Notes

Generation of Versatile Reagents Derived from R_2Zn and a Vanadium(III) or a Vanadium(IV) Complex and Their Application to Organic Synthesis

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Although it is known that dialkylzinc reagents, R_2Zn, are generally inert to carbonyl compounds, addition of a catalytic amount of an amino alcohol[1] or certain transition metal complexes[2] can enhance their nucleophilicity and make them reactive toward carbonyl compounds. It is reported that R_2Zn can reduce vanadium(IV) complexes and produce low-valent vanadium(II) species,[3] but application of the latter to organic synthesis has not appeared so far. During the course of our study to examine the reactivity of the combination of R_2Zn and several vanadium complexes, we have found that reagents derived from R_2Zn and VCl_4 or $VCl_3(thf)_3$ showed different reactivity toward carbonyl compounds depending on the reaction conditions for preparation of the reagents. We describe here three types of organic reactions using a $R_2Zn-VCl_4$ or a $R_2Zn-VCl_3(thf)_3$ system: (i) the alkylation of carbonyl compounds, (ii) the pinacol-coupling reaction, and (iii) the deoxygenative coupling reaction of carbonyl compounds (Scheme 1).

Scheme 1. $R_2Zn-VCl_4$ or $VCl_3(thf)_3$ System in THF

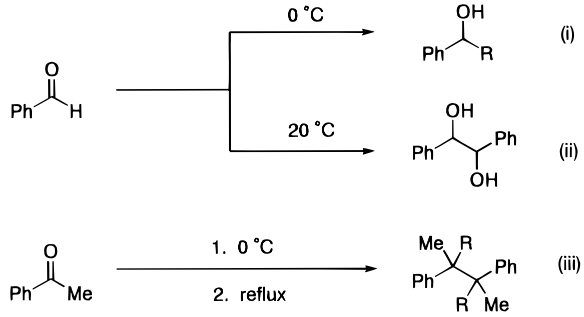
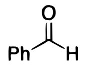
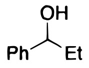
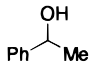
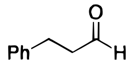
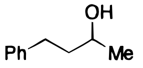
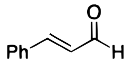
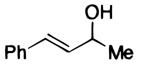
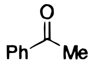
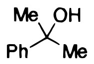
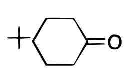
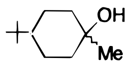
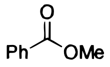


Table 1. Alkylation of Several Carbonyl Compounds Mediated by R_2Zn and VCl_4 or $VCl_3(thf)_3$[a]

run	carbonyl compound	vanadium compound	alkylzinc	product	yield (%)[b]
1		VCl_4	Et_2Zn	 **1a**	97
2		$VCl_3(thf)_3$	Et_2Zn		94
3		VCl_4	Me_2Zn	 **1b**	99
4		$VCl_3(thf)_3$	Me_2Zn		91
5		VCl_4	Me_2Zn	 **1c**	82
6		VCl_4	Me_2Zn	 **1d**	88
7		VCl_4	Me_2Zn	 **1e**	81[c]
8		$VCl_3(thf)_3$	Me_2Zn		80[c]
9		VCl_4	Et_2Zn	n. r.[d]	
10		$VCl_3(thf)_3$	Et_2Zn	n. r.[d]	
11		VCl_4	Me_2Zn	 **1f**	78[e,f]
12		$VCl_3(thf)_3$	Me_2Zn		98[e,g]
13		VCl_4	Me_2Zn	n. r.[h]	
14		$VCl_3(thf)_3$	Me_2Zn	n. r.[h]	

[a] Carbonyl compound (1.0 equiv) was treated with R_2Zn (1.0 equiv) in the presence of VCl_4 or $VCl_3(thf)_3$ (1.0 equiv) in THF at 0 °C for 5 h. [b] Isolated yield. [c] The reaction was conducted at 20 °C for 10 h. [d] No reaction. The reaction was conducted at 20 °C for 10 h. [e] The reaction was conducted at 20 °C for 12 h. [f] Axial alcohol:equatorial alcohol = 73:27. [g] Axial alcohol:equatorial alcohol = 73:27. [h] No reaction. The reaction was conducted at 20 °C for 12 h.

Representative results of the alkylation of several carbonyl compounds using R_2Zn and VCl_4 or $VCl_3(thf)_3$ are shown in Table 1. A mixture of VCl_4 (1.0 equiv) and Et_2Zn (1.0 equiv) in THF was stirred at −78 °C for 1 h under Ar, and then to the reaction mixture was added a solution of benzaldehyde (1.0 equiv) in THF at the same temperature. The reaction temperature was raised gradually to 0 °C. At about −20 °C, the reaction mixture changed from a red-purple suspension to a purple solution. After the resulting mixture was stirred at 0 °C for 5 h, 1-phenylpropanol (**1a**) was obtained in 97% isolated yield (Table 1, run 1). In this reaction, if only 1/3 equiv of VCl_4 per 1 equiv of $ZnEt_2$ was employed the yield of **1a** decreased to 8% and 72% of benzaldehyde was recovered. Thus, the system needs a stoichiometric amount of V(IV). When $VCl_3(thf)_3$[4] was employed instead of VCl_4, the addition of an ethyl group also proceeded to give **1a** in 94% isolated yield (Table 1, run 2). When a vanadium(II) complex such as $VCl_2(tmeda)_2$[5] or [V_2-

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(1) (a) Noyori, R. *Asymmetric Catalysis In Organic Synthesis*; John Wiley & Sons: New York, 1994; Chapter 5. (b) Noyori, R.; Suga, S.; Kawai, K.; Okada, S.; Kitamura, M.; Oguni, N.; Hayashi, M.; Kaneko, T.; Matsuda, Y. *J. Organomet. Chem.* **1990**, *382*, 19−37. (c) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49−69. (d) Soai, K.; Niwa, S. *Chem. Rev. (Washington, D.C.)* **1992**, *92*, 833−856.

(2) (a) Oguni, N.; Omi, T.; Yamamoto, Y.; Nakamura, A. *Chem. Lett.* **1983**, 841−842. (b) Yoshioka, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 1657−1660. (c) Takahashi, H.; Kawakita, T.; Yoshioka, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 7095−7098. (d) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 99−101.

(3) (a) Jacob, V. K.; Wagner, S.; Schumann, W.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1976**, *427*, 75−84. (b) Folting, K.; Huffmman, J. C.; Bansemer, R. L.; Caulton, K. G.; Martin, J. L.; Smith, P. D. *Inorg. Chem.* **1984**, *23*, 4589−4592. (c) Smith, P. D.; Martin, J. L.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G. *Inorg. Chem.* **1985**, *24*, 2997−3002.

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(5) Edema, J. J. H.; Stauthamer, W.; van Bolhuis, F.; Gambarotta, S.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1990**, *29*, 1302−1306.

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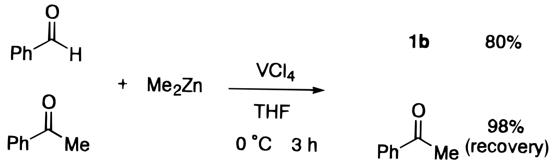
$Cl_3(thf)_6]_2[Zn_2Cl_6]$[6] was used, however, the pinacol coupling of benzaldehyde occurred predominantly and **1a** was not obtained at all. Since the presence of the vanadium(II) species in the reaction mixture immediately induces the pinacol coupling of an aldehyde,[7] the combination of Et_2Zn and VCl_4 or $VCl_3(thf)_3$ probably does not afford a vanadium(II) species but provides some higher-valent vanadium species. It may be of interest to know whether only one or both Et groups of Et_2Zn add to carbonyls in these reactions. Thus, we examined the reaction using 2 equiv of benzaldehyde in the reaction of run 1 (Table 1). Although during 5 h of reaction at 0 °C only 40% of **1a** besides 38% of the unreacted benzaldehyde was obtained, after 24 h of reaction 36% of **1a** and 30% of propiophenone were obtained accompanied by 8% of the starting benzaldehyde and 27% of benzyl alcohol; in the latter reaction about 1.3 equiv of Et groups have been transferred.[8] This indicates that one of the two ethyl groups was transferred easily to carbonyls but the transfer of the second ethyl group proceeds only slowly, though both ethyl groups can add to carbonyl groups.

It is known that Me_2Zn shows extremely low reactivity toward a carbonyl compound compared to Et_2Zn when combined with an amino alcohol.[1] Me_2Zn, combined with a vanadium(III) or a vanadium(IV) compound, however, was also sufficiently effective for the methylation of benzaldehyde. Reaction of Me_2Zn with benzaldehyde in the presence of VCl_4 afforded 1-phenylethan-1-ol (**1b**) quantitatively under similar conditions to those applied to the system, $Et_2Zn-VCl_4$ (Table 1, run 3). Employing $VCl_3(thf)_3$, **1b** was also obtained in 91% yield (Table 1, run 4).

An aliphatic aldehyde was also treated with $Me_2Zn-VCl_4$ to afford the corresponding methylated alcohol (Table 1, run 5). In the reaction of an α,β-unsaturated aldehyde, the 1,2-addition proceeded exclusively (Table 1, run 6). Although it is reported that an alkylzinc activated by an amino alcohol did not react with ketones,[1] two ketones were transformed to the corresponding alcohols by using $Me_2Zn-VCl_4$ (Table 1, runs 7, 8, 11, and 12). To obtain a satisfactory yield, a prolonged reaction time and a little higher temperature (20 °C) were needed. In contrast to the reactivity of alkylzinc reagents activated by amino alcohols, the activity of the $Me_2Zn-VCl_4$ or $VCl_3(thf)_3$ system was much higher than that of the Et_2Zn system. Alkylation of acetophenone using Et_2Zn instead of Me_2Zn did not proceed at all, and acetophenone was recovered (Table 1, runs 9 and 10). Methylation of 4-*tert*-butylcyclohexanone using the $Me_2Zn-VCl_4$ system resulted in the preferential formation of the axial alcohol (axial alcohol:equatorial alcohol = 73:27) (Table 1, run 11). The selectivity did not change by using $VCl_3(thf)_3$ instead of VCl_4 (Table 1, run 12) and is similar to that of methylation with MeLi (axial alcohol: equatorial alcohol = 79:21).[10] The methylation of an ester (methyl benzoate) using the $ZnEt_2-VCl_4$ or $VCl_3(thf)_3$ was not successful, and the ester was recovered quantitatively (Table 1, runs 13 and 14).

In the methylation of carbonyl compounds using the $Me_2Zn-VCl_4$ system, the consumption of aldehyde was much faster than that of ketone. Thus, a competitive reaction between an aldehyde and a ketone was examined. When a mixture of benzaldehyde (1.0 equiv) and acetophenone (1.0 equiv) was reacted with Me_2Zn (1.0 equiv) in the presence of VCl_4 (1.0 equiv) in THF at 0 °C, only the methylation of benzaldehyde proceeded and the alcohol **1b** was obtained in 80% yield along with unreacted acetophenone in 98% yield (eq 1).



(1)

In the methylation of acetophenone with the Me_2Zn/V system, we have also examined whether both of the methyl substituents can add to the carbonyl or not. Thus, 2 equiv of acetophenone was treated in THF at ambient temperature with a methylating reagent prepared from 1 equiv of Me_2Zn and 1 equiv of $VCl_3(thf)_3$. After 38 h of reaction, 34% of the alcohol **1b** accompanied with 14% of a coupling product, 2,2-dimethyl-2,2-diphenylbutane (**3**) (*vide infra*), was obtained. The remaining 37% of acetophenone was unreacted. This indicates that only 0.96 equiv of the available 2 equiv of methyl groups had been utilized; only one of the two zinc methyls can add to ketone under the reaction conditions. This propensity of the methylating reagent is also responsible for the high chemoselectivity between aldehyde and ketone shown in the above competitive experiment.

Which is the actual reactive species in this alkylation, an alkylzinc reagent or an alkylvanadium reagent? It has been reported that in the alkylation of an aldehyde using $Ti(O^iPr)_4$ and Et_2Zn an ethyltitanium reagent prepared in situ reacts with the aldehyde.[2b,c] Although vanadium is also an early transition metal like titanium, a C−V bond is more unstable compared to a C−Ti bond. Thus, a nucleophilic attack of an alkylvanadium species to carbonyl compounds does not readily occur unless stabilizing additive such as HMPA is present.[11] In our alkylation of carbonyl compounds mediated by a dialkyl-

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(6) (a) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377−1378. (b) Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715−2718. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913−917.

(7) For pinacol-type coupling of carbonyl compounds by vanadium(II) species, see: (a) Freudenberger, J. H.; Konradi, A. W.; Pedersen S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014−8016. (b) Takahara, P. M.; Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *Tetrahedron Lett.* **1989**, *30*, 7177−7180. (c) Konradi, A. W.; Pedersen, S. F. *J. Org. Chem.* **1990**, *55*, 4506−4508. (d) Park, J.; Pedersen, S. F. *J. Org. Chem.* **1990**, *55*, 5924−5926. (e) Annunziata, R.; Cinquini, M.; Cozzi, F.; Giaroni, P. *Tetrahedron Asymmetry* **1990**, *1*, 355−358. (f) Annunziata, R.; Cinquini, M.; Cozzi, F.; Giaroni, P.; Benaglia, M. *Tetrahedron* **1991**, *47*, 5737−5758. (g) Raw, A. S.; Pedersen, S. F. *J. Org. Chem.* **1991**, *56*, 830−833. (h) Kemp, D. J.; Sowin, T. J.; Doherty, E. M.; Hannick, S. M.; Codavoci, L.; Henry, R. F.; Green, B. E.; Spanton, S. G.; Norbeck, D. W. *J. Org. Chem.* **1992**, *57*, 5692−5700. (i) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Giaroni, P. *J. Org. Chem.* **1992**, *57*, 782−784. (j) Konradi, A. W.; Pedersen, S. F. *J. Org. Chem.* **1992**, *57*, 28−32. (k) Park, J.; Pedersen, S. F. *Tetrahedron* **1992**, *48*, 2069−2080. (l) Kraynack, E. A.; Pedersen, S. F. *J. Org. Chem.* **1993**, *58*, 6114−6117. (m) Konradi, A. W.; Kemp, S. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1994**, *116*, 1316−1323. (n) Kammermeier, B.; Beck, G.; Jacobi, D.; Jendralla, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 685−687. (o) Kammermeier, B.; Beck, G.; Holla, W.; Jacobi, D.; Napierski, B.; Jendralla, H. *Chem. Eur. J.* **1996**, *2*, 307−315. (p) Hirao, T.; Hasegawa, T.; Muguruma, Y.; Ikeda, I. *J. Org. Chem.* **1996**, *61*, 366−367.

(8) Formation of propiophenone could be formally explained by a β-hydride elimination from vanadium alcoholate of **1a**[9] liberating a "V−H" species, which may reduce benzaldehyde to give benzyl alcohol. The details of the reaction will be reported separately.

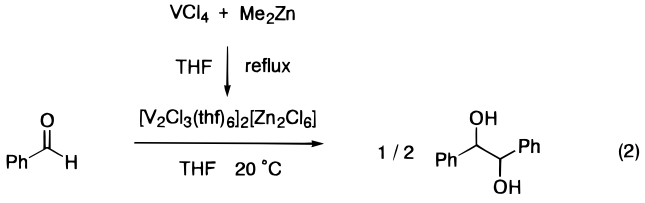
(9) Hirao, T.; Misu, D.; Agawa, T. *J. Am. Chem. Soc.* **1985**, *107*, 7179−7181.

(10) MacDonald, T. L.; Still, W. C. *J. Am. Chem. Soc.* **1975**, *97*, 5280−5281.

(11) Kataoka, Y.; Makihira, I.; Tani, K. *Tetrahedron Lett.* **1996**, *37*, 7083−7086.

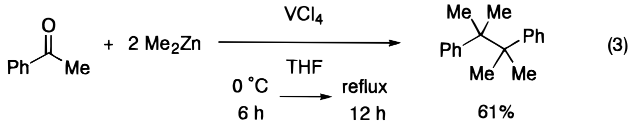
zinc−vanadium system, the reaction of vanadium(III) or -(IV) with R_2Zn should afford an alkylated Zn−V hetero polymetallic complex similar to those reported by Thiele,[3a] which may contain both alkylzinc species and vanadium species. The real alkylating reagent may be the alkylzinc part, and the higher-valent vanadium part may function as an activator of the carbonyl compounds by coordination as a Lewis acid. However, as the reaction requires 1 equiv of vanadium per 1 equiv of alkylzinc (vide supra), cooperation of the zinc and the vanadium parts as a whole in the heteropolymetallic species may play an important role. This cooperative function of the alkylzinc moieties and the higher-valent vanadium species would give a higher reactivity to the $R_2Zn−VCl_4$ or $R_2Zn−VCl_3(thf)_3$ system compared to the R_2Zn−amino alcohol system.

Interestingly, when a reaction similar to that of run 3 in Table 1, i.e., the reaction of benzaldehyde with Me_2Zn in the presence of VCl_4, was conducted at 20 °C, the pinacol coupling product of the aldehyde was obtained in 57% yield besides the alcohol **1b** (32% yield). When the temperature of the reaction mixture was raised to 20 °C before the addition of benzaldehyde, the reaction mixture became a dark-greenish violet suspension. An IR spectrum of the greenish precipitate obtained from the $Me_2Zn−VCl_4$ reaction mixture revealed that $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ was produced.[8] At about 20 °C the alkylated Zn−V heteropolymetallic complex, prepared from VCl_4 and Me_2Zn at 0 °C, should be reduced to some vanadium(II) species by the alkylzinc. These results prompted us to prepare a vanadium(II) species from a vanadium(III) or a vanadium(VI) complex with R_2Zn and to apply it to the pinacol coupling of aldehyde as a typical vanadium(II)-mediated reaction.[7] Experiments to elucidate the reaction of a dialkylzinc and a vanadium complex have demonstrated that a vanadium(II) species was produced quantitatively from VCl_4 and Me_2Zn in THF under reflux conditions. For example, VCl_4 reacted with 1.0 equiv of Me_2Zn in THF at 0 °C for 30 min to give a purple-colored solution. The resulting reaction mixture was refluxed for 1 h, and then a THF solution of benzaldehyde (1.0 equiv) was added at 20 °C to give a pinacol coupling product **2** in 89% isolated yield with high *dl* selectivity (*dl*:*meso* = 97:3) (eq 2).



2 89% (*dl* : *meso* = 97 : 3)

We have recently reported a C−C bond-forming reaction by a deoxygenative radical coupling from ketones, MeMgBr, and a vanadium(II) complex in the presence of a catalytic amount of molecular oxygen.[12] This is a characteristic reaction of a vanadium(II) complex, which is essential for the removal of an oxygen atom from a C−O bond. A combination of VCl_4 and Me_2Zn can also promote this reaction (eq 3). For example, VCl_4 reacted with 2.0 equiv of Me_2Zn in THF at 0 °C for 30 min to give a purple-colored solution. The resulting reaction mixture was reacted with acetophenone (1.0 equiv) at 0 °C for 6 h and then heated under reflux for 12 h to give a reductive coupling product **3** in 61% isolated yield. Although the details of the reaction pathway are not clear at present, a vanadium(II) species should be produced during the reaction because the coupling product cannot be obtained without a vanadium(II) species.[12] If in this reaction $VCl_3(thf)_3$ was employed instead of VCl_4, the coupling product **6** was obtained in 83% yield.



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In conclusion, we have developed a new activation method of dialkylzinc with a tri- or a tetravalent vanadium complex. By using this method, alkylation of carbonyl compounds with dialkylzinc, which generally proceeds only very slowly or not at all without a relevant additive, occurred smoothly. In addition, by controlling reaction conditions, a pinacol coupling reaction or a deoxygenative C−C single bond formation reaction can also proceed by using the same system.

Experimental Section

All manipulations were conducted under argon atmosphere with standard Schlenk methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used after distillation. THF was distilled from sodium benzophenone ketyl under argon prior to use. VCl_4 was obtained from commercial suppliers (Aldrich) and was used as received. $VCl_3(thf)_3$ was prepared according to the published procedure.[4] Column chromatography was conducted by using silica gel 60 (230−400 mesh). The melting points are uncorrected. ^1H NMR spectra were recorded at 270.05 MHz, and chemical shifts are expressed in ppm downfield from Me_4Si using a δ scale ($CHCl_3$ was used as an internal standard δ 7.26).

1-Phenylpropan-1-ol (1a).[13] To a red-purple suspension of VCl_4 (172 mg, 0.89 mmol) in THF (10 mL) was added a hexane solution of Et_2Zn (1.0 mol/L, 0.89 mL, 0.89 mmol) at −78 °C to produce a pink suspension. After the reaction mixture was stirred for 1 h at −78 °C, a THF solution of benzaldehyde (94 mg, 0.89 mmol) was added at the same temperature and then the temperature was raised gradually to 0 °C. The pink suspension changed the color to purple above −20 °C. The resulting purple solution was stirred for 5 h at 0 °C, resulting in a black solution, which was treated with 1 N HCl (30 mL) and then extracted with ether (3 × 10 mL). The combined extracts were washed with H_2O (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to provide an oil. This oil was purified by column chromatography on silica gel (hexane: AcOEt = 2:1) to afford **1a** (117 mg, 97%) as a colorless oil. The alcohol **1a** was obtained in 94% yield when $VCl_3(thf)_3$ was employed instead of VCl_4: ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.4 Hz, 3H), 1.70−1.83 (m, 2H), 2.43 (s, 1H), 4.54 (t, J = 6.7 Hz, 1H), 7.25−7.37 (m, 5H).

1-Phenylethan-1-ol (1b).[14] This compound was prepared similarly from benzaldehyde using VCl_4 and Me_2Zn in 99% yield as a colorless oil. The alcohol **1b** was obtained in 91% yield when $VCl_3(thf)_3$ was employed instead of VCl_4: ^1H NMR ($CDCl_3$) δ 1.43 (d, J = 6.4 Hz, 3H), 2.42 (s, 1H), 4.81 (q, J = 6.4 Hz, 1H), 7.21−7.33 (m, 5H).

4-Phenylbutan-2-ol (1c).[15] This compound was prepared from 3-phenylpropanal, Me_2Zn, and VCl_4 as described for

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[12] Kataoka, Y.; Akiyama, H.; Makihira, I.; Tani, K. *J. Org. Chem.* **1996**, *61*, 6094−6095.

[13] Seebach, D.; Plattner, D. A.; Beck, A. K.; Wang, Y. M.; Hunziker, D.; Petter, W. *Helv. Chim. Acta* **1992**, *75*, 2171−2209.

[14] *Handbook of Proton-NMR Spectra and Data*; Asahi Research Center Co., Ltd., Ed.; Academic Press: New York, 1985.

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compound **1a**: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, $J = 6.2$ Hz, 3H), 1.67−1.79 (m, 2H), 1.98 (s, 1H), 2.58−2.79 (m, 2H), 3.73−3.84 (m, 1H), 7.12−7.29 (m, 5H).

(*E*)-4-Phenylbut-3-en-2-ol (1d).[16] This compound was prepared from 3-phenylprop-2-enal, Me_2Zn, and VCl_4 as described for compound **1a**: ^{1}H NMR ($CDCl_3$) δ 1.37 (d, $J = 6.4$ Hz, 3H), 2.66 (s, 1H), 4.45−4.50 (m, 1H), 6.26 (dd, $J = 15.8$, 6.2 Hz, 1H), 6.56 (d, $J = 15.8$ Hz, 1H), 7.21−7.40 (m, 5H).

2-Phenylpropan-2-ol (1e).[14] This compound was prepared from acetophenone, Me_2Zn, and VCl_4 as described for compound **1a**, except the reaction mixture was stirred for 10 h at 20 °C after addition of acetophenone: ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 6H), 2.28 (s, 1H), 7.17−7.47 (m, 5H).

4-*tert*-Butyl-1-methylcyclohexanol (1f).[17] This compound was prepared from 4-*tert*-butylcyclohexanone, Me_2Zn, and VCl_4 as described for compound **1a**, except the reaction mixture was stirred for 12 h at 20 °C after addition of 4-*tert*-butylcyclohexanone. The ratio of the axial and the equatorial alcohols was determined by GLC (axial alcohol:equatorial alcohol = 73:27). GLC conditions: Simadzu capillary column, CBP1-M25-025; column temperature, 100 °C; retention time, 8.7 min (the axial alcohol), 9.5 min (the equatorial alcohol).

Typical Procedure for the Pinacol Coupling Reaction of Benzaldehyde Using a VCl_4−Me_2Zn System (Eq 2). To a red-purple suspension of VCl_4 (200 mg, 1.0 mmol) in THF (10 mL) was added a hexane solution of Me_2Zn (1.0 mol/L, 1.0 mL, 1.0 mmol) at 0 °C to give a purple suspension. After being stirred for 0.5 h at 0 °C, the reaction mixture was heated under reflux for 1 h. To the resulting black solution containing greenish precipitates was added a THF solution of benzaldehyde (106 mg, 1.0 mmol) at 20 °C. The resulting mixture was stirred for 12 h at 20 °C, to give a brown solution, which was treated with H_2O (20 mL) and then extracted with ether (3 × 10 mL). The combined extracts were washed with H_2O (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to provide an oil. This oil was purified by column chromatography on silica gel (hexane:AcOEt = 2:1) to afford ***dl*- and *meso*-1,2-diphenyl-1,2-ethanediol (2)**[18] (96 mg, 89%) as a colorless solid. ***dl*- and *meso*-2.** The two diastereomers could not be separated and their ratio was determined by ^{1}H NMR analysis (*dl*:*meso* = 97:3): ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 2H), 4.52 (s, 2H, *dl*), 4.65 (s, 2H, *meso*), 6.92−7.16 (m, 10H).

Typical Procedure for the Deoxygenative Coupling Reaction (Eq 3). To a red-purple suspension of VCl_4 (193 mg, 1.0 mmol) in THF (10 mL) was added a hexane solution of Me_2Zn (1.0 mol/L, 2.0 mL, 2.0 mmol) at 0 °C to give a purple suspension. After the reaction mixture was stirred for 0.5 h at 0 °C, a THF solution of acetophenone (120 mg, 1.0 mmol) was added at 0 °C. The resulting purple solution was stirred for 6 h at 0 °C and then heated under reflux for 12 h, resulting in a black solution. After being treated with HCl (0.1 N, 20 mL), the reaction mixture was extracted with ether (20 mL). The combined extracts were washed with H_2O (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to provide an oil. This oil was purified by column chromatography on silica gel (hexane) to afford **2,3-dimethyl-2,3-diphenylbutane (3)** (72 mg, 61%) as a colorless solid. **3**: $R_f = 0.36$ (hexane); mp 115−116 °C; ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 12H), 7.04−7.18 (m, 10H); IR (Nujol) 3089, 3051, 3014, 2954, 2925, 2855, 2723, 1955, 1895, 1814, 1686, 1599, 1577, 1496, 1458, 1443, 1379, 1216, 1148, 1089, 1066, 1030, 1001, 919, 840, 774, 731, 702, 588, 517, 429 cm^{-1}. Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.94; H, 9.46.

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