

# Synthesis of (arylimido)vanadium complexes and their application for oxidative coupling reactions of silyl enol ether derivatives†

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(Arylimido)vanadium(v) complexes, V(NAr)(OEt)Cl<sub>2</sub> [Ar = C<sub>6</sub>H<sub>5</sub>, *p*-BrC<sub>6</sub>H<sub>4</sub>, *p*-(MeO)C<sub>6</sub>H<sub>4</sub>] or V(NAr)Cl<sub>3</sub> [Ar = *o*-BrC<sub>6</sub>H<sub>4</sub>, *o*-(MeO)C<sub>6</sub>H<sub>4</sub>] were synthesized by the reaction of VO(OEt)Cl<sub>2</sub> or VOCl<sub>3</sub>, respectively, with the corresponding aryl isocyanates. X-Ray crystal structure determination for V(NAr)(OEt)Cl<sub>2</sub> (Ar = C<sub>6</sub>H<sub>5</sub> and *p*-BrC<sub>6</sub>H<sub>4</sub>) elucidates the alkoxido-bridged dimeric building blocks [V(NAr)(OEt)Cl<sub>2</sub>]<sub>2</sub>, wherein the substituent on the benzene ring was found to affect the character of the imido nitrogen. The <sup>51</sup>V NMR spectroscopic measurements indicated that the electronic state of the vanadium metal centre depends on the ligands connecting to the vanadium and the substituents on the benzene ring. The selective oxidative cross-coupling reaction of silyl ketene acetal with silyl enol ether was achieved using V(*Np*-BrC<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub> or V(*No*-BrC<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub>.

## Introduction

Oxo and imido ligands are recognized to stabilize highly oxidized transition metals through extensive ligand-to-metal π-donation.<sup>1</sup> (Imido)vanadium(v) complexes have attracted much attention<sup>2</sup> because of their potential application as catalysts for olefin polymerization,<sup>3</sup> C–H activation<sup>4</sup> and related reactions.<sup>5</sup> Ligands connecting to the vanadium metal centre have been reported to influence the reactivity.<sup>3c,3e,3h,3i</sup> Compared with oxo ligands, imido ligands can possess a substituent on the imido nitrogen so that the steric and electronic characters of the metal centre are considered to be controlled by the properties of the nitrogen substituent. In such a sense, the design of (arylimido)vanadium(v) complexes is one of key factors in the development of efficient reagents. In previous papers, the *p*-substituent on the benzene ring of (arylimido)vanadium(v) complexes was demonstrated to affect the nature of the vanadium metal centre and imido bond through π-conjugation.<sup>6</sup> On the other hand, oxovanadium(v) alkoxydichloride is allowed to induce the oxidative coupling reaction of silyl enol ethers.<sup>7</sup> We herein report the structural characterization of (arylimido)vanadium(v) complexes and their application as a one-electron oxidant in the oxidative coupling reaction of silyl enol ether derivatives.

## Results and discussion

The reaction of VO(OEt)Cl<sub>2</sub> or VOCl<sub>3</sub> with substituted aryl isocyanates in octane at reflux temperature was performed to give the corresponding (*p*-substituted phenylimido)vanadium(v) ethoxydichlorides [V(*Np*-R<sup>1</sup>C<sub>6</sub>H<sub>4</sub>)(OEt)Cl<sub>2</sub> (**1a**: R<sup>1</sup> = MeO, **1b**: R<sup>1</sup> = H, **1c**: R<sup>1</sup> = Br) and (*p*- or *o*-substituted phenylimido)vanadium(v) trichlorides [V(*Np*-R<sup>1</sup>C<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub> (**2a**: R<sup>1</sup> = MeO,<sup>2c</sup> **2b**: R<sup>1</sup> = H,<sup>2d</sup> **2c**: R<sup>1</sup> = Br<sup>2e</sup>) and V(*No*-R<sup>2</sup>H<sub>4</sub>)Cl<sub>3</sub> (**2d**: R<sup>2</sup> = MeO, **2e**: R<sup>2</sup> = Br)].

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**Table 1** Synthesis and <sup>51</sup>V NMR spectra of (arylimido)vanadium(v) complexes **1** and **2**

Complex <b>1</b> or <b>2</b>	R <sup>1</sup>	R <sup>2</sup>	Yield/%	<sup>51</sup> V NMR/ppm
<b>1a<sup>a</sup></b>	MeO	H	89	−4
<b>1b<sup>a</sup></b>	H	H	82	−136
<b>1c<sup>a</sup></b>	Br	H	85	−146
<b>2a<sup>b</sup></b>	MeO	H	88	429
<b>2b<sup>b</sup></b>	H	H	73	260
<b>2c<sup>b</sup></b>	Br	H	75	263
<b>2d<sup>b</sup></b>	H	MeO	89	385
<b>2e<sup>b</sup></b>	H	Br	85	258

<sup>a</sup> This work. <sup>b</sup> Ref. 2c. <sup>c</sup> Ref. 2d.

Complexes **1** and **2** were characterized by <sup>1</sup>H NMR spectra. The <sup>51</sup>V NMR spectroscopic measurements clarified the substituent effect on the electronic environment of the vanadium metal centre. Compared with the <sup>51</sup>V chemical shifts of **2**, the shifts of **1** were observed at a higher field with the electron donation from the ethoxido group (Table 1). The <sup>51</sup>V chemical shifts of **1** were observed at a lower field with an increase in the electron-donating capability of the substituent on the benzene ring. In the <sup>51</sup>V NMR spectra of the d<sup>0</sup> diamagnetic vanadium complexes, the vanadium metal centre becomes increasingly shielded as the electronegativity of the imido ligand increases.<sup>2c</sup> The chemical shifts indicate that the vanadium metal centre of a (*p*-methoxyphenylimido)vanadium(v) complex is more electron-rich than that of non-substituted or bromo substituted complexes. The π-conjugation between the aryl group and the imido bond is considered to control the electronic

**Table 2** Crystallographic data for **1b** and **1c**

	<b>1b</b>	<b>1c</b>
Formula	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> N <sub>1</sub> Cl <sub>2</sub> V <sub>1</sub>	C <sub>8</sub> H <sub>8</sub> O <sub>1</sub> N <sub>1</sub> Br <sub>1</sub> Cl <sub>2</sub> V <sub>1</sub>
Formula weight	274.02	336.92
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i> (no. 61)	<i>P2<sub>1</sub>/n</i> (no. 14)
<i>a</i> /Å	11.6418(14)	7.6595(10)
<i>b</i> /Å	7.8118(8)	11.7903(14)
<i>c</i> /Å	24.194(3)	13.1806(19)
$\alpha$ /°		
$\beta$ /°		101.426(4)
$\gamma$ /°		
<i>V</i> /Å <sup>3</sup>	2200.2(4)	1166.7(3)
<i>Z</i>	8	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.558	1.918
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	13.465	47.082
<i>T</i> /°C	-100 ± 1	-100 ± 1
$\lambda$ (Mo-K $\alpha$ )/Å	0.71075	0.71075
<i>R<sub>1</sub></i> <sup>a</sup>	0.0331	0.0484
<i>wR<sub>2</sub></i> <sup>b</sup>	0.0781	0.1275

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

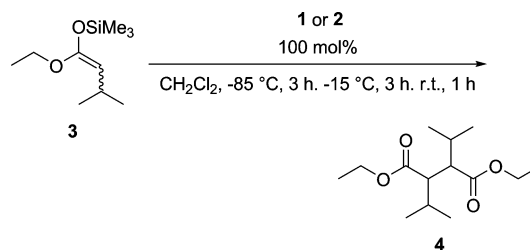
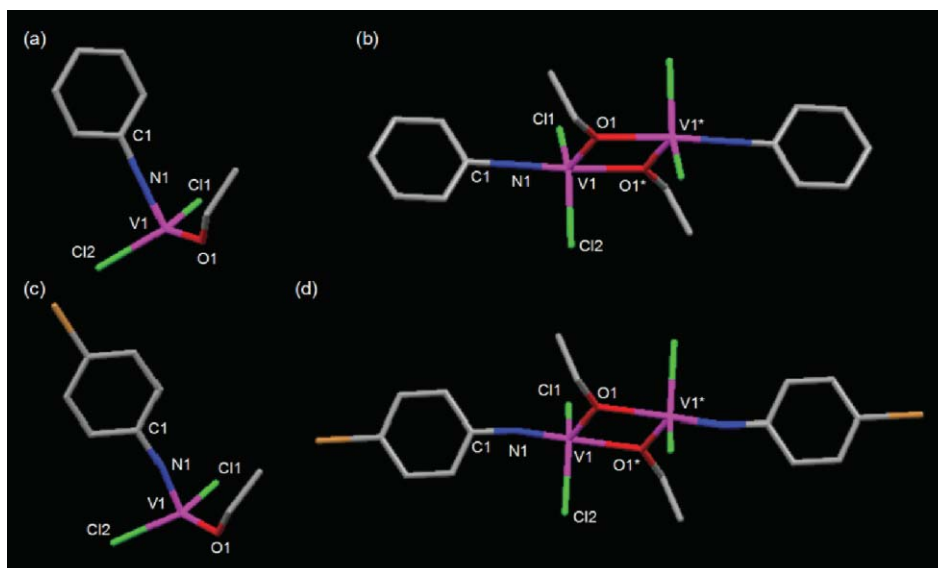
properties of the vanadium metal centre. The <sup>51</sup>V NMR spectra of **2** indicate that the electron-donating substituent on the benzene ring is related to the shielding effect of the imido nitrogen.

(*p*-Tolyl)imido vanadium(v) trichloride has been reported to be present in chlorido-bridged polymeric building blocks,<sup>8</sup> although (arylimido)vanadium(v) triisopropoxide<sup>2i,3g,6b</sup> and (arylimido)vanadium(v) dialkoxychloride<sup>2c</sup> form an alkoxido-bridged packing structure. On the contrary, the assembled structure of (arylimido)vanadium(v) alkoxydichloride has not been reported, although these complexes have already been synthesized.<sup>2c,3f</sup> To clarify the association properties of (arylimido)vanadium(v) alkoxydichloride, the single-crystal X-ray structure determinations of **1b** and **1c** were studied (Table 2).

As observed in the crystal structures of the dialkoxide<sup>2c</sup> and trialkoxide complexes,<sup>2i,3g,6b</sup> V(NC<sub>6</sub>H<sub>5</sub>)(OEt)Cl<sub>2</sub> (**1b**) was found to form dimeric building blocks, in which each vanadium atom

is coordinated in a trigonal-bipyramidal geometry, bridging to the second vanadium atom *via* the ethoxido group in an apical position (Fig. 1b). The V(1)–N(1) distance of 1.6554(14) Å and the nearly linear C(1)–N(1)–V(1) angle of 173.46(13)° suggest the participation of an sp-hybridized character in the imido nitrogen. The ethoxido-bridged dimeric building blocks were also formed in the case of **1c**, bearing the bromo group on the benzene ring (Fig. 1d). No notable difference was observed with the V(1)–Cl(1), V(1)–Cl(2), C(1)–N(1) and V(1)–V(1\*) lengths (Table 3). A nearly linear V(1)–N(1)–C(1) angle was also observed with **1c**. However, as compared with **1b**, the imido angle is almost 4° bent. This result indicates that there is less contribution of an sp-hybridized character from the imido nitrogen of **1c**. This is probably due to the conjugation of the electron-withdrawing group, the bromo group might weaken the sp-hybridized character. Such a relationship between the imido bond character and the substituent effect was also reported with V(NAr)(Oi-Pr)<sub>3</sub>.<sup>6c</sup>

To evaluate the effect of the aryl substituents and the ligands binding to the vanadium on the reactivity of the (arylimido)vanadium(v) complexes, the oxidative homo-coupling reaction of silyl ketene acetal **3** was examined, as shown in Scheme 1 and Table 4. By using V(*Np*-(MeO)C<sub>6</sub>H<sub>4</sub>)(*Oi*-Pr)<sub>3</sub>,<sup>6b</sup> the homo-coupled product **4**<sup>7d</sup> was not produced (entry 1). On the other hand, with the (arylimido)vanadium(v) ethoxydichlorides **1**, the homo-coupled product **4** was obtained. Interestingly, probably due to the electron-withdrawing properties of the bromo group,

**Scheme 1** The homo-coupling reaction of **3**, using **1** or **2**.**Fig. 1** (a) The crystal structure of **1b**, (b) the crystal structure of **1b** arising from dimeric building blocks, (c) the crystal structure of **1c** and (d) the crystal structure of **1c** arising from dimeric building blocks (hydrogen atoms are omitted for clarity).

**Table 3** Selected bond lengths and angles for **1b** and **1c**

	<b>1b</b>	<b>1c</b>
Bond lengths/Å		
V(1)–N(1)	1.6554(14)	1.661(3)
V(1)–Cl(1)	2.2266(5)	2.2249(12)
V(1)–Cl(2)	2.2151(5)	2.2232(10)
V(1)–O(1)	1.8187(12)	1.814(2)
V(1)–O(1 <sup>a</sup> )	2.2019(12)	2.203(2)
C(1)–N(1)	1.381(2)	1.374(4)
C(4)–Br(1)		1.896(3)
V(1)–V(1 <sup>a</sup> )	3.2225(4)	3.2200(9)
Bond angles/°		
C(1)–N(1)–V(1)	173.46(13)	169.5(2)
N(1)–V(1)–Cl(1)	96.33(5)	98.89(12)
N(1)–V(1)–Cl(2)	97.29(5)	95.17(10)
N(1)–V(1)–O(1)	99.91(6)	100.95(13)
N(1)–V(1)–O(1 <sup>a</sup> )	173.66(6)	173.90(14)
O(1)–V(1)–Cl(1)	118.12(4)	115.05(8)
O(1 <sup>a</sup> )–V(1)–Cl(1)	86.00(3)	86.33(7)
O(1)–V(1)–Cl(2)	121.21(4)	122.55(9)
O(1 <sup>a</sup> )–V(1)–Cl(2)	87.00(3)	85.25(7)
O(1)–V(1)–O(1 <sup>a</sup> )	78.84(4)	73.84(10)
Cl(1 <sup>a</sup> )–V(1)–Cl(2)	115.12(2)	116.21(4)
V(1)–O(1)–V(1 <sup>a</sup> )	106.16(5)	106.16(11)

<sup>a</sup> **1b**:  $-x + 1, -y + 1, -z + 1$ , **1c**:  $-x + 1, -y, -z$ .

**Table 4** The homo-coupling reaction of **3**, using **1** or **2**

Entry	Complex	Yield of <b>4</b> /% <sup>a</sup>
1	V(N <i>p</i> -(MeO) <sub>6</sub> H <sub>4</sub> )(O <i>i</i> -Pr),	No reaction
2	<b>1a</b>	8
3	<b>1b</b>	6
4	<b>1c</b>	18
5	<b>2a</b>	63
6	<b>2b</b>	73
7	<b>2c</b>	75
8	<b>2d</b>	65
9	<b>2e</b>	79

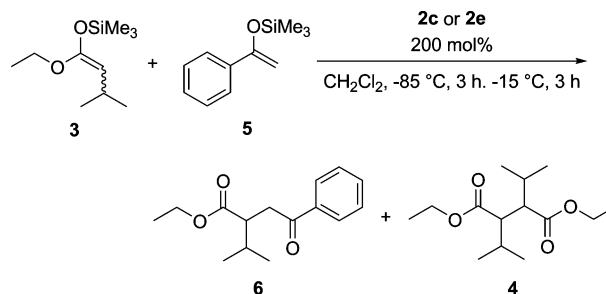
<sup>a</sup> Determined by <sup>1</sup>H NMR using durene as an internal standard.

the use of **1c** resulted in an approximately 10% higher yield than that when using **1a** or **1b** (entries 2–4). From the above-mentioned insufficient reactivity of **1**, (arylimido)vanadium(v) trichloride **2** was employed. The yield of **4** was raised to 63% by use of V(N*p*-(MeO)<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub> (**2a**). The oxidative homo-coupling reaction of **3** was found to depend largely on the ligands connecting to the vanadium. Then, the position and electronic properties of the substituent on the benzene ring were changed to study the substituent effect. As shown in entries 5 and 8 or entries 7 and 9, the position of the substituent was not found to affect the reactivity of the complex. On the other hand, as shown in the reactivity of **1**, the reaction was dependent on the electronic character of the substituent. Use of (bromophenylimido)vanadium(v) trichlorides **2c** and **2e** resulted in higher yields than those resulting from the use of non-substituted or methoxido-substituted complexes (entries 5–9). The reactivity of the (arylimido)vanadium(v) complexes was found to be changed dramatically by the ligands binding to the vanadium metal centre and tuned finely by the electronic properties of the substituent on the benzene ring. These findings are consistent with the above-mentioned chemical shifts of <sup>51</sup>V NMR (Table 1).

The redox process of the vanadium species for this coupling reaction was investigated. After the reaction of entry 7, doublet peaks of the aromatic ring in <sup>1</sup>H NMR and a broad peak in the <sup>51</sup>V NMR disappeared. EPR spectra at room temperature in acetonitrile solution revealed a resonance at  $g = 1.990$  with the characteristic octet pattern [ $A_{\text{iso}}(^{51}\text{V}) = 107 \times 10^{-4} \text{ cm}^{-1}$ ] expected for the interaction of an unpaired electron of V<sup>IV</sup> with the <sup>51</sup>V nucleus ( $I = 7/2$ ). These findings indicate that the vanadium(v) species is reduced to vanadium(IV) through a one-electron redox process.

In the homo-coupling reaction of silyl enol ether **5** with **2c** or **2e**, which are reactive oxidants towards **3**, the homo-coupled product was not obtained, indicating that **5** is less reactive than **3**. This difference in the reactivity was applied to the selective cross-coupling reaction of silyl enol ether **5** and silyl ketene acetal **3** to give 1,4-keto ester **6**<sup>7c</sup> (Scheme 2). Treatment of **3** with an equal amount of **5** in the presence of **2c** or **2e** led to the predominant formation of the cross-coupled keto ester **6**, with a small amount of the homo-coupled by-product **4** (Table 5, entries 1 and 2). The yield using **2e** was 15% lower than that using **2c**. It should be noted that the reaction is more selective with 200 mol% of **5** and the formation of the by-product **4** was completely suppressed by using **2c**.

In summary, (arylimido)vanadium(v) ethoxydichloride V(NAr)(OEt)Cl<sub>2</sub> [Ar = C<sub>6</sub>H<sub>5</sub> (**1b**), *p*-BrC<sub>6</sub>H<sub>4</sub> (**1c**)] was demonstrated to form dimeric building blocks, wherein the substituent on the benzene ring was found to affect the character of the imido nitrogen. Ligands connecting to the vanadium metal centre and the substituents on the benzene ring were elucidated to affect the electronic properties of the vanadium nuclei and control the reactivity. These findings permitted the selective oxidative coupling reaction of silyl ketene acetal and silyl enol ether to provide a useful synthetic protocol. The application of (arylimido)vanadium(v) complexes to other oxidation reactions is currently under way.

**Scheme 2** The cross-coupling reaction of **3** with **5**, using **2c** or **2e**.**Table 5** The cross-coupling reaction of **3** with **5**, using **2c** or **2e**

Entry	Complex <b>2</b>	Amount of <b>5</b> used/mol%	Yield/% <sup>a</sup>	
			<b>6</b>	<b>4</b>
1	<b>2c</b>	100	74	17
2	<b>2e</b>	100	59	18
3	<b>2c</b>	200	84	0
4	<b>2e</b>	200	80	trace

<sup>a</sup> Determined by <sup>1</sup>H NMR using durene as an internal standard.

## Experimental

### General procedures and instrumentation

All manipulations were carried out under an atmosphere of nitrogen in a drybox or using standard Schlenk techniques. All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. The solvents employed were dried by refluxing in the presence of appropriate drying reagents, distilled under an atmosphere of argon, de-gassed and stored in a drybox. The complexes V(*Np*-(MeO)C<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub> (**2a**),<sup>2b</sup> V(NC<sub>6</sub>H<sub>5</sub>)Cl<sub>3</sub> (**2b**)<sup>2d</sup> and V(*Np*-BrC<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub> (**2c**),<sup>2b</sup> the silyl ketene acetal **3**<sup>9</sup> and the silyl enol ether **5**<sup>10</sup> were obtained as reported. <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-ECP 400 (400 MHz) or a Varian MERCURY 300 (300 MHz) spectrometer. The chemical shifts were referenced to the residual resonances of deuterated solvents. <sup>51</sup>V NMR spectra were obtained with a JEOL JNM-ECP 400 (105 MHz) spectrometer with VOCl<sub>3</sub> as an external standard.

### Synthesis of (arylimido)vanadium(v) ethoxydichloride

[V(*Np*-(MeO)C<sub>6</sub>H<sub>4</sub>)(OEt)Cl<sub>2</sub>] (**1a**), V(NC<sub>6</sub>H<sub>5</sub>)(OEt)Cl<sub>2</sub> (**1b**), V(*Np*-BrC<sub>6</sub>H<sub>4</sub>)(OEt)Cl<sub>2</sub> (**1c**)

A mixture of the isocyanate (3.0 mmol) and oxovanadium(v) ethoxydichloride (3.0 mmol) was stirred in octane (30 mL) under an atmosphere of nitrogen at reflux temperature for 16 h. Solvent was evaporated under reduced pressure and the thus-obtained compound was washed with hexane. Saturated hexane solution was chilled at -30 °C to give the desired crystal.

**1a**: Isolated yield 89%, <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.50 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 5.56 (br, 2H), 3.86 (s, 3H), 1.65 (br, 3H), <sup>51</sup>V NMR (105 MHz, CD<sub>2</sub>Cl<sub>2</sub>) -4 ppm.

**1b**: Isolated yield 89%, <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.26–7.46 (multi, 5H), 5.57 (q, *J* = 6.9 Hz, 2H), 1.62 (t, *J* = 6.9 Hz, 3H), <sup>51</sup>V NMR (105 MHz, CD<sub>2</sub>Cl<sub>2</sub>) -136 ppm.

**1c**: Isolated yield 85%, <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.53 (q, *J* = 6.9 Hz, 2H), 1.58 (t, *J* = 6.9 Hz, 3H), <sup>51</sup>V NMR (105 MHz, CD<sub>2</sub>Cl<sub>2</sub>) -146 ppm.

### Synthesis of (*o*-substituted phenylimido)vanadium(v) trichloride

[V(*No*-(MeO)C<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub>] (**2d**), V(*No*-BrC<sub>6</sub>H<sub>4</sub>)Cl<sub>3</sub> (**2e**)

A mixture of the isocyanate (3.0 mmol) and oxovanadium(v) trichloride (3.0 mmol) was stirred in octane (30 mL) under an atmosphere of nitrogen at reflux temperature for 16 h. Solvent was evaporated under reduced pressure and the thus-obtained compound was washed with hexane. The desired compound was collected by filtration and dried *in vacuo*.

**2d**: Isolated yield 89%, <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.28 (dd, *J* = 8.1, 7.5 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.92 (dd, *J* = 7.8, 7.5 Hz, 1H), 4.03 (s, 3H), <sup>51</sup>V NMR (105 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 385 ppm.

**2e**: NMR yield 85%, <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.74 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 7.8, 7.5 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.8 Hz, 1H), <sup>51</sup>V NMR (105 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 258 ppm

### A representative procedure for the oxidative homo-coupling reaction of **3**

The silyl ketene acetal **3** (20.2 mg, 0.10 mmol) in dichloromethane (500 μL) was added dropwise to a suspension of the (arylimido)vanadium(v) complex (0.10 mmol) in dichloromethane (500 μL) at -85 °C. The suspension was stirred at -85 °C for 3 h, at -15 °C for 3 h and then the solution was stirred at room temperature for 1 h. 5% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.5 mL) and ether (3 mL) were added to the reaction mixture, which was extracted with ether (6 mL × 3). The combined ethereal solution was washed with saturated aqueous NaHCO<sub>3</sub> (1.5 mL) and saturated aqueous NaCl (1.5 mL), dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The yield was determined by using durene (6.7 mg, 0.05 mmol) as an internal standard.

### A representative procedure for the oxidative cross-coupling reaction of **3** with **5**

The silyl ketene acetal **3** (20.2 mg, 0.10 mmol) dissolved in dichloromethane (0.5 mL) was added dropwise to a suspension of the (arylimido)vanadium(v) complex (0.20 mmol) and the silyl enol ether **5** (19.2 mg, 0.10 mmol) in dichloromethane (1.5 mL) at -85 °C. The suspension was stirred at -85 °C for 3 h and at -15 °C for 3 h. 5% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (1 mL) and ether (6 mL) were added to the reaction mixture, which was extracted with ether (6 mL × 3). The combined ethereal solution was washed with saturated aqueous NaHCO<sub>3</sub> (1.5 mL) and saturated aqueous NaCl (1.5 mL), dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The yield was determined by using durene (13.4 mg, 0.1 mmol) as an internal standard.

### X-Ray structure analysis

All measurements for **1b** and **1c** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The structures of **1b** and **1c** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are summarized in Table 2. Selected bond lengths and bond angles are listed in Table 3.

### EPR measurement

The silyl ketene acetal **3** (20.2 mg, 0.10 mmol) in dichloromethane (500 μL) was added dropwise to a suspension of the imidovanadium(v) complex **2c** (32.7 mg, 0.10 mmol) in dichloromethane (500 μL) at -85 °C. The suspension was stirred at -85 °C for 3 h, at -15 °C for 3 h and at room temperature for 1 h and then was taken into a drybox. The suspension was concentrated *in vacuo* and was washed with hexane. The thus-obtained dark compound was re-precipitated with ether at -30 °C and dissolved in acetonitrile (10<sup>-3</sup> M). EPR spectrum was recorded on a JEOL JES-RE1XE spectrometer under irradiation of a high-pressure mercury lamp (USH-1005D) by focusing at the sample cell in the EPR cavity at 298 K. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (*S/N*) ratio of the observed



spectrum under non-saturating microwave power conditions. The  $g$  value was calibrated using a  $Mn^{2+}$  marker.

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