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**.

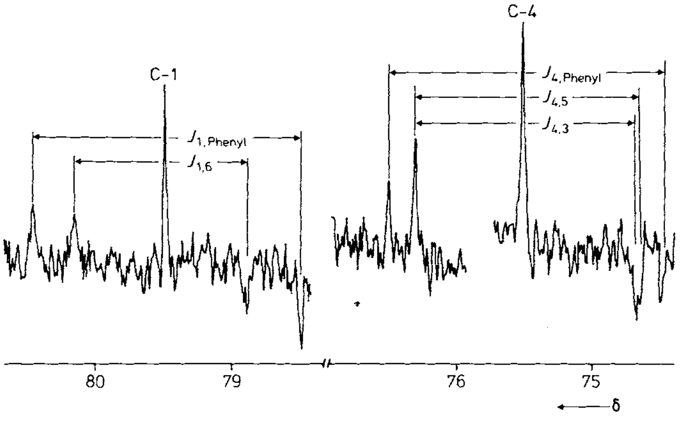

Fig. 2. Part of the one-dimensional ^{13}C-INADEQUATE-NMR spectrum of **3** at 25 MHz. Sample solution: 1 g **3** and *ca.* 10 mg Cr(acac)$_3$ in 1.5 mL CDCl$_3$. Pulse sequence as in Fig. 1; τ adjusted for $J_{CC} = 45$ Hz. 33400 sweeps, repetition time 6.1 s (total measurement time 57 h). The residual signals of the solvent were not recorded.

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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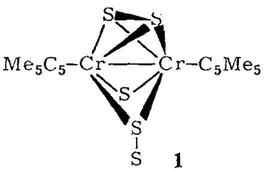
A General Method for the Synthesis of Heterometal Clusters of the $M_2Fe_2S_4$-Cubane Type (M = Cr, Mo)

By *Henri Brunner, Heike Kauermann,* and
Joachim Wachter[*]

Interest in the cubane-like molecules $Cp_4M_4S_4$ ($Cp = \eta^5$-C_5H_5; M = Cr, Mo, Fe, Co) has so far been directed at the problem of the metal-metal bond[1] rather than at expanding the system with new ligand-metal combinations. The multifarious properties of cubane-like Fe_3MoS_4 clusters[2] stimulated a search for generally applicable methods for the synthesis of such heterometal clusters. Expansion of a precursor containing four sulfur atoms and two cyclopentadienyl-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 M_4S_4 skeletal framework. This concept was successfully tested by reaction of the sulfur-rich pentamethylcyclopentadienyl complexes $Cp'_2Cr_2S_5$ **1** and $Cp'_2Mo_2S_4$ **2** with $Co_2(CO)_8$ to give $Cp'_2M_2Co_2S_4(CO)_2$ ($Cp' = \eta^5$-C_5Me_5; M = Cr, Mo)[3].



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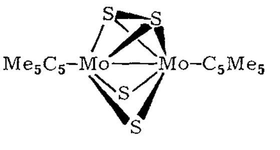

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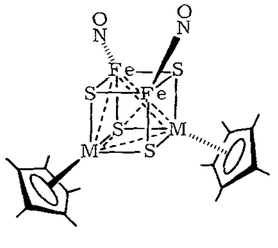

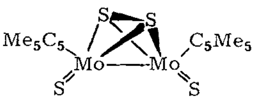

5

3: M = Cr
4: M = Mo

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 $[Fe(CO)_3NO][Ph_3PNPPh_3]$ affords the red-brown diamagnetic complexes **3** and **4**, respectively, in 40—50% yield[4a]. The isomer of **2** containing terminal sulfur ligands, complex **5**, also reacts analogously. The composition of the products $Cp'_2M_2Fe_2S_4(NO)_2$ 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 $Mo_2Fe_2S_4$ 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 ^{1}H-NMR spectra, at $\delta = 1.90$ in the case of **3** and at 1.96 in the case of **4** ($CDCl_3$ solution). The IR spectra[4b] contain absorption bands for the NO- and the C_5Me_5-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 μ_2,η^2-S_2- and μ_2,η^1-S_2-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 μ_3-ligands.

The novel heterometal clusters **3** and **4** represent a link between the $Cp_4Mo_4S_4$ cluster, for which MO considerations point to metal-metal interactions[5a], and the isoelectronic $(NO)_4Fe_4S_4$ complex, for which X-ray structure investigations have confirmed a distorted cubane-structure with four Fe—Fe bonds[5b].

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[4] a) General procedure: A solution of 0.5 mmol of **1** or **2**, respectively, and 708 mg (1.0 mmol) of $[Fe(CO)_3NO][Ph_3PNPPh_3]$ in 230 mL of THF is ir-

radiated for 20 h in an immersion lamp apparatus (125 W Hg-lamp). The reaction mixture is concentrated and chromatographed on SiO_2 (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.—b) IR (KBr, cm^{-1}): **3**: $\nu_{NO} = 1738, 1712$ vs (toluene 1725), $\nu_{Cr-NO} = 592$ w, $\nu_{CH} = 1373, 1017$ s; **4**: $\nu_{NO} = 1734, 1708$ vs (toluene 1720), $\nu_{Mo-NO} = 595$ w, $\nu_{CH} = 1374, 1022$ s.

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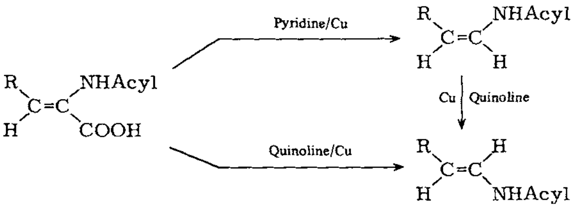
Biomimetic Synthesis of Primary Enamides by Decarboxylation of α,β-Dehydroamino Acids[**]

By *Ulrich Schmidt*[*] and *Albrecht Lieberknecht*

Dedicated to Professor Adolf Steinhofer 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*-acyldehydroamino 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*-acyldehydroamino 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*-acyldehydroamino acids in diglyme react with copper powder and pyridine to give predominantly (*Z*)-enamides ($Z:E \approx 80:20$); in contrast, with quinoline and copper powder predominantly (*E*)-enamides are obtained ($Z:E \approx 10:90$). 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 $KHSO_4$ solution. After medium pressure chromatography on silica gel Lichroprep Si60 (15—25 μ) using ethyl acetate/petroleum ether 19 mg *cis*- and 102 mg *trans*-β-acetylaminostyrene were isolated.

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

No.	R	Acyl	Catalyst	Yield [%]	*Z* : *E*
1	C_6H_5	CH_3CO	Py/Cu	67	84 : 16
2	C_6H_5	CH_3CO	Quin/Cu	75	16 : 84
3	4-CH_3O–C_6H_4	CH_3CO	Py/Cu	50	71 : 29
4	4-CH_3O–C_6H_4	CH_3CO	Quin/Cu	77	20 : 80
5	3,4-$(CH_3O)_2C_6H_3$	CH_3CO	Py/Cu	60	0 : 100
6	3,4-$(CH_3O)_2C_6H_3$	CH_3CO	Quin/Cu	60	0 : 100
7	C_6H_5	Boc-Ile	Quin/Cu	68	14 : 86
8	3,4,5-$(CH_3O)_3C_6H_2$	Boc-Trp	Quin/Cu	63	22 : 78
9	*i*C_5H_{11}	C_6H_5CO	Quin/Cu	45	0 : 100
10	*n*C_5H_{11} [b]	CH_3CO	Quin/Cu	51	73 : 27

[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 dioxane, autoclave with glass insert, 60 min, 145 °C.

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Asymmetry of Emission Quenching and Product Formation in an Asymmetrically Sensitized Photoreaction[**]

By *Hermann Rau*[*] and *Richard Ratz*

Asymmetry in photoreactions of chiral molecules sensitized by one enantiomer of a chiral donor may be monitored by determining the asymmetry of emission quenching and the optical induction found in the remaining educt and/or in the photoproduct[1]. *Irie et al.*[2] have observed asymmetries ($\kappa = k_q(S-R)/k_q(R-R)$) in electron-transfer emission quenching of (−)-(*R*)-1,1′-binaphthyl by enantiomeric pairs of optically active amines to the extent of up to $\kappa = 7.9$ at −10 °C. The highest asymmetry observed at room temperature ($\kappa = 4.0$), if maintained in an overall photochemical decomposition reaction, would lead to an enantiomeric purity of the educt $P_{en} = (c_R - c_S)/(c_R + c_S)$ of more than 60% at 63% extent of reaction. If this could be realized, then asymmetric photochemistry would become a viable preparative method.

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