sphere, the trimethyltin substituent is cleaved with methyllithium at −78 °C. Conditions for transmetalation of α-stannyl ethers, organic analogs of our metal α-stannylalkoxides, had been developed previously by Still.[3]



In general, interaction of the incipient carbanion with the metal center may lead to an η^2-(C,O)-coordination mode if the intermediate α-stannylalkoxide complex is coordinatively unsaturated and/or contains an ancillary ligand that may be lost. If such an ancillary ligand is anionic, neutral complexes may form, otherwise anionic complexes should result. Appropriate organometallic precursors to test both of these situations are found in Cp$_2$ZrCl$_2$ and Cp$_2$Zr(Me)Cl. With these reagents the requisite zirconocene (α-stannylalkoxide) complexes form cleanly over several hours in tetrahydrofuran (thf).

Low temperature transmetalation with methyllithium in thf or dimethoxyethane (DME) readily converts **1**–**3** to

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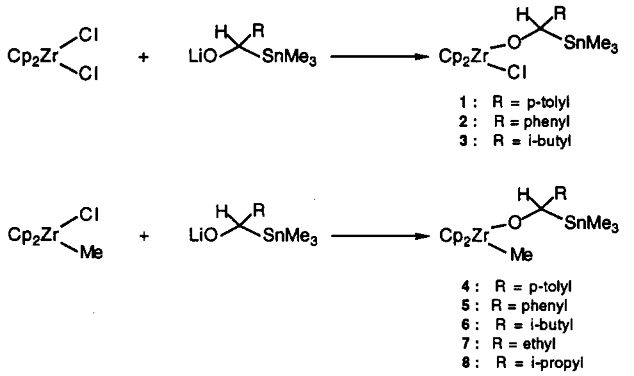
[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1993.

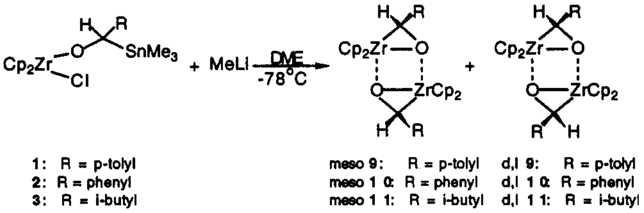
[1] Dombek, B. D. *Adv. Catal.* 1983, *32*, 325–416.

[2] Garner, C. M.; Mendez, N. Q.; Kowalczyk, J. J.; Fernandez, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* 1990, *112*, 5146. Waymouth, R. M.; Clauser, K. R.; Grubbs, R. H. *J. Am. Chem. Soc.* 1986, *108*, 6385–6387. Waymouth, R. M.; Grubbs, R. H. *Organometallics* 1988, *7*, 1631–1635.

[3] Still, W. C. *J. Am. Chem. Soc.* 1978, *100*, 1481.

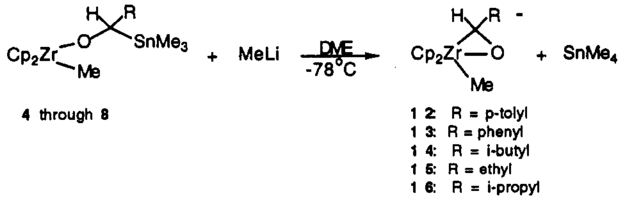


the neutral zirconaoxiranes **9–11**. The products of this reaction are dimeric, as expected from precedence supplied by Erker's zirconocene(η^2-benzophenone)[4] and zirconocene(η^2-formaldehyde)[5] complexes.



Our neutral complexes differ from any aldehyde complexes previously reported in that they are homodimers containing a chiral center in each monomer, leading to the production of meso and racemic diastereomers. Syntheses of **11** provide 2:1 mixtures of the meso and *d,l* isomers while syntheses of **9** and **10** result in meso:*d,l* ratios of 6:1. The aldehyde's η^2-coordination mode causes the cyclopentadienyl ligands on each zirconium atom to be inequivalent, which is reflected in the ^{1}H and ^{13}C NMR spectra. Confirmation of the nature of these compounds and assignment of the NMR parameters for meso and *d,l* isomers is provided by an X-ray crystallographic study of the isovaleraldehyde complex *meso*-**11** (Figure 1). The meso isomers are less soluble than the *d,l* isomers in nonpolar solvents (e.g., benzene, ether, hexane) and may be isolated free of the *d,l* form. The *d,l* complexes are more difficult to separate from the remaining meso isomer and have not been isolated in isomerically pure form but only as samples enriched in the *d,l* isomer.

The anionic aldehyde complexes **12** through **16** may be obtained by exposure of **4** through **8** to transmetalation conditions. Compounds **12** and **13** may be synthesized in either thf or DME, but for compounds **14–16**, DME must be used as solvent.



NMR spectra display inequivalent cyclopentadienyls and also a zirconium bound methyl group. An X-ray crystal structure of complex **14** confirms the nature of these anionic complexes (Figure 2). Compounds **12–14** have also been obtained by treatment of tetrahydrofuran solutions of **9–11** with methyllithium.

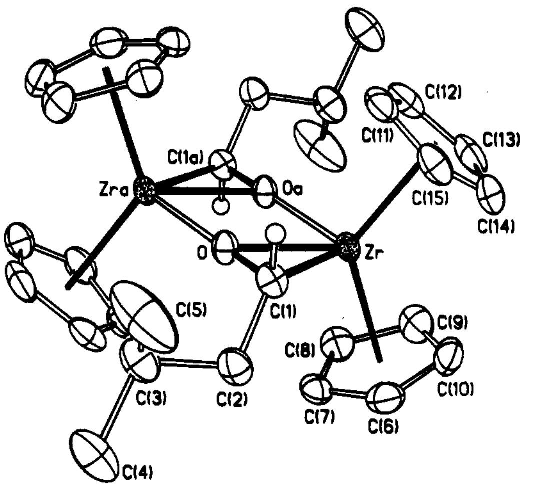


Figure 1. ORTEP drawing and labeling scheme for *meso*-**11** with selected bond distances and angles: Zr–C(1) 2.266(3), Zr–O 2.101(2), O–C(1) 1.421(3), Zr–O(a) 2.170(2) Å; O–Zr–C(1) 37.7(1), Zr–O–C(1) 77.4(1), Zr–C(1)–O 64.8(1), O–Zr–O(a) 69.6(1), Zr–O–Zr(a) 110.3(1), C(1)–O–Zr(a) 170.0(2)°.

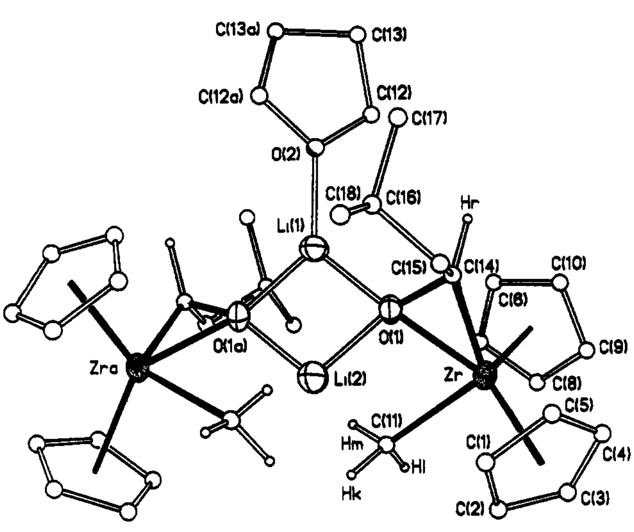


Figure 2. ORTEP drawing and labeling scheme for **14** with selected bond distances and angles: Zr–O(1) 2.147(4), Zr–C(14) 2.262(7), Zr–C(11) 2.392(8), C(14)–O(1) 1.425(7), C(11)–H(k) 1.06(5), C(11)–H(l) 0.94(5), C(11)–H(m) 0.89(6), O(1)–Li(1) 1.85(1), O(1)–Li(2) 1.83(1), Li(1)–O(2) 1.91(2) Å; O(1)–Zr–C(14) 37.6(2), O(1)–C(14)–Zr 66.8(3), Zr–O(1)–C(14) 75.6(3), O(1)–Zr–C(11) 78.7(2), O(1)–Li(1)–O(1a) 99.1(7), O(1)–Li(1)–O(2) 130.4(4), O(1a)–Li(1)–O(2) 130.4(4), O(1)–Li(2)–O(1a) 100(1)°.

Before this work anionic aldehyde complexes were virtually unknown, the only previous example[6] being CpMo(CO)$_2$(MeCHO)$^-$, although related anionic ketene complexes have been reported by Grubbs.[7] This new synthetic method provides a convenient route for complexation of aldehydes to the zirconocene fragment, providing access to neutral and anionic zirconaoxiranes in good to excellent overall yields (65–88%).

II. Crystal Structures of *meso*-11 and -14. As with the (benzophenone)zirconocene[4] and (formaldehyde)-

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[4] Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668.

[5] Erker, G.; Hoffmann, U.; Zwettler, R.; Betz, P.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630–631.

[6] Gauntlett, J. T.; Taylor, B. F.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 420–421.

[7] Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210–2211. Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499–5500.

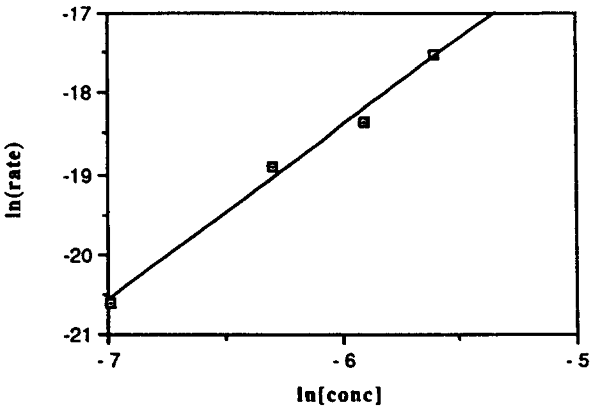

Figure 3. Plot for the determination of the isomerization reaction order at 69 °C (r^2 = 0.99).

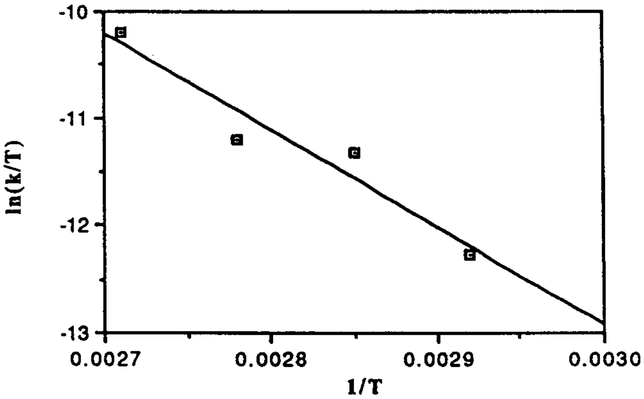

Figure 4. Plot for the determination of the isomerization activation parameters (r^2 = 0.93).

zirconocene[5] complexes, *meso*-**11** exists as a tightly bound dimer in the solid state. Thus, the Zr–Oa bond (2.170(2) Å) responsible for the dimerization in *meso*-**11** is comparable in length to that found for the formaldehyde complex (2.200(2) Å) and significantly shorter than that found for the benzophenone complex (2.287(2) Å). The Zr–O (2.101(2) Å), Zr–C(1) (2.266(3) Å), and C(1)–O (1.421(3) Å) bond lengths are typical of complexes where the zirconaoxirane resonance structure is known to be dominant. The two monomeric units of *meso*-**11** are related to each other by a crystallographically imposed inversion center causing the Zr_2O_2 core to be rigorously flat. The CNT1-Zr-CNT2 plane is essentially perpendicular to the Zr_2O_2 plane (89.2°) while the Zr–O–C(1) plane is tipped 5.6° from a coplanar arrangement.

Complex **14** also crystallizes as a dimeric species, but the zirconium centers are not involved in the dimerization interaction. Instead, dimerization occurs through bridging of the two aldehyde oxygen atoms by lithium counterions. The two monomeric units are related to each other by a crystallographic 2-fold axis running through the lithium atoms.

The bond distances observed in the zirconaoxirane subunit (Zr–O(1), 2.147(4) Å; Zr–C(14), 2.262(7) Å; C(14)–O(1), 1.425(7) Å) are quite similar to those observed for *meso*-**11**, the only significant difference being a small increase in the Zr–O distance. An analogous trend has been observed for related neutral and anionic ketene complexes reported by Grubbs.[7] An interesting feature of the solid-state structure of **14** is found in the lithium coordination environments. Li(1) is stabilized by interactions with three oxygen donors in an approximately trigonal planar geometry. In contrast, Li(2) has only two oxygen donor ligands. Further stabilization of Li(2) apparently occurs through interaction with the C(11)–H(k) bonds of the terminal methyl ligands on each zirconium. This interaction is reflected in elongation of the C–H(k) bond (1.06(5) Å) relative to the other two C–H bonds of the methyl group (0.94(5), 0.89(6) Å). A pseudotetrahedral environment around Li(2) is thereby attained.

III. Coordinatively Unsaturated Intermediate. Zirconocene complexes of η^2-bound unsaturated ligands have demonstrated great promise as reagents for carbon–carbon bond formation to unsaturated organic substrates. Thus, coupling reactions involving zirconocene alkyne,[8] alkene,[8] and imine[9] complexes and zirconocene mediated cyclizations[10] of α,ω-dienes, -diynes, and -enynes have been known for some time. Erker has shown that a dimeric (benzophenone)zirconocene complex will insert alkynes regioselectively, yielding zirconaoxacyclopentenes.[4,11]

The most plausible mechanism for such reactions involves complexation of substrate by a coordinatively unsaturated intermediate followed by a metallacycle expansion step. Although the solid-state structure of neutral, dimeric zirconaoxiranes shows that each zirconium atom is coordinatively saturated, a coordinatively unsaturated complex must be accessible in solution. Erker has postulated that an equilibrium between dimeric and monomeric (benzophenone)zirconocene complexes is established in solution and that the monomeric complex is the species responsible for reactivity.[4,11] The relative stereochemical label in our neutral aldehyde complexes supplied by the presence of two chiral centers, one in each monomeric unit, provides the first opportunity to probe the nature of the reactive intermediate generated in solution from dimeric zirconaoxiranes. We have found that the reaction of the dimeric isovaleraldehyde complexes, **11**, with carbon monoxide proceeds through a mechanism which *excludes* monomeric zirconaoxiranes from the reaction coordinate.

Reaction of benzene or thf solutions of isomerically pure *meso*-**11** with 1 atm of CO at room temperature produces a single bimetallic complex **17** in which CO has inserted into only one of the two zirconaoxirane subunits.[12] Although we have not been able to isolate *d,l*-**11** completely free from *meso*-**11**, exposure of mixtures of *meso*- and *d,l*-**11** to carbon monoxide result in formation of **17** and its isomer **18** in ratios corresponding to the original meso:*d,l* ratio. Since *meso*-**11** has been shown to produce **17**

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[8] Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–58 and references therein.

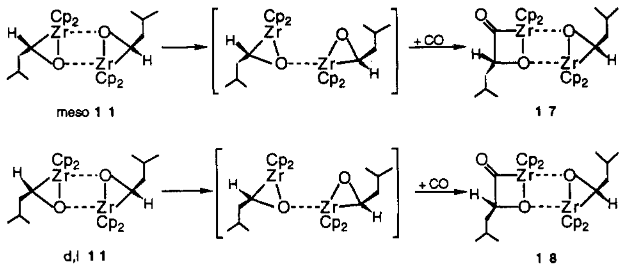
[9] Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321. Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486.

[10] Negishi, E. *Chem. Scr.* **1989**, *29*, 457–468. Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahshi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105. Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435. Rajan Babu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128. Parshal, G. W.; Nugent, W. A.; Chan, D. M.-T.; Tam, W. *Pure Appl. Chem.* **1985**, *57*, 1815. Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244. Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. Yousaf, S. M.; Farona, M. F.; Shively, R. J.; Youngs W. J. *J. Organomet. Chem.* **1989**, *363*, 281.

[11] Rosenfeldt, F.; Erker, G. *Tetrahedron Lett.* **1980**, *21*, 1637. Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29–42. Erker, G.; Rosenfeldt, F. *Tetrahedron* **1982**, *38*, 1285.

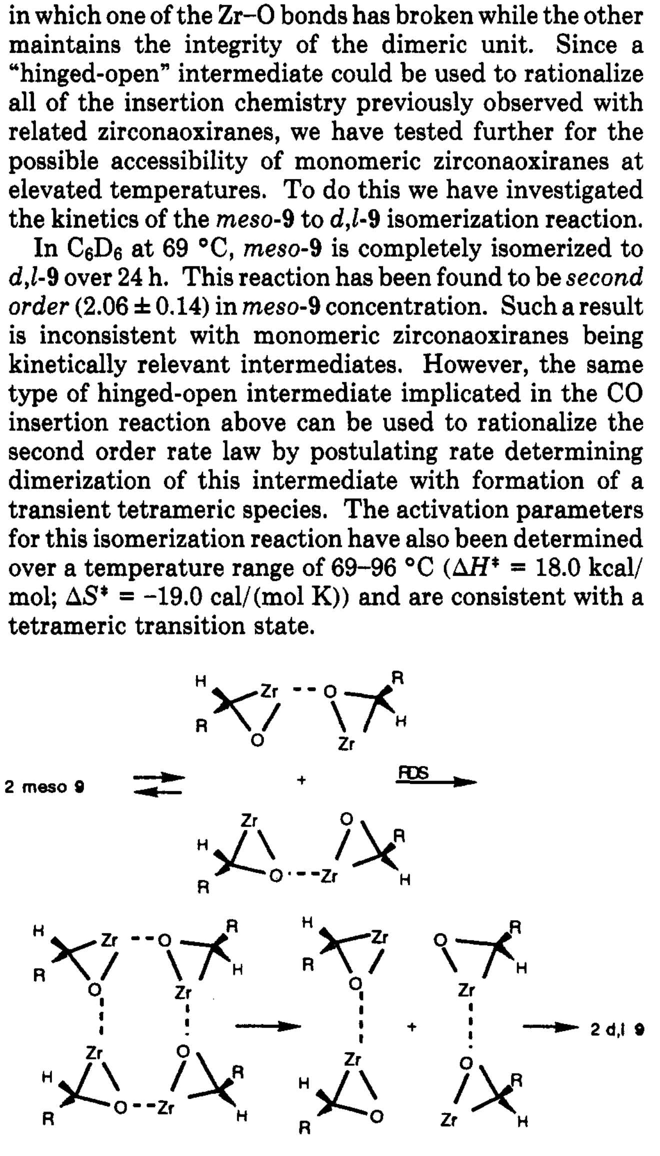
[12] Erker has reported an analogous reaction with $[Cp_2Zr(OCHPh)][Cp_2Zr(OCH_2)]$ under 100 atm of CO. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

selectively, this result implies stereoselective conversion of *d,l*-**11** to **18** as well.



We explain the complete stereoselectively of these reactions by invoking a new "hinged-open" intermediate in which one of the Zr–O bonds has broken while the other maintains the integrity of the dimeric unit. Since a "hinged-open" intermediate could be used to rationalize all of the insertion chemistry previously observed with related zirconaoxiranes, we have tested further for the possible accessibility of monomeric zirconaoxiranes at elevated temperatures. To do this we have investigated the kinetics of the *meso*-**9** to *d,l*-**9** isomerization reaction.

In C_6D_6 at 69 °C, *meso*-**9** is completely isomerized to *d,l*-**9** over 24 h. This reaction has been found to be *second order* (2.06 ± 0.14) in *meso*-**9** concentration. Such a result is inconsistent with monomeric zirconaoxiranes being kinetically relevant intermediates. However, the same type of hinged-open intermediate implicated in the CO insertion reaction above can be used to rationalize the second order rate law by postulating rate determining dimerization of this intermediate with formation of a transient tetrameric species. The activation parameters for this isomerization reaction have also been determined over a temperature range of 69–96 °C ($\Delta H^{\ddagger}$ = 18.0 kcal/mol; $\Delta S^{\ddagger}$ = −19.0 cal/(mol K)) and are consistent with a tetrameric transition state.



Thus, it is likely that hinged-open complexes, not monomeric zirconaoxiranes, are the intermediates which first bind substrates during all insertion reactions into dimeric zirconaoxiranes.

Conclusion

A general and efficient synthesis of both neutral and anionic (η^2-aldehyde)zirconocene complexes has been developed. The first X-ray structure of an anionic aldehyde complex has been obtained. Mechanistic studies indicate that hinged-open dimeric complexes, not monomeric zirconaoxiranes, are the reactive intermediates generated in solution from neutral, dimeric zirconaoxiranes.

Experimental Section

General Procedures. All manipulations were performed under a dry nitrogen atmosphere using standard glovebox and Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM 250 or Bruker AM 250 spectrometer. Chemical shifts were measured relative to residual solvent peaks. NMR data for *d,l*-**9**, *d,l*-**10**, and *d,l*-**11** were derived from spectra of *meso-d,l* mixtures by subtraction. Solvents were dried and redistilled from Na/K alloy prior to use. Zirconocene dichloride, trimethyltin chloride, lithium diisopropylamide, and methyllithium were purchased from Aldrich Chemical Co. and used as received. All aldehydes were purchased from Aldrich and redistilled prior to use. Trimethyltin hydride[13] and zirconocene methyl chloride[14] were prepared by literature procedures. All aldehyde complexes were hydrolyzed (1 M H_2SO_4 saturated with Na_2SO_4) to provide the corresponding free alcohols which were identified by NMR comparison to authentic materials.

Synthesis of 12. Me_3SnH (0.69 g, 4.2 mmol) was diluted with 15 mL of tetrahydrofuran, and the resulting solution was cooled to 0 °C. Lithium diisopropylamide (2.80 mL of a 1.5 M solution, 4.2 mmol) was added dropwise and the mixture stirred for 15 min. The solution was then cooled to −78 °C, neat *p*-tolualdehyde was added by syringe, and the cold solution was stirred for 30 min. After warming to room temperature, the solution was added rapidly to a solution of $Cp_2Zr(Me)Cl$ (1.14 g, 4.2 mmol) in 15 mL of thf and then stirred for 1 h. Solvent was then removed under vacuum and the (α-stannylalkoxide)zirconocene extracted into diethyl ether. After filtration from LiCl the ether was removed and the product was redissolved in thf. The solution was cooled to −78 °C and MeLi (3.00 mL of a 1.4 M solution, 4.2 mmol) was then added dropwise by syringe. The reaction mixture was stirred for 40 min before warming to room temperature and removing volatiles under vacuum. The product was suspended in hexane, isolated by filtration, washed with additional hexane and dried under vacuum. This gives $Cp_2Zr(Me)$(*p*-tolualdehyde)Li(thf) as a pale yellow solid (1.62 g, 88%). $Cp_2Zr(Me)\{OCH(SnMe_3)C_6H_4\text{-}Me\}$, **4**: ^{1}H NMR (benzene-d_6) δ 7.03 (AB, 4H, C_6H_4), 5.82 (s, 5H, Cp), 5.75 (s, 5H, Cp), 5.53 (s, 1H, $^2J_{Sn-H}$ = 24 Hz, CHO), 2.16 (s, 3H, Ph–CH_3), 0.35 (s, 3H, Zr–CH_3), 0.08 (s, 9H, $^2J_{Sn-H}$ 51, 49 Hz, Sn–CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 145.21, 133.83, 129.21, 122.99 (C_6H_4), 110.51 (Cp), 110.36 (Cp), 84.10 (CHO), 21.02 (Ph–CH_3), 19.23 (Zr–CH_3), −10.15 (Sn–CH_3). $Cp_2Zr(Me)(OCHC_6H_4\text{-}Me)Li$, **12**: ^{1}H NMR (tetrahydrofuran-d_8) δ 6.68 (AB, 4H, C_6H_4), 5.46 (s, 5H, Cp), 5.12 (s, 5H, Cp), 3.35 (s, 1H, CHO), 2.17 (s, 3H, Ph–CH_3), −0.58 (s, 3H, Zr–CH_3); $^{13}C\{^1H\}$ NMR (dichloromethane-d_2) δ 152.92, 129.84, 128.85, 120.55 (C_6H_4), 107.13 (Cp), 106.84 (Cp), 69.94 (CHO), 20.93 (Ph–CH_3), 2.93 (Zr–CH_3). HRMS: calc 355.06346; meas, 355.0652.

The synthesis of 13 was the same as for **12**. $Cp_2Zr(Me)(OCHC_6H_5)Li$, **13**: yield = 83%; ^{1}H NMR (THF-d_8) δ 6.92 (t, 2H, C_6H_5), 6.76 (br s, 2H, C_6H_5), 6.46 (t, 1H, C_6H_5), 5.47 (s, 5H, Cp), 5.14 (s, 5H, Cp), 3.39 (s, 1H, CHO), −0.56 (s, 3H, Zr–CH_3); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 160.33, 127.50, 120.81, 118.37 (C_6H_5), 106.76 (Cp), 105.84 (Cp), 67.04 (CHO), 9.89 (Zr–CH_3).

The synthesis of 14–16 were as for **12** except that dimethoxyethane was substituted for tetrahydrofuran as the solvent in the transmetalation reaction. This provides anionic complexes solvated by DME. $Cp_2Zr(Me)\{OCH(SnMe_3)CH_2CHMe_2\}$, **6**: ^{1}H NMR (benzene-d_6) δ 5.79 (s, 5H, Cp), 5.78 (s, 5H, Cp), 4.58 (t, 1H, ^3J = 8.2 Hz, CHO), 1.70 (m, 2H), 1.33 (m, 1H), 0.92 (d, 3H, ^3J = 5.7 Hz), 0.90 (d, 3H, ^3J = 5.7 Hz), 0.28 (s, 3H, Zr–CH_3), 0.14 (s, 9H, $^2J_{Sn-H}$ = 50, 49 Hz, Sn–CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6)

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δ 110.34 (Cp), 110.22 (Cp), 79.44 (CHO), 48.34 (CH_2), 23.55 (CH_3), 21.95 (CH_3), 20.24 (Zr–CH_3), −10.24 (Sn–CH_3). $Cp_2Zr(Me)(OCHCH_2CHMe_2)Li$, **14**: yield = 65%; ^1H NMR (tetrahydrofuran-d_8) δ 5.35 (s, 5H, Cp), 5.34 (s, 5H, Cp), 2.03 (dd, 1H, ^3J = 4.7, 7.3 Hz, CHO), 1.39 (m, 3H, $CHCH_2$), 0.98 (d, 6H, ^3J = 6.8 Hz, 2 CH_3), −0.86 (s, 3H, Zr–CH_3); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 105.28 (Cp), 105.26 (Cp), 62.19 (CHO), 51.55 (CH_2), 31.23 (CH), 24.35 (CH_3), 23.57 (CH_3), 2.53 (Zr–CH_3). $Cp_2Zr(Me)(OCHCH_2CH_3)Li$, **15**: yield = 69%; ^1H NMR (tetrahydrofuran-d_8) δ 5.33 (s, 5H, Cp), 5.31 (s, 5H, Cp), 1.78 (dd, 1H, CHO), 1.40–1.27 (m, 2H, CH_2), 1.02 (t, 3H, CH_3), −0.84 (s, 3H, Zr–CH_3); $^{13}C\{^1H\}$ NMR (tetrhaydrofuran-d_8) δ 105.11 (2Cp), 67.00 (CHO), 33.90 (CH_2), 14.88 (CH_3), 3.88 (Zr–CH_3). $Cp_2Zr(Me)(OCHCHMe_2)Li$, **16**: yield = 65%; ^1H NMR (tetrahydrofuran-d_8) δ 5.36 (s, 5H, Cp), 5.32 (s, 5H, Cp), 1.45 (d, 1H, CHO), 1.12 (m, 1H, $CHMe_2$), 1.11 (d, 3H, CH_3), 0.95 (d, 3H, CH_3), −0.92 (s, 3H, Zr–CH_3); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 105.2 (2 Cp), 73.7 (CHO), 37.6 ($CHMe_2$), 26.67 (CH_3), 24.5 (CH_3), 20.97 (Zr–CH_3).

Syntheses of 9–11. Synthesized as for **12** except that Cp_2ZrCl_2 was substituted for $Cp_2Zr(Me)Cl$ and the final product was extracted into diethyl ether and filtered to remove LiCl. $Cp_2Zr(Cl)\{OCH(SnMe_3)C_6H_4Me\}$, **1**: ^1H NMR (benzene-d_6) δ 7.04 (AB, 4H, C_6H_4), 6.02 (s, 5H, Cp), 5.93 (s, 5H, Cp), 5.65 (s, 1H, $^2J_{Sn-H}$ = 24 Hz, CHO), 2.14 (s, 3H, Ph–CH_3), 0.20 (s, 9H, $^2J_{Sn-H}$ = 52, 50 Hz, Sn–CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 144.45, 134.23, 129.35, 123.27 (C_6H_4), 113.58 (Cp), 113.30 (Cp), 86.86 (CHO), 21.00 (Ph–CH_3), −9.62 (Sn–CH_3). *meso*-$[Cp_2Zr(OCHC_6H_4Me)]_2$, *meso*-**9**: ^1H NMR (tetrahydrofuran-d_8) δ 6.86 (AB, 4H, C_6H_4), 5.80 (s, 5H, Cp), 5.42 (s, 5H, Cp), 4.07 (s, 1H, CHO), 2.24 (s, 3H, Ph–CH_3); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 153.7, 130.0, 128.6, 122.0 (C_6H_4), 109.3 (Cp), 108.5 (Cp), 76.3 (CHO), 21.0 (Ph–CH_3). *d,l*-$[Cp_2Zr(OCHC_6H_4Me)]_2$, *d,l*-**9**: ^1H NMR (tetrahydrofuran-d_8) δ 6.96 (AB, 4H, C_6H_4), 6.08 (s, 5H, Cp), 5.83 (s, 5H, Cp), 3.97 (s, 1H, CHO), 2.29 (s, 3H, Ph–CH_3); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 150.4, 131.4, 129.9, 121.6 (C_6H_4), 110.9 (Cp), 109.7 (Cp), 81.9 (CHO), 21.5 (Ph–CH_3) (combined yield of **9** = 85%). *meso*-$[Cp_2Zr(OCHC_6H_5)]_2$, *meso*-**10**: ^1H NMR (tetrahydrofuran-d_8) δ 7.09–6.65 (m, 5H, C_6H_4), 5.81 (s, 5H, Cp), 5.43 (s, 5H, Cp), 4.10 (s, 1H, CHO); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 156.7, 127.8, 121.9, 121.2 (C_6H_5), 109.3 (Cp), 108.5 (Cp), 76.3 (CHO). *d,l*-$[Cp_2Zr(OCHC_6H_5)]_2$, *d,l*-**10**: ^1H NMR (tetrahydrofuran-d_8) δ 7.27–6.80 (m, 5H, C_6H_5), 6.10 (s, 5H, Cp), 5.84 (s, 5H, Cp), 4.02 (s, 1H, CHO); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 154.9, 128.3, 122.4, 121.5 (C_6H_5), 110.9 (Cp), 109.8 (Cp), 82.0 (CHO) (combined yield of **10** = 82%). $Cp_2Zr(Cl)\{OCH(SnMe_3)CH_2CHMe_2\}$, **3**: ^1H NMR (benzene-d_6) δ 5.98 (s, 5H, Cp), 5.97 (s, 5H, Cp), 4.71 (dd, 1H, ^3J = 5, 10 Hz, CHO), 1.77 (m, CH_2, 2H), 1.37 (m, CH, 1H), 0.92 (d, 3H, ^3J = 7 Hz, CH_3), 0.90 (d, 3H, ^3J = 7 Hz, CH_3), 0.23 (s, 9H, $^2J_{Sn-H}$ = 52, 50 Hz, Sn–CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 113.35 (Cp), 113.11 (Cp), 82.44 (CHO), 47.74 (CH_2), 24.94 (CH), 23.50 (CH_3), 21.99 (CH_3), −9.80 (Sn–CH_3). *meso*-$[Cp_2Zr(OCHCH_2CHMe_2)]_2$, *meso*-**11**: ^1H NMR (benzene-d_6) δ 5.78 (s, 5H, Cp), 5.70 (s, 5H, Cp), 2.69 (dd, 1H, ^3J = 3, 8 Hz, CHO), 1.63 (m, 3H, CH_2CH), 1.12 (d, 3H, ^3J = 6 Hz, CH_3), 1.11 (d, 3H, ^3J = 6 Hz, CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 108.25 (Cp), 108.06 (Cp), 77.24 (CHO), 48.24 (CH_2), 30.88 (CH), 23.93 (CH_3), 22.57 (CH_3). *d,l*-$[Cp_2Zr(OCHCH_2CHMe_2)]_2$, *d,l*-**11**: ^1H NMR (benzene-d_6) δ 5.77 (s, 5H, Cp), 5.71 (s, 5H, Cp), 2.62 (dd, 1H, ^3J = 3, 9 Hz, CHO), 1.62 (m, 3H, CH_2CH), 1.12 (d, 3H, ^3J = 6 Hz, CH_3), 1.11 (d, 3H, ^3J = 6 Hz, CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 108.34 (Cp), 108.12 (Cp), 77.13 (CHO), 48.94 (CH_2), 31.29 (CH), 24.06 (CH_3), 22.48 (CH_3) (combined yhield of **11** = 77%). HRMS: calc, 612.11128, meas, 612.1114.

Reaction of *meso*-11 with CO To Give 17. Pure *meso*-**11**, obtained by recrystallization from benzene, was dissolved in benzene-d_6 or tetrahydrofuran-d_8 in a 5-mm NMR tube. The solvent was frozen using liquid nitrogen and the head space evacuated. Carbon monoxide (1 atm) was introduced, and the tube was then sealed and allowed to warm to room temperature. The reaction was monitored by ^1H NMR and after 28 h the reaction was complete. No **18** could be detected in the NMR spectra. This reaction is readily reversible. Removal of the CO atmosphere results in reversion of the product to *meso*-**11**. **17**: ^1H NMR (benzene-d_6) δ 5.75 (s, 5H, Cp), 5.69 (s, 5H, Cp), 5.65 (2 s, 10H, 2 Cp), 4.44 (d, 1H, ^{3} = 6, 7 Hz, O=CCH), 2.91 (dd, 1H, ^3J = 4, 8 Hz, CHO), 2.14 (t, 2H, ^3J = 7 Hz, CH_2), 1.70 (m, 4H, Me_2CHCH_2CH), 1.12 (d, 3H, J = 6 Hz, CH_3), 1.11 (d, 3H, J = 6 Hz, CH_3), 1.05 (d, 3H, J = 7 Hz, CH_3), 1.04 (d, 3H, J = 7 Hz, CH_3); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 300.23 (C=O), 110.15 (Cp), 110.02 (Cp), 108.52 (Cp), 108.48 (Cp), 102.48 (O=CCH), 81.78 (CHO), 48.91 (CH_2), 43.35 (CH_2), 30.51 (CH), 24.82 (CH), 24.25 (CH_3), 23.63 (CH_3), 23.06 (CH_3), 22.71 (CH_3). IR (thf): ν_{CO} = 1657 cm^{-1}.

Table I. Crystallographic Data for $[C_{15}H_{20}O_2Zr]_2$, *meso*-11

(a) Crystal Parameters			
formula	$C_{30}H_{40}O_2Zr_2$	V, Å^3	1388.4(4)
fw	615.90	Z	2
cryst syst	monoclinic	cryst dimens, mm	0.30 × 0.45 × 0.65
space group	$P2_1/c$	cryst color	pale yellow
a, Å	9.729(2)	D(calc), g cm^{-3}	1.471
b, Å	18.733(4)	μ(Mo Kα), cm^{-1}	7.52
c, Å	8.098(1)	temp, K	297
β, deg	109.84(1)		
(b) Data Collection			
diffractometer	Nicolet R3m	no. of rflns collcd	3519
monochromator	graphite	no. of indpt rflns	3191
radiation	Mo Kα (λ = 0.710 73 Å)	no. of indpt obsvd rflns $F_0 \geq n(F_o)$ (n = 5)	2496
2θ scan range, deg	4–55	std rflns	3 std/ 197 rflns
data collected (h,k,l)	±13,±25,±11	var in stds	<2
(c) Refinement			
$R(F)$, %	2.78	$\Delta(\rho)$, e Å^{-3}	0.358
$R_w(F)$, %	3.00	N_o/N_v	10.7
Δ/σ(max)	0.017	GOF	1.067

Reaction of *d,l*-11 with CO To Give 18. A mixture of *d,l*-**11** and *meso*-**11** (4:1) was reacted with CO as above. This provided a mixture of **18** and **17** (4:1). **18**: ^1H NMR (benzene-d_6) δ 5.76 (s, 5H, Cp), 5.69 (s, 5H, Cp), 5.65 (2 s, 10H, 2 Cp), 4.22 (t, 1H, ^3J = 7 Hz, O=CCH), 2.97 (dd, 1H, ^3J = 3, 8 Hz, CHO), 2.13 (t, 2H, ^3J = 7 Hz, CH_2), 1.70 (m, 4H, Me_2CHCH_2CH), 1.12 (d, 3H, J = 6 Hz, CH_3), 1.11 (d, 3H, J = 6 Hz, CH_3), 1.05 (d, 3H, J = 7 Hz, CH_3), 1.04 (d, 3H, J = 7 Hz, CH_3); $^{13}C\{^1H\}$ NMR (tetrahydrofuran-d_8) δ 302.74 (C=O), 110.22 (Cp), 110.11 (Cp), 108.74 (Cp), 108.61 (Cp), 103.67 (O=CCH), 81.64 (CHO), 49.66 (CH_2), 44.24 (CH_2), 30.69 (CH), 24.47 (CH), 24.16 (CH_3), 23.65 (CH_3), 23.19 (CH_3), 22.48 (CH_3). IR (thf): ν_{CO} = 1657 cm^{-1}.

Kinetics of the *meso*-9 to *d,l*-9 Isomerization. Four C_6D_6 solutions of *meso*-**9** of concentrations 4.38, 3.27, 2.18, and 1.09 mM were prepared and concentration versus time data obtained by ^1H NMR in a probe thermostated at 69 ± 0.5 °C by observing the decrease in cyclopentadienyl intensity of the meso complex versus total Cp intensity. These measurements were repeated at temperatures of 78, 87, and 96 °C. This reaction is very clean with no decomposition products observed over the course of the isomerization. Initial rates were determined, and the reaction order at each temperature was derived by plotting the log of the initial rate versus the log of the initial concentration. The experimental orders at each temperature were found to be 2.16 (69 °C), 2.01 (78 °C), 2.17 (87 °C), and 1.92 (96 °C), giving 2.06 ± 0.14 as the average of these four separate order determinations. Activation parameters were determined from these kinetic runs via plots of $\ln(k/T)$ versus $1/T$ according to standard transition state theory.

X-ray Crystallography. Pale yellow crystals of *meso*-**11** were obtained by slow evaporation of a benzene solution. The crystal was sealed in a glass capillary, and data were collected on a Nicolet R3m diffractometer at ambient temperature (23 ± 1 °C) using Mo Kα radiation (λ = 0.710 73 Å). The unit cell was found to be monoclinic, $P2_1/c$, a = 9.7293(19) Å, b = 18.733(4) Å, c = 8.0984(13) Å, β = 109.838(13)°, V = 1388.4(4) Å^3, Z = 2, μ = 7.52 cm^{-1}, and D_{calcd} = 1.471 g cm^{-3}. Of the 3519 reflections collected (4 ≤

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for *meso*-11

	x	y	z	U^a
Zr	1207(1)	725(1)	372(1)	29(1)
O	911(2)	−307(1)	1210(2)	35(1)
C(1)	2247(3)	−91(1)	2496(3)	37(1)
C(2)	3459(3)	−629(1)	2773(4)	44(1)
C(3)	3238(4)	−1331(2)	3630(4)	54(1)
C(4)	4271(5)	−1910(2)	3429(5)	79(2)
C(5)	3416(7)	−1238(3)	5530(6)	120(3)
C(6)	3571(3)	594(2)	−232(5)	56(1)
C(7)	2598(3)	110(2)	−1370(4)	45(1)
C(8)	1494(4)	499(2)	−2600(4)	49(1)
C(9)	1774(4)	1225(2)	−2234(4)	59(1)
C(10)	3063(4)	1283(2)	−794(5)	62(2)
C(11)	174(4)	1276(2)	2607(4)	49(1)
C(12)	−533(4)	1623(2)	1043(4)	53(1)
C(13)	502(4)	2022(1)	594(5)	60(1)
C914)	1854(4)	1919(2)	1940(5)	60(1)
C(15)	1647(4)	1461(2)	3158(4)	53(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Crystallographic Data for $[C_{16}H_{23}OLiZr]_2\cdot(THF)$, 14

	(a) Crystal Parameters		
formula	$[C_{16}H_{23}OLiZr]_2\cdot$ (THF)	V, Å^3	3475.7(16)
fw	731.14	Z	4
cryst syst	orthorhombic	cryst dimens, k mm	0.10 × 0.40 × 0.40
space group	*C2cb* (No. 41)	cryst color	pale green-yellow
a, Å	11.9227(38)	D(calc), g cm^{-3}	1.358
b, Å	20.3074(43)	μ(Mo Kα), cm^{-1}	6.11
c, Å	14.7684(36)	temp, K	296
	(b) Data Collection		
diffractometer	Nicolet 42m	no. of rflns collected	1981
monochromator	graphite	no. of indpt flns	1854
radiation	Mo Kα (λ = 0.710 73 Å)	no. of indpt obsvd rflns $Fx_o \geq n\sigma(F_o)$ (n = 4)	1439
2θ scan range, deg	4–52	std rflns	3 std/ 197 rflns
data collected (h,x",l)	+15,+26,+19	var in stds	~4
	(c) Refinement		
$R(F)$, %	3.56	$\Delta(\rho)$, e Å^{-3}	0.397
$R_w(F)$, %	3.51	N_o/N_v	7.0
Δ/σ(max)	0.366	GOF	0.974

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 14

	x	y	z	U^a
Zr	5000	8566.3(2)	9230.1(3)	33.8(1)
O(1)	5896(4)	9306(2)	9977(3)	34(1)
O(2)	8502(5)	10000	10000	53(2)
C(1)	3507(7)	8419(5)	10423(6)	81(2)
C(2)	2937(7)	8411(4)	9632(8)	90(3)
C(3)	3227(8)	7859(4)	9137(6)	83(2)
C(4)	3990(8)	7509(4)	9663(5)	71(2)
C(5)	4159(8)	7856(4)	10459(5)	72(2)
C(6)	6718(8)	8603(5)	8206(5)	89(2)
C(7)	5886(10)	8807(4)	7677(5)	88(2)
C(8)	5202(8)	8279(4)	7569(5)	82(2)
C(9)	5594(8)	7766(4)	8014(5)	83(2)
C(10)	6588(9)	7956(5)	8458(5)	95(2)
C(11)	4075(8)	9547(4)	8733(5)	59(2)
C(12)	9187(7)	9578(4)	9458(5)	66(2)
C(13)	10365(6)	9649(4)	9809(6)	87(2)
Li(1)	6903(12)	10000	10000	41(3)
Li(2)	4913(8)	10000	10000	52(3)
C(14)	6271(6)	8698(3)	10352(4)	36(2)
C(15)	6157(6)	8659(3)	11364(4)	40(2)
C(16)	6893(6)	9140(3)	11908(4)	41(2)
C(17)	8109(7)	8925(4)	11924(5)	55(2)
C(18)	6452(7)	9224(4)	12971(4)	56(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2θ ≤ 55°), 3191 were independent and 2496 were observed with $F_o \geq 5\sigma(F_o)$. Intensity data were not corrected for adsorption (well-shaped crystal, low μ). Solution by Patterson map located the Zr atom, non-hydrogen atoms were anisotropically refined, and the aldehydic hydrogen atom was found and refined isotropically while all other hydrogens were placed in idealized positions. $R(F)$ = 2.78%, $R_w(F)$ = 3.00%, GOF = 1.067, and $\Delta\rho$(max) = 0.358 e Å^{-3}.

Pale yellow crystals of 14 were obtained by recrystallization from diethyl ether. The crystal was sealed in a glass capillary, and data were collected on a Nicolet R3m diffractometer at ambient temperature (23 ± 1 °C) using Mo Kα radiation (λ = 0.710 73 Å). The unit cell was found to be orthorhombic, *C2cb* (a nonstandard setting for *Aba*2), a = 11.923(4) Å, b = 20.307(4) Å, c = 14.768(4) Å, V = 3575.7(16) Å^3, Z = 4, and D_{calcd} = 1.358 g cm^{-3}. The noncentrosymmetric space group was chosen on the basis of E statistics and the successful refinement of the structure. The centrosymmetric alternative *Cmca* could be rejected on the basis of the strict absence of mirror-plane symmetry. Solution by Patterson map located the Zr atom, and non-hydrogen atoms were anisotropically refined. All hydrogens except H_r, H_k, H_l, and H_m were calculated in idealized positions. H_r, H_k, H_l, and H_m were then located and refined isotropically. Of the 1981 reflections collected (4 ≤ 2θ ≤ 52°), 1439 were observed with $F_o \geq 4\sigma(F_o)$. $R(F)$ = 3.56%, $R_w(F)$ = 3.51%, GOF = 0.974, and $\Delta\rho$(max) = 0.397 e Å^{-3}.

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Supplementary Material Available: Details of the X-ray crystal structures of *meso*-11 and 14 including tables of atomic coordinates, bond lengths, bond angles, and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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