

## Copper(I) Complexes with Unsaturated Nitrogen Ligands. Part IV\*. Synthesis and Structure of Copper(I) Monoazadiene Complexes

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### Abstract

Monoazadienes,  $R-N=CR'-CR''=CH-R'''$  (mad), readily form complexes with copper(I) salts. Complexes with a monoazadiene:copper ratio between 1:1 and 3:1 have been synthesized. The stoichiometry of the complexes formed is dependent on the nature of the anion of the copper(I) salt, the monoazadiene and the reaction conditions.

The crystal and molecular structures of four complexes with different copper to monoazadiene ratios have been determined by X-ray diffraction methods.  $[(mad)_3Cu]^+[O_3SCF_3]^-$  (1) (mad =  $C_6H_5CH=CH-CH=N-C_6H_4-p-CH_3$ ): space group  $R3$ ,  $a = 13.373(5)$ ,  $c = 44.626(36)$  Å,  $Z = 6$ ,  $R = 0.084$  for 1518 reflections;  $(mad)_2CuCl$  (2) (same mad): space group  $C2/c$ ,  $a = 12.7965(5)$ ,  $b = 13.855(5)$ ,  $c = 15.809(6)$  Å,  $\beta = 98.67(4)^\circ$ ,  $Z = 4$ ,  $R = 0.048$  for 1947 reflections;  $[(mad)_2Cu]_2Cl^+[CuCl_2]^-$  (7) (same mad): space group  $C2/c$ ;  $a = 16.994(7)$ ,  $b = 15.408(5)$ ,  $c = 22.807(4)$  Å,  $\beta = 102.62(2)^\circ$ ,  $Z = 4$ ,  $R = 0.055$  for 2783 reflections; and  $(mad)CuCl_2$  (8) (mad =  $C_6H_5CH=CH-CH=N-CH(ipr)_2$ ): space group  $P2_12_12_1$ ,  $a = 12.399(4)$ ,  $b = 14.418(6)$ ,  $c = 19.399(19)$  Å,  $Z = 4$ ,  $R = 0.054$  for 1815 reflections.

All four examples are complexes with trigonal planar geometry around the copper atom. This underlines the importance of the coordination number three in copper(I) chemistry. The monoazadiene ligand, different from enones, coordinates in all cases via the nitrogen lone pair only and shows the all-*trans* configuration.

### Introduction

Recently we investigated copper(I) complexes with diazadienes ( $R-N=CR'-CR''=N-R$ ) and carbon monoxide, olefines or acetylenes [1]. These complexes as well as similar complexes with other nitrogen containing chelating ligands [2, 3] show a

distorted tetrahedral or trigonal planar coordination geometry. Monoazadiene ligands (mad =  $R-N=CH-CH=CH-R'$ ) in principle have three accessible coordination sites, the C=C and the C=N  $\pi$  electrons and the nitrogen lone pair. As monodentate nitrogen donors they should form less rigid complexes than the bidentate diazadienes and therefore seemed to be interesting candidates to get additional information about influences that determine the coordination number of copper(I) compounds. With other transition metals like iron or nickel, binding via the olefinic double bond plays an important role, and a number of compounds with different coordination geometries are well known from these metals [4, 5]. Our general interest in the coordination chemistry of conjugated imines has led us to investigate the interaction of monoazadienes with copper(I) compounds. We report here on the preparation and crystal and molecular structures of monoazadiene copper(I) complexes.

### Experimental

All syntheses were performed under an inert atmosphere with Schlenk equipment. All solvents were dried and distilled under nitrogen before use.  $CuO_3SCF_3 \cdot \frac{1}{2}C_6H_6$  was prepared from  $Cu_2O$  and  $HOSO_2CF_3$  (1:1 molar ratio) in benzene with separation of water by azeotropic distillation. The mad ligands were prepared by condensation of cinnamylidene aldehyde with the appropriate amine. All complexes reported gave satisfactory elemental analyses. Infrared spectra were recorded as Nujol mulls. NMR spectra were measured in  $CDCl_3$  using TMS as an internal standard.

#### *Tris(cinnamylidene-p-toluidine)copper(I) Trifluoromethanesulfonate Dichloromethane Solvate (1)*

Copper(I) trifluoromethanesulfonate benzene solvate  $CuO_3SCF_3 \cdot \frac{1}{2}C_6H_6$  (0.67 g, 2.6 mmol) and the mad ligand (8 mmol) are stirred in 20 ml of dichloromethane for 1 h at room temperature. Then 20 ml of hexane are added and the reaction mixture is

\*Part III is ref. 1.

warmed to 50 °C and filtrated. A slow precipitation of hexagonal orange crystals follows. Yield 0.82 g (35%). IR (cm<sup>-1</sup>): 1620, 1580, 1570, 1505, 1270, 1173, 1160, 1038, 818, 756, 640. <sup>1</sup>H NMR (ppm): 8.32 (d, CH=N, <sup>3</sup>J = 8.8 Hz); 7.6–6.9 (CH, 11H); 5.27 (s, CH<sub>2</sub>Cl<sub>2</sub>); 2.32 (s, CH<sub>3</sub>). Found: C, 66.11; H, 5.18; N, 4.68; Cl, 1.91. Calc. for C<sub>49</sub>H<sub>45</sub>CuF<sub>3</sub>N<sub>3</sub>·O<sub>3</sub>·½CH<sub>2</sub>Cl<sub>2</sub>: C, 66.01; H, 5.09; N, 4.67; Cl, 1.97%.

#### General Procedure for the Preparation of (mad)<sub>2</sub>CuX

10 mmol of the copper(I) halide and 20 mmol of the corresponding mad derived from cinnamic aldehyde are heated in 40 to 60 ml of acetone for 15 min until all of the copper halide is dissolved. The product crystallizes while the solution is allowed to cool to room temperature. For other mad ligands the stoichiometry of the solid products obtained might be different.

#### Bis(cinnamylidene-*p*-toluidine)chlorocopper(I) (2)

IR (cm<sup>-1</sup>): 1617, 1572, 1563, 1500, 1263, 1163, 995, 810, 758, 690. <sup>1</sup>H NMR (ppm): 8.1 (CH=N, 1H); 7.6–7.0 (CH, 11H); 2.31 (s, CH<sub>3</sub>). Yield: 83% of red crystals. Found: C, 71.17; H, 5.53; N, 5.21. Calc. for C<sub>32</sub>H<sub>30</sub>ClCuN<sub>2</sub>: C, 70.97; H, 5.58; N, 5.17%.

Crystallization from less concentrated solutions gave mixtures of 2 (red) and 7 (orange crystals).

#### Bis(cinnamylidene-*p*-toluidine)bromocopper(I) (3)

IR (cm<sup>-1</sup>): 1618, 1572, 1563, 1500, 1163, 994, 810, 757, 690. The preparation can be performed in dichloromethane. Yield: 71% of red crystals. Found: C, 65.22; H, 4.95; N, 4.83. Calc. for C<sub>32</sub>H<sub>30</sub>BrCuN<sub>2</sub>: C, 64.58; H, 4.70; N, 5.02.

#### Bis(cinnamylideneaniline)chlorocopper(I) (4)

IR (cm<sup>-1</sup>): 1622, 1578, 1567, 1487, 1447, 1168, 990, 760, 690. Recrystallization from acetone gave 74% of red crystals. Found: C, 69.94; H, 5.15; N, 5.38. Calc. for C<sub>30</sub>H<sub>26</sub>ClCuN<sub>2</sub>: C, 70.17; H, 5.10; N, 5.45%.

#### Bis(cinnamylideneaniline)bromocopper(I) (5)

IR (cm<sup>-1</sup>): 1623, 1578, 1565, 1488, 1445, 1168, 990, 760, 690. Yield 56% of red crystals. Found: C, 52.12; H, 3.98; N, 3.76. Calc. for C<sub>30</sub>H<sub>26</sub>BrCuN<sub>2</sub>: C, 52.69; H, 4.15; N, 3.84%.

#### Bis(cinnamylidene-*t*-butylamine)chlorocopper(I) (6a)

IR (cm<sup>-1</sup>): 1625, 1598, 1587, 1162, 990, 747, 687, 516. <sup>1</sup>H NMR (ppm): 7.5–7.1 (CH, 8H), 1.37 (s, CH<sub>3</sub>). Found: C, 66.91; H, 7.72; N, 5.98. Calc. for C<sub>26</sub>H<sub>34</sub>ClCuN<sub>2</sub>: C, 65.96; H, 7.19; N, 5.92%.

Some other complexes of composition (mad)<sub>2</sub>-CuCl are obtained as oils or glassy products, when the starting compounds are reacted in the appropriate stoichiometry, e.g. bis(cinnamylideneisopropylamine)chlorocopper(I): IR (cm<sup>-1</sup>): 1620, 1320,

1145, 980, 746, 685. <sup>1</sup>H NMR (ppm): 7.8–7.0 (=CH, 8H), 3.6 (sept., CHMe<sub>2</sub>, 1H), 1.4 (d, CH<sub>3</sub>, 6H).

#### Bis(cinnamylidene-2,6-diisopropylaniline)chlorocopper(I) (6b)

Quantitative yield of orange oil, solidifying below 0 °C. <sup>1</sup>H NMR (ppm): 8.4 (d, CH=N, 1H), 7.6–7.1 (mult., =CH, 10H), 3.09 (sept., CHMe<sub>2</sub>, 2H), 1.18 (d, CH<sub>3</sub>, 12H).

#### Bis(crotonylidene-2,4-dimethylpent-3-ylamine)chlorocopper(I) (6c)

In thf a quantitative yield of an orange oil is obtained after reacting the components in the appropriate stoichiometry at room temperature and evaporating the solvent. IR (cm<sup>-1</sup>): 1645, 1600, 1195, 1108, 970. <sup>1</sup>H NMR (ppm): 7.72 (d, CH=N, 1H), 6.6–6.5 (mult., =CH, 2H), 2.53 (t, CH–ipr<sub>2</sub>, 1H), 2.02 (mult, CHMe<sub>2</sub>, 2H), 1.93 (d, CH<sub>3</sub>–C=, <sup>3</sup>J = 5.3 Hz), 0.98 (d, CH<sub>3</sub>, 6H, <sup>3</sup>J = 6.6 Hz), 0.86 (d, CH<sub>3</sub>, 6H, <sup>3</sup>J = 6.6 Hz).

#### Bis(crotonylidene-2,6-diisopropylaniline)chlorocopper (6d)

Quantitative yield of an orange–red oil. IR (cm<sup>-1</sup>): 1640, 1620, 1587, 1460, 1438, 1380, 1360, 1180, 1170, 990, 960, 933, 798, 760. <sup>1</sup>H NMR (ppm): 7.69 (d, CH=N, 1H, <sup>3</sup>J = 8.4 Hz), 7.13 (arom. H, 3H), 6.8–6.5 (m, =CH, 2H), 3.00 (sept., 2H, <sup>3</sup>J = 6.9 Hz), 1.98 (d, 3H, CH<sub>3</sub>–C=, <sup>3</sup>J = 5.6 Hz), 1.16 (d, CH<sub>3</sub>, 12H).

#### Bis(crotonylidene-*tert*-butylamine)chlorocopper(I) (6e)

The yellowish oil is obtained quantitatively from a reaction in thf after removing all of the solvent. <sup>1</sup>H NMR (ppm): 7.81 (d, CH=N, 1H, <sup>3</sup>J = 5.9 Hz), 6.5–6.3 (m, CH=, 2H), 1.87 (d, CH<sub>3</sub>, 3H, <sup>3</sup>J = 5.3 Hz), 1.28 (s, CH<sub>3</sub>, 9H).

#### {μ-Chloro-bis[bis(cinnamylidene-*p*-toluidine)chlorocopper(I)]} Dichlorocuprate (7)

Copper(I) chloride (0.2 g, 2 mmol) and cinnamylidene-*p*-toluidine (0.66 g, 3 mmol) are stirred with 70 ml of acetone until all of the copper chloride is dissolved. Then the solution is heated for a short time. After cooling to 0 °C the orange product crystallizes. Yield 0.4 g (68%). IR (cm<sup>-1</sup>): 1612, 1578, 1560, 1500, 1164, 980, 950, 842, 812, 753, 747, 683, 412. Found: C, 65.37; H, 5.18; N, 4.77. Calc. for C<sub>64</sub>H<sub>60</sub>Cl<sub>3</sub>Cu<sub>3</sub>N<sub>4</sub>: C, 65.48; H, 5.30; N, 4.77%.

#### Di-μ-chlorobis[cinnamylidene-2,4-dimethylpent-3-ylamine-copper(I)] (8)

Copper(I) chloride (0.9 g, 9 mmol) and cinnamylidene-2,4-dimethylpent-3-ylamine (2.5 g, 11 mmol) are stirred in 40 ml of hexane. Then 40 ml of diethylether are added. Slowly a homogeneous orange

TABLE I. Crystallographic Data for (mad)<sub>3</sub>Cu(O<sub>3</sub>SCF<sub>3</sub>) (1), (mad)<sub>2</sub>CuCl (2), [(mad)<sub>2</sub>Cu<sub>2</sub>Cl](CuCl<sub>2</sub>) (7) and [(mad)CuCl<sub>2</sub>]<sub>2</sub> (8)

	1	2	7	8
Formula	C <sub>49</sub> H <sub>45</sub> CuF <sub>3</sub> N <sub>3</sub> O <sub>3</sub> S· $\frac{1}{2}$ CH <sub>2</sub> Cl <sub>2</sub>	C <sub>32</sub> H <sub>30</sub> ClCuN <sub>2</sub>	C <sub>64</sub> H <sub>60</sub> Cu <sub>3</sub> N <sub>4</sub>	C <sub>32</sub> H <sub>46</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>2</sub>
Molecular weight	918.98	541.60	1182.20	656.73
Crystal system	trigonal	monoclinic	monoclinic	orthorhombic
Space group	R3	C2/c	C2/c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	13.3732(54)	12.7963(54)	16.994(7)	12.3993(42)
b (Å)		13.8551(45)	15.408(5)	14.4180(55)
c (Å)	44.6259(360)	15.8085(59)	22.807(4)	19.3990(188)
β (°)		98.673(36)	102.62(2)	
V (Å <sup>3</sup> )	6911.8(71)	2770.7(18)	5827.2(31)	3468.0(38)
Z	6	4	4	4
D <sub>calc</sub> (g/cm <sup>3</sup> )	1.325	1.298	1.348	1.258
Crystal size (mm <sup>3</sup> )	0.5 × 0.5 × 0.4	0.4 × 0.3 × 0.3	0.7 × 0.3 × 0.3	0.35 × 0.3 × 0.3
μ (cm <sup>-1</sup> )	6.30	9.08	12.68	14.06
2θ range (°)	4.5–50	0–50	2–50	4–45
h/k/l range			0/0/–27 –20/19/27	0/0/–5 –14/16/21
No. reflections measured	2725	2443	5374	3202
No. reflections used	1518 (I ≥ 3σ(I))	1947 (I ≥ 1.5σ(I))	2783 (I ≥ 2σ(I))	1815 (I ≥ 3σ(I))
No. variables refined	174	191	371	174
R	0.084	0.048	0.055	0.054
R <sub>w</sub>	0.055 (w = 5.4539)	0.037 (w = 1.677)	0.029 (w = 1.9459)	0.042 (w = 2.0646)
Max. e/Å <sup>3</sup>	0.6	0.5	0.5	0.5
Max. shift/e.s.d.	0.05	0.001	0.02	0.3

solution develops. Within 24 h a yellow precipitate appears. It is redissolved by adding 20 ml of ether and 20 ml of thf. Then 20 ml of hexane are added and the solution is cooled to 0 °C. After 24 h yellow crystals can be separated by filtration. Yield 1.7 g (58%). IR (cm<sup>-1</sup>): 1645, 1620, 1500, 980, 755, 695, 560, 517. <sup>1</sup>H NMR (ppm): 7.9 (CH=N, 1H), 7.6–7.3 (CH, 7H), 2.7 (t, CH–N, 1H), 2.27 (oct., CH–CH<sub>3</sub>), 1.09 (d, CH<sub>3</sub>, <sup>3</sup>J = 6.7 Hz), 0.93 (d, CH<sub>3</sub>, <sup>3</sup>J = 6.7 Hz). Found: C, 58.76; H, 7.13; N, 4.41. Calc. for C<sub>32</sub>H<sub>46</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub>: C, 58.53; H, 7.06; N, 4.27%.

#### Cinnamylidene-*p*-toluidinecopper(I) Trifluoromethanesulfonate (9)

From the reaction of 0.63 g (2.5 mmol) CuO<sub>3</sub>SCF<sub>3</sub>· $\frac{1}{2}$ C<sub>6</sub>H<sub>6</sub> and 0.55 g (2.5 mmol) of cinnamylidene-*p*-toluidine (stirring at room temperature for 24 h in dichloromethane) a low yield (0.27 g, 25%) of a yellow powder resulted, analyzing for a 1:1 complex. IR (cm<sup>-1</sup>): 1620, 1578, 1500, 1290, 1177, 1029, 1008, 829, 751, 631. Found: C, 47.26; H, 3.52; N, 3.23. Calc. for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>CuNO<sub>3</sub>S: C, 47.06; H, 3.48; N, 3.23%. No crystals could be obtained to perform a single crystal X-ray diffraction study.

#### X-ray Crystallographic Measurements

The crystals chosen were encapsulated in a glass capillary under a nitrogen atmosphere. They were mounted on a SYNTEX P2<sub>1</sub> (7, 8) or a Hilger and Watts (1, 2) four circle diffractometer using graphite-

monochromated Mo Kα radiation (λ = 0.70926 Å), which was used for all crystallographic measurements. Cell parameters were obtained and refined on the basis of 13 (1), 22 (2), 17 (7) or 20 (8) computer centered reflections chosen from diverse regions of the reciprocal space. The parameters pertaining to data collection, structure solution and refinement are reported in Table I. Intensity data were collected by the θ/2θ scan technique at room temperature. During the data collection, three standard reflections were collected every 100 reflections. There was no significant variation of the intensities during the data collection. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structures were solved by direct [6] (1, 7, 8) or Patterson [7] (2) methods and subsequent difference-Fourier syntheses. In this way all oxygen, nitrogen and carbon atoms could be located. When they could be unambiguously located, hydrogen atoms were added in following least-square cycles, all other hydrogen positions were calculated geometrically. Methyl groups were allowed to rotate freely. All non-hydrogen atoms were calculated with anisotropic temperature factors, except for 8, where only the copper and the chlorine atoms were made anisotropic and the solvent in 1. Refinement by full-matrix least-squares [7] progressed to the reported R values (Table I), the function minimized was: [Σw(F<sub>o</sub> – F<sub>c</sub>)<sup>2</sup>/σ<sub>(F<sub>o</sub>)</sub><sup>2</sup>][Σw × F<sub>o</sub><sup>2</sup>/σ<sub>(F<sub>o</sub>)</sub><sup>2</sup>]<sup>-1</sup>. The plots (Figs. 1 through 4) were drawn with the SCHAKAL [8] program.

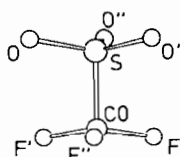
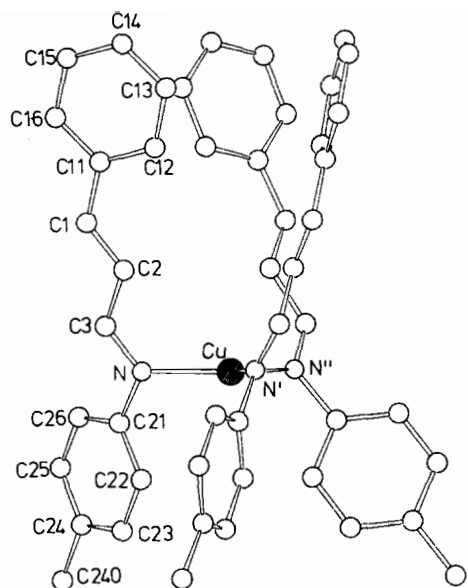


Fig. 1. Molecular structure and numbering scheme of 1.

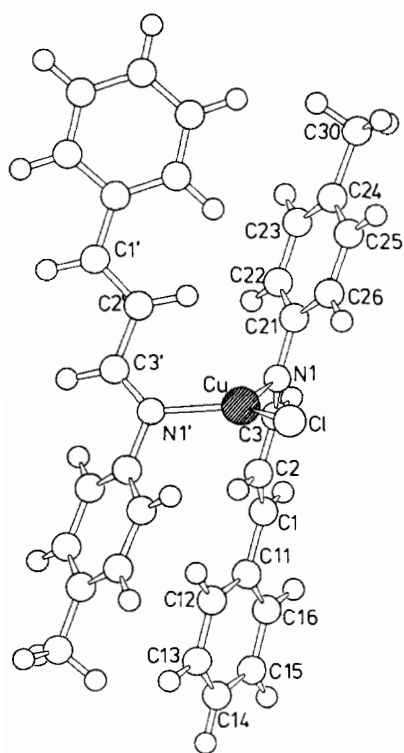


Fig. 2. Molecular structure and numbering scheme of 2.

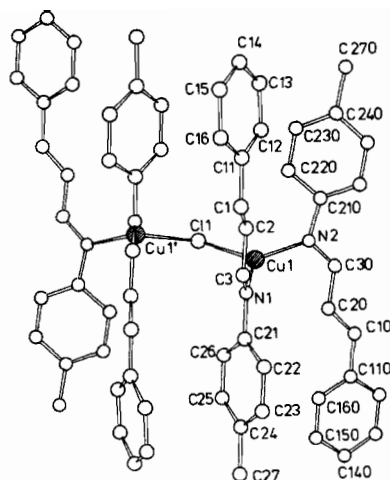


Fig. 3. Molecular structure and numbering scheme of 7. (The  $[\text{CuCl}_2]^-$  anion is not shown:  $d(\text{Cu}-\text{Cl}) = 2.09 \text{ \AA}$ , angle  $\text{Cl}-\text{Cu}-\text{Cl} = 177.2^\circ$ .)

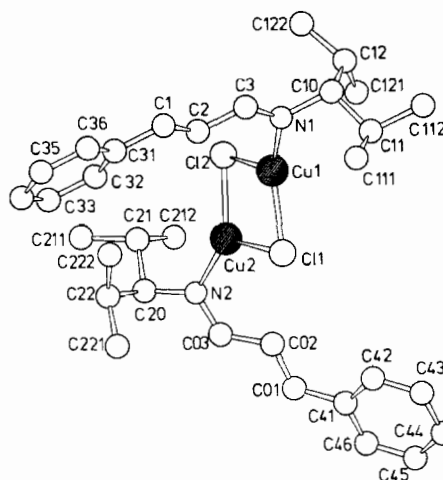
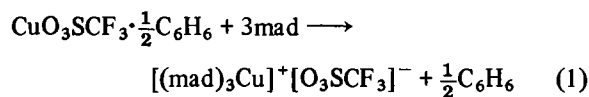


Fig. 4. Molecular structure and numbering scheme of 8.

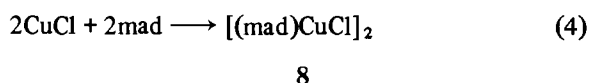
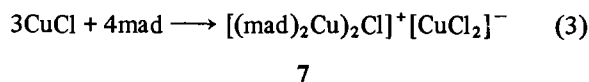
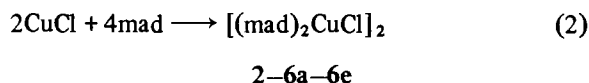
## Results and Discussion

### Syntheses and Properties

The preparation of monoazadiene copper(I) complexes is outlined in eqns. (1)–(4). Reaction of the appropriate copper(I) salt with the monoazadiene in the desired stoichiometry in polar solvents results in the formation of mad complexes. Sometimes equilibria between complexes of different stoichiometry are possible, and in these cases conditions (solvent, concentrations, temperature) have to be carefully controlled in order to crystallize the desired isomer.



1



In a number of cases, oily or glassy products  $(\text{mad})_2\text{CuCl}$  resulted from the reaction of copper(I) chloride with some mad ligands. A 1:1 complex of copper(I) trifluoromethanesulfonate with cinnylidene-*p*-toluidine could only be obtained as a yellow powder. The structure of these products could not be determined, although for the former compounds solution NMR spectra could be performed.

#### Crystal Structures

The molecular and crystal structures of the complexes 1, 2, 7 and 8 have been determined by X-ray diffraction methods. Crystallographic data are collected in Table I, positional parameters in Table II. Figures 1-4 show pictures of the molecules. Important bond lengths and angles of the structures are given in Table III.

All four complexes show the coordination number three and a trigonal planar environment for all copper atoms (except for the  $[\text{CuCl}_2]^-$  ion). The coordinating atoms can be three nitrogen atoms (1), a chlorine and two nitrogen atoms (2), a bridging chlorine and two nitrogen atoms (7) or two bridging chlorine and one nitrogen atom (8). Except for the symmetrical complex 1 there are some deviations from the regular trigonal planar geometry ( $120^\circ$  angles) of up to  $20^\circ$ . Copper-nitrogen distances vary between 1.94 and 2.02 Å, copper-chlorine distances between 2.18 (terminal chlorine) and 2.23 or 2.41 Å (bridging chlorine). Detailed discussions on the factors influencing Cu(I)-halide distances have been published [9]. The deviations in the copper-nitrogen/chlorine distances and the deviations from the regular trigonal geometry can be correlated. A relatively short distance of copper to the coordinating atom A  $d(\text{Cu}-\text{A})$  results in a small angle at copper to the other two coordinating atoms B, C and vice versa. This is equivalent to say that approaching the coordination number two (large angle A-Cu-B) will place the third ligand C at a large distance. This fact is best

TABLE II. Atomic Positional Parameters of Complexes 1, 2, 7 and 8

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
<b>1</b>				
Cu	0.0000(0)	0.0000(0)	0.7204(1)	0.065(1)
C11 <sup>a</sup>	0.0000(0)	0.0000(0)	0.0059(26)	0.592(28)
C12 <sup>a</sup>	0.0000(0)	0.0000(0)	0.0486(7)	0.459(17)
S	0.0000(0)	0.0000(0)	0.4216(2)	0.186(12)
S1 <sup>a</sup>	-0.0223(14)	-0.0856(15)	0.4365(3)	0.169(10)
F	0.0060(7)	-0.1017(7)	0.4654(2)	0.264(16)
O	0.0068(5)	0.1218(5)	0.4153(1)	0.206(11)
N	-0.1091(5)	-0.1703(4)	0.7210(1)	0.072(7)
CO	0.0000(0)	0.0000(0)	0.4615(5)	0.287(47)
C1	-0.0865(6)	-0.2651(6)	0.7955(1)	0.079(9)
C2	-0.0609(6)	-0.1972(6)	0.7715(1)	0.072(9)
C3	-0.1253(6)	-0.2361(6)	0.7438(1)	0.075(9)
C11	-0.0359(4)	-0.2348(5)	0.8257(1)	0.078(9)
C12	0.0564(4)	-0.1258(5)	0.8327(1)	0.091(10)
C13	0.0984(4)	-0.1006(5)	0.8619(1)	0.104(11)
C14	0.0482(4)	-0.1845(5)	0.8842(1)	0.129(14)
C15	-0.0441(4)	-0.2935(5)	0.8773(1)	0.113(13)
C16	-0.0861(4)	-0.3187(5)	0.8480(1)	0.101(11)
C21	-0.1877(4)	-0.2201(4)	0.6958(1)	0.060(8)
C22	-0.1423(4)	-0.1786(4)	0.6674(1)	0.064(8)
C23	-0.2131(4)	-0.2205(4)	0.6422(1)	0.074(9)
C24	-0.3294(4)	-0.3038(4)	0.6454(1)	0.083(10)
C25	-0.3748(4)	-0.3453(4)	0.6738(1)	0.077(9)
C26	-0.3039(4)	-0.3034(4)	0.6990(1)	0.072(9)
C30	-0.4091(7)	-0.3474(7)	0.6179(1)	0.113(12)
<b>2</b>				
Cu	0.0000(0)	0.2015(1)	0.2500(0)	0.050(1)
C1	0.0000(0)	0.0444(1)	0.2500(0)	0.059(1)
N1	-0.1088(2)	0.2902(2)	0.1848(2)	0.046(3)
C1	-0.2471(3)	0.3948(2)	0.3468(2)	0.049(3)
C2	-0.1749(3)	0.3447(2)	0.3099(2)	0.049(4)
C3	-0.1709(3)	0.3462(3)	0.2212(2)	0.050(3)
C11	-0.2578(2)	0.3949(2)	0.3467(2)	0.047(3)
C12	-0.1831(3)	0.3554(2)	0.5000(2)	0.052(4)
C13	-0.1966(3)	0.3573(2)	0.5844(2)	0.060(4)
C14	-0.2873(3)	0.3987(2)	0.6084(2)	0.059(4)
C15	-0.3613(3)	0.4378(3)	0.5460(2)	0.064(4)
C16	-0.3476(3)	0.4372(2)	0.4618(2)	0.058(4)
C21	-0.1086(2)	0.2993(3)	0.0957(2)	0.045(3)
C22	-0.1039(2)	0.2161(2)	0.0485(2)	0.056(4)
C23	-0.1034(3)	0.2213(3)	-0.0389(2)	0.064(4)
C24	-0.1050(3)	0.3093(3)	-0.0810(2)	0.062(4)
C25	-0.1066(3)	0.3923(3)	-0.0317(2)	0.066(4)
C26	-0.1079(33)	0.3880(3)	0.0550(2)	0.059(4)
C30	-0.1058(4)	0.3152(4)	-0.1762(2)	0.093(6)
<b>7</b>				
Cu1	0.5517(1)	0.5387(1)	0.3367(1)	0.063(1)
Cl1	0.5000(0)	0.6147(1)	0.2500(0)	0.064(2)
Cu2	0.5000(0)	0.1030(1)	0.2500(0)	0.079(1)
Cl2	0.3937(1)	0.1064(1)	0.1835(1)	0.103(2)
N1	0.5913(2)	0.4201(3)	0.3263(2)	0.055(5)
N2	0.5485(3)	0.5929(3)	0.4145(2)	0.059(5)
C1	0.4326(4)	0.2925(4)	0.3280(3)	0.070(8)

(continued)

TABLE II. (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
C2	0.4638(3)	0.3596(2)	0.3321(2)	0.062(7)
C3	0.5463(3)	0.3517(4)	0.3258(2)	0.058(6)
C11	0.3272(3)	0.2951(4)	0.3308(2)	0.066(7)
C12	0.2936(3)	0.3652(4)	0.3560(2)	0.078(7)
C13	0.2112(4)	0.3656(4)	0.3552(3)	0.098(9)
C14	0.1627(4)	0.2967(5)	0.3310(3)	0.101(11)
C15	0.1967(4)	0.2279(4)	0.3064(3)	0.103(10)
C16	0.2270(4)	0.2264(4)	0.3059(3)	0.093(9)
C21	0.6747(3)	0.4085(3)	0.3227(2)	0.055(6)
C22	0.7220(3)	0.3408(4)	0.3519(2)	0.073(7)
C23	0.8032(3)	0.3340(4)	0.3480(3)	0.080(8)
C24	0.8378(3)	0.3928(4)	0.3148(2)	0.074(7)
C25	0.7892(3)	0.4594(4)	0.2864(2)	0.072(7)
C26	0.7088(3)	0.4680(3)	0.2902(2)	0.064(6)
C27	0.9257(3)	0.3823(4)	0.3110(3)	0.099(8)
C10	0.7611(3)	0.6308(4)	0.4806(3)	0.075(8)
C20	0.6943(3)	0.6063(4)	0.4414(3)	0.069(7)
C30	0.6160(3)	0.6160(4)	0.4520(3)	0.072(7)
C110	0.8447(3)	0.6244(4)	0.4735(2)	0.066(7)
C120	0.9052(3)	0.6618(4)	0.5174(3)	0.093(8)
C130	0.9853(4)	0.6587(5)	0.5111(3)	0.115(11)
C140	1.0046(4)	0.6192(5)	0.4617(3)	0.116(11)
C150	0.9446(4)	0.5826(4)	0.4189(3)	0.113(10)
C160	0.8655(3)	0.5838(4)	0.4247(3)	0.087(8)
C210	0.4718(3)	0.6020(3)	0.4315(2)	0.058(6)
C220	0.4033(3)	0.6033(3)	0.3859(2)	0.062(6)
C230	0.3266(3)	0.6080(3)	0.3991(2)	0.071(7)
C240	0.3173(3)	0.6117(3)	0.4581(3)	0.070(7)
C250	0.3874(3)	0.6090(4)	0.5030(2)	0.093(8)
C260	0.4642(3)	0.6039(4)	0.4908(2)	0.083(8)
C270	0.2345(3)	0.6169(4)	0.4728(3)	0.091(8)
8				
Cu1	0.3547(1)	0.5943(1)	0.7051(1)	0.095(1)
Cu2	0.1567(1)	0.4901(1)	0.7300(1)	0.077(1)
C11	0.3203(2)	0.4488(3)	0.6729(2)	0.124(4)
N1	0.4798(6)	0.67325	0.71895	0.056(3)
N2	0.0420(6)	0.4006(5)	0.7475(5)	0.059(3)
C1	0.5509(9)	0.6101(7)	0.8939(6)	0.063(4)
CO1	0.0376(9)	0.2514(8)	0.5941(6)	0.066(4)
C2	0.4912(9)	0.6205(7)	0.8355(6)	0.066(4)
CO2	0.0710(9)	0.3214(8)	0.6372(6)	0.060(4)
C3	0.5298(9)	0.6734(7)	0.7774(6)	0.057(3)
CO3	0.0155(8)	0.3352(7)	0.7029(6)	0.060(4)
C10	0.5272(8)	0.7278(7)	0.6598(5)	0.051(3)
C11	0.5620(9)	0.6591(7)	0.6033(6)	0.068(4)
C12	0.4491(10)	0.8054(8)	0.6349(6)	0.075(4)
C20	-0.0230(8)	0.4020(7)	0.8114(5)	0.059(3)
C21	-0.0629(9)	0.5034(8)	0.8232(5)	0.064(3)
C22	0.0517(10)	0.3673(8)	0.8724(7)	0.089(4)
C31	0.5171(6)	0.5545(5)	0.9541(4)	0.062(4)
C32	0.4130(6)	0.5196(5)	0.9623(4)	0.080(4)
C33	0.3876(6)	0.4660(5)	1.0200(4)	0.089(5)
C34	0.4664(6)	0.4474(5)	1.0694(4)	0.087(4)
C35	0.5705(6)	0.4823(5)	1.0612(4)	0.092(4)
C36	0.5958(6)	0.5360(5)	1.0036(4)	0.076(4)
C41	0.0832(7)	0.2305(5)	0.5274(5)	0.064(4)

(continued)

TABLE II. (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
C42	0.1824(7)	0.2664(5)	0.5067(5)	0.091(4)
C43	0.2236(7)	0.2447(5)	0.4418(5)	0.123(6)
C44	0.1655(7)	0.1871(5)	0.3975(5)	0.103(5)
C45	0.0662(7)	0.1511(5)	0.4183(5)	0.098(5)
C46	0.0251(7)	0.1728(5)	0.4832(5)	0.084(4)
C111	0.6420(11)	0.5795(7)	0.6317(6)	0.091(4)
C112	0.6152(11)	0.7121(8)	0.5412(6)	0.096(5)
C121	0.3489(11)	0.7681(10)	0.5982(7)	0.115(5)
C122	0.4146(10)	0.8673(8)	0.6950(7)	0.103(5)
C211	-0.1324(9)	0.5035(8)	0.8917(6)	0.084(4)
C212	-0.1354(9)	0.5322(7)	0.7622(7)	0.090(4)
C221	0.0889(11)	0.2695(9)	0.8575(7)	0.113(5)
C222	0.1493(11)	0.4277(9)	0.8907(7)	0.118(5)

<sup>a</sup>Cocrystallizing solvent CH<sub>2</sub>Cl<sub>2</sub>.

exemplified by complex 8. Unsymmetrical chlorine bridges were also detected in a tetrahedral complex [(dad)CuCl]<sub>2</sub> [10] (dad = chelating 1,4-diaza-1,3-diene ligand R-N=CR'-CR'=N-R). Even the Cu-N distances in three- and four-coordinate complexes with dad ligands (dad)CuCl or [(dad)<sub>2</sub>Cu]<sup>+</sup> show considerable Cu-N bond length differences, which correlate with larger bond angles facing the longer bonds to copper [11].

The monoazadiene ligand shows the expected all-*trans* conformation (E-s)E-E in the examined complexes. The angle between the N=C-C=C π plane and the copper coordination plane varies between 69° and 86°, except for 8, in which one of the mad systems is almost orthogonal to the Cu coordination plane, while the other one shows an interplane angle of only 37°. The obvious tendency of the N=C-C=C system to be orthogonal to the main complex plane is counteracted by interligand repulsion and packing effects in the solid state. This can clearly be seen in the complex 8, where the two halves of the molecule show quite different conformations. The normal quasi-orthogonal position of the mad is also encountered in square planar d<sup>8</sup> metal complexes of mad and mono-coordinate dad [12] with the same total number of electrons as the three-coordinate d<sup>10</sup> complexes described here. But there is no strong downfield <sup>1</sup>H NMR shift for H2 as in the mad-Pd(II) or mad-Rh(I) complexes. The phenyl rings at C1, the C terminal side of the mad system, are only slightly tilted with regard to the mad π system (6°-20°), the N terminal phenyl rings are substantially more so (24°-46°).

Copper(I) has a strong affinity for nitrogen donor ligands. When trifluorosulfonate or other very poorly coordinating counterions are present, ligands such as carbon monoxide, olefines or alkynes are readily bonded to copper together with two N ligands [1-3]. Chloride is very competitive on the other hand, and

TABLE III. Selected Interatomic Distances (Å) and Angles (°)

Distances					
<b>(mad)<sub>3</sub>Cu(O<sub>3</sub>SCF<sub>3</sub>) (1)</b>					
Cu–N	199.9(5)	N–C3	128.8(9)	C1–C11	147.1(7)
		C3–C2	144.8(8)	N–C21	145.5(6)
		C2–C1	133.4(9)		
<b>(mad)<sub>2</sub>CuCl (2)</b>					
Cu–N1	202.0(2)	N1–C3	130.4(4)	C1–C11	144.8(5)
Cu–Cl	217.7(1)	C3–C2	141.1(5)	N1–C21	141.6(4)
		C2–C1	135.7(5)		
<b>[((mad)<sub>2</sub>Cu)<sub>2</sub>Cl](CuCl<sub>2</sub>) (7)</b>					
Cu1–N1	197.8(4)	N1–C3	130.0(7)	C1–C11	146.7(8)
Cu1–Cl1	230.1(1)	C3–C2	144.5(8)	N1–C21	145.0(6)
		C2–C1	134.1(9)		
Cu1–N2	197.3(4)	N2–C30	129.6(6)	C10–C110	146.7(8)
		C30–C20	144.4(8)	N2–C210	144.7(7)
		C2–C1	133.7(7)		
<b>[(mad)CuCl]<sub>2</sub> (8)</b>					
Cu1–N1	194.3(8)	N1–C3	129.4(16)	C1–C31	147.9(13)
Cu1–Cl1	222.9(4)	C3–C2	144.2(16)	N1–C10	150.9(14)
Cu1–C12	241.4(3)	C2–C1	136.0(16)		
Cu2–N2	195.1(8)	N2–CO3	132.1(14)	CO1–C41	144.2(14)
Cu2–Cl1	238.5(4)	CO3–CO2	146.3(16)	N2–C20	147.8(14)
Cu2–C12	225.6(3)	CO2–CO1	137.5(16)		
<b>Angles</b>					
<b>(mad)<sub>3</sub>Cu(O<sub>3</sub>SCF<sub>3</sub>) (1)</b>					
N–Cu–N'	120.0	C3–N–C21	117.5(6)		
C2–C1–C11	128.5(7)	C1–C2–C3	122.5(7)		
N–C3–C2	124.2(7)				
<b>(mad)<sub>2</sub>CuCl (2)</b>					
N1–Cu–N1'	105.0(1)	N1–Cu–Cl	127.5(1)		
N1–C3–C2	123.0(3)	C1–C2–C3	123.3(4)		
C2–C1–C11	126.5(3)	C3–N1–C21	118.7(3)		
<b>[((mad)<sub>2</sub>Cu)<sub>2</sub>Cl](CuCl<sub>2</sub>) (7)</b>					
N1–Cu–N2	125.1(1)	N1–Cu1–Cl1	116.3(1)		
N2–Cu1–Cl1	118.5(1)	Cu1–Cl1–Cu1'	118.8(1)		
C3–N1–C21	118.7(4)	C2–C1–C11	127.6(6)		
C1–C2–C3	123.9(6)	N1–C3–C2	120.8(5)		
C30–N2–C210	119.5(4)	C20–C10–C110	127.4(5)		
C10–C20–C30	123.6(5)	N2–C30–C20	124.6(5)		
<b>[(mad)CuCl]<sub>2</sub> (8)</b>					
Cl1–Cu1–Cl2	101.8(1)	Cl1–Cu2–Cl2	101.9(1)		
N1–Cu1–Cl1	138.0(3)	N1–Cu1–Cl2	119.2(3)		
N2–Cu2–Cl1	122.5(3)	N2–Cu2–Cl2	135.7(3)		
N1–C3–C2	121.7(10)	C1–C2–C3	121.9(10)		
N2–CO3–CO2	123.5(9)	CO1–CO2–CO3	119.2(10)		
C3–N1–C10	118.6(9)	CO3–N2–C20	115.1(8)		
C2–C1–C31	124.3(10)	CO2–CO1–C41	125.4(10)		

almost inevitably it enters the coordination sphere if present together with N ligands. The chelate effect may counteract to some extent. Thus for example, with biacetylbis(2,6-dimethylphenylimine) as a chelating dad ligand, copper(I) chloride forms crystals, which contain both [(dad)<sub>2</sub>Cu]<sup>+</sup>[CuCl<sub>2</sub>]<sup>–</sup>

and (dad)<sub>2</sub>CuCl molecules in the unit cell [11]. We expected that monoazadienes with an olefinic double bond in the vicinity to the N atom might form complexes, where both coordination sites are utilized for complex formation, as encountered for isoelectronic Ni(0) [4]. Neither did we find the involvement of the

C=C double bond nor the C=N double bond in any of the solid state structures. This is probably due to the rather good shielding of the copper atom by the mad ligands utilized in this work. It has been demonstrated that three-coordinate copper complexes often show interactions with a fourth ligand at longer distances, even if this ligand has generally poor donor qualities, e.g. with one oxygen of the  $\text{CF}_3\text{SO}_3^-$  anion in (DAD)Cu(CO) complexes [1] or with a phenyl ring double bond of a tetraphenylborate anion in a (N N)Cu(CO) complex [13]. Even in the complex of type 7 a bridging chloride is sufficient to compete with the double bonds held in the vicinity of the copper nucleus. This is also encountered for some rhodium(I) complexes, where C=C double bonds remain pendant and are not competitive with a single chloro bridge [14]. Also for a complex of 1:1 stoichiometry, such as 8, chloride bridges are preferred over C=C double bonds as ligands. Compound 9, with the trifluoromethanesulfonate anion in 1:1 ratio with a mad ligand, might be a polymer, in which the mad displays a bridging function via the N lone pair and the C=C double bond. Unfortunately no crystals could be obtained.

Although ligands, which are stronger bases than chloride (e.g. carbanions  $\text{R}^-$ ) might disfavour the N bonded mad relative to the C=C bonded mad, it seems reasonable to expect a different reaction path of organocuprates with monoazadienes as compared to  $\alpha,\beta$ -unsaturated carbonyl compounds (mono-oxadienes) [15]. In preliminary experiments we found that the addition of Grignard reagents to (dad)Cu(I) complexes gave the N alkylated reduction product of the ligand [16] and this was also observed for monoazadienes [17].

### Supplementary Material

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-52851, the names of the authors, and the journal citation.

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