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Organometallic Radical-Initiated Carbon−Sulfur Bond Cleavage and Carbon−Carbon Coupling in Dithiocarbamate and Thiocarbenoid Cyclopentadienylchromium Complexes

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Cothermolysis of the dithiocarbamate complex $CpCr(CO)_2(S_2CNEt_2)$ (**2b**) with $[CpCr(CO)_3]_2$ (**1**) in toluene at 110 °C for 2 h led to the isolation of a yellowish red low-melting solid of $CpCr(CO)_2(CNEt_2)$ (**3b**; 6%), a dark red viscous liquid of $CpCr(CO)_2(SCNEt_2)$ (**4b**; 19%), dark red crystalline solids of $CpCr(CO)_2(\eta^2(C,O)\text{-}C(O)C(NEt_2)CH(NEt_2))$ (**5b**; 4%), dark green solids of $Cp_4Cr_4S_4$ (30%), dark brown solids of the double cubane $Cp_6Cr_8S_8(C(S)NEt_2)_2$ (**6b**; 13%), and blue solids of $Cr(S_2CNEt_2)_3$ (**8b**; 9% yield). Except for **5b**, the same product composition (**3b**, 11%; **4b**, 14%; **6b**, 37%; $Cp_4Cr_4S_4$, 20%) was obtained from a similar thermal treatment of **8b** with **1**. A similar reaction of the thiocarbenoid complex $CpCr(CO)_2(SCNMe_2)$ (**4a**) yielded yellow crystalline solids of $CpCr(CO)_2(CNMe_2)$ (**3a**, 16%), a dark brown solid of $Cp_4Cr_4S_2(CO)(CNMe_2)$ (**7a**, 36%), $Cp_4Cr_4S_4$ (10% yield), and $Cp_2Cr_2(CO)_4$ (17%). Complexes **3a**, **5b**, and **7a** have been characterized by single-crystal X-ray diffraction analysis. The structures of **3a** and **5b** possess a metal−carbyne and a metal−alkenylacyl moiety, respectively. Complex **7a** is a μ_3-aminocarbyne cubane complex.

Introduction

Carbon−carbon and carbon−sulfur bond-making and -breaking reactions bear relevance to many significant biological and industrial processes.[1,2] They are becoming an increasingly common feature in the reactivity of dithiocarbamates, since the first observation of carbon−sulfur bond cleavage in a Mo complex in 1972.[3] In some of these cases, a single C−S cleavage in the reaction of the dithiocarbamate anion with the metal substrate results in a complex in which the cleaved S atom assumes a distinctly different coordination mode, e.g., in bridged species of μ-S M_2,[3a−c] μ_3-S M_3, and μ-η^1(C):η^2(S) M_2[3d] types or in an M═S bond.[3e] In other instances, C−S bond cleavage is initiated by reaction with external reagents, e.g. with $Co_2(CO)_8$,[3f] with thiophilic PEt_3 to abstract the sulfur atom,[3c,g] with $Ru_3(CO)_{12}$,[3h] and with an organic isocyanate.[3c] Some examples are known where double C−S bond cleavage could be effected merely by thermal activation.[3c,h,i] Recently we have also encountered such an occurrence in the complex $CpCr(CO)_2(S_2CNEt_2)$ (**2b**), which resulted in the formation of the thiocarbenoid complex $CpCr(CO)_2(SCNEt_2)$ (**4b**) and a dithiooxamide-bridged double cubane additionally linked by a Cr−Cr bond.[4] We report here a hitherto unknown organometallic radical initiated C−S cleavage and C−C coupling leading to the isolation of a variety of cyclopentadienylchromium complexes, which include a new η^2(*C*,*O*)-bis(amino)alkenylacyl compound and an aminocarbyne cubane.

Experimental Section

General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in an M. Braun Labmaster 130 inert gas system. NMR spectra were measured on a Bruker 300 MHz FT NMR spectrometer (^1H at 300.14 MHz and ^{13}C at 75.43 MHz); ^1H and ^{13}C chemical shifts were referenced to residual C_6H_6 in C_6D_6. IR spectra in Nujol mulls or KBr disks were measured in the range 4000−400 cm^{-1} on a BioRad FTS-165 FTIR instrument. Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in house. $[CpCr(CO)_3]_2$ (**1**) was synthesized as described by Manning[9] from chromium hexacarbonyl (98% purity from Fluka). $CpCr(CO)_2(\eta^2\text{-}S_2CNEt_2)$ (**2b**), $CpCr(CO)_2(\eta^2\text{-}SCNMe_2)$ (**4a**), and $Cr(S_2CNEt_2)_3$ (**8b**) were obtained as described in the preceding paper

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in this issue.[5] All solvents were dried over sodium/benzophenone and distilled before use. Silica gel (Merck Kieselgel 60, 230−400 mesh) was dried at 140 °C overnight before chromatographic use.

Cothermolysis of $CpCr(CO)_2(\eta^2\text{-}S_2CNEt_2)$ (2b) with $[CpCr(CO)_3]_2$ at 110 °C. A dark brown mixture of $[CpCr(CO)_3]_2$ (**1**) (100 mg, 0.25 mmol) and $CpCr(CO)_2(\eta^2\text{-}S_2CNEt_2)$ (**2b**) (144 mg, 0.45 mmol) in toluene (8 mL) was stirred at 110 °C for 2 h. The resultant dark brown reaction mixture was concentrated to ca. 3 mL and loaded onto a silica gel column (2.5 × 15 cm) prepared in *n*-hexane. Elution gave five fractions. (i) A yellow eluate in *n*-hexane/toluene (1:2, 5 mL) was obtained, which on concentration gave a reddish yellow liquid of $CpCr(CO)_2(CNEt_2)$ (**3b**) (8 mg, 0.03 mmol, 6% yield). (ii) A dark red eluate in toluene (10 mL) was isolated, which on concentration gave dark red "oily" solids of $CpCr(CO)_2(\eta^2\text{-}SCNEt_2)$ (**4b**) (28 mg, 0.10 mmol, 19% yield). (iii) A dark brown eluate in toluene (15 mL) was collected, from which was obtained a brown solid; extraction of this with *n*-hexane/toluene (1:2, 3 × 3 mL) separated the less soluble $Cp_4Cr_4S_4$ as dark green solids (22 mg, 0.04 mmol, 30% yield), giving a solution which after concentration to 2 mL was chromatographed on a silica gel column (2 × 8 cm). A red eluate in toluene (5 mL) led to the isolation of red crystalline solids of $CpCr(CO)_2(\eta^2(C,O)\text{-}C(O)C(NEt_2)CH(NEt_2))$ (**5b**) (8 mg, 0.02 mmol, 4% yield); a reddish brown eluate in toluene (8 mL) was also collected, from which was isolated $Cp_6Cr_8S_8(\mu\text{-}\eta^2{:}\eta^2\text{-}SCNEt_2)_2$ (**6b**) (10 mg, 0.01 mmol, 12% yield).[4,5] (iv) A blue eluate in toluene (8 mL) was obtained, from which was isolated a blue solid of $Cr(S_2CNEt_2)_3$ (**8b**) (21 mg, 0.04 mmol, 9% yield). (v) A brown eluate in THF (10 mL) was obtained, which gave a dark brown solid (12 mg), consisting of a mixture of $Cp_4Cr_4S_2(CO)_2$ and an unidentified compound.

Cothermolysis of $CpCr(CO)_2(\eta^2\text{-}SCNMe_2)$ (4a) with $[CpCr(CO)_3]_2$ at 110 °C. A dark brown mixture of $[CpCr(CO)_3]_2$ (**1**) (80 mg, 0.20 mmol) and $CpCr(CO)_2(\eta^2\text{-}SCNMe_2)$ (**4a**) (52 mg, 0.20 mmol) in toluene (10 mL) was stirred at 110 °C for 3 h. The resultant dark brown reaction mixture was concentrated to ca. 3 mL and loaded onto a silica gel column (3 × 16 cm) prepared in *n*-hexane. Elution gave four fractions. (i) A dark green eluate in *n*-hexane/toluene (1:1, 8 mL) was collected, which on concentration gave dark green solids of $Cp_2Cr_2(CO)_4(Cr{\equiv}Cr)$ (12 mg, 0.03 mmol, 17% yield). (ii) A yellow eluate in *n*-hexane/toluene (1:4, 8 mL) was obtained, which on concentration gave reddish yellow crystalline solids of $CpCr(CO)_2(CNMe_2)$ (**3a**) (15 mg, 0.07 mmol, 16% yield). (iii) A dark green eluate in toluene (10 mL) was obtained, which on concentration gave dark green solids of $Cp_4Cr_4S_4$ (6 mg, 0.01 mmol, 10% yield). (iv) A brown eluate in toluene/THF (4:1, 10 mL) was obtained, from which was isolated a highly air-sensitive dark brown solid of $Cp_4Cr_4S_2(CO)(CNMe_2)$ (**7a**) (22 mg, 0.04 mmol, 36%).

Cothermolysis of $Cr(S_2CNEt_2)_3$ (8b) with $[CpCr(CO)_3]_2$ at 110 °C. A blue-green mixture of $[CpCr(CO)_3]_2$ (**1**) (40 mg, 0.10 mmol) and $Cr(S_2CNEt_2)_3$ (**8b**) (34 mg, 0.07 mmol) in toluene (5 mL) was stirred at 110 °C for 2 h. The resultant dark brown reaction mixture was concentrated to ca. 2 mL and loaded onto a silica gel column (2 × 10 cm) prepared in *n*-hexane. Elution gave four fractions. (i) A yellow eluate in *n*-hexane/toluene (1:2, 5 mL) was obtained, which on concentration gave $CpCr(CO)_2(CNEt_2)$ (**3b**) (6 mg, 0.02 mmol, 12% yield). (ii) A dark red eluate in toluene (6 mL) was collected, which on concentration gave $CpCr(CO)_2(SCNEt_2)$ (**4b**) (8 mg, 0.03 mmol, 14% yield). (iii) A dark brown eluate in toluene (15 mL) was isolated, from which was obtained a brown solid; extraction of this with *n*-hexane/toluene (1:2, 2 × 3 mL) separated insoluble dark green solids of $Cp_4Cr_4S_4$ (6 mg, 0.01 mmol, 20% yield) from a solution which on concentration yielded $Cp_6Cr_8S_8(\mu\text{-}\eta^2,\eta^2\text{-}SCNEt_2)_2$ (**6b**)[4,5] (12 mg, 0.01 mmol, 37% yield). (iv) A brown eluate in THF (10 mL) gave a dark brown unidentified solid (5 mg).

Data for the Compounds Obtained. Compound 3a. ^1H NMR (C_6D_6): δ 4.75 (s, 5H, Cp), 2.31 (6H, CH_3). ^{13}C NMR (C_6D_6): δ 88.6 (Cp); 41.1 (CH_3); 282.0 ($C{\equiv}Cr$); 245.3 (CO). IR (KBr, cm^{-1}): ν(CO) 1940 (s), 1863 (s); ν(CN) 1588 (m); $\nu(NC_2)$ 1170 (m). MS FAB$^+$ (*m*/*z*): 229 $[M]^+$, 201 $[M - CO]^+$, 173 $[M - 2CO]^+$, 117 $[CpCr]^+$, 52 $[Cr]^+$. Anal. Calcd for $C_{10}H_{11}NO_2Cr$: C, 52.40; H, 4.84; N, 6.11. Found: C, 52.07; H, 4.74; N, 6.18.

Compound 3b. ^1H NMR (C_6D_6): δ 4.74 (s, 5H, Cp), 2.66 (q, $J = 7$ Hz, 4H, CH_2), 0.89 (t, $J = 7$ Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 88.5 (Cp); 48.0 (CH_2); 14.8 (CH_3); 282.1 ($C{\equiv}Cr$); 245.6 (CO). IR (KBr, cm^{-1}): ν(CO) 1947 (s), 1864 (s); ν(CN) 1562 (m); $\nu(NC_2)$ 1163 (m). MS FAB$^+$ (*m*/*z*): 257 $[M]^+$, 229 $[M - CO]^+$, 201 $[M - 2CO]^+$, 117 $[CpCr]^+$, 52 $[Cr]^+$. HR-MS FAB$^+$ (*m*/*z*): for $[M]^+$ 257.0506 (found), 257.0508 (calcd). This compound is an oil (mp <-5 °C). No satisfactory elemental analysis was obtained. The proton NMR spectrum of a pure sample is given as Supporting Information.

Compound 5b. ^1H NMR (C_6D_6): δ 8.45 (s, 1 H, CH), 4.70 (s, 5 H, Cp), 3.84 (unres q, $J = 7$ Hz, 2 H, CH_2), 2.83 (q, $J = 7$ Hz, 2 H, CH_2), 2.75 and 2.71 (overlapping q, $J = 7$ Hz, 4 H, CH_2), 0.93 (t, $J = 7$ Hz, 3 H, CH_3), 0.86 (t, $J = 7$ Hz, 6 H, CH_3), 0.81 (t, $J = 7$ Hz, 3 H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 90.6 (Cp); 51.2, 48.1, 42.5 (CH_2); 14.9, 13.6, 13.3 (CH_3); 162.2 ($=CH$); 119.0 ($=C$); 389.5 (very weak, C(O)); 227.2, 258.0 (CO). IR (toluene, cm^{-1}): ν(CO) 1936 (s), 1844 (s); $\nu(C{=}C)$, $\nu(\eta^2\text{-}C(O))$, or ν(CN) 1633 (m), 1534 (m), 1470 (w), 1425 (w); $\nu(NC_2)$ 1151 (m). MS FAB$^+$ (*m*/*z*): 370 $[M]^+$, 314 $[M - 2CO]^+$, 286 $[M - 3CO]^+$, 169 $[C(NEt_2)CH(NEt_2)]^+$. HR-MS ESI$^+$ (*m*/*z*): for $[M + H]^+$ 371.1435 (found), 371.1426 (calcd); for $[M + Na]^+$ 393.1238 (found), 393.1246 (calcd). It was not possible to completely remove the trace amounts of $Cp_4Cr_4S_4$ contaminant. The proton NMR spectrum of a sample is given as Supporting Information.

Compound 7a. ^1H NMR (C_6D_6): δ 16.2 (s, $\nu_{1/2} = 22$ Hz, Cp), 15.0 (s, $\nu_{1/2} = 33$ Hz, Cp), 11.6 (s, $\nu_{1/2} = 138$ Hz, Cp). IR (Nujol, cm^{-1}): ν(CO) 1600 (s), ν(CN) 1567 (m), $\nu(NC_2)$ 1103 (m). MS EI$^+$: *m*/*z* 588 $[M - CO]^+$, 471 $[Cp_3Cr_3S_2(CNMe_2)]^+$, 117 $[CpCr]^+$, 52 $[Cr]^+$. This compound was highly air-sensitive, resulting in unsatisfactory elemental analysis data. The proton NMR spectrum of a pure sample is given as Supporting Information.

Thermolysis of $CpCr(CO)_2(SCNEt_2)$ (4b). A red solution of $CpCr(CO)_2(SCNEt_2)$ (**4b**) (9 mg, 0.03 mmol) in toluene-d_8 (0.5 mL) in a septum-capped 5 mm NMR tube under argon was maintained at ca. 110 °C, and its proton NMR spectrum was scanned at intervals to 2 h.

Crystal Structure Analyses. Diffraction-quality single crystals were obtained at −29 °C as follows: **3a** as reddish yellow needles and **5b** as red needles after 5 and 32 days, respectively, from solutions in toluene layered with hexane; **7a** as dark brown rhombuses from solutions in THF layered with hexane after 3 days.

The crystals were mounted on quartz fibers. The air-sensitive crystal of **7a** was coated with grease. X-ray data were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data were corrected for Lorentz and polarization effcts with

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Table 1. Data Collection and Processing Parameters

	3a	**5b**	**7a**
formula	$C_{10}H_{11}CrNO_2$	$C_{18}H_{26}CrN_2O_3$	$C_{24}H_{26}Cr_4NOS_2 \cdot THF$
M_r	229.20	370.41	688.68
temp, K	223(2)	223(2)	153(2)
cryst color, habit	red-yellow, needle	red, needle	dark brown, rhombus
cryst size, mm	0.10 × 0.24 × 0.32	0.06 × 0.22 × 0.34	0.39 × 0.20 × 0.19
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/m$	*Pbca*	*Pnma*
a, Å	5.9268(2)	12.7127(4)	17.3950(15)
b, Å	10.7263(4)	16.0862(5)	10.6646(9)
c, Å	8.3862(3)	18.3629(6)	14.7196(13)
α, deg	90	90	90
β, deg	97.171(2)	90	90
γ, deg	90	90	90
V, Å^3	528.96(3)	3755.2(2)	2730.6(4)
Z	2	8	4
density, g cm^{-3}	1.439	1.310	1.675
abs coeff, mm^{-1}	1.054	0.626	1.730
F(000)	236	1568	1412
θ range for data collecn, deg	2.45−30.74	2.22−26.37	2.34−25.03
index ranges	$-8 \le h \le 8, 0 \le k \le 14, 0 \le l \le 11$	$0 \le h \le 15, 0 \le k \le 20, 0 \le l \le 22$	$0 \le h \le 20, 0 \le k \le 12, 0 \le l \le 17$
no. of rflns collected	4520	29 008	19 114
no. of indep rflns	1604	3836	2555
max, min transmissn	0.928, 0.715	0.928, 0.567	0.801, 0.602
no. of data/restraints/ params	1604/0/93	3836/0/217	2555/2/171
final R indices ($I > 2\sigma(I)$)^{a,b}	R1 = 0.0369, wR2 = 0.0964	R1 = 0.0537, wR2 = 0.1182	R1 = 0.0850, wR2 = 0.2066
R indices (all data)	R1 = 0.0401, wR2 = 0.0981	R1 = 0.0855, wR2 = 0.1312	R1 = 0.1036, wR2 = 0.2170
goodness of fit on F^2 ^{c}	1.061	0.964	1.145
large diff peak, hole, e Å^{-3}	0.578, −0.263	0.531, −0.295	1.356, −0.809

[a] $R1 = (\sum|F_o| - |F_c|)\sum|F_o|$. [b] $wR2 = [(\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $GOF = [(\sum w|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

the SMART suite of programs[10] and for absorption effects with SADABS.[11] Structure solution and refinement were carried out with the SHELXTL suite of programs.[12] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The Cp and alkyl hydrogens were placed in calculated positions. The data collection and processing parameters are given in Table 1.

Results and Discussion

Products and Reaction Pathways. The cothermolysis of $CpCr(CO)_2(S_2CNEt_2)$ (**2b**) with $[CpCr(CO)_3]_2$ (**1**) in refluxing toluene for 2 h led to the isolation of the chromium carbyne complex $CpCr(CO)_2(CNEt_2)$ (**3b**) as reddish yellow low-melting solids (6% yield), the thiocarbenoid complex $CpCr(CO)_2(SCNEt_2)$ (**4b**) as dark red "oily solids" (19%), the aminoacyl complex $CpCr(CO)_2(\eta^2(C,O)\text{-}C(O)C(NEt_2)CH(NEt_2))$ (**5b**) as dark red crystalline solids (4%), the double cubane $Cp_6Cr_8S_8(C(S)NEt_2)_2$ (**6b**) as dark brown solids (13%), the coordination compound $Cr(S_2CNEt_2)_3$ (**8b**) as blue solids (9%), and the cubane $Cp_4Cr_4S_4$ as dark green solids (30%), as presented in Scheme 1. It was truly unexpected that except for the low-yield complex **5b**, the same product composition (**3b**, 11%; **4b**, 14%; **6b**, 37%; $Cp_4Cr_4S_4$, 20%) was obtained from a similar cothermolysis of **8b** with **1** (Scheme 2). Among these products, **4b**, **6b**, **8b**, and $Cp_4Cr_4S_4$ were obtained also by thermal degradation of **2b** alone, which also produced the thermally unstable bis(dithiocarbamate) doubly bridged dicubane $Cp_6Cr_8S_8(S_2CNEt_2)_2$ (**9**),[4,5] which in this present study was found to react with **1** at 90 °C within 1 h, transforming to noncharacterizable paramagnetic species. A comparison of the products and their yields from these three reactions and the analogous reaction of **4a** is given in Table 2. This shows that while the cleavage of one sulfur atom from **2** is a thermally achievable process, double desulfurization requires assistance from **1a**, the incumbent monomer of **1** arising from its facile dissociation.[13] The detection of $Cp_4Cr_4S_2(CO)_2$ (^1H NMR: δ(Cp) 9.74 and 5.66) and the isolation of the previously characterized cubane $Cp_4Cr_4S_4$ in substantial amounts in all these thermolytic reactions provide evidence for the initial formation of the precursor complex $[CpCr(CO)_2]_2S$,[6] a finding congruent with the observed thiophilicity of the $CpCr(CO)_3^{\bullet}$ species **1a**.[7] In the reaction between **8b** and **1**, a transfer of dithiocarbamate ligands from the tris(dithiocarbamate) coordination compound to **1a** has been effected, undoubtedly initiated by cleavage of the chelate rings in **8b**. The thermolytic desulfurization of the thiocarbenoid complex **4a** with **1** was found to yield the carbyne complex $CpCr(CO)_2(CNMe_2)$ (**3a**) as yellow crystalline solids in 16% yield and dark brown solids of the aminocarbyne cubane $Cp_4Cr_4S_2(CO)(CNMe_2)$ (**7a**) as the major product (36%), together with dark green solids of $Cp_4Cr_4S_4$ (10%) and $Cp_2Cr_2(CO)_4$ (17%), as shown in Scheme 3. It was demonstrated that complexes **3a**/**3b** and **7a**/**7b** did not originate from thermal degradation of the thiocarbene complex **4a**/**4b**, which remained unchanged after 2 h in refluxing toluene-d_8. The intermediate formation of the carbenoid species R_2NC: is indicated by the presence of alkene and alkenyl moieties in the structural com-

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(10) SMART version 4.05; Siemens Energy & Automation Inc., Madison, WI.

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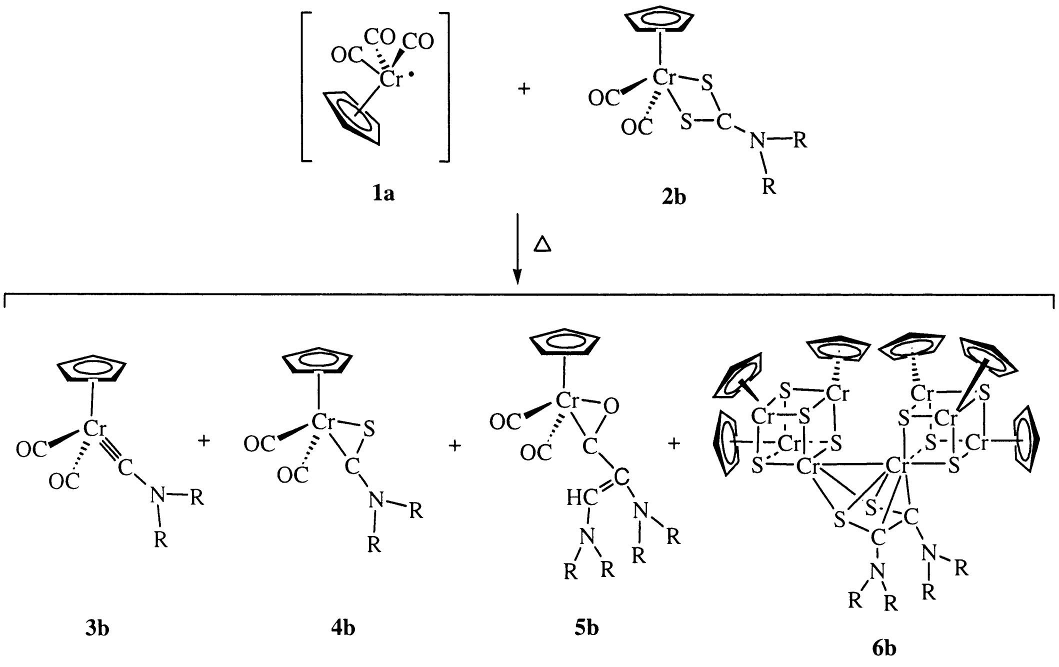
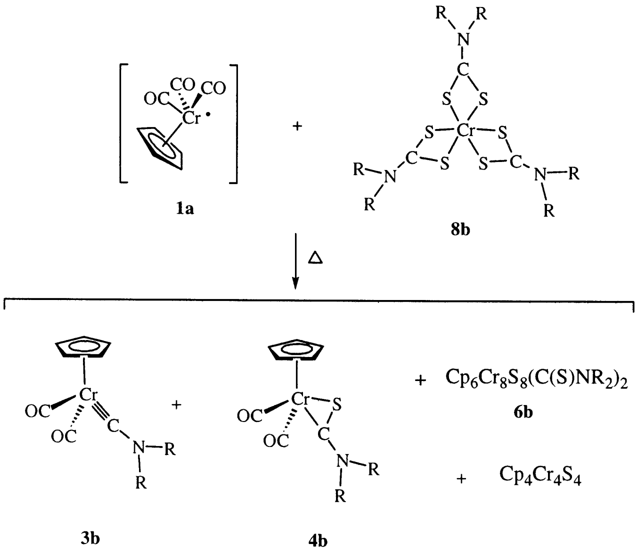
Scheme 1[a]



+ $Cp_4Cr_4S_4$

[a] R = Et. The six Cr−Cr bonds in each of the cubanes **6b** are omitted for clarity.

Scheme 2[a]



[a] R = Et.

positions of **6b** and **5b**, respectively, suggestive of carbene dimerization, which is a well-established process.[14] The carbyne moiety $R_2NC\equiv$ is evident in the structures of **3a** and **7a**. The thermal instability of **5b** in solution ($t_{1/2}$ = ca. 1.5 h at 110 °C) explains its extremely low isolated yield and frustrates our efforts to detect its immediate precursor. However, it is likely that the insertion of CO into the Cr−C bond involved in its formation originated from ligated CO, since these thermal degradations were found to be suppressed under an atmosphere of CO. The product complexes show that, with respect to sulfur cleavage, the reaction pathways fall into three categories in which (i) the dithiocarbamate (DTC) ligand remains intact, as in compounds **8** and **9**, (ii) the DTC ligand has undergone mono sulfur cleavage, producing species of types I and II, as found in the thiocarbenoid complex **4** and the dithiooxamide dicubane **6**, and (iii) the DTC ligand has suffered double sulfur cleavage, generating species of types III−V, as found in the Cr−aminocarbyne complex **3**, the alkenylacyl compound **5**, and the aminocarbyne cubane **7**, respectively (Scheme 4).

Spectral Features. The ^{1}H and ^{13}C NMR spectra of the mononuclear complex **3** show the Cp resonances (δ 4.75 and 88.6 for **3a**; δ 4.74 and 88.5 for **3b**) in the range observed for other CpCr moieties;[7] the C≡Cr resonances in the ^{13}C NMR spectrum (δ 282.0 for **3a**; δ 282.1 for **3b**) are comparable to that of the analogous complex $CpCr(CO)_2(CN\textit{i}\text{-}Pr_2)$ (δ 281.7).[8a] The two equivalent cis-oriented carbonyl ligands in complex **3** show only one resonance in the ^{13}C NMR spectrum (δ 245.3 for **3a**; δ 245.6 for **3b**). This is consistent with the observation in $CpCr(CO)_2(CN\text{-}\textit{i}\text{-}Pr_2)$ (δ 245.7).[8a] The Cp resonance of the acyl complex **5b** is observed in the ^{1}H NMR spectrum at δ 4.70 and at δ 90.6 in the ^{13}C NMR spectrum, which also shows the two carbonyl ligands at δ 227.2 and 258.0, respectively. The acyl resonance in ^{13}C NMR is barely visible at δ 389.5 (range observed for metal−acyl complexes δ 136.5−391.6),[15] and the alkenyl carbon atoms appear at δ 162.2 and 119.0, respectively. Four nonequivalent CH_2 protons were observed at δ 3.84, 2.83, 2.75, and 2.71. Three sets of CH_3 protons were found at δ 0.93 (3 H), 0.86 (6 H), and 0.81 (3 H). The proton Cp resonances of **7a** were seen

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[14] (a) Fischer, H.; Kreissl, F. R.; Schubert, U.; Hofmann, P.; Dötz, K. H.; Weiss, K. *Transition Metal Carbene Complexes*; VCH: Weinheim, Germany, 1984; pp 94−96. (b) Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. I, p 190. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

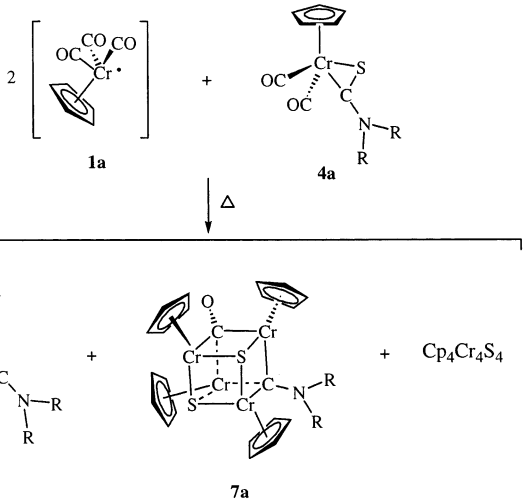
[15] Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059 and references therein.

Table 2. Yield (%) of Products[a]

	products													
	3		**4**		**5**		**6**		**7**		**8**			
reacn	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**	**7a**	**7b**	**8a**	**8b**	**9**	$Cp_4Cr_4S_4$
2b + **1** at 110 °C/2 h		6 (7)		19 (22)		4 (5)		13		*b*		9 (10)	0	30
8b + **1** at 110 °C/2 h		12 (33)		14 (40)		0		37		0			0	20
4a + **1** at 110 °C/2 h	16 (33)				0		0		36		0		0	10
thermolysis of **2b** at 90 °C/2 h[5]		0		11		*b*		7		0		19	11	22

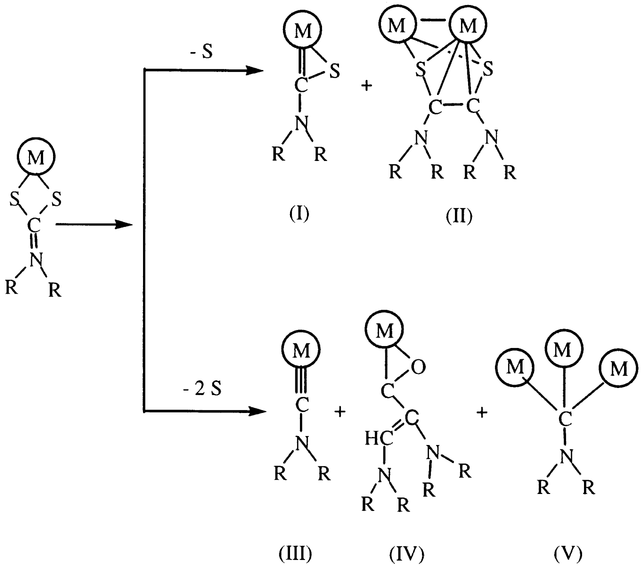
[a] Yields are based on **1** (values in parentheses are based on the respective substrates). [b] A trace observed in the ^{1}H NMR spectrum of the product mixture but lost in the chromatographic separation.

Scheme 3[a]



[a] R = Me. The six Cr−Cr bonds in the cubane core of **7a** are omitted for clarity.

Scheme 4



at *δ* 16.2, 15.0, and 11.6, as broad peaks, in accord with paramagnetism arising from an odd valence electron count (57 electrons) in the cubane molecule. In fact, such low-field resonances for Cp rings have been observed previously for other paramagnetic cyclopentadienylchromium complexes.[13c,16] Unfortunately, accurate integrals for the broad peaks could not be obtained. The *N*-methyl signals could not be observed.

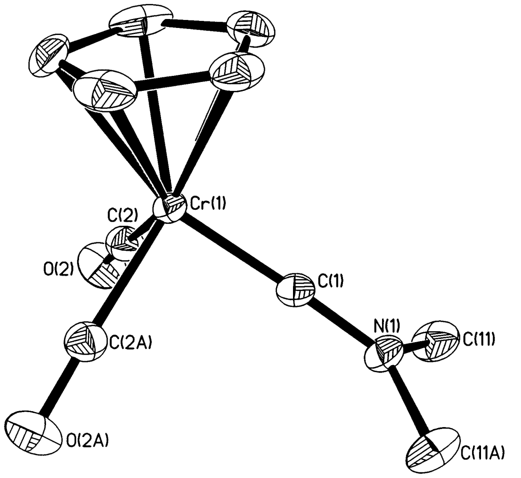


Figure 1. Molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level.

Structures. The molecular structures of **3a**, **5b**, and **7a** have been determined. The ORTEP diagrams are shown in Figures 1−3, and selected bond parameters are given in Tables 3−5 for these complexes.

The complex **3a** (Figure 1) belongs to the rare group of aminocarbyne chromium complexes, the first example of which was isolated fairly recently by Filippou and co-workers from a multiple-step synthesis from $Cr(CO)_6$.[8] The structure shows a CpCr moiety bonded to an aminocarbyne and two CO ligands, similar to the case for the W analogue. The $Cr-C_{carbyne}$ (1.740(2) Å) bond is longer than that of $CpCr(CO)_2(\equiv CPh)$[8c] (1.705(2) Å) but is shorter than the $Cr-C_{carbonyl}$ bond (1.8313(18) Å). The C−N bond (1.461(2) Å) is longer than that of $CpCr(CO)_2(S_2CNMe_2)$ (1.325(3) Å).[5] The Cr−C−N linkage (angle Cr(1)−C(1)−N(1) 177.7(2)°) is almost linear.

The structure of **5b**, illustrated in Figure 2, contains a metal−acyl unit, the bond parameters of which are given in Table 4; Table 6 shows a similarity of this structure to those of analogous Mo and W complexes. Noting that Δ((M−O) − (M−C)) is inversely proportional to the strength of the metal−acyl group interaction,[17] the data indicate that the Cr−acyl bond is stronger than those reported for similar Mo and W complexes. The short C(1)−C(2) distance (1.378(4) Å) is in close agreement with that of a double bond (1.335(3) Å), while that of C(1)−C(33) (1.415(4) Å) tends more toward the C−C

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[16] Goh, L. Y.; Leong, W. K.; Leung, P. H.; Weng, Z.; Haiduc, I. *J. Organomet. Chem.* **2000**, *607*, 64.

[17] (a) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. (b) Carmona, E.; Sánchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214. (c) Skagestad, V.; Rømming, C.; Tilset, M. *Inorg. Chem.* **1995**, *34*, 3194. (d) Adams, H.; Cubbon, R. J.; Sarsfield, M. J.; Winter, M. J. *Chem. Commun.* **1999**, 491. (e) Debad, J. D.; Legzdins, P. *Organometallics* **1993**, *12*, 2094.

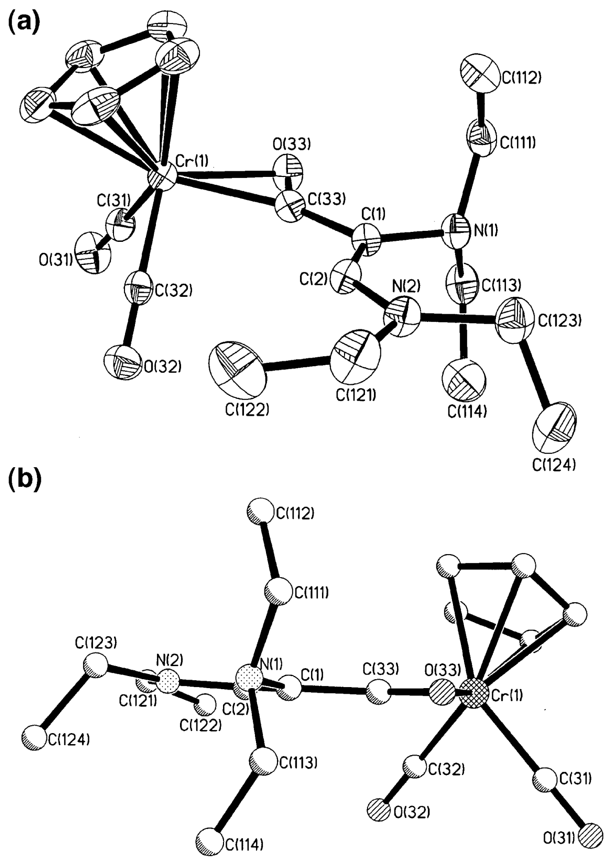

Figure 2. Two views of the molecular structure of **5b**. Thermal ellipsoids are drawn at the 50% probability level.

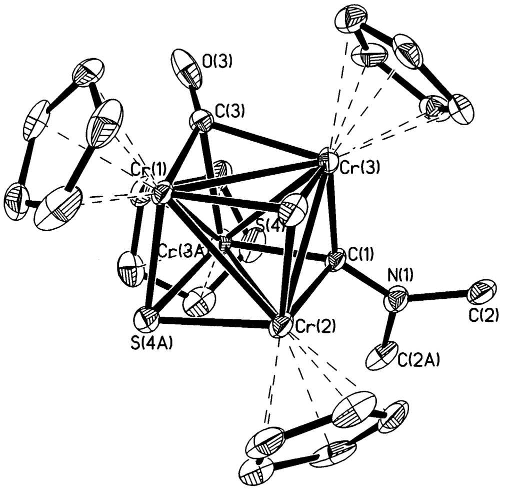

Figure 3. Molecular structure of **7a**. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Distances and Angles for 3a

Bond Distances (Å)			
Cr(1)−C(1)	1.740(2)	Cr(1)−C(2)	1.8313(18)
C(1)−N(1)	1.297(3)	N(1)−C(11)	1.461(2)
C(2)−O(2)	1.151(2)		
Bond Angles (deg)			
Cr(1)−C(1)−N(1)	177.7(2)	C(1)−N(1)−C(11)	121.89(11)
C(11)−N(1)−C(11A)	116.2(2)		

Table 4. Selected Bond Distances and Angles for 5b

Bond Distances (Å)			
Cr(1)−C(33)	1.977(3)	Cr(1)−O(33)	2.104(2)
C(1)−C(2)	1.378(4)	C(1)−C(33)	1.415(4)
C(1)−N(1)	1.439(3)	C(2)−N(2)	1.320(3)
C(33)−O(33)	1.242(3)	N(1)−C(111)	1.473(4)
N(1)−C(113)	1.480(4)	N(2)−C(121)	1.486(4)
N(2)−C(123)	1.472(4)	C(31)−O(31)	1.154(3)
C(32)−O(32)	1.154(4)		
Bond Angles (deg)			
Cr(1)−C(33)−O(33)	77.92(17)	Cr(1)−O(33)−C(33)	66.80(16)
O(33)−Cr(1)−C(33)	35.27(9)	Cr(1)−C(33)−C(1)	151.8(2)
O(33)−C(33)−C(1)	130.1(3)	N(1)−C(1)−C(2)	125.2(3)
C(33)−C(1)−N(1)	120.8(2)	C(33)−C(1)−C(2)	113.9(2)
C(2)−C(1)−N(1)	125.2(3)	C(1)−C(2)−N(2)	133.3(3)
N(2)−C(2)−C(1)	133.3(3)	C(1)−N(1)−C(113)	112.6(2)
C(1)−N(1)−C(111)	112.8(2)	C(111)−N(1)−C(113)	111.2(2)
C(2)−N(2)−C(121)	124.9(3)	C(2)−N(2)−C(123)	120.9(3)
C(121)−N(2)−C(123)	114.0(3)		

Table 5. Selected Bond Distances and Angles for 7a

Bond Distances (Å)			
Cr(1)−Cr(2)	2.752(2)	Cr(1)−Cr(3)	2.7817(19)
Cr(2)−Cr(3)	2.746(2)	Cr(1)−S(4)	2.268(2)
Cr(2)−S(4)	2.249(2)	Cr(3)−S(4)	2.253(3)
Cr(1)−C(3)	2.020(13)	Cr(3)−C(3)	2.209(9)
C(3)−O(3)	1.010(13)	Cr(2)−C(1)	2.212(11)
Cr(3)−C(1)	1.962(7)	C(1)−N(1)	1.365(14)
Bond Angles (deg)			
Cr(2)−Cr(1)−Cr(3)	59.51(5)	Cr(1)−Cr(2)−Cr(3)	60.79(5)
Cr(1)−Cr(3)−Cr(2)	59.70(5)	C(3)−Cr(1)−S(4)	101.6(2)
S(4)−Cr(1)−S(4A)	103.18(13)	C(3)−Cr(1)−Cr(2)	99.8(3)
S(4)−Cr(1)−Cr(2)	52.17(6)	C(3)−Cr(1)−Cr(3)	51.9(3)
S(4)−Cr(1)−Cr(3)	51.78(7)	C(1)−Cr(2)−S(4)	96.89(18)
S(4)−Cr(2)−S(4A)	104.37(13)	C(1)−Cr(2)−Cr(3)	45.04(19)
S(4)−Cr(2)−Cr(3)	52.48(7)	C(1)−Cr(2)−Cr(1)	91.9(3)
S(4)−Cr(2)−Cr(1)	52.78(6)	C(1)−Cr(3)−C(3)	99.0(3)
C(1)−Cr(3)−S(4)	104.6(3)	C(3)−Cr(3)−S(4)	96.5(3)
C(1)−Cr(3)−Cr(2)	52.9(3)	C(3)−Cr(3)−Cr(2)	95.3(3)
S(4)−Cr(3)−Cr(2)	52.36(7)	C(1)−Cr(3)−Cr(1)	96.7(3)
C(3)−Cr(3)−Cr(1)	46.0(3)	S(4)−Cr(3)−Cr(1)	52.27(7)
Cr(2)−S(4)−Cr(3)	75.17(9)	Cr(2)−S(4)−Cr(1)	75.05(8)
Cr(3)−S(4)−Cr(1)	75.95(9)	C(1)−N(1)−C(2)	123.6(5)
C(2)−N(1)−C(2A)	112.6(10)	O(3)−C(3)−Cr(1)	139.9(11)
O(3)−C(3)−Cr(3)	127.5(7)	Cr(1)−C(3)−Cr(3)	82.1(4)
Cr(3)−C(3)−Cr(3A)	74.8(4)	N(1)−C(1)−Cr(3)	135.0(3)
N(1)−C(1)−Cr(2)	115.0(8)	Cr(3)−C(1)−Cr(2)	82.0(4)
Cr(3)−C(1)−Cr(3A)	86.3(4)		

single-bond value of 1.532(2) Å. The unsymmetrical nature of substituents on the C(1)−C(2) alkenyl moiety has resulted in very different values of the C−NEt$_2$ distances. Of the two such distances, C(2)−N(2) (1.320(3) Å) is indicative of double-bond character (C−N = 1.47 Å and C=N = 1.27 Å),[18] in agreement with an sp^2 N center possessing a planar conformation. The second such distance, C(1)−N(1) (1.439(3) Å), is closer to the C−N single-bond distances in the amino side chains (1.472(4)−1.486(4) Å), in keeping with a pyramidal geometry at N(1), which is 0.418 Å above the C(1)−C(111)−C(113) plane. The C(33)−O(33) distance (1.242(3) Å) is slightly longer than the corresponding distance (1.154(4) Å) in the terminal CO ligands. The atoms O(33), C(33), C(1), C(2), N(2), C(121), and C(123) are coplanar, with Cr(1) and N(1) located on opposite sides of the plane, while the atoms N(1), C(111), and C(113) of the other tetraalkylamino "branch" are in a perpendicular plane.

The ORTEP plot of the cubane complex **7a** is illustrated in Figure 3. The structure contains a unique combination of three varieties of triply bridging ligands, viz., one μ_3-CO, one μ_3-CNR$_2$, and two μ_3-S ligands. As

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[18] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 224−229.

Table 6. Bond Distances (Å) and Angles (deg) of the Tricyclo Acyl Unit in 5b and Related Complexes

complexes	M−C	M−O	C−O	Δ((M−O) − (M−C))	M−C−O	M−O−C	O−M−C
$CpCr(CO)_2(\eta^2(C,O)\text{-}C(O)(CNEt_2)(CHNEt_2))$ (**5b**)	1.977(3)	2.104(2)	1.242(3)	0.127	77.92(17)	66.80(16)	35.27(9)
$TpMo(CO)_2(\eta^2\text{-}COMe)$[17a]	2.018(8)	2.222(5)	1.23(1)	0.204	82.6(5)	64.2(4)	33.2(3)
$TpMo(CO)_2(\eta^2\text{-}COPh)$[17a]	2.021(5)	2.189(3)	1.224(6)	0.168	80.8(3)	65.7(3)	33.5(2)
$TpMo(CO)(P(OMe)_3)(\eta^2\text{-}COMe)$[17a]	2.003(6)	2.200(4)	1.896(7)	0.197	82.2(4)	64.4(4)	33.4(2)
$TpMo(CO)(PEt_3)(\eta^2\text{-}COMe)$[17a]	2.002(8)	2.246(5)	1.898(8)	0.244	84.2(5)	62.5(4)	33.23
$Mo(\eta^2\text{-}COCH_2SiMe_3)Cl(CO)(PMe_3)_3)$[17b]	2.024(6)	2.324(4)	1.234(6)	0.30	87.5(4)	60.5(3)	32.0(2)
$CpW(NCMe_2)(Br)(\eta^2\text{-}COMe)^+BF_4^-$ [17c]	1.960(17)	2.158(10)	1.278(19)	0.62	80.6(9)	63.6(9)	35.7(6)
$TpW(CO)_2(\eta^2\text{-}C(O)(c\text{-}C_3H_5))$[17d]	2.02(2)	2.217(10)	1.25(2)	0.197			34.0(4)
$Cp^*W(NO)(\eta^2\text{-}C(O)CH_2CMe_3)(Ph)$ [17e]	2.046(4)	2.202(3)	1.236(5)	0.156	80.2(2)		33.6(1)

far as we are aware, this is the first case of a cubane containing a μ_3-aminocarbyne ligand; the closest examples of bridging aminocarbyne ligands are found in μ_2-CNR_2 complexes of tungsten[3g] and ruthenium.[3f,19] The cubane core of **7a** possesses a plane of symmetry which passes through Cr(1), Cr(2), C(3)O(3), and C(1)N-(1). The aminocarbyne ligand is planar at its N atom, indicative of sp^2 character and consistent with the double-bond character of the C−N bond, as reflected in its short distance of 1.365(14) Å. The Cr−C(3)−Cr angles (74.8(4), 82.1(4)°) at the μ_3-CO group are smaller than those at the μ_3-CNR_2 group (Cr−C(1)−Cr = 82.0(4), 86.3(4)°). Other bond parameters are comparable to those in the allied mixed μ_3-CO/μ_3-S cubane complex $Cp_4Cr_4S_2(CO)_2$, the structure of which has been previously determined.[6a] The C−O distance of μ_3-CO in **7a** (1.010(13) Å) is much shorter than the corresponding distance in terminal CO ligands in **5b** but very close to those in $Cp_4Cr_4S_2(CO)_2$ (1.041(10) and 1.006(11) Å). It is seen that the replacement of a μ_3-CO by a μ_3-CNR_2 ligand in the cubane core does not have any significant effect on the corresponding bond parameters of the two cubes.

Concluding Remarks

This study demonstrates the effectiveness of the organometallic radical $CpCr(CO)_3^{\bullet}$ in mono- and disulfur cleavage of η^2-dithiocarbamate ligands in cyclopentadienylchromium and chromium(III) complexes, leading to the formation of various types of cyclopentadienylchromium compounds belonging to the thiocarbene, carbyne, (amino)alkenylacyl, triply bridging aminocarbyne cubane, and doubly bridged dithiooxamido double-cubane varieties.

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Supporting Information Available: ORTEP diagrams and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and all bond lengths and angles for the structures of **3a**, **5b**, and **7a** and figures giving proton NMR spectra of **3b**, **5b**, and **7a** in C_6D_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Bodensieck, U.; Stoeckli-Evans, H.; Rheinwald, G.; Süss-Fink, G. *J. Organomet. Chem.* **1992**, *433*, 167.