Stabilizing Effect of HMPA (Hexamethylphosphoric Triamide) on Vanadium−Carbon Bonds and Their Application to Carbon−Carbon Bond Formation Reactions

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Allylation of carbonyl compounds with allyl halides mediated by a vanadium(II) complex in a mixed solvent system of THF and HMPA has been accomplished. The addition of HMPA stabilized a vanadium−carbon bond of an allyl vanadium species and prevented dimerization of allyl halides or pinacol coupling of carbonyl compounds. Other alkylations such as a benzylation of carbonyl compounds or a Reformatsky-type reaction could also be mediated by a low-valent vanadium(II) species and benzyl bromide or bromo acetate in a THF−HMPA solvent system. By isolation of the vanadium−HMPA complex, $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$ (HMPA = hexamethylphosphoric triamide), and clarification of its structure, it became clear that the coordination of bulky HMPA to vanadium centers played an important role in the carbon−carbon bond-forming reactions.

Introduction

Recently, various low-valent early transition metal complexes, which have a strong reducing ability and a high oxophilicity, have been used in the field of organic synthesis.[1] However, low-valent vanadium(II) complexes have scarcely been applied to organic synthesis except in radical reactions induced by one-electron reduction ability of vanadium(II). Though vanadium belongs to group V, it has similar characteristics to other early transition metals.[2−4] For example, both low-valent complexes of titanium and chromium, which belong to the same transition series as vanadium, have been used for the allylation of carbonyl compounds.[5] However, allylation of carbonyl compounds using allyl vanadium species derived from an allyl halide and a low-valent vanadium(II) complex have not been reported so far. One reason is that the vanadium−carbon bond is so reactive that dimerization of the allyl group or β-elimination preferentially takes place.[2h,6] In order to generate a vanadium−carbon bond having an appropriate stability, it is necessary to control the electronic character on the vanadium by selecting or designing a ligand.

Hexamethylphosphoric triamide (HMPA) has a unique property as a polar aprotic solvent and has been used in many reactions.[7] It is known that the addition of HMPA sometimes has dramatic effects on samarium(II)-mediated organic reactions.[8] This may result from the increase of the electron density on the samarium atom

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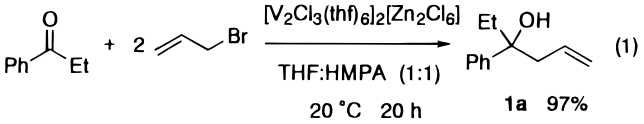
and the enhanced stability of Sm(III) species.[9] In a preliminary report, we have described that the addition of HMPA also had a great influence on the stability and the reactivity of an allyl vanadium species and made it useful for the allylation of carbonyl compounds.[10] We have further investigated the effect of adding HMPA and found that relatively stable organovanadium reagents can be generated from a vanadium(II) complex and several organohalide compounds in a mixed solvent of THF and HMPA and can be used for several anionic reactions such as allylation or benzylation of carbonyl compounds and Reformatsky-type reactions. In addition, we have described the isolation and the X-ray analysis of a new vanadium(II)−HMPA complex, $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$, which can also be applied to these anionic reactions.

Results and Discussion

Allylation of Carbonyl Compounds Mediated by Vanadium(II) Complexes. Allylation of carbonyl compounds mediated by low-valent vanadium complexes proceeds smoothly in the presence of HMPA. For example, the reaction of propiophenone (1.0 equiv) with allyl bromide (2.0 equiv) in the presence of the binuclear vanadium(II) complex, $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.0 equiv; 4.0 equiv as vanadium(II) metal), prepared in advance and purified,[11] in a mixed solvent of THF and HMPA (1:1) at 20 °C for 20 h afforded the homoallyl alcohol **1a** in 97% isolated yield after hydrolysis of the reaction mixture (eq 1). This is the first example of the application of an allyl vanadium reagent, generated *in situ* from a vanadium(II) complex and allyl bromide, in organic synthesis.[12] When only a stoichiometric amount of the allyl vanadium reagent (vanadium(II):allyl bromide: carbonyl compound = 2:1:1) was employed, the reaction did not proceed to completion and the yield of the homoallyl alcohol decreased (75%), accompanied by 14% of the unreacted starting propiophenone. The use of excess allyl vanadium reagent gave better yields. Employing $VCl_2(tmeda)_2$[13] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) as another vanadium(II) source, the homoallyl alcohol **1a** was also obtained in 90% isolated yield. In the absence of HMPA, however, allylation using $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ did not proceed at all and propiophenone was recovered quantitatively, probably partially due to insufficient solubility of the vanadium complex in THF. Although $VCl_2(tmeda)_2$ was soluble in THF, the homoallyl alcohol was obtained in only 19% isolated yield without HMPA and the remaining propiophenone was recovered unchanged. No other product was detected except 1,5-hexadiene, a reductive coupling product of allyl bromide. The allyl vanadium species derived from $VCl_2(tmeda)_2$ and allyl bromide in THF may not be sufficiently stable and decompose to give 1,5-hexadiene prior to the allylation of propiophenone. HMPA could enhance the solubility of a vanadium(II) complex and also stabilize the allyl vanadium species.



(1)

The results of the reaction between allyl halides and carbonyl compounds mediated by vanadium(II) complexes in THF−HMPA are summarized in Table 1. When ketones were employed as the carbonyl compounds, the corresponding homoallyl alcohols were obtained in good yields. Allylation of aldehydes also proceeded, but formation of the pinacol-coupling products induced by the low-valent vanadium(II) complex was not completely avoided. Especially in the allylation of benzaldehyde, the pinacol-coupling product was the main product. In vanadium(II)-mediated allylations, HMPA should play an important role in suppressing the pinacol-coupling reaction.

It is well-established that allylation of carbonyl compounds with crotyl bromide mediated by early transition metal complexes gives γ-substituted products with high regio- and stereoselectivity.[17] In the vanadium(II)-mediated allylation in THF and HMPA, only γ-substituted products were also obtained but the anti-stereoselectivities were not high. For example, when decanal was used as a carbonyl compound, the ratio of the syn- to anti-homoallyl alcohol was 21:79 (run 9) and the allylation of a more bulky aldehyde, 2,2-dimethylpropanal, afforded almost equal amounts of both of the isomeric homoallyl alcohols (run 13). These results can be explained as follows: an allyl vanadium species is produced in the reaction mixture and then reacts with carbonyl compounds *via* a six-membered transition state to produce γ-substituted products. Coordination of bulky HMPA to vanadium or a bulky substituent of aldehyde impedes the chair-form transition state, thus anti-selectivity significantly decreases. The result is similar to that of allylation mediated by low-valent chromium complexes in DMF or using a bulky aldehyde.[17b] Allylation of 4-*tert*-butylcyclohexanone afforded a mixture of the axial and equatorial alcohol in 85% isolated yield, but the isomeric selectivity was not high (axial alcohol:equatorial alcohol = 48:52, run 14).

The binuclear vanadium(II) complex, $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, showed higher activity toward the allylation than $VCl_2(tmeda)_2$. Although the difference in activity between $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ and $VCl_2(tmeda)_2$ was not observed for the allylation using allyl bromide (run 1 vs 2), the yield of homoallyl alcohol derived from the

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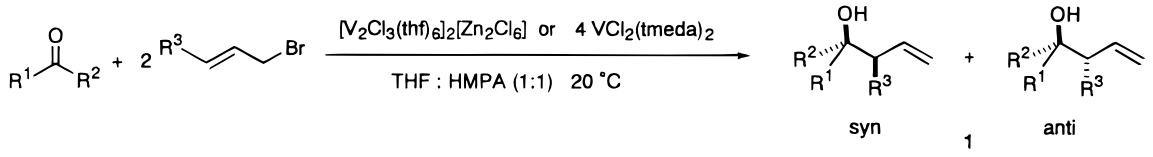
Table 1. Allylations of Carbonyl Compounds Mediated by Vanadium(II) Complexes in THF−HMPA[a]



run	R^1R^2CO R^1	R^2	allyl halide R^3	vanadium	time (h)	products	yield (%)[b]	syn/anti[c]	pinacol coupling products (%)
1	Ph	Et	H	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	20	**1a**	97		0
2	Ph	Et	H	$VCl_2(tmeda)_2$	20	**1a**	90		0
3	Ph	Et	Me	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	20	**1b**	86	39/61[d]	0
4	Ph	Et	Me	$VCl_2(tmeda)_2$	20	**1b**	16	41/59[d]	0
5	$PhCH_2CH_2$	Me	H	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	3	**1c**	97		0
6	$PhCH_2CH_2$	Me	Me	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	3	**1d**	89	(49/51)[e]	0
7	$PhCH_2CH_2$	H	H	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	3	**1e**	64		13
8	$CH_3(CH_2)_8$	H	H	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	1	**1f**	75		22
9	$CH_3(CH_2)_8$	H	Me	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	1	**1g**	80	21/79[f]	19
10	Ph	H	H	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	0.5	**1h**	20		79
11	Ph	H	Me	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	0.5	**1i**	32	26/74[f]	62
12	^{t}Bu	H	H	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	1	**1j**	74		0
13	^{t}Bu	H	Me	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	1	**1k**	73	47/53[f]	0
14	$-CH_2CH_2CH(^tBu)CH_2CH_2-$		H	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	6	**1l**	85	48/52[g]	0

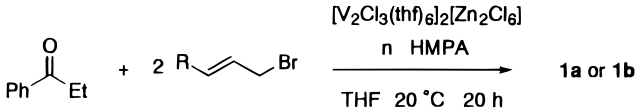
[a] Carbonyl compound (1 equiv) and allyl halide (2 equiv) were added to a solution of vanadium(II) (4 equiv) in THF and HMPA (1:1). [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] Reference 14. [e] Which is syn or anti was not defined. [f] Reference 15. [g] The ratio of axial alcohol and equatorial alcohol, see ref 16.

less reactive crotyl bromide was drastically decreased in the $VCl_2(tmeda)_2$-mediated reaction (run 3 vs 4). One reason is that TMEDA might reduce the Lewis acidity of the vanadium complex which is necessary for activation of the carbonyl compounds. The binuclear vanadium(II) complex salt, $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, dissolves in THF−HMPA to produce a "zinc species" (*vide infra*) which might act as a Lewis acid in the reaction mixture. The allyl vanadium species may then react with an electronically activated carbonyl compound to afford the homoallyl alcohol more efficiently.[18]

The best solvent system of those examined so far for the vanadium-mediated allylation is a combination of THF and HMPA. The allylation of propiophenone in pure HMPA also gave the alcohol **1a** in 97% isolated yield, but the reaction mixture became a muddy suspension which was hard to handle. When dichloromethane or DMF was used as a solvent, in which $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ is soluble, the allylation of propiophenone scarcely proceeded and the starting ketone was recovered quantitatively. Ureas such as 1,3-dimethyl-2-imidazolidinone (DMI) have been used as alternatives to HMPA.[19] $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ is also soluble in DMI. The allylation of propiophenone with the allyl vanadium species in DMI gave **1a** in 95% yield, which is a result similar to that in a HMPA-THF solvent system. However, when crotyl bromide was used instead of allyl bromide, the reactivity decreased. The homoallyl alcohol **1b** was obtained in 78% yield with a similar diastereoselectivity (syn:anti = 36:64).

The vanadium-mediated allylation is influenced by the amount of HMPA (Table 2). In this allylation, HMPA was generally employed as a co-solvent (10 mL,

Table 2. Influence of the Amount of HMPA on Vanadium-Mediated Allylations[a]



run	equiv of HMPA	R	yield (%)[b]	syn/anti[c]	recovery of propiophenone (%)
1	8	H	58		35
2[d]	8	H	57		38
3	12	H	82		10
4	14	H	93		4
5	16	H	97		0
6	57	H	97		0
7	8	Me	23	50/50	74
8	12	Me	46	44/56	52
9	14	Me	52	43/57	44
10	16	Me	67	42/58	33
11	24	Me	75	41/59	20
12	57	Me	86	39/61	0

[a] Propiophenone (1.0 equiv), allyl bromide (2.0 equiv), and $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.0 equiv) were employed. [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] The reaction time was extended to 50 h.

ca. 57 equiv per 1 equiv of a carbonyl compound, ca. 14 equiv per vanadium metal, run 6). When the amount of HMPA was reduced to 2.0 equiv per vanadium metal ($n = 8$ in a $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6] - n$HMPA system, run 1), the homoallyl alcohol **1a** was obtained in only 58% isolated yield and propiophenone was recovered in 35% isolated yield. Even if the reaction time was prolonged to 50 h, the yield of **1a** did not change (run 2). After 20 h, the allyl vanadium species in the reaction mixture was completely consumed. The yield of the homoallyl alcohol was improved gradually with increasing the amount of HMPA. When more than 4.0 equiv of HMPA per 1.0 equiv of vanadium ($n = 16$, run 4) was added, the homoallyl alcohol was obtained quantitatively. In the allylation of propiophenone with crotyl bromide, however, addition of 4.0 equiv of HMPA was not sufficient. In order to get the homoallyl alcohol **1b**

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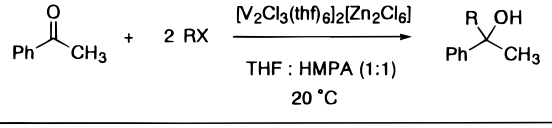
Table 3. Reaction of Various Alkyl Halides with Acetophenone Mediated by $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$[a]



run	RX	time/h	yield/%[b]	
1	$BrCH_2COOCH_3$	2	66	(2)
2		1	86[c]	(3)
3	$PhCH_2Br$	1	86	(4)
4	MeI	48	0[d]	
5	PhI	48	0[d]	

[a] Acetophenone (1.0 equiv) and RX (2.0 equiv) were added to a solution of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.0 equiv) in THF and HMPA (1:1). [b] Isolated yield. [c] Allenyl alcohol was obtained in 6% yield. [d] Acetophenone was recovered in 47% yield, and the pinacol coupling product of acetophenone was obtained in 29% yield. [e] Acetophenone was recovered in 12% yield, and the pinacol coupling product of acetophenone was obtained in 83% yield.

quantitatively, a large excess of HMPA had to be added to the reaction mixture.

The role of the added HMPA in the vanadium-mediated allylation can be explained as follows: Coordination of HMPA to vanadium may stabilize an allyl vanadium species and suppress its reductive decomposition to give biallyl compounds. The reactivity of the allyl vanadium species toward a carbonyl compound increased, and thus, the homoallyl alcohol was obtained in good yields.

Other Alkylations of Carbonyl Compounds Mediated by Vanadium(II) Complexes. Next, we examined the scope and limitation of the present allylation of carbonyl compounds. We found that not only allylations but also Reformatsky-type reactions and alkylation of ketones could be mediated by a low-valent alkyl vanadium species generated in a THF−HMPA solvent system. Representative results using acetophenone as a ketone are shown in Table 3. Although a Reformatsky-type reaction can be induced by the reductive influence of low-valent metal species,[20] vanadium(II) complexes such as $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ or $VCl_2(tmeda)_2$ were not effective. Reaction of acetophenone with an α-bromo ester or propargyl bromide in the presence of a vanadium(II) complex in THF−HMPA afforded β-hydroxy ester or homopropargyl alcohol in good yields (run 1 and 2). The reaction conditions tolerate the ester functionality. Although the reaction with benzyl bromide gave the corresponding alcohol in 86% isolated yield (run 3), simple alkyl or aryl halides such as MeI and PhI did not give the corresponding alcohol in the presence of the vanadium(II) complexes and only the pinacol-coupling product was obtained along with the unreacted ketone (run 4 and 5). Interestingly, when PhI was employed as an alkylating reagent, the pinacol-coupling product was obtained in good yield (83%); the pinacol-coupling of acetophenone cannot be promoted by the low-valent vanadium (II) species alone.

(20) Review: (a) Rathke, M. W. *Org. React.* **1975**, *22*, 423−460. (b) Fürstner, A. *Synthesis* **1989**, 571−590.

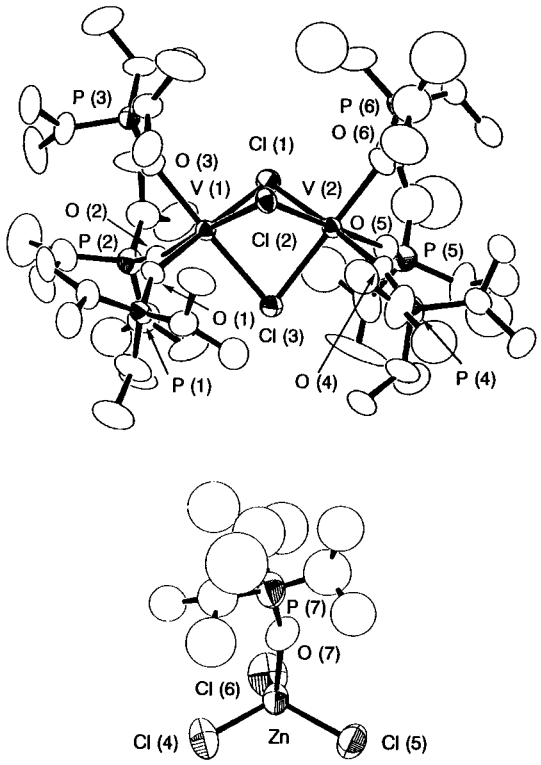


Figure 1. Molecular structure of $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$ **5**: the cationic (top) and the anionic part (bottom).

Preparation, Characterization, and Reactions of a Vanadium(II)−HMPA Complex. In order to investigate the role of HMPA in the vanadium(II)-mediated allylations, isolation of a vanadium(II)−HMPA complex was attempted. Reaction of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ with excess HMPA in THF at 20 °C afforded extremely air-sensitive green crystals of $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$, **5**, in 50% isolated yield after recrystallization from THF−ether (eq 2).

$$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6] + \text{excess HMPA} \xrightarrow[\text{THF, 20 °C}]{} \underset{\mathbf{5}\quad 50\%}{2\,[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]} \qquad (2)$$

Complex **5** was characterized by the usual spectroscopic methods and elemental analysis. The ^{31}P NMR (toluene-d_8, 35 °C) spectrum showed two broad singlets at δ 25.6 ($\Delta\nu_{1/2}$ = 200 Hz) and 129 ($\Delta\nu_{1/2}$ = 870 Hz) in a 6:1 intensity ratio, indicating the presence of two kinds of magnetically inequivalent HMPA groups in the complex. The ^1H NMR (toluene-d_8, 35 °C) spectrum, however, showed only a broad singlet at δ 2.46 ($\Delta\nu_{1/2}$ = 22 Hz) for the methyl protons of HMPA, reflecting the paramagnetic nature of the vanadium(II) metal. The structure of **5** has finally been confirmed by single-crystal X-ray diffraction. The molecular structure is shown in Figure 1, and selected bond distances and angles are given in Table 4. Complex **5** is composed of a monocationic binuclear vanadium(II) species and a mononuclear zinc counteranion.

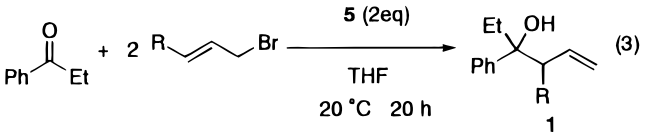
The structure of the cationic part of **5** is a trichloride-bridged binuclear complex which resembles that found in $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$,[11] and each vanadium(II) atom has an octahedral *fac* geometry. Three HMPA molecules coordinate to each vanadium(II) atom via the

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$ (5)

V(1)−V(2)	3.167(1)	V(1)−O(1)	2.134(9)
V(1)−Cl(1)	2.515(4)	V(1)−O(2)	2.120(10)
V(1)−Cl(2)	2.519(5)	V(1)−O(3)	2.127(9)
V(1)−Cl(3)	2.542(4)	V(2)−O(4)	2.114(9)
V(2)−Cl(1)	2.535(5)	V(2)−O(5)	2.117(9)
V(2)−Cl(2)	2.526(4)	V(2)−O(6)	2.101(10)
V(2)−Cl(3)	2.524(4)	(V−O) av	2.119(10)
(V−Cl) av	2.527(9)	O(1)−P(1)	1.472(9)
O(2)−P(2)	1.452(9)	O(3)−P(3)	1.480(9)
O(4)−P(4)	1.458(9)	O(5)−P(5)	1.482(9)
O(6)−P(6)	1.487(10)	(O−P) av	1.472(13)
V(1)−Cl(1)−V(2)	77.7(1)	V(1)−Cl(3)−V(2)	77.4(1)
V(1)−Cl(2)−V(2)	77.8(1)		

oxygen atom, which is a similar coordination mode to that found in other HMPA complexes.[9] The vanadium metal is surrounded by the bulky HMPA. The V−V separation of 3.167(1) Å is significantly longer than that (2.993(1) Å) in $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, and the average V−Cl bond distance in complex **5** (2.527(9) Å) is also longer than that (2.478(3) Å) found in the complex $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$. The observed average V−Cl−V angle is 77.6(1)°, whereas that in $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ is 74.4°. These structural features suggest the presence of a strong steric repulsion between bulky HMPA molecules. Z. Hou and H. Yamazaki reported that the P−O bond distance and other structural features of a coordinated HMPA ligand in transition metal complexes do not significantly change depending on the complexes.[9b] This propensity is also observed in the complex **5**: the P−O distance of 1.472(13) Å is similar to those found in other HMPA complexes. In contrast to the anionic part of the complex $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, the anionic part of **5** is a mononuclear monoanion and has a slightly distorted tetrahedral geometry. A more strongly coordinating ligand, HMPA, also coordinates to the zinc atom and, thus, prevents the formation of a binuclear species. Thus, complex **5** forms a 1:1 electrolyte instead of a 2:1 electrolyte which was found in the THF complex. A total of seven molecules of HMPA have been included in the complex. This is the first example of HMPA-coordinated vanadium or zinc complexes, to the best of our knowledge, of which the structure has been determined.[21]

The vanadium−HMPA complex **5** itself can also promote the allylation efficiently in THF. When propiophenone was treated with allyl bromide or crotyl bromide in the presence of **5** in THF (without additional HMPA) at 20 °C for 20 h, the propiophenone was completely consumed and the homoallyl alcohol **1a** or **1b** was obtained in 94% or 52% isolated yield, respectively (eq 3). The activity is similar to that of allylation



a : R = H 94%
b : R = Me 52% (syn / anti = 44 / 56)

with $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ in the presence of 3.5 equiv of HMPA per 1.0 equiv of vanadium in THF (n = 14 in Table 2).

(21) Martin, J.; Normant, H. *C.R. Seances Acad. Sci., Ser. C* **1969**, *268C*, 152−155.

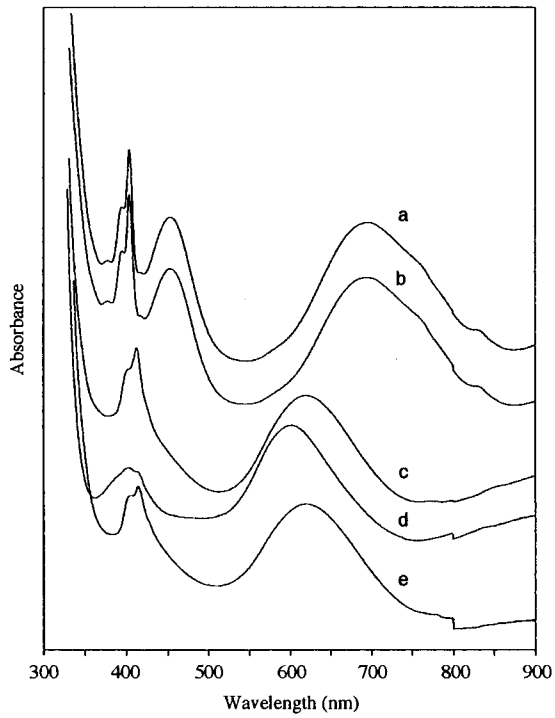
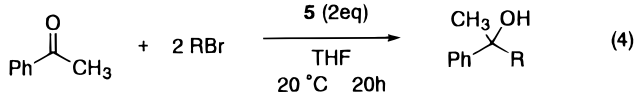


Figure 2. UV−vis spectra of several vanadium(II) complexes in THF and/or HMPA: (a) $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$, **5**, in THF; (b) $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ in THF, after addition of 3.5 equiv of HMPA per V; (c) HMPA complex **5** after addition of 4 equiv of TMEDA per **5** in THF; (d) $VCl_2(tmeda)_2$ in THF; (e) a mixture of $VCl_2(tmeda)_2$ and excess amount of HMPA in THF.

The vanadium(II) complex **5** was also effective for a Reformatsky-type reaction and benzylation of acetophenone in pure THF (eq 4). The vanadium−HMPA



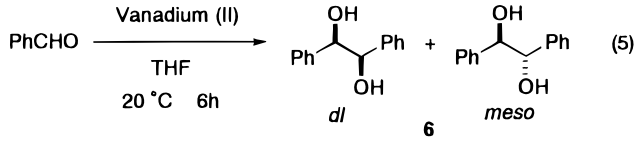
R = $CH_2CO_2CH_3$ (**2**) 60%
R = CH_2Ph (**4**) 91%

complex **5** is the first vanadium(II) complex to be applied to anionic organic reactions as a promoter; by utilizing the reducing power of a vanadium(II) complex, a vanadium−carbon bond is prepared *in situ* from several organic halides and then the organic group can be transferred to a carbonyl carbon to form a new carbon−carbon bond not *via* a radical mechanism but by using the nucleophilicity of the vanadium complex.

Figure 2 shows UV−vis spectra of the HMPA complex **5**, $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, and $VCl_2(tmeda)_2$ taken in THF and/or HMPA. Spectrum a is the spectrum of the HMPA complex **5** measured in THF solvent. It is very similar to the spectrum of $[V_2Cl_3(thf)_6]B(C_6H_5)_4$ measured in THF[11c] and shows four major bands at 395 (ϵ = 14), 404 (ϵ = 20), 455 (ϵ = 13), and 698 nm (ϵ = 13). The spectrum showed unique relatively sharp and strong bands around 400 nm, which can be assigned to double spin-flip transitions of the coupled pair of V^{2+} ions.[11c] The relatively weak and broad bands at ca. 450 and 700 nm should be due to the spin-allowed ligand-field transitions. This spectrum is very similar to the spectrum of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ and HMPA (HMPA:V = 3.5:1) in THF (spectrum b). On the other hand,

spectrum c, which is the spectrum of HMPA complex **5** obtained after addition of 4.0 equiv of TMEDA per vanadium in THF, resembles that of $VCl_2(tmeda)_2$ by itself (spectrum d) or a mixture of $VCl_2(tmeda)_2$ and an excess amount of HMPA (spectrum e). In spectra c and e, the bands at around 450 and 700 nm showed a blue-shift to around 400 and 600 nm and the sharper and stronger bands, due to the double spin-flip transitions of the coupled pair of V^{2+}, being apparently weakened. These observations indicate that TMEDA coordinates to a vanadium(II) metal more strongly than HMPA and that the vanadium complex becomes a mononuclear species. In fact, when an excess amount of TMEDA was added to a THF solution of the vanadium−HMPA complex **5**, $VCl_2(tmeda)_2$ precipitated from the reaction mixture. The strong coordinating ability of TMEDA should cause a decrease of the Lewis acidity of the vanadium complex.

The pinacol coupling of an aldehyde is also a typical reaction induced by low-valent vanadium(II) complexes.[3] The HMPA complex **5** can promote the pinacol coupling. For example, the reaction of benzaldehyde in the presence of 0.5 equiv of $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$ in THF at 20 °C for 6 h afforded the pinacol-coupling product in 86% yield (*dl*:*meso* = 83:17; eq 5). The pinacol-



Vanadium (II)	yield/%	*dl*/*meso*
$[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$ (0.5 equiv)	86	83/17
$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (0.25 equiv)	97	96/4
$VCl_2(tmeda)_2$ (1.0 equiv)	87	99/1

coupling reaction mediated by $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ or $VCl_2(tmeda)_2$ was completed within 6 h with much higher *dl*-selectivity (*dl*:*meso* = 96:4 and 99:1), eq 5. This may imply that coordination of HMPA to vanadium prevents the aldehyde from getting near the vanadium center and interrupts a vanadium-bridging control in the transition state which is responsible for the high *dl*−diol selectivity.[22]

Conclusion

We have achieved the generation of a relatively stable organovanadium species from vanadium(II) and several organic halides in the presence of HMPA and applied them to ionic carbon−carbon bond-forming reactions, such as allylation and benzylation of carbonyl compounds and Reformatsky-type reactions. The addition of HMPA stabilized the vanadium−carbon bond of the organovanadium species and prevented its homolytic cleavage. Isolation of the vanadium−HMPA complex, $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$, and clarification of its structure made it clear that the coordination of bulky HMPA to the vanadium center played an important role in the carbon−carbon bond-formation reactions.

(22) (a) Clerici, A.; Porta, O. *Tetrahedron Lett.* **1982**, *23*, 3517−3520. (b) Clerici, A.; Porta, O. *J. Org. Chem.* **1985**, *50*, 76−81. (c) Clerici, A.; Clerci, L.; Porta, O. *Tetrahedron Lett.* **1996**, 37, 3035−3038.

Experimental Section

All manipulations were conducted under an argon atmosphere with standard Schlenk methods. Unless otherwise noted, the carbonyl compounds and allyl halides were obtained from commercial suppliers and were used after distillation. THF was distilled from sodium benzophenone ketyl under argon prior to use. HMPA, DMF, CH_2Cl_2, and DMI were distilled from calcium hydride under argon prior to use. $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$[11] and $VCl_2(tmeda)_2$[13] were prepared according to published procedures. Column chromatography was conducted by using silica gel 60 (E. Merck, 230−400 mesh). The melting points were uncorrected. ^1H and ^{31}P NMR spectra were recorded at 270.05 and 109.25 MHz, respectively. The chemical shifts of the ^1H NMR results are expressed in ppm downfield from Me_4Si using δ scale ($CHCl_3$ was used as an internal standard, δ 7.26), and those of ^{31}P NMR are referred to 85% H_3PO_4 as an external reference.

General Procedure for Allylation of Carbonyl Compounds Mediated by Vanadium(II) Complexes (Table 1). To a solution of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.0 mmol) in THF (10 mL) and HMPA (10 mL) was added a THF (3 mL) solution of a carbonyl compound (1.0 mmol) and an allyl bromide (2.0 mmol) at 20 °C. After the reaction mixture was stirred for 20 h at 20 °C, the reaction mixture was treated with H_2O (30 mL) and then extracted with ether (50 mL). The extracts were washed with H_2O (2 × 30 mL) and dried over $MgSO_4$. After being concentrated *in vacuo*, the residual oil was purified by column chromatography on silica gel to afford the homoallyl alcohol.

3-Phenylhex-5-en-3-ol (1a):[23] ^1H NMR ($CDCl_3$) δ 0.76 (t, J = 7.3 Hz, 3H), 1.77−1.91 (m, 2H), 2.03 (s, 1H), 2.49 (dd, J = 12.9, 8.6 Hz, 1H), 2.71 (dd, J = 13.5, 5.9 Hz, 1H), 5.06−5.16 (m, 2H), 5.50−5.66 (m, 1H), 7.18−7.40 (m, 5H).

(3*S,4*R**)- and (3*R**,4*R**)-4-Methyl-3-phenylhex-5-en-3-ol (1b)**:[14] The two diastereomers could not be separated, and their ratio was determined by ^1H NMR analysis ((3*S**,4*R**):(3*R**,4*R**) = 39:61). ^1H NMR ($CDCl_3$): δ 0.67 (t, J = 6.4 Hz, 3H (3*S**,4*R**)), 0.73 (t, J = 7.4 Hz, 3H (3*R**,4*R**)), 0.81 (d, J = 6.9 Hz, 3H (3*S**,4*R**)), 1.02 (d, J = 6.9 Hz, 3H (3*R**,4*R**)), 1.68−2.00 (m, 3H (3*S**,4*R**) + 3H (3*R**,4*R**)), 2.54−2.67 (m, 1H (3*S**,4*R**) + 1H (3*R**,4*R**)), 5.00−5.16 (m, 2H (3*S**,4*R**) + 2H (3*R**,4*R**)), 5.57−5.60 (m, 1H (3*R**,4*R**)), 5.78−5.92 (m, 1H (3*S**,4*R**)), 7.17−7.39 (m, 5H (3*S**,4*R**) + 5H (3*R**,4*R**)).

3-Methyl-1-phenylhex-5-en-3-ol (1c):[24] ^1H NMR ($CDCl_3$) δ 1.23 (s, 3H), 1.59 (s, 1H), 1.73−1.79 (m, 2H), 2.28 (d, J = 7.4 Hz, 2H), 2.65−2.72 (m, 2H), 5.09−5.17 (m, 2H), 5.80−5.95 (m, 1H), 7.12−7.29 (m, 5H).

(3*R,4*R**)- and (3*R**,4*S**)-3,4-Dimethyl-1-phenylhex-5-en-3-ol** (1d): The two diastereomers could not be separated, and their ratio was determined by ^1H NMR analysis ((3*R**,4*R**):(3*R**,4*S**) = 49:51). R_f = 0.42 (hexane:EtOAc = 5:1). ^1H NMR ($CDCl_3$): δ 1.03 (d, J = 5.0 Hz, 3H (3*R**,4*R**)), 1.06 (d, J = 4.9 Hz, 3H (3*R**,4*S**)), 1.16 (s, 3H (3*R**,4*S**)), 1.19 (s, 3H (3*R**,4*R**)), 1.49 (s, 1H (3*R**,4*R**)), 1.59 (s, 1H (3*R**,4*S**)), 1.70−1.81 (m, 2H (3*R**,4*R**) + 2H (3*R**,4*S**)), 2.28−2.34 (m, 1H (3*R**,4*R**) + 1H (3*R**,4*S**)), 2.61−2.76 (m, 2H (3*R**,4*R**) + 2H (3*R**,4*S**)), 5.04−5.15 (m, 2H (3*R**,4*R**) + 2H (3*R**,4*S**)), 5.72−5.92 (m, 1H (3*R**,4*R**) + 1H (3*R**,4*S**)), 7.12−7.29 (m, 5H (3*R**,4*R**) + 5H (3*R**,4*S**)). MS (EI): m/z 149 ($M^+ - C_4H_7$). IR (neat, mixture of syn:anti = 49:51): 3445, 3063, 3026, 2974, 2937, 2875, 1994, 1802, 1718, 1636, 1604, 1542, 1496, 1454, 1419, 1376, 1279, 1193, 1155, 1100, 1066, 1031, 1001, 941, 911, 742, 699, 514 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.15; H, 9.70.

1-Phenylhex-5-en-3-ol (1e):[25] ^1H NMR ($CDCl_3$) δ 1.71−1.90 (m, 3H), 2.12−2.36 (m, 2H), 2.62−2.83 (m, 2H), 3.62−

(23) Guijarro, D.; Mancheño, B.; Yus, M. *Tetrahedron* **1994**, *50*, 8551−8558.

(24) Barluenga, J.; Flórez, J.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, *12*, 3019−3026.

(25) Sano, H.; Miyazaki, Y.; Okawara, M.; Ueno, Y. *Synthesis* **1986**, 776−777.

3.71 (m, 1H), 5.08−5.17 (m, 2H), 5.74−5.89 (m, 1H), 7.07−7.32 (m, 5H).

Tridec-1-en-4-ol (1f):[26] ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.4 Hz, 3H), 1.26−1.76 (m, 17H), 2.07−2.19 (m, 1H), 2.23−2.37 (m, 1H), 3.63 (br m, 1H), 5.07−5.15 (m, 2H), 5.75−5.90 (m, 1H).

(3*R,4*R**)- and (3*S**,4*R**)-3-Methyltridec-1-en-4-ol (1g)**:[15] The two diastereomers could not be separated, and their ratio was determined by ^{1}H NMR analysis ((3*R**,4*R**):(3*S**,4*R**) = 21:79). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.7 Hz, 3H (3*R**,4*R**) + 3H (3*S**,4*R**)), 1.02 (d, J = 6.9 Hz, 3H (3*R**,4*R**)), 1.03 (d, J = 6.9 Hz, 3H (3*S**,4*R**)), 1.27−1.58 (m, 17H (3*R**,4*R**) + 17H (3*S**,4*R**)), 2.17−2.27 (m, 1H (3*R**,4*R**) + 1H (3*S**,4*R**)), 3.39 (br m, 1H (3*R**,4*R**) + 1H (3*S**,4*R**)), 5.04−5.12 (m, 2H (3*R**,4*R**) + 2H (3*S**,4*R**)), 5.70−5.83 (m, 1H (3*R**,4*R**) + 1H (3*S**,4*R**)).

1-Phenylbut-3-en-1-ol (1h):[27] ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 1H), 2.48−2.59 (m, 2H), 4.74 (t, J = 6.3 Hz, 1H), 5.11−5.20 (m, 2H), 5.73−5.89 (m, 1H), 7.25−7.36 (m, 5H).

(1*S,2*R**)- and (1*S**,2*S**)-2-Methyl-1-phenylbut-3-en-1-ol (1i)**:[15] The two diastereomers could not be separated, and their ratio was determined by ^{1}H NMR analysis ((1*S**,2*R**):(1*S**,2*S**) = 26:74). ^{1}H NMR ($CDCl_3$): δ 0.86 (d, J = 6.9 Hz, 3H (1*S**,2*S**)), 1.00 (d, J = 6.9 Hz, 3H (1*S**,2*R**)), 2.13 (br s, 1H (1*S**,2*R**) + 1H (1*S**,2*S**)), 2.43−2.57 (m, 1H (1*S**,2*R**) + 1H (1*S**,2*S**)), 4.34 (d, J = 7.7 Hz, 1H (1*S**,2*S**)), 4.63 (d, J = 5.7 Hz, 1H (1*S**,2*R**)), 5.00−5.20 (m, 2H (1*S**,2*R**) + 2H (1*S**,2*S**)), 5.67−5.87 (m, 1H (1*S**,2*R**) + 1H (1*S**,2*S**)), 7.21−7.35 (m, 5H (1*S**,2*R**) + 5H (1*S**,2*S**)).

2,2-Dimethylhex-5-en-3-ol (1j):[28] ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 9H), 1.59 (s, 1H), 1.92−2.05 (m, 1H), 2.33−2.41 (m, 1H), 3.26 (dd, J = 10.6, 2.0 Hz, 1H), 5.12−5.19 (m, 2H), 5.79−5.95 (m, 1H).

(3*S,4*R**)- and (3*S**,4*S**)-2,2,4-Trimethylhex-5-en-3-ol (1k)**:[15] The two diastereomers could not be separated, and their ratio was determined by ^{1}H NMR analysis ((3*S**,4*R**):(3*S**,4*S**) = 47:53). ^{1}H NMR ($CDCl_3$): δ 0.93 (s, 9H (3*S**,4*S**)), 0.96 (s, 9H (3*S**,4*R**)), 1.05 (d, J = 6.9 Hz, 3H (3*S**,4*R**)), 1.12 (d, J = 6.9 Hz, 3H (3*S**,4*S**)), 1.51 (br s, 1H (3*S**,4*R**) + 1H (3*S**,4*S**)), 2.45−2.60 (m, 1H (3*S**,4*R**) + 1H (3*S**,4*S**)), 3.13 (s, 1H (3*S**,4*S**)), 3.23 (d, J = 4.0 Hz, 1H (3*S**,4*R**)), 4.96−5.09 (m, 2H (3*S**,4*R**) + 2H (3*S**,4*S**)), 5.82−6.03 (m, 1H (3*S**,4*R**) + 1H (3*S**,4*S**)).

***cis*-4-*tert*-Butyl-1-(2-propenyl)-cyclohexan-1-ol (1l)**:[16] ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 9H), 1.30−1.42 (m, 5H), 1.52−1.77 (m, 5H), 2.19 (dd, J = 7.6, 1.0 Hz, 2H), 5.05−5.15 (m, 2H), 5.81−5.96 (m, 1H).

***trans*-4-*tert*-Butyl-1-(2-propenyl)-cyclohexan-1-ol (1l)**:[16] ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 9H), 1.01−1.17 (m, 3H), 1.34−1.43 (m, 2H), 1.60−1.80 (m, 5H), 2.29 (d, J = 7.3 Hz, 2H), 5.10−5.19 (m, 2H), 5.81−5.97 (m, 1H).

Typical Procedure for Allylation of Propiophenone in 1,3-Dimethyl-2-imidazolidinone (DMI). To a solution of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.65 g, 1.0 mmol) in DMI (10 mL) was added a DMI (3 mL) solution of propiophenone (134 mg, 1.0 mmol) and allyl bromide (0.17 mL, 2.0 mmol) at 20 °C. After the reaction mixture was stirred for 20 h at 20 °C, the reaction mixture was treated with H_2O (30 mL) and then extracted with ether (30 mL). The extracts were washed with H_2O (2 × 30 mL) and dried over $MgSO_4$. After being concentrated *in vacuo*, the residual oil was purified by column chromatography on silica gel (hexane:AcOEt = 5:1) to afford **1a** (168 mg, 95%) as a colorless oil.

Methyl 3-Hydroxy-3-phenyl-butanoate (2):[29] To a solution of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.63 g, 1.0 mmol) in THF (10 mL) and HMPA (10 mL) was added a THF (3 mL) solution of acetophenone (120 mg, 1.0 mmol) and methyl bromoacetate (0.19 mL, 2.0 mmol) at 20 °C. After the reaction mixture was stirred for 2 h at 20 °C, the reaction mixture was treated with H_2O (30 mL) and then extracted with ether (50 mL). The extracts were washed with H_2O (2 × 30 mL) and dried over $MgSO_4$. After being concentrated *in vacuo*, the residual oil was purified by column chromatography on silica gel (hexane:AcOEt = 2:1) to afford **2** (129 mg, 66%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 3H), 2.80 (d, J = 16.1 Hz, 1H), 2.98 (d, J = 16.1 Hz, 1H), 3.60 (s, 3H), 4.26 (s, 1H), 7.20−7.46 (m, 5H).

2-Phenylpent-4-yn-2-ol (3):[30] ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 3H), 2.03 (t, J = 2.6 Hz, 1H), 2.54 (s, 1H), 2.70 (ddd, J = 23.4, 16.5, 2.6 Hz, 2H), 7.21−7.51 (m, 5H).

1,2-Diphenylpropan-2-ol (4):[31] To a solution of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.63g, 1.0 mmol) in THF (10 mL) and HMPA (10 mL) was added a THF (3 mL) solution of acetophenone (120 mg, 1.0 mmol) and benzyl bromide (0.24 mL, 2.0 mmol) at 20 °C. After the reaction mixture was stirred for 1 h at 20 °C, the reaction mixture was treated with H_2O (30 mL) and then extracted with ether (50 mL). The extracts were washed with H_2O (2 × 30 mL) and dried over $MgSO_4$. After being concentrated *in vacuo*, the residual oil was purified by column chromatography on silica gel (hexane:AcOEt = 5:1) to afford **4** (183 mg, 86%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.52 (s, 3H), 1.96 (s, 1H), 3.04 (dd, J = 29.0, 13.2 Hz, 2H), 6.94−7.40 (m, 10H).

Preparation of $[V_2Cl_3(hmpa)_6][ZnCl_3(hmpa)]$ (hmpa = Hexamethylphosphoric Triamide) (5). To a suspension of $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ (1.07 g, 0.66 mmol) in THF (10 mL) was added HMPA (4.6 mL, 26.4 mmol) at 20 °C, and the resultant green solution was stirred for 30 min. After the solvent was evaporated *in vacuo*, the residual solid was washed with ether (2 × 30 mL) and redissolved in THF (5 mL) and ether (20 mL). After the insoluble materials were removed and the filtrate was allowed to stand overnight at −18 °C, green crystals of **5** were obtained (1.08 g, 50%). ^{1}H NMR (toluene-d_8): δ 2.46 (br s, $\Delta\nu_{1/2}$ = 22 Hz). ^{31}P NMR (toluene-d_8): δ 25.6 (6P, $\Delta\nu_{1/2}$ = 200 Hz), 129 (1P, $\Delta\nu_{1/2}$ = 870 Hz). IR (Nujol mull): 1303, 1192, 1146, 1069, 990, 842, 753, 479 cm^{-1}. Mp 188−190 °C (dec). MS (FAB): m/z 479, 481 ($VCl_2(hmpa)_2^+$). Anal. Calcd for $C_{42}H_{126}Cl_6N_{21}O_7P_7V_2Zn$: C, 30.87; H, 7.77; N, 18.00. Found: C, 30.53; H, 7.36; N, 17.68.

Crystallographic Data Collection and Structure Determination of 5. A crystal of **5** suitable for X-ray diffraction sealed in a glass capillary under an argon atmosphere was mounted on a Rigaku AFC-7R rotating anode automatic four-cycle diffractometer for data collection, using graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods with SHELX86[32] and expanded using Fourier techniques.[33] The crystal structure was refined by full-matrix least-squares methods on F. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp. Selected interatomic distances and angles are listed in Table 4. Crystallographic data are given in Table 5. We have deposited atomic coordinates for **5** with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

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Table 5. Crystallographic Data for 5

formula	$C_{42}H_{126}Cl_6N_{21}O_7P_7V_2Zn$
fw	1634.39
cryst syst	triclinic
space group	*P*1 (No. 2)
a, Å	18.411 (6)
b, Å	18.691 (8)
c, Å	15.128 (4)
α, deg	110.64 (2)
β, deg	93.18 (3)
γ, deg	61.03 (3)
V, Å^3	4219 (2)
Z	2
D_{calcd}, g cm^{-3}	1.286
λ(Mo Kα), Å	0.710 69
cryst size, mm	0.43 × 0.27 × 0.13
temperature, K	293(1)
2*θ* limit, deg	50
collection region	$0 \le h \le 24$, $-24 \le k \le 24$, $-20 \le l \le 20$
intensity variation, %	−12.4 (a linear correction factor was applied.)
no. of measd reflns	13 037
$T_{(min, max)}$	0.9193, 0.9994
no. of unique reflns	12 608
R_{int}	0.07
criterion for obsd reflns	$I > 3.0\sigma(I)$
no. of obsd reflns	4487
no. of vaiable params	668
R, R_w	0.080, 0.062
w	$1/\sigma^2(F_0)$
$\Delta/\sigma_{(max)}$	0.01
GOF	3.29
$\Delta\rho_{(min, max)}$, e$^-$/Å^3	−0.61, 0.78

General Procedure for Alkylation Mediated by [V_2Cl_3(hmpa)$_6$][$ZnCl_3$(hmpa)]. To a solution of [V_2Cl_3(hmpa)$_6$][$ZnCl_3$(hmpa)] (2.0 mmol) in THF (10 mL) was added a THF (3 mL) solution of a ketone (1.0 mmol) and an organic halide (2.0 mmol) at 20 °C. After the reaction mixture was stirred for 20 h at 20 °C, the reaction mixture was treated with H_2O (30 mL) and then extracted with ether (30 mL). The extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel to afford the alcohol.

Typical Procedure for Pinacol Coupling of Benzaldehyde Mediated by [V_2Cl_3(hmpa)$_6$][$ZnCl_3$(hmpa)]. To a solution of [V_2Cl_3(hmpa)$_6$][$ZnCl_3$(hmpa)] (1.00 g, 0.61 mmol) in THF (10 mL) was added a THF (3 mL) solution of benzaldehyde (130 mg, 1.23 mmol) at 20 °C. After the reaction mixture was stirred for 6 h at 20 °C, the reaction mixture was treated with 0.1 M HCl(aq) (20 mL) and then extracted with ether (20 mL). The extracts were washed with H_2O (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane:AcOEt = 2:1) to afford 1,2-diphenyl-1,2-ethanediol, **6,** as a white solid (113 mg, 86%).

***dl* and *meso*-1,2-Diphenyl-1,2-ethanediol (6).**[22b] The two diastereomers could not be separated, and their ratio was determined by ^{1}H NMR analysis (*dl*:*meso* = 83:17). ^{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).

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Supporting Information Available: Text giving the experimental details of X-ray analysis and tables of the X-ray structure determination, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **5** (42 pages). Ordering information is given on any current masthead page.

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