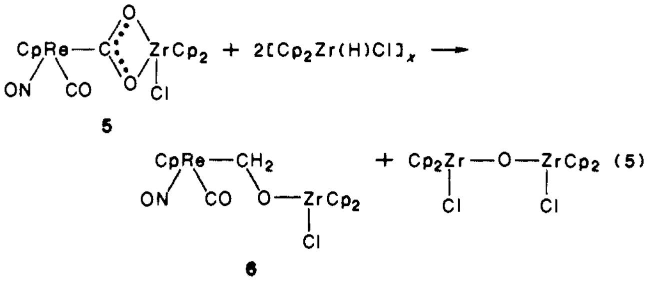
Those bridging two zirconocene centers (using Cp and C_5Me_5 ligands) are especially noteworthy for mediating carbon monoxide fixation by zirconocene hydrides.[20] Two such bis(zirconocene) (μ-oxymethylene) complexes have been intercepted and fully characterized as $\mu(\eta^1\text{-O}:\eta^2)$ formaldehyde (or μ-metallaoxirane $\overline{\text{ZrCH}_2\text{O}}\text{Zr}$) 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**.

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Catalytic Asymmetric Induction. Highly Enantioselective Addition of Dialkylzincs to Aldehydes

M. Kitamura, S. Suga, K. Kawai, and R. Noyori*

Department of Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

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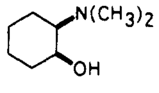
Several examples have been reported for highly enantioselective alkylation of aldehydes by organometallic compounds combined with chiral modifiers.[1] In all cases, however, the procedures require stoichiometric or even excess amounts of the chiral sources.[2] Accordingly, development of efficient chiral 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]



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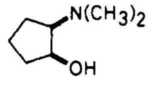

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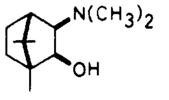

3, DAIB

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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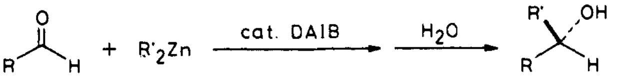
Table I. Enantioselective Addition of Dialkylzincs to Aldehydes[a]

aldehyde	alkylating agent	conditions		alkylated product		
		solvent	time, h	% yield[b]	$[\alpha]^{22}_D$, deg (*c*, solvent)	% ee[c] (confign)
C_6H_5CHO	$(C_2H_5)_2Zn$	toluene	6	97	−47.6 (6.11, $CHCl_3$)[d]	98 (*S*)[e]
C_6H_5CHO	$(C_2H_5)_2Zn$	hexane–toluene	6	94[f]		98 (*S*)
C_6H_5CHO	$(C_2H_5)_2Zn$	ether–toluene	6	98[f]		99 (*S*)
C_6H_5CHO	$(C_2H_5)_2Zn$	THF–toluene	64	44[f]		91 (*S*)
C_6H_5CHO	$(CH_3)_2Zn$	toluene	70	59[f]	−49.7 (2.01, *c*-C_5H_{10})[g]	91[h] (*S*)
p-ClC_6H_4CHO	$(C_2H_5)_2Zn$	toluene	12	86	−23.5 (0.82, C_6H_6)[i]	93 (*S*)
p-$CH_3OC_6H_4CHO$	$(C_2H_5)_2Zn$	toluene	12	96	−32.1 (1.25, C_6H_6)[i]	93 (*S*)
(*E*)-$C_6H_5CH{=}CHCHO$	$(C_2H_5)_2Zn$	toluene	6	81	−5.7 (100, $CHCl_3$)[j]	96 (*S*)
$C_6H_5CH_2CH_2CHO$	$(C_2H_5)_2Zn$	toluene	12	80	+23.9 (1.44, C_2H_5OH)[k]	90[l] (*S*)
n-$C_6H_{13}CHO$	$(C_2H_5)_2Zn$	toluene	24	81	+5.1 (1.31, $CHCl_3$)[m]	61[l] (*S*)

[a] Reaction was carried out in degassed solvent at 0 °C by using 2 mol % (−)-DAIB and 1.2 equiv of the alkylating agent per aldehyde. [b] Isolated yield. [c] Determined by HPLC using a Bakerbond DNBPG chiral column unless otherwise specified. [d] See ref 8. [e] Absolute configuration: MacLeod, R.; Welch, F. J.; Mosher, H. S. *J. Am. Chem. Soc.* **1960**, *82*, 876. [f] HPLC analysis. [g] $[\alpha]^{20}_D$ +43.1° (*c* 7.19, *c*-C_5H_{10}) for (*R*)-1-phenylethanol: Yamaguchi, S.; Mosher, H. S. *J. Org. Chem.* **1973**, *38*, 1870. [h] Determined by HPLC analysis of the (*R*)-α-methoxy-α-[(trifluoromethyl)phenyl]-acetate (Develosil 100-5 column, 1:100 ethyl acetate–hexane eluent). [i] Reported values for (*S*)-1-(*p*-chlorophenyl)propanol in 43% ee and (*S*)-1-(*p*-methoxyphenyl)propanol in 51% ee are $[\alpha]^{22}_D$ −10.4° (*c* 5, C_6H_6) and $[\alpha]^{22}_D$ −17.2° (*c* 5, C_6H_6), respectively [Capillon, J.; Guettē, J. *Tetrahedron* **1979**, *35*, 1817]. [j] $[\alpha]^{23}_D$ −6.6° (*c* 3.18, $CHCl_3$) for (*S*)-1-phenylpent-1-en-3-ol in 75% ee: Sato, T., Gotoh, Y.; Wakabayashi, Y.; Fujisawa, T. *Tetrahedron Lett.* **1983**, *24*, 4123. [k] $[\alpha]_D$ +26.8° (*c* 5.0, C_2H_5OH) for (*S*)-1-phenyl-3-pentanol: see ref in footnote *j*. [l] Determined by HPLC analysis of the (*R*)-1-(1-naphthyl)ethyl carbamate (Develosil 100-3, 1:2 ether–hexane). [m] $[\alpha]^{24}_D$ +9.6° (*c* 8.3, $CHCl_3$) for (*S*)-3-nonanol: Mukaiyama, T.; Hojo, K. *Chem. Lett.* **1976**, 893.

context. Under the influence of 2 mol % of (−)-DAIB, diethylzinc reacted with benzaldehyde (1.2:1 molar ratio) in toluene smoothly at 0 °C, and (*S*)-1-phenylpropanol was obtained in 98–99% ee and in 98% chemical yield. Table I exemplifies the efficient asymmetric alkylation. The enantiomeric excess was determined carefully by HPLC analysis using a chiral stationary phase. Enantioselectivity of the reaction of *p*-substituted benzaldehydes is generally high. Certain α,β-unsaturated or aliphatic aldehydes can be also alkylated with a high degree of enantioselectivity. Use of nonpolar solvents such as hexane, toluene, ether, or their mixtures gave consistently satisfactory results. THF as solvent retarded the reaction and lowered the enantioselectivity to some extent. Attempted alkylation of acetophenone failed.



Notably, stoichiometry of the substrate, alkylating agent, and auxiliary has marked effects on the reaction rate and course. Benzaldehyde does not react with diethylzinc at 0 °C in toluene. When a 1:1:1 or 1:2:2 mixture of benzaldehyde, diethylzinc, and (−)-DAIB in toluene was allowed to stand at 0 °C, the aldehyde was consumed slowly but only benzyl alcohol was obtained. No ethylation product could be detected. If, however, the amount of diethylzinc to (−)-DAIB was doubled, the ethylation reaction took place smoothly, as under the above described catalytic conditions, leading to the desired alcohol in 98% ee and in 88% (benzaldehyde:diethylzinc:DAIB = 1:2:1, 12 h) or 49% (1:1:0.5 ratio, 12 h) yield. These results indicate that two zinc species per aldehyde are responsible for the alkylation reaction.

This method is practical and operationally very simple. A typical procedure is illustrated as follows: In a frame-dried Schlenk tube was placed (−)-DAIB (371 mg, 1.88 mmol) and dry toluene (200 mL), and the whole mixture was degassed and covered with argon. To this was added a 4.19 M toluene solution of diethylzinc (27.0 mL, 113 mmol) and the resulting solution was stirred at 15 °C for 15 min (ethane evolution was confirmed by ^{1}H NMR). After cooling to −78 °C, benzaldehyde (10.0 g, 94.2 mmol) was then added and the mixture was warmed up to 0 °C, stirred for 6 h, and quenched by adding a saturated ammonium chloride solution. Usual extractive workup and distillation gave (*S*)-1-phenylpropanol in 98% ee (12.4 g, 97% yield) as an oil, $[\alpha]^{22}_D$ −47.6° (*c* 6.11, $CHCl_3$) [lit.[8] $[\alpha]_D$ −45.45° (*c* 5.15, $CHCl_3$)]. The ee was determined by HPLC analysis (column, Bakerbond DNBPG; eluent, 0.25% 2-propanol in hexane; flow rate, 1.0 mL/min; detection, 254-nm light). Racemic 1-phenylpropanol exhibited two base-line-separated peak arising from the *S* isomer (t_R 47.8 min) and *R* isomer (t_R 50.0 min) with equal intensities, whereas the synthetic alcohol showed these peaks in ratio of 99.2:0.8.

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Two-Dimensional Chemical Exchange NMR in the Solid: Proton Dynamics in Phthalocyanine

B. H. Meier, Carlyle B. Storm, and William L. Earl*

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Received December 11, 1985

Carbon-13 solid-state cross-polarization magic angle spinning (CP-MAS) has proved to be a powerful method for investigating dynamical processes in solids.[1] In investigations of molecules with several resonances, the intrinsically lower resolution of CP-MAS NMR spectra compared to liquid-state spectra makes the interpretation of the spectra cumbersome due to peak overlap. In some cases, such as porphyrins or phthalocyanines, these problems arising in the ^{13}C spectra have been overcome by observing ^{15}N instead of ^{13}C.[2-4] This requires considerable synthetic effort because the NMR measurements must be performed on an enriched sample to overcome the low sensitivity. We present here results which show that ^{13}C 2-D exchange exchange spectroscopy[5,6] can extend the resolution, allowing the spectroscopist to extract the details of the exchange process from a natural abundance sample even when the ^{13}C resonances strongly overlap in the one-dimensional spectrum. There is another example in which 2-D exchange spectroscopy has been exploited in a solid to determine a proton exchange rate but it was in a system where

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