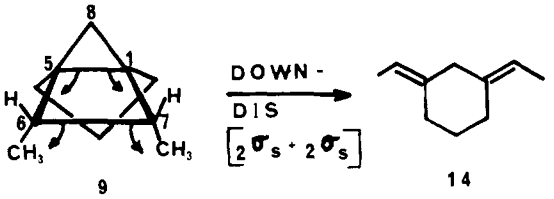
$J_{cd} < 0.35$ and $J_{bd} = 0.68$ Hz for diene **14**, which confirm the assignments based on criterion 1.); (3) nuclear Overhauser effects (proton–proton), maximized by spectral subtraction, which were detected for two pairs (H_d/H_a and H_d/H_b) in **12** (about 5% each, saturation of H_d) and for two pairs (H_a/H_b and H_a/H_d) in **14** (about 8% for H_b, saturation of H_a), in agreement with the above assignments.

Individual pyrolyses of propellanes **9–11** were carried out by flash vacuum (5×10^{-6} torr) pyrolysis (FVP) at temperatures between 520 and 690 °C and by static pyrolysis (sealed tubes, 100–200 torr) at 321 °C. At 520 °C, the total material balance was 97–99%. The percent yields of **12**, **13**, and **14**, respectively, were from **9**, 0.1, 0.5, and 99.4%, from **10**, 39.6, 47.8, and 12.6%, and from **11**, 3.6, 41.4, and 55.0%. Control experiments showed that the product compositions were not affected by interconversions among the stereoisomeric reactants or products and that the rates of pyrolysis of **9–11** did not differ significantly.

Our present interpretation of the data assumes that in the absence of strongly countervailing steric factors, the favored cycloreversion of [3.2.1]propellanes follows the "down-disrotatory" pathway exemplified by the highly stereospecific transformation **9** → **14**. This mode benefits from the same kind of steric preference that causes 3-methylcyclobutene to give *trans*-1,3-pentadiene,[10] but it also causes a steric clash of the exo substituents at C_6 and C_7 of the propellane with the syn hydrogen at C_8 in the transition state. Apparently, when one or both of the exo C_6 and C_7 groups are CH_3, as in **10** and **11**, the energy cost is sufficient to divert the cycloreversion into other pathways.



9

14

The underlying basis for the "down-disrotatory" preference is not obvious. As a $[_2\sigma_s + {}_2\sigma_s]$ process, this mode is formally forbidden to be concerted by orbital symmetry. Moreover, the alternative mechanism via biradical **5** receives no support from presently available theory.[9] Extended Hückel calculations suggest that stretching of the bridge bond (C_1–C_5) of [3.2.1.]propellane leads neither to a total molecular energy minimum at the biradical geometry nor to a crossing of the antisymmetric and symmetric frontier energy levels. Such a crossing would be needed to produce the A-below-S ordering conducive to symmetry-allowed disrotatory cleavage of **5**.

A speculative interpretation of the "down-disrotatory" pathway as an orbital symmetry forbidden reaction facilitated by efficient overlap of the C_1–C_5 and C_6–C_7 orbitals in the transition state merits consideration.[11]

Acknowledgment. We thank the National Science Foundation (CHE-8011399 and 7916210) for partial support of this work and of the NSF Northeast Regional NMR Facility at Yale University. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Professor K. B. Wiberg provided helpful discussions.

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Synthesis and Structure of $[PPN]_2[(\mu_2\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)Cr(CO)_5]$: A Chromium Cluster[1]

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Up to now, no fully characterized homogeneous chromium cluster has been known. There is only one compound reported in literature that should belong to this type of complexes, the $Na_2[Cr_3(CO)_{14}]$,[2] with either a linear or cyclic array of three chromium atoms, but no spectroscopic or structural details have been published so far. We were able to synthesize and characterize such a complex. Starting from the $[Cr_2(CO)_{10}SH]^-$ anion,[3] we enhanced the nucleophilicity of the complex by deprotonating[4] it to the deep green $[Cr_2(CO)_{10}S]^{2-}$ **1**. Treatment of **1** with excess $(CO)_5CrTHF$ (molar ratio = 1:2.2) leads to a change in color from green to red. After addition of [PPN]Cl[5] and recrystallization from acetone/ether, dark red crystals of **2**[6] can be obtained.

$$[PPN][\{(CO)_5Cr\}_2SH] \xrightarrow[THF]{NaH} Na[PPN][\{(CO)_5Cr\}_2S] \xrightarrow[2.\ [PPN]Cl]{1.\ (CO)_5CrTHF} \underset{\mathbf{2}}{[PPN]_2[(\mu_2\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)Cr(CO)_5]}$$

In the solid state, **2** can be kept in air for some days without apparent decomposition.

An X-ray crystal-structure determination of **2**[7] revealed discrete cations and anions. The PPN cation shows no abnormities.[8] The anion (Figure 1) consists of a chromium triangle capped with a $SCr(CO)_5$ group. The basal chromium atoms are connected by single bonds, but there is no binding interaction with the other metal atom. All four S–Cr distances are in the range of single bonds; S–Cr4 is the longest of them. There are three terminal and two bridging CO ligands attached to each of the three basal chromium atoms, totaling to nine terminal and three bridging carbon monoxide ligands for the cluster part of the anion. If the metal–metal bonds are neglected, each of these three chromium atoms has a roughly octahedral surrounding with bond angles ranging from 163.5 (6)° to 175.4 (4)° (Table I) for opposite ligands. Cr4 carriers 5 terminal CO groups and is octahedrally coordinated. The whole $(CO)_5Cr$ group is somewhat bent toward Cr3. All carbon monoxide bridges are asymmetric, two of them to an extent as to classify them as semibridging.[9] Therefore, the bond lengths of the carbon monoxide bridges to one of the chromium atoms (Cr1) are quite different with 192.3 (12) pm

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(5) Solution in C_2H_5OH; molar ratio $[PPN]_2[\{(CO)_5Cr\}_2S]/[PPN]Cl$ = 1/1; $[PPN]^+$ = bis(triphenylphosphane)nitrogenium. *Chemical Abstracts* recommended name for $[PPN]^+$ is: bis(triphenylphosphoranediyl)nitrogen(1+).

(6) 37% yield, mp 163 °C, correct C, H, N, Cr elemental analysis, purification leads to composition $[PPN]_2[(CO)_{17}Cr_4S]\cdot(H_3C)_2CO$. The acetone can be removed by application of vacuum.

(7) The dark red crystals crystallize in the triclinic space group $P\bar{1}$, with unit cell constants $a = 1477.2$ (5), $b = 1703.1$ (3), $c = 1950.0$ (4) pm, $\alpha = 86.94$ (2)°, $\beta = 72.08$ (2)°, $\gamma = 70.84$ (2)°. The structure was refined to values $R_F = 0.083$ and $R_W = 0.100$. 5902 independent reflections with $|F| \geq 3\sigma(F)$ were used.

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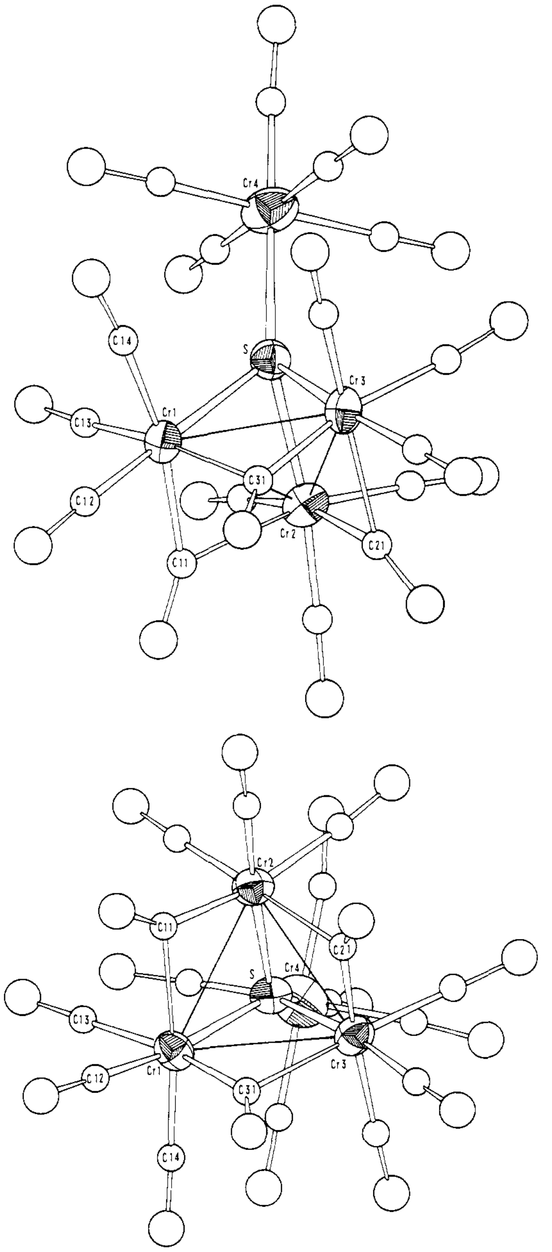

Figure 1. Molecular geometry of **2**. View from the side and from below. The anisotropically refined chromium and sulfur atoms are designated as 50% probability thermal ellipsoides.

Table I. Selected Anion Bond Lengths (ppm) and Bond Angles (deg) of Compound **2**

Cr-Cr	285.0 (9) mean	
Cr1,2,3-S	230.5 (5) mean	
Cr4-S	246.8 (3)	
Cr4-C_a	174.8 (14)	Δ = 10.6
Cr4-C_e	185.4 (15)	
Cr1-C14	184.1 (13) (trans to C11)	
Cr1-C13	178.6 (12) (trans to C31)	
Cr1-C12	178.7 (13) (trans to S)	
Cr1-C31	233.8 (11)	Δ = 39.4
Cr3-C31	194.4 (13)	
Cr2-C21	196.8 (12)	Δ = 26.5
Cr3-C21	223.3 (14)	
Cr1-C11	192.3 (12)	Δ = 39.6
Cr2-C11	231.9 (15)	
Cr1,2,3-S-Cr1,2,3	76.40 (3) mean	
Cr1-S-Cr4	134.20 (16)	
Cr2-S-Cr4	138.23 (15)	
Cr3-S-Cr4	130.59 (14)	
C12-Cr1-S	175.40 (4)	
C13-Cr1-C31	173.70 (5)	
C14-Cr1-C11	163.50 (6)	

(to C11) compared to 233.8 (11) pm (to C31). Since we have a terminal CO in an opposite position in each case, we are able to look for a trans effect of asymmetric CO bridges for the first time, and indeed, the distance C13–Cr1 is considerably shorter than C14–Cr1 (Table I). The electron-donating abilities of the sulfur atom can be evaluated from the $(CO)_5Cr$ group. The difference between equatorial and axial Cr–C bonds amounts to 10.6 pm. Comparable large effects are shown solely by ligands (sulfur as ligator), which are regarded as possessing only donor but no acceptor abilities.[10] If sulfur donates two electrons to each of the four chromium atoms, both parts of the molecule are electronically saturated.[11] Therefore, the sulfur ligand can be regarded formally as an eight-electron-donating sulfide ligand. In most other cases, where a bare sulfur atom is tetrahedrally surrounded by four metal atoms, it is best considered as a formal six-electron donor.[12]

As there is not apparent electronic reason for the observed deviation of the cluster part from C_{3v} symmetry as well as for the asymmetric arrangement of the $Cr(CO)_5$ group, we think that this is caused by package effects.

Infrared spectra, taken in THF and in KBr, show that the structure as determined in the solid state is essentially the same persistent in solution. In the CO valency region, seven bands are observed at 2061 vw, 2014 vw, 1968 vs, 1932 m, 1914 s, 1868 s, and 1796 vw(broad) cm^{-1} (THF solution). The habitus of the latter band is characteristic for the considered type of asymmetric CO bridges.[13] At −60 °C, we find two signals at 221.9 and 216.7 ppm (intensity ratio 1:3) in the ^{13}C NMR spectra, which are attributable to the cluster part of **2**. At −10 °C, there is already total carbonyl scrambling in this part of the molecule, as now only one signal is observed at 216.8 ppm. The $Cr(CO)_5$ group gives rise to two signals at 232.6 (cis) and 224.4 (trans) ppm with a 4:1 ratio (δ values relative to external Me_4Si, THFd_8 as solvent). The large downfield shift of the signal of the cis CO ligands ($Cr(CO)_5$ group) is interesting, since with other $LCr(CO)_5$ compounds, the resonance signal of the cis CO ligands is located at higher field than that of the trans CO.[14]

Acknowledgment. We are indebted to Fonds der Chemischen Industrie and to Prof. Dr. Th. Kruck for their support of this work, as well as to Dr. R. Froehlich for technical assistance.

Supplementary Material Available: Seven tables listing details of the structural work, three figures with numbering schemes, and two drawings, showing the packing (20 pages). Ordering information is given on any current masthead page.

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Effective Route to Azetidines from Azetidin-2-ones Using Hydroalanes as Specific Reducing Agents

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Although the chemistry and biochemistry of azetidin-2-ones have been extensively studied with regard to various β-lactam antibiotics,[2] less attention has been drawn to those of azetidines.