by its two separate components.

The plot of susceptibility vs. temperature for compound **4** showed behavior typical of an antiferromagnetically coupled linear-chain polymer[12] and, upon analysis, gave $g = 2.139$ (8) and $J = -36.3$ (2) cm^{-1}. Data are available in Table S1.[11]

Differences in the solid-state infrared spectra of **3** and **4** compared with that of the mononuclear complex (Experimental Section) in the 1500–1700-cm^{-1} (C=N, C=C) region may be diagnostic of the mode of imidazole binding.

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Registry No. 3, 74911-59-4; 4, 74911-55-0; Cu(deimH)(ClO$_4$)$_2$, 74947-52-7; Cu(PMDT)(ClO$_4$)$_2$·2CH$_3$CN, 74911-61-8; 1,1-dimethyldiethylenetriamine, 24229-53-6; 4(5)-(formyl)imidazole, 3034-50-2.

Supplementary Material Available: Table S1 reporting the observed and calculated temperature dependent magnetic susceptibilities for Cu$_2$(deim)(PMDT)(ClO$_4$)$_3$ and [Cu(deim)(ClO$_4$)]$_n$ (2 pages). Ordering information is given on any current masthead page.

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Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy, and Istituto di Strutturistica Chimica, Università di Parma, 43100 Parma, Italy

Carbonyl Sulfide Activation: COS Disproportionation to Dithiocarbonate and Carbon Monoxide Promoted by Vanadocene

Marco Pasquali,[1a] Carlo Floriani,*[1a] Angiola Chiesi-Villa,[1b] and Carlo Guastini[1b]

Two strategies for studying molecular activation promoted by transition-metal complexes are the utilization of "model compounds" and "equivalent molecules". These approaches were recently applied to the problems associated with the activation of CO$_2$ by transition-metal complexes.[2a] While carbodiimides,[2b] phenyl isocyanate,[3] and diphenylketene[4] imitate CO$_2$ in many respects, carbon disulfide, which appears as the most obvious CO$_2$ analogue and which has a very rich organometallic chemistry,[5] is apparently a poor model. We expect that COS would more closely resemble CO$_2$ in its activation by transition metals. Very few reports have been concerned, however, with the reaction of COS with transition-metal complexes. In these cases, π coordination to the

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Table I. Summary of Crystal Data and Intensity Data Collection for [Cp$_2$V)$_2$(COS$_2$)]·C$_6$H$_6$

a, Å	16.317 (5)
b, Å	10.566 (2)
c, Å	15.416 (5)
α, deg	90.0
β, deg	114.72 (4)
γ, deg	90.0
Z	4
M_r	532.5
d_{calcd}, g cm^{-3}	1.465
space group	$P2_1/c$
radiation	Nb-filtered Mo Kα (λ = 0.710 69 Å)
μ, mm^{-1}	0.93
$\mu \bar{r}$	0.1
scan type	θ–2θ
scan range	±0.5° from peak center
scan speed, deg θ/min	2.5–10
bkgd	stationary cryst at ±0.5°
2θ limits, deg	5–48
criterion for obsn	$I > 2\sigma(I)$
unique obsd data	2318
unique total data	3791
cryst dimens, mm^3	0.34 × 0.10 × 0.48

metal center through the C=S double bond has been proposed.[6,7]

$L_nM = Pt(PPh_3)_2$,[6] $Rh(Cl)(PCy_3)_2$[7]
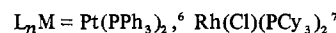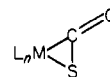
With group 8 metals in low oxidation states, COS tends to resemble CS$_2$ more than CO$_2$. We report here the reaction between COS and vanadocene, whose reactivity with other CO$_2$ equivalents has been described recently.[8,9] Vanadocene promotes a disproportionation of COS to COS$_2^{2-}$ and CO, resulting in the complexes (Cp$_2$V)$_2$(COS$_2$) and Cp$_2$V(CO).

Experimental Section

All the experimental operations were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Vanadocene was prepared as described in the literature.[10] Carbonyl sulfide is commercially available from Aldrich. IR spectra were recorded with a Perkin-Elmer 282 spectrophotometer. Magnetic susceptibility measurements were made with a Faraday balance.

Reaction of Vanadocene with Carbonyl Sulfide. A 250-mL flask containing the violet solution of vanadocene (1.0 g, 5.52 mmol) in benzene (30 mL) was evacuated and then filled with COS at room temperature. The color of the solution turned suddenly to blue. When the solution was allowed to stand, gas evolution occurred along with change of the color to deep maroon. A crystalline maroon solid separated (ca 60%). Anal. Calcd for C$_{21}$H$_{20}$V$_2$OS$_2$: C, 55.50; H, 4.40; S, 14.10. Found: C, 55.12; H, 4.88; S, 14.10. The complex has a magnetic moment of 2.72 μ_B at 297 K. The IR spectrum (Nujol) does not show any significant band above 1600 cm^{-1}. The solid is very sensitive to air and contains variable amounts of solvent, which is lost very easily. The X-ray analysis was performed on [(Cp$_2$V)$_2$(COS$_2$)]·C$_6$H$_6$.

The same reaction was carried out with an excess of vanadocene over COS as follows: a toluene solution (30 mL) of vanadocene (2.13 g, 11.76 mmol) was reacted with 100 mL of COS (ca 4 mmol). The IR spectrum shows the presence in solution of a strong carbonylic band at 1880 cm^{-1} corresponding to that of Cp$_2$V(CO).[11]

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Table II. Atomic Coordinates ($\times 10^4$), with Estimated Standard Deviations in Parentheses, for $[(Cp_2V)_2COS_2)]\cdot C_6C_6$

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
V(1)	10110 (1)	1789 (1)	3895 (1)	C(24)	2901 (6)	2794 (11)	3015 (8)
V(2)	6588 (1)	2743 (1)	3789 (1)	C(25)	2736 (6)	1521 (11)	2761 (8)
S(1)	7946 (1)	2982 (2)	3461 (1)	C(26)	3094 (6)	583 (11)	3455 (8)
S(2)	7760 (1)	1208 (2)	4735 (1)	H(1)	9913	−984	3582
O	9204 (3)	1296 (5)	4400 (4)	H(2)	8436	474	2596
C(30)	8441 (4)	1767 (7)	4229 (5)	H(3)	8988	2374	1802
C(1)	9889 (6)	−123 (7)	3177 (6)	H(4)	10738	2177	2343
C(2)	9130 (5)	635 (8)	2661 (6)	H(5)	11320	103	3441
C(3)	9413 (6)	1629 (8)	2262 (5)	H(6)	9969	3342	5440
C(4)	10323 (6)	1523 (7)	2539 (5)	H(7)	10083	4632	4002
C(5)	10618 (5)	440 (7)	3098 (5)	H(8)	11389	3564	3637
C(6)	10448 (6)	3157 (9)	5127 (6)	H(9)	12091	1685	4862
C(7)	10505 (7)	3814 (7)	4381 (7)	H(10)	11242	1539	5976
C(8)	11182 (6)	3269 (8)	4203 (6)	H(11)	6230	−79	3369
C(9)	11544 (5)	2307 (8)	4830 (7)	H(12)	5006	1233	3695
C(10)	11101 (6)	2213 (9)	5402 (5)	H(13)	4684	3332	2637
C(11)	5964 (9)	861 (9)	3055 (8)	H(14)	5768	3379	1765
C(12)	5341 (8)	1496 (13)	3222 (9)	H(15)	6718	1245	2210
C(13)	5181 (6)	2597 (12)	2687 (10)	H(16)	5411	3292	4822
C(14)	5727 (6)	2619 (14)	2225 (7)	H(17)	5323	4882	3453
C(15)	6215 (7)	1526 (15)	2469 (9)	H(18)	7105	5445	3857
C(16)	5994 (8)	3686 (14)	4732 (10)	H(19)	8096	4010	5300
C(17)	5924 (10)	4517 (15)	4027 (9)	H(20)	7087	2728	5895
C(18)	6847 (11)	4784 (8)	4237 (9)	H(21)	3891	202	4948
C(19)	7355 (6)	4055 (9)	4988 (7)	H(22)	4182	2467	5374
C(20)	6839 (9)	3409 (9)	5290 (7)	H(23)	3543	4110	4126
C(21)	3617 (6)	917 (11)	4403 (8)	H(24)	2612	3487	2451
C(22)	3782 (6)	2190 (11)	4657 (8)	H(25)	2321	1222	2025
C(23)	3424 (6)	3128 (11)	3963 (8)	H(26)	2960	−421	3273

X-ray Data Collection. The crystal chosen for data collection was wedged into thin-walled glass capillary which was sealed under nitrogen. Preliminary examination of rotation and Weissenberg photographs provided approximate cell dimensions and showed the space group to be $P2_1/c$. An accurate determination of the unit cell parameters was obtained by a least-squares fit of 20 reflections whose θ values were refined ($\theta > 15°$). A summary of crystal data and intensity data collection is given in Table I. Three-dimensional intensity data were collected at room temperature on a single-crystal Siemens AED automated diffractometer. The pulse-height discriminator was set up to accept 90% of the incident radiation. For measuring intensity and background, the "five-point technique"[12] was used. One reflection was monitored after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during the data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established by Wilson's method.[13] In view of the rather low absorbance ($\mu\bar{r} = 0.1$) and the irregular shape of the sample, no corrections for absorption were applied.

Structure Determination and Refinement.[14] Positional parameters for the two independent vanadium atoms were deduced from a vector analysis of a three-dimensional Patterson function, and those of the other nonhydrogen atoms were obtained by successive Fourier syntheses. Refinement was by full-matrix least squares, isotropically down to $R = 0.110$ and anisotropically down to $R = 0.061$. Throughout the refinement the benzene solvent molecule was considered as a regular hexagon of carbon atoms having fixed C–C bond lengths of 1.395 Å.

The hydrogen atoms could not be accurately located in a difference Fourier map but were added at idealized positions, as fixed-atom contributions with isotropic temperature factors of their parent carbon atoms. After two further cycles of least squares, the R index converged to the final value of 0.058 ($R_w = 0.057$). In the last stage of the refinement no parameter shifted by more than 0.3 times its standard

deviation. In the final difference electron density map, no peak higher than 0.55 e Å^{-3} was observed. The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The function minimized during least-squares refinement was $\sum w|\Delta F|^2$, and the reflections were weighted according to the expression $w = k/[\sigma_{F_o}^2 + (\text{abs}(g))(F_o^2)]$ on the basis of counting statistics (the error in observation of unit weight is 1.00). k and g were redetermined after each structure factor calculation and refined by fitting $(F_o - F_c)^2$ to $[\sigma_{F_o} + (\text{abs}(g))(F_o^2)]/k$. In our final refinement, $k = 1.0000$ and $g = 0.003$. The atomic scattering factors were those of ref 15 for V, those of Cromer and Mann[16] for S, O, and C, and those of Stewart, Davidson, and Simpson[17] for H.

The final atomic coordinates are listed in Table II.

Results and Discussion

Carbonyl sulfide reacts with a toluene or benzene solution of vanadocene, Cp_2V ($Cp = \eta^5\text{-}C_5H_5$), as reported in eq 1.

$$2Cp_2V + 2COS \rightarrow (Cp_2V)_2(COS_2) + CO \qquad (1)$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
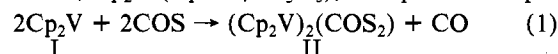
The presence and the origin of carbon monoxide was easily identified by carrying out reaction 1 with an excess of vanadocene over COS. In this case, the toluene solution contains $Cp_2V(CO)$ ($\nu_{CO} = 1880$ cm^{-1}),[11] and the transformation undergone by COS can be represented in reaction 2. Complex

$$3Cp_2V + 2COS \rightarrow (Cp_2V)_2(COS_2) + Cp_2V(CO) \qquad (2)$$
$$\text{II} \qquad\qquad\qquad \text{III}$$
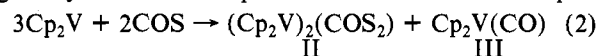
III behaves, in many cases, as a vanadocene source losing carbon monoxide.[18] Therefore, the excess of COS in reaction 1 converts all the starting vanadocene into II, evolving carbon monoxide.

Complex II crystallizes with a molecule of benzene, which is very easily lost even in a stream of nitrogen. The analytical data correspond to the unsolvated species. Spectroscopic and magnetic results are inconclusive concerning the molecular

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Table III. Bond Distances (Å) and Angles (Deg), with Estimated Standard Deviations in Parentheses, for [(Cp$_2$V)$_2$(COS$_2$)]·C$_6$H$_6$^{a}

V(1)-C(1)	2.259 (8)	V(1)-C(6)	2.264 (9)	V(2)-C(11)	2.304 (10)	V(2)-C(16)	2.286 (15)
V(1)-C(2)	2.262 (9)	V(1)-C(7)	2.270 (8)	V(2)-C(12)	2.270 (14)	V(2)-C(17)	2.270 (16)
V(1)-C(3)	2.295 (7)	V(1)-C(8)	2.244 (10)	V(2)-C(13)	2.218 (13)	V(2)-C(18)	2.250 (9)
V(1)-C(4)	2.275 (8)	V(1)-C(9)	2.243 (10)	V(2)-C(14)	2.230 (10)	V(2)-C(19)	2.229 (10)
V(1)-C(5)	2.254 (8)	V(1)-C(10)	2.252 (8)	V(2)-C(15)	2.265 (14)	V(2)-C(20)	2.286 (10)
average	2.271 (9)	average	2.256 (7)	average	2.259 (17)	average	2.260 (12)
V(1)-O	2.006 (6)	V(2)-S(1)	2.483 (4)	V(2)-Cp(3)	1.941 (13)	C(30)-O	1.262 (9)
V(1)-Cp(1)	1.939 (7)	V(2)-S(2)	2.466 (3)	V(2)-Cp(4)	1.950 (12)	C(30)-S(1)	1.704 (8)
V(1)-Cp(2)	1.930 (9)					C(30)-S(2)	1.708 (8)
C(1)-C(2)	1.41 (1)	C(6)-C(7)	1.38 (1)	C(11)-C(12)	1.33 (2)	C(16)-C(17)	1.36 (2)
C(2)-C(3)	1.39 (1)	C(7)-C(8)	1.37 (2)	C(12)-C(13)	1.39 (2)	C(17)-C(18)	1.43 (3)
C(3)-C(4)	1.37 (1)	C(8)-C(9)	1.36 (1)	C(13)-C(14)	1.35 (2)	C(18)-C(19)	1.35 (2)
C(4)-C(5)	1.39 (1)	C(9)-C(10)	1.36 (1)	C(14)-C(15)	1.36 (2)	C(19)-C(20)	1.31 (2)
C(5)-C(1)	1.38 (1)	C(10)-C(6)	1.39 (1)	C(15)-C(11)	1.34 (2)	C(20)-C(16)	1.32 (2)
average	1.39 (1)	average	1.37 (1)	average	1.35 (2)	average	1.35 (2)
C(1)-V(1)-C(2)	36.3 (3)	C(6)-V(1)-C(7)	35.4 (4)	C(11)-V(2)-C(12)	33.8 (5)	C(16)-V(2)-C(17)	34.9 (5)
C(2)-V(1)-C(3)	35.5 (3)	C(7)-V(1)-C(8)	35.4 (4)	C(12)-V(2)-C(13)	36.0 (5)	C(17)-V(2)-C(18)	36.9 (6)
C(3)-V(1)-C(4)	34.8 (4)	C(8)-V(1)-C(9)	35.2 (3)	C(13)-V(2)-C(14)	35.4 (4)	C(18)-V(2)-C(19)	35.0 (4)
C(4)-V(1)-C(5)	35.8 (3)	C(9)-V(1)-C(10)	35.2 (3)	C(14)-V(2)-C(15)	35.3 (5)	C(19)-V(2)-C(20)	33.7 (4)
C(5)-V(1)-C(1)	35.6 (3)	C(10)-V(1)-C(6)	35.9 (4)	C(15)-V(2)-C(11)	34.0 (5)	C(20)-V(2)-C(16)	33.5 (5)
average	35.7 (3)	average	35.4 (2)	average	35.0 (5)	average	34.6 (6)
O-V(1)-Cp(1)	108.7 (3)	S(1)-V(2)-Cp(3)	108.0 (4)	Cp(3)-V(2)-Cp(4)	136.6 (6)	V(1)-O-C(30)	129.7 (5)
O-V(1)-Cp(2)	108.1 (3)	S(1)-V(2)-Cp(4)	108.5 (5)	O-C(30)-S(1)	125.6 (6)	V(2)-S(1)-C(30)	89.2 (3)
Cp(1)-V(1)-Cp(2)	142.9 (4)	S(2)-V(2)-Cp(3)	107.1 (4)	O-C(30)-S(2)	122.8 (6)	V(2)-S(2)-C(30)	89.7 (3)
S(1)-V(2)-S(2)	69.5 (1)	S(2)-V(2)-Cp(4)	107.2 (4)	S(1)-C(30)-S(2)	111.6 (4)		
C(5)-C(1)-C(2)	107.0 (7)	C(10)-C(6)-C(7)	107.8 (9)	C(15)-C(11)-C(12)	109.9 (1.1)	C(20)-C(16)-C(17)	112.3 (1.4)
C(1)-C(2)-C(3)	107.7 (8)	C(6)-C(7)-C(8)	107.2 (8)	C(11)-C(12)-C(13)	106.1 (1.2)	C(16)-C(17)-C(18)	102.6 (1.2)
C(2)-C(3)-C(4)	108.6 (7)	C(7)-C(8)-C(9)	108.6 (8)	C(12)-C(13)-C(14)	109.0 (1.2)	C(17)-C(18)-C(19)	107.0 (1.2)
C(3)-C(4)-C(5)	108.1 (8)	C(8)-C(9)-C(10)	109.0 (9)	C(13)-C(14)-C(15)	106.1 (1.2)	C(18)-C(19)-C(20)	110.3 (1.2)
C(4)-C(5)-C(1)	108.7 (8)	C(9)-C(10)-C(6)	107.3 (8)	C(14)-C(15)-C(11)	108.9 (1.2)	C(19)-C(20)-C(16)	107.7 (1.0)
average	108.0 (5)	average	107.9 (5)	average	108.0 (1.0)	average	107.7 (1.6)

^{a} All the average values have been calculated using the formulas

$$x_m = \frac{\Sigma w_i x_i}{\Sigma w_i} \qquad \sigma_m = \left[\frac{1}{N-1}\left(\frac{\Sigma w_i x_i^2}{\Sigma w_i} - x_m^2\right) + \frac{1}{\Sigma w_i}\right]^{1/2} \qquad w_i = \sigma_i^{-2}$$

Cp(1), Cp(2), Cp(3), and Cp(4) are referred to the centroids of the rings C(1)-C(5), C(6)-C(10), C(11)-C(15), and C(16)-C(20), respectively.

complexity of II and the bonding mode of the dithiocarbonato ligand. Therefore the nature of II was clarified by X-ray analysis, which was performed on [(Cp$_2$V)$_2$(COS$_2$)]·C$_6$H$_6$.

Figure 1 shows a view of the dimeric unit (Cp$_2$V)$_2$(COS$_2$), and bond distances and angles are given in Table III. Each vanadium atom is η^5 bonded to two Cp rings, bent away from the horizontal plane containing the COS$_2$$^{2-}$ bridging ligand, which is nearly coplanar with V(1) and V(2). The C–C bond distances within the planar Cp rings, as well as the V–C and V–Cp(1) distances, fall in the usual range.[8,9,19-21] The Cp–V–Cp angles vary from 142.9 (4)° around V(1) to 136.6 (6)° around V(2). The relative orientation of the two Cp rings is eclipsed around V(1) and rotated by 17° from an eclipsed conformation around V(2). The V–S bond distances [V-(2)-S(1) = 2.483 (4) and V(2)-S(2) = 2.466 (3) Å] can be compared with those found in Cp$_2$V(CS)$_2$[21] (IV) [2.432 (2) Å] and in [Cp$_2$V(SCSMe)]I$_3$[21] [2.452 (4) Å]. The V–O bond distance [2.006 (6) Å] falls in the range found for Cp$_2$V-(PhC=C=O)[8] [2.020 (4) Å] and [Cp$_2$V(OCMe$_2$)](BPh$_4$) [2.081 (4) Å].[8]

Bond distances and angles within the COS$_2$$^{2-}$ unit compare well with those reported for other dithiocarbonato complexes, where the COS$_2$$^{2-}$ ligand is chelated to only one metal center through both sulfur atoms.[22] C–S and C–O have a significant double-bond character, indicating an electronic delocalization
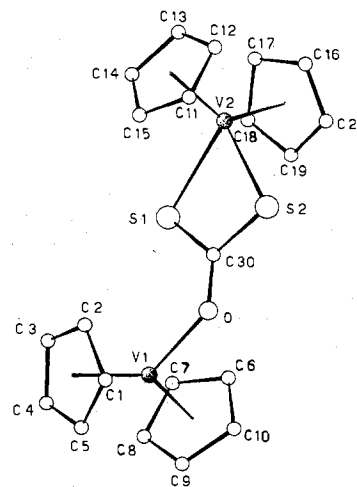

Figure 1. View of the molecular structure of (Cp$_2$V)$_2$(COS$_2$).

all over the COS$_2$$^{2-}$ unit. The absence of any vibrational band in the IR spectrum above 1600 cm^{-1} agrees with this observation. The magnetic moment (2.72 μ_B at 297 K) shows the presence of two unpaired electrons per two vanadium atoms, which cannot be magnetically equivalent. Therefore, complex II could be considered either as a mixed-valence vanadium-(IV)–vanadium(II) compound or as a compound containing one diamagnetic and one paramagnetic vanadium(III).[23]

The vanadocene-promoted transformation of COS is summarized in reaction 3, which is one of the two possible so-called

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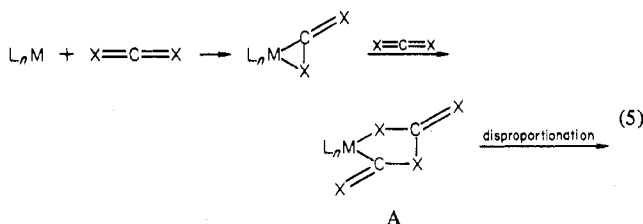
(23) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 203.

$$2COS + 2e^- \rightarrow COS_2^{2-} + CO \qquad (3)$$
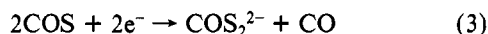
disproportionation paths of COS, the second one being reaction 4. Many cumulenes like CO_2,[2a] carbodiimides,[2b] and iso-

$$2COS + 2e^- \rightarrow CO_2S^{2-} + CS \qquad (4)$$
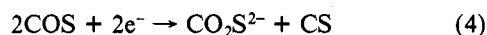
cyanates[3] undergo disproportionation in the reaction with metal complexes. The action of the metal is exemplified in (5). The

$$(5)$$

A

head-to-tail dimerization (A) of the functional group C=X seems to be the key intermediate preceding the disproportionation of the cumulene. It is rather difficult, however, to envisage such a mechanism for reaction 1, since when vanadocene reacts with functional groups like –C≡C–,[19] >C=O,[8] and >C=N–,[9] it forms 1:1 adducts only:

X = S; Y = S[20]
X = NR; Y = NR[22]
X = O; Y = CPh$_2$[19]
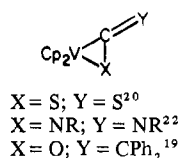
In the same studies we found that the nucleophilicity of the uncoordinated heteroatom (Y = S, NR) is rather high, so that its alkylation occurs with CH_3I under mild conditions.[9,21] On the basis of some considerations outlined above, we can propose the pathway shown by (6) for reaction 1.

$$(6)$$
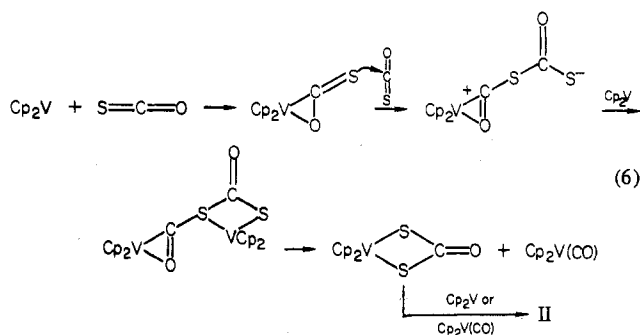
We must emphasize that COS is formally reduced by two electrons in its addition to the metal. The nucleophilic attack by the uncoordinated sulfur on the electrophilic carbon of another molecule of COS gives a head-to-tail linkage between two COS molecules, which is, probably, the prerequisite to the disproportionation.[24] A species like B may react with either Cp$_2$V(CO) or Cp$_2$V to produce a vanadium derivative like II. Such a reaction was observed to occur between Cp$_2$VX$_2$ (X = Cl, SR) and Cp$_2$V.[25] The usual COS decomposition pathways cannot account for the formation of COS_2^{2-}.[26] While the disproportionation of CO_2 to CO_3^{2-} and CO is a well-established metal-promoted transformation,[2a] the generation of CS_3^{2-} from CS_2 is interpreted as occurring via the reaction of CS_2 on preformed metal–sulfido complexes.[27]

It can be noticed that, as suggested by this piece of vanadocene chemistry, the head-to-tail dimerization across two metal centers can account for the metal-induced disproportionation of cumulenes, including CO_2.[24]

Supplementary Material Available: Listings of structure factor amplitudes, thermal parameters (Table IV), and least-squares planes (Table V) (18 pages). Ordering information is given on any current masthead page.

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Molybdenum and Tungsten Complexes of Bidentate Bis(aryldiazenato) Ligands

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As an extension of a study of the synthesis and reactivity of chelating bidentate nitrile and isocyanide ligands,[2] we report herein the preparation and chemical properties of potentially chelating bidentate bis(aryldiazenato) ligands of the structure

R = H, *t*-Bu
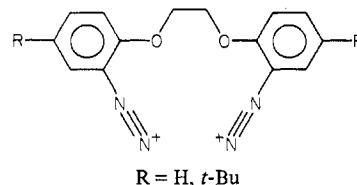
The ligands are abbreviated as DiN$_2$$^{2+}$ (R = H) and *t*-Bu-DiN$_2$$^{2+}$ (R = *t*-Bu). Molecular models indicate that these ligands should chelate best to octahedral or square-planar complexes where the angle between the donor groups is 90°. However, the formation of polymeric derivatives, owing to the flexibility of the alkyl chain, is also possible. To our knowledge, there are no reports in the literature of this type of ligand.

Recent interest[3] in aryldiazenato (ArN$_2$$^+$) ligands stems, in part, from studies of the similarities and differences of NO$^+$, N$_2$, and ArN$_2$$^+$. Only recently, several authors reported the syntheses, by different routes, of the rare complexes containing two aryldiazenato ligands.[4] The existence of these complexes suggested that derivatives containing the chelating DiN$_2$$^{2+}$ and *t*-BuDiN$_2$$^{2+}$ ligands could be prepared. It was toward this end that the following study was undertaken.

Experimental Section

General Procedures. All reactions involving organometallic compounds were carried out under an atmosphere of dry nitrogen.

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