pairs of satellites (in part, overlaid) with coupling constants 41.8, 42.6, and 52.3 Hz: the first coupling constant is also observed on the signal of the carbonyl C atom, the second on that of an allenic C atom, and the third on that of an aromatic C atom. These results are consistent only with structure 3.

The advantage of the INADEQUATE pulse sequence is that it enables structures such as 1 and 2, or 3 and 4 to be differentiated unequivocally, without having to draw upon reference compounds.

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A General Method for the Synthesis of Heterometal Clusters of the M₂Fe₂S₄-Cubane Type (M = Cr, Mo)
By Henri Brunner, Heike Kauermann, and Joachim Wachter*

Interest in the cubane-like molecules Cp₂M₂S₄ (Cp=η⁵-C₅Me₅; M=Cr, Mo, Fe, Co) has so far been directed at the problem of the metal-metal bond rather than at expanding the system with new ligand-metal combinations. The multifarious properties of cubane-like Fe₂Mo₂S₄ clusters stimulated a search for generally applicable methods for the synthesis of heterometal clusters. Expansion of a precursor containing four sulfur atoms and two cyclotriadene-6A metal groups by two each of the isoelectronic groups MCp (M=Cr, Mo), Mn(CO)₂, Fe(NO) or Co(CO) offers a facile entry to the M₄S₄ skeletal framework. This concept was successfully tested by reaction of the sulfur-rich pentamethylcyclopentadienyl complexes Cp₃Cr₂S₄ 1 and Cp₃Mo₂S₄ 2 with CO₂(CO)₅ to give Cp₃M₂Co₂S₄(CO)₂ (Cp'=η⁵-C₅Me₅; M=Cr, Mo) [3].

We have now been able to confirm the general validity of the concept: Irradiation of the green and blue solutions, respectively, of 1 and 2 in tetrahydrofuran in the presence of two equivalents of [Fe(CO)₅NO][Ph₃P(NPPh₃)] affords the red-brown diamagnetic complexes 3 and 4, respectively, in 40-50% yield [4]. The isomer of 2 containing terminal sulfur ligands, complex 5, also reacts analogously. The composition of the products Cp₃M₂Fe₂S₄(NO)₂ is confirmed by elemental analysis and mass spectra. Since we have so far been unable to grow single crystals of the products, the confirmation of the structure rests primarily on spectroscopic data. The 70 eV mass spectrum of 4 shows the molecular ion and the successive cleavage of all ligands from the Mo₂Fe₂S₄ skeleton, with appearance also of the doubly positively charged ion for each fragment, whereas the molecular ion 3 can be observed only in the field-desorption mass spectrum (from toluene solution). A single sharp methyl signal appears in each of the ¹H-NMR spectra in the case of 3 and at δ = 1.96 in the case of 4 (CDCl₃ solution). The IR spectra contain absorptions for the NO- and the C,MeS-groups, but no further metal-ligand vibration bands. The disappearance of the strong ν(MO=S) bands of 5 (485 cm⁻¹) and of the absorptions of the δ₂,S₂- and δ₃,S₂-ligands in 1 (599, 495, 445 cm⁻¹) in favor of a weak absorption at 386 cm⁻¹ can best be interpreted in terms of an equal distribution of four S-atoms over all metal centers in the form of μ₃-ligands.

The novel heterometal clusters 3 and 4 represent a link between the Cp₃Mo₂S₄ cluster, for which MO considerations point to metal-metal interactions, and the isoelectronic (NO)₅Fe₂S₄ complex, for which X-ray structure investigations have confirmed a distorted cubane-structure with four Fe–Fe bonds.

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[4] a) General procedure: A solution of 0.5 mmol of 1 or 2, respectively, and 708 mg (3.0 mmol) of [Fe(CO)₅NO][Ph₃P(NPPh₃)] in 230 mL of THF is ir-

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Footnotes:
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radiated for 20 h in an immersion lamp apparatus (125 W Hg lamp). The reaction mixture is concentrated and chromatographed on SiO₂ (40 × 3.5 cm column), the complexes 3 and 4, respectively, being eluted as red-brown zones with toluene. Recrystallization from toluene/pentane (6:1) furnishes analytically pure amorphous crystals. — IR (KBr, cm⁻¹): 3: νmₐ = 1738, 1712 vs (toluene 1725), νC=O = 1733, 1017 s; 4: νmₐ = 1734, 1708 vs (toluene 1720), νC=O = 1734, 1022 s.


**Biomimetic Synthesis of Primary Enamides by Decarboxylation of α,β-Dehydroamino Acids**

By Ulrich Schmidt* and Albrecht Lieberknecht

Dedicated to Professor Adolf Steinhefer on the occasion of his 75th birthday

Primary enamides[1] are produced by lower organisms from amino acids, probably by decarboxylation of α,β-dehydroamino acids. We have also succeeded in performing this reaction in vitro. Decarboxylation of aliphatic and aromatic N-acetyldideoxyamin acids[2] offers the simplest route to primary enamides; it is superior to previously described methods[3] and, in addition, opens the possibility of synthesizing (E)- and (Z)-enamides stereoselectively.

Aromatic and aliphatic N-acetyldideoxyamin acids[4] decarboxylate within an hour at 145°C in the presence of bases and copper powder to afford enamides in 50—75% yield. On the whole, the reaction can be stereoselectively controlled (exceptions: examples 5 and 10 in Table 1): solutions of aromatic (Z)-N-acetyldideoxyamin acids in di- glyme react with copper powder and pyridine to give predominantly (Z)-enamides (Z: E ≈ 80:20); in contrast, with quinoline and copper powder predominantly (E)-enamides are obtained (Z: E ≈ 10:90). Under these conditions (Z)-enamides rearrange to (E)-enamides. The decarboxylation can also be performed on dehydropeptides (examples 7 and 8).

**Procedure**

A solution of α-(N-acetylamino)cinnamic acid (205 mg), copper powder (200 mg), and quinoline (166 mg) in 5 mL diglyme under nitrogen is heated to 145°C in an oil bath. The volatile components are subsequently removed in vacuo: the residue is taken up in chloroform, filtered, and extracted with KHSO₄ solution. After medium pressure chromatography on silica gel Lichroprep Si60 (15—25 μ) using

![Diagram of decarboxylation process](image)

Table 1. Decarboxylation of N-acetyldideoxyamin acids to afford enamides [a].

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Acyl</th>
<th>Catalyst</th>
<th>Yield [Z : E]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅</td>
<td>CH₃CO</td>
<td>Py/Cu</td>
<td>67 : 84</td>
</tr>
<tr>
<td>2</td>
<td>C₆H₅</td>
<td>CH₃CO</td>
<td>Quin/Cu</td>
<td>75 : 16</td>
</tr>
<tr>
<td>3</td>
<td>4-CH₃O-C₆H₅</td>
<td>CH₃CO</td>
<td>Py/Cu</td>
<td>50 : 71</td>
</tr>
<tr>
<td>4</td>
<td>4-CH₃O-C₆H₅</td>
<td>CH₃CO</td>
<td>Quin/Cu</td>
<td>70 : 20</td>
</tr>
<tr>
<td>5</td>
<td>3,4-(CH₃O)₂C₆H₅</td>
<td>CH₃CO</td>
<td>Py/Cu</td>
<td>60 : 0</td>
</tr>
<tr>
<td>6</td>
<td>3,4-(CH₃O)₂C₆H₅</td>
<td>CH₃CO</td>
<td>Quin/Cu</td>
<td>60 : 0</td>
</tr>
<tr>
<td>7</td>
<td>C₆H₅</td>
<td>CH₃CO</td>
<td>CuCl₂</td>
<td>0 : 100</td>
</tr>
<tr>
<td>8</td>
<td>3,4,5-(CH₃O)₃C₆H₅</td>
<td>CH₃CO</td>
<td>Quin/Cu</td>
<td>63 : 22</td>
</tr>
<tr>
<td>9</td>
<td>C₆H₅</td>
<td>CH₃CO</td>
<td>CuCl₂</td>
<td>45 : 0</td>
</tr>
<tr>
<td>10</td>
<td>nC₈H₁₇</td>
<td>[b] CH₃CO</td>
<td>Quin/Cu</td>
<td>51 : 73</td>
</tr>
</tbody>
</table>

[a] 1 mmol dehydroamino acid, 200 mg copper powder, 1,2 mmol pyridine (Py) or quinoline (Quin), 5 mL diglyme, autoclave with glass insert, 60 min, 145°C. [b] 1 mmol dehydroamino acid, 200 mg copper powder, 1,2 mmol quinoline, 5 mL dioxide, autoclave with glass insert, 60 min, 145°C.

ethyl acetate/petroleum ether 19 mg cis- and 102 mg trans-β-acetylaminoester were isolated.

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![Image of decarboxylation reaction](image)