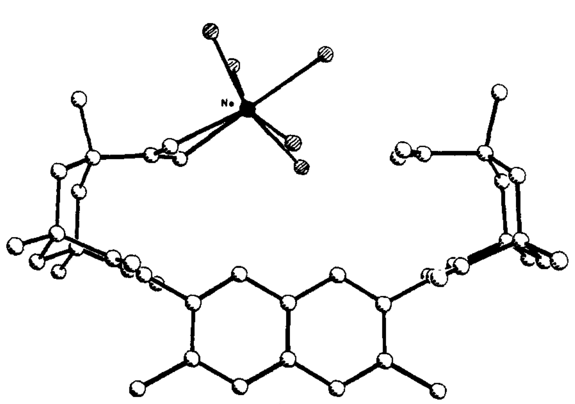


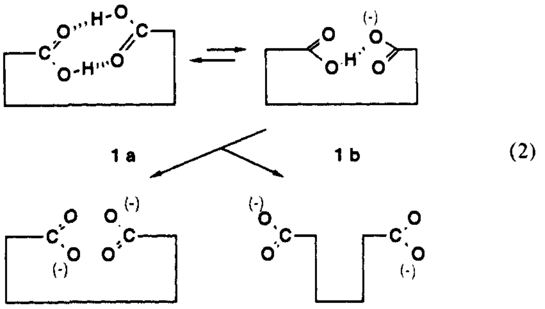
10

Figure 1. Crystal structure of the monosodium salt of **2**. The oxygens of the water molecules indicated by shaded circles; all hydrogens have been omitted for clarity.

is also about 3 Å, but the conformation forces the convergence of the syn lone pairs in the dianion. The result of such high electron density in a limited volume is seen in the extraordinary ΔpK_a of 6.3 units.

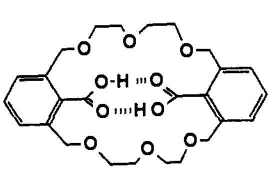
At first glance, the poor access of solvent to the syn lone pairs in the dianion of **1a** could be due to its instability. But even when hydroxylic solvents have access to the carboxyl groups an orientation effect of the lone pairs is observed. Specifically, the diacid **2** binds alcohols tenaciously,[10] and the crystal structure[11] of the monosodium salt, reproduced in **10** (Figure 1), shows extensive solvation by water. The distance that separates the carboxyl oxygens in **2** is seen to be 5.8 Å, or about 1 Å *larger* than that involved in **5**. *Yet the dianion of 2 is less stable.* The enforced convergence of the syn lone pairs in **2** vs. **5** accommodates this result quite nicely.

The effects of intramolecular hydrogen bonding are, admittedly, difficult to quantify in these systems. For example, **1a** may be unique in this group of acids in that its first ionization destroys one intramolecular hydrogen bond but improves[12] the remaining one. The loss of the latter upon the second ionization doubtless contributes to the very large ΔpK_a observed (eq 2).



(2)

Perhaps a measure of this contribution is provided by **1b**. Here, the dianion surely assumes a divergent conformation, since rotations about the C_{aryl}–N bond are rapid at room temperature.[3] If the monoanion of **1b** enjoys an intramolecular hydrogen bond similar to that of **2a**, then a large part of the $\Delta pK_a = 2.6$ represents the cost of breaking it[13] (eq 2). Otherwise, a very small ΔpK_a could be expected. In the monoanions of **6–8** such bonding is also possible but structural limitations force the anti lone pair to interact with the anti acid as in **11**. What effect this has on ΔpK_a is not easily assessed.[14] The $\Delta pK_a = 1.7$ observed for **9**, for example, has been interpreted as inconsistent with an intramolecular hydrogen bond in the monoanion.[7]



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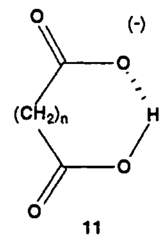

11

In comparison of molecules which differ in more than one respect, the data generally admit to alternative interpretations. The present case is no exception, and the series **1a**, **2**, and **3** are merely readily accessible points in a continuum of structures. When intermediate distances and orientations become available, some finer tuning of the interpretations is also likely to follow. In the meantime, the orientation effects described here support the contention[1d] that the modest efficiency of processes such as A is a result of stereoelectronic effects at carboxyl oxygen.

Acknowledgment. We thank the National Science Foundation for support and Dr. Jaime Abola for his assistance in the crystallographic study.

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(11) General methods for the X-ray studies may be found in ref 3; details will be reported elsewhere.

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Heterobimetallic $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ Carbon Dioxide and $\mu(\eta^1\text{-C,O})$ Formaldehyde Complexes $Cp(NO)(CO)Re\text{-}C(O)O\text{-}Zr(Cl)Cp_2$ and $Cp(NO)(CO)Re\text{-}CH_2O\text{-}Zr(Cl)Cp_2$

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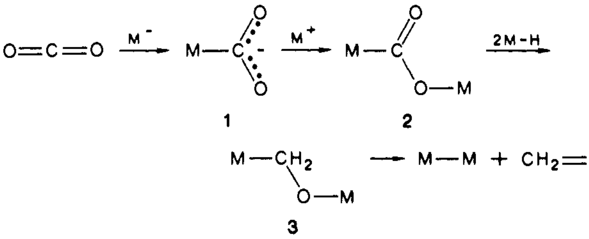
Reducing carbon dioxide[1] to formaldehyde with transition organometallic complexes has as one approach the bimetallic coordination–activation of C_1 fragments. For example (eq 1), an



η^1-C CO_2 complex (or metallocarboxylate) **1** could form a bimetallic $\mu(\eta^1\text{-C,O})$ carboxylate derivative **2**, which upon treating with a metal hydride gives a $\mu(\eta^1\text{-C,O})$ formaldehyde compound **3**. A few metallocarboxylates **1** have been characterized as a result of either coordinating CO_2 to an electron-rich transition-metal center,[2] or by adding excess hydroxide to a ligated carbonyl (eq

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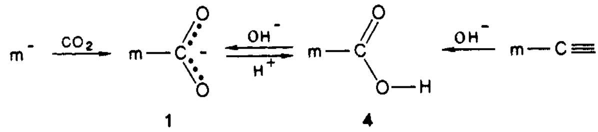
(1) (a) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Ebel, E. W., Eds.; Pergamon Press: New York, 1982, Vol. 8, Chapter 50.4. (b) Ito, T.; Yamamoto, A. In *Organic and Bio-Organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (c) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (d) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel: Boston, 1983; pp 169–219. (g) Floriani, C. *Pure Appl. Chem.* **1983**, *55*, 1; **1982**, *54*, 59.

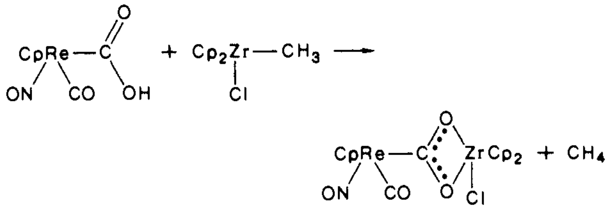
0002-7863/86/1508-6069$01.50/0

2).[3] Two examples of bimetallic $\mu(\eta^1$-C,O) carboxylates **2**, fully characterized $Cl(4\text{-}t\text{-}Bu(pyd))(PPh_3)_2Ir(\mu\text{-}O)(\mu\text{-}CO_2)Os(O)_2(4\text{-}t\text{-}Bu(pyd))_2$[4,5] and the postulated intermediate $Cp_2(Cl)TiOC(O)Ti(Cl)Cp_2$,[6,7] have been noted. No subsequent reductive chemistry of the C_1 ligand in these examples of **2** has been demonstrated.


(2)

We now report syntheses of the bimetallic μ-carboxylate $Cp(CO)(NO)ReC(O)OZr(Cl)Cp_2$ (**5**) and of the μ-formaldehyde compound $Cp(CO)(NO)ReCH_2OZr(Cl)Cp_2$ (**6**), in which the bridging C_1 ligands (**2** and **3**, respectively) originate in a metallocarboxylic acid[8] **4**.

Treatment of $Cp_2(Cl)Zr\text{-}CH_3$[9] in toluene with the metallocarboxylic acid $Cp(NO)(CO)Re\text{-}CO_2H$[3d,8d,10] thus affords a yellow solution (with gas evolution—presumably methane[9,11]). IR spectral monitoring after a few minutes indicated that all of the metallocarboxylic acid had been consumed, and adding hexane precipitated $Cp(NO)(CO)Re\text{-}C(O)O\text{-}Zr(Cl)Cp_2$ (**5**) (82% yield), eq 3, as an analytically pure, light-yellow powder. IR and ^1H and ^{13}C NMR spectral data of this stable product superpose those of $Cp(NO)(CO)ReC(O)OCH_3$[10b] and of $Cp_2(Cl)ZrOC(O)CH_3$[12] for all ligands except the μ-carboxylate.[13] Here the ^{13}C NMR spectral assignment (δ 212.6) differs from that of the Re carboxylate ester (δ 184.2) and of the Zr acetate (δ 187.1).

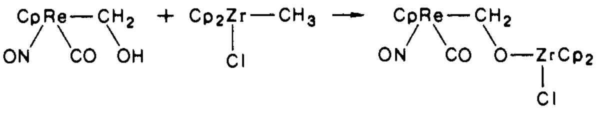

(3)

5

Structural assignment of **5** as a $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ carboxylate, chelating the Zr center, follows from consideration of its IR spectral data. The $\nu(OCO)_{asym}$ 1350 cm^{-1} and $\nu(OCO)_{sym}$ 1278 cm^{-1} absorptions, although displaced to lower energies with respect to analogous ν(OCO) of 1528 and 1477 cm^{-1} for $Cp_2(Cl)ZrOC(O)CH_3$,[12] are consistent with those of chelating carboxylates.[14] Corresponding $\Delta\nu$(OCO) values [for $\nu(OCO)_{asym} - \nu(OCO)_{sym}$] of 72 and 50 cm^{-1} for **5** and for the zirconocene acetate, respectively, also are in the right range (≤ 100 cm^{-1}). Monodentate carboxylate ligands, in contrast, invariably have an IR $\nu(OCO)_{asym}$ above 1600 cm^{-1} and $\Delta\nu$(OCO) values greater than 250 cm^{-1}.[15] That **5** retains the Re carboxylate as a bidentate ligand to Zr is precedented by the existence of a number of $Cp_2(Cl)Zr(XY)$ complexes (XY is a bidentate ligand),[11] including the important class of η^2-acyl complexes.[16]

Bridging carboxylate **5** nevertheless reacts as a typical metalloester (alkoxycarbonyl complex)[17] with electrophiles. Either acid ($HBF_4\cdot OMe_2$) or $Et_3O^+PF_6^-$ in CH_2Cl_2 solution immediately consumes **5** and releases $Cp(NO)(CO)_2Re^+$,[10] which is isolated in over 85% yield.

The sensitivity of the Zr–methyl bond on $Cp_2(Cl)Zr\text{-}CH_3$ toward hydroxylic cleavage[9,11] again proved useful in its reaction with a hydroxymethyl ligand. This zirconocene methyl instantaneously couples with $Cp(NO)(CO)ReCH_2OH$[10b,c] in toluene solution (with gas evolution); adding hexane precipitates analytically pure $Cp(NO)(CO)Re\text{-}CH_2O\text{-}Zr(Cl)Cp_2$ (**6**) (85% yield) as a pale orange powder (eq 4).[18] Its spectral data support a $\mu(\eta^1$-C,O) formaldehyde unit having a Re center that is electronically equivalent to the starting hydroxymethyl. The presence of diastereotopic and chemical shift nonequivalent Cp ligands on Zr and methylene hydrogens further signals, as expected,[10b] a chiral Re center.


(4)

6

Complex **6** joins a relatively small group of formaldehyde complexes,[19] some involving the C_1 ligand bridging two metals.[19g-j]

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(13) $Cp(NO)(CO)Re\text{-}CO_2\text{-}Zr(Cl)Cp_2$ (**5**): IR (CH_2Cl_2) 1997 cm^{-1} (vs, br) (CO), 1729 cm^{-1} (vs, br) (NO), 1352 cm^{-1} (m) $(\nu_{OCO})_{asym}$, 1265 cm^{-1} (s, br) $(\nu_{OCO})_{sym}$; IR (KBr) 1982 cm^{-1} (vs, br) (CO), 1713 cm^{-1} (vs, br) (NO), 1430–1240 cm^{-1} [half-intensity band-width maxima: 1350 cm^{-1} $(\nu_{OCO})_{asym}$, 1278 cm^{-1} $(\nu_{OCO})_{sym}$]; ^1H NMR ($CDCl_3$) δ 6.28 (s, 10 H, $ZrCp_2$), 5.82 (s, 5 H, ReCp); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 212.6 (CO_2), 201.4 (CO), 114.6 (CpZr), 93.7 (CpRe). Acceptable analysis.

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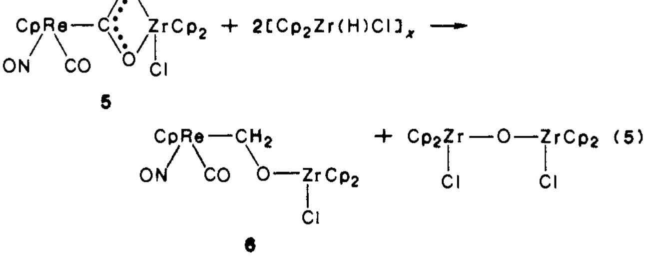
(18) $Cp(NO)(CO)Re\text{-}CH_2O\text{-}Zr(Cl)Cp_2$ (**6**): IR (CH_2Cl_2) 1960 cm^{-1} (vs) (CO), 1688 cm^{-1} (vs) (NO); ^1H NMR (C_6D_6) δ 6.11 (s, 5 H, CpZr), 5.98 (s, 5 H, CpZr), 5.05 (s, 5 H, CpRe), 6.27 (d, J = 8.8 Hz, 1 H, CH_2), 5.72 (d, J = 8.8 Hz, 1 H, CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 210.4 (CO), 113.4 and 112.5 (CpZr), 92.3 (CpRe), 53.1 (CH_2O) ($^1J_{C\text{-}H}$ = 147 Hz; gated decoupling). Acceptable analysis.

Those bridging two zirconocene centers (using Cp and C_5Me_5 ligands) are especially noteworthy for mediating carbon monoxide fixation by zirconocene hydrides.[20] Two such bis(zirconocene) (μ-oxymethylene) complexes have been intercepted and fully characterized as $\mu(\eta^1\text{-O}:\eta^2)$ formaldehyde (or μ-metallaoxirane $ZrCH_2OZr$) compounds.[19i,j] The facile dyotropic shift—degenerate rearrangement equilibrating the $Cp_2(X)Zr$ units[16,19i,j,21]—exhibited by these latter compounds in solution is not evident for **6**.[22,23]

A significant feature of these (Re,Zr) μ-C_1 complexes is that the μ-CO_2 compound **5** reduces to its μ-CH_2O derivative **6** (eq 5). Thus, 2 equiv of $[Cp_2Zr(H)Cl]_x$[24] in THF (1 h) transforms **5** into **6** and the known[25] μ-oxo $[Cp_2(Cl)Zr]_2O$, with 61% conversion evident by NMR and IR spectroscopy. The corresponding methyl ester, $Cp(CO)(NO)ReCO_2CH_3$, under similar conditions, quantitatively affords **6**; whereas, with 1 equiv of $[Cp_2Zr(H)Cl]_x$, 50% conversion to **6** occurs.



The reaction chemistry of {Re,Zr} μ-carboxylate **5** and μ-formaldehyde **6** compounds may model binding of CO_2 between two metal centers and then reducing the resulting $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ carboxylate to ligated formaldehyde (cf., eq 1). In this study, the hydroxycarbonyl group or Re carboxylic acid precursor to **5** (eq 3) originates from a carbonyl ligand (as does the hydroxymethyl group used in independently synthesizing **6**). Work in progress, however, is directed toward the synthesis of other examples of heterobimetallic μ-carboxylates **3** directly from the CO_2 adduct **1**.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8305484) is gratefully acknowledged.

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(23) ^1H NMR data of **6** is best compared with that of $Cp_2(Cl)Zr–CH(R)O–Zr(Cl)Cp_2$ (R = cyclohexylmethyl),[21a] both in C_6D_6. The diastereotopic Cp groups on the μ-cyclohexylacetaldehyde complex absorb as two singlets for each Zr center: δ 5.76, 5.73 for (η^2-C,O) C-bound Zr and δ 6.12, 6.04 for (η^1-O) O-bound Zr.

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Catalytic Asymmetric Induction. Highly Enantioselective Addition of Dialkylzincs to Aldehydes

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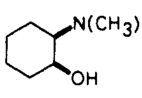
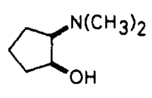
Several examples have been reported for highly enantioselective alkylation of aldehydes by organometallic compounds combined with chiral modifiers.[1] In all cases, however, the procedures require stoichiometric or even excess amounts of the chiral sources.[2] Accordingly, development of efficient chiral multiplication methods in the carbonyl alkylation constitutes a veritable challenge.[3] We here disclose a highly efficient asymmetric induction which provides the first solution to this significant synthetic problem.

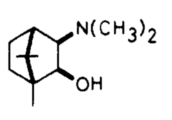
Monomeric dialkylzincs having an sp-hybridized linear geometry are inert to carbonyl compounds, but the reactivity can be enhanced by the structural modification by appropriate ligands or auxiliaries.[4] Replacement of one alkyl group by an electronegative substituent increases the acceptor character of the zinc atom and the donor property of the remaining alkyl group, thereby accelerating the reaction with carbonyl substrates. Recently Oguni and Omi reported that reaction of diethylzinc and benzaldehyde in the presence of a catalytic amount of (*S*)-leucinol (a primary amino alcohol) give (*R*)-1-phenylpropanol in 48.8% ee.[5] Encouraged by this result, we surveyed a variety of β-amino alcohols for activation of dialkylzinc reagents and observed the most impressive rate enhancement with some sterically constrained, tertiary amino alcohols. In the reaction of diethylzinc and benzaldehyde, for instance, (±)-*cis*-1-(dimethylamino)-2-hydroxycyclohexane (**1**) and -cyclopentane (**2**) proved to be 10–100 times as effective as related acyclic amino alcohols or primary and secondary amino analogues of **1** and **2**.[6]



1



2



3, DAIB

With such information in hand, we employed a camphor-derived homochiral amino alcohol possessing the requisite structure. Thus (−)-3-*exo*-(dimethylamino)isoborneol (DAIB) (**3**),[7] $[\alpha]^{14}{}_D$ −9.40° (*c* 4.31, C_2H_5OH), serves as an excellent chiral auxiliary in this

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