the entering-ligand dependence, though small it may be, cannot be excluded as in the case of a set of substituted salicylic acid systems.[14]

Enhanced Reactivity of $GaOH^{2+}$. As seen from Table III, k^*_{GaOH} is almost 2 orders of magnitude higher than k^*_{Ga}. The effect of bound ligands on the ease of replacement of the remaining water molecule has been interpreted by their ability to donate electrons to the central metal ion.[23,39,40] This effect is also reflected in the lower activation enthalpy for the k_{GaOH} path than for the k_{Ga} path (Table II).

For the complexation reactions dissociatively activated, values of $k_M/K_{os} = k^*_M$ and $k_{MA}/K_{os} = k^*_{MA}$ do not differ much from $k_M^{-H_2O}$, the rate constant of water exchange at M, and $k_{MA}^{-H_2O}$, the rate constant of water exchange at MA, respectively, if the compared rate constants are determined under similar conditions.[2,41] The bound-ligand effect on the water exchange has been interpreted by eq 9,[23,39,40] where E(A)

$$\log k_{MA}^{-H_2O} = \log k_M^{-H_2O} + \gamma E(A) \qquad (9)$$

refers to the electron donor constant of the coordinated ligand A and γ is a constant characteristic of the metal ion M. Taking into account the statistical factor arising from the number of water molecule available for exchange, the water-exchange rate constant at $GaOH^{2+}$ is expressed as

$$\log (k_{GaOH}^{-H_2O}/5) = \log (k_{Ga}^{-H_2O}/6) + 1.65\gamma$$

where 1.65 is the electron donor constant of OH^- as proposed by Edwards.[42] By the use of the rate constants listed in Table III, the γ value for Ga(III) is estimated to be 1.3. As stated previously,[23,40] a hard metal ion such as Ga(III) has higher γ value than less hard metal ions such as Co(II) ($\gamma = 0.47$), Ni(II) ($\gamma = 0.40$), and Zn(II) ($\gamma = 0.30$).

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Registry No. Gallium, 7440-55-3; tropolone, 533-75-5.

Supplementary Material Available: Listings of conditional rate constants $k_{o(H)}$ at atmospheric pressure (Table SI) and at high pressure (Tables SII and SIII) and a plot of {log ([GaA⁻]/[H₂A²⁻]) – log [Ga′]} vs. –log [H⁺] (Figure S1) (7 pages). Ordering information is given on any current masthead page.

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Reactivity of Decamethylvanadocene with Phenyl Isothiocyanate and Carbonyl Sulfide: Reactions Related to the Desulfurization of the Thiocarbonyl Group

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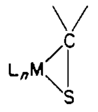
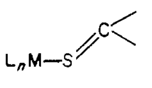
The reaction of decamethylvanadocene (I) with phenyl isothiocyanate gave $[(\eta^5\text{-}C_5Me_5)_2V(PhNCS)]$ (II) containing a η^2-C,S-bonded isothiocyanate unit. The X-ray structure of II showed that the CS fragment is accommodated in the cavity provided by the two bent C_5Me_5 ligands [V–C = 2.042 (7) Å; V–S = 2.444 (2) Å; C–S = 1.745 (7) Å]. Complex II is thermally labile, and it undergoes a thermal transformation occurring with the migration of the metal-bonded carbon to one of the C_5Me_5 rings. The resulting complex was $[(\eta^5\text{-}C_5Me_5)V(PhN\text{–}C(S)\text{–}C_5Me_5)_2]$ (III) whose structure was determined by an X-ray analysis. Complex III is a vanadium(III) derivative ($\mu_{eff} = 2.98$ μ_B at 297 K) containing a η^5-C_5Me_5 ring and two bidentate chelating thioamido groups [V–S = 2.458 (4), 2.449 (3) Å; V–N = 2.154 (4), 2.150 (4) Å]. Carbonyl sulfide reacted with $[(\eta^5\text{-}C_5Me_5)_2V]$ to form a rather labile crystalline adduct $[(\eta^5\text{-}C_5Me_5)_2V(COS)]$ [ν(C=O) = 1625 cm^{-1}] undergoing thermal transformation to $[(\eta^5\text{-}C_5Me_5)_2V(S_2)]$ and $[(\eta^5\text{-}C_5Me_5)_2V(CO)]$ by a pathway that is probably different from that of PhNCS. Crystallographic details for complex II: space group $P2_1/n$ (monoclinic), $a = 9.876$ (3) Å, $b = 14.650$ (5) Å, $c = 16.784$ (6) Å, $\beta = 94.40$ (3)°, $Z = 4$, $V = 2421$ (1) Å^3, $D_{calcd} = 1.25$ g cm^{-3}. The R final factor was 0.052 for 1686 observed reflections. Crystallographic details for complex III: space group $Pbca$ (orthorhombic), $a = 29.971$ (7) Å, $b = 14.292$ (4) Å, $c = 18.698$ (5) Å, $Z = 8$, $V = 7961$ (4) Å^3, $D_{calcd} = 1.21$ g cm^{-3}. The R final factor was 0.045 for 2644 observed reflections.

Introduction

The thiocarbonyl functional group has been largely used for modeling studies concerning the desulfurization of substrates like thioketones, isothiocyanates, and carbonyl sulfide promoted by mononuclear[1-6] or polynuclear[5b] metal complexes. Such a reaction proceeds via a preliminary coordination to the metal of the >C=S unit, which can display either a η^2-C,S (A) or a η^1-S (B) bonding mode.



A



B

Both kinds of (>C=S)–(metal) interactions have been identified and structurally proven in thioketones,[6-8] while the side-on coordination is preferred by isothiocyanates[9] and carbonyl sulfide.[10] Other bonding modes for thioketones have

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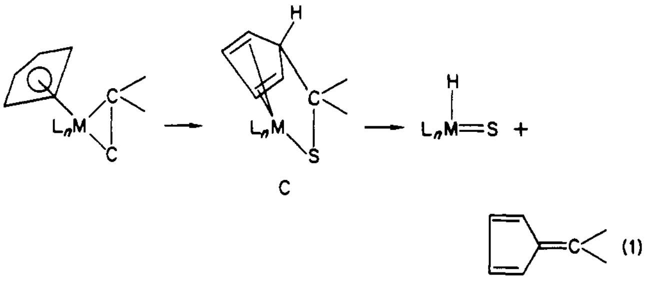
been discovered,[11] but their role in the desulfurization reaction seems to be less relevant. Formation of adducts like A or B is followed, in the desulfurization reaction, by the probable generation of a reactive carbon center, namely a free radical or a carbanion, from the metal–carbon bond cleavage (structure A) or by an electron transfer (structure B). Such a carbon-reactive intermediate can be trapped by another ligand on the metal. Cyclopentadienyl (cp ≡ η^5-C_5H_5) ligands have been found to undergo the transformation into fulvenes,[1,6] as exemplified in the following reaction:



(1)

Formation of fulvenes from reaction 1 is associated with the presence of hydrogen substituents on the cp ring.[1,6] Provided there is another substituent, it would be possible to trap the intermediate (C). Alper reported, however, that the desulfurization of thioketones did not occur when a (pentamethylcyclopentadienyl)iron complex was used instead of the unsubstituted one, $[cpFe(CO)_2]^-$.[1] Vanadocene was reported to react with thiobenzophenone to form a complex containing a η^2-C,S-metal-bonded thioketone unit, which underwent a thermal desulfurization to diphenylfulvene, in such a way that the bonding mode of the >C=S unit can be related to the desulfurization reaction.[6] The present study concerning the reactivity of decamethylvanadocene with phenyl isothiocyanate and carbonyl sulfide will provide significant support to the desulfurization pathways of the >C=S unit by metals. Although coordination of phenyl isothiocyanate to a transition metal is a rather common reaction,[3] only recently has a single structural report appeared for a complex containing PhNCS as ligand.[9] This is due to the fact that in most instances, even though the RNCS molecule appears initially to form a 1:1 complex,[3,12] the metal promotes further transformations of the organic molecule like desulfurization and reductive disproportionation. The present report is concerned with the isolation and the structural identification of a metal-η^2-C,S-bonded PhNCS and the products formed from its thermal decomposition.

Experimental Section

All the reactions described above have been carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Decamethylvanadocene was synthesized as previously reported.[13] IR spectra were measured with a Perkin-Elmer 283 spectrophotometer. Magnetic susceptibility was measured with a Faraday balance.

Reaction of Decamethylvanadocene with Phenyl Isothiocyanate. (a) Reaction at Room Temperature. A *n*-hexane solution (50 mL) of $[(\eta^5\text{-}C_5Me_5)_2V]$ (0.82 g, 2.55 mmol) was reacted with neat PhNCS (0.40 mL, 3.34 mmol). The resulting red solution, which was kept standing for 5 weeks at room temperature in the dark, gave bright green crystals (0.45 g). Anal. Calcd for $[(\eta^5\text{-}C_5Me_5)_2V(PhNCS)]$ (II), $C_{27}H_{35}NSV$: C, 71.05; H, 7.67; N, 3.07; S, 7.02. Found: C, 71.46; H, 7.83; N, 2.99; S, 7.08. The IR spectrum (Nujol) showed a strong >C=N– band at 1610 cm^{-1}. The complex has a magnetic moment of 1.77 μ_B at 297 K.

Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes II and III

	complex II	complex III
	$C_{27}H_{35}NSV$	$C_{44}H_{55}N_2S_2V$
cryst system	monoclinic	orthorhombic
space group	$P2_1/n^a$	*Pbca* [D_{2h}^{15}; No.61]
cell params[b]		
a, Å	9.876 (3)	29.791 (7)
b, Å	14.650 (5)	14.292 (4)
c, Å	16.784 (6)	18.698 (5)
α, deg	90	90
β, deg	94.40 (3)	90
γ, deg	90	90
V, Å^3	2421 (1)	7961 (4)
Z	4	8
D_{calcd}, g cm^{-3}	1.25	1.21
mol wt	456.6	727.0
cryst dimens, mm	0.27 × 0.32 × 0.64	0.17 × 0.20 × 0.32
linear abs coeff, cm^{-1}	4.92	32.9
diffractometer	Philips PW 1100	Siemens AED
scan type	$\omega/2\theta$	$\theta/2\theta$
scan speed	0.075°/s	3–12°/min
scan width, deg	1.40	*c*
radiation	graphite monochromated, Mo Kα (λ = 0.7107 Å)	Ni filtered Cu Kα (λ = 1.5418 Å)
2θ range, deg	6–48	6–120
reflcns measd	±*h*,*k*,*l*	*h*,*k*,*l*
total no. of unique data	3794	5201
criterion for obsd	$I > 3\sigma(I)$	$I > 2\sigma(I)$
no. of unique obsd data	1686	2644
no. of variables	271	441
overdetermination ratio	6.2	6.0
R factor	0.052	0.045

[a] A nonstandard setting of C_{2h}^5; No. 14. Coordinates of equivalent positions: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$. [b] Unit cell parameters were obtained by least-squares analysis of the setting angles of 20 carefully centered reflections chosen from diverse regions of reciprocal space.
[c] $(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$ $[\Delta\theta = ((\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda) \tan\theta]$.

(b) Reaction in Refluxing *n*-Heptane. To an *n*-heptane solution (50 mL) of $[(\eta^5\text{-}C_5Me_5)_2V]$ (0.94 g, 2.93 mmol) was added PhNCS (0.35 mL, 2.93 mmol). The resulting solution was refluxed for 60 h until the complete consumption of PhNCS, as checked by the IR spectrum. The resulting red-brown solution cooled at –30 °C gave on standing a brown, crystalline, and very air-sensitive solid (0.28 g). Anal. Calcd for $[(C_5Me_5)V(PhN\text{-}C(S)\text{-}C_5Me_5)_2]$ (III), $C_{44}H_{55}N_2S_2V$: C, 72.73; H, 7.58; N, 3.86; S, 8.82. Found: C, 72.44; H, 7.64; N, 3.65; S, 8.69. μ_{eff} = 2.98 μ_B at 297 K. The IR spectrum (nujol) shows a weak band at 1655 cm^{-1}. A small amount of unidentified product can be recovered from the solution.

(c) Thermal Decomposition of $[(\eta^5\text{-}C_5Me_5)_2V(PhNCS)]$. An *n*-heptane (50 mL) suspension of $[(\eta^5\text{-}C_5Me_5)_2V(PhNCS)]$ (0.63 g) was refluxed for 7 h. The resulting red-brown solution, concentrated to a small volume, gave on standing at –30 °C for 1 week complex III, as a brown crystalline solid.

Reaction of Decamethylvanadocene with Carbonyl Sulfide. An *n*-hexane (50 mL) solution of $[(\eta^5\text{-}C_5Me_5)_2V]$ (0.91 g, 2.83 mmol) was exposed to a COS atmosphere. On standing at room temperature for 1 week, the solution turned brown and deep yellow crystals of $[(\eta^5\text{-}C_5Me_5)_2VS_2]$[14] (XI) formed. Anal. Calcd for $C_{20}H_{30}VS_2$: C, 62.34; H, 7.79; S, 16.62. Found: C, 62.60; H, 7.82; S, 15.27. The mother liquor showed a strong CO band at 1850 cm^{-1} due to $[(\eta^5\text{-}C_5Me_5)V(CO)]$ (XII).[13b] If the reaction of $[(\eta^5\text{-}C_5Me_5)_2V]$ with COS is carried out at –30 °C a small amount of black crystalline solid can be recovered, $[(\eta^5\text{-}C_5Me_5)_2V(COS)]$ (X). Its thermal lability prevented any microanalytical determination. The solution did not show

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for Complex II

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
V	2441 (1)	2521 (1)	1101 (1)	C12	5520 (7)	1944 (6)	292 (5)
S	4229 (2)	1835 (1)	1995 (1)	C13	3151 (9)	474 (6)	275 (5)
N	4981 (6)	3662 (4)	1734 (3)	C14	515 (8)	1436 (6)	−473 (5)
C	4240 (7)	2959 (5)	1651 (4)	C15	1197 (9)	3558 (6)	−727 (5)
C1	3473 (8)	2989 (5)	−54 (4)	C16	−596 (9)	1419 (6)	1434 (6)
C2	4036 (7)	2141 (5)	176 (4)	C17	−950 (8)	3329 (6)	619 (5)
C3	2992 (8)	1490 (5)	127 (4)	C18	1365 (8)	4664 (5)	1369 (5)
C4	1778 (7)	1934 (5)	−155 (4)	C19	2647 (8)	3717 (7)	2915 (5)
C5	2073 (8)	2855 (5)	−267 (4)	C20	1508 (10)	1656 (7)	2937 (6)
C6	339 (8)	2239 (5)	1598 (5)	C21	6266 (7)	3732 (5)	2186 (4)
C7	241 (7)	3069 (5)	1187 (4)	C22	6953 (7)	3014 (6)	2572 (5)
C8	1160 (7)	3684 (5)	1572 (4)	C23	8218 (8)	3188 (7)	2996 (5)
C9	1792 (7)	3250 (6)	2246 (4)	C24	8721 (8)	4052 (8)	3032 (5)
C10	1270 (8)	2340 (6)	2261 (5)	C25	8061 (9)	4750 (7)	2656 (6)
C11	4246 (9)	3863 (6)	−133 (5)	C26	6824 (8)	4598 (6)	2228 (5)

Table III. Fractional Atomic Coordinates ($\times 10^4$) for Complex III

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
V	1491 (1)	3894 (1)	1575 (1)	C21	1893 (2)	5034 (5)	164 (3)
S1	845 (1)	4945 (1)	1421 (1)	C22	1986 (2)	4368 (5)	−356 (4)
S2	1710 (1)	2601 (1)	790 (1)	C23	2325 (3)	4555 (6)	−866 (4)
N1	1550 (1)	4841 (3)	684 (2)	C24	2568 (2)	5389 (7)	−823 (5)
N2	1017 (1)	2760 (3)	1555 (3)	C25	2474 (2)	6033 (6)	−301 (4)
C1	1789 (2)	4896 (4)	2392 (4)	C26	2139 (2)	5855 (5)	207 (4)
C2	1527 (2)	4243 (6)	2762 (3)	C27	1168 (2)	5276 (4)	698 (3)
C3	1734 (3)	3382 (5)	2691 (5)	C31	982 (2)	1327 (4)	749 (3)
C4	2114 (3)	3499 (6)	2273 (5)	C32	816 (2)	617 (4)	1290 (4)
C5	2151 (2)	4440 (5)	2088 (4)	C33	384 (2)	473 (5)	1192 (4)
C6	1714 (3)	5940 (5)	2398 (5)	C34	217 (2)	1070 (5)	623 (4)
C7	1119 (3)	4474 (8)	3210 (4)	C35	551 (2)	1583 (4)	367 (3)
C8	1609 (4)	2480 (7)	3075 (6)	C36	1301 (2)	837 (4)	225 (4)
C9	2466 (4)	2758 (8)	2103 (7)	C37	1136 (3)	147 (5)	1800 (4)
C10	2546 (3)	4903 (8)	1703 (5)	C38	93 (3)	−203 (6)	1605 (5)
C11	993 (2)	5977 (4)	151 (3)	C39	−270 (2)	1116 (5)	390 (5)
C12	1205 (2)	6940 (4)	223 (4)	C40	548 (3)	2314 (5)	−225 (4)
C13	1384 (2)	7199 (5)	−391 (4)	C41	577 (2)	2614 (4)	1856 (3)
C14	1326 (2)	6444 (5)	−910 (4)	C42	211 (2)	3062 (4)	1554 (4)
C15	1107 (2)	5735 (4)	−615 (3)	C43	−215 (2)	2916 (5)	1840 (4)
C16	471 (2)	6088 (5)	210 (4)	C44	−270 (3)	2364 (7)	2440 (5)
C17	1173 (3)	7485 (5)	916 (4)	C45	102 (3)	1928 (6)	2744 (4)
C18	1626 (3)	8103 (5)	−542 (5)	C46	529 (2)	2049 (5)	2462 (4)
C19	1497 (3)	6521 (6)	−1671 (4)	C47	1191 (2)	2208 (4)	1078 (3)
C20	959 (3)	4844 (5)	−945 (4)				

any band due to a carbonylic species. The IR spectrum (Nujol) showed an intense >C═O stretching frequency at 1625 cm^{-1}.

Reaction of Decamethylvanadocene with Thiobenzophenone. From the reaction of an *n*-heptane solution of decamethylvanadocene with Ph_2CS was recovered $[(\eta^5\text{-}C_5Me_5)_2V]$ substantially unconverted after some weeks.

X-ray Crystallography. Crystals of the complexes were sealed in thin-walled glass capillaries under nitrogen. The reduced cells were obtained by using TRACER.[15] A summary of the data collection is given in Table I.

The intensity data were collected at room temperature (22 °C). Individual reflection profiles[16] were analyzed for complex II, while the three-point technique was used for complex III. The structure factor amplitudes were obtained after the usual Lorentz and polarization reduction,[17] and the absolute scale was established by the Wilson method.[18] No absorption corrections were applied to the data because of the small linear absorption coefficient for complex II and because of the small crystal size for complex III. The structures were solved by a combination of Patterson and Fourier syntheses and refined by full-matrix least squares. Atomic scattering factors were taken from ref 19 for V, from ref 20 for S, C, and N, and from ref 21 for H. Anomalous dispersion terms were included for all atoms.[19] All the hydrogen atoms were located from difference Fourier syntheses and included prior to the final refinement as fixed contributors (B_{iso} = 7.8 Å^2). The final model converged to R = 0.052 and R_w = 0.051[22] for complex II and R = 0.045 for complex III. For complex II weights

Table IV. Bond Distances (Å) and Angles (deg) for Complex II

V–S	2.444 (2)	V–cp1	2.015 (7)	S–C	1.745 (7)
V–C	2.042 (7)	V–cp2	2.000 (7)	C–N	1.265 (9)
				N–C21	1.431 (9)

cp1–V–cp2	143.1 (3)	V–S–C	55.4 (2)
C–V–cp1	104.1 (3)	V–C–N	141.4 (6)
C–V–cp2	107.6 (3)	S–C–N	138.6 (6)
S–V–cp1	108.4 (2)	C–N–C21	126.8 (6)
S–V–cp2	107.3 (2)	N–C21–C26	115.2 (6)
S–V–C	44.7 (2)	N–C21–C22	125.2 (7)
V–C–S	80.0 (3)		

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(22) $R = \|F_o| - |F_c\|/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table V. Bond Distances (Å) and Angles (deg) for Complex III

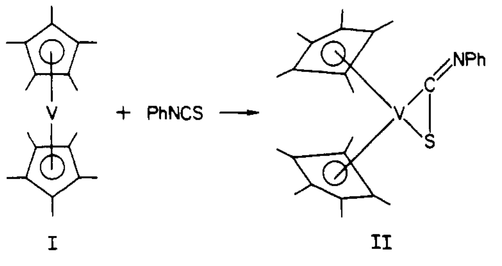
V-S1	2.458 (4)	V-N2	2.150 (4)
V-S2	2.449 (3)	V-cp1	1.983 (7)
V-N1	2.154 (4)		
S1-C27	1.726 (6)	S2-C47	1.731 (7)
N1-C27	1.297 (7)	N2-C47	1.299 (8)
N1-C21	1.437 (7)	N2-C41	1.441 (7)
C11-C27	1.524 (8)	C31-C47	1.534 (8)
C11-C16	1.567 (8)	C31-C36	1.534 (9)
C11-C12	1.520 (8)	C31-C32	1.516 (9)
C11-C15	1.512 (8)	C31-C35	1.514 (8)
C12-C13	1.319 (10)	C32-C33	1.316 (9)
C13-C14	1.461 (10)	C33-C34	1.452 (10)
C14-C15	1.325 (9)	C34-C35	1.325 (9)
N2-V-cp1	119.3 (3)	S2-V-N1	89.4 (1)
N1-V-cp1	119.8 (2)	S1-V-cp1	116.5 (2)
N1-V-N2	120.9 (2)	S1-V-N2	86.8 (1)
S2-V-cp1	116.6 (2)	S1-V-N1	65.8 (1)
S2-V-N2	66.2 (1)	S1-V-S2	126.8 (1)
V-S1-C27	79.8 (2)	V-S2-C47	79.7 (2)
V-N1-C27	102.4 (3)	V-N2-C47	102.0 (3)
V-N1-C21	134.6 (3)	V-N2-C41	134.4 (4)
C21-N1-C27	123.1 (5)	C41-N2-C47	122.9 (4)
N1-C27-C11	127.0 (5)	N2-C47-C31	127.8 (5)
S1-C27-N1	111.9 (4)	S2-C47-N2	111.9 (4)
S1-C27-C11	121.0 (4)	S2-C47-C31	120.3 (4)
C27-C11-C15	114.1 (5)	C47-C31-C35	109.6 (5)
C27-C11-C16	111.0 (5)	C47-C31-C36	112.3 (5)
C27-C11-C12	113.2 (5)	C47-C31-C32	114.5 (5)
C12-C11-C15	101.4 (5)	C32-C31-C35	101.5 (5)
C12-C11-C16	108.3 (5)	C32-C31-C36	108.8 (5)
C15-C11-C16	108.2 (5)	C35-C31-C36	109.5 (5)
C11-C12-C13	110.2 (6)	C31-C32-C33	109.3 (6)
C12-C13-C14	108.8 (6)	C32-C33-C34	110.2 (6)
C13-C14-C15	110.3 (6)	C33-C34-C35	109.4 (6)
C14-C15-C11	109.3 (5)	C34-C35-C31	109.4 (5)

were applied according to the scheme $w = [\sigma^2(F_o) + 0.0003F_o^2]^{-1}$, based on counting statistics, and this gave a satisfactory analysis of variance, $\sum w\Delta F^2$ vs. $|F|$, $\sin\theta$, and indices. The error in an observation of unit weight[23] was 2.1. Unit weights were used for complex III. No corrections for extinction were deemed necessary. In the final difference Fourier syntheses there were no peaks above the general background.

The final positional parameters for complexes II and III are given in Tables II and III, respectively; selected bond distances and angles are given in Tables IV, and V, respectively. The anisotropic thermal parameters, positional parameters for the hydrogen atoms, and nonessential bond lengths and angles are available as supplementary material.

Results and Discussion

Decamethylvanadocene reacted very slowly with phenyl isothiocyanate to form complex II at room temperature in *n*-hexane solution. Addition of a carbene-type metal complex like I to an organic functional group >C=X is a rather common reaction in vanadocene chemistry,[6,24,25] while it is quite rare in the case of decamethylvanadocene.[13b] The size of the cavity provided by the two bent C_5Me_5 rings and the greater basicity of the metal center are the major factors inducing such a change in the reactivity of the metal center vs. that observed in the case of unsubstituted vanadocene.[13b] Vanadocene reacted with thiobenzophenone to form $[(cp)_2V(\eta^2\text{-}Ph_2CS\text{-}C,S)]$,[6] while no reaction between I and Ph_2CS was observed. This can mainly be ascribed to the steric hindrance of the two phenyl groups bonded to the >C=S unit. A less crowded >C=S group like that in PhN=C=S reacts as shown in reaction 2. Complex II has been isolated as bright green crystals, with a magnetic moment of 1.77 μ_B at 297 K. The η^2-C,S bonding mode of the isothiocyanate group is largely accepted in the literature,[3,12] in spite of the fact that the only structural evidence for this is rather recent.[9] The IR spectrum (Nujol Mull) exhibits bands at 1610 and 620 cm^{-1}, for the C=N stretching vibration and for the MCS vibration, respectively.[3] The rather low value for the C=N frequency is due to significant electron transfer to the -NCS unit from the metal, which is very electron rich in decamethylvanadocene.[13b]



I II

(2)

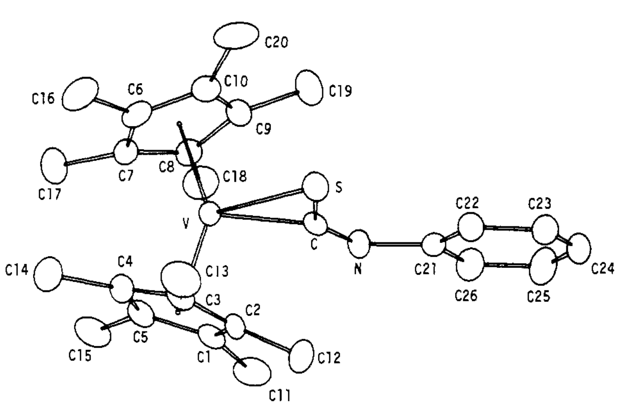
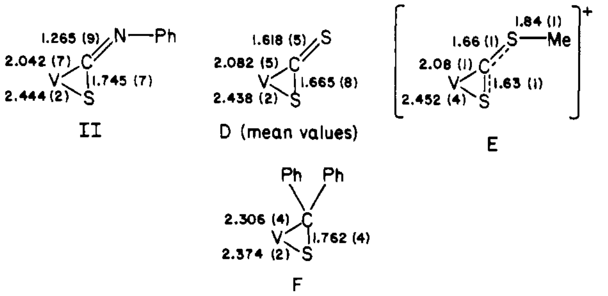


Figure 1. ORTEP diagram of complex II (30% probability ellipsoids).

Chart I



The structure of complex II consists of monomeric units of $[(\eta^5\text{-}C_5Me_5)_2V(PhNCS)]$ (Figure 1), where the two pentamethylcyclopentadienyl ligands are η^5 bonded to the metal in a bent arrangement to make a cavity in the equatorial plane for the -NCS ligand η^2-C,S bonded to the metal. The reciprocal orientation of the two cyclopentadienyl rings is nearly staggered. The presence of C_5Me_5 instead of cp ligands around vanadium causes a significant lengthening of the $(\eta^5\text{-}C_5Me_5)$-V distances [2.015 (7), 2.000 (7) Å] vs. the cp-V distances (1.92-1.97 Å)[6,24,25] and an enlargement of the $(\eta^5\text{-}C_5Me_5)$-V-$(\eta^5\text{-}C_5Me_5)$ angle [143.1 (3)°], which is in the highest range found for vanadocene derivatives.[6,24,25] These values are close however to those observed in $[(\eta^5\text{-}C_5Me_5)_2V(\eta^2\text{-}S_2)]$[14] [V-$(\eta^5\text{-}C_5Me_5)$ = 2.02 (2) Å; $(\eta^5\text{-}C_5Me_5)$-V-$(\eta^5\text{-}C_5Me_5)$ = 141.7 (4)°]. As found in decamethylvanadocene derivatives,[13b] the mutual repulsion of the methyl groups on the rings in complex II is reduced by their deviation out of the planes of

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[23] Defined as $[\sum w(|F_o| - |F_c|)^2/(\text{No} - \text{Nv})]^{1/2}$, where No is the number of observations and Nv is the number of variable parameters.

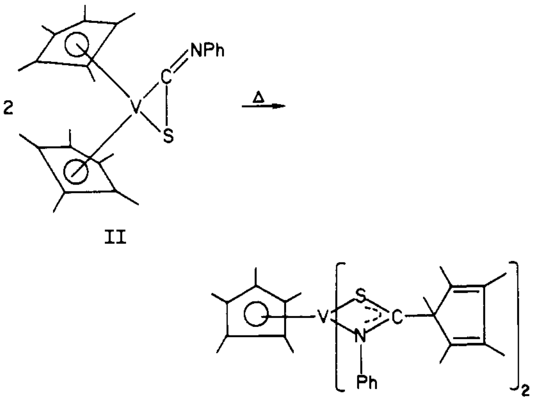
[24] (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 1918-1924. (b) *Ibid.* **1982**, *104*, 2019-2020. (c) Pasquali, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 165-171. (d) *Ibid.* **1981**, *20*, 1173-1178.

[25] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1612-1617.

the rings [from 0.080 (8) to 0.454 (8) Å], which assume a butterfly conformation (Table SVII). The atoms V, C, S, and N are coplanar (Table SVII), and the V–S bond distance [2.444 (2) Å] is close to those found in other vanadocene derivatives containing V–S bonds.[6,25,26] It would be useful to compare the geometry of the VCS unit with the corresponding ones found in $[(cp)_2V(CS_2)]$ (D),[25] $[(cp)_2V(CS_2Me)]^+$ (E),[25] and $[(cp)_2V(SCPh_2)]$ (F)[6] (Chart I).

The V–C bond distance in complex II is close to those found in D and E, even if significantly shorter, while the C–S distance is comparable with that found in F.[6] The planarity of the VCSN unit and the bond angles around the C carbon atom indicate an sp^2 hybridization state for this atom. Although the trend of bond distances seems to indicate a high localization of the double bond on the C–N unit [C–N = 1.265 (9) Å corresponds to the value (1.26 Å) accepted for a $C_{sp^2} = N_{sp^2}$ double bond], some delocalization all over the VSCNPh fragment is rather plausible, the dihedral angle between the equatorial plane and the phenyl ring being only 6.3 (3)°. This is further proven by the rather low C═N band occurring at 1610 cm^{-1}.[3]

Complex II was found to be thermally labile and, when heated in refluxing *n*-heptane, transformed according to eq 3. The original vanadium was transformed partially to III and to a complex (IV) that was not identified. Complex III has two unpaired electrons (2.98 μ_B at 297 K) and an IR spectrum showing a weak >C═N– band at 1655 cm^{-1}. The structure of complex III, whose nature was ascertained by an X-ray analysis, is crucial for understanding its genesis.

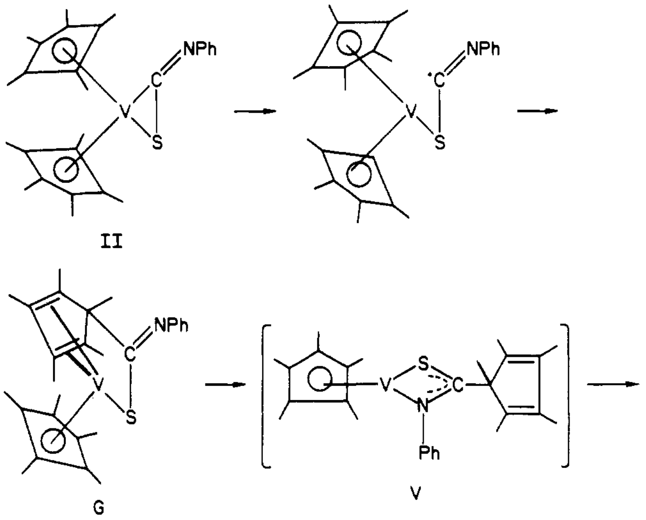


II

III

+ IV (3)

The structure of complex III consists of monomeric units of $[(\eta^5\text{-}C_5Me_5)V(PhN\text{–}C(S)\text{–}C_5Me_5)_2]$ (Figure 2) where only one cyclopentadienyl ring is η^5 bonded to the metal and two thioamido ligands are chelating vanadium through the sulfur and nitrogen atoms. The coordination polyhedron can be described as a severely distorted trigonal bipyramid with the V–N1–N2–$(\eta^5\text{-}C_5Me_5)$ group as the equatorial plane and the sulfur atoms at the apices. The distortion from a regular polyhedron is evidenced by the departure of the angles S1–V–N1 [65.8 (1)°] and S2–V–N2 [66.2 (1)°] from 90° and of the angle S1–V–S2 [126.8 (1)°] from 180°, and it is clearly due to the N- - -S bite. The V–S [2.458 (4), 2.449 (3) Å] and S–C [S1–C27 = 1.726 (6) Å; S2–C47 = 1.731 (7) Å] distances are not significantly different from those in complex II. The differences between the N–C distances in the two complexes are not particularly significant [N1–C27 = 1.297(7) Å; N2–C47 = 1.299 (8) Å]. The V–N distances [V–N1 = 2.154 (4) Å; V–N2 = 2.150 (4) Å] are close to those observed in other vanadocene derivatives,[24c] while the V–$(\eta^5\text{-}C_5Me_5)$ distance [mean value 2.007 (7) Å] is comparable to those in complex II. The differences between the N–C distances in the two complexes are not particularly significant [N1–C27 = 1.297(7) Å; N2–C47 = 1.299 (8) Å]. The V–N distances [V–N1 = 2.154 (4) Å; V–N2 = 2.150 (4) Å] are close to those observed in other vanadocene derivatives,[24c] while the V–$(\eta^5\text{-}C_5Me_5)$ distance [mean value 2.007 (7) Å] is comparable to those in complex II. The two coordination rings, rotated with respect to each other by 69.6 (1)°, show significant deviations from planarity (Table SVII), and this can be a consequence of steric hindrance between the bulky substituents at the thioamido ligand. The η^5-metal-bonded cyclopentadienyl ring is planar, and the methyl carbons are slightly outside the plane in the opposite direction to the metal, as in complex II [from 0.095 (8) to 0.180 (10) Å]. It is worthy to notice that, except for the substituents at the C_{sp^3} carbon atoms (C11 and C31), the methyl carbons of the two cyclopentadienyl substituents of the thioamido ligand lie on the respective ring planes (Table SVII). Carbon–carbon double bonds are localized in both rings [C12–C13 = 1.319 (10) Å; C14–C15 = 1.325 (9) Å; C32–C33 = 1.316 (9) Å; C34–C35 = 1.325 (9) Å]. The geometries of the two thioamido ligands are quite similar and differ only in the orientation of the C_5Me_5 and Ph rings with respect to the coordination rings [dihedral angles: V–S1–N1–C27 ∧ C21···C26, 69.7 (2)°; V–S1–N1–C27 ∧ C11···C15, 74.1 (2)°; V–S2–N2–C47 ∧ C41···C46, 80.6 (2)°; V–S2–N2–C47 ∧ C31···C35, 84.3 (2)°]. The transformation of II into III involved primarily the migration of the C_5Me_5 fragment from the metal to the carbon atom of the >C═S functional group. Such a process was observed in the metal cyclopentadienyl complexes, promoting desulfurization of thioketones.[1,6] The presence of hydrogen substituents on the cp ring was responsible, however, for a further evolution of such a proposed intermediate. The following reaction can take into account the results outlined above:



III (4)

The thermal decomposition will promote the cleavage of the metal–carbon bond, forming a reactive carbon species like a free radical attacking the C_5Me_5 ring. The transformation of the intermediate (G) is different from that shown for the related species (C) in reaction 1 because of the absence of hydrogen substituents at the cyclopentadienyl ring. Therefore, the intermediate (G) rearranges, forming a thioamido ligand. Such an organic fragment is the precursor of fulvenes from thioketones (see reaction 1) in the case of unsubstituted cyclopentadienyls, but it has never been identified. Complex V containing a thioamido ligand may be the most plausible precursor of complex III via a disproportionation of vanadium(II) and a ligand redistribution reaction. It seems that the desulfurization reaction of the >C═S organic functionality

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(26) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1980**, *19*, 3847–3850.

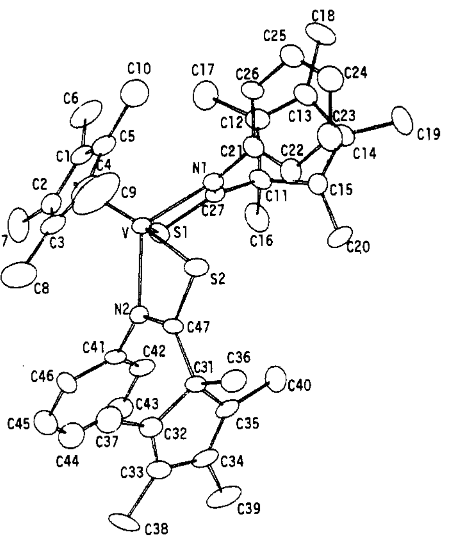
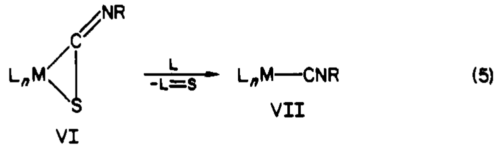


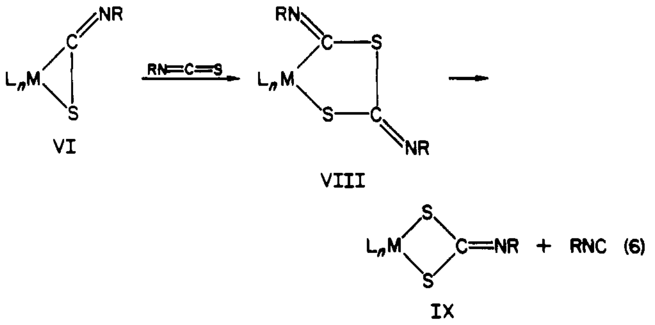
Figure 2. ORTEP diagram of complex III (30% probability ellipsoids).

is strictly related to its η^2-C,S anchoring mode and to the subsequent thermally induced carbon–metal bond cleavage. The carbon–metal bond cleavage could be either homolytic or heterolytic, and carbanion formation as well can occur.

Metal-promoted transformations of organic isothiocyanates, RNCS, lead, normally, either to the desulfurization[3,4,12] of the organic substrate with the consequent formation of RNC (reaction 5) or to its head-to-tail dimerization preceding the so-called disproportionation (reaction 6).[3,4,12] For both transformations, however, it seems that the M–S rather than the M–C cleavage is the key step.

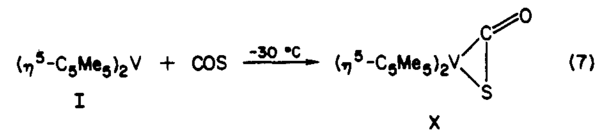


(5)



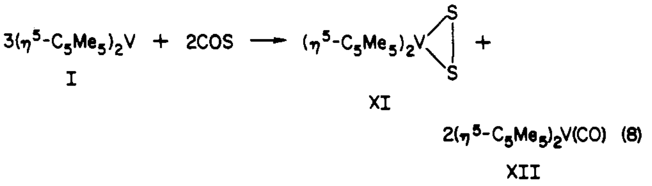
(6)

We did expect to find in the reaction of I with carbonyl sulfide a relationship with the reaction reported for PhNCS. This similarity was found, however, only in a few aspects. When reaction 7 was carried out at −30 °C, a 1:1 adduct was



(7)

isolated, though its characterization was difficult, because of the lability of X. Complex X was isolated in a crystalline form, though unstable at room temperature. The ν(C=O) stretching frequency is at 1625 cm^{-1} (Nujol mull). When reaction 7 was carried out at room temperature, desulfurization of COS and formation of a disulfur complex, XII, occurred, while carbon

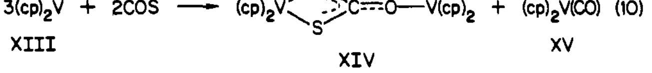


(8)

monoxide was complexed by I in the form of $(\eta^5\text{-}C_5Me_5)_2V(CO)$. The structure and a different synthesis of XI have been recently reported.[14] Reaction of COS with transition-metal complexes has been proposed to form in a preliminary step a 1:1 adduct like XI,[3,10,27] though no structural information is available so far on this type of complex. Carbonyl sulfide complexes can undergo desulfurization by phosphine ligands to the corresponding carbonyls,[3,10] or they can be involved in the so-called reductive disproportionation of COS[3,10]

$$2COS + 2e^- \rightarrow COS_2^{2-} + CO \qquad (9)$$

as exemplified by the reaction occurring with vanadocene:[26]

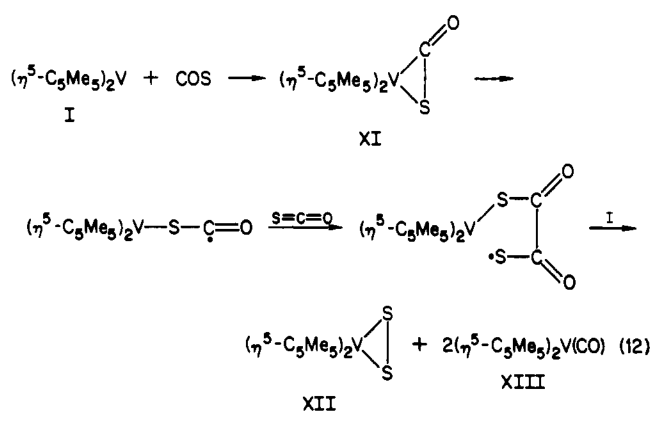


(10)

Desulfurization of COS by $[cpMn(CO)_2(thf)]$[28] is parallel to the reaction with decamethylvanadocene:

$$\underset{\text{XVI}}{4cpMn(CO)_2(thf)} + 2COS \xrightarrow{-THF} \underset{\text{XVII}}{\{[cpMn(CO)_2]_2S_2\}} + \underset{\text{XVIII}}{2cpMn(CO)_3} \qquad (11)$$

There is no suggestion, however, as to how reaction 8 can occur. The results outlined in the case of PhNCS and the isolation of X may justify the sequence proposed in eq 12,



(12)

where the key step is the V–C bond cleavage and the resulting free radical reacts with another molecule of COS.

Registry No. I, 74507-60-1; II, 91898-71-4; III, 91898-72-5; X, 91898-73-6; XI, 88423-78-3; XII, 83260-22-4.

Supplementary Material Available: Listings of observed and calculated structure factors, nonrefined hydrogen coordinates for complexes II (Table SI) and III (Table SII), thermal parameters (Tables SIII and SIV), nonessential bond distances and angles (Tables SV and SVI), and least-squares planes (Table SVII) (44 pages). Ordering information is given on any current masthead page.

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(27) Baird, M. C.; Wilkinson, G. *J. Chem. Soc., A* **1967**, 865–872. van Gaal, H. L. M.; Verlaan, J. P. J. *J. Organomet. Chem.* **1977**, *133*, 93–105.

(28) Herberhold, M.; Reiner, D.; Zimmer-Gasser, B.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1281–1285.