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Chlorozirconocene Carboxylate Complexes Cp$_2$ClZr(OCOR) (R = H, CH$_3$, *t*-Bu, Ph) and Their Reactions with Zirconium Hydride Reagents. Metal Hydride Reduction of Ligated Carboxylate

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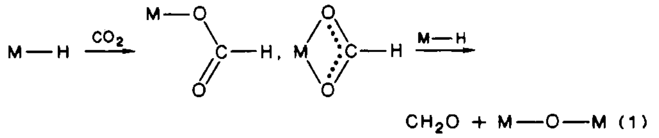
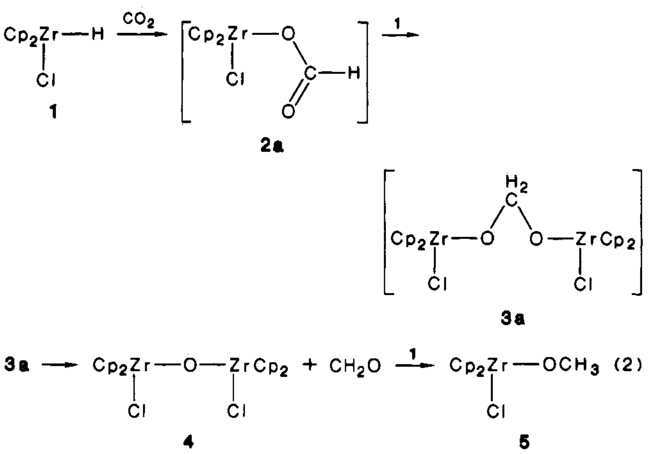
The chlorozirconocene carboxylates Cp$_2$(Cl)ZrOC(O)R, with formate (**2a**, R = H), acetate (**2b**, R = CH$_3$), pivalate (**2c**, R = C(CH$_3$)$_3$), and benzoate (**2d**, R = Ph) as the carboxylate ligands, have been prepared and characterized, and their reactions with the zirconium hydride reagents [Cp$_2$Zr(H)Cl]$_x$ (**1**) and [(C$_5$H$_4$Me)$_2$Zr(H)(μ-H)]$_2$ (**6**) have been studied. These carboxylates **2a–d** are available by treating [Cp$_2$(Cl)Zr]$_2$O with an excess of the requisite carboxylic acid. In CH$_2$Cl$_2$ solution or as KBr pellets, **2a–d** have IR spectra that are consistent with the presence of a chelating, bidentate (η^2-O,O′) carboxylate ligand, although the formate also has equilibrium amounts of unidentate (η^1-O) carboxylate. In THF solution, however, all exist as solvated η^1-O carboxylate complexes, possibly Cp$_2$(Cl)Zr(OC(O)R)(THF). Of these zirconocene carboxylates, all but the pivalate react in THF (but not in toluene) with **1** and yield the requisite aldehyde plus the μ-oxo compound [Cp$_2$(Cl)Zr]$_2$O. Yields of acetaldehyde and benzaldehyde are 92–93%. No direct evidence for the postulated μ-η^1-O,O′ *gem*-diolate intermediates Cp$_2$(Cl)ZrOCH(R)-OZr(Cl)Cp$_2$ (**3a,b,d**) during this reduction of ligated carboxylate was obtained. Reduction of the acetate **2b** with **6**, however, regioselectively affords the μ-oxo compound Cp$_2$(Cl)ZrOZr(OCH$_2$CH$_3$)Cp$_2$, which is consistent with transience of a μ-η^1-O,O′ *gem*-diolate.

Introduction

Homogeneous reduction of carbon dioxide, with transition-metal organometallic hydrido complexes, could presage the conversion of this abundant feedstock into the C$_1$ molecules formaldehyde or methanol.[1] A number of organometallic hydrides accordingly incorporate CO$_2$ and produce η^1-O or η^2-O,O′ metalloformate complexes (eq 1).[2,3] The subsequent reductive chemistry of ligated formate (or of other coordinated carboxylates) has not been studied.[4]



Reduction of ligated formate, however, is implicit as hydridochlorozirconocene, [Cp$_2$Zr(H)Cl]$_x$[5] (**1**), reduces CO$_2$, which is perhaps the premier example of a metal hydride fixing CO$_2$ (eq 2). Floriani[6] and others[7] established that 2 equiv of **1** rapidly converts CO$_2$ to formaldehyde (plus (μ-oxo) dichlorozirconocene (**4**)[8]), and a third equivalent further incorporates the CH$_2$O to give the chlorozirconocene methoxide **5**.[9] This methoxide upon hydrolysis then affords methanol. The plausible ligand reactions extant in this CO$_2$-fixation scheme (eq 2) are the zirconium hydride **1** first generating the metalloformate **2a**. A second equivalent of **1** then adds across **2a** and generates the *gem*-diolate **3a**, which extrudes formaldehyde. Intermediacy of the η^1-O



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formate **2a**, heretofore an unknown compound, and of the μ-η^1-O,O′ *gem*-diolate **3a**, however, is assumed.

We are interested in establishing that metal hydrides will reduce formate and other carboxylate ligands. In a previous study, FpOC(O)R and bimetallic $FpOC(R)OFp^+$ carboxylate complexes (Fp = $Cp(CO)_2Fe$; R = H, CH_3) were synthesized in an attempt to generate the *gem*-diolate compound $FpOCH_2OFp$.[10,11] Nucleophilic hydride donors cleaved these bimetallic μ-carboxylates by direct displacement at an iron center, however, and no evidence was found (from labeling studies) for hydride addition to bridging formate.

The reduction of Zr(IV) carboxylates by Zr hydride reagents, in an attempt to detect the μ-η^1-O,O′ compound **3a** and homologous acetals, is now addressed. We report (1) preparation and characterization of the chlorozirconocene carboxylates $Cp_2Zr(Cl)O_2CR$ (containing the carboxylates formate (**2a**, R = H), acetate (**2b**, R = CH_3), pivalate (**2c**, R = *t*-Bu), and benzoate (**2d**, R = Ph)) and (2) reaction of these carboxylates with the zirconium hydrides $[Cp_2Zr(H)Cl]_x$ (**1**) and $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (**6**).

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere and with standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air- and/or moisture-sensitive organometallics.[12]

Infrared spectra were recorded on a Perkin-Elmer Model No. 297 spectrophotometer, using the polystyrene 1601-cm^{-1} calibration. The IR spectral data so recorded are believed accurate to ± 2 cm^{-1} below and ± 5 cm^{-1} above 2000 cm^{-1}; they are reported over the 2400–1100-cm^{-1} range. ^1H NMR spectra were obtained on Varian T-60A and XL-200 NMR spectrometers; ^{13}C NMR spectral data came from an IBM WP-100 SY instrument. Chemical shifts are in δ units downfield from the $SiMe_4$ internal standard. The $CDCl_3$ solvent used in collecting the NMR spectral data was first filtered through activity 1 alumina. GLC analyses were carried out with a GOW-Mac Model 205 instrument fitted with 4 ft by $^1/_4$ in. Cu columns, which were packed with carbowax-20 M (20%) or DC-200 (20%) on Chromosorb P (80/100 mesh). Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed by Mic Anal, Tucson, AZ.

Inorganic and organic reagents were procured commercially and used as received. The following solvents were additionally purified by distilling under nitrogen: methylene chloride and hexane from P_2O_5; benzene, toluene, ether, and tetrahydrofuran (THF) from sodium benzophenone ketyl. Literature procedures were used in preparing $(Cp_2ZrCl)_2O$ (**4**),[8c] $[Cp_2Zr(H)Cl]_x$,[8c] $Cp_2Zr(CH_3)Cl$ (**7**),[13] $[(C_5H_4Me)_2ZrCl]_2O$,[8d] $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (**6**),[14] and $Cp_2Ti(OCOPh)_2$.[15] The insoluble hydridochlorozirconocene oligomer **1**, inevitably contaminated with NaCl, was assayed for its hydride content by reacting it with acetylferrocene. A known excess of $FcCOCH_3$ in benzene solution thus was treated with **1** for 2 h (with stirring). The solvent was evaporated, and the residue was dissolved in $CDCl_3$ for ^1H NMR spectral quantification of $FeCH(CH_3)OZr(Cl)Cp_2$.[7a] Concentrations of this reduced product were determined from the ratio of its integrated methyl absorption (a doublet, $J = 6.5$ Hz, at δ 1.44) to that of the unreacted $FcCOCH_3$ methyl singlet (δ 2.33). Dimeric **6** was recrystallized from THF prior to use.

Preparation of $Cp_2ZrCl(OCOH)$ (2a). To a solution of $(Cp_2ZrCl)_2O$ (**4**; 800 mg, 1.51 mmol) in 60 mL of benzene was added 98% formic acid (490 mg, 10.6 mmol). After the mixture stood for 1 h, the clear solution was evaporated, and the white residue was precipitated from CH_2Cl_2–hexane, yielding 754 mg (83%) of $Cp_2ZrCl(OCOH)$ (**2a**) as an off-white solid, mp 110–114 °C. IR (KBr): $\nu(CO_2)$ 1628 (m, br), 1562 (m), 1372 (m), 1313 (w) cm^{-1}; 1438 (m) cm^{-1} (for Cp_2ZrCl). IR (CH_2Cl_2): $\nu(CO_2)$ 1726 (w, br), 1643 (s), 1560 (s), 1378 (s), 1313 (m) cm^{-1}. IR (THF): $\nu(CO_2)$ 1729 (s), 1655 (m, br), 1562 (m, br), 1367 (m, br). CH_2Cl_2 solutions of **2a** (1 mmol) containing 10% or 50% (by volume) THF also have an IR $\nu(CO_2)$ band at 1729 cm^{-1}, but at 0.1 or 0.3 relative intensity, respectively, of that measured in THF solution. ^1H NMR ($CDCl_3$): δ 8.30 (s, 1 H, O_2CH), 6.33 (s, 10 H, Cp). ^{13}C NMR ($CDCl_3$): δ 171.4 (O_2CH), 115.1 (Cp). Anal. Calcd for $C_{11}H_{11}O_2ClZr$: C, 43.74; H, 3.68. Found: C, 43.64; H, 3.83.

Preparation of $Cp_2ZrCl(OCOCH_3)$ (2b). A benzene solution (50 mL) containing $(Cp_2ZrCl)_2O$ (**4**; 500 mg, 0.94 mmol) was added to an acetic anhydride (98 mg, 0.96 mmol)–glacial acetic acid (336 mg, 5.6 mmol) solution in benzene (10 mL). This clear solution (allowed to stand 1 h) was evaporated, and the residue was recrystallized from CH_2Cl_2–hexane (−20 °C) and dried under vacuum, which afforded $Cp_2ZrCl(OCOCH_3)$ (**2b**) as a creamy white solid (446 mg, 75% yield), mp 142–144 °C (lit.[16] mp 137–138 °C). IR (KBr): 1639 (w, br), 1590–1370 cm^{-1} (half-height width; peak maxima at 1520, 1470, 1438, 1415 cm^{-1}). IR (CH_2Cl_2): 1635 (w, br), 1528 (m, $\nu(CO_2)$), 1477 (s, $\nu(CO_2)$) cm^{-1}. IR (THF): 1751 (s), 1728 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.29 (s, 10 H, Cp), 2.03 (s, 3 H, $OCOCH_3$). ^{13}C NMR ($CDCl_3$): δ 187.1 (OCO), 114.7 (Cp), 22.7 (CH_3). Anal. Calcd for $C_{12}H_{13}O_2ClZr$: C, 45.60; H, 4.15. Found: C, 45.49; H, 4.09.

As an alternative synthesis, a benzene solution (10 mL) containing $Cp_2Zr(Cl)CH_3$ (**7**; 462 mg, 1.70 mmol) was treated with 110 mg (1.83 mmol) of glacial acetic acid in benzene (10 mL). Brisk gas evolution (presumably methane) immediately ensued. The clear solution after 1 h was evaporated and the residue recrystallized from CH_2Cl_2-hexane, producing spectroscopically pure $Cp_2ZrCl(OCOCH_3)$ (**2b**), yield 433 mg (81%).

Preparation of $Cp_2ZrCl[OCOC(CH_3)_3]$ (2c). $(Cp_2ZrCl)_2O$ (**4**; 1000 mg, 1.89 mmol) as a benzene solution (80 mL) was treated with 2,2-dimethylpropionic acid (1361 mg, 13.3 mmol) in benzene (25 mL), and after 1 h the resulting clear solution was evaporated under reduced pressure. This residue was dissolved in 7 mL of CH_2Cl_2, layered with hexane (80 mL), and stored at −20 °C for 12 h. Tannish white crystals were filtered, washed with hexane, and vacuum-dried, yielding 1070 mg (79%) of $Cp_2Zr(Cl)OCOC(CH_3)_3$ (**2c**), mp 152–154 °C. IR (KBr): 1581 (w), 1488 (s, br), 1440 (s, br), 1383 (m), 1360 (s), 1225 (s) cm^{-1}. IR (CH_2Cl_2): 1500 (sh), 1493 (s), 1442 (s), 1423 (sh), 1366 (w), 1225 (m) cm^{-1}. IR (THF): 1728 (m, br), 1520–1410 (m, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.21 (s, 10 H, Cp), 1.22 (s, 9 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 193.8 (OCO), 114.5 (Cp), 39.1 (CMe_3), 26.1 (CH_3). Anal. Calcd for $C_{15}H_{19}O_2ClZr$: C, 50.30; H, 5.35. Found: C, 50.18; H, 5.35.

Preparation of $Cp_2ZrCl(OCOPh)$ (2d). Benzoic acid (1426 mg, 11.7 mmol) was added to a benzene solution (120 mL) of $(Cp_2ZrCl)_2O$ (**4**; 1000 mg, 1.89 mmol); the clear solution (1 h) was evaporated. The residue was dissolved in a minimum volume of CH_2Cl_2 (20 mL); this solution was layered with 60 mL of hexane and then kept at −20 °C (12 h) to produce creamy white crystals. These were recrystallized from CH_2Cl_2–hexane as analytically pure white crystals of $Cp_2ZrCl(OCOPh)$ (**2d**): 967 mg (68% yield); mp 162–163 °C (lit.[16] mp 160.5–161.5 °C). IR (KBr): 1590 (m), 1493 (m), 1450–1350 (s, br). IR (CH_2Cl_2): 1601 (m), (1511, 1501) (s), 1455–1410 (s, br), 1323 (w). IR (THF): 1721 (s), 1600 (m), (1512, 1502) (s), 1430 (s, br), 1320 (m, br). ^1H NMR ($CDCl_3$): δ 8.23–7.92 (m, 2 H, Ph), 7.60–7.26 (m, 3 H, Ph), 6.32 (s, 10 H, Cp). ^{13}C NMR ($CDCl_3$): δ 171.9 (OCO), 133.6, 131.2, 129.7, 128.3 (Ph), 114.7 (Cp). Anal. Calcd for $C_{17}H_{15}O_2ClZr$: C, 54.00; H, 4.00. Found: C, 53.73; H, 3.92.

Reaction of $Cp_2Zr(H)Cl$ (1) and $Cp_2ZrCl(OCOH)$ (2a). A THF suspension (5 mL) of $Cp_2Zr(H)Cl$ (**1**; 0.42 mmol) was treated with $Cp_2ZrCl(OCOH)$ (**2a**; 126 mg, 0.42 mmol) and stirred. The reaction mixture formed a clear solution within 15 min; an IR spectrum accordingly indicated that all the starting **2a** had been consumed. Treating the solution with hexane (30 mL) and cooling (−20 °C) overnight resulted in the deposition of white crystals. These were filtered, vacuum-dried, and identified as spectroscopically pure **4**, yield 212 mg (96%).

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[11] Al alternative approach to fixing CO_2 ligated between two metal centers involves μ-η^1-C,O carboxylates. The synthesis and reductive chemistry of the bimetallic μ-η^1-C,O carboxylate Cp(CO)(NO)ReC(O)OZr(Cl)Cp_2, giving its μ-η^1-C,O formaldehyde derivative $[Re]CH_2O[Zr]$, has been accomplished: Tso, C. C.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

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Reduction of $Cp_2ZrCl(OCOCH_3)$ (2b) and $Cp_2ZrCl(OCOPh)$ (2d) with $[Cp_2Zr(H)Cl]_x$ (1). A solution of $Cp_2ZrCl(OCOCH_3)$ (**2b**; 253 mg, 0.80 mmol) in THF (6 mL) was aded to a suspension of $[Cp_2Zr(H)Cl]_x$ (**1**; 0.80 mmol) in 4 mL of THF. The reaction mixture provided a clear solution within 3 min; an IR spectrum confirmed that the acetaldehyde (ν(CO) 1726 cm^{-1}) had replaced the acetate absorption (1751, 1728 cm^{-1}). Quantitative IR spectral analysis with a Beer's law plot for acetaldehyde further established a 93% yield. The reaction mixture then was trap-to-trap-distilled (10^{-3} mm, receiver cooled in liquid N_2), and the distillate was analyzed by GLC using a toluene internal standard: acetaldehyde (the only organic product) was formed in 95% yield. The residue remaining after distillation was dissolved in 3 mL of THF and treated with hexane (30 mL). This precipitated spetroscopically pure $(Cp_2ZrCl)_2O$ (**4**; yield 393 mg, 93%) after filtering and vacuum drying.

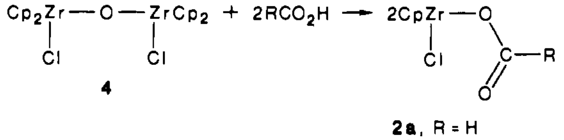
A solution of $Cp_2ZrCl(OCOPh)$ (**2d**; 250 mg, 0.66 mmol) in THF (8 mL) was added to a $[Cp_2Zr(H)Cl]_x$ (**1**; 0.66 mmol)–THF (3 mL) suspension, which formed a clear solution within 10 min. IR spectral monitoring was consistent with replacement of the benzoate absorption (1722 cm^{-1}) by the benzaldehyde ν(CO) (1705 cm^{-1}); quantitative IR spectral analysis with a Beer's law plot for benzaldehyde demonstrated a 97% yield. The reaction mixture was treated with hexane (60 mL) and kept cold (−20 °C) overnight to precipitate a white solid. This was collected, vacuum-dried, and identified as spectroscopically pure $(Cp_2ZrCl)_2O$ (**4**; yield 321 mg, 92%). The supernatant was analyzed qualitatively (GLC) to confirm benzaldehyde as the only organic product.

Reaction of $Cp_2ZrCl(OCOCH_3)$ (2b) and $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (6). A clear toluene solution (5 mL) containing $Cp_2ZrCl(COCH_3)$ (**2b**; 276 mg, 0.88 mmol) and $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (**6**; 276 mg, 0.44 mmol) was unchanged after being stirred at room temperature (2 h). An IR spectrum of this solution established that the starting **2b** was consumed, although acetaldehyde was not evident. The solution then was diluted with hexane (70 mL) and was stored at −20 °C (8 h); the resulting precipitate was removed and discarded. Concentrating the supernatant produced a gum (328 mg), but attempts to further purify this extremely hygroscopic/unstable material proved unsuccessful. Its ^1H NMR data nevertheless is in accord with that for $(Cp_2ZrCl)(\mu\text{-}O)[(C_5H_4Me)_2ZrOCH_2CH_3]$ (**8a**; 54% yield) that is contaminated by $(Cp_2ZrCl)(\mu\text{-}O)[(C_5H_4Me)_2ZrCl]$ (**9**; 12%). ^1H NMR (200 MHz, $CDCl_3$): δ 6.26 (s, 5 H, Cp), 6.18 (s, 5 H, Cp), 6.3–5.8 (br m, 8 H, C_5H_4Me), 4.0–4.4 (br m, 2 H, OCH_2), 2.23 (s, 3 H, C_5H_4*Me*), 2.17 (s, 3 H, C_5H_4*Me*), 1.21 (br t, $J \approx 6.5$ Hz, 3 H, OCH_2CH_3). Proton spin–spin decoupling experiments: irradiating the apparent pair of a doublet of quartets at δ 4.1 gave a methyl singlet at δ 1.19; irradiating the δ 1.2 signal afforded two methylene singlets at δ 4.08 and 4.17.

$(Cp_2ZrCl)(\mu\text{-}O)[(C_5H_4Me)_2ZrOCH_2CH_3]$ (**8a**) was generated in toluene on a 1.0-mmol scale from $Cp_2ZrCl(OCOCH_3)$ (**2b**) and $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (**6**). The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (60 mL) and treated with aqueous HCl (5 mL, 0.1 g of HCl). After the mixture was stirred for 10 min, the organic layer was separated and dried over anhydrous $MgSO_4$ (45 min). The solvent was evaporated and the residue reprecipitated (CH_2Cl_2–hexane) to give a colorless solid (428 mg) for analytically pure $(Cp_2ZrCl)(\mu\text{-}O)[(C_5H_4Me)_2ZrCl]$ (**9**): 77% yield; mp 170–172 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 6.32 (s, 5 H, Cp), 6.30 (s, 5 H, Cp), 6.14 (br t, J = 2.3 Hz, 4 H, C_5H_4Me ($H_{2,5}$)), 6.09 (br s, 2 H, C_5H_4Me ($H_{3(4)}$)), 5.89 (br s, 2 H, C_5H_4Me ($H_{4(3)}$)), 2.24 (s, 3 H, $C_5H_4CH_3$), 2.23 (s, 3 H, $C_5H_4CH_3$). Anal. Calcd for $C_{22}H_{24}Cl_2OZr_2$: C, 47.35; H, 4.34. Found: C, 47.40; H, 4.48.

Results and Discussion

Preparation and Characterization of Chlorozirconocene Carboxylates $Cp_2ClZrOCOR$ (R = H, CH_3, *t*-Bu, and Ph). The importance of Cp_2Zr^{IV} or "zirconocene" compounds to transition-metal organometallic chemistry in general,[5b,17] and to CO_2 fixation in particular,[6,7] contrasts with the information available on their Zr(IV) carboxylate derivatives. Early attempts to prepare the mono- and bis(acetates) $Cp_2Zr(Cl)O_2CCH_3$ (**2b**) and $Cp_2Zr(O_2CCH_3)_2$ by treating Cp_2ZrCl_2 and $(Cp_2ZrH_2)_x$, respectively, with acetic acid cleaved the Zr–Cp units.[18,19] Both trifluoroacetate analogues, however, are prepared by these and other routes.[18-20] The bis(acetate) $Cp_2Zr(O_2CCH_3)_2$ apparently results from the reaction of Cp_2ZrCl_2 and $Na^+(O_2CCH_3)^-$ in refluxing benzene, although further details were not reported.[13] Protonating Schwartz's reagent, $[Cp_2Zr(H)Cl]_x$ (**1**), with carboxylic acids apparently eliminates hydrogen and gives the zirconocene carboxylate;[5b] with ferrocenecarboxylic acid, $FcCO_2H$, for example, **1** gives the chlorozirconocene carboxylate $Cp_2(Cl)ZrOC(O)Fc$.[7] Finally, Brainina and co-workers isolated the chlorozirconocene acetate (**2b**) and benzoate (**2d**) compounds after treating the μ-oxo compound **4** with the requisite carboxylic acid (eq 3),[16] again without benefit of supporting IR or NMR spectral data.

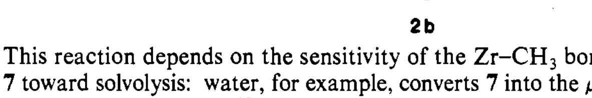

(3)

4

2a, R = H
b, R = CH_3
c, R = $C(CH_3)_3$
d, R = Ph

We used Brainina's procedure for syntheszing the four chlorozirconcene carboxylates **2a–d** (eq 3). As detailed in the Experimental Section, these straightforward preparations afford the corresponding formate **2a** (83%), acetate **2b** (75%), pivalate **2c** (79%), and benzoate **2d** (68%) in good to moderate yields as moisture-sensitive, but otherwise stable, white solids.

The acetate **2b** also results in good yield (81%) after treating the methylchlorozirconocene compound **7** with acetic acid (eq 4).


(4)

7

2b

This reaction depends on the sensitivity of the Zr–CH_3 bond of **7** toward solvolysis: water, for example, converts **7** into the μ-oxo compound **4** plus CH_4.[13]

All four carboxylate complexes are fully characterized by their IR, ^1H, and ^{13}C NMR spectral data and by their elemental analyses. ^{13}C NMR spectral data, for example, are consistent with carboxylate ligands that absorb (carbonyl carbons) from δ 171 (**2a**) to 194 (**2c**).

Both ^1H and ^{13}C NMR spectra of the formate **2a** (in $CDCl_3$) at −50 °C, however, clearly show the presence of two isomers. Two sets of narrow Cp resonances (δ 6.38, 6.35 and 114.9, 114.5, respectively) and of formate absorptions (δ 8.42, 8.35 and 175.6, 171.6), in 1:1 relative intensity, thus are evident. This doubling of NMR resonances upon cooling is reversible. Warming the solutions to room temperature and recording the NMR spectra regenerate the original spectra corresponding to a single isomer in solution. In contrast, both ^1H and ^{13}C NMR spectra of the acetate **2b** at −50 °C remain unchanged (without peak broadening) from room-temperature spectra; only one isomer is evident in solution.

IR spectral data are used to discern among three solvent-dependent carboxylate ligand bonding modes:[21] unidentate η^1-O (A), bidentate or chelating η^2-O,O′ (B),[22] and solvated unidentate (C).[23] Assignments for the **2a–d** carboxylate $\nu(CO_2)_{asym}$ and

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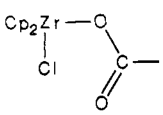
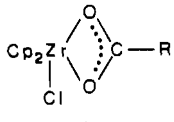
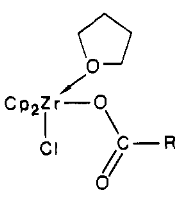
(22) Discerning between chelating carboxylate in B and μ-η^1-O,O′ bridging carboxylate, e.g., $Cp_2ClZr(\mu\text{-}OC(R)O)_2ZrClCp_2$, by IR spectroscopy is not reliable.[21] We assume structure B, as it is consonant with the established propensity of chlorozirconocene toward η^2 chelation of acyl and other bidentate ligands.[17]



A



B



C

$\nu(CO_2)_{sym}$ absorptions in the 1750–1250-cm^{-1} carboxylate and ester $\nu(CO_2)$ region[26] have been made. The acetate (**2b**), pivalate (**2c**), and benzoate (**2d**) complexes accordingly are structurally similar and differ from the formate **2a**.

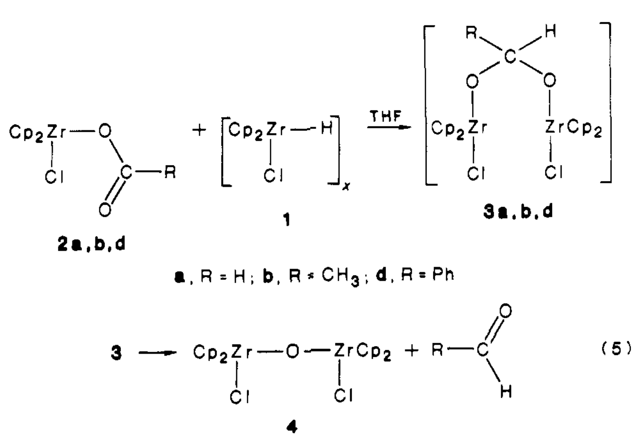
The formate **2a** as a KBr pellet or in CH_2Cl_2 solution exists as a mixture of unidentate η^1-O (A; $\nu(CO_2)_{asym}$ 1628 cm^{-1}/$\nu(CO_2)_{sym}$ 1372 cm^{-1}) and of bidentate η^2-O,O′ (B; $\nu(CO_2)_{asym}$ 1562 cm^{-1}/$\nu(CO_2)_{sym}$ 1372 cm^{-1}) structures. These assignments for **2a** (A) may be compared with those of $Cp_2Ti(O_2CPh)_2$ (1625 cm^{-1}/1338 cm^{-1}, respectively (KBr pellet)), in which both benzoate ligands are unidentate in the solid state.[15,27] Our assignments for **2a**, moreover, are consonant with those for a number of other transition-metal formate complexes—$\nu(CO_2)_{asym}$ for unidentate η^1-O formates (only) absorb above 1600 cm^{-1}.[2a,21c] The $\Delta\nu$ separation between the asymmetric and symmetric $\nu(CO_2)$ bands, moreover, is greatest (~300 cm^{-1}) with the unidentate formates.[21]

Both the NMR and IR spectral studies on **2a** thus are consistent with the presence of two isomers in $CDCl_3$ and CH_2Cl_2 solution, respectively. A reasonable deduction is that **2a** (A) and **2a** (B) are these two isomers and that their equilibration at room temperature is sufficiently rapid to afford time-averaged ^{1}H and ^{13}C NMR spectra.

In THF solution, the chlorozirconocene formate **2a** evidently forms a THF adduct **2a** (C)[23] that exhibits an intense $\nu(CO_2)_{asym}$ band at 1729 cm^{-1} and a weaker $\nu(CO_2)_{sym}$ band at 1367 cm^{-1}. This solvation is not quantitative, as other IR $\nu(CO_2)_{asym}$ bands of weaker intensity (1655 and 1562 cm^{-1}) indicate that some A and B tautomers remain in solution. Recrystallizing THF-solvated **2a** from CH_2Cl_2–hexane returns unsolvated **2a**.

The other three chlorozirconocene carboxylates **2b–d** favor the chelating form B in the solid state and in CH_2Cl_2 solution. In CH_2Cl_2 solution, for example, $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ values are assigned: **2b** (1528, 1477 cm^{-1}), **2c** (1493, 1442 cm^{-1}), and **2d** (1511, 1501, 1455–1410 cm^{-1}). (Phenyl ring vibrational modes for the benzoate **2d** preclude precise $\nu(CO_2)$ assignments.) Only the acetate **2b** has even a weak IR $\nu(CO_2)$ absorption (1639 cm^{-1}) above 1600 cm^{-1}. When dissolved in THF, however, all three carboxylates generate intense $\nu(CO_2)_{asym}$ bands above 1720 cm^{-1}, consistent with the presence of solvated **2b–d** (C). It is worth noting that this dramatic shift in the IR $\nu(CO_2)_{asym}$ band upon THF solvation of **2a–d** is not general for group 4 metal carboxylate complexes, as the analogous $Cp_2Ti(OCOPh)_2$[15] evidently does not ligate THF.[27] The observation that $\Delta\nu(CO_2)$ values (for $\nu(CO_2)_{asym} - \nu(CO_2)_{sym}$) of **2b** and **2c** (51 cm^{-1}) are significantly less than that for **2a** (B) (182 cm^{-1}) is precedented.[21]

Reduction of Chlorozirconocene Carboxylate Complexes. Three of the four chlorozirconocene carboxylates, **2a,b,d**, readily react with the oligomeric hydride complex $[Cp_2Zr(H)Cl]_x$ (**1**) in THF to produce the μ-oxo compound **4** plus the requisite aldehyde (eq 5). These reactions are complete after the reaction mixtures are stirred a few minutes at room temperature. The insoluble **1** then has dissolved, and IR spectral monitoring is consistent with $\nu(CO_2)_{asym}$ for **2a,b,d** being replaced by $\nu(CO)$ for the acetaldehyde (from **2b**) and for benzaldehyde (from **2d**). The μ-oxo complexes were isolated in over 90% yields from **2a,b,d** and acetaldehyde and benzaldehyde were quantified (in 92–93% yields) by both IR spectral and GLC procedures.



2a,b,d **1** **3a,b,d**

a, R = H; **b**, R = CH_3; **d**, R = Ph

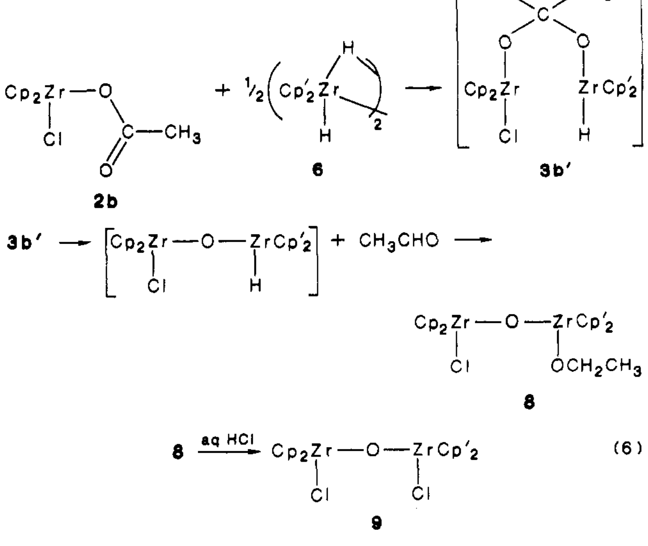
3 **4** (5)

Hydridochlorozirconocene (**1**) suspended in benzene or toluene does not react (i.e., dissolve) over 8 h with either the acetate **2b** or the benzoate **2d** complexes. Conceivably, small amounts of **1** dissolve in THF but not in benzene or toluene in order to drive the reaction with **2b,d**. The pivalate complex **2c**, in contrast, does not react at all (8 h) with **1** in either THF or toluene. Presumably the sterically bulky *t*-Bu group on **2c** blocks its reaction with **1**.

Transience of the μ-η^1-O,O′ *gem*-diolate complexes **3a,b,d** during the reduction of the requisite carboxylate complex **2** with **1** can be postulated (cf. eq 2). These acetal complexes apparently degrade in a fast step by ejecting the aldehyde RCHO and leaving the μ-oxo compound **4**, the two observed products. Attempts at directly detecting **3a,b,d** at lower temperatures proved unsuccessful: The reactions between **2** and **1** progress slowly, and no reaction occurs in THF between **2b** and **1** at −20 °C (4 h). Raising this temperature to 0 or 22 °C, with close IR spectral monitoring, confirmed that acetaldehyde concentration increased in concert with **1** dissolving.

By switching from **1** to $[(\eta^5\text{-}C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (**6**), we were able to use a soluble zirconium hydride.[14b] Moreover, the methyl tag on the substituted Cp ligands (designated Cp′) serves as a convenient label in NMR spectra. If **6** thus reduces $Cp_2ZrCl(OCOCH_3)$ (**2b**) by a mechanism similar to that in eq 5, then unsymmetrical μ-oxo $Cp_2ZrOZrCp'$ derivatives should result.

$[Cp'_2ZrH(\mu\text{-}H)]_2$ (**6**) in fact instantly reduces ligated acetate on **2b** in either THF or toluene solution (eq 6). The resulting



2b **6** **3b′** **8** **9** (6)

Cp′ = η^5-C_5H_4Me

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[23] IR spectral studies of course will not ascertain the extent of solvation. Incorporating one THF molecule into **2** (as C), however, fully utilizes all of the "bent" zirconocene valence orbitals;[24] an 18-electron complex results. As precedent, results of an X-ray crystallographic determination of $Cp_2Zr(OSO_2CF_3)_2\cdot THF$ establishes the presence of two η^1-O triflates and one THF additionally ligating the zirconocene moiety.[25]

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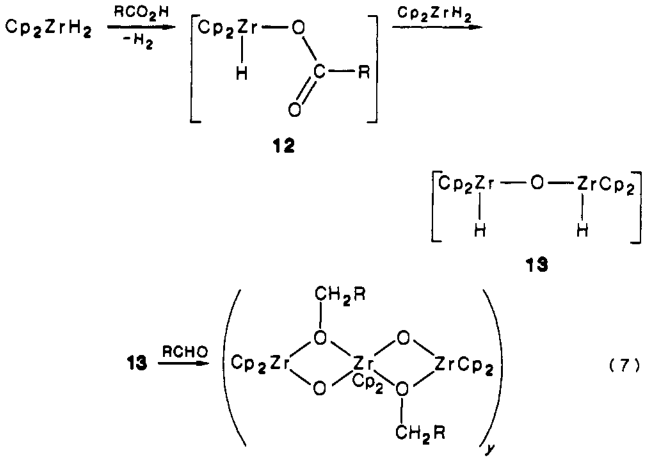
[27] IR data for $Cp_2Ti(OCOPh)_2$: in KBr, 1625 (s, br), 1360–1240 cm^{-1} (half-height width; peak maxima at 1338, 1315, 1292 cm^{-1}); in CH_2Cl_2, 1635 (s, br), 1350–1240 (s, br) cm^{-1}; in THF, 1642 (s) cm^{-1}.

μ-oxo chloro ethoxide **8**, obtained in 54% yield, always was contaminated with the μ-oxo dichloride **9**. Attempts to further purify **8** inevitably gave uncharacterized decomposition products.[28] Structural characterization of **8** rests on interpretation of its ^{1}H NMR spectrum and on derivatization as the unsymmetrical μ-oxo dichloride **9**. This analytically pure derivative remained (77% yield) after treating **8** with aqueous HCl.

The complicated ^{1}H NMR spectra of the Zr_2 complexes **8** and **9** require further comment. Their assignment rests on explaining the differences between the NMR spectra of the starting materials $(\eta^5\text{-}C_5H_4Me)_2ZrCl_2$ (**10**) and $(\eta^5\text{-}C_5H_4Me)_2Zr(Cl)OZr(Cl)(\eta^5\text{-}C_5H_4Me)_2$ (**11**).[8d,29] For **10**, the substituted Cp ligands afford two A_2B_2 triplets (the $H_{3,4}$ multiplet absorbs upfield from that of $H_{2,5}$) and a methyl singlet, whereas for **11**, the $H_{3,4}$ triplet is replaced by two quartets (one for H_3 on both rings and the other for H_4), while the compound retains a triplet for $H_{2,5}$ and a methyl singlet. This chemical shift nonequivalence of the methyl Cp ring protons H_3 and H_4 on **11** originates in their being diastereotopic.[31,32]

The ^{1}H NMR spectrum of the unsymmetrical μ-oxo dichloride **9** differs from that of **11**, in that the prochiral Zr centers on **9** are now also diastereotopic. Hence, we see two magnetically nonequivalent Cp ligands, as well as two chemical-shift-nonequivalent methyl singlets for the Cp′ ligands. The remaining Cp′ ring proton pairs $H_{3(4)}$ and $H_{2(5)}$ have absorptions that resemble those on **11**, except that the two $H_{3(4)}$ multiplets are not fully resolved. The ^{1}H NMR spectrum of the μ-oxo chloro ethoxide **8**, in turn, resembles that of **9**. Cp′ protons $H_{2(5)}$ and $H_{3(4)}$, however, absorb as three poorly resolved multiplets (relative intensities 2:1:1) between δ 6.3 and 5.8. Two additional multiplets, a poorly resolved pair of doublets of quartets (δ 4.0–4.4) and a broadened triplet (δ 1.21), represent the ethoxy group. Results of double-irradiation experiments confirm that the methylene protons are indeed chemical-shift-nonequivalent. These methylene protons are diastereotopic by virtue of double nonequivalence involving the prochiral Zr center.[31]

Wailes and Weigold reported using the insoluble $(Cp_2ZrH_2)_x$ in first generating and then reducing carboxylate ligands (eq 7).[19]



12

13

13

(7)

14: R = CH_3 ($y < 2$), CF_3 ($y = 1$), Ph ($y >> 1$)

Intermediates **12** and **13** offer a plausible pathway in accounting for the oligomeric μ-oxo μ-alkoxide complexes **14** that form. Subsequent reactions of these intermediates, furthermore, closely parallel those postulated in eq 6.

In summary, the chlorozirconocene formate, acetate, pivalate, and benzoate complexes **2a–d** are readily available and fully characterized. Of these, all but the pivalate react in THF with $[Cp_2Zr(H)Cl]_x$ (**1**) and yield the requisite aldehyde plus the μ-oxo compound $Cp_2(Cl)ZrOZr(Cl)Cp_2$ (**4**). Yields of acetaldehyde and benzaldehyde are 92–93%; the identity (and high yield) of formaldehyde is assumed on the basis of Floriani's work (and our high yield of **4**). No direct evidence for the postulated μ-η^1-O,O′ *gem*-diolate intermediates $Cp_2(Cl)ZrOCH(R)OZr(Cl)Cp_2$ (**3a,b,d**) during this reduction of ligated carboxylate exists. Reaction of the zirconium hydride $[Cp'_2ZrH(\mu\text{-}H)]_2$ (**6**) with $Cp_2Zr(Cl)(OCOCH_3)$ (**2b**), however, regioselectively affords the μ-oxo compound $Cp_2(Cl)ZrOZr(OCH_2CH_3)Cp'_2$ (**8**), which is consonant with intermediacy of the μ-η^1-O,O′ acetal **3b′**. We conclude that the two zirconium hydrides **1** and **6** readily reduce zirconocene–carboxylate(η^1-O) ligands in a reaction that parallels the reduction of organic esters by **1**.[5b,7]

Acknowledgment. This research was supported by NSF Grant CHE-8305485. We also thank Professor Carlo Floriani (Columbia University) for helpful discussions.

Registry No. **1**, 37342-97-5; **2a**, 109283-27-4; **2b**, 60876-22-4; **2c**, 109306-36-7; **2d**, 109283-28-5; **4**, 12097-04-0; **6**, 77965-67-4; **7**, 1291-45-8; **8a**, 109283-29-6; **9**, 109306-37-8; 2,2-dimethylpropionic acid, 75-98-9; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7.

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[28] (a) Complex **8** proved to be more unstable than the known[8a,9] chlorozirconocene ethoxide $Cp_2Zr(Cl)(OCH_2CH_3)$. Our samples of this ethoxide, prepared according to the procedure of Gray and Brubaker,[9] were handled easily once its high reactivity toward hydrolysis was accounted for: $Cp_2Zr(Cl)(OCH_2CH_3)$ ^{1}H NMR ($CDCl_3$): δ 6.29 (s, 10 H, Cp), 4.06 (quartet, $J = 7$ Hz, 2 H, OCH_2), 1.12 (t, $J = 7$ Hz, 3 H, $ZrOCH_2CH_3$). (b) The related compound $Cp_2(Cl)ZrOZr(OCH_2CH_3)Cp_2$ has been reported as the product of atmospheric hydrolysis during crystallization of $Cp_2Zr(Cl)(OCH_2CH_3)$.[8a] No spectral data, however, are available.

[29] Our ^{1}H NMR data (200 MHz) are in substantial agreement with those of Samuel.[8d] $(C_5H_4Me)_2ZrCl_2$ (**10**) ^{1}H NMR ($CDCl_3$): δ 6.30 (t (A_2B_2), $J = 2.6$ Hz, 4 H, Cp′ ($H_{2,5}$)), 6.19 (t (A_2B_2), $J = 2.6$ Hz, 4 H, Cp′ ($H_{3,4}$)), 2.28 (s, 6 H, CH_3). $(C_5H_4Me)_2ZrClOZrCl(C_5H_4Me)_2$ (**11**) ^{1}H NMR ($CDCl_3$): δ 6.14 (t, $J = 2.6$ Hz, 4 H, Cp′ ($H_{2,5}$)), 6.08 (quartet, $J = 2.6$ Hz, 2 H, Cp′ ($H_{3(4)}$)), 5.88 (quartet, $J = 2.6$ Hz, 2 H, Cp′ ($H_{4(3)}$)), 2.23 (s, 6 H, CH_3). The starting **10** contained less than 5% Cp_2ZrCl_2. ^{1}H NMR ($CDCl_3$): δ 6.47. The correspondng Cp resonance for $Cp_2ClZrOZrClCp_2$ occurs at δ 6.23. Assignments of the $\eta^5\text{-}C_5H_4Me$ ring ($H_{3,4}$ absorbing upfield of $H_{2,5}$) follow from the results of studies with the appropriate ferrocene derivatives.[30]

[30] Rausch, M.; Siegel, A. *J. Organomet. Chem.* **1969**, *17*, 117. Slocum, D. W.; Ernst, C. R. *Adv. Organomet. Chem.* **1972**, *10*, 79.

[31] VanGorkum, V.; Hall, G. E. *Q. Rev., Chem. Soc.* **1968**, *22*, 14. Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307.

[32] That only one set ($H_{3(4)}$) of diastereotropic protons is chemical shift nonequivalent, but not the other ($H_{2(5)}$), is precedented: Cerarotti, E.; Kagan, H. B.; Goddard, R.; Kruger, C. *J. Organomet. Chem.* **1978**, *162*, 297.