Table I

−78 °C	−116 °C	−196 °C
Data Reported[6]		
Br_2	SF_5Br, Br_2	SF_6, SF_5, SOF_2, SiF_4, S_2F_{10}
Data Obtained by Following the Reported Procedure[6]		
−78 °C	−116 °C	−196 °C
Br_2, SF_5Br, S_2F_{10}	SF_5Br, Br_2	SF_4, SF_5Br, SF_6
Data Obtained in the Modified Procedure		
−68 °C[a]	−116 °C	−196 °C
Br_2, S_2F_{10}	SF_5Br, Br_2	SF_6, SF_4

[a] Pyrex beads used in the trap.

°C) was carried out with continuous pumping for 4 h. The yield we obtained was 45%. After the reaction was repeated five times (with use of recovered bromine with 10 mmol of S_2F_{10} each time), the yield increased to 75%. The ^{19}F NMR spectroscopy showed the presence of large amounts of SF_5Br and unreacted S_2F_{10} in the −78 °C trap. Fox had stated that this trap contained only bromine. There was also some SF_5Br found in the −196 °C trap as detected by NMR signals at −5 and −88 ppm[7] with respect to SF_6.

The reaction was repeated with 10 mmol of S_2F_{10} and 100 mmol of Br_2 (150 °C, 16 h). The conditions of the fractionation were changed by (a) increasing the temperature of the first trap to −63 °C in order to allow a better transfer of SF_5Br from the first to second trap and (b) using glass beads in order to increase the surface area of the traps at −63 and −116 °C to prevent escape of Br_2 from the first into the second and of SF_5Br from the second into the third trap. The NMR spectra of the contents of the traps at −63 and −196 °C showed no presence of SF_5Br. SF_5Br was found only in the −116 °C trap, along with small amounts of bromine. Purification of SF_5Br from traces of bromine was completed by addition of a few milliliters of mercury to the SF_5Br trap at 0 °C.[6]

Table I compares the compounds in each trap for each method.

The yield that we obtained in our method was about 85% for SF_5Br and was not dependent on reusing the bromine or removal of a deleterious contaminant from the bromine, as suggested by Kovacina, Berry, and Fox.[6]

Registry No. SF_5Br, 15607-89-3; S_2F_{10}, 5714-22-7; Br_2, 7726-95-6.

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(7) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, **1**, 215 (1962).

Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy, and the Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica CNR, Università di Parma, 43100 Parma, Italy

Thiobenzophenone η^2-C,S Bonded to Vanadocene: A Precursor in Desulfurization Reactions

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Received June 8, 1982

The organometallic chemistry of thioketones has undergone a substantial recent development by Alper and his group.[1] Thioketones have been used as model substrates for studying the desulfurization reaction and for testing the thiophilicity of low-valent metal complexes.[1-5] The activation of the thiocarbonyl function depends on the interaction mode in a preliminary step of the >C=S unit with the metal. Thioketones, usually, coordinate to a metal center by using the lone pairs on the sulfur atom,[3] while a unique thioketone η^2-C,S bonded to a molybdenum complex was very recently structurally identified.[1] The ortho metalation of aromatic thioketones, occurring with a transformed[4] or retained[5] thiocarbonyl function and the desulfurization reaction,[6,7] producing carbenes, can be considered as the step following the preliminary thioketone–metal interaction.

We decided to use vanadocene, $(cp)_2V$ (cp = η^2-C_5H_5), in the reaction with a thioketone function, since vanadocene adds as a carbene-like species to a variety of organic functions and small molecules.[8] Vanadocene produces a remarkable change in the chemical properties of the metal-bonded unit by a significant electron transfer from the metal to the functional group.

The present report concerns the reaction occurring between vanadocene and thiobenzophenone leading to a η^2-C,S metal-anchored thiocarbonyl function. The thermal decomposition of such a complex generates a sulfur-containing vanadium complex and diphenylfulvene.

Experimental Section

All the reactions described were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Tetracarbonyl(η^5-cyclopentadienyl)vanadium(I),[9] bis(η^5-cyclopentadienyl)vanadium(II),[10] and thiobenzophenone[11] were prepared as in the literature. IR spectra were measured with a Perkin-Elmer 283 spectrometer. Magnetic measurements were made with a Faraday balance.

Synthesis of $[(cp)_2V(Ph_2CS)]$ (II). A toluene (15 mL) solution of vanadocene (0.55 g, 3.04 mmol) was reacted with thiobenzophenone (0.68 g, 3.43 mmol). The color of the solution changed rapidly from deep violet to deep red. The solution gave on standing for 12 h dark red crystals of $[(cp)_2V(Ph_2CS)]$ (0.65 g, 56%). The solid is very sensitive to air. Anal. Calcd for $[(cp)_2V(Ph_2CS)]$, $C_{23}H_{20}VS$: C, 72.82; H, 5.27; S, 8.44. Found: C, 72.92; H, 5.22; S, 8.20. The magnetic moment is 1.74 μ_B at 292 K.

Reaction of Complex II with Methyl Iodide. An *n*-hexane (50 mL) suspension of complex II (1.29 g, 3.40 mmol) was reacted with methyl iodide (2.0 mL, 32.0 mmol). When the mixture was heated for 10 min at 50 °C, $(cp)_2VI$[12] was formed as a maroon-green solid in almost quantitative yield. A toluene solution of II reacted with I_2 gave in quantitative yield (ca. 90%) $(cp)_2VI_2$.[8]

Thermal Decomposition of Complex II. A toluene (30 mL) solution of complex II (1.05 g, 2.77 mmol) was heated at 100 °C for 4 h. The color of the solution changed to maroon, and a brown microcrystalline solid was formed (0.19 g, 46% yield). Anal. Calcd for $[cpVS]_n$,

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(1) Alper, H.; Silavwe, N. D.; Birnbaum, G. I.; Ahmed, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6582–8 and references cited therein.
(2) Omae, I. *Coord. Chem. Rev.* **1979**, *28*, 97–115.
(3) Gingerich, R. G. W.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *132*, 377–86. Karcher, B. A.; Jacobson, R. A. *Ibid.* **1977**, *132*, 387–93. Alper, H.; Paik, H. N. *Ibid.* **1978**, *155*, 47–52. Dettlaf, G.; Behrens, U.; Weiss, E. *Ibid.* **1978**, *152*, 95–9.
(4) Alper, H.; Chan, A. S. K. *J. Am. Chem. Soc.* **1973**, *95*, 4905–13. Alper, H.; Root, W. G. *Ibid.* **1975**, *97*, 4251–7.
(5) Alper, H. *Inorg. Chem.* **1976**, *15*, 962–4; *J. Organomet. Chem.* **1974**, *80*, C29–C30.
(6) Alper, H.; Paik, H. N. *J. Am. Chem. Soc.* **1978**, *100*, 508–12.
(7) Alper, H. *J. Org. Chem.* **1975**, *40*, 2694; *J. Organomet. Chem.* **1974**, *73*, 359–64.
(8) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019–20. Pasquali, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 165–71, 1173–8 and references therein.
(9) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046–9.
(10) Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 2205–12.
(11) Gofton, B. F.; Braude, E. A. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 927–8.
(12) De Liefde Mejer, H. J.; Janssen, M. J.; Van der Kerk, G. H. J. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 831–45.

0020-1669/83/1322-0841$01.50/0

Table I. Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses for Complex II

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
V	2944 (1)	1917 (1)	310 (1)	C(25)	3590 (4)	554 (4)	3652 (3)
S	4721 (1)	771 (1)	1031 (1)	C(26)	4084 (4)	770 (3)	2908 (2)
C(30)	4311 (3)	2014 (3)	1610 (2)	H(1)	1726 (46)	4166 (44)	−389 (31)
C(1)	2584 (4)	3670 (3)	−433 (2)	H(2)	4032 (49)	4331 (42)	527 (31)
C(2)	3829 (4)	3753 (3)	77 (2)	H(3)	5613 (50)	2694 (45)	−36 (31)
C(3)	4636 (4)	2882 (4)	−203 (2)	H(4)	4358 (46)	1649 (44)	−1192 (30)
C(4)	3885 (4)	2259 (3)	−887 (2)	H(5)	1775 (48)	2607 (46)	−1573 (29)
C(5)	2635 (4)	2749 (4)	−1032 (2)	H(6)	2208 (46)	363 (44)	1622 (31)
C(6)	1732 (4)	661 (4)	1028 (3)	H(7)	615 (47)	2318 (46)	1214 (30)
C(7)	1030 (4)	1734 (4)	879 (3)	H(8)	217 (47)	2515 (46)	−349 (28)
C(8)	676 (4)	1856 (5)	−7 (4)	H(9)	1210 (46)	617 (41)	−1034 (30)
C(9)	1190 (5)	856 (5)	−396 (3)	H(10)	2318 (49)	−693 (44)	46 (32)
C(10)	1820 (5)	133 (4)	239 (3)	H(12)	4175 (46)	4212 (43)	2226 (30)
C(11)	5354 (3)	2977 (3)	1795 (2)	H(13)	5681 (45)	5770 (40)	2509 (31)
C(12)	5084 (3)	4095 (3)	2114 (2)	H(14)	8050 (49)	5227 (42)	2285 (30)
C(13)	6056 (3)	4950 (4)	2314 (3)	H(15)	8487 (46)	3369 (41)	1759 (31)
C(14)	7314 (3)	4725 (4)	2206 (3)	H(16)	6860 (48)	1961 (43)	1467 (30)
C(15)	7615 (3)	3638 (5)	1891 (3)	H(22)	2619 (47)	3278 (43)	2342 (29)
C(16)	6652 (3)	2768 (3)	1683 (2)	H(23)	1429 (47)	2896 (43)	3451 (30)
C(21)	3719 (3)	1769 (3)	2404 (2)	H(24)	2169 (48)	1155 (46)	4392 (32)
C(22)	2818 (4)	2554 (3)	2689 (3)	H(25)	3859 (49)	−240 (42)	3992 (30)
C(23)	2333 (4)	2329 (4)	3452 (3)	H(26)	4728 (48)	194 (44)	2717 (31)
C(24)	2720 (5)	1332 (4)	3931 (3)				

C_5H_5VS: C, 40.54; H, 3.38; S, 21.62. Found: C, 40.52; H, 3.40; S, 19.94. The mother solution, which was chromatographed on silica gel and eluted with toluene, gave, as an orange crystalline solid, diphenylfulvene, which was identified by comparison with an authentic sample (63% yield). The same desulfurization reaction can be achieved under milder conditions in the presence of PPh_3.

Reaction of [cpV(CO)$_4$] with Elemental Sulfur. Elemental sulfur, S_8 (0.70 g, 2.7 mmol), was refluxed for 4 h with [cpV(CO)$_4$] (0.74 g, 3.07 mmol) in toluene (25 mL) to give a microcrystalline maroon solid (0.14 g, 31%). Anal. Calcd for $[cpVS]_n$, C_5H_5VS: C, 40.54; H, 3.38; S, 21.62. Found: C, 39.93; H, 3.31; S, 21.90. The IR spectrum is identical with that of the compound formed from the thermal decomposition of complex II. The magnetic moment was 1.36 μ_B/vanadium atom at 292 K.

X-ray Crystal Structure Analysis of Complex II. A crystal of dimensions 0.13 × 0.20 × 0.53 mm was mounted on a Lindemann glass fiber under nitrogen. The choice of space group and preliminary lattice parameters were determined from rotation and Weissenberg photographs. Accurate unit cell dimensions were obtained from the least-squares refinement of the 2θ values of 20 general reflections ($2\theta > 60°$) measured on a Siemens AED automated X-ray diffractometer.

Crystal Data: $C_{23}H_{20}SV$; $M_r = 379.4$; monoclinic; $a = 10.280$ (1), $b = 11.249$ (1), $c = 15.889$ (2) Å; $\beta = 99.27$ (1)°; $V = 1813.3$ Å^3; $Z = 4$; $D_c = 1.390$ g cm^{-3}; $F(000) = 788$; Cu Kα radiation; $\lambda = 1.5418$ Å; μ(Cu Kα) = 56.7 cm^{-1}; space group $P2_1/n$ from systematic absences.

Data Collection. The crystal was mounted with its [001] axis parallel to the ϕ axis of the Siemens diffractometer. A total of 3050 independent reflections were measured ($6° < 2\theta < 130°$), of which 2516 with intensity $> 2\sigma(I)$ were considered observed and used for the structure determination. Nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) was used and the θ–2θ scan method employed with a scan speed related to the number of counts on the peak (lowest speed 2.5° min^{-1}). One reflection was remeasured after 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection. Intensities were measured with use of the "five-point" technique.[13] The data were corrected for Lorentz and polarization effects. No absorption correction was made ($\mu\bar{r} = 0.4$) due to the irregular shape of the crystal and the difficulties in indexing crystal faces. Thermal coefficients are therefore influenced by this omission.

Structure Solution and Refinement.[14] The structure was solved by the heavy-atom method starting from a three-dimensional Patterson synthesis, which gave the position of the vanadium atom. The remainder of the molecule was located from a Fourier synthesis phased by the metal atom. Refinement was by full-matrix least squares, first isotropically to an R value of 0.110 and then anisotropically to $R = 0.072$. At this stage a difference Fourier synthesis located all the hydrogen atoms, which were refined with isotropic thermal parameters in the final cycles. Convergence was obtained at an R value of 0.056 with the weighted residual R_w of 0.058. The weighting scheme used in minimizing the funciton was $\sum w|\Delta F|^2$, where $w = k/[\sigma^2(F_o) + |g|F_o^2]$; k is determined after each structure factor calculation and refined by fitting $(|F_o| - |F_c|)^2$ to $(\sigma^2(F_o) + |g|(F_o^2)/k$. The value for g was that giving the smallest variation of the mean value of $w(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o; in the final refinement $k = 1.000$ and $g = 0.002$. The error in an observation of unit weight was 1.27. The overdetermination ratio was NO:NV = 2516:306 = 8.2:1. In the final refinement no parameter shifted by more than 0.3 times its standard deviation. A final difference Fourier synthesis was featureless with no significant peak above the general background. No evidence for secondary extinction was found. Anomalous scattering corrections were included in all structure factor calculations. Scattering factors were taken from ref 15 for V, from ref 16 for S and C, and from ref 17 for H. Final atomic positions are quoted in Table I. Thermal parameters are listed in Table SI; bond distances and angles are in Tables II and SII.[18]

Table II. Selected Bond Distances[a] (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for Complex II, $[(cp)_2V(Ph_2CS)]$

V–S	2.374 (2)	S–C(30)	1.762 (4)
V–C(30)	2.306 (4)	C(30)–C(11)	1.519 (5)
V–cp(1)[b]	1.972 (4)	C(30)–C(21)	1.512 (4)
V–cp(2)[b]	1.971 (4)		

V–C(30)–S	70.0 (1)	S–V–C(30)	44.2 (1)
V–C(30)–C(11)	121.1 (2)	S–V–cp(1)	112.5 (1)
V–C(30)–C(21)	118.0 (2)	S–V–cp(2)	108.4 (1)
S–C(30)–C(11)	116.5 (2)	C(30)–V–cp(1)	110.4 (1)
S–C(30)–C(21)	117.0 (2)	C(30)–V–cp(2)	113.6 (2)
C(11)–C(30)–C(21)	109.6 (3)	cp(1)–V–cp(2)	133.9 (2)
V–S–C(30)	65.9 (1)		

[a] C–H distances range from 0.94 (5) to 1.14 (5) Å. [b] cp(1) and cp(2) are referred to the centroids of the rings C(1)–C(5) and C(6)–C(10), respectively.

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(13) Hoppe, W. *Acta Crystallogr., Sect. A* **1969**, *A25*, 67–76.

(14) Computer programs used on a Cyber 7600 computer of the "Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Casalecchio, BO)" were those of the SHELX-76 system (G. M. Sheldrick, University of Cambridge, England). Calculations were performed with the financial support of the University of Parma.

(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–4.

(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

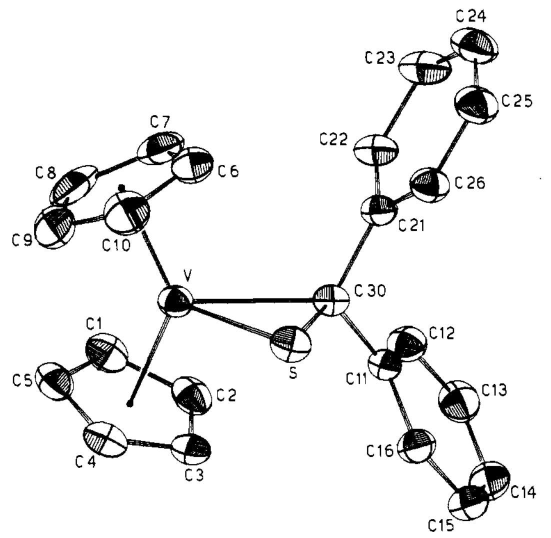
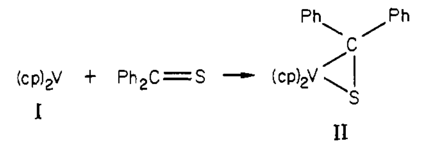


Figure 1. ORTEP view of the molecular structure of $[(cp)_2V(Ph_2CS)]$.

Results and Discussion

A toluene solution of vanadocene (I) reacted with thiobenzophenone, $Ph_2C{=}S$, according to eq 1. Complex II was



(1)

$$(cp)_2V + Ph_2C{=}S \rightarrow (cp)_2V(Ph_2CS)$$

cp = η^5-C_5H_5

obtained as very air-sensitive red crystals. The thiocarbonyl function is displaced from II by the action of I_2 and CH_3I, to form $(cp)_2VI_2$[8] and $(cp)_2VI$,[12] respectively. Complex II, which can be viewed as resulting from the carbene-like addition of the metal to the thiocarbonyl function, has a magnetic moment of 1.74 μ_B at 292 K.

The structure proposed for complex II is based mainly on the results of the X-ray analysis. Figure 1 shows an ORTEP view of the molecular structure of II. The most relevant bond distances and angles are reported in Table II. The two cp rings, which are η^5 bonded to vanadium, are bent away (cp(1)–V–cp(2), 133.9 (2)°) to make a room in the equatorial plane of the molecule for the $>C{=}S$ unit. The reciprocal orientation of the cp rings is eclipsed and the V–cp($\perp$) distances are as follows: V–cp(1), 1.972 (4) Å; V–cp(2), 1.971 (4) Å (Table II). All the other structural parameters concerning the $[(cp)_2V]$ unit moiety are as expected.[8,9] The structural features of the [VCS] unit deserve great attention, and they are compared in Figure 2 with the corresponding ones found in the complexes $[(cp)_2V(CS_2)]$[20] (III) and $[(cp)_2V(CS_2Me)]^+$ (IV).[20] V–S bond distances are comparable in the three complexes, while C–S and V–C bond distances within the [VCS] unit are significantly longer in complex II. The carbenoid nature of the carbon atom in complexes III and IV, having a π interaction with adjacent heteroatoms, causes an electronic delocalization over all the three atoms of the CS_2 unit. A comparable C–S bond distance (1.769 (2) Å) is found in the thiocamphor molybdenum complex, where the thioketone displays a similar η^2-C,S bonding mode.[1] The C–S bond distance is significantly longer than that found in free $Ph_2C{=}S$ (1.636 (9) Å).[21] Very few data are so far available on vanadocenes bearing an additional V–C bond.[8,19] In all cases, however, the V–C bond distance is significantly shorter than that found in complex II.

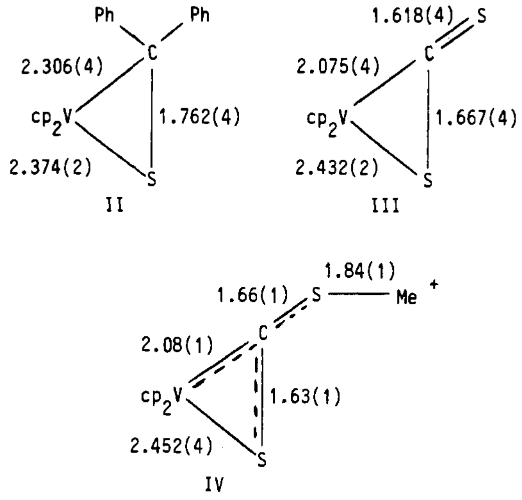
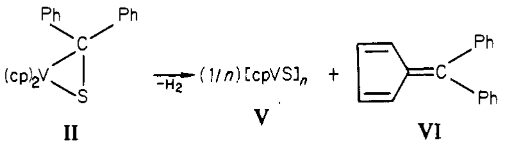


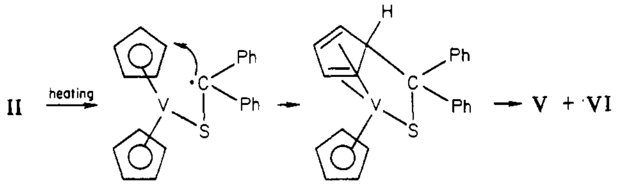
Figure 2.

Complex II is thermally labile, and when it is heated at 100 °C in toluene solution, it undergoes the transformation

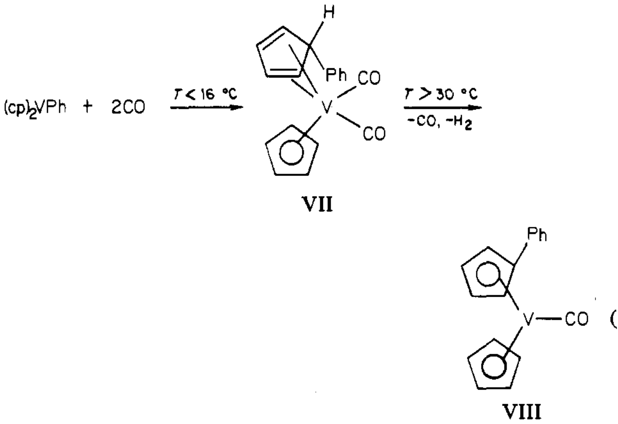


(2)

The highly insoluble complex V crystallized, while diphenylfulvene was isolated from the solution in a significant yield. Such a transformation of complex II can be achieved under milder conditions in the presence of PPh_3. Few hypotheses can be made on the occurrence of the vanadocene-promoted desulfurization of thiobenzophenone (reaction 2). The thermal lability of the V–C σ bond may be the reason for a homolytic cleavage of the V–C bond in complex II.[12] It can occur in a preliminary step, generating a carbon free radical, which then attacks one of the cp rings (eq 3). Migration of a phenyl group to one of the cp rings of the vanadocene unit was observed in the reaction of $[(cp)_2VPh]$ with carbon monoxide[22] (eq 4). Conversion of VII into VIII with the



(3)



(4)

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[18] See paragraph at end of paper regarding supplementary data.

[19] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282–7.

[20] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1612–7.

[21] Rindorf, G.; Carlsen, L. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1179–82.

subsequent loss of hydrogen occurs on gentle heating. Reaction 4 is strongly reminiscent of reaction 3. A similar mechanism was proposed by Alper to interpret the desulfurization of thiobenzophenones by $[cpM(CO)_n]^-$ (M = Fe, $n = 2$; M = Mo or W, $n = 3$).[6] Such a reaction led to the cleavage of the cp–metal bond and to the formation of diarylfulvenes.

For clarification of the nature of V, the reaction of elemental sulfur with $[cpV(CO)_4]$[9] was carried out (eq 5). Compound

$$[cpV(CO)_4] + {}^1/_8S_8 \rightarrow (1/n)\underset{\mathrm{V}}{[cpVS]_n} + 4CO \qquad (5)$$

V was obtained as a microcrystalline solid from reaction 5. There is, however, a striking difference in composition, magnetic properties, and IR spectrum between complex V and $[(cp)_2V_2S_5]_n$ proposed to form in the reaction of $[cpV(CO)_4]$ with elemental sulfur in refluxing toluene for 16 h. Such a difference may be due to the significant difference in the experimental conditions.[23] The crucial point is, probably, the fact that the final solution was handled in the air. This might cause the transformation of a preliminary compound coming from reaction 5. We did not achieve a satisfactory knowledge of the nature of V because of its low solubility. Analytical data agree with the proposed formula, for which we found a magnetic moment of 1.36 μ_B at 292 K per vanadium atom. This cannot help in proposing a plausible structure for V in the absence of any information concerning its molecular complexity. We would draw attention to the close similarity between the desulfurization of thiobenzophenone and the deoxygenation of N_2O,[24] both promoted by vanadocene. The latter reaction produces a polynuclear monocyclopentadienylvanadium complex, $[(cp)_5V_5O_6]$ (IX). The resemblance between V and IX is not only restricted to their origin but can be extended, eventually, to their molecular complexity and to their magnetic properties.

Acknowledgment. We thank the CNR (Rome) for financial support.

Registry No. I, 1277-47-0; II, 84332-78-5; V, 84332-80-9; I_2, 7553-56-2; CH_3I, 74-88-4; $Ph_2C{=}S$, 1450-31-3; $[CpV(CO)_4]$, 12108-04-2; sulfur, 7704-34-9.

Supplementary Material Available: Listings of structure factor amplitudes, thermal parameters (Table SI), and bond distances and angles (Table SII) (15 pages). Ordering information is given on any current masthead page.

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(22) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 203–8.

(23) Schunn, R. A.; Fritchie, C. J.; Prewitt, C. T. *Inorg. Chem.* **1966**, *5*, 892–9.

(24) Bottomley, F.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 28–9.

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Fluoro-Containing Complexes of Chromium(III). 12. Preparation and Resolution of the *cis*-Fluoroamminebis(ethylenediamine)chromium(III) Cation[1]

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Received June 22, 1982

In 1975 Wong and Kirk[2] reported the first successful preparation of solid salts of the *cis*- and *trans*-$[Cr(en)_2FNH_3]^{2+}$ (en = ethylenediamine) cations via the ammonolysis of *trans*-$[Cr(en)_2FBr]Br$. The synthetic method, which involved Cr–Br bond rupture and Cr–NH_3 bond formation, produced both isomers with a cis/trans ratio of approximately 60/40. This preparative method, coupled with the rather high solubility of the cis isomer, resulted in a low overall yield of the cis isomer. Assignments of the cis and trans structures were made on the basis of the differences in molar absorptivities. This was necessary since both isomers have the same local site symmetry (C_{4v}), a situation which requires that the number of spin-allowed electronic transitions be the same for both isomers and that the wavelengths of maximum and minimum absorptions be essentially constant.

During the course of stereochemical investigations in this laboratory, it became necessary to develop a synthetic route that could be used to prepare the cis isomer in quantity and to establish unequivocally its structure; hence, the present study was undertaken.

Experimental Section

Caution! Perchlorate salts of metal complexes with reducing ligands such as amines are potentially explosive, and care should be exercised when handling these materials.

Preparation of Starting Materials. (±)-*cis*-$[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$ was prepared as previously described.[3] (±)-*cis*-$[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$ was converted to (±)-*cis*-$[Cr(en)_2F(OH_2)]I_2\cdot H_2O$ and then to (±)-*cis*-$[Cr(en)_2FCl]I$ via the published methods.[3,4] (±)-*cis*-$[Cr(en)_2FCl]I$ was utilized to obtain (±)-*cis*-$[Cr(en)_2FNH_3]ICl$ by the method used to prepare *trans*-$[Cr(tn)_2FNH_3]ICl$ (tn = 1,3-propanediamine) except that the ammonia was dried over sodium prior to use instead of being condensed directly from the cylinder.[5]

In a typical preparation of $[Cr(en)_2FNH_3]ICl$, a 6.2-g (17.5-mmol) sample of (±)-*cis*-$[Cr(en)_2FCl]I$ was reacted with 30–40 mL of dry liquid ammonia. The yield was 6.1 g (94%) of crude product. The electronic spectrum of the crude product in 0.1 M perchloric acid was characterized by λ_{max} 495 nm (ϵ 62.0 M^{-1} cm^{-1}), λ_{min} 416 (ϵ 17.7), and λ_{max} 359 (ϵ 38.6).

Isolation of (±)-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$. A 1.0-g (2.7-mmol) sample of crude $[Cr(en)_2FNH_3]ICl$ was dissolved in 1.0 mL of 0.1 M perchloric acid, the orange solution was filtered, and the cold filtrate was diluted with perchloric acid as described by Wong and Kirk.[2] This method produced 0.30 g (27%) of the desired product. Anal. Calcd for (±)-*cis*-$[Cr(en)_2FNH_3](ClO_4)_2$: C, 11.79; H, 4.66; N, 17.19. Found: C, 11.56; H, 4.42; N, 17.23. The electronic spectrum in 0.1 M perchloric acid was characterized by λ_{max} 496 nm (ϵ 64.9 M^{-1} cm^{-1}), λ_{min} 418 (ϵ 16.3), and λ_{max} 362 (ϵ 34.5) [lit.:[2] λ_{max} 494 (ϵ 64.9), λ_{min} 417 (ϵ 16.6), and λ_{max} 360 (ϵ 34.4)].

Isolation of (±)-*cis*-$[Cr(en)_2FNH_3]I_2$. A 5.5-g (14.8-mmol) sample of crude (±)-*cis*-$[Cr(en)_2FNH_3]ICl$ was dissolved in 10 mL of water at room temperature, and the solution was quickly filtered. The orange filtrate was diluted with 5 mL of 47% hydriodic acid and cooled in an ice bath for 15 min. The orange product was collected, washed with acetone, and air-dried. The yield was 5.2 g (76%).

An 11.6-g (25.1-mmol) sample of crude (±)-*cis*-$[Cr(en)_2FNH_3]I_2$ was dissolved with constant stirring in 50 mL of water at 25–30 °C. The orange solution was filtered, and the filtrate was cooled in an ice bath for 1 h. The orange solid was collected, washed with acetone, and air-dried. The yield was 6.0 g (52%). The electronic spectrum in 0.1 M perchloric acid was characterized by λ_{max} 495 nm (ϵ 65.9 M^{-1} cm^{-1}), λ_{min} 418 (ϵ 17.4), and λ_{max} 357 (ϵ 39.6). Anal. Calcd for (±)-*cis*-$[Cr(en)_2FNH_3]I_2$: C, 10.39; H, 4.11; N, 15.15; F, 4.11. Found: C, 10.48; H, 4.25; N, 15.08; F 3.98.

Resolution of (±)-*cis*-$[Cr(en)_2FNH_3]I_2$. A 5.0-g (10.8-mmol) sample of recrystallized (±)-*cis*-$[Cr(en)_2FNH_3]I_2$ in 40 mL of water at room temperature was added to a solution of 9.42 g (21.6 mmol) of $(+)_{589}$-silver bromocamphor-π-sulfonate[6] in 50 mL of water at 45–55

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(1) Part 11: Vaughn, J. W. *J. Cryst. Spec. Res.*, in press.

(2) Wong, C. F. C.; Kirk, A. D. *Can. J. Chem.* **1975**, *53*, 3388.

(3) Vaughn, J. W.; Yeoman, A. M. *Inorg. Chem.* **1976**, *15*, 2320.

(4) Vaughn, J. W.; Yeoman, A. M. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 165.

(5) Vaughn, J. W. *Inorg. Chem.* **1981**, *20*, 2397.

(6) Halloran, L. J.; Gillie, A. L.; Legg, J. I. *Inorg. Synth.* **1978**, *18*, 103.

0020-1669/83/1322-0844$01.50/0