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Synthesis and properties of isocyanate and isothiocyanate d^1- and d^2-complexes of vanadocene

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Abstract

The reactions of vanadocene and its halides Cp_2VCl and Cp_2VCl_2 with R_3MNCX ($M = Sn, Si, X = O, S$) and $R_2M(NCX)_2$ in various molar ratios have been studied. The reactions proceed either by an exchange of groups, with no change in the oxidation state of vanadium, or by an oxidative addition of pseudohalide ligand: $V^{II} \rightarrow V^{III}$; $V^{III} \rightarrow V^{IV}$. Oxidative addition results in the formation of $(R_3M)_2$ or gaseous hydrogen (in the reaction with HCl) in the reaction products.

We have prepared the first ever monomeric and readily oxidisable d^2-complexes of V^{III} of Cp_2VNCX-type and asymmetric d^1-complexes of $Cp_2V(Cl)NCX$ type, which, although rather stable in air, undergo disproportionation into symmetric d^1-complexes on heating. In transmetallation reactions the ligand activity is found to increase in the order $Cl < NCO < NCS$. The complexes were characterised by GLC analysis, IR and ESR spectroscopy. A general scheme for the disproportionation reaction of asymmetric complexes of vanadocene is supported by differential thermal analysis data.

Introduction

The carbenoid properties of vanadocene have been of great use for obtaining mono- and dicyclopentadienyl complexes in reactions with halogen derivatives, acyl peroxides, carbonic acids, etc. [1–3]. Vanadium is well-known for a great number of highly specific oxidative-reductive processes which result mainly in the formation of V^{IV} and V^{II} in the case of asymmetric covalent derivatives of V^{III} [4] or in the formation of V^{III} in the case of vanadocene derivatives [5]:

$$Cp_2VR_2 + Cp_2V \rightarrow 2Cp_2VR$$

Isocyanate and isothiocyanate derivatives of vanadocene have not been studied in detail, except the d^1-complexes of $Cp_2V(NCX)_2$ ($X = O, S$) type [6]. However, the

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presence of the pseudohalide ligand in these compounds led us to the idea of using them as biologocally-active compounds while investigating oxidative-reductive processes in the d^3-, d^2-, d^1-complexes of vanadocene. Here we examine the exchange reactions of vanadocene and its chlorides with organotin and -silicon isocyanates and isothiocyanates.

Results and discussion

As a follow-up to the investigation of organometallic heterocumulenes [7] we have carried out the first ever reaction of vanadocene and its mono- and dichlorides with organotin and -silicon isocyanates and isothiocyanates. Reaction of vanadocene with tributylstannylisocyanate, -isothiocyanate, trimethylsilylisothiocyanate or dibutylstannyldiisothiocyanate results in novel d^2-complexes of vanadocene: bis(π-cyclopentadienyl)vanadiumisocyanate (I) and bis(π-cyclopentadienyl)vanadium-isothiocyanate (II) (sealed ampoule, hexane or toluene, 20 °C, 3–20 d.; 120 °C, 4–5 h) [8]:

$$R_3MNCX + Cp_2V \rightarrow \underset{\text{(I), (II)}}{Cp_2VN{=}C{=}X} + 1/2(R_3M)_2 \qquad (1a)$$

$$\text{I: } X = O, \text{ II: } X = S$$

$$Bu_2Sn(NCS)_2 + 2Cp_2V \rightarrow 2Cp_2VNCS + 1/n(Bu_2Sn)_n \qquad (1b)$$

Neither an excess of the original isocyanate (2 : 1 to 4 : 1) nor further heating (150 °C, 5–8 h) resulted in the subsequent oxidation of V^{III} to V^{IV}. Neither was $Cp_2V(NCS)_2$ formed when the corresponding d^2-complex was heated with Me_3SiNCS under more severe conditions (190 °C, 10–15 h). However, reaction with $Bu_2Sn(NCS)_2$ or Bu_3SnNCS, Cp_2V led to the partial transformation of compound II into the d^1-complex, $Cp_2V(NCS)_2$.

Compounds I and II can also be obtained in high yields (up to 80%) in exchange reactions (eqs. 2a, 2b):

$$R_3MNCX + Cp_2VCl \rightarrow Cp_2VN{=}C{=}X + R_3MCl \qquad (2a)$$

$$(R_3M = Me_3Si,\ Et_3Sn,\ Bu_3Sn;\ X = O,\ S)$$

$$Bu_2Sn(NCS)_2 + 2Cp_2VCl \rightarrow 2Cp_2VN{=}C{=}S + Bu_2SnCl_2 \qquad (2b)$$

Reaction of the monochloride Cp_2VCl, with a double excess of R_3MNCX yields vanadocene d^1-complex with concomitant oxidation of V^{III} to V^{IV}. The reaction of tributylstannylisocyanate, -isothiocyanate or trimethylsilylisothiocyanate with Cp_2VCl (2 : 1) proceeds according to eq. 3 under conditions similar to those for reactions 1 and 2:

$$2R_3MNCX + Cp_2VCl \rightarrow Cp_2V(N{=}C{=}X)_2 + R_3MCl + 1/2(R_3M)_2 \qquad (3)$$

$$(R_2M = Me_3Si,\ Bu_3Sn,\ X = S;\ R_3M = Bu_3Sn,\ X = O)$$

In these reactions the formation of asymmetric d^1-complex $Cp_2V(NCX)Cl$ as an intermediate takes place. Special experiments have shown it to symmetrize into $[Cp_2V(NCX)_2 + Cp_2VCl_2]$ at 150–190 °C (eq. 4).

$$\underset{\text{(III)}}{2Cp_2V(NCS)Cl} \xrightarrow[150\,°C]{\text{toluene}} Cp_2V(NCS)_2 + Cp_2VCl_2 \qquad (4)$$

Asymmetric d^1-complexes have been obtained in exchange reactions from dichloride at room temperature:

$$R_3MNCX + Cp_2VCl_2 \rightarrow \underset{(III),\,(IV)}{Cp_2V(NCX)Cl} + R_3MCl \qquad (5)$$

$(R_3M = Bu_3Sn,\ X = O;\ R_3M = Me_3Si,\ X = S)$

A two-fold excess of Me_3SiNCS in reaction 5 also gives an asymmetric product, but an exact 1 : 1 stoichiometry is required in the case of tributylstannylisocyanate (100–150 ° C, 1–2 h). Here besides $Cp_2V(NCO)Cl$ (IV) a symmetric diisocyanate of vanadocene is formed, probably as a result of the symmetrization mentioned above. Asymmetric product was isolated after reaction of isocyanate (I) with hydrogen chloride in dioxane:

$$Cp_2VNCO \xrightarrow[\text{dioxane}]{\text{HCl}} \underset{(IV)}{Cp_2V(NCO)Cl} + 1/2H_2 \qquad (6)$$

Similarly, HCl transforms isothiocyanate II into the asymmetric d^1-complex, III.

When a mixture of Cp_2VCl_2 (or Cp_2TiCl_2) and Me_3SiNCS (or Bu_3SnNCO with molar ratio 1 : 2) is heated total substitution by Cl atoms of iso(or isothio)cyanate fragments takes place:

$$2R_3MNCX + Cp_2M'Cl_2 \rightarrow Cp_2M'(NCX)_2 + 2R_3MCl \qquad (7)$$

$R_3M = Bu_3Sn,\ X = O,\ S;\ R_3M = Me_3Si,\ X = S;\ M' = Ti,\ V$

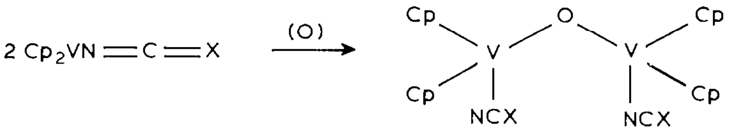
Diisocyanates of vanadocene are obtained in yields of over 90%, isothiocyanates – almost quantitatively, and the derivatives of titanocene – in yields of about 80%.

Thus, it has been found that pseudohalide ligands of N=C=X type readily displace halogen atoms from vanadocene and titanocene chlorides. In separate experiments we have shown that one pseudohalide ligand can be substituted by another, the substitution activity increasing in the following sequence: Cl < N=C=O < N=C=S. The reactivity of organotin pseudohalide is higher than that of organosilicon pseudohalide. For example, reaction with Bu_3SnNCS at room temperature in toluene solution readily transforms isocyanate I into isothiocyanate II (98%), whereas $Cp_2V(NCO)_2$ to transformed gradually into $Cp_2V(NCS)_2$ by reaction with Me_3SiNCS:

$$Bu_3SnNCS + Cp_2VNCO \rightarrow Cp_2VNCS + Bu_3SnNCO \qquad (8)$$

An attempt to prepare asymmetric isocyanate or isothiocyanate d^1-complex of vanadocene in the reaction of $Cp_2V(NCO)_2$ with Me_3SiNCS (1 : 1) was unsuccessful, and a mixture of symmetric vanadocene d^1-complexes was obtained in this case.

Compounds III and IV as well as most of Cp_2V d^1-complexes, green crystals of different shades, are not oxidized by atmospheric oxygen, whereas the blue-violet, monomeric d^2-complexes I and II, are readily oxidized to form the corresponding oxides V and VI similar to those for titanocene and zirconocene [6,8]:



(V: X = O , VI : X = S)

Table 1

Elemental analysis and some physical and chemical constants of vanadocene complexes.

Compound (N)	Colour	ESR [a]		IR [b] ν(cm^{-1})		Found (calc.)(%)				Empirical formula
		A_i(^{51}V) E	g_i	N=C=X	Cp	C	H	N	V	
Cp_2VNCO (I) [c]	blue-violet	–	–	2210	3100, 1005 800	59.73 (59.20)	4.56 (4.52)	5.74 (6.28)	22.81 (22.83)	$C_{11}H_{10}NOV$
Cp_2VNCS (II) [d]	black-violet	–	–	2060	3100, 1015 1005, 810	55.62 (55.23)	4.87 (4.21)	5.55 (5.86)	21.56 (21.30)	$C_{11}H_{10}NSV$
$Cp_2V(NCS)Cl$ (III) [e]	dark-green	73.5	1.9846	2090 2080	3090, 1025 1005, 830	47.69 (48.10)	3.74 (3.67)	5.14 (5.10)	18.45 (18.55)	$C_{11}H_{10}ClNSV$
$Cp_2V(NCO)Cl$ (IV) [f]	light-green	75.2	1.9831	2220	3100, 1015 1005, 830	50.97 (51.09)	4.20 (3.90)	5.39 (5.41)	20.09 (19.700	$C_{11}H_{10}ClNOV$
$[Cp_2V(NCO)]_2O$ (V)	green-brown	–	–	2210	3090, 1015 1005, 805	57.59 (57.16)	4.85 (4.36)	– (6.06)	22.27 (22.04)	$C_{22}H_{20}N_2O_3V_2$
$[Cp_2V(NCS)]_2O$ (VI)	brown	–	–	2060	3090, 1015 840	53.67 (53.44)	4.72 (4.08)	– (5.66)	20.56 (20.61)	$C_{22}H_{20}N_2OS_2V_2$
$Cp_2V(NCO)_2$ [g]	intense green	76.0 (76.1)	1.9786 (1.985)	2240, 2220 (2239, 2213)	3100, 1020 1010, 835					
$Cp_2V(NCS)_2$ [g]	yellow-green	73.1 (73.0, 73.4)	1.9816 (1.991, 1.982)	2082, 2062 (2092, 2066)	3090, 1025 1010, 840					
$Cp_2Ti(NCO)_2$ [g]	orange red	–	–	2230, 2200 (2235, 2196)	3100, 1030 1015, 825					
$Cp_2Ti(NCS)_2$ [g]	red-brown	–	–	2040 2020 (2058, 2017)	3090, 1015 825					

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[a] In THF: accuracy: A_i (^{51}V) ± 0.1 E, g_i ± 0.0001; data from ref. 8 are given in parentheses. [b] Data from ref. 9 are given in parentheses. [c] Found: M, 230.8, calc: 223.1 (cryoscopy in benzene). [d] Found: M, 291.0, calc: 239.2. [e] Found: Cl 12.76, calc: 12.91%. [f] Found: Cl 13.26, calc: 13.71%. [g] Known compounds.

The reaction of vanadocene with bis(dibutylstannyl)oxydiisocyanate $Bu_2Sn(NCO)OSn(NCO)Bu_2$ (toluene, 120 °C, 10 h) also yields compound V, which was confirmed by their IR spectra.

The composition and structure of new compounds was confirmed by elemental analysis, cryoscopic molar mass determination, and ESR- and IR-spectroscopy (Table 1).

In order to determine phase transitions and melting/decomposition points, compounds I–VI as well a $Cp_2V(NCO)_2$ and $Cp_2V(NCS)_2$ have been investigated by use of differential thermal analysis (DTA). From DTA data, isocyanate I melts at 173° C (reversible endothermic effect) and decomposes with exothermic effect in the range 230–260 ° C with maximum at 250 ° C (Fig. 1, curve 1). Decomposition of compound V proceeds in two steps (150–170 ° C, 200–250 ° C) with the first exothermic effect with maximum at 165 ° C, and the second with a maximum at 225 ° C (Fig. 1, curve 2). Isothiocyanate II decomposes in two steps without melting; the first irreversible exothermic effect being observed in the range 140–170 ° C with a maximum at 161° C, and the second – in the range 215–255 ° C with a maximum at 243° C (Fig. 1, curve 3). The decomposition of compound VI is slightly endothermic at 175 ° C and becomes pronounced in the range 220–270 ° C, with maximum at 240 ° C (Fig. 1, curve 4).

When heated $Cp_2V(NCO)_2$, decomposes in two steps with the first exothermic effect being observed between 210–250 °C, with a maximum at 230 °C and the second, which is less pronounced, in the range 260–290 °C (Fig. 2, curve 1).

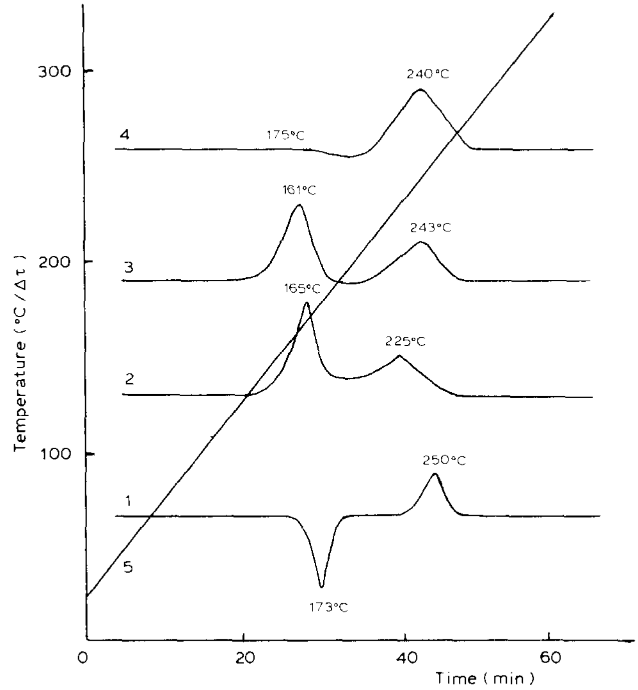

Fig. 1. Thermogram: 1 – Cp_2VNCO (I), 2 – $[Cp_2V(NCO)]_2O$ (V), 3 – Cp_2VNCS (II), 4 – $[Cp_2V(NCS)]_2O$ (VI), 5 – temperature change.

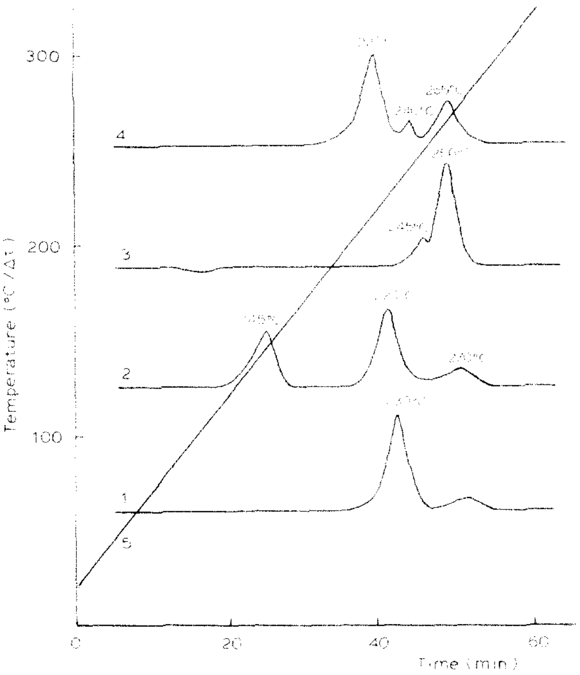

Fig. 2. Thermogram: 1 – $Cp_2V(NCO)_2$; 2 – $Cp_2V(NCO)Cl$ (IV); 3 – $Cp_2V(NCS)_2$; 4 – $Cp_2V(NCS)Cl$ (III); 5 – temperature change.

Thermal decomposition of $Cp_2VCl(NCO)$ occurs in three steps. Exothermic effects are observed between 130–150 °C, 215–240 °C and 250–280 °C, with maxima at 145, 220 and 270 °C, respectively (Fig. 2, curve 2). Decomposition of $Cp_2V(NCS)_2$ produces two exothermic effects: one – in the range 240–250 °C with a maximum at 245 °C, and another, which is more pronounced, from 250 to 275 °C with a maximum at 266 °C (Fig. 2, curve 3). Decomposition of $Cp_2V(NCS)Cl$ is similar to that of $Cp_2V(NCO)Cl$, i.e. it proceeds in three steps: the first exothermic effect is observed between 200–230 °C with a maximum at 220 °C, the second – from 235 to 250 °C with a maximum at 240 °C and the third – from 250 °C to 280 °C with a maximum at 265 °C (Fig. 2, curve 4).

The DTA data confirm the fact that under the action of atmospheric oxygen, compounds I and II are irreversibly transformed into new products, although no marked changes are observed in their IR spectra, and complexes $Cp_2V(NCX)Cl$ in the first step of decomposition are symmetrized into $Cp_2V(NCX)_2$ and Cp_2VCl_2 and then decompose further in their characteristic temperature ranges.

Experimental

All reactions were carried out under argon or under vacuum. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer. ESR data were recorded with a Bruker-ER-200D-SRC spectrometer in X-range with a working frequency of 9.4 GHz. The standard for the determination of the g-factor values was Mn^{2+} in the

Table 2

Reaction products of vanadocene, vanadocene chlorides and titanocene dichloride with organotin and -silicon pseudohalides.

Original compounds		Reaction conditions		Reaction products	
Reagent (mmol)	Substrate (mmol)	T, (° C)	Time, h	$Cp_2V(Ti)$-heterocumulene mmol (yield (%))	Other products, mmol (yield (%))
Cp_2V (9.45)	Bu_3SnNCO (9.49)	20	480	Cp_2VNCO, 3.80 (40)	$(Bu_3Sn)_2$ [b], 1.41 (30)
Cp_2V (5.18)	Me_3SiNCS (10.37)	120	4	Cp_2VNCS, 4.94 (95)	$(Me_3Si)_2$ [c], Me_3SiNCS [c]
Cp_2V (12.68)	Bu_3SnNCS (12.68)	20	48	Cp_2VNCS, 11.04 (87)	$(Bu_3Sn)_2$ [d], 4.88 (77)
Cp_2V (6.14)	$Bu_2Sn(NCS)_2$ (3.07)	20	240	Cp_2VNCS, 4.18 (68)	$(Bu_2Sn)_n$
Cp_2VCl (2.32)	Bu_3SnNCO (2.32)	20	72	Cp_2VNCO, 0.77 (33)	Bu_3SnCl, 2.00 (86)
Cp_2VCl (2.89)	Bu_3SnNCO (5.78)	120	3	$Cp_2V(NCO)_2$, 1.17 (40)	Bu_3SnCl 1.63 (56); $(Bu_3Sn)_2$ [b], 0.31 (22)
Cp_2VCl (1.41)	Me_3SiNCS (1.41)	20	480	Cp_2VNCS, 1.03 (73)	Me_3SiCl [c], 0.46 (33)
Cp_2VCl (4.20)	Me_3SiNCS (8.40)	120–150	10	$Cp_2V(NCS)_2$, 3.19 (76)	Me_3SiCl [c], 3.08 (73), $(Me_3Si)_2$ [c], 0.68 (32)
Cp_2VCl (2.77)	Bu_3SnNCS (2.77)	20	480	Cp_2VNCS, 2.10 (75)	Bu_3SnCl, 1.90 (68)
Cp_2VCl (3.30)	Bu_3SnNCS (6.60)	120	2	$Cp_2V(NCS)_2$, 2.36 (71)	Bu_3SnCl, 4.30 (65); $(Bu_3Sn)_2$ [b], 0.17 (11)
Cp_2VCl (2.86)	$Bu_2Sn(NCS)_2$ (1.43)	20	240	Cp_2VNCS, 2.01 (70)	Bu_2SnCl_2, 1.32 (92)
Cp_2VCl_2 (1.89)	Bu_3SnNCO (3.78)	20	240	$Cp_2V(NCO)_2$, 1.55 (82)	Bu_3SnCl 2.98 (79)
Cp_2VCl_2 (1.98)	Bu_3SnNCO (1.98)	150	2	$Cp_2V(NCO)Cl$, 1.66 (84)	Bu_3SnCl, 1.66 (84)
Cp_2VCl_2 (1.98)	Bu_3SnNCS (3.96)	20	120	$Cp_2V(NCS)_2$, 1.97 (99)	Bu_3SnCl, 3.35 (84.5)
Cp_2VCl_2 (3.97)	Me_3SiNCS (7.94)	120–150	5	$Cp_2V(NCS)_2$, 3.83 (96.5)	Me_3SiCl [b], 1.84 (23)
Cp_2VCl_2 (5.95)	Me_3SiNCS (11.90)	20	200	$Cp_2V(NCS)Cl$, 5.46 (92)	Me_3SiCl [b], Me_3SiNCS [b]
Cp_2VNCO (1.58)	Bu_3SnNCS (1.58)	20	72	Cp_2VNCS, 1.57 (99)	Bu_3SnNCO, 0.48 (30)
Cp_2TiCl_2 (4.01)	bu_3SnNCO (8.02)	120–150	10	$Cp_2Ti(NCO)_2$, 3.15 (78.5)	Bu_3SnCl, 7.46 (93)
Cp_2TiCl_2 (2.02)	Me_3SiNCS (4.04)	120–150	10	$Cp_2Ti(NCS)_2$, 1.60 (79)	Me_3SiCl [b]

[a] Reactions were carried out in toluene or hexane in evacuated sealed ampoules. [b] $(Bu_3Sn)_2$ is determined by iodometry in toluene. [c] $(Me_3Si)_2$ is determined by GLC.

crystal lattice of MgO. GLC analysis of products as carried out on a Tsvet-129 chromatograph with a catarometer detector, using a 300 × 0.4 cm column packed with SE-30 (5%) on Chromaton N-AW-HMDS (0.20–0.25 mm) (T 60 °C), with helium as the carrier gas (rate, 20 ml/min). Melting points and decomposition temperatures were determined by DTA using evacuated capillaries. Al_2O_3 was used as the standard. The temperature was incrased at a rate of 5 °C/min. The experimental data are given in Table 2.

Preparation of bis(π-cyclopentadienyl)vanadium isocyanate (I)

A mixture of tributylstannylisocyanate (3.15 g, 9.49 mmol) and vanadocene (1.71 g, 9.45 mmol) in 30 ml of hexane was kept for 20 d at room temperature in an evacuated sealed ampoule, and 0.85 g (40%) of a blue-violet, fine crystalline compound (I) was found to have separated. Found: C, 59.73; H, 4.56; N, 5.74; V, 22.11. $C_{11}H_{10}NOV$ calc: C, 59.20; H, 4.52; N, 6.28; V, 22.83%. $(Bu_3Sn)_2$ (0.82 g, 30%) was disilled from the reaction solution in vacuo. The yield of hexabutyldistannane was also checked by iodometric titration.

Similarly, a mixture of tributylstannylisocyanate (1.97 g, 5.93 mmol) and Cp_2V (0.54 g, 2.99 mmol) in hexane was heated at 120 °C for 4 h from the resulting mixture was isolated 0.20 g (30%) of compound I and 0.42 g (48%) of $(Bu_3Sn)_2$. Heating a mixture of Bu_3SnNCO (0.77 g, 2.32 mmol) and Cp_2VCl (0.50 g, 2.32 mmol) in toluene solution at 20 °C for 36 h yielded 0.17 g (33%) of compound (I) and 0.65 g (86%) of tributylstannylchloride.

Preparation of bis(π-cyclopentadienyl)vanadiumisothiocyanate (II)

Reaction of tributylstannylisothiocyanate (4.41 g, 12.68 mmol) with Cp_2V (2.30 g, 12.68 mmol) (20 °C, 48 h) yielded 2.64 g (87%) of compound II (blue-black fine crystalline powder). Found: C, 55.62; H, 4.87; N, 5.55; V, 21.56. $C_{11}H_{10}NSV$ calcd.: C, 55.23; H, 4.21; N, 5.86; V, 21.30%. 2.83 g (77%) of hexabutyldistannane was detected in the reaction solution.

In a similar way reaction of 0.31 g (1.41 mmol) of Cp_2VCl and 0.18 g (1.41 mmol) of Me_3SiNCS gave 0.25 g (73%) of compound (II) and 0.05 g (33% by GLC) of trimethylchlorosilane.

Reaction of Cp_2V (0.94 g, 5.18 mmol) with Me_3SiNCS (1.36 g, 10.37 mmol), Cp_2VCl (0.60 g, 2.77 mmol) with Bu_3SnNCS (0.96 g, 2.77 mmol), Cp_2V (1.11 g, 6.14 mmol) with $Bu_2Sn(NCS)_2$ (1.07 g, 3.07 mmol) or Cp_2VCl (0.62 g, 2.86 mmol) with $Bu_2Sn(NCS)_2$ (0.50 g, 1.43 mmol) gave 1.18 g (95%), 0.50 g (75%), 1.0 g (68%) or 0.49 g (71%) of compound II and $(Me_3Si)_2$ (GLC), Bu_3SnCl (0.62 g, 68%), $(Bu_2Sn)_n$ or Bu_2SnCl_2 (0.4 g, 92%), respectively.

Similarly, reaction of Bu_3SnNCS (0.55 g, 1.58 mmol) and Cp_2VNCO (0.35 g, 1.58 mmol) (hexane, 20 °C, 72 h) gave 0.37 g (97% of Cp_2VNCS. 0.16 g (31%) of Bu_3SnNCO was isolated by distillation in vacuo.

Preparation of bis(π-cyclopentadienyl)vanadiumisothiocyanate chloride (III)

A mixture of trimethylsilylisothiocyanate (1.56 g, 11.89 mmol) and Cp_2VCl_2 (1.5 g, 5.95 mmol) in toluene (35 ml) was vigorously stirred at room temperature for 200 h in a sealed ampoule. The ampoule was opened in air, the resulting dark-green fine crystalline precipitate was washed with successively toluene, alcohol and ether, and then dried to yield 1.50 g (92%) of compound III. Found: C, 47.69; H, 3.74; Cl, 12.76; N, 5.14; V, 18.45. $C_{11}H_{10}ClNSV$ calcd.: C, 48.10; H, 3.67; Cl, 12.91; N, 5.10;

V, 18.55%. Trimethylchlorosilane and an excess of Me_3SiNCS was detected (GLC) in the filtrate.

Preparation of bis(π-cyclopentadienyl)vanadiumisocyanate chloride (IV)

A mixture of triethylstannylisocyanate (1.13 g, 4.56 mmol) and Cp_2VCl (0.99 g, 4.56 mmol) in toluene (15 ml) was kept at room temperature for 24 h in an evacuated sealed ampoule till the colour of the reaction mixture changed from blue (Cp_2VCl) to an intense blue-violet (Cp_2VNCO). HCl in dioxane (0.34 g, 9.32 mmol) was added to the mixture in vacuo. The ampoule was opened in air, and after 24 h the reaction products were washed successively with toluene, alcohol and ether to give 0.50 (42%) of a green finely-divided precipitate of compound IV.

Preparation of bis(π-cyclopentadienyl)vanadiumdiisocyanate *

A mixture of tributylstannylisocyanate (1.25 g, 3.78 mmol) and Cp_2VCl_2 (0.48 g, 1.89 mmol) in toluene (30 ml) was kept in an evacuated sealed ampoule at room temperature for 240 h, to give 0.41 g (82%) of $Cp_2V(NCO)_2$ and 0.97 g (79%) of Bu_3SnCl. A mixture of Bu_3SnNCO (1.92, 5.78 mmol) and Cp_2VCl (0.63 g, 2.89 mmol) in toluene (30 ml) was kept at room temperature for 120 h. The resulting violet solution was heated at 120–150 °C for 3 h, then the ampoule was opened in air, and the brown precipitate washed with alcohol. The residue was extracted with acetone and the resulting green crystals were washed with alcohol and then CCl_4 to give 0.31 g (40%) of $Cp_2V(NCO)_2$. The filtrates were found to contain 0.53 g (56%) of Bu_3SnCl and 0.18 g (22%) of hexabutyldistannane.

Preparation of bis(π-cyclopentadienyl)vanadiumdiisothiocyanate *

A mixture of trimethylsilylisothiocyanate (1.10 g, 8.40 mmol) and Cp_2VCl (0.91 g, 4.20 mmol) in toluene (30 ml) was heated at 120–150 °C for 10 h to give 0.95 g (76%) of Cp_2V $(NCS)_2$. The filtrate contained 0.33 g (73%) of trimethylchlorosilane and 0.10 g (32%) of hexamethyldisilane based on GLC data. Similarly, reaction of Bu_3SnNCS (2.3 g, 6.60 mmol) with Cp_2VCl (0.71 g, 3.30 mmol) (120 °C, 2 h), Me_3SiNCS (1.04 g, 7.94 mmol) with Cp_2VCl_2 (1.0 g, 3.97 mmol) (120–150 °C, 5 h) or Bu_3SnNCS (1.38 g, 3.96 mmol) with Cp_2VCl_2 (0.5 g, 1.98 mmol) 20 °C, 120 h) gave 0.70 g (71%) of $Cp_2V(NCS)_2$, 1.4 g (65%) of Bu_3SnCl and 0.10 g (11%) of $(Bu_3Sn)_2$, 1.14 g (96.5%) of $Cp_2V(NCS)_2$ and 0.20 g (23%) of Me_3SiCl or 0.58 g (99%) of $Cp_2V(NCS)_2$ and 1.09 g (85.5%) of Bu_3SnCl, respectively.

Preparation of bis(π-cyclopentadienyl)titaniumdiisocyanate and -diisothiocyanata **

Similarly, reaction of Me_3SiNCS (0.53 g, 4.04 mmol) with Cp_2TiCl_2 (0.5 g, 2.02 mmol) or Bu_3SnNCO (2.68 g, 8.08 mmol) with Cp_2TiCl_2 (1.0 g, 4.04 mmol) yielded 0.47 g (80%) of $Cp_2Ti(NCS)_2$ and Me_3SiCl or 0.83 g (78.5%) of $Cp_2Ti(NCO)_2$, and 2.43 g (93%) of Bu_3SnCl, respectively.

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* A known compound

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