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A Catalytic System for the Activation of Diorganozinc Reagents

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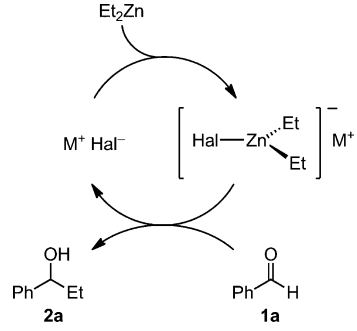
We report a novel catalytic system for the activation of diorganozinc reagents. We assumed that the nucleophilic activation of diethylzinc should be efficiently performed by simple alkali metal salts. Indeed, the combination of sodium salts and 15-crown-5 significantly accelerates the rate of diethylzinc addition to benzaldehyde under mild conditions. The activity of the catalytic system strongly depends on the nature of the anion, decreasing in the order $I^- > Br^- > Cl^- > F^-$. Under the optimized reaction conditions, various aryl, hetero aryl, and aliphatic aldehydes were converted with diethylzinc and the corresponding product was obtained in excellent yields. The first X-ray absorption spectroscopy measurements on such type of reactions provide initial insights that support the proposed catalytic cycle and suggest the formation of a zincate complex.

Introduction

Among organic reactions, those that form new carbon–carbon bonds are of major interest for synthetic chemists. The nucleophilic addition of different organometallic reagents to carbonyl compounds has long been known and offers a very elegant opportunity to form a broad variety of different products.[1] Along with organolithium and Grignard compounds, zinc organyls are among the most important reagents for such transformations. Although known for a long time, their application in organic synthesis has only developed significantly over the last few decades.[2] In contrast to other organometallic reagents,[2d] zinc organyls constitute a unique class of compounds because they tolerate a large number of functional groups[3] and often react stereo- and chemoselectively in the presence of a suitable catalyst.[4] Positive effects of halides as additives in transition-metal-catalyzed processes have been reported frequently.[5] In our efforts to employ phosphonium salts as Lewis acidic catalysts, we reported their application in the conversion of diethylzinc with aldehydes.[6] Notably, we observed that the catalytic activity of the phosphonium salts strongly depends on the nature of the anion.[6a] Recently, Song et al. reported synergistic effects of quaternary ammonium salts on the asymmetric addition of diethylzinc to aldehydes as well as their utilization as catalysts in the addition of Grignard reagents to ketones.[7] In this context, we were interested in the nucleophilic activation of diethylzinc by simple alkali metal salts (Scheme 1). Similar nucleophilic activation has been proposed and might be expected for σ-donor ligands, for example iodide.[3a,3b,5a,5b,8] Moreover organozincates[9] are valuable reagents, and anions of the type shown in Scheme 1 have been reported by Richey Jr. and co-workers.[9k] We chose the addition of diethylzinc to benzaldehyde **1a** as a model reaction to investigate the envisioned nucleophilic activation by the halogen anion of these salts.



Scheme 1. Proposed catalytic cycle for the addition of Et_2Zn to benzaldehyde (**1a**). Product **2a** is obtained after aqueous work up.

Results and Discussion

Initial experiments showed that simple phosphonium salts efficiently catalyzed the addition of diethylzinc to benzaldehyde (**1a**).[6b] The activity of those catalysts mainly depended on the nature of the anion (Table 1). In the absence of a catalyst the reaction proceeded sluggishly and the desired product was obtained in only low yields up to 11% (entry 1). The addition of crown ethers had no influence on the outcome of the reaction (entries 2–4). In the presence of sodium fluoride, chloride, bromide, or iodide the yield was slightly improved to 33% (entries 5–8). The utilization

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of the corresponding lithium and potassium salts had no significant influence (entries 9 and 10). Finally, crown ethers were employed as co-catalysts to improve the activity of the anions further. Crown ethers are known to generate activated "naked anions" in aprotic organic solvents in situ by forming a chelate complex with the cation.[10] The utilization of sodium salts in a 1:1 molar ratio with 15-crown-5 led to significantly increased conversions and yields (entries 11–14). The best result was obtained for NaI in combination with the crown ether, giving the desired product **2a** in 98% yield (entry 10). Reducing the reaction time to 6 h led to 94% yield (entry 15), however, significantly lower yield was obtained when the reaction time was reduced further to 3 h (entry 16). The utilization of LiCl and KCl in combination with 12-crown-4 and 18-crown-6, respectively (entries 17 and 18), had no significant influence on the outcome of the reaction compared with that using the NaCl/15-crown-5 system (entry 12).

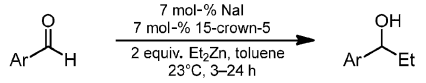
Table 1. Catalyst screening for the conversion of **1a** with diethylzinc.[a]

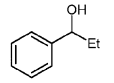
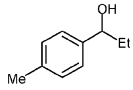
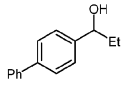
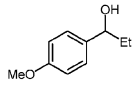
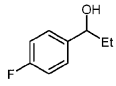
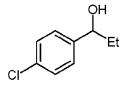
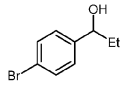
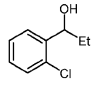
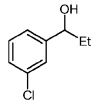
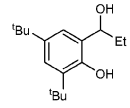
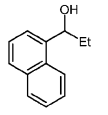
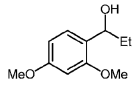
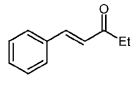
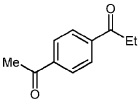
Entry	Catalyst	*t* [h]	Conv. **1a** [%][b]	Yield **2a** [%][b]
1	–	24	14	11
2	12-crown-4	24	10	8
3	15-crown-5	24	18	11
4	18-crown-6	24	15	10
5	NaF	24	23	21
6	NaCl	24	33	30
7	NaBr	24	31	29
8	NaI	24	36	33
9	LiCl	24	35	33
10	KCl	24	31	31
11	NaF/15-crown-5	24	46	35
12	NaCl/15-crown-5	24	91	86
13	NaBr/15-crown-5	24	>99	94
14	NaI/15-crown-5	24	>99	98, 97[c]
15	NaI/15-crown-5	6	94	94, 75[d], 40[e]
16	NaI/15-crown-5	3	85	80
17	LiCl/12-crown-4	24	88	87
18	KCl/18-crown-6	24	93	90

[a] Reaction conditions: NaX/15-crown-5 (1:1, 7 mol-%), benzaldehyde (**1a**; 1.0 equiv.), Et_2Zn (2.0 equiv.), anhydrous toluene, 23 °C. [b] Determined by GC analysis with hexadecane as internal standard. [c] In THF. [d] Et_2Zn (1.0 equiv.). [e] Et_2Zn (0.5 equiv.).

Encouraged by the initial results, we next evaluated the effectiveness of the system in the conversion of diethylzinc with aryl aldehydes **1** into the corresponding alcohols **2** (Table 2). Conversion of the model substrate **1a** gave the desired product **2a** after 24 h reaction time in 99% isolated yield. In general, shorter reaction times were possible and **2a** could be obtained in 80% yield after 3 h (entry 1). When $[Bu_4P]Cl$ was employed as the catalyst the yield of **2a** was only 72% after 6 h. This result shows the increased reactivity of the new catalytic system. The conversion of other substrates was monitored by GC analysis and the reaction was stopped when full conversion was reached. *para*-Methyl and *para*-phenyl-substituted aldehydes **1b** and **1c** could be quantitatively converted into the corresponding alcohols **2b** and **2c**, respectively, in 12 h (entries 2 and 3). The corresponding methoxy-substituted derivative **2d** was isolated in

Table 2. Conversion of aryl aldehydes **1** with Et_2Zn.



Entry	Product		*t* / h	Yield **2** / %[a]
1		**2a**	24 (3)	99 (80[b])
2		**2b**	12	99
3		**2c**	12	98
4		**2d**	12	74
5		**2e**	6	93
6		**2f**	6	96
7		**2g**	6	92
8		**2h**	6	88
9		**2i**	12	91
10		**2j**	48	99
11		**2k**	12	99
12		**2l**	24	94
13		**2m**	24	37[b]
14		**2n**	24	50[b]

[a] Product **2** was obtained after aqueous work up. Isolated yields are given. [b] Determined by GC analysis with hexadecane as internal standard.

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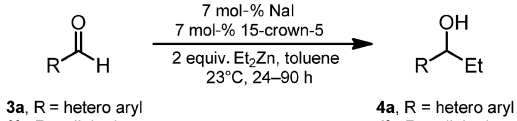
good yield (74%; entry 4). In contrast, *para*-halogen-functionalized products **2e**–**g** were obtained in excellent yields (>90%) after 6 h (entries 5–7). The yield was independent of the substitution pattern, for example *ortho*- (**2h**), *meta*- (**2i**), and *para*-chlorobenzaldehyde (**2f**) were obtained in 88–96% yield (entries 6, 8, and 9), although longer reaction time was necessary for full conversion of **1i** (entry 9). Notably, the conversion of base-sensitive phenol derivative **1j** gave the desired product **2j** in excellent yield of 99%. Moreover, naphthalene-1-carbaldehyde (**1k**) and dimethoxybenzaldehyde (**1l**) were converted into the corresponding alcohol in 99 and 94% yield, respectively (entries 11 and 12).

The chemoselectivity of the reaction was tested in the conversion of cinnamaldehyde (**1m**) and 4-acetylbenzaldehyde (**1n**) with diethylzinc for 24 h at room temperature in the presence of 7 mol-% NaI/15-crown-5. In both cases, exclusive 1,2-addition to the aldehyde functionality was observed. The corresponding products **2m** and **2n** were obtained in 37 and 50% yield, respectively. The formation of byproducts was not observed. Furthermore, we were interested in examining the scope and limitations of the reaction. To this end, we investigated the conversion of hetero aryl and aliphatic aldehydes under the same reaction conditions (Table 3). The obtained yields were still good but they were considerably lower than in the conversion of aryl aldehydes **1** shown in Table 2. The conversion of pyridine-2-carbaldehyde (**3aa**) only led to 62% yield of the desired product **4aa** even after 90 h reaction time (Table 3, entry 1). The same reaction time was needed for full conversion of furan-2-carbaldehyde (**3ab**) and product **4ab** was obtained in good yield of 75% (entry 2). The reaction of thiophene-2-carbaldehyde (**3ac**) with diethylzinc gave **4ac** in 79% yield after 48 h (entry 3). Similar results were obtained in the conversion of aliphatic aldehydes **3b**. The conversion of *n*-hexanal (**3ba**) was complete after 24 h, giving 76% yield of **4ba**, whereas 3-phenylpropanal (**3bb**) and citronellal (**3bc**) gave the desired products **4ba** and **4bc** in 71 and 63% yield, respectively (entries 4–6).

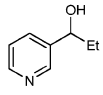
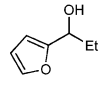
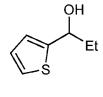
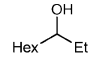
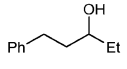
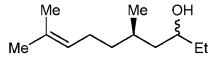
Finally, the utilization of other readily available diorganozinc reagents (R_2Zn, R = Me, *n*Bu, *i*Pr, Ph) in the conversion of **1a** under the same reaction conditions was investigated (Table 4). Although other R_2Zn compounds could be converted, the yields of the corresponding products **5** were only moderate or even low. The best result was obtained with dimethylzinc (R = Me), which gave **5a** in 71% yield (entry 1). The conversion of **1a** with dibutyl- and diisopropylzinc gave 1-phenyl-1-pentanol (**5b**) and 2-methyl-1-phenylpropanol (**5c**) in only 48 and 31% yield, respectively (entries 2 and 3). In contrast, diphenylmethanol (**5d**) could be observed in moderate yield of 60% (entry 4).

Table 3. Conversion of hetero aryl **3a** and aliphatic aldehydes **3b** with Et_2Zn; product **4** was obtained after aqueous workup.



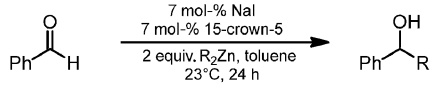
3a, R = hetero aryl
3b, R = aliphatic

4a, R = hetero aryl
4b, R = aliphatic

Entry	Product		*t* / h	Yield **4** / %[a]
1		**4aa**	90	62
2		**4ab**	90	75
3		**4ac**	48	79
4		**4ba**	24	76
5		**4bb**	48	71
6		**4bc**	48	63

[a] Isolated yield.

Table 4. Conversion of benzaldehyde **1a** with various R_2Zn compounds; product **5** was obtained after aqueous workup.



1a **5**

Entry	R_2Zn	Product		Yield **2** / %[a]
1	Me_2Zn		**5a**	71
2	nBu_2Zn		**5b**	48
3	iPr_2Zn		**5c**	31
4	Ph_2Zn		**5d**	60

[a] Determined by ^1H NMR spectroscopic analysis with 1,3,5-trimethylbenzol as internal standard.

To gain initial insights into the mechanism of the described reaction, X-ray absorption spectroscopy (XAS) techniques were applied. This method is able to provide information about the oxidation state and coordination geometry by XANES (X-ray absorption near edge structure) of a metal atom in an element-sensitive manner.[11] Additionally, EXAFS (extended X-ray absorption fine structure) delivers the number, type, and distance of coordinating atoms around a metal atom. As model systems to study the mechanism of this reaction, a solution of Et_2Zn in toluene (a) and with stoichiometric amounts of NaI and 15-crown-5 (b), as well as this mixture with a stoichiometric amount of **1a** (c) were studied by XAS. Figure 1 shows the XANES spectra of the solutions, and Figure 2 shows the Fourier-transformed EXAFS spectra. The structural parameters obtained by fitting the experimental spectra with theoretical models are summarized in Table 5.

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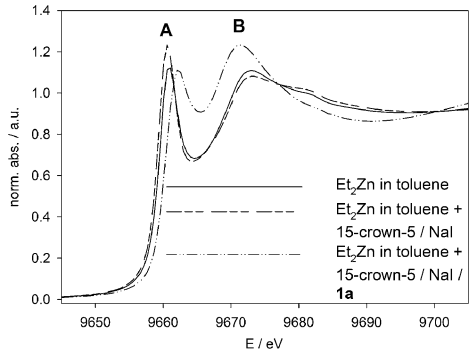

Figure 1. XANES spectra of Et_2Zn in toluene, with 15-crown-5 and NaI, and with additional **1a**. The resonances discussed in the text are indicated with **A** and **B**.

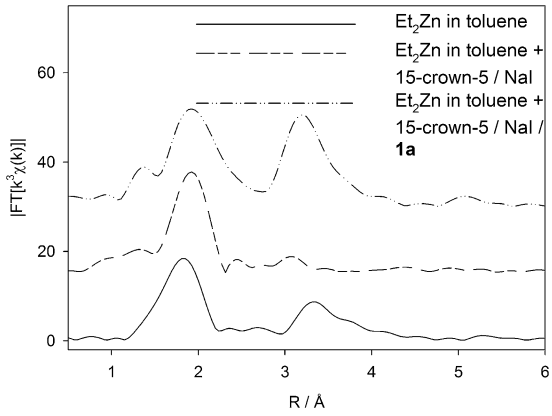

Figure 2. Fourier transformed EXAFS spectra of Et_2Zn in toluene, with 15-crown-5 and NaI, and with additional **1a**. The signals are discussed in the text.

Table 5. Structural parameters obtained by fitting the experimental EXAFS data with theoretical models.

Sample	Abs-Bs[a]	N(Bs)[b]	R(Abs-Bs) /Å[c]
Et_2Zn in toluene (a)			
	Zn-C	2.6 ± 0.3	1.97 ± 0.02
	Zn-C	3.1 ± 0.6	3.40 ± 0.03
Et_2Zn in toluene + 15-crown-5/NaI (b)			
	Zn-C	2.6 ± 0.3	1.96 ± 0.02
	(Zn-I)	0.8 ± 0.2	3.21 ± 0.03
Et_2Zn in toluene + 15-crown-5/NaI/**1a** (c)			
	Zn-C	2.3 ± 0.2	2.00 ± 0.02
	Zn-O	2.0 ± 0.2	2.11 ± 0.02
	Zn-Zn	1.2 ± 0.2	3.07 ± 0.03
	Zn-C	0.9 ± 0.1	2.94 ± 0.03
	Zn-C	2.4 ± 0.4	3.51 ± 0.04

[a] Abs = X-ray absorbing atom, Bs = backscattering neighbor. [b] Number of backscattering neighbor atoms. [c] Distance between absorber and backscatterer.

The XANES spectrum of Et_2Zn is in accordance with previous reports.[12] The sharp resonance **A** found at approximately 9660 eV in Figure 1 is due to a 1s-4p transition. According to the linear coordination in Et_2Zn in toluene, the intensity of this resonance is rather large. This is also reflected in the structural parameters obtained by fitting the EXAFS data with theoretical models (Table 5).

Two carbon shells are found at distances of 1.97 and 3.40 Å, with the according coordination numbers. No Zn–Zn contributions that would be characteristic for higher aggregates were detected. Addition of NaI and 15-crown-5 leaves the intensity of **A** almost unchanged, indicating that no significant change in the orbital structure behind the 1s-4p transition occurs. In the linear structure of Et_2Zn, the final p states are the degenerate $p_{x,y}$ states and p_z with a slightly higher energy. In case of a trigonal planar structure there are still two degenerate final states, but now the $p_{y,z}$, have a higher energy than the single p_x.[13] With the resolution of our experiments, these cases are difficult to distinguish from the XANES spectra, therefore the linear and trigonal planar structure are both plausible after the addition of NaI and 15-crown-5.

Unfortunately, the EXAFS results are also not equivocal; 2.6 carbon neighbors could be fitted, which is in agreement with an unchanged Zn–C coordination. Clearly, this number is too small for coordinating 15-crown-5, therefore, complexation of Zn by 15-crown-5 can be excluded. The coordination of I^- to Zn^{2+} is assumed because the halide ion has significant influence on the catalytic activity. The inclusion of a direct Zn–I pair in the EXAFS fit is feasible, and the fitting results given in Table 5 are reproducible. However, the Zn–I is not of statistical significance, that is, it does not increase the quality of fit in comparison to a single shell fit with only Zn–C. Moreover, the Zn–I shell suffers from large thermal disorder, which could explain the lack of significance. Additionally, destructive interference effects are well-known in X-ray absorption spectroscopy,[14] which lead to the annihilation of two backscattering signals, and it cannot be excluded that such effects contribute to the weak Zn–I signal. Nonetheless, the Zn–I pair is given in parentheses in Table 5. Still, together with the slightly changed XANES signature and the first Zn–C shell, which is identical to pure Et_2Zn, we interpret these results as indicating the formation of a zincate complex as given in Scheme 1.

Support for this conclusion is provided by the results obtained after addition of **1a**. It is assumed that **1a** substitutes the I^- of the zincate complex. Since in this sample the Zn–C shell is visible again, the hypothesis of destructive interference caused by iodine is supported. Moreover, a second light atom nearest neighbor (denoted as Zn–O) and a second Zn–C shell can be detected at 2.11 and 2.94 Å, respectively, which is characteristic of coordinating **1a**. The fourfold coordination of the Zn center is also reflected in the XANES spectrum, in which the position of **A** shifts to higher energies, and the ratio between the first (**A**) and second resonance (**B**) is also altered, which is characteristic of a tetrahedral coordination geometry.[12a] Finally, a dimeric structure is formed by coordination of **1a**, because a Zn–Zn shell significantly increased the quality of fit.

Conclusions

We have established a new method for the activation of diorganozinc reagents with catalytic amounts of sodium

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iodide in the presence of 15-crown-5. Although other diorganozinc reagents could be employed, the procedure proved to be most efficient in the acceleration of diethylzinc addition to a variety of aromatic, heteroaromatic, and aliphatic aldehydes under mild conditions. The corresponding alcohols were usually obtained in good to excellent yields. XAS experiments support the formation of a zincate complex as the active species, although further experiments are required to resolve this issue. This simple system might be useful to enhance reactivity and selectivity in organozinc addition reactions or halogen–zinc exchange reactions, respectively.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk techniques. Toluene was dried with sodium and freshly distilled before use. All starting materials were commercially available and used without further purification. TLC was performed on Macherey–Nagel silica gel plates 60 (UV254). Preparative column chromatography was carried out using Macherey–Nagel M60 silica gel (0.04–0.063 mm) with cyclohexane and ethyl acetate (EtOAc) as eluents for flash column chromatography.

General Procedure for the Addition of Et_2Zn: The aldehyde (1.0 equiv.) was added to a mixture of 15-crown-5 (7 mol-%) and sodium iodide (7 mol-%) in toluene [c(aldehyde) = 2.5 mol L^{-1}]. Subsequently, Et_2Zn in toluene (c = 1.1 mol L^{-1}, 2.0 equiv.) was added dropwise at 0 °C. The solution was warmed to 23 °C and stirring was continued for 3–90 h. The mixture was diluted with HCl (1 N, 3.3 mL per mmol of aldehyde). The aqueous layer was extracted with CH_2Cl_2 (3 × 6.5 mL·per mmol of aldehyde) and the combined organic layers were dried (Na_2SO_4). All volatiles were removed in vacuo and the residue was purified by chromatography (SiO_2; cyclohexane/EtOAc).

1-Phenylpropan-1-ol (2a):[15] Compound **1a** (159 mg, 1.50 mmol) was converted for 24 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 10:1; R_f = 0.68), **2a** was obtained as a colorless oil (201 mg, 1.48 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, J = 7.3 Hz, 3 H), 1.59–1.79 (m, 2 H), 1.94 (br. s, 1 H), 4.50 (t, J = 6.9 Hz, 1 H), 7.16–7.29 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.09 (CH_3), 31.82 (CH_2), 75.96 (CH), 125.93 (2CH), 127.44 (CH), 128.34 (2CH), 144.54 (C) ppm. MS (EI, 70 eV): m/z (%) = 136 (12) $[M]^+$, 107 (100), 79 (70), 77 (39), 51 (26).

1-(4-Methylphenyl)propan-1-ol (2b):[16] Compound **1b** (180 mg, 1.50 mmol) was converted for 12 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.83), **2b** was obtained as a colorless oil (224 mg, 1.49 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.4 Hz, 3 H), 1.66–1.90 (m, 2 H), 1.92 (d, J = 3.0 Hz, 1 H), 2.35 (s, 3 H), 4.55 (dt, J = 2.6, 6.8 Hz, 1 H), 7.14–7.19 (m, 2 H), 7.21–7.27 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.16 (CH_3), 21.07 (CH_3), 31.75 (CH_2), 75.84 (CH), 125.89 (2CH), 129.03 (2CH), 137.09 (C), 141.60 (C) ppm. MS (EI, 70 eV): m/z (%) = 150 (9) $[M]^+$, 121 (100), 93 (47), 91 (43), 77 (25), 65 (10).

1-(Biphenyl-4-yl)propan-1-ol (2c):[16] Compound **1c** (273 mg, 1.50 mmol) was converted for 12 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 10:1; R_f = 0.69), **2c** was obtained as a colorless solid (308 mg, 1.47 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.4 Hz, 3 H), 1.72–1.97 (m, 3 H), 4.66 (dt, J = 3.0, 6.4 Hz, 1 H), 7.32–7.38 (m, 1 H), 7.31–7.50 (m, 4 H), 7.56–7.77 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.16 (CH_3), 31.85 (CH_2), 75.74 (CH), 126.39 (2CH), 127.04 (2CH), 127.13 (2CH), 127.22 (CH), 128.73 (2CH), 140.40 (C), 140.84 (C), 143.59 (C) ppm. MS (EI, 70 eV): m/z (%) = 212 (15) $[M]^+$, 194 (22), 184 (14), 183 (100), 178 (10), 155 (44), 154 (10), 153 (16), 152 (20), 77 (12).

1-(4-Methoxyphenyl)propan-1-ol (2d):[16] Compound **1d** (204 mg, 1.50 mmol) was converted for 12 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.66), **2d** was obtained as a colorless oil (185 mg, 1.11 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.6 Hz, 3 H), 1.71–1.92 (m, 2 H), 1.97–2.00 (m, 1 H), 3.85 (s, 3 H), 4.58 (dt, J = 2.3, 7.3 Hz, 1 H), 6.91–6.95 (m, 2 H), 7.28–7.33 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.16 (CH_3), 31.72 (CH_2), 55.22 (CH_3), 75.59 (CH), 113.72 (2CH), 127.16 (2CH), 136.74 (C), 158.94 (C) ppm. MS (EI, 70 eV): m/z (%) = 166 (10) $[M]^+$, 148 (28), 147 (16), 137 (100), 109 (22), 94 (17), 77 (22).

1-(4-Fluorophenyl)propan-1-ol (2e):[16] Compound **1e** (186 mg, 1.50 mmol) was converted for 6 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.47), **2e** was obtained as a colorless oil (215 mg, 1.39 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.4 Hz, 3 H), 1.57–1.76 (m, 2 H), 2.00 (br. s, 1 H), 4.48 (t, J = 6.6 Hz, 1 H), 6.91–6.98 (m, 2 H), 7.18–7.24 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.17 (CH_3), 31.09 (CH_2), 75.45 (CH), 115.28 (d, $^2J_{C,F}$ = 21.3 Hz, 2CH), 127.70 (d, $^3J_{C,F}$ = 7.9 Hz, 2CH), 140.39 (d, $^4J_{C,F}$ = 3.0 Hz, C), 163.75 (d, $^1J_{C,F}$ = 245.2 Hz, C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.0 ppm. MS (EI, 70 eV): m/z (%) = 154 (6) $[M]^+$, 125 (100), 97 (46), 95 (14), 77 (14).

1-(4-Chlorophenyl)propan-1-ol (2f):[16] Compound **1f** (210 mg, 1.49 mmol) was converted for 6 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.66), **2f** was obtained as a colorless oil (245 mg, 1.44 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.4 Hz, 3 H), 1.54–1.81 (m, 2 H), 1.84–1.88 (m, 1 H), 1.86 (br. s, 1 H), 4.50 (dt, J = 3.3, 6.4 Hz, 1 H), 7.17–7.21 (m, 2 H), 7.22–7.27 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.90 (CH_3), 31.86 (CH_2), 75.20 (CH), 127.26 (2CH), 128.43 (2CH), 132.99 (C), 142.91 (C) ppm. MS (EI, 70 eV): m/z (%) = 170 (10) $[M]^+$, 143 (34), 142 (10), 141 (100), 139 (12), 117 (15), 115 (17), 113 (16), 77 (56), 51 (10), 32 (43) ppm.

1-(4-Bromophenyl)propan-1-ol (2g):[17] Compound **1g** (277 mg, 1.50 mmol) was converted for 6 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.77), **2g** was obtained as a colorless oil (296 mg, 1.38 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.4 Hz, 3 H), 1.62–1.87 (m, 2 H), 1.98 (br. s, 1 H), 4.56 (t, J = 6.6 Hz, 1 H), 7.18–7.23 (m, 2 H), 7.43–7.49 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.94 (CH_3), 31.87 (CH_2), 75.26 (CH), 121.13 (C), 127.67 (CH), 131.41 (CH), 143.47 (C) ppm. MS (EI, 70 eV): m/z (%) = 216 (11) $[MH]^+$, 214 (10), 187 (94), 185 (100), 159 (15), 157 (20), 78 (29), 77 (58), 51 (10).

1-(2-Chlorophenyl)propan-1-ol (2h):[16] Compound **1h** (210 mg, 1.49 mmol) was converted for 6 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.55), **2h** was obtained as a colorless oil (223 mg, 1.31 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.4 Hz, 3 H), 1.55–1.83 (m, 2 H), 2.02 (br. s, 1 H), 4.95–5.05 (m, 1 H), 7.08–7.14 (m, 1 H), 7.18–7.33 (m, 2 H), 7.43–7.54 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.99 (CH_3), 30.40 (CH_2), 71.89 (CH), 126.95 (CH), 127.08 (CH), 128.28 (CH), 129.29 (CH), 131.90 (C), 141.92

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(C) ppm. MS (EI, 70 eV): *m/z* (%) = 170 (7) $[M]^+$, 143 (34), 142 (9), 141 (100), 113 (15), 77 (52), 51 (9).

1-(3-Chlorophenyl)propan-1-ol (2i):[16] Compound **1i** (210 mg, 1.49 mmol) was converted for 12 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.48), **2i** was obtained as a yellow oil (231 mg, 1.35 mmol, 91%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.4 Hz, 3 H), 1.65–1.88 (m, 2 H), 2.01 (br. s, 1 H), 4.58 (t, J = 6.5 Hz, 1 H), 7.18–7.31 (m, 3 H), 7.33–7.36 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.92 (CH_3), 31.86 (CH_2), 75.26 (CH), 124.07 (CH), 126.09 (CH), 127.51 (CH), 129.61 (CH), 134.23 (C), 146.59 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 170 (12) $[M]^+$, 143 (33), 142 (8), 141 (100), 115 (15), 113 (14), 77 (66), 51 (8).

2,4-Di-*tert*-butyl-6-(1-hydroxypropyl)phenol (2j):[18] Compound **1j** (351 mg, 1.50 mmol) was converted for 48 h according to the general procedure (note: 10 mol-% NaI/15-crown-5 was employed) After chromatography (SiO_2; cyclohexane/EtOAc, 25:1; R_f = 0.86), **2j** was obtained as a colorless oil (396 mg, 1.50 mmol, 99%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.3 Hz, 3 H), 1.30 (s, 9 H), 1.44 (s, 9 H), 1.80–2.04 (m, 2 H), 2.44 (d, J = 2.3 Hz, 1 H), 4.69–4.74 (m, 1 H), 6.81 (d, J = 2.4 Hz, 1 H), 7.25 (d, J = 2.4 Hz, 1 H), 8.19 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.54 (CH_3), 29.69 (CH_2), 29.70 ($3CH_3$), 31.62 ($3CH_3$), 34.16 (CH), 35.06 (C), 79.08 (CH), 122.11 (CH), 123.27 (CH), 126.30 (C), 136.74 (C), 140.94 (C), 152.46 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 246 (21) $[M - H_2O]^+$, 232 (18), 231 (100).

1-(Naphthalen-1-yl)propan-1-ol (2k):[16] Compound **1k** (234 mg, 1.50 mmol) was converted for 12 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 25:1; R_f = 0.71), **2k** was obtained as a yellow oil (275 mg, 1.48 mmol, 99%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, J = 7.4 Hz, 3 H), 1.85–2.11 (m, 3 H), 5.39 (dd, J = 5.1, 7.5 Hz, 1 H), 7.44–7.57 (m, 3 H), 7.61–7.68 (m, 1 H), 7.77–7.84 (m, 1 H), 7.86–7.93 (m, 1 H), 8.09–8.18 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.47 (CH_3), 31.02 (CH_2), 72.52 (CH), 122.84 (CH), 123.18 (CH), 125.34 (CH), 125.42 (CH), 125.85 (CH), 127.81 (CH), 128.82 (CH), 130.44 (C), 133.75 (C), 140.16 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 186 (29) $[M]^+$, 168 (12), 158 (12), 157 (100), 153 (24), 152 (12), 130 (11), 129 (99), 128 (55), 127 (32).

1-(2,4-Dimethoxyphenyl)propan-1-ol (2l):[19] Compound **1l** (249 mg, 1.50 mmol) was converted for 24 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 10:1; R_f = 0.38), **2l** was obtained as a colorless oil (277 mg, 1.41 mmol, 94%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.4 Hz, 3 H), 1.74–1.87 (m, 2 H), 2.44–2.50 (m, 1 H), 3.80 (s, 3 H), 3.82 (s, 3 H), 4.72 (q, J = 6.0 Hz, 1 H), 6.44–6.47 (m, 1 H), 6.47–6.49 (m, 1 H), 7.17–7.21 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.53 (CH_3), 30.11 (CH_2), 55.25 (CH_3), 55.33 (CH_3), 72.02 (CH), 98.64 (CH), 103.95 (CH), 124.91 (C), 127.63 (CH), 157.73 (C), 159.95 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 196 (5) $[M]^+$, 178 (11), 168 (10), 167 (100), 151 (14), 137 (18).

1-(Pyridin-2-yl)propan-1-ol (4aa):[20] Compound **3aa** (160 mg, 1.49 mmol) was converted for 90 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.68), **4aa** was obtained as a pale-yellow oil (126 mg, 0.92 mmol, 62%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.5 Hz, 3 H), 1.56–1.72 (m, 1 H), 1.74–1.89 (m, 1 H), 4.23 (br. s, 1 H), 4.62 (dd, J = 6.9, 4.8 Hz, 1 H), 7.08–7.15 (m, 1 H), 7.16–7.21 (m, 1 H), 7.56–7.65 (m, 1 H), 8.44–8.49 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.36 (CH_3), 31.28 (CH_2), 73.72 (CH), 120.34 (CH), 122.16 (CH), 136.54 (CH), 148.09 (CH), 161.96 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 137 (12) $[M]^+$, 120 (14), 109 (77), 108 (100), 106 (12), 80 (21), 79 (20), 78 (36), 53 (12), 52 (14), 51 (11).

1-(Furan-2-yl)propan-1-ol (4ab):[16] Compound **3ab** (144 mg, 1.50 mmol) was converted for 90 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.68), **3ab** was obtained as a pale-yellow oil (141 mg, 1.12 mmol, 75%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.5 Hz, 3 H), 1.76–1.96 (m, 2 H), 2.04 (br. s, 1 H), 4.59 (t, J = 6.6 Hz, 1 H), 6.21–6.24 (m, 1 H), 6.31–6.34 (m, 1 H), 7.35–7.38 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.89 (CH_3), 28.55 (CH_2), 69.15 (CH), 105.85 (CH), 110.04 (CH), 141.84 (CH), 156.61 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 126 (15) $[M]^+$, 97 (100), 69 (12), 41 (18), 39 (12) ppm.

1-(Thien-2-yl)propan-1-ol (2ac):[19] Compound **4ac** (168 mg, 2.50 mmol) was converted for 48 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 20:1; R_f = 0.68), **4ac** was obtained as a colorless oil (168 mg, 1.18 mmol, 79%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.5 Hz, 3 H), 1.68–1.90 (m, 2 H), 2.12 (br. s, 1 H), 4.74 (t, J = 6.6 Hz, 1 H), 6.86–6.91 (m, 2 H), 7.14–7.18 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.09 (CH_3), 32.14 (CH_2), 71.66 (CH), 123.71 (CH), 124.40 (CH), 126.50 (CH), 148.55 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 142 (16) $[M]^+$, 113 (100), 85 (50), 45 (11).

Nonan-3-ol (4ba):[19] Compound **3ba** (171 mg, 1.50 mmol) was converted for 24 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 25:1; R_f = 0.86), **4ba** was obtained as a colorless oil (164 mg, 1.14 mmol, 76%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.3 Hz, 3 H), 0.92 (t, J = 7.5 Hz, 3 H), 1.22–1.34 (m, 8 H), 1.34–1.56 (m, 4 H), 3.47–3.54 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.82 (CH_3), 14.02 (CH_3), 22.58 (CH_2), 25.59 (CH_2), 29.35 (CH_2), 30.09 (CH_2), 31.81 (CH_2), 36.93 (CH_2), 73.26 (CH) ppm. MS (EI, 70 eV): *m/z* (%) = 144 (10) $[M]^+$, 115 (30), 97 (72), 69 (18), 59 (100), 58 (11), 57 (16), 55 (73), 43 (22), 41 (30), 31 (14), 29 (16).

1-Phenyl-3-pentanol (4bb):[16] Compound **3bb** (134 mg, 1.00 mmol) was converted for 48 h according to the general procedure After chromatography (SiO_2; cyclohexane/EtOAc, 2:1; R_f = 0.41), **4bb** was obtained as a colorless oil (116 mg, 0.71 mmol, 71%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00–1.07 (m, 3 H), 1.47–1.71 (m, 2 H), 1.75–1.91 (m, 3 H), 2.69–2.81 (m, 1 H), 2.83–2.95 (m, 1 H), 3.57–3.70 (m, 1 H), 7.23–7.43 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.78 (CH_3), 30.16 (CH_2), 31.98 (CH_2), 38.48 (CH_2), 72.50 (CH), 125.68 (CH), 128.29 (2CH), 128.33 (2CH) ppm. MS (EI, 70 eV): *m/z* (%) = 164 (4) $[M]^+$, 146 (43), 117 (65), 104 (33), 91 (100), 78 (15), 65 (13), 59 (12), 51 (6).

2,6-Dimethyldec-2-ene-8-ol (4bc):[21] Compound **3bc** (154 mg, 1.00 mmol) was converted for 48 h according to the general procedure. After chromatography (SiO_2; cyclohexane/EtOAc, 10:1; R_f = 0.55), **4bc** was obtained as a colorless oil (117 mg, 0.63 mmol, 63%, 1:1 mixture of diastereoisomers). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (dd, J = 5.9, 6.5 Hz, 3 H), 0.93 (t, J = 7.5 Hz, 3 H), 1.06–1.55 (m, 7 H), 1.60 (s, 3 H), 1.67 (s, 3 H), 1.90–2.07 (m, 2 H), 3.57–3.66 (m, 1 H), 5.12–5.06 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.74 (CH_3), 9.91 (CH_3), 17.60 (CH_3), 19.10 (CH_3), 20.29 (CH_3), 25.31 (CH_2), 25.45 (CH_2), 25.67 (CH_3), 28.85 (CH), 28.23 (CH), 30.33 (CH_2), 30.99 (CH_2), 36.61 (CH_2), 37.94 (CH_2), 44.39 (CH_2), 44.59 (CH_2), 70.88 (CH), 71.20 (CH), 124.75 (CH), 131.12 (C), 131.17 (C) ppm. MS (EI, 70 eV): *m/z* (%) = 184 (2), 155 (15), 137 (9), 123 (20), 109 (58), 99 (70), 95 (62), 82 (100), 69 (71), 67 (47), 59 (29), 55 (47).

X-ray Absorption Measurements: XAS measurements were performed at beamline X1 at the Hamburger Synchrotron Strahlungs-

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labor (HASYLAB) under ambient conditions at 293 K. A Si(111) double crystal monochromator was used for measurements at the Zn *K*-edge (9.659 keV). The second monochromator crystal was tilted for optimal harmonic rejection. The spectra were recorded in transmission mode with ionization chambers filled with nitrogen. The individual pressures were adjusted to optimize the signal-to-noise ratio. Energy calibration was performed with a zinc metal foil, which was measured simultaneously with the samples between the second and third ionization chamber. To avoid errors in the XANES region due to small changes in the energy calibration between two measurements, all spectra were calibrated to the edge position of the zinc foil. The liquid samples were measured in a specially designed transmission sample cell for air- and moisture-sensitive samples, which was equipped with tabs to be connected to a Schlenk line. The cell could be evacuated under elevated temperature and flushed with argon prior to the measurements. Air-sensitive samples could be added by using a syringe under inert conditions. Operando studies were carried out with a set-up described previously.[22]

Data evaluation started with background absorption removal from the experimental absorption spectrum by subtracting a Victoreen-type polynomial. Due to several inflection points in the absorption edge, the threshold energy E_0 was determined consistently by taking the energy at half the edge jump;[23] for copper metal, this procedure causes a shift of the energy scale in comparison with the most published data by around 5 eV. All spectra were corrected in a consistent way so this shift does not lead to misinterpretations. To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used; it was adjusted in such a way that the low-R components of the resulting Fourier transform were minimal. After division of the background-subtracted spectrum by its smooth part, the photon energy was converted into photoelectron wave numbers k. The resulting $\chi(k)$-function was weighted with k^3 and Fourier transformed using a Hanning window function. Data analysis was performed in k-space with Fourier filtered data. The filtered range was chosen according to the range of significant data and is given in Table 5 together with the results of the fitting procedure. Adjustment of the common theoretical EXAFS expression

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} S_0^2(k) F_j(k) e^{-2k^2\sigma_j^2} e^{-2r_j/\lambda} \sin\left[2kr_j + \delta_j(k)\right] \quad (1)$$

(N_j: one type of neighbor atoms j in a shell, r_j: distance of atoms j from the X-ray absorbing atom, S_0^2: amplitude reduction factor, F_j: backscattering amplitude, σ^2: Debye-Waller like factor, δ_j : overall phaseshift) according to the curved wave formalism of the EXCURV98 program with XALPHA phase and amplitude functions.[24] The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI set to –4.00 eV). An inner potential correction E_f was introduced when fitting experimental data with theoretical models that accounts for an overall phase shift between the experimental and calculated spectra.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra.

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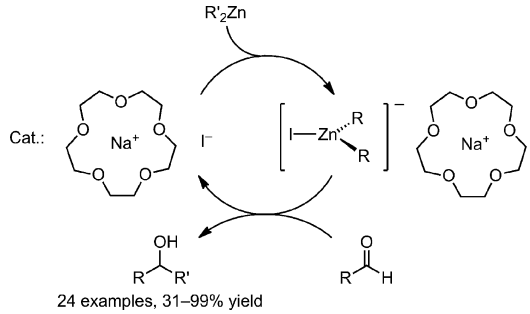

Sodium salts in combination with crown ethers efficiently activate diorganozinc. Catalytic amounts of sodium iodide and 15-crown-5 promote the conversion of various aldehydes. Efforts to apply EXAFS techniques to verify the mode of activation are described.

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