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Organoimido and organodi-imido vanadium complexes†

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Abstract—Reactions of the *p*-tolylimido vanadium(V) complex [V(NTol)Cl_3], **1**, with sodium dithiocarbamate salts Na[S_2CNR_2] yield an homologous series of organoimido vanadium(V) dithiocarbamate systems [$TolN{\equiv}V(S_2CNR_2)_xCl_{(3-x)}$] [$x = 1$: R = Et (**2a**), Me (**2b**); $x = 2$: R = Et (**3a**), Me (**3b**); $x = 3$: R = Et (**4a**), Me (**4b**)]; the electronic and ^{51}V NMR spectra of these complexes are described. Zn reduction of complexes **3** affords impure products whose ESR spectra are consistent with the presence of the V(IV) systems [V(NTol)$(S_2CNR_2)_2$], **5**. Reaction of $VOCl_3$ with 0.5 equiv. of *p*-OCN—C_6H_4–NCO yields the *p*-phenylenediimido complex [$Cl_3V{\equiv}NC_6H_4N{\equiv}VCl_3$], **6**. Dissolution of **6** in THF produces an adduct [$(THF)_3Cl_3V{\equiv}NC_6H_4N{\equiv}VCl_3(THF)_3$], **7**, whose THF ligands are weakly bound. $VOCl_3$ reacts with an equimolar amount of *p*-OCN—C_6H_4—NCO to produce the mononuclear complex *p*-[$Cl_3V{\equiv}NC_6H_4$—NCO], **8**. The reaction of **8** with $OWCl_4$ in refluxing toluene affords an insoluble product analyzing as the expected heterobinuclear system [$Cl_3V{\equiv}NC_6H_4N{\equiv}WCl_4$], **9**, but treatment of this product with THF yields a mixture shown by ^1H NMR to contain both **7** and its ditungsten analogue [$(THF)Cl_4W{\equiv}NC_6H_4N{\equiv}WCl_4(THF)$], indicating that an unusual intermetallic exchange of imido ligands has occurred. The chloride ligands of **6** can be substituted by [S_2CNEt_2] or [O^tBu] anions to afford [$(Et_2NCS_2)_3V{\equiv}NC_6H_4N{\equiv}V(S_2CNEt_2)_3$], **11**, and [$(^tBuO)_3V{\equiv}NC_6H_4N{\equiv}V(O^tBu)_3$], **12**, respectively. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: organoimido vanadium(V) dithiocarbamate systems; intermetallic exchange; imido ligands.

The first examples of vanadium dithiocarbamate complexes, $V(S_2CNR_2)_4$, were prepared by Bradley and Gitlitz by the action of CS_2 on the corresponding tetrakis(dialkylamides) $V(NR_2)_4$ [1]. Subsequent investigations [2] revealed that $V(S_2CNEt_2)_4$ was thermally and oxidatively unstable and that upon exposure to O_2, the oxo vanadium dithiocarbamates $O{\equiv}V(S_2CNEt_2)_3$ [3] and $O{\equiv}V(S_2CNEt_2)_2$ [4] were produced. Since oxo and organoimido ligands are isoelectronic, and often form congruent sets of transition metal complexes [5], we became interested in the arylimido analogues of these oxo-vanadium systems. In this contribution, we report an homologous series of tolylimido vanadium dithiocarbamate complexes of the form [$TolN{\equiv}V(S_2CNR_2)_xCl_{(3-x)}$] and describe the preparation and preliminary reactivity studies of a divanadium phenylenedi-imido complex *viz.*, [$Cl_3V{\equiv}NC_6H_4N{\equiv}VCl_3$].

RESULTS AND DISCUSSION

Tolylimido vanadium(V) complexes

The starting material for these syntheses is *p*-tolylimido vanadium(V) trichloride [6], V(NTol)Cl_3, **1**, which is one of a large number of arylimido vanadium(V) complexes conveniently prepared from the reaction of $VOCl_3$ with the corresponding arylisocyanate ArNCO [7]. The substitution reactions of **1** with anhydrous sodium dithiocarbamates Na[S_2CNR_2] (R = Me, Et) in CH_2Cl_2 at room temperature occur as shown in eq. (1). All of these solid products display good solubility in chlorinated hydrocarbon solvents and are moderately soluble in toluene, with the diethyl dithiocarbamate species as a class displaying higher solubility than the dimethyl derivatives.

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† Dedicated with respect to Professor Donald C. Bradley, an inspiring scientist and a true gentleman.

$$\mathbf{1} + x\,\mathrm{Na[S_2CNR_2]} \xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{TolN{\equiv}V(S_2CNR_2)_xCl_{(3-x)}} + x\,\mathrm{NaCl} \qquad (1)$$

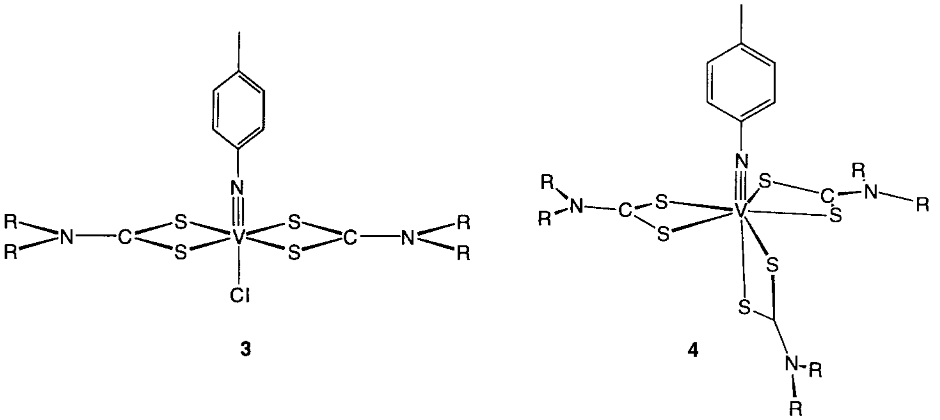
$x = 1$: R = Et, **2a**; R = Me, **2b**

$x = 2$: R = Et, **3a**; R = Me, **3b**

$x = 3$: R = Et, **4a**; R = Me, **4b**

The ^{1}H NMR spectra of the monosubstituted species **2a** and **2b** each reveal a single environment for the alkyl groups within the dithiocarbamate ligands, suggesting that the dithiocarbamates bind in the equatorial plane *cis* to the tolylimido ligand, but this observation alone is insufficient to deduce their probable geometries. For the disubstituted systems **3a** and **3b**, ^{1}H NMR spectra again indicate that the dithiocarbamates are contained in the equatorial plane *cis* to the tolylimido ligand: for **3a**, the S_2CNEt_2 groups produce a single methyl triplet δ 1.27 and a pair of methylene ABX_3 multiplets (due to the diastereotopic CH_2 protons) centered at δ 3.78 while for **3b**, a single resonance for the S_2CNMe_2 groups is observed at δ 3.36. These observations are consistent with a pseudo-octahedral structure for complexes **3** in which the chlorine atom occupies the position *trans*-to the tolylimido ligand as shown in Fig. 1. For the trisubstituted complexes **4**, ^{1}H NMR spectra suggest the adoption of a pentagonal bipyramidal structure (Fig. 1). Thus, the methyl groups of the S_2CNEt_2 ligands of **4a** appear as two triplets of relative intensity 5 : 1, as observed for the isoelectronic species $[\mathrm{PhN{\equiv}Mo(S_2CNEt_2]^+}$ [9]; the methyl groups of the S_2CNMe_2 ligands of **4b** appears as five singlets of relative intensity 2 : 1 : 1 : 1 : 1 : 1. Pentagonal bipyramidal structures have been established crystallographically both for $\mathrm{O{\equiv}V(S_2CNEt_2)_3}$ [3b] and $[\mathrm{Ph_3CN{\equiv}Mo(S_2CNMe_2)_3]^+}$ [10].

The ^{51}V NMR spectra of these complexes have been recorded as $CDCl_3$ solutions and the results are collected in Table 1. For the mono-substituted complexes **2**, the ^{51}V chemical shifts are perturbed only slightly upfield of that of the $\mathrm{V(NTol)Cl_3}$ parent (**1**, 305; **2a**, 301; **2b**, 289 ppm). Incorporation of a second dithiocarbamate ligand induces a moderate upfield shift (**3a**, 166; **3b**, 161 ppm), while extreme upfield shifts are observed for the tris(dithiocarbamate) complexes (**4a**,



3

4

Fig. 1. Proposed structures for complexes 3 and 4.

Table 1. ^{51}V NMR[a] and visible spectral[b] Data for $\mathrm{V(NTol)(S_2CNR_2)_xCl_{(3-x)}}$ Complexes

Complex	$\delta(^{51}V)$ (ppm)	fwhm (Hz)	λ_{max} (nm)
$\mathrm{V(NTol)(S_2CNEt_2)Cl_2}$ (**2a**)	301	415	530
$\mathrm{V(NTol)(S_2CNMe_2)Cl_2}$ (**2b**)	289	439	520
$\mathrm{V(NTol)(S_2CNEt_2)_2Cl}$ (**3a**)	166	2610	393
$\mathrm{V(NTol)(S_2CNMe_2)_2Cl}$ (**3b**)	161	1870	540
$\mathrm{V(NTol)(S_2CNEt_2)_3}$ (**4a**)	−565	1780	520
$\mathrm{V(NTol)(S_2CNMe_2)_3}$ (**4b**)	−574	1530	393

[a] $CDCl_3$ solution, 298 K, 105.2 MHz, relative to external $VOCl_3/CDCl_3$ (75% v/v), positive values denote downfield chemical shifts.

[b] $C_6H_5CH_3$ solution, 298 K.

-565; **4b**, -574 ppm). The linewidths of these resonances in all cases are sufficiently broad (*ca* 400–2600 Hz) so as to preclude the resolution of ^{51}V–^{14}N spin coupling; such coupling constants have been observed to range from 92–112 Hz in related V(NR)X$_3$ systems (R = alkyl, aryl; X = alkoxide, aryloxide, alkyl) [7b,11]. Within each set, the ^{51}V chemical shift of a given S$_2$CNMe$_2$ complex is observed at slightly higher field than that of its S$_2$CNEt$_2$ counterpart, an observation which is consistent with the greater electron donation capability of the S$_2$CNMe$_2$ ligand. It is interesting to note that the progressive upfield shift in $\delta(^{51}\text{V})$ observed upon successive replacement of chloride by S$_2$CNR$_2$ ligands in this series is opposite to the effect induced by replacement of chloride by monodentate thiolates. Thus, Preuss [12] finds that successive substitution of chloride by *tert*-butyl thiolate in the series [V(N^{t}Bu)(S^{t}Bu)$_x$Cl$_{(3-x)}$] drives the ^{51}V chemical shifts downfield (x = 0, 8; x = 1, 232; x = 2, 330; x = 3, 467 ppm).

The electronic spectra of complexes **2**, **3**, and **4** in the range 350–700 nm have been recorded as toluene solutions (Table 1). In all cases, shoulders in the visible region are observed superimposed upon an intense and broad feature tailing out of the UV region. The energies of these visible region absorptions increase with progressive incorporation of dithiocarbamate ligands. As previously noted for the series [V(NTol)(OR)$_x$Cl$_{(3-x)}$] (R = ^{t}Bu,2,6-Me$_2$C$_6$H$_3$) [7b], there is a correlation between $\delta(^{51}\text{V})$ and (ΔE^{-1}) for the [V(NTol)(S$_2$CNR$_2$)$_x$Cl$_{(3-x)}$] complexes as shown in Fig. 2. Such a correlation implies that the dominant factor governing the observed ^{51}V chemical shifts is the paramagnetic shielding term σ_{para} [7b,13].

Attempts to generate the d^1 systems [V(NTol)(S$_2$CNR$_2$)$_2$] from the corresponding [V(NTol)(S$_2$CNR$_2$)$_2$Cl] complexes **3**, as shown in eq. (2), have been only partially successful. Thus, treatment of either **3a** or **3b** with an excess of Zn powder in CH$_2$Cl$_2$ at room temperature afforded dark yellow–brown solutions after 18 h reaction time. Workup led to dark brown powders which displayed broad and indistinct ^{1}H NMR spectra. ESR spectra of these products (298 K, CDCl$_3$ solution) revealed the characteristic eight line spectra expected for V(IV) with a d^1_{xy} configuration (**5a**: g = 1.976, $A(^{51}\text{V})$ = 89.1 G; **5b**: g = 1.991, $A(^{51}\text{V})$ = 89.9 G). While these values are very close to those reported for the analogous vanadyl complexes [2,4b], elemental analysis results on complexes **5** indicated that these products were not obtained in a pure state.

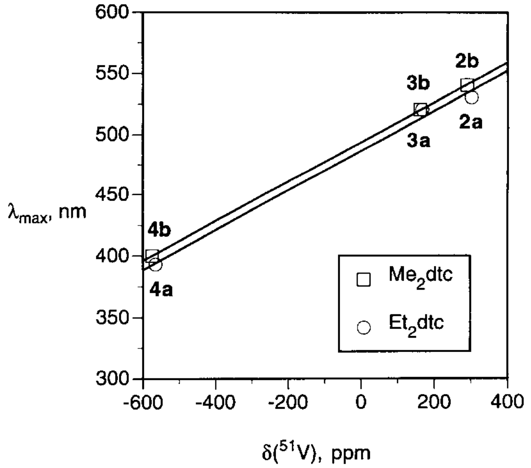
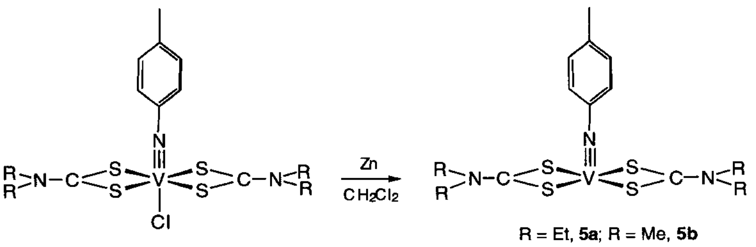


Fig. 2. Correlation of $\delta(^{51}\text{V})$ with visible region λ_{max}. See text for numbering scheme.

Phenylenedi-imido vanadium(V) complexes

A variety of organodi-imido bridged systems [L$_n$M≡N—R—N≡ML$_n$] are known for M = Mo, W, Re and U, but to our knowledge no such complexes have been reported for vanadium [14–17]. An entry point to such systems is provided by the *p*-phenylenedi-imido complex [Cl$_3$V≡NC$_6$H$_4$N≡VCl$_3$], **6**, which can be prepared in high yield as shown in eq. (3). **6** is obtained as a brown solid which is soluble (with adduct formation) in THF, but which is insoluble in other common organic solvents suggesting that unsolvated **6** exists as an intermolecularly associated species in the solid state. When **6** is dissolved in THF, an intense yellow–brown solution is formed from which a brown solid product **7** can be obtained. The ^{1}H NMR spectrum of **7** reveals the incorporation of three THF ligands per vanadium atom [eq. (4)].

The THF ligands are easily lost from **7**; storage *in vacuo* induces the formation of a complex shown by elemental analysis to be a mono-THF complex of **6**, *viz*. [Cl$_3$V≡NC$_6$H$_4$N≡VCl$_3$]·THF, in which we believe the THF molecule to be simply a guest in the



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R = Et, **5a**; R = Me, **5b**

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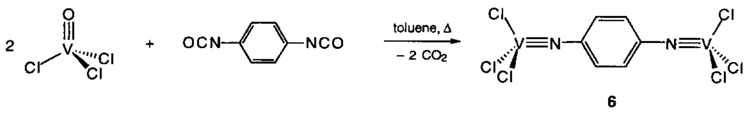

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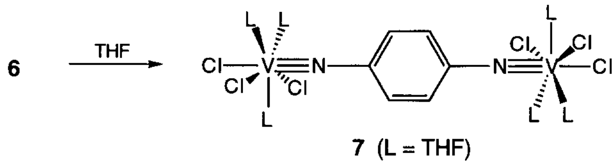


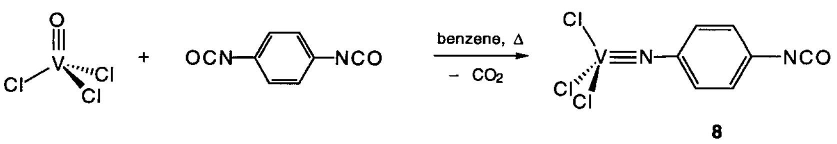
(4)

lattice. Similar facile loss of coordinated THF has been noted for analogous [ArN$\equiv$VCl$_3$] systems, for which both mono- and bis-THF adducts can be isolated [7b,18]. The ^{51}V NMR spectrum (CDCl$_3$, 298 K) of **7** displays a broad (fwhm = 2200 Hz) resonance at δ 380 ppm; the corresponding resonance for [TolN$\equiv$VCl$_3$(THF)] is observed at δ 374 ppm (fwhm = 1900 Hz) [7b].

The reaction between VOCl$_3$ and an equimolar amount of *p*-phenylene diisocyanate affords the mononuclear complex [OCN—C$_6$H$_4$N$\equiv$VCl$_3$], **8**, in high yield as shown in eq. (5). The ^{51} NMR resonance for **8** is observed at δ 283 ppm (fwhm = 750 Hz), within the range previously observed for various *p*-substituted phenylimido vanadium trichloride complexes, [X—C$_6$H$_4$N$\equiv$VCl$_3$] [7b].

The presence of the pendant isocyanate function within **8** suggested the possibility of using it to construct heterobimetallic phenylenedi-imido systems of the type [Cl$_3$V$\equiv$NC$_6$H$_4$N$\equiv$ML$_n$], but our preliminary investigations of such reactions have uncovered unexpected results. Thus, reaction between **8** and WOCl$_4$ in refluxing toluene [eq. (6)] produces a brown powder whose elemental analysis is a reasonable agreement with that expected for the presumptive product [Cl$_3$V$\equiv$NC$_6$H$_4$N$\equiv$WCl$_4$], **9**. As observed for **6**, **9** is insoluble in common non-donor solvents, but is readily soluble in THF. Surprisingly, however, the ^{1}H NMR spectrum of the material obtained after workup of a solution of **9** in THF revealed the presence of both **7** and its ditungsten analogue [(THF)Cl$_4$W$\equiv$N-C$_6$H$_4$N$\equiv$WCl$_4$(THF)] [14c]; the spectrum contained no resonances attributable to a THF complex of **9**. Thus, we conclude that an unusual example of an intermetal exchange of imido ligands [19] has occurred leading to a net disproportionation of **9**. As shown in Scheme 1 (which is a simplistic representation that does not attempt to account for additional intermolecular associations), a plausible intermediate in this redistribution reaction is a heterobimetallic *bis*-(μ-imido) species. At this stage, the actual nature of the brown product isolated from the reaction of eq. (6) remains uncertain—as does any potential involvement of THF in promoting the disproportionation—and distinguishing among the possibilities shown in Scheme 1 (i.e. authentic **9**, or the *bis*-(μ-imido) species, or a 1 : 1 mixture of homobimetallic species **6** and **10**) is not yet possible.

The chloride ligands of **6** undergo substitution by dithiocarbamates and *tert*-butoxide in reactions analogous to those of eq. (1) but, in reactions designed to replace either one or two chlorides at each vanadium center, ^{1}H NMR spectra of the products indicated that mixtures of variously substituted products were obtained. A pure product, **11**, has been obtained in the case of complete substitution of all six chlorides by [S$_2$CNEt$_2$] as shown in eq. (7). **11** is obtained as a mahogany solid in *ca* 60% yield. No discernable ^{51}V NMR resonance could be observed for **11**, presumably due to the extreme breadth of the signal. Similarly, the reaction of **6** with 6 equiv. of KO^{t}Bu proceeds with complete chloride substitution to pro-



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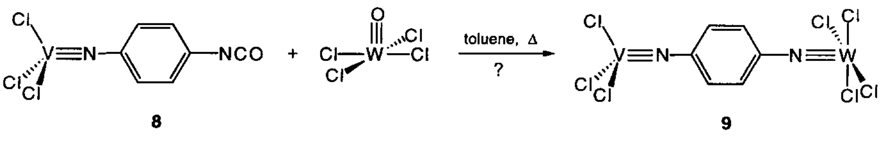

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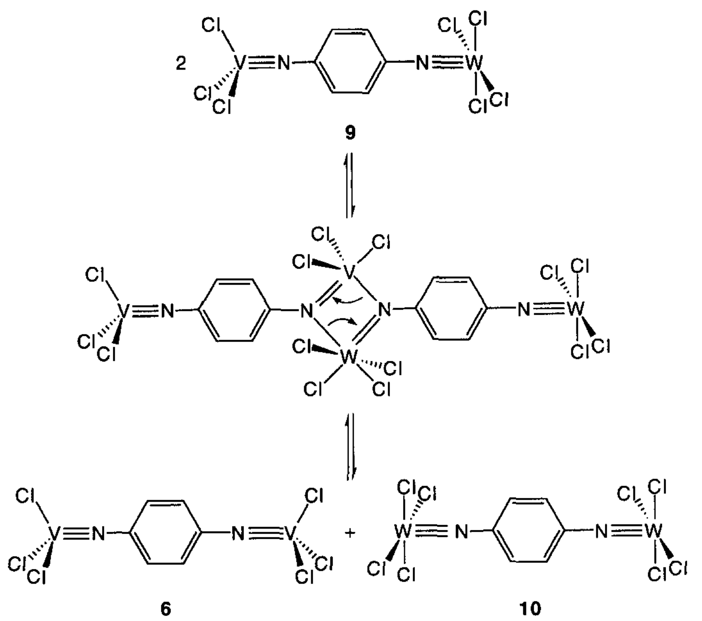
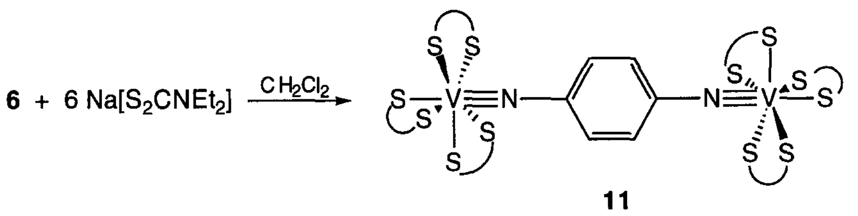
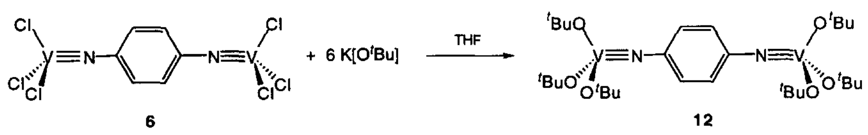


Scheme 1. A possible pathway for the disproportionation of **9**.



(7)



(8)

duce the hexakis(*tert*-butoxide) product **12** [eq. (8)]. **12** is obtained as a dark orange powder which is extremely soluble in common organic solvents, including hexane. The ^{51}V NMR resonance for **12** is observed at δ −638, a value only slightly downfield of that for the corresponding tolylimido system [TolN≡V(O^{t}Bu)$_3$] (δ −654) [7b]. Although the resonance for **12** is relatively narrow (fwhm = 345 Hz), ^{51}V–^{14}N spin coupling could not be resolved in this case; for [TolN≡V(O^{t}Bu)$_3$], this coupling constant was observed to be 111 Hz [7b].

EXPERIMENTAL

All reactions and manipulations were carried out either *in vacuo* or under an atmosphere of purified dry nitrogen. Solvents employed were dried and distilled prior to use. Sodium dialkyldithiocarbamate salts were prepared by treatment of the corresponding amine with NaOH in the presence of CS$_2$, and were dried *in vacuo* at 100°C prior to use. V(NTol)Cl$_3$ was prepared as previously described [7b]. Other reagents were obtained from commercial sources.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. ^{1}H (400.1 MHz) and ^{51}V (105.2 MHz) NMR spectra were obtained on an IBM/Bruker WM-400 instrument at 298 K and are referenced to internal Me$_4$Si and external VOCl$_3$/CDCl$_3$ (75% v/v), respectively. ESR spectra were recorded with a Bruker ER 200D spectrometer operating near 9.27 GHz and were calibrated using DPPH as an external field marker. Electronic spectra in the range 350–700 nm were recorded with a Cary 14 spectrophotometer.

V(NTol)(S$_2$CNEt$_2$)Cl$_2$ (2a)

A portion of V(NTol)Cl$_3$ (0.500 g, 1.91 mmol) was placed in a reaction flask and *ca* 5 g of Celite was added as a filtration aid. An addition sidearm containing $Na(S_2CNEt_2]$ (0.326 g, 1.91 mmol) was attached, and 25 cm^3 of CH_2Cl_2 was introduced by vacuum distillation. After complete dissolution of the vanadium complex, the dithiocarbamate salt was added to the stirred solution at room temperature, causing a rapid color change from dark green to orange–red. After 30 min, the reaction was filtered on a medium porosity sintered glass frit and the filtrate was taken to dryness. The dark red–purple solid product was triturated with pentane (*ca* 30 cm^3), collected by filtration and dried *in vacuo*. If necessary, the product can be recrystallized to remove traces of $V(NTol)(S_2CNEt_2)_2Cl$ (**3a**) by the addition of hexane to a concentrated CH_2Cl_2 solution. Anal. Calcd (found) for $C_{12}H_{17}N_2S_2Cl_2V$: C, 38.41 (38.92) ; H, 4.57 (4.89) ; N, 7.47 (7.49). ^1H NMR ($CDCl_3$) : δ 7.24 (AA′BB′ q, $J_{AB} = 7.92$ Hz, 4 H, $C_6H_4CH_3$), 3.86 (q, 4H, CH_2CH_3), 2.43 (*s*, 3H, $C_6H_4CH_3$), 1.34 (t, 6H, CH_2CH_3). ^{51}V NMR ($CDCl_3$): δ 301 (fwhm = 415 Hz). λ_{max} ($C_6H_5CH_3$) : 530 nm.

$V(NTol)(S_2CNMe_2)Cl_2$ (**2b**)

Prepared and purified as for **2a**, using $V(NTol)Cl_3$ (0.500 g, 1.91 mmol) and $Na[S_2CNMe_2]$ (0.273 g, 1.91 mmol); the product is a dark red solid. ^1H NMR ($CDCl_3$): δ 7.24 (AA′BB′ q, $J_{AB} = 8.02$ Hz, 4H, $C_6H_4CH_3$), 3.36 (s, 6H, CH_3), 2.43 (s, 3H, $C_6H_4CH_3$). ^{51}V NMR ($CDCl_3$): δ 289 (fwhm = 439 Hz). λ_{max} ($C_6H_5CH_3$) : 540 nm.

$V(NTol)(S_2CNEt_2)_2Cl$ (**3a**)

Prepared as for **2a**, using $V(NTol)Cl_3$ (0.500 g, 1.91 mmol) and $Na[S_2CNEt_2]$ (0.652 g, 3.80 mmol) and stirring at room temperature for 60 min. The dark red product is obtained as the CH_2Cl_2 hemisolvate. Anal. Calcd (found) for $C_{17.5}H_{28}N_3Cl_2S_4V$: C, 39.19 (39.07) ; H, 5.23 (5.53) ; N, 7.84 (7.72). ^1H NMR ($CDCl_3$) : δ 7.30 (AA′BB′ q, $J_{AB} = 8.32$ Hz, 4 H, $C_6H_4CH_3$), 5.29 (s, 1H, CH_2Cl_2) 3.82 (ABX_3 m, 4H, CH_2CH_3), 3.74 (ABX_3 m, 4H, CH_2CH_3), 2.43 (s, 3H, $C_6H_4CH_3$), 1.27 (t, 12H, CH_2CH_3). ^{51}V NMR ($CDCl_3$): δ 166 (fwhm = 2610 Hz). λ_{max} ($C_6H_5CH_3$) : 520 nm.

$V(NTol)(S_2CNMe_2)_2Cl$ (**3b**)

Prepared as for **2a**, using $V(NTol)Cl_3$ (0.500 g, 1.91 mmol) and $Na[S_2CNMe_2]$ (0.545 g, 3.81 mmol), and stirring at room temperature for 60 min ; the product is a dark red solid which can be purified by recrystallization from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$) : δ 7.31 (AA′BB′ q, $J_{AB} = 8.06$ Hz, 4 H, $C_6H_4CH_3$), 3.36 (s, 12H, CH_3), 2.42 (s, 3H, $C_6H_4CH_3$). ^{51}V NMR ($CDCl_3$) : δ 161 (fwhm = 1870 Hz). λ_{max} ($C_6H_5CH_3$) : 520 nm.

$V(NTol)(S_2CNEt_2)_3$ (**4a**)

Prepared as for **2a**, using $V(NTol)Cl_3$ (0.500 g, 1.91 mmol) and $Na[S_2CNEt_2]$ (0.978 g, 5.72 mmol), and stirring at room temperature for 90 min ; the product is a dark yellow solid which can be purified by recrystallization from CH_2Cl_2/hexane. Anal. Calcd (found) for $C_{22}H_{37}N_4S_6V$: C, 43.98 (43.60) ; H, 6.21 (6.22) ; N, 9.24 (9.18). ^1H NMR ($CDCl_3$): δ 7.03 (AA′BB′ q, $J_{AB} = 8.08$ Hz, 4H, $C_6H_4CH_3$), 3.81 (m, br, 12H, CH_2CH_3), 2.27 (s, 3H, $C_6H_4CH_3$), 1.27 (t, br, 15H, CH_2CH_3), 1.17 (t, br, 3H, CH_2CH_3). ^{51}V NMR ($CDCl_3$): δ −565 (fwhm = 1780 Hz). λ_{max} ($C_6H_5CH_3$) : 393 nm.

$V(NTol)(S_2CNMe_2)_3$ (**4b**)

Prepared as for **2a**, using $V(NTol)Cl_3$ (0.500 g, 1.91 mmol) and $Na[S_2CNMe_2]$ (0.818 g, 5.72 mmol), and stirring at room temperature for 90 min ; the product is a dark yellow solid which can be purified by recrystallization from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$) : δ 7.04 (AA′BB′ q, $J_{AB} = 8.14$ Hz, 4 H, $C_6H_4CH_3$), 3.42 (s, 6H, CH_3), 3.37, 3.35, 3.31, 3.28 (s, 3H each, CH_3), 2.27 (s, 3H, $C_6H_4CH_3$). ^{51}V NMR ($CDCl_3$) : δ −574 (fwhm = 1530 Hz). λ_{max} ($C_6H_5CH_3$) : 390 nm.

$V(NTol)(S_2CNEt_2)_2$ (**5a**)

A reaction vessel was charged with **3a** (0.300 g, 0.616 mmol) and Zn powder (1.45 g; 22.2 mmol), and CH_2Cl_2 (*ca* 50 cm^3) was admitted by vacuum distillation. The reaction mixture was stirred at room temperature for 24 h, and the color of the solution changed from orange–red to yellow–brown. The mixture was filtered, the filtrate was taken to dryness and the resultant dark brown powder was triturated with pentane, and dried *in vacuo*. Elemental analyses were not satisfactory. ESR ($CDCl_3$, 298 K): octet, $g = 1.976$, $A(^{51}V) = 89.1$ G.

$V(NTol)(S_2CNME_2)_2$ (**5b**)

Prepared as for **5a**, using **3b** (0.300 g, 0.695 mmol) and Zn powder (1.36 g, 20.8 mmol) and stirring at room temperature for 18 h; the product is a dark brown powder. Elemental analyses were not satisfactory. ESR ($CDCl_3$, 298 K): octet, $g = 1.991$, $A(^{51}V) = 89.9$ G.

p-$[Cl_3V{\equiv}NC_6H_4N{\equiv}VCl_3]$ (**6**)

A portion of $VOCl_3$ (2.5 cm^3, 26 mmol) in toluene (*ca* 120 cm^3) was added to a reaction flask bearing a reflux condenser, and an additional sidearm containing *p*—OCN—C_6H_4—NCO (2.00 g, 12 mmol) was attached. As the solution was being warmed to reflux temperature, the diiocyanate was added in portions over a few minutes. After 45 h of refluxing, the dark green–brown solution was cooled and the dark brown solid product was collected by filtration, washed with CH_2Cl_2 until the washings were colorless, and dried *in vacuo* at 55°C for 12 h to yield 4.23 g (84%) of **6**. anal. Calcd (found) for $C_6H_4N_2Cl_6V_2$: C, 17.21 (17.35); H, 0.96 (1.11); N, 6.69 (6.79).

p-$[(THF)_3Cl_3V{\equiv}NC_6H_4N{\equiv}VCl_3(THF)_3]$ (**7**)

At room temperature, 0.25 g of **6** were dissolved in 50 cm^3 of THF, and the intense yellow–brown solution was stirred at room temperature for 30 min. Evaporation of the solvent afforded a brown solid, which was dried *in vacuo* for 6 h. ^1H NMR ($CDCl_3$): δ 7.78 (s, 4 H, C_6H_4), 4.04 (t, 24H, OCH_2CH_2), 1.96 (quintet, 24H, OCH_2CH_2). ^{51}V NMR ($CDCl_3$): δ 380 (fwhm = 2200 Hz). The THF ligands of **7** are weakly bound and storage *in vacuo* induces the loss of five of them, forming a brown mono(THF) adduct, **6**·THF. Anal. Calcd (found) for $C_{10}H_{12}N_2OCl_6V_2$: C, 24.47 (24.69); H, 2.46 (2.92); N, 5.71 (5.76).

p-$[Cl_3V{\equiv}NC_6H_4{-}NCO]$ (**8**)

A solution of $VOCl_3$ (2.8 cm^3, 29 mmol) in 25 cm^3 of benzene was added dropwise over the course of 1 h to a stirred solution of *p*-OCN—C_6H_4—NCO (4.88 g, 30 mmol) in *ca* 100 cm^3 of benzene at 60°C. The green solution was refluxed for 36 h and solvent was removed *in vacuo*. The brown solid residue was washed with hexane (*ca* 30 cm^3), collected by filtration and dried *in vacuo* at 60°C to yield 6.74 g (79%) of **8**. Anal. Calcd (found) for $C_7H_4N_2OCl_3V$: C, 29.05 (28.94); H, 1.39 (1.45); N, 9.65 (9.68). ^1H NMR ($CDCl_3$): δ 7.32 (AA′BB′ q, J_{AB} = 8.30 Hz, 4 H, C_6H_4). ^{51}V NMR ($CDCl_3$): δ 283 (fwhm = 750 Hz).

p-$[Cl_3V{\equiv}NC_6H_4N{\equiv}WCl_4]$ (**9**)

A mixture of $WOCl_4$ (0.36 g, 1.03 mmol) and **8** (0.30 g, 1.03 mmol) was dissolved in toluene (*ca* 50 cm^3) forming a green solution. The solution was refluxed for 24 h, during which time the color became yellow–brown. After cooling to room temperature, the brown solid product was collected by filtration, washed with CH_2Cl_2 until the washings no longer showed a green color, and dried under vacuum to yield 0.36 g (60%) of a product analyzing as **9**. Anal. Calcd (found) for $C_6H_4N_2Cl_7VW$: C, 12.27 (12.36); H, 0.69 (1.20); N, 4.77 (4.07).

p-$[(Et_2NCS_2)_3V{\equiv}NC_6H_4N{\equiv}V(S_2CNEt_2)_3]$ (**11**)

A portion of $Na[S_2CNEt_2]$ (1.03 g, 6.0 mmol) was added to a suspension of **6** (0.42 g, 1.0 mmol) in 50 cm^3 CH_2Cl_2 containing *ca* 5 g of Celite as a filtration aid. The red reaction mixture was stirred at room temperature for 90 min and filtered. The residue remaining on the frit was washed with CH_2Cl_2 (2 × 50 cm^3); these washings were combined with the filtrate and taken to dryness. The dark red solid residue was washed with hexane (50 mL) and dried under vacuum to yield 0.65 g (59%) of mahogany **11**. anal Calcd (found) for $C_{36}H_{64}N_8S_{12}V_2$: C, 39.46 (39.86); H, 5.89 (6.06); N, 10.23 (10.33). ^1H NMR ($CDCl_3$): δ 6.78 (s, 4H, C_6H_4), 3.80 (m, br, 24H, CH_2), 1.25, 1.16 (overlapped m, br, 36H, CH_3).

p-$[(^tBuO)_3V{\equiv}NC_6H_4N{\equiv}V(O^tBu)_3]$ (**12**)

A portion of $K[O^tBu]$ (2.50 g, 22.3 mmol) was added to a solution of **6** (1.50 g, 3.58 mmol) in 100 mL of THF containing *ca* 3 g of Celite as a filtration aid. An orange color developed immediately and the reaction was stirred at room temperature for 18 h, filtered and the filtrate was taken to dryness. The solid residue was extracted into hexane (50 cm^3), filtered and taken to dryness yielding 1.77 g (77%) of dark orange **12**. ^1H NMR($CDCl_3$): δ 7.06 (s, 4H, C_6H_4), 1.41 (s, 54H, CH_3). ^{51}V NMR ($CDCl_3$): δ −638 (fwhm = 345 Hz).

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