

## Modeling Heterogeneous Catalysts with Homogeneous Catalysts. 2. Modeling Catalytic Hydrodenitrogenation

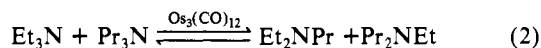
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Received October 1, 1981

Hydrodenitrogenation (HDN), the process by which nitrogen is removed (as ammonia) from nitrogenous materials by hydro-treating, is a major component of the complete process for converting crude oil to fuels. With the advent of the energy crisis and the need to develop coal, oil shale, and tar sands as alternative sources of fuel, HDN has become an even more important industrial process since these sources can contain up to 20% nitrogenous compounds. For example, one-third of the cost of producing synthetic fuel from oil shale is vested in the hydro-treating process. The major portion of the cost of hydro-treating is in HDN. Thus, the development of new and better HDN catalysts could allow the production of synthetic fuels from non-crude-oil sources that could be economically competitive with crude-oil-derived fuels.

We have recently shown<sup>1</sup> that it is possible to model the catalytic interactions of tertiary amines with palladium black, a heterogeneous catalyst, using a homogeneous catalyst based on Ru<sub>3</sub>(CO)<sub>12</sub>. In this modeling study, Ru<sub>3</sub>(CO)<sub>12</sub> and Os<sub>3</sub>(CO)<sub>12</sub> were found to be very efficient catalysts for the deuterium (D) for hydrogen (H) exchange reaction, (1), and the alkyl exchange reaction, (2).<sup>2,3</sup>



Since the major objective in HDN is to remove nitrogen as NH<sub>3</sub> by cleaving C-N bonds, the observation of C-N bond cleavage in reaction 2 suggested that it might be possible to model HDN with these same homogeneous catalysts. If it is possible to fully understand the mechanisms that promote catalytic C-N bond cleavage in the HDN process, then it may be possible to develop better HDN catalysts.<sup>4</sup>

We report here results that indicate that it is possible 1) model several aspects of heterogeneously catalyzed HDN using a ho-

Table I. Catalytic Deuterium for Hydrogen Exchange on Tertiary Amines. Site Selectivities ( $\alpha:\beta:\gamma$  Ratios) for Various Catalysts<sup>a-d</sup>

catalyst	temp, °C	Et <sub>3</sub> N	Pr <sub>3</sub> N	Bu <sub>3</sub> N
Pd black <sup>e</sup>	150	0.38:1	0.80:1	1.50:1
Ru <sub>3</sub> (CO) <sub>12</sub> <sup>e</sup>	150	0.29:1	1.30:1	2.10:1
Rh <sub>6</sub> (CO) <sub>16</sub> <sup>f</sup>	150	0.25:1	0.33:1	0.46:1:0.20
Rh <sub>6</sub> (CO) <sub>16</sub>	200	0.38:1	0.40:1:0.06	0.44:1:0.07
Rh metal <sup>g</sup>	232	0.22:1		
CoMo	237	0.24:1	0.25:1	0.36:1
CoMo	260	0.20:1	0.27:1:0.08	0.29:1:0.10
Mo metal <sup>h</sup>	230	0.26:1		

<sup>a</sup> The values shown represent  $\alpha:\beta:\gamma$  site selectivity ratios determined by <sup>2</sup>H NMR spectrometry using a Nicolet 360-MHz instrument. CDCl<sub>3</sub> was used as an internal standard. <sup>b</sup> Reaction solutions for the homogeneously catalyzed reactions contained 43 mmol of amine, 0.1 mmol of Rh<sub>6</sub>(CO)<sub>16</sub>, and 100 mmol of D<sub>2</sub>O under 800 psi of CO. Reaction solutions were heated as indicated for the times listed in Table II. <sup>c</sup> Reaction solutions for the heterogeneously catalyzed reactions contained 43 mmol of amine, 0.3-0.7 g of Ketjenfine CoMo catalyst, and 100 mmol of D<sub>2</sub>O under 250 psi of D<sub>2</sub>. Solutions were heated at listed temperatures for times listed in Table II. The Ketjenfine catalyst composition is 4% CoO and 12% MoO<sub>3</sub> on  $\gamma$ -alumina. Catalyst was activated by heating in flowing H<sub>2</sub> at 475 °C for 16 h before use. <sup>d</sup> Blanks run with alumina showed negligible deuterium incorporation. <sup>e</sup> From ref 2. <sup>f</sup> Data from ref 3. <sup>g</sup> At this temperature the Rh<sub>6</sub>(CO)<sub>16</sub> catalyst visibly decomposed to fine metal particles that catalyze D for H exchange. <sup>h</sup> Mo metal was formed by decomposition of Mo(CO)<sub>6</sub>. Reaction conditions: 6.0 mL of Et<sub>3</sub>N; 0.1 mmol of Mo(CO)<sub>6</sub>; 2.0 mL of D<sub>2</sub>O; 250 psi of D<sub>2</sub>; 230 °C.

mogeneous catalyst system in which the catalyst precursor is Rh<sub>6</sub>(CO)<sub>16</sub>. We have previously<sup>1-3</sup> determined the reactivity patterns of several homogeneous group 8 transition-metal catalysts with triethylamine (Et<sub>3</sub>N), tri-*n*-propylamine (Pr<sub>3</sub>N), and tri-*n*-butylamine (Bu<sub>3</sub>N) for reactions 1 and 2. Thus, it was logical to establish the reactivity patterns of a common industrial HDN catalyst, Ketjenfine cobalt-molybdenum (CoMo) on  $\gamma$ -alumina,<sup>5</sup> for reactions 1 and 2 with the same tertiary amines.

The results of the D for H exchange experiments (reaction 1) are shown in Tables I and II. The results for the alkyl-exchange study are shown in Table III. In the Pd black modeling studies, the homogeneous catalytic systems based on Ru<sub>3</sub>(CO)<sub>12</sub> and Os<sub>3</sub>(CO)<sub>12</sub> provided the most comparable reactivity patterns. In the present studies the reactivity patterns of the Rh<sub>6</sub>(CO)<sub>16</sub>-derived homogeneous catalyst most closely resemble those of the CoMo heterogeneous catalyst.

Unlike what was found in the Pd black modeling studies, the site selectivities ( $\alpha:\beta:\gamma$  ratios)<sup>6</sup> for the CoMo- and Rh<sub>6</sub>(CO)<sub>16</sub>-catalyzed reactions do not undergo dramatic changes on changing the amine from Et<sub>3</sub>N to Pr<sub>3</sub>N to Bu<sub>3</sub>N (see Table I for comparison). In the present study, there appears to be a slight increase in  $\alpha$  abstraction relative to  $\beta$  abstraction as the amine becomes bulkier. Similarly, there are no significant changes in product selectivity patterns as the amines change, again unlike what is found in the Pd black modeling studies. As shown in Table II, the same two major products are obtained for each amine with the CoMo- or Rh<sub>6</sub>(CO)<sub>16</sub>-based catalysts. The only difference

(5) (a) The Ketjenfine catalyst is composed of 4% CoO and 12% MoO<sub>3</sub> on  $\gamma$ -alumina. The catalyst comes as pellets and was crushed in a mortar and pestle and sieved before activation. Activation was accomplished by heating the catalyst to 475 °C in flowing hydrogen for 16 h. Despite attempts to maintain consistent conditions, catalyst activity varied from batch to batch and thus reliable kinetic data (turnover frequencies for moles amine reacted per unit time) for the various reactions and amines studied could not be obtained as was done in ref 1. (b) HDN is normally run with sulfided CoMo catalysts; however, sulfiding was omitted in the present study to minimize variables. Unsulfided CoMo catalysts are also active HDN catalysts [Sonnenmans, J.; Van Den Berg, G. H.; Mars, P. *J. Catal.* 1973, 31, 220-230]. Comparison of reactivity patterns for sulfided and unsulfided CoMo catalysts will be the subject of future reports.

(6) Because of the higher sensitivity of the Nicolet 360-MHz <sup>2</sup>H NMR spectrometer used in this study, we are now able to see evidence of  $\gamma$  D for H exchange. However,  $\gamma$  exchange rarely amounted to more than 10% of the deuterium-exchanged material and was only evident in the longer time and higher temperature runs.

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(1) Shvo, Y.; Thomas, D. W.; Laine, R. M.; *J. Am. Chem. Soc.* 1981, 103, 2461.

(2) Shvo, Y.; Laine, R. M.; *J. Chem. Soc., Chem. Commun.* 1980, 753.

(3) Laine, R. M.; Thomas, D. W.; Cary, L. W.; Buttrill, S. E. *J. Am. Chem. Soc.* 1978, 100, 6527.

(4) Considerable effort has been invested in studying HDN with use of model compounds such as quinoline, indole, and pyridine. See for example the excellent work of Satterfield. (a) Cocchette, J. F.; Satterfield, C. N. *Ind. Eng. Chem. Process Des. Dev.* 1981, 20, 49. (b) Satterfield, C. N.; Gultekin, S. *Ibid.* 1981, 20, 62. (c) Shih, S. S.; Katzer, J. R.; Kwart, H.; Stiles, A. B. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* 1977, 22, 919. (d) Stern, E. W. *J. Catal.* 1979, 57, 390. While many extremely useful observations have been made in these reports concerning the pathways (reaction networks) by which nitrogen is extracted from the organic product, to date only rate constants and thermodynamic information about the reaction networks have been described. No one, to date, has attempted to describe the catalytic mechanisms of C-N bond cleavage. Nelson and Levy [(e) Nelson, N.; Levy, R. B. *Ibid.* 1979, 58, 485] have suggested that most C-N bond cleavage arises from Hofmann degradation. In contrast to this idea, the results we report here indicate that no organic chemistry (C-N bond cleavage) occurs even at 260 °C with a  $\gamma$ -alumina blank over extended periods of time. Only in the presence of a metal catalyst is C-N bond cleavage observed. Thus our results do not support Hofmann degradation as the mechanism for C-N bond cleavage in HDN at the temperatures studied.

Table II. Patterns of Deuterium for Hydrogen Exchange for CoMo and Rhodium for Several Tertiary Amines<sup>a</sup>

catalyst	temp, °C	run time, h	Et <sub>3</sub> N-d <sub>1</sub>	Et <sub>3</sub> N-d <sub>2</sub>	Et <sub>3</sub> N-d <sub>3</sub>	Et <sub>3</sub> N-d <sub>4</sub>
Os <sub>3</sub> (CO) <sub>12</sub> <sup>b</sup>	150	20	α (0.5)	β (0.7)	β (1.2)	β (2.6)
Rh <sub>6</sub> (CO) <sub>16</sub> <sup>c</sup>	150	20	β (0.5)	β (1.4)	β (5.6)	α (9.5)
Rh <sub>6</sub> (CO) <sub>16</sub>	200	3.5	β (0.1)	β (0.1)	β (0.4)	α (1.0)
Rh <sup>d</sup>	232	2.5	? (16.2)	? (14.4)	? (9.5)	? (5.3)
CoMo	237	20	β (0.5)	β (3.4)	β (12.1)	α (6.3)
CoMo <sup>e</sup>	260	6	β (0.1)	β (1.3)	β (4.78)	α (3.6)
Mo metal <sup>f,g</sup>	230	20	β (0.0)	β (0.2)	β (0.6)	α (0.7)

catalyst	temp, °C	run time, h	Pr <sub>3</sub> N-d <sub>1</sub>	Pr <sub>3</sub> N-d <sub>2</sub>	Pr <sub>3</sub> N-d <sub>3</sub>	Pr <sub>3</sub> N-d <sub>4</sub>
Ru <sub>3</sub> (CO) <sub>12</sub>	150	20	α (15.0)	β (8.0)	β (5.0)	
Rh <sub>6</sub> (CO) <sub>16</sub>	150	20	β (0.3)	β (0.7)	α (1.6)	
Rh <sub>6</sub> (CO) <sub>16</sub>	200	3.5	β (0.0)	β (0.4)	α (2.6)	? (0.3)
CoMo	237	20	β (0.2)	β (3.0)	α (1.7)	? (0.5)
CoMo	260	20	β (2.7)	β (6.1)	α (3.3)	(1.2)

catalyst	temp, °C	run time, h	Bu <sub>3</sub> N-d <sub>1</sub>	Bu <sub>3</sub> N-d <sub>2</sub>	Bu <sub>3</sub> N-d <sub>3</sub>	Bu <sub>3</sub> N-d <sub>4</sub>
Ru <sub>3</sub> (CO) <sub>12</sub>	150	20	α (20.9)	β (8.3)	β (3.1)	
Rh <sub>6</sub> (CO) <sub>16</sub>	150	20	β (0.2)	β (0.4)	α (0.5)	
Rh <sub>6</sub> (CO) <sub>16</sub>	200	3.5	β (0.5)	β (1.0)	α (2.4)	? (0.3)
CoMo	237	40	β (3.7)	β (7.4)	α (6.1)	? (1.8)
CoMo	260	20	β (0.8)	β (1.3)	α (1.0)	? (0.5)

<sup>a</sup> See Table I for reaction conditions and catalyst preparation. Values in parentheses represent percent of total amines recovered (usually 98%). <sup>b</sup> Reference 2. <sup>c</sup> Reference 3. <sup>d</sup> At this temperature the Rh<sub>6</sub>(CO)<sub>16</sub> decomposes giving visible metal particles that actively catalyze D for H exchange. <sup>e</sup> Blank reactions with Condea alumina give negligible D for H exchange. <sup>f</sup> Mo metal was formed by decomposition of Mo(CO)<sub>6</sub>. Reaction conditions: 6.0 mL of Et<sub>3</sub>N; 0.1 mmol of Mo(CO)<sub>6</sub>; 2.0 mL of D<sub>2</sub>O; 250 of psi D<sub>2</sub>. Total decomposition in 1 h. <sup>g</sup> Note that Mo metal has the same product selectivity as the rhodium catalysts.

Table III. Extent of Formation of Mixed-Alkyl- or Dialkylamines from Catalytic Alkyl Exchange between Et<sub>3</sub>N and Pr<sub>3</sub>N<sup>a,b</sup>

catalyst	temp, °C	Et <sub>2</sub> NH	Et <sub>2</sub> NPr	EtNPr <sub>2</sub>	HNPr <sub>2</sub>	Et <sub>2</sub> NBu
Os <sub>3</sub> (CO) <sub>12</sub>	150		26.7	28.4		
Pd black <sup>c,d</sup>	150		0.2	0.6		
Rh <sub>6</sub> (CO) <sub>16</sub>	150		1.6	1.6		
Rh <sub>6</sub> (CO) <sub>16</sub>	200	0.2	5.2	4.6	0.1	0.6
CoMo <sup>e</sup>	260	3.9	3.1	4.2	5.2	
Rh <sub>6</sub> (CO) <sub>16</sub> <sup>f</sup>	200	0.4				0.2 <sup>h</sup>
Os <sub>3</sub> (CO) <sub>12</sub> <sup>f,g</sup>	200	4.6				0.4 <sup>h</sup>
CoMo <sup>f</sup>	260	2.0				1.8 <sup>h</sup>

<sup>a</sup> The numerical values correspond to (mol mixed amine/total mol amine) × 100 and are reproducible to within 10% of the indicated value. <sup>b</sup> Reaction conditions for the homogeneously catalyzed reactions involve heating a mixture of Et<sub>3</sub>N (14 mmol), Pr<sub>3</sub>N (14 mmol), 0.1 mL of H<sub>2</sub>O and 0.05 mmol of catalyst under 100 psi of N<sub>2</sub> for Os<sub>3</sub>(CO)<sub>12</sub> and Pd black and 400 psi of CO for the Rh<sub>6</sub>(CO)<sub>16</sub> catalyzed reactions for 20 h. <sup>c</sup> Reference 2. <sup>d</sup> 1.0 mmol catalyst. <sup>e</sup> The reaction conditions are the same as in *b* except 250 psi of H<sub>2</sub> and 0.5 g of catalyst (freshly activated) are used. <sup>f</sup> The reaction conditions are identical with those in *b* except 43 mmol of Et<sub>3</sub>N is used. <sup>g</sup> As in *f* except 250 psi of H<sub>2</sub> is employed instead of N<sub>2</sub>. <sup>h</sup> Note that the ethyl lost in the Et<sub>3</sub>N C-N bond cleavage results in the formation of small quantities of Et<sub>2</sub>NBu and ethanol in both the homogeneously and heterogeneously catalyzed reactions. We observe no formation of ethane in the gases above the reaction solutions.

is that the second major product for the Rh<sub>6</sub>(CO)<sub>16</sub>-catalyzed reaction is always the major product for the CoMo-catalyzed reaction and vice versa.

There are several possible explanations for the observed inversion of product selectivity. Thus, the differences in product selectivity (i) are simply a consequence of differences in reaction temperature as was found in the Pd black D for H exchange studies, (ii) arise because of the different metallic properties of CoMo compared with the rhodium catalyst, (iii) are the result of support interactions with CoMo that modify its catalytic properties, and (iv) occur because of alloy properties extant in CoMo that are unobtainable with the homogeneous rhodium catalyst.

Combinations of these possibilities could also explain the inversion. The first explanation is not valid because increasing the reaction temperature of the rhodium-catalyzed reaction (from 150 to 200 °C)<sup>7-9</sup> did not result in a change in product selectivities.

We are currently investigating the other three explanations. If product inversion results because of either of the latter two possibilities, then the model system may be a valuable probe of catalyst-support interactions or alloying effects (see footnote *g*, Table II).

The alkyl-exchange studies (Table III) reveal that CoMo does catalyze alkyl exchange, but only inefficiently, as was found with the Rh<sub>6</sub>(CO)<sub>16</sub> catalyst. Coincidentally, CoMo catalysis of the first step in the HDN of Et<sub>3</sub>N and Pr<sub>3</sub>N occurs as witnessed by the observance of C-N bond cleavage of these tertiary amines at 260 °C to obtain Et<sub>2</sub>NH and Pr<sub>2</sub>NH (Table III).

The parallels between the Rh<sub>6</sub>(CO)<sub>16</sub> homogeneous catalyst system and the CoMo catalyst system for site selectivity and product selectivity in the D for H exchange in Et<sub>3</sub>N, Pr<sub>3</sub>N, and in the alkyl-exchange reaction provide good evidence that the homogeneous rhodium catalyst system can be used to model the catalytic reactions of CoMo with amines.

The key question to be answered is whether or not the homogeneous rhodium catalyst can be used to model CoMo catalysis of HDN. That is, can it catalytically cleave C-N bonds to form N-H bonds, a necessary step in the HDN process. Table III shows that *both rhodium and osmium catalytically cleave C-N bonds in Et<sub>3</sub>N to form Et<sub>2</sub>NH*. This is the same initial step in the CoMo-catalyzed HDN of Et<sub>3</sub>N, thus establishing the validity of the model. Further support in favor of a valid model comes from our observations that the same rhodium catalyst system can catalyze reactions similar to those observed for CoMo-catalyzed HDN, where pyridine is the substrate<sup>10</sup> (eq 3). *N*-pentyl-piperidines similar to **1** have been found as intermediates in HDN modeling studies with CoMo catalysts and pyridine.<sup>11</sup>

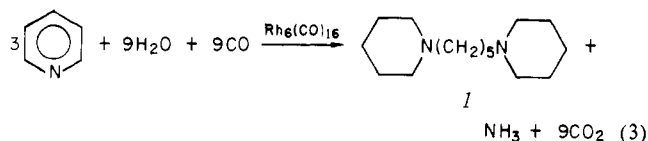
(7) In the <sup>2</sup>H NMR spectrum of the Pr<sub>3</sub>N/Rh<sub>6</sub>(CO)<sub>16</sub> (200 °C) reaction we were fortunate enough to observe two very clean peaks, one a doublet and the other a quintet. This observation provides proof of the mass spectral analysis in that the predicted major product Pr<sub>2</sub>NCHD<sub>2</sub>CH<sub>3</sub> should, by proton coupling, give a doublet and a quintet in the <sup>2</sup>H NMR spectrum.

(8) We have observed (by IR spectroscopy) the presence of Rh<sub>12</sub>(CO)<sub>30</sub><sup>2-</sup> and Rh<sub>5</sub>(CO)<sub>15</sub><sup>-</sup> in all the rhodium-catalyzed D for H exchange reactions.

(9) Note that when the temperature of the homogeneous rhodium-catalyzed D for H exchange was raised to 230 °C, rhodium metal was deposited in the reactor. This metal proved to be an active catalyst for D for H exchange. The important point is that the metal exhibited a totally different behavior from the homogeneous catalyst in that D<sub>1</sub> products predominated. This was confirmed in the <sup>2</sup>H NMR spectrum, which showed several products.

(10) Laine, R. M.; Thomas, D. W. *J. Org. Chem.* 1979, 44, 4964.

(11) Sonnemans, J.; Neyens, W. J.; Maxs, P. *J. Catal.* 1974, 34, 230. See ref 5b as well.



Finally, HDN C-N cleavage normally results in the formation of N-H and C-H bonds.<sup>4</sup> Analysis of the gas phase above the CoMo reactions in which Et<sub>2</sub>NH was observed revealed only hydrogen. The ethyl groups lost are observed by GC-mass spectroscopy as Et<sub>2</sub>NBu and EtOH. The mechanism of transformation of two ethyl groups to a butyl group or one ethyl group to ethanol is not apparent; however, in the rhodium and osmium modeling studies of CoMo, Et<sub>3</sub>N is also observed to lose ethyl groups to obtain Et<sub>2</sub>NH and coincidentally to produce Et<sub>2</sub>NBu and EtOH. This represents an additional reaction parameter that supports reliable modeling of the reactivity patterns of the heterogeneous HDN catalyst, CoMo, using a homogeneous catalyst derived from Rh<sub>6</sub>(CO)<sub>16</sub>.

Sufficient information is now available from the catalytic and stoichiometric reactions of amines with organometallic compounds to propose and test a complete mechanistic scheme for C-N bond cleavage in the HDN process.<sup>12</sup>

**Acknowledgment.** We thank the National Science Foundation for their generous support of this work through CHE Grant No. 78-25069. RML would also like to thank Professor Michel Blanchard and the Université de Poitiers for a sabbatical leave position.

**Registry No.** Rh<sub>6</sub>(CO)<sub>16</sub>, 28407-51-4; Ru<sub>3</sub>(CO)<sub>12</sub>, 15243-33-1; Os<sub>3</sub>(CO)<sub>12</sub>, 15696-40-9; Et<sub>3</sub>N, 121-44-8; Pr<sub>3</sub>N, 102-69-2; Bu<sub>3</sub>N, 102-82-9.

(12) Laine, R. M., to be submitted for publication.

### Synthesis and Crystal Structure of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cr<sub>2</sub>S<sub>5</sub> Containing an Unusual η<sup>1</sup>-(μ-Disulfide) Ligand

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Received November 5, 1981

Among transition-metal complexes with a metal-metal triple bond, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mo]<sub>2</sub> plays a unique role because of its versatile reaction possibilities.<sup>1</sup> In contrast, little is known concerning the reactivity of its chromium analogue, for which only the reactions with small nucleophiles, e.g., CO<sub>2</sub> and RC≡CR,<sup>3</sup> have been observed to give well-defined products. We chose [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(CO)<sub>2</sub>Cr]<sub>2</sub> as starting material for the reaction with elemental sulfur, because we expected the five methyl substituents at the cyclopentadienyl ligand to favor the reaction.<sup>4</sup>

The reaction of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(CO)<sub>2</sub>Cr]<sub>2</sub> with an excess of sulfur in toluene<sup>5</sup> gives as the only isolable product black-green crystals

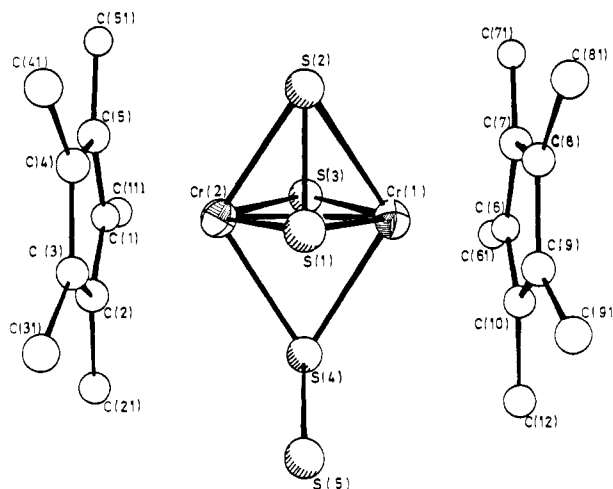


Figure 1. View of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cr<sub>2</sub>S<sub>5</sub>.

Table I. Selected Bond Lengths *d* (Å) and Bond Angles ω (Deg)

bond	<i>d</i>	angle	ω
Cr(1)-Cr(2)	2.489 (2)	Cr(1)-S(1)-Cr(2)	65.6 (1)
Cr(1)-S(1)	2.295 (4)	Cr(1)-S(1)-S(2)	62.1 (1)
Cr(1)-S(2)	2.297 (3)	Cr(1)-S(2)-Cr(2)	65.7 (1)
Cr(1)-S(3)	2.239 (3)	Cr(1)-S(2)-S(1)	62.1 (1)
Cr(1)-S(4)	2.344 (4)	Cr(1)-S(3)-Cr(2)	67.6 (1)
Cr(1)-C(C <sub>5</sub> Me <sub>5</sub> )	2.233 (9)	Cr(1)-S(4)-Cr(2)	64.0 (1)
Cr(2)-S(1)	2.302 (4)	Cr(1)-S(4)-S(5)	108.8 (1)
Cr(2)-S(2)	2.292 (3)	Cr(2)-S(1)-S(2)	61.9 (1)
Cr(2)-S(3)	2.238 (3)	Cr(2)-S(2)-S(1)	62.3 (1)
Cr(2)-S(4)	2.354 (4)	Cr(2)-S(4)-S(5)	108.8 (2)
Cr(2)-C(C <sub>5</sub> Me <sub>5</sub> )	2.227 (9)	S(1)-Cr(1)-S(2)	55.8 (1)
S(1)-S(2)	2.149 (5)	S(1)-Cr(1)-S(4)	76.1 (1)
S(4)-S(5)	2.101 (5)	S(2)-Cr(1)-S(3)	84.0 (1)
		S(3)-Cr(1)-S(4)	74.1 (1)

of the diamagnetic complex (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cr<sub>2</sub>S<sub>5</sub>. The compound has been characterized by total elemental analysis. The 70-eV mass spectrum consists of the parent ion followed by consecutive loss of three sulfur atoms, giving the most stable fragment (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cr<sub>2</sub>S<sub>2</sub><sup>+</sup>. The <sup>1</sup>H NMR spectrum exhibits only one singlet at 2.13 ppm (CDCl<sub>3</sub>), which indicates a symmetric structure with respect to the C<sub>5</sub>Me<sub>5</sub> groups. Infrared absorptions (KBr disk) at 598 w, 495 m, and 445 w cm<sup>-1</sup> may be attributed to different Cr-S bonding modes. As these spectroscopic data were not sufficient for a structural characterization of the new complex, an X-ray crystal structure was carried out. The monoclinic crystals crystallize in the space group C<sub>2h</sub>-P2<sub>1</sub>/c, with cell constants *a* = 13.970 (5) Å, *b* = 10.188 (3) Å, *c* = 16.482 (5) Å; β = 92.46 (3)°; *V* = 2343.6 Å<sup>3</sup>; *Z* = 4. Of 3210 measured reflections (Mo Kα radiation), 2212 with *I* ≥ 2.5σ(*I*) were used for the refinement of the structure (*R*<sub>F</sub> = 0.062).

The dominating feature of the structure (Figure 1) is the plane of the five sulfur atoms, perpendicular to the metal-metal bond and parallel to the two η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> planes. It contains three different types of sulfur ligands: (i) a μ-S ligand, S(3), bridging the two Cr atoms in the usual way;<sup>6</sup> (ii) a η<sup>2</sup>(μ-S, μ-S) ligand, S(1)S(2), forming a side-on bonded disulfide bridge;<sup>7</sup> (iii) a η<sup>1</sup>(μ-S) ligand, representing a novel type of disulfide bridge in which S(4) is coordinated to both Cr atoms, leaving S(5) uncoordinated. Whereas the atoms S(1)-S(4) are in a nearly square-planar arrangement around the Cr-Cr axis, the bond S(4)-S(5) is bent with respect to the plane Cr(1)-S(4)-Cr(2) with S(5) oriented

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(5) A mixture of 1.46 g (3 mmol) of [(C<sub>5</sub>Me<sub>5</sub>)(CO)<sub>2</sub>Cr]<sub>2</sub> and 0.38 g (1.48 mmol) of S<sub>8</sub> in 100 mL of toluene was stirred at 45 °C for 17 h. The reaction mixture was filtered, concentrated, and chromatographed (30 × 3 cm, SiO<sub>2</sub>). Unreacted starting material was eluted with toluene as a green band, followed by a dark green band of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cr<sub>2</sub>S<sub>5</sub> (22% yield), eluted with 3:1 toluene:ether. Black-green prisms were obtained by recrystallization from toluene at -35 °C.

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