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Crystal and Molecular Structures of Bis[(η^5-cyclopentadienyl)dicarbonylchromium] Sulfide, a Novel Organometallic Complex Possessing a Cr≡S≡Cr Linkage

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The reaction of $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$ with $S_3N_3Cl_3$ in tetrahydrofuran affords the new bimetallic complex, $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$, in 34% yield. This complex crystallizes with two independent molecules in space group $P\bar{1}$ of the triclinic system in a cell of dimensions $a = 8.152$ (1) Å, $b = 10.288$ (1) Å, $c = 18.441$ (2) Å, $\alpha = 88.01$ (1)°, $\beta = 81.51$ (1)°, and $\gamma = 89.28$ (1)°. The structure has been refined by full-matrix least-squares methods to values of R and R_w of 0.045 and 0.073, respectively, for 42 anisotropic atoms and 4882 observed reflections. The most chemically interesting feature of the structure is the unprecedented, central CrSCr linkage which is essentially linear and very short (average Cr–S = 2.074 Å). These facts can be interpreted in terms of Cr≡S≡Cr multiple bonding, a rationale which is consistent with the relative chemical inertness of this linkage and the observed stereochemical nonrigidity of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ in solution at ambient temperature.

Introduction

It has been communicated previously that the reaction between $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$ and $S_3N_3Cl_3$ in tetrahydrofuran at −78 °C affords $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ in 21% yield.[1] We now wish to report that another product formed in this reaction is the bimetallic compound $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$, which is the first organometallic member of a whole new class of metal–sulfur complexes.[2] In this paper we describe the results of a single-crystal diffraction analysis of this unusual complex as well as some of its physical and chemical properties.

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents either were purchased from commercial suppliers or were prepared according to published procedures, and their purity was checked by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use, and all manipulations were performed in an atmosphere of prepurified dinitrogen unless otherwise indicated.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} absorption band of a polystyrene film. Proton magnetic resonance spectra were obtained on a Varian Associates T60 spectrometer with tetramethylsilane (Me_4Si) being employed as an internal standard. Carbon-13 NMR spectra were recorded on a Varian Associates CFT20 spectrometer with reference to the solvent used, but all ^{13}C chemical shifts are reported in ppm downfield from Me_4Si. The mass spectrum was recorded at 70 eV on an Atlas CH4B spectrometer by using the direct-insertion method with the assistance of Mr. J. W. Nip. Elemental analyses were performed by Mr. P. Borda of this department.

Isolation of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$. Typically, after $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ had been isolated from the final reaction mixture,[1] the combined reaction residues were partially dissolved in ~10 mL of toluene, and the resulting dark green slurry was transferred under N_2 to the top of a Florisil column (4 × 28 cm). Elution of the column with toluene developed an olive green band which was collected. Removal of solvent from the eluate in vacuo produced a solid which was recrystallized from dichloromethane–hexanes to obtain dark green crystals (1.29 g, 34% yield based on Cr) of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$.

Anal. Calcd for $C_{14}H_{10}Cr_2O_4S$: C, 44.45; H, 2.67; S, 8.48. Found: C, 44.47; H, 2.64; S, 8.19. IR (hexanes): ν_{CO} 2000, 1960, 1932, 1924 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.87 (s). ^{13}C NMR ($CDCl_3$): δ 245.9 (s, CO), 89.0 (s, C_5H_5). The melting point (in air) was 112–113 °C dec.

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ with Nitrosyl Chloride. A dichloromethane solution of ClNO[3] was added dropwise to a stirred solution of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ (0.38 g, 1.0 mmol) in the same solvent (40 mL) at room temperature. Gas evolution occurred, the solution became bright green, and a fine yellow precipitate formed. Just enough ClNO was added to react with all of the sulfur complex, as monitored by infrared spectroscopy. The final mixture was reduced in vacuo to 10 mL and was transferred to the top of a 2 × 5 cm Florisil column. Elution of the column with CH_2Cl_2 resulted in the development of a single, golden band which was collected and taken to dryness at reduced pressure. The residue was identified as $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$[4] (0.26 g, 60% yield) by its characteristic physical properties.

The reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$[5] with ClNO proceeded similarly and produced $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ in 42% yield.

Treatment of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ with Carbon Monoxide. A toluene solution (15 mL) containing 0.38 g (1.0 mmol) of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ was transferred under an argon atmosphere to a 45-mL Parr pressure bomb. The bomb was flushed three times with 60 atm of CO and was then pressurized to 100 atm with CO. This pressure was maintained for 18 h at ambient temperature. The CO was then released, the bomb was flushed with argon, and the solution was transferred under argon to a 100-mL three-necked flask. Removal of the solvent in vacuo afforded a yellow-green residue which was identified as unreacted $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ by its distinctive spectroscopic properties.

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$ with Nitrogen Monoxide. Prepurified nitrogen monoxide was bubbled slowly through a toluene solution (25 mL) containing 0.45 g (1.3 mmol) of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$[5] for 12 h at room temperature. During this period, the originally green solution developed an orange coloration. The final solution was concentrated in vacuo to ~10 mL and then transferred to the top of a 3 × 5 cm Florisil column made up in dichloromethane. Elution of the column with dichloromethane developed a single orange band that was collected and taken to dryness under reduced pressure. Sublimation of the residue at ambient temperature (5 × 10^{-3} mm) onto a dry ice cooled probe afforded 0.23 g (1.1 mmol, 43% yield) of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[3] which was identified by its infrared and mass spectra.

The Florisil column was then eluted with tetrahydrofuran to produce a dark green band which also was collected and taken to dryness in vacuo. Crystallization of the resulting solid from CH_2Cl_2–hexanes yielded green crystals of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO)_2)$[6] (0.20 g, 35% yield) which were identified by its characteristic physical properties.

Analogous treatment of a toluene solution of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ with NO produced no changes in the infrared spectrum of the solution.

X-ray Diffraction Study of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$. Crystals of the title compound suitable for X-ray work were grown by slow cooling of a hexane solution of the complex from 60 °C to room temperature. A series of precession photographs from a single crystal mounted in air provided the Laue symmetry $\bar{1}$ and initial unit cell dimensions. A least-squares analysis of the setting angles of 25 reflections (20° < 2θ < 28°) automatically located and centered on a Nonius CAD-4 diffractometer with Mo Kα radiation provided accurate unit cell parameters (Table I). Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer;[7] the pertinent details are given in Table I. Standard Lorentz and polarization corrections were followed by an absorption correction using the Gaussian integration method.[8]

The structure was solved by direct methods using 744 $|E|$ values greater than 1.8 provided by a K-curve method.[9] The $|E|$ statistics were all consistent with the space group $P\bar{1}$. An outstanding solution was obtained from a symbolic addition procedure,[10] and the 744 E values in this set afforded an E map which clearly revealed the Cr

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Table I. Crystal Data and Nonius CAD-4 Data Collection Procedures for $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$

formula	$C_{14}H_{10}Cr_2O_4S$	α	88.01 (1)°
mol wt	378.3	β	81.51 (1)°
space grp	$P\bar{1}$	γ	89.28 (1)°
a	8.152 (1) Å	V	1528.8 Å^3
b	10.288 (1) Å	Z	4
c	18.441 (2) Å		

ρ_c	1.643 g/cm^3
radiation	graphite monochromated Mo K$_\alpha$
bounding planes	{001}, {100}, $\{\bar{1}10\}$
cryst vol	0.0324 mm^3
linear abs coeff (Mo Kα)	15.28 cm^{-1}
transmission factors	0.530–0.839
monochromator angle	12.20° (2θ)
scan type	ω–2θ
scan width	$\Delta\omega = [0.90 + 0.35 \tan\theta]°$
aperture width	$[1.5 + 1.0 \tan\theta]$ mm
SIGPRE	0.667 (3σ)
SIGMA	0.033 (30σ)
NPIPRE	3(6.71°/min)
ITMAX	90 s
collectn range	$+h, \pm k, \pm l$, $2.5° \leqslant 2\theta \leqslant 57°$
no. of data	7737 total; 4882 unique with $I > 3\sigma(I)$ ($p = 0.04$)

and S positions. A subsequent Patterson synthesis confirmed both the space group and the heavy-atom positions. The other nonhydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier techniques. After one cycle of refinement using anisotropic thermal parameters for all known atoms, a difference Fourier synthesis suggested that disorder of the η^5-C_5H_5 rings was present at each position. Attempted least-squares refinement in which each ring was replaced by two alternative isotropic rings failed to establish an acceptable geometry for various fixed occupancy ratios; anisotropic refinement of the disordered model proved to be impossible. Further attempts using idealized rigid groups gave a large increase in R and suggested that in some cases the η^5-C_5H_5 ring located initially by Fourier methods was only a minor contributor. Consequently, the approximation of one anisotropic η^5-C_5H_5 ring at each position was considered to be the most satisfactory. The final cycle of full-matrix least-squares refinement converged to values of R and R_w of 0.045 and 0.073, respectively, for the 42 anisotropic atoms and 4882 observed reflections. Anomalous scattering components[11] for Cr and S were included, and atomic scattering factors for all atoms were those of Cromer and Mann.[12] The weights used were $1/\sigma^2(F)$, and weighting analyses confirmed their suitability. The error in an observation of unit weight was 1.10 electrons, and peaks in the final difference Fourier map ranged from –0.8 (1) to +0.6 (1) e/Å^3. Attempts at refinement of the structure in $P1$ or reduction to a cell of higher symmetry were both unsuccessful.

Final positional and thermal parameters are tabulated in Tables II and III.[13] Values of $|F_o|$ vs. $|F_c|$ for the 7737 reflections are given in Table IV.[14]

Results and Discussion

A surprising product resulting from the reaction of Na[$(\eta^5$-$C_5H_5)Cr(CO)_3$] with $S_3N_3Cl_3$ in tetrahydrofuran (THF) is the novel bimetallic complex $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$, which can be isolated in 34% yield. The carbonyl anion thus functions as a desulfurization reagent during this conversion,[15] but the detailed mechanism of the process remains to be elucidated. The sulfur-containing product is a green, air-stable, diamagnetic solid (mp 112–113 °C) which is freely soluble in common organic solvents (except paraffin hydrocarbons) and sublimes without attendant decomposition at 80 °C under a dynamic vacuum (5×10^{-3} mm) onto a water-cooled probe. Its low-resolution mass spectrum (Table V) confirms its bimetallic nature and exhibits a fragmentation pattern which indicates that the Cr_2S grouping is quite resistant to cleavage. The exact features of this grouping have been established from a single-crystal X-ray study of the complex.

Table II. Final Fractional Positional Parameters with Estimated Standard Deviations (Esd's) in Parentheses[a]

atom	x	y	z
Cr(11)	42004 (8)	93167 (6)	85516 (3)
Cr(12)	46368 (7)	74414 (6)	65795 (3)
S(1)	44143 (12)	82977 (10)	75926 (5)
C(111)	6431 (6)	9405 (5)	8514 (3)
O(111)	7899 (5)	9496 (4)	8468 (3)
C(112)	4172 (6)	7835 (5)	9184 (3)
O(112)	4120 (5)	6947 (4)	9574 (2)
C(121)	2361 (5)	7485 (5)	6561 (2)
O(121)	981 (4)	7533 (5)	6540 (2)
C(122)	4512 (6)	5714 (5)	6940 (3)
O(122)	4497 (6)	4653 (4)	7136 (3)
Cp(111)	3440 (9)	11329 (5)	8289 (3)
Cp(112)	3972 (8)	11260 (6)	9008 (5)
Cp(113)	2878 (9)	10432 (6)	9464 (3)
Cp(114)	1735 (8)	9976 (6)	9058 (4)
Cp(115)	2063 (8)	10527 (6)	8353 (4)
Cp(121)	4963 (7)	8311 (6)	5460 (3)
Cp(122)	5995 (7)	8996 (5)	5882 (3)
Cp(123)	7150 (6)	8107 (5)	6107 (3)
Cp(124)	6892 (7)	6903 (6)	5852 (3)
Cp(125)	5511 (8)	7005 (6)	5441 (3)
Cr(21)	3251 (7)	54037 (6)	15617 (3)
Cr(22)	–3374 (7)	72213 (6)	35551 (3)
S(2)	–1403 (12)	63039 (10)	25599 (5)
C(211)	883 (6)	6937 (5)	1035 (3)
O(211)	1264 (6)	7881 (4)	710 (2)
C(212)	–1828 (6)	5553 (4)	1341 (2)
O(212)	–3128 (4)	5611 (4)	1194 (2)
C(221)	–1032 (6)	5735 (4)	4111 (2)
O(221)	–1498 (6)	4842 (4)	4466 (2)
C(222)	–2537 (5)	7708 (5)	3583 (2)
O(222)	–3881 (4)	8028 (5)	3609 (2)
Cp(211)	1507 (8)	3675 (5)	1978 (3)
Cp(212)	2715 (6)	4366 (6)	1510 (4)
Cp(213)	2231 (8)	4413 (6)	792 (3)
Cp(214)	734 (9)	3740 (6)	843 (4)
Cp(215)	283 (8)	3284 (5)	1558 (4)
Cp(221)	60 (9)	9033 (8)	4090 (6)
Cp(222)	875 (15)	9093 (8)	3372 (6)
Cp(223)	2037 (10)	8195 (12)	3307 (4)
Cp(224)	2049 (8)	7476 (7)	3943 (6)
Cp(225)	788 (9)	7990 (7)	4459 (3)

[a] $\times 10^5$ for Cr and S; $\times 10^4$ for all other atoms.

The crystal structure of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ consists of a closely packed array of two discrete molecular units which are crystallographically independent of each other (Figure 1). The two independent molecules possess only C_1 symmetry and are approximately identical in terms of their gross stereochemical features. The structure of molecule 1 is shown in Figure 2. Bond distances and angles for the two molecules are tabulated in Tables VI and VII, respectively, with average molecular dimensions being summarized in Table VIII. Apart from the parameters involving the η^5-C_5H_5 rings, which are approximations to an apparently disordered situation at each position, the largest deviation from the mean values is exhibited by the Cr(11)–C(111)–O(111) group. Both the Cr(11)–C(111) and C(111)–O(111) bond lengths differ by ca. 8σ from the average values, but the large thermal parameters for O(111) suggest that this deviation may be due to a disorder in this particular carbonyl group.

While the bond distances and angles exhibit only small differences between the two independent molecules (Table VIII), this similarity is not evident from the torsion angles presented in Table IX. However, if the dihedral angles about the Cr→Cr vector are considered, the majority of this difference may be recognized as being due to the direction of displacement of each sulfur atom from collinearity with its two bonded chromium atoms, as shown in Figure 3. Furthermore, the nonbonded contact distances given in Table X allow the minor differences in dimensions between the two molecules to be explained in terms of a reasonably crowded lattice. All but six of the η^5-C_5H_5 carbon atoms, C(111),

Table III. Final Thermal Parameters and Their Esd's (Å^2)[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(11)	476 (3)	466 (4)	335 (3)	111 (3)	−104 (3)	−116 (3)
Cr(12)	381 (3)	473 (4)	331 (3)	−3 (3)	−47 (2)	−111 (3)
S(1)	488 (5)	554 (6)	367 (5)	62 (4)	−80 (4)	−158 (4)
C(111)	51 (2)	69 (3)	76 (3)	2 (2)	−14 (2)	−13 (2)
O(111)	117 (3)	182 (4)	248 (5)	−5 (3)	−36 (3)	−38 (4)
C(112)	64 (3)	69 (3)	59 (3)	18 (2)	9 (2)	−19 (2)
O(112)	112 (3)	70 (2)	77 (3)	28 (2)	27 (2)	24 (2)
C(121)	47 (2)	76 (3)	50 (2)	7 (2)	−9 (2)	−11 (2)
O(121)	46 (2)	128 (4)	102 (3)	18 (2)	−17 (2)	−9 (3)
C(122)	53 (2)	62 (3)	59 (3)	−3 (2)	−2 (2)	−9 (2)
O(122)	110 (3)	55 (2)	123 (4)	−5 (2)	−5 (3)	18 (2)
Cp(111)	110 (5)	54 (3)	78 (4)	33 (3)	−1 (3)	−1 (3)
Cp(112)	95 (4)	61 (3)	152 (7)	35 (3)	−50 (5)	−63 (4)
Cp(113)	120 (5)	70 (4)	60 (3)	50 (4)	−10 (3)	−23 (3)
Cp(114)	75 (4)	90 (4)	107 (5)	42 (3)	9 (4)	−26 (4)
Cp(115)	89 (4)	87 (4)	83 (4)	53 (4)	−34 (3)	−22 (3)
Cp(121)	85 (4)	103 (4)	42 (2)	−13 (3)	−8 (2)	10 (3)
Cp(122)	70 (3)	73 (3)	57 (3)	−17 (3)	1 (2)	7 (2)
Cp(123)	48 (2)	73 (3)	69 (3)	−6 (2)	5 (2)	7 (3)
Cp(124)	66 (3)	83 (4)	69 (3)	9 (3)	28 (3)	−7 (3)
Cp(125)	104 (4)	90 (4)	42 (3)	−24 (3)	19 (3)	−25 (3)
Cr(21)	401 (3)	438 (4)	316 (3)	70 (3)	−25 (2)	−81 (3)
Cr(22)	352 (3)	449 (4)	316 (3)	0 (2)	−41 (2)	−80 (2)
S(2)	401 (5)	574 (6)	339 (5)	52 (4)	−36 (4)	−125 (4)
C(211)	60 (3)	53 (3)	55 (3)	6 (2)	16 (2)	−7 (2)
O(211)	115 (3)	66 (2)	98 (3)	11 (2)	39 (3)	7 (2)
C(212)	59 (3)	52 (2)	53 (3)	0 (2)	−11 (2)	−14 (2)
O(212)	61 (2)	86 (3)	101 (3)	7 (2)	−33 (2)	−17 (2)
C(221)	60 (3)	52 (2)	46 (2)	−2 (2)	−13 (2)	−10 (2)
O(221)	129 (3)	58 (2)	74 (2)	−21 (2)	−19 (2)	8 (2)
C(222)	52 (2)	69 (3)	41 (2)	9 (2)	−5 (2)	−12 (2)
O(222)	52 (2)	133 (4)	86 (3)	35 (2)	−12 (2)	−18 (2)
Cp(211)	92 (4)	66 (3)	70 (3)	35 (3)	−9 (3)	1 (3)
Cp(212)	53 (3)	77 (4)	107 (5)	27 (3)	−8 (3)	−17 (3)
Cp(213)	103 (5)	78 (4)	63 (3)	50 (3)	26 (3)	1 (3)
Cp(214)	113 (5)	73 (4)	77 (4)	40 (4)	−26 (4)	−38 (3)
Cp(215)	96 (4)	48 (3)	105 (5)	15 (3)	−8 (4)	−17 (3)
Cp(221)	81 (4)	94 (5)	209 (9)	2 (4)	−52 (6)	−91 (6)
Cp(222)	173 (9)	89 (5)	113 (7)	−66 (6)	−76 (7)	32 (5)
Cp(223)	86 (5)	183 (10)	84 (5)	−84 (6)	19 (4)	−39 (6)
Cp(224)	66 (4)	96 (5)	160 (7)	−9 (3)	−56 (4)	−36 (5)
Cp(225)	104 (5)	111 (5)	59 (3)	−57 (4)	−26 (3)	−12 (3)

[a] ×10^4 for Cr and S; ×10^3 for all other atoms. The anisotropic thermal parameters employed in the refinement are U_{ij} in the expression $f = f^0 \exp(-2\pi^2 \Sigma_{i,j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*)$. For isotropic atoms $f = f^0 \exp(-8\pi^2 U(\sin^2 \theta)/\lambda^2)$.

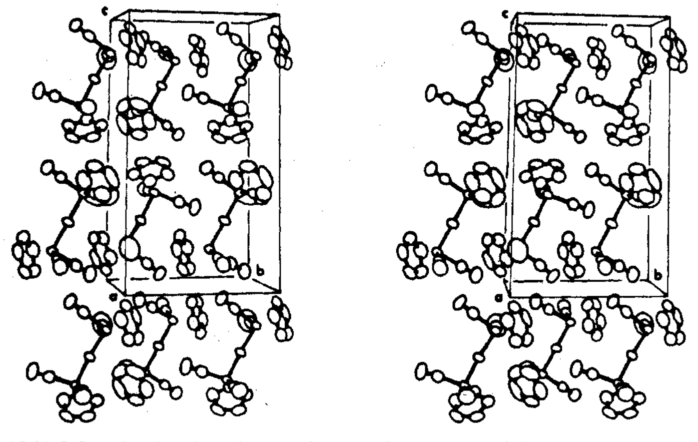

Figure 1. Packing of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ molecules viewed approximately down *a* toward the origin (ORTEP diagram; 50% probability ellipsoids).

C(122), and C(121), have nonbonded intermolecular contacts of less than 3.5 Å.

The peripheral molecular dimensions of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ are comparable to those found in other cyclopentadienylchromium carbonyls.[17] Indeed, the bond lengths and angles within each $(\eta^5\text{-}C_5H_5)Cr(CO)_2$ fragment are completely consistent with the view that the $\eta^5\text{-}C_5H_5$ ring functions as a formal five-electron donor to the metal center and that the terminal carbonyl groups are normal two-electron donor ligands. Hence, prior to incorporation of the sulfur atom, each end of the bimetallic complex can be viewed as containing a chromium atom having a formal 15-electron valence configuration.

The most striking aspect of the molecular structure is the central, essentially linear Cr–S–Cr linkage. The average Cr–S bond length of 2.074 Å (with individual values ranging from 2.071 (1) to 2.077 (1) Å) is the shortest such distance yet reported, and it implies the existence of multiple bonding

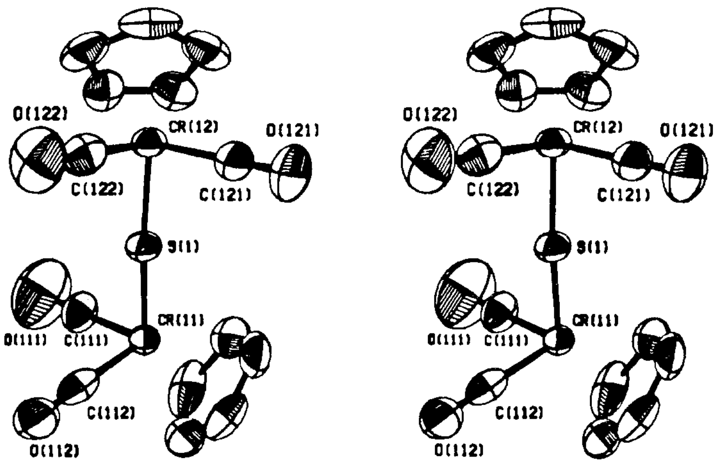

Figure 2. Stereoscopic view of one $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ molecule (ORTEP diagram; 50% ellipsoids).

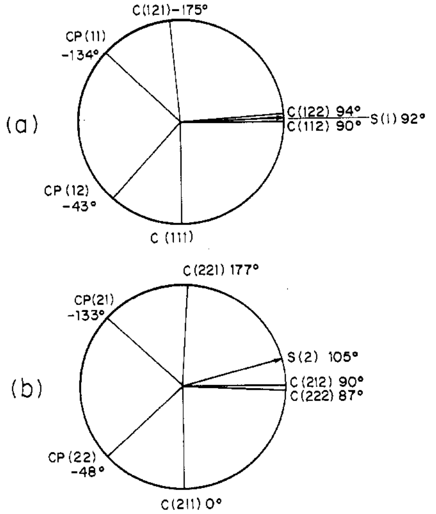

Figure 3. Dihedral angles about the Cr→Cr vector showing the direction of displacement of S for (a) molecule 1 viewed from Cr(11) toward Cr(12) and (b) molecule 2 viewed from Cr(21) toward Cr(22).

Table V. Low-Resolution Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$[a]

m/e	rel abund	assignt[b]
378	20	$(C_5H_5)_2Cr_2(CO)_4S^+$
322	14	$(C_5H_5)_2Cr_2(CO)_2S^+$
294	25	$(C_5H_5)_2Cr_2(CO)S^+$
266	100	$(C_5H_5)_2Cr_2S^+$
201	18	$(C_5H_5)Cr_2S^+$
182	96	$(C_5H_5)_2Cr^+$
136	28	Cr_2S^+
133	18	$(C_5H_5)_2Cr_2S^{2+}$
117	30	$(C_5H_5)Cr^+$
52	75	Cr^+

[a] Probe temperature ~90 °C. [b] The assignments involve the most abundant naturally occurring isotopes in each fragment.

Table VI. Bond lengths and Esd's (Å)[a]

molecule 1		molecule 2	
Cr(11)-S(1)	2.071 (1)	Cr(21)-S(2)	2.072 (1)
Cr(12)-S(1)	2.076 (1)	Cr(22)-S(2)	2.077 (1)
Cr(11)-CP(11)	1.849	Cr(21)-CP(21)	1.838
Cr(12)-CP(12)	1.842	Cr(22)-CP(22)	1.840
Cr(11)-C(111)	1.813 (5)	Cr(21)-C(211)	1.849 (5)
Cr(11)-C(112)	1.885 (5)	Cr(21)-C(212)	1.863 (5)
Cr(12)-C(121)	1.861 (5)	Cr(22)-C(221)	1.857 (5)
Cr(12)-C(122)	1.874 (5)	Cr(22)-C(222)	1.849 (5)
C(111)-O(111)	1.192 (5)	C(211)-O(211)	1.145 (6)
C(112)-O(112)	1.141 (5)	C(212)-O(212)	1.132 (5)
C(121)-O(121)	1.132 (5)	C(221)-O(221)	1.145 (5)
C(122)-O(122)	1.137 (6)	C(222)-O(222)	1.135 (5)
Cr(11)-Cp(111)	2.212 (5)	Cr(21)-Cp(211)	2.182 (5)
Cr(11)-Cp(112)	2.191 (5)	Cr(21)-Cp(212)	2.202 (5)
Cr(11)-Cp(113)	2.208 (5)	Cr(21)-Cp(213)	2.209 (5)
Cr(11)-Cp(114)	2.197 (5)	Cr(21)-Cp(214)	2.193 (5)
Cr(11)-Cp(115)	2.197 (5)	Cr(21)-Cp(215)	2.182 (5)
Cr(12)-Cp(121)	2.202 (5)	Cr(22)-Cp(221)	2.189 (6)
Cr(12)-Cp(122)	2.218 (5)	Cr(22)-Cp(222)	2.169 (5)
Cr(12)-Cp(123)	2.212 (5)	Cr(22)-Cp(223)	2.171 (5)
Cr(12)-Cp(124)	2.187 (5)	Cr(22)-Cp(224)	2.191 (6)
Cr(12)-Cp(125)	2.176 (5)	Cr(22)-Cp(225)	2.192 (6)
Cp(111)-Cp(112)	1.45 (1)	Cp(211)-Cp(212)	1.39 (1)
Cp(112)-Cp(113)	1.41 (1)	Cp(212)-Cp(213)	1.44 (1)
Cp(113)-Cp(114)	1.37 (1)	Cp(213)-Cp(214)	1.40 (1)
Cp(114)-Cp(115)	1.39 (1)	Cp(214)-Cp(215)	1.38 (1)
Cp(115)-Cp(111)	1.39 (1)	Cp(215)-Cp(211)	1.42 (1)
Cp(121)-Cp(122)	1.43 (1)	Cp(221)-Cp(222)	1.39 (1)
Cp(122)-Cp(123)	1.40 (1)	Cp(222)-Cp(223)	1.31 (1)
Cp(123)-Cp(124)	1.37 (1)	Cp(223)-Cp(224)	1.37 (1)
Cp(124)-Cp(125)	1.45 (1)	Cp(224)-Cp(225)	1.41 (1)
Cp(125)-Cp(121)	1.41 (1)	Cp(225)-Cp(221)	1.42 (1)

[a] CP(11), CP(12), CP(21), and CP(22) are the centroids of the $\eta^5\text{-}C_5H_5$ rings.

between the three atoms. This inference is supported by two previous structural determinations. The Cr–S distance of 2.510 (2) Å in $(CO)_5CrSPMe_3$ has been assigned to a formal single bond between the two elements,[18] and the Cr–S distance of 2.351 Å in $(CO)_5CrSFeCo_2(CO)_9$ has been interpreted in terms of synergic σ and π bonding between the two atoms.[19] Consequently, to account for the extreme shortness of the Cr–S bonds and the diamagnetism of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ and to provide each chromium atom in the complex with the favored 18-electron configuration, it is best to represent the bonding in the central linkage as Cr≡S≡Cr in which principally chromium 3d orbitals of σ and π symmetry overlap with appropriate sulfur orbitals. Obviously, the bonding within the Cr_2S unit can only be treated adequately by sophisticated molecular orbital techniques, but it should be noted that the rationale presented above does account for the documented ability of sulfur to linearly bridge nickel- and cobalt-containing moieties which also contain the metals in initial 15-electron configurations.[2]

The spectroscopic properties of the sulfur complex can be readily understood in terms of its molecular structure. In hexanes it exhibits infrared absorptions at 2000, 1960, 1932, and 1924 cm^{-1} which can be attributed to the terminal carbonyl ligands. A similar four-band ν_{CO} pattern persists when the complex is dissolved in solvents such as CH_2Cl_2 and THF or suspended in a Nujol mull, thereby suggesting that the asymmetric molecular structure observed in the solid state is maintained in these solutions. However, the ^1H NMR spec-

Table VII. Bond Angles and Esd's (deg)[a]

molecule 1		molecule 2	
Cr(11)-S(1)-Cr(12)	174.70 (6)	Cr(21)-S(2)-Cr(22)	173.95 (6)
S(1)-Cr(11)-C(111)	92.4 (1)	S(2)-Cr(21)-C(211)	93.8 (1)
S(1)-Cr(11)-C(112)	95.6 (1)	S(2)-Cr(21)-C(212)	96.2 (1)
C(111)-Cr(11)-C(112)	89.6 (2)	C(211)-Cr(21)-C(212)	90.0 (2)
CP(11)-Cr(11)-S(1)	128.7	CP(21)-Cr(21)-S(2)	128.6
CP(11)-Cr(11)-C(111)	122.0	CP(21)-Cr(21)-C(211)	120.7
CP(11)-Cr(11)-C(112)	119.0	CP(21)-Cr(21)-C(212)	118.5
S(1)-Cr(12)-C(121)	93.3 (1)	S(2)-Cr(22)-C(221)	94.2 (1)
S(1)-Cr(12)-C(122)	96.6 (1)	S(2)-Cr(22)-C(222)	95.7 (1)
C(121)-Cr(12)-C(122)	90.9 (2)	C(221)-Cr(22)-C(222)	88.8 (2)
CP(12)-Cr(12)-S(1)	127.6	CP(22)-Cr(22)-S(2)	126.5
CP(12)-Cr(12)-C(121)	120.5	CP(22)-Cr(22)-C(221)	122.3
CP(12)-Cr(12)-C(122)	119.4	CP(22)-Cr(22)-C(222)	120.2
Cr(11)-C(111)-O(111)	177.6 (5)	Cr(21)-C(211)-O(211)	178.5 (5)
Cr(11)-C(112)-O(112)	178.4 (4)	Cr(21)-C(212)-O(212)	177.9 (4)
Cr(12)-C(121)-O(121)	178.7 (5)	Cr(22)-C(221)-O(221)	177.8 (4)
Cr(12)-C(122)-O(122)	176.9 (4)	Cr(22)-C(222)-O(222)	178.6 (4)
Cp(111)-Cp(112)-Cp(113)	107.8 (5)	Cp(211)-Cp(212)-Cp(213)	107.7 (5)
Cp(112)-Cp(113)-Cp(114)	108.3 (6)	Cp(212)-Cp(213)-Cp(214)	107.1 (5)
Cp(113)-Cp(114)-Cp(115)	108.5 (6)	Cp(213)-Cp(214)-Cp(215)	109.1 (5)
Cp(114)-Cp(115)-Cp(111)	110.4 (6)	Cp(214)-Cp(215)-Cp(211)	108.3 (6)
Cp(115)-Cp(111)-Cp(112)	105.1 (6)	Cp(215)-Cp(211)-Cp(212)	107.9 (5)
Cp(121)-Cp(122)-Cp(123)	107.8 (5)	Cp(221)-Cp(222)-Cp(223)	108.3 (8)
Cp(122)-Cp(123)-Cp(124)	109.7 (5)	Cp(222)-Cp(223)-Cp(224)	112.0 (7)
Cp(123)-Cp(124)-Cp(125)	108.0 (5)	Cp(223)-Cp(224)-Cp(225)	106.5 (7)
Cp(124)-Cp(125)-Cp(121)	107.3 (5)	Cp(224)-Cp(225)-Cp(221)	106.2 (6)
Cp(125)-Cp(121)-Cp(122)	107.2 (5)	Cp(225)-Cp(221)-Cp(222)	107.0 (7)

[a] CP(11), CP(12), CP(21), and CP(22) are the centroids of the η^5-C_5H_5 rings bonded to the Cr of the same number.

Table VIII. Average Intramolecular Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$

	molecule 1	molecule 2
Cr-S	2.0735	2.0745
Cr-C(O)	1.858	1.855
C-O	1.151	1.139
Cr-Cp[12]	2.200	2.188
Cr-CP[a]	1.846	1.839
Cr-S-Cr	174.70	173.95
S-Cr-C(O)	94.5	95.0
S-Cr-CP	128.2	127.6
C(O)-Cr-C(O)	90.3	89.4
CP-Cr-C(O)	120.2	120.4
Cp-Cp	1.41	1.39
Cp-Cp-Cp	108.0	108.0
Cr-C-O	177.9	178.2

[a] CP represents the centroid of the cyclopentadienyl rings.

Table IX. Torsion Angles (deg)[a]

molecule 1		molecule 2	
Cr(11)-(S-Cr)-C(121)	-87	Cr(21)-(S-Cr)-C(221)	-109
Cr(11)-(S-Cr)-C(122)	-178	Cr(21)-(S-Cr)-C(222)	162
Cr(11)-(S-Cr)-CP(12)	47	Cr(21)-(S-Cr)-CP(22)	28
Cr(12)-(S-Cr)-C(111)	-88	Cr(22)-(S-Cr)-C(211)	-75
Cr(12)-(S-Cr)-C(112)	-178	Cr(22)-(S-Cr)-C(212)	-166
Cr(12)-(S-Cr)-CP(11)	47	Cr(22)-(S-Cr)-CP(21)	60

[a] See footnote to Table VI.

Table X. Intermolecular Nonbonded Contacts Less Than 3.5 Å[a]

O(111)-Cp(215)^{i}	3.203 (7)	O(122)-C(212)^{iv}	3.292 (6)
O(111)-O(211)^{ii}	3.268 (7)	O(122)-C(222)^{iv}	3.341 (6)
O(111)-Cp(211)^{i}	3.404 (7)	Cp(111)-O(212)^{v}	3.317 (7)
C(112)-O(211)^{iii}	3.403 (6)	Cp(112)-O(212)^{v}	3.303 (7)
O(112)-O(211)^{iii}	3.061 (6)	Cp(114)-O(211)^{v}	3.262 (7)
O(112)-O(212)^{iv}	3.200 (6)	Cp(115)-O(211)^{v}	3.425 (7)
O(112)-Cp(213)^{i}	3.261 (7)	Cp(121)-O(222)^{v}	3.427 (6)
O(112)-Cp(212)^{i}	3.325 (7)	Cp(123)-O(121)^{vi}	3.376 (6)
O(112)-C(211)^{iii}	3.481 (6)	Cp(124)-O(221)^{vi}	3.474 (7)
C(121)-O(221)^{iv}	3.250 (6)	Cp(125)-O(222)^{vi}	3.470 (7)
O(121)-O(221)^{iv}	3.106 (6)	O(221)-O(221)^{iv}	3.382 (8)
O(121)-Cp(211)^{iv}	3.364 (7)	Cp(224)-O(222)^{vi}	3.337 (8)
O(122)-O(212)^{iv}	3.121 (6)	Cp(223)-O(222)^{vi}	3.456 (10)
O(122)-O(222)^{iv}	3.202 (6)		

[a] Symmetry code: (i) $1-x$, $1-y$, $1-z$; (ii) $1-x$, $2-y$, $1-z$; (iii) x, y, $1+z$; (iv) $-x$, $1-y$, $1-z$; (v) $-x$, $2-y$, $1-z$; (vi) $1+x$, y, z.

trum of the compound in $CDCl_3$ consists of a single sharp resonance at δ 4.87 due to the cyclopentadienyl ring protons, and its ^{13}C NMR spectrum ($CDCl_3$) displays single resonances at δ 245.9 and 89.0 which are assignable to the carbonyl and cyclopentadienyl ligands, respectively. These NMR results indicate that the four CO and two η^5-C_5H_5 ligands are each magnetically equivalent on the time scale of the experiment at ambient temperature and that $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ is thus stereochemically nonrigid in solution. To reconcile the IR and NMR data, it is tempting to speculate that a low-energy process such as rotation of the $(\eta^5\text{-}C_5H_5)Cr(CO)_2$ groups about the Cr≡S≡Cr axis enables the ligand environments to be time-averaged, but elucidation of the rearrangement processes operative in this system must await a variable-temperature NMR study. In this connection, it can be noted that similar spectroscopic properties have been reported[20] for the complexes $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC{\equiv}CR)$ [R = H, Et, Ph] which contain an asymmetric $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ unit bridged by the acetylene group. Detailed studies of these complexes have provided evidence for rearrangement processes which average the environment of the CO ligands at room temperature sufficiently rapidly to result in only one ^{13}C NMR resonance due to these ligands while the IR spectrum still exhibits four carbonyl absorptions.[20]

That the CrSCr multiple bond in $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ is reasonably strong is evidenced by the inertness of the complex to reagents that transform the Cr≡Cr linkage in the related dimer $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$.[21] Toluene solutions of the sulfur complex do not react with CO at 100 atm, PPh_3 at reflux, nor NO at ambient temperature. In contrast, $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$ is converted by NO to $(\eta^5\text{-}C_5H_5)Cr(CO)_2$-

(NO) (43% yield) and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ (35% yield) under identical experimental conditions. It has previously been reported that the carbonyl dimer in benzene reacts with CO (100 atm) to form $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[22] and with phosphines to form unisolable products. Both bimetallic compounds are transformed by ClNO in CH_2Cl_2 to the well-known $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, the sulfur-containing reagent being converted in higher yields (60% vs. 42%).

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Registry No. $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$, 71549-26-3; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$, 54667-87-7; $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, 36312-04-6; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$, 68013-60-5; ClNO, 2696-92-6.

Supplementary Material Available: Table IV, a listing of structure amplitudes (67 pages). Ordering information is given on any current masthead page.

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Organometallic Nitrosyl Chemistry. 10.[1] Synthesis, X-ray Structural Characterization, and Properties of Dicarbonyl(η^5-cyclopentadienyl)(thionitrosyl)chromium

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The novel organometallic thionitrosyl complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ can be isolated in 21% yield from the reaction of $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$ and $S_3N_3Cl_3$ in tetrahydrofuran at −78 °C. The complex crystallizes in space group $P2_1/m$ of the monoclinic system in a cell of dimensions $a = 6.528$ (1) Å, $b = 9.641$ (1) Å, $c = 7.096$ (1) Å, and $\beta = 99.22$ (1)°. The structure has been refined by full-matrix least-squares methods to values of R and R_w of 0.025 and 0.033, respectively, for 848 observed reflections. Each molecule of the complex has crystallographic m symmetry and is in a "piano stool" configuration with the NS ligand being coordinated essentially linearly to the metal via the nitrogen atom. Important intramolecular dimensions are Cr–N = 1.694 (2) Å, N–S = 1.551 (2) Å, and the angle Cr–N–S = 176.8 (1)°. Several physical and chemical properties of the complex have been determined and have been compared with those displayed by its isostructural nitrosyl analogue, $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. Such a comparison results in a dichotomy concerning the relative electron-accepting and -donating properties of NS and NO ligands.

Introduction

It has been known for many years that nitric oxide can coordinate to transition metals in a wide range of oxidation states to form metal nitrosyls.[2] Analogous thionitrosyl complexes are markedly less abundant, a fact which reflects primarily the present lack of reagents which can be utilized to introduce the thionitrosyl group onto a transition metal. The few thionitrosyl complexes which have been prepared result from the reaction of elemental sulfur, propylene sulfide, or disulfur dichloride with coordinated nitrido ligands in the precursors.[3] We now report that during its reaction with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^-$, trithiazyl trichloride, $S_3N_3Cl_3$, functions as a source of NS to afford the novel organometallic complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$. We also provide full details of an X-ray investigation of this unique compound and describe some of its characteristic physical and chemical properties. Portions of this work have been communicated previously.[4]

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was confirmed by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use; all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared (IR) spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton and carbon-13 magnetic resonance spectra