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Monomeric and Dimeric Cyclooctyne-Stabilized Complexes of Copper(I)[1]

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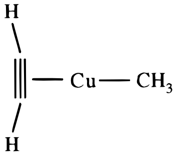
The syntheses and structures of cyclooctyne halogeno copper(I) complexes are described. The dimeric compounds [CuX(cyclooctyne)]$_2$ (**5**: **5a**, X = Cl; **5b**, X = Br; **5c**, X = I) are formed by reaction of equimolar amounts of cyclooctyne and copper(I) halide. X-ray structure analyses of all three compounds **5** show the copper(I) ion in a trigonal-planar coordination with bridging halide ligands. The complexes **5** react with an excess of cyclooctyne to give the monomeric bis(alkyne) complexes [CuX(cyclooctyne)$_2$] (**7**: **7a**, X = Cl; **7b**, X = Br; **7c**, X = I). Here, the three X-ray structure determinations prove that two η^2-coordinated alkyne ligands are bound to a monomeric copper(I) halide unit. The reaction of the bromo complex **5b** with 3,3,6,6-tetramethyl-l-thia-4-cycloheptyne (S-alkyne) affords the first mixed-alkyne copper complex [(cyclooctyne)CuBr$_2$Cu(S-alkyne)] (**9**). Compound **9** forms dinuclear molecules in solution but a polymeric bent chain in the solid state (X-ray structure determination), in which one copper remains in a trigonal-planar environment and the other copper has a tetracoordinated structure.

Introduction



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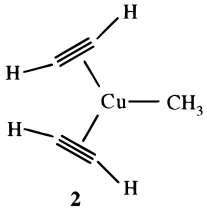

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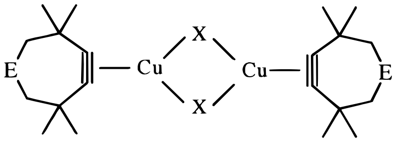

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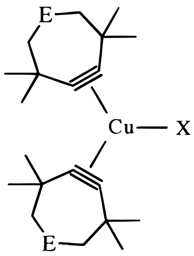
(X = Cl, Br, I)

(E = CH$_2$, S, SiMe$_2$, SO$_2$)

3a: E = SO$_2$, X = Cl
3b: E = SO$_2$, X = Br
3c: E = SO$_2$, X = I
3d: E = S, X = Cl

Kovacs and Frenking have recently reported a theoretical study of bis(η^2-alkyne) complexes of copper(I), silver(I), and gold(I).[2] The authors claimed that it seems highly unlikely that Cu(I) complexes with two nonbridging alkyne ligands can be isolated, because the addition of a second acetylene to the molecule (C$_2$H$_2$)CuCH$_3$ (**1**) to give (C$_2$H$_2$)$_2$CuCH$_3$ (**2**) results only in a marginal energy gain of 2.6 kcal/mol. It was further noted that copper(I) complexes containing one alkyne ligand may become available under appropriate conditions. In this context it is worth mentioning that our research group was able to synthesize many copper alkyne complexes of the type [(alkyne)CuX]$_n$ (e.g., **3**) with some special bulky, highly strained, and thereby activated cycloheptynes.[3] Indeed, we have never observed a complex of the type [CuX(cycloheptyne)$_2$] (**4**; X = negatively charged group), which we attribute to the bulkiness of the particular substituted cycloheptynes used. A detailed inspection of the literature revealed that already in 1972



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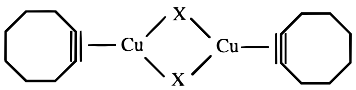
Wittig and Fischer reported on the copper(I) bromide complex [CuBr(cyclooctyne)$_2$], in which two cyclooctyne ligands are obviously coordinated to the CuBr unit.[4] The compound [CuBr(cyclooctyne)$_2$] was only characterized by chemical analysis and its IR spectrum. A further copper(I) cyclooctyne bromide complex, [CuBr(cyclooctyne)], with only one alkyne ligand bound to copper, was also reported by Wittig and Fischer.[4]

In the course of our systematic investigations of group 11 organometallic compounds of angle-strained alkynes we again prepared the two cyclooctyne copper(I) bromide complexes mentioned above and synthesized the related copper cyclooctyne chloride and iodide compounds [CuX(cyclooctyne)] and [CuX(cyclooctyne)$_2$] (X = Cl, I) for the first time. The molecular structures of all six complexes have been determined by X-ray diffraction, and some selected reactions of the dimeric compounds [CuX(cyclooctyne)]$_2$ (**5**) have been studied.



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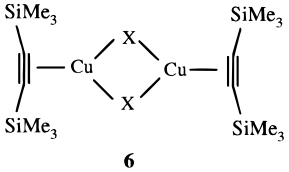
5a: X = Cl
5b: X = Br
5c: X = I

Results and Discussion

1. Synthesis and Spectroscopic Properties of the Dimeric Cyclooctyne Copper(I) Complexes [CuX(cyclooctyne)]$_2$ (5a, X = Cl; 5b, X = Br; 5c, X = I). The reaction of equimolar amounts of the copper(I) halides CuCI, CuBr, and CuI with cyclooctyne in tetrahydrofuran at 20 °C afforded the dimeric cyclooctyne copper(I) complexes **5a**−**c** in high yields. The complexes were recrystallized from hot cyclopentane and isolated as colorless crystalline solids (yield: 60−63% for **5a**,**c**; 99% for **5b**). The determination of the molecular mass in chloroform showed that compounds **5** are dimeric in this solvent. In acetonitrile, however, monomers are formed.

In Table 1 some selected spectroscopic data for **5** are listed (IR $\nu(C\equiv C)$ and ^{13}C NMR $\delta(C\equiv C)$). For comparison, corresponding values for the free ligand cyclooctyne and the related complexes [CuX(SO$_2$-cycloheptyne)]$_2$ (**3**; E = SO$_2$) and [CuX(Me$_3$SiC≡CSiMe$_3$)]$_2$ (**6**) are included.[3c,5]



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6a: X = Cl
6b: X = Br
6c: X = I

On coordination of cyclooctyne to copper(I) in the complexes **5** shifts of 174 cm^{-1} (**5a**), 166 cm^{-1} (**5b**), and 155 cm^{-1} (**5c**) to lower wavenumbers are observed for the C≡C stretch in the IR spectrum. As both donation and back-donation from the alkyne to copper(I) weakens the C≡C triple bond, these shift values are a direct indication for the strength of the alkyne−copper bonding, which obviously is weaker for the iodo complex **5c** than for the chloro compound **5a**. For the cycloheptyne complexes **3a**−**c** a shift of 170 cm^{-1} is observed. For the bis(trimethylsilyl)acetylene compounds **6** shifts of about 160 cm^{-1} are found. Thus, only slightly different values for the shift on coordination in the copper(I) complexes **5**, **3**, and **6** are observed, although the SO$_2$-cycloheptyne gives a stronger bonding to copper(I) than the cyclooctyne ligand and the (trimethylsilyl)acetylene. This can be seen from the copper−carbon bonding distances, which are approximately 0.02 Å longer for the cyclooctyne complexes **5** than for the SO$_2$-cycloheptyne compounds **3** and 0.07 Å longer for the bis(trimethylsilyl)-acetylene complexes **6** than for SO$_2$-cycloheptyne compounds **3** (see section 2). The ^{13}C NMR signal for the carbon atoms of the C≡C triple bond is only slightly shifted on coordination to copper(I). A small downfield shift is observed, which increases on going from the chloro to the iodo complex. The same observation holds for the SO$_2$-cycloheptyne and the (trimethylsilyl)acetylene complexes **3** and **6** (see Table 1).

Table 1. Selected Spectroscopic Data for the Dimeric Dicopper Complexes [(cyclooctyne)CuX]$_2$ (5) and the Related Complexes [(SO$_2$-cycloheptyne)CuX]$_2$ (3; E = SO$_2$)[3c] and [(Me$_3$SiC≡CSiMe$_3$)CuX]$_2$ (6)[5] and for the Bis(cyclooctyne) Copper Complexes [(cyclooctyne)$_2$CuX] (7)[a]

compd	IR $\nu(C\equiv C)$ (cm^{-1}) (KBr or Nujol)	^{13}C NMR $\delta(C\equiv C)$ (ppm) (CDCl$_3$)
cyclooctyne	2216	94.7
5a (X = Cl)	2042	98.7
5b (X = Br)	2050	99.5
5c (X = I)	2061	100.9
SO$_2$-cycloheptyne	2177	101.7
3a (X = Cl)	2016, 1994	104.9
3b (X = Br)	2019, 1995	105.3
3c (X = I)	2020, 1994	107.6
Me$_3$SiC≡CSiMe$_3$	2110	113.0
6a (X = Cl)	1949	115.2
6b (X = Br)	1949	115.2
6c (X = I)	1953	116.4
cyclootyne	2216	94.7
7a (X = Cl)	2073	97.2
7b (X = Br)	2076	98.2
7c (X = I)	2072	98.4

[a] For comparison corresponding values for the free ligands cyclooctyne, SO$_2$-cycloheptyne,[3c] and Me$_3$SiC≡CSiMe$_3$ are also listed.

2. Solid-State Structures of the Dimeric Cyclooctyne Copper(I) Complexes [CuX(cyclooctyne)]$_2$ (5a, X = Cl; 5b, X = Br; 5c, X = I). The molecular structures in the solid state of the compounds **5a**−**c** have been determined by X-ray diffraction analysis. All three complexes have the same dimeric molecular structure, which is shown in Figure 1. The crystallographic data and selected bond lengths and angles for the compounds **5** are listed in Tables 2 and 3, respectively. For comparison, corresponding values for the related copper−alkyne complexes **3** (E = SO$_2$) and **6** are also given.[3c,6] These five compounds have the same dimeric molecular structure as the complexes **5**.

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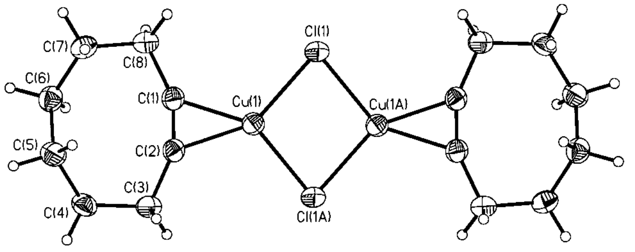


Figure 1. Molecular structure of $[CuCl(cyclooctyne)]_2$ (**5a**). The complexes **5b** and **5c** have the same structure.

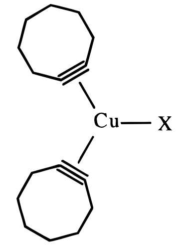
Table 2. Crystallographic Data for Compounds 5a−c

	5a	**5b**	**5c**
formula	$C_{16}H_{24}Cl_2Cu_2$	$C_{16}H_{24}Br_2Cu_2$	$C_{16}H_{24}Cu_2I_2$
fw	414.34	503.25	597.23
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	5.273(1)	4.789(2)	4.981(3)
b, Å	7.620(2)	7.837(1)	9.192(4)
c, Å	10.972(2)	23.697(5)	10.763(6)
α, deg	83.21(1)	90	85.39(4)
β, deg	89.00(2)	92.52(3)	80.17(6)
γ, deg	82.02(2)	90	81.45(5)
V, $Å^3$	433.5(2)	888.5(4)	479.4(4)
ρ_{calcd}, g cm^{-3}	1.587	1.881	2.069
Z	1	2	1
cryst size, mm	0.9 × 0.3 × 0.2	0.9 × 0.3 × 0.1	0.8 × 0.5 × 0.3
diffractometer	Siemens P4	Siemens P4	Siemens P4
μ, mm^{-1}	2.75^a	6.88^a	5.43^b
radiation	Mo Kα	Mo Kα	Mo Kα
temp, K	173	173	173
$2\theta_{max}$, deg	55	45	55
index ranges	$-5 \le h \le 6$ $-9 \le k \le 9$ $-14 \le l \le 14$	$-5 \le h \le 1$ $-8 \le k \le 1$ $-25 \le l \le 25$	$-6 \le h \le 4$ $-11 \le k \le 11$ $-13 \le l \le 13$
no. of unique rflns	1981	1101	2201
no. of rflns with $I > 2\sigma(I)$	1848	865	2007
ref param	92	182	109
min/max resid electron density, e $Å^{-3}$	0.40/−0.59	0.36/−0.31	1.78/−1.93
R1/wR2 ($I > 2\sigma(I)$)	0.028/0.077	0.032/0.070	0.060/0.152
R1/wR2 (all)	0.031/0.079	0.049/0.076	0.063/0.156

[a] Absorption correction applied using program DIFABS.[17] [b] Absorption correction applied (ψ scans).

The coordination sphere of the copper(I) ions in the alkyne complexes **5** is trigonal planar with two bridging halide ions and an η^2-bonded alkyne ligand which is located in the coordination plane. The copper···copper distance for **5** increases on going from chloride (2.936 Å, **5a**) to bromide (2.986 Å, **5b**); the same is valid for the complexes **3** and **6**. To our surprise, the Cu···Cu distance is shortest for the iodo complex **5c** (2.875 Å). In compound **3c**, on the other hand, it is the longest (3.084 Å). The copper−halide bond lengths increase as expected from chloride (2.268 Å, **5a**) and bromide (2.388 Å, **5b**) to iodide (2.558 Å, **5c**). The Cu−η^2(C≡C) bonds have lengths of 1.974 Å (**5a**), 1.980 Å (**5b**), and 2.015 Å (**5c**). Thus, a clear influence of the halide ligand on the strength of the copper−alkyne bonding is observed, with the iodo complex **5c** having the weakest Cu−alkyne interaction. The C≡C bonds have lengths of 1.211 Å (**5c**), 1.200 Å (**5b**), and 1.230 Å (**5a**). For the noncoordinated cyclooctyne a value of 1.232 Å has been measured.[7] This value does not seem to be very accurate, as for cyclononane 1.212 Å was observed and for the cycloheptyne 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne 1.209 Å was found.[8,9] Thus, free cyclooctyne should have a C≡C bond length of 1.21 Å. This value was also found for our iodo and bromo complexes **5c** and **5b**, whereas a slightly longer C≡C bond length was observed for the chloro compound **5a**, which also shows the strongest interaction with the copper(I) ion. The cycloheptyne complexes **3a**−**c** show C≡C bond lengths between 1.225 and 1.230 Å[3c] and the bis(trimethylsilyl)acetylene complexes **6a**,**b** C≡C lengths of 1.227 and 1.239 Å.[6] The C≡C−C bond angles for the complexes **5** are observed to be around 155°. For the free cyclooctyne a value of 158.5° has been determined.[7] Therefore, on coordination this angle is reduced. Noncyclic alkynes here show an even larger effect when coordinated to a transition metal; e.g., the bis(trimethylsilyl)acetylene changes the C≡C−C angle from linearity to 164.0° (**6b**) and 165.3° (**6a**) on coordination to the copper atom (see Table 2).[6]

3. Synthesis and Spectroscopic Properties of the Monomeric Bis(cyclooctyne)copper(I) Complexes [CuX(cyclooctyne)$_2$] (7a, X = Cl; 7b, X = Br; 7c, X = I). The dinuclear copper(I) cyclooctyne complexes **5** react with an excess of cyclooctyne in tetrahydrofuran (**5a**) or cyclopentane (**5b**,**c**) at 20 °C to give the mononuclear bis(cyclooctyne)copper(I) complexes **7a**−**c**. The complexes were recrystallized from cyclopentane and isolated as colorless crystalline solids (yield: 56% for **7a**, 83% for **7b**, and 64% for **7c**). When the solid compounds are heated under vacuum (0.1 mbar) to 50 °C, cyclooctyne is slowly emitted and the starting complexes **5** are re-formed. The determination of the molecular mass of the bis(cyclooctyne) complexes **7** in chloroform (concentration 0.02 mol/L, temperature 25 °C) gave values indicating some release of cyclooctyne in solution, especially for the chloro and iodo compounds **7a**,**c** (data are listed in the Experimental Section).



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7a: X = Cl
7b: X = Br
7c: X = I

In Table 1 some selected spectroscopic data for **7** are listed (IR ν(C≡C) and ^{13}C NMR δ(C≡C)). For comparison, corresponding values for cyclooctyne are also presented. On coordination of two cyclooctyne molecules to one copper(I) halide in the complexes **7** a shift of 140−144 cm^{-1} is observed for the C≡C stretch in the IR spectrum. This is a smaller shift to lower wavenumbers than for the dimeric dicopper complexes **5**. As expected, two alkyne ligands coordinate more weakly to the copper(I) ion than does one acetylene ligand. This can also be seen from the copper−carbon bonding distances, which are approximately 0.08 Å longer for the bis(cyclooctyne) complexes **7** than for the dicopper compounds **5** (see section 4). The ^{13}C NMR signal of the carbon atoms of the C≡C triple bond is only slightly shifted on coordination to copper(I). A small downfield shift is observed which increases on going from the

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Table 3. Selected Bond Lengths (Å) and Angles (deg) of Compounds 5a−c[a]

	5a (X = Cl)	**5b** (X = Br)	**5c** (X = I)	**3a** (X = Cl)	**3b** (X = Br)	**3c** (X = I)	**6a** (X = Cl)	**6b** (X = Br)
				Bond Lengths				
Cu···Cu	2.936(1)	2.986(3)	2.875(2)	2.949(1)	2.999(1)	3.084(1)	3.032(1)	3.130(1)
Cu−X[b]	2.268(1)	2.388(2)	2.558(2)	2.266(1)	2.392(1)	2.563(1)	2.280(1)	2.407(1)
Cu−C[b]	1.974(2)	1.980(9)	2.015(6)	1.947(2)	1.967(6)	1.986(4)	2.018(3)	2.044(7)
C≡C	1.230(3)	1.200(9)	1.211(10)	1.225(3)	1.227(8)	1.230(6)	1.227(5)	1.239(9)
				Bond Angles				
X−Cu−X	99.3(1)	102.6(1)	111.6(1)	97.8(1)	100.9(1)	104.4(1)	96.6(1)	98.9(1)
Cu−X−Cu	80.7(1)	77.4(1)	68.4(1)	81.2(1)	77.6(1)	74.0(1)	83.4(1)	81.1(1)
C≡C−C[a]	155.2(2)	153.5(9)	155.1(6)	148.8(2)	149.1(6)	148.9(5)	165.3(3)	164.0(8)

[a] For comparison values of the related complexes [(SO_2-cycloheptyne)CuX]$_2$ (**3**; E = SO_2)[3c] and [($Me_3SiCCSiMe_3$)CuX]$_2$ (**6**)[6] are also listed. [b] Averaged values.

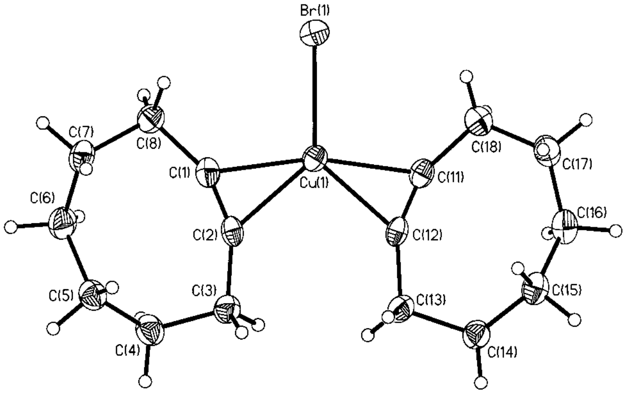
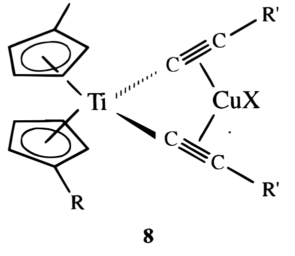


Figure 2. Molecular structure of [CuBr(cyclooctyne)$_2$] (**7b**). The complexes **7a** and **7c** have the same structure.

chloro to the iodo complex. The same observation holds for the cyclooctyne complexes **5** (see Table 1).

4. Solid-State Structures of the Bis(cyclooctyne)copper(I) Complexes [CuX(cyclooctyne)$_2$] (7a, X = Cl; 7b, X = Br; 7c, X = I). The molecular structures in the solid state of the compounds **7a**−**c** have been determined by X-ray diffraction analysis. The three copper complexes have the same monomeric molecular structure, which is shown in Figure 2. The chloro compound **7a** crystallizes in the space group $P2_1/c$ with two independent molecules per asymmetric unit. The complexes **7b**,**c** are isostructural and crystallize in the space group *Pbca* with one molecule per asymmetric unit. The crystallographic data and selected bond lengths and angles for the compounds **7** are listed in Tables 4 and 5, respectively. The coordination sphere of the copper(I) ions in the bis(alkyne) complexes **7** is trigonal planar with two η^2-bonded alkyne ligands located in the coordination plane (maximum deviation of 0.12 Å for a carbon atom of a C≡C bond in complex **7a**). A similar bonding arrangement is present in the bis(σ-alkynyl) compounds **8**, which can be considered as organometallic π-tweezer complexes.[10] The copper−halide bond lengths of the complexes **7** have almost the values expected for a pure copper−halogen single bond (the covalent radius of a copper atom (sp^2-hybridization of the valence orbitals) is 1.20 Å; the covalent radii of the halogens are 0.99 Å (Cl), 1.14 Å (Br), and 1.33 Å (I)[3c]). The copper−alkyne bond lengths show two slightly different values (e.g. 2.041 Å (Cu−C1) and 2.080 Å (Cu−C2) for compound **7a**; C1 and C2 are the adjacent carbon atoms of the same cycloalkyne ligand, see Figure 2). Significantly longer copper−alkyne distances (0.049−0.106 Å) are found for the bis(alkyne) complexes **7** than for the dimeric mono(alkyne) complexes **5** (see Tables 3 and 5). In the chloro complex **8a** even longer Cu−η^2-(C≡C) bond lengths are observed (2.05 and 2.19 Å) than in complex **7a**, indicating in **8a** a weaker metal−alkyne interaction. Hence, a shorter Cu−Cl bond is found for complex **8a** (2.182 Å (**8a**), 2.220 Å (**7a**)). As in the complexes **5**, a clear influence of the halide ligand on the strength of the copper−alkyne bonding is observed for the compounds **7**, the iodo complex again having the



8

8a: X = Cl, R = $SiMe_3$, R' = Phenyl

Table 4. Crystallographic Data for Compounds 7a−c

	7a	**7b**	**7c**
formula	$C_{16}H_{24}ClCu$	$C_{16}H_{24}BrCu$	$C_{16}H_{24}CuI$
fw	315.34	359.80	406.79
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	*Pbca*	*Pbca*
a, Å	13.101(1)	14.790(9)	15.109(1)
b, Å	15.991(1)	9.315(7)	9.330(1)
c, Å	15.166(1)	22.093(15)	22.679(1)
α, deg	90	90	90
β, deg	106.17(1)	90	90
γ, deg	90	90	90
V, Å^3	3051.6(1)	3044(4)	3197.0(1)
ρ_{calcd}, g cm^{-3}	1.373	1.570	1.690
Z	8	8	8
cryst size, mm	0.4 × 0.4 × 0.3	0.4 × 0.2 × 0.2	0.5 × 0.4 × 0.2
diff model	SMART CCD	CAD4	SMART CCD
μ, mm^{-1}	1.59[a]	4.92[b]	3.28[a]
radiation	Mo Kα	Cu Kα	Mo Kα
temp, **K**	173	173	173
$2\theta_{max}$, deg	58	153	57
index ranges	$-17 \le h \le 13$ $-19 \le k \le 21$ $-12 \le l \le 20$	$18 \le h \le 0$ $-11 \le k \le 0$ $0 \le l \le 27$	$-20 \le h \le 19$ $-9 \le k \le 12$ $-25 \le l \le 30$
no. of unique rflns	7874	3193	3967
no. of rflns with $I > 2\sigma(I)$	6192	2131	3239
ref param	344	164	165
min/max resid electron density, e Å^{-3}	0.45/−0.51	0.62/−0.63	1.30/−1.28
R1/wR2 ($I > 2\sigma(I)$)	0.036/0.074	0.048/0.120	0.031/0.069
R1/wR2 (all)	0.053/0.081	0.097/0.142	0.041/0.072

[a] Absorption correction applied using the program SADABS.[18] [b] Absorption correction applied using the program DIFABS.[17]

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(10) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of Compounds 7a−c[a]

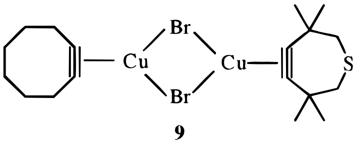
	7a (X = Cl)	**7b** (X = Br)	**7c** (X = I)	**8a** (X = Cl)
		Bond Lengths		
Cu−X	2.220(1)[b]	2.358(2)	2.535(1)	2.182(3)
Cu−C1[b]	2.041(2)	2.052(5)	2.064(3)	2.19(1)
Cu−C2[b]	2.080(2)	2.086(5)	2.092(2)	2.05(1)
$C{\equiv}C$[b]	1.216(3)	1.212(7)	1.219(4)	1.23(1)
		Bond Angles		
X−Cu−M[c]	113.6(1),[b] 114.8(1)[b]	114.2(1), 115.1(1)	113.5(1), 114.8(1)	116.9(3), 117.3(3)
M−Cu−M′	131.4(1)[b]	130.7(2)	131.7(1)	125.8(3)
$C{\equiv}C{-}C$[b]	152.9(2), 155.8(2)	154.1(5), 155.9(5)	153.6(3), 154.6(3)	161.0(3), 162.7(3)

[a] For comparison values of the structurally related complex $[(Cp'_2Ti(C{\equiv}CPh)_2)CuCl]$ (**8a**)[5] are also listed. [b] Averaged values. [c] Center of the $C{\equiv}C$ bond.

weakest Cu−alkyne interaction (see Table 5). The $C{\equiv}C$ bonds have lengths of 1.212−1.219 Å. Similar values were found for the complexes **5**. As expected, the bond angles around the copper atoms are close to the ideal value of 120°, the M−Cu−M′ angle (M = midpoint of the $C{\equiv}C$ bond) being a bit wider (130.7−131.7°) because of the steric demand of the in-plane alkyne ligands. The $C{\equiv}C{-}C$ bond angles are around 155°, as in the complexes **5**.

5. Reaction of the Dimeric Cyclooctyne Copper(I) Complex [CuBr(cyclooctyne)]$_2$ (5b) with 3,3,6,6-tetramethyl-l-thia-4-cycloheptyne (S-alkyne): Solid-State Structure of the Polymeric Complex [(cyclooctyne)CuBr$_2$Cu(S-alkyne)] (9). The dinuclear copper(I) cyclooctyne complexes **5** show a reaction chemistry similar to that for the cycloheptyne complexes **3**. For example, the reaction of **5b** with sodium acetylacetonate (Na-acac) affords the volatile monomeric copper complex [Cu(acac)(cyclooctyne)], the reaction of **5b** with diethylamine ($HNEt_2$) gives the monomeric copper complex [CuBr($HNEt_2$)(cyclooctyne)], and the reaction with triphenylphosphane (PPh_3) yields the dimeric copper complex [(cyclooctyne)CuBr$_2$Cu(PPh_3)$_2$]. Such types of copper alkyne compounds were reported by us during the past few years with the special cycloheptyne 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (S-alkyne) instead of cyclooctyne.[3e,11]

A new type of complex, the mixed cyclooctyne/S-alkyne dicopper(I) compound **9**, could now be obtained by reacting complex **5b** with an equimolar amount of 3,3,6,6-tetramethyl-l-thia-4-cycloheptyne (S-alkyne) in tetrahydrofuran. The complex **9** was recrystallized from tetrahydrofuran/cyclopentane and isolated as light brown blocks (yield: 74%). The determination of the molecular mass in chloroform showed that the compound **9** is dinuclear in this solvent (formula: [(cyclooctyne)CuBr$_2$Cu(S-alkyne)]). In the solid state compound **9** forms a polymeric structure (see X-ray structure analysis).



9

In the IR spectrum (Nujol) three bands for the $C{\equiv}C$ stretch are observed: 2078 cm^{-1} as well as 2003 and 1981 cm^{-1}. By comparison with the IR spectra of the pure cyclooctyne and S-alkyne complexes **5b** (ν($C{\equiv}C$) 2050 cm^{-1}) and **3d** (ν($C{\equiv}C$) 2005, 1981 cm^{-1})[3c] can be concluded that the stretch at 2078 cm^{-1} originates from the cyclooctyne ligand and those at 2003 and 1981 cm^{-1} originate from the S-alkyne ligand. The marked increase of the wavenumber for the cyclooctyne ligand from 2050 cm^{-1} (complex **5b)** to 2078 cm^{-1} (complex **9)** indicates a different bonding mode for the cyclooctyne ligand in complex **9** in comparison to complex **5b.** Indeed the X-ray structure determination of compound **9** reveals that in **9** the cyclooctyne is bound to a four-coordinated copper atom (weaker bonding; see Figure 3), whereas in complex **6b** the usual trigonal-planar copper atom is present (stronger bonding). This finding is also consistent with the decrease of the $C{\equiv}C$ stretch of the coordinated cyclooctyne to 2052 cm^{-1} when the IR spectrum of complex **9** is recorded in chloroform solution, where the polymeric solid-state structure is lost and a normal dinuclear complex with two trigonal-planar copper atoms formed.

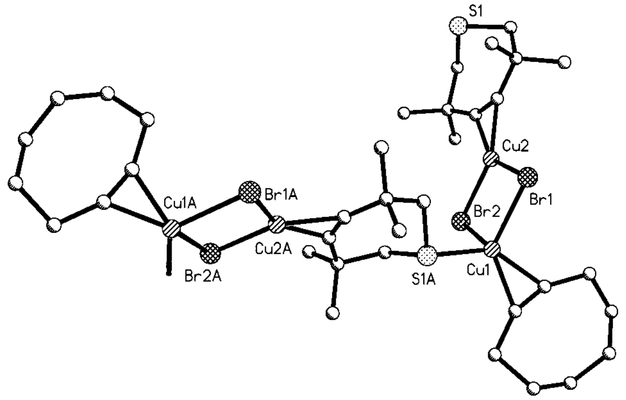


Figure 3. Polymeric structure of [(cyclooctyne)CuBr$_2$Cu-(S-alkyne)] (**9**) in the solid state (two asymmetric units are shown).

The structure of compound **9** has been determined by X-ray diffraction analysis. As already mentioned, complex **9** forms in the solid state a bent polymeric structure, which is shown in Figure 3. Crystallographic data and selected bond distances and angles are given in Tables 6 and 7, respectively. Dinuclear units of the composition [(cyclooctyne)CuBr$_2$Cu(S-alkyne)] (one is shown in Figure 4) form the polymeric structure by interconnecting these asymmetric units via strong sulfur−copper bonds from one S-alkyne ligand of one unit to a copper atom (Cu1) of a second adjacent unit (see Figure 3). The copper atom Cu1, which carries the cyclooctyne ligand, thus gets the coordination number 4 (CN = 4). The copper atom Cu2 remains in a trigonal-planar geometry coordinated by two bromo ligands and the $C{\equiv}C$-bound S-alkyne ligand. For the copper atom Cu2 we

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(11) (a) Schmidt, G.; Behrens, U. *J. Organomet. Chem.* **1996**, *509*, 49. (b) Olbrich, F.; Behrens, U.; Schmidt, G.; Weiss, E. *J. Organomet. Chem.* **1993**, *463*, 249.

Table 6. Crystallographic Data for Compound 9

formula	$C_{18}H_{28}Br_2Cu_2S$
fw	563.36
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	13.405(3)
b, Å	11.605(2)
c, Å	14.831(3)
α, deg	90
β, deg	110.06(3)
γ, deg	90
V, Å^3	2167.2(8)
ρ_{calcd}, g cm^{-3}	1.727
Z	4
cryst size, mm	0.4 × 0.3 × 0.2
diff model	SMART CCD
μ, mm^{-1}	5.74[a]
radiation	Mo Kα
temp, K	173
$2\theta_{max}$, deg	58
index ranges	$-18 \le h \le 9$ $-15 \le k \le 15$ $-14 \le l \le 20$
no. of unique rflns	5533
no. of rflns with $I > 2\sigma(I)$	3390
ref param	215
min/max resid electron density, e Å^{-3}	1.30/−0.95
R1/wR2 ($I > 2\sigma(I)$)	0.047/0.104
R1/wR2 (all)	0.091/0.118

[a] Absorption correction applied using the program SADABS.[18]

Table 7. Selected Bond Lengths (Å) and Angles (deg) of Compound 9

	Cu1	Cu2
	Bond Lengths	
Cu···Cu	3.273(1)	
Cu−Brl	2.465(1)	2.388(1)
Cu−Br	2.768(1)	2.354(1)
Cu−S	2.307(1)	
Cu−Cl	2.032(5)	1.966(5)
Cu−C	2.040(5)	1.968(5)
C≡C	1.195(7)[a]	1.224(7)[b]
	Bond Angles	
Br−Cu−Br	91.3(1)	104.4(1)
Cu−Br−Cu	84.8(1)[c]	79.0(1)[d]
C≡C−C	155.6(6)[a]	148.0(5)[b]

[a] Cyclooctyne. [b] S-alkyne. [c] Angle at Br1. [d] Angle at Br2.

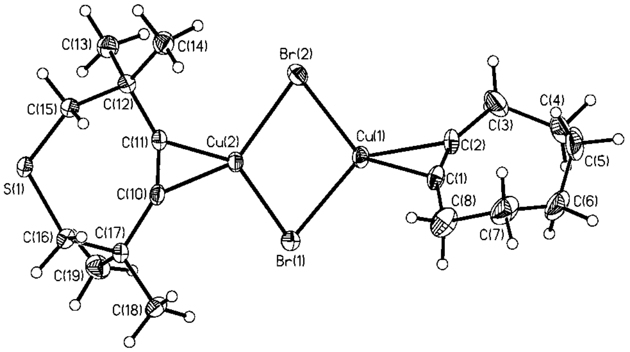

Figure 4. Asymmetric unit of [(cyclooctyne)CuBr$_2$Cu(S-alkyne)] (**9**).

observe very similar bond distances Cu−Br (2.354 and 2.388 Å) and Cu−η^2(C≡C) (1.967 Å) as in complex **3b** (see Table 3) because in both complexes the coordination geometry around the copper atom is the same. The four-coordinated copper atom Cu1 bonds more weakly to the cyclooctyne ligand (Cu1−η^2(C≡C) = 2.036 Å). In the trigonal-planar cyclooctyne copper complex **5b** a Cu−η^2(C≡C) bond length of only 1.980 Å is found (see Table 3). As expected, an alkyne ligand in a four-coordinated copper(I) complex forms a weaker bond to the metal ion than in a copper complex of coordination number 3. Two very different Cu1−Br distances are present in complex **9** (2.465 and 2.768 Å). It is thus appropriate to speak of a 3 + 1 coordination of the copper atom Cul. Four-coordinated copper is quite rare for alkyne−copper(I) complexes. We know of only two further examples, [CuI(S-alkyne)]$_3$ and [CuCl(S-alkyne)]$_6$.[3c] In both compounds there are two bridging halide ligands, one halide being 0.43 Å farther from the four-coordinated copper atom than the other one. For the bromo complex **9** this difference is only 0.30 Å. It should be mentioned in this context that there are a few polymeric (alkyne)CuCl complexes where the copper(I) ion in principle exhibits a trigonal-pyramidal coordination.[12] The trigonal plane is composed of the alkyne and two chloro ligands, a third chloro ligand being in an apical position. We do not consider such a complex as having a four-coordinated copper structure because the apical Cl ligand is more than 0.7 Å farther away from the copper(I) ion than the two chloro ligands in the trigonal plane (Cu−Cl$_{trigonal}$ = 2.255−2.295 Å, Cu−Cl$_{apical}$ = 3.037−3.102 Å).[12] The two alkyne ligands in the asymmetric unit of compound **9** form an angle of 71.8° with each other because the C atoms of the cyclooctyne ligand are in a trans position to the strongly bound S and Br donor atoms and not in a trans position to the two bromo ligands, as the S-alkyne at copper Cu2 is.

Experimental Section

General Procedures. All operations (except the determination of the molecular weights) were performed under an atmosphere of argon with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Cyclooctyne and 3,3,6,6-tetramethyl-l-thia-4-cycloheptyne (S-alkyne) were prepared according to literature methods.[13] Infrared data were collected on a Perkin-Elmer 1720 FI-IR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Gemini 200 FT-NMR spectrometer at 200 MHz (^{1}H) or 50.3 MHz (^{13}C) with TMS as standard. Molecular weights were taken by vapor-pressure osmometry in chloroform and acetonitrile (apparatus from Dr. Herbert Knauer & CO GmbH, Berlin).

Synthesis of [CuCl(cyclooctyne)]$_2$ (5a). Cyclooctyne (2.0 g, 18.5 mmol) was added to 1.53 g (15.5 mmol) of copper(I) chloride in 100 mL of tetrahydrofuran. The suspension was stirred at 20 °C. Within 1 h an almost clear solution formed. After filtration the solvent was removed under vacuum and the residue crystallized from 55 mL of hot cyclopentane. Yield: 1.92 g (60%) of product was obtained as colorless crystals. Mp: 113 °C. Solubility: good in tetrahydrofuran, chloroform, and acetonitrile, less good in *n*-hexane and cyclopentane. Anal. Calcd for $C_{16}H_{24}Cu_2Cl_2$ (414.36): C, 46.38; H, 5.84. Found: C, 46.37; H, 5.97. Molecular mass: 452 (in chloroform), 219 (in acetonitrile). IR (Nujol): ν(C≡C) 2042 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.69 (m, CH$_2$, C5/6), 1.91 (m, CH$_2$, C4/7), 2.49 (m, CH$_2$, C3/8) ppm. ^{13}C NMR (CDCl$_3$) δ 23.9 (C3/8), 29.2 (C5/6), 32.5 (C4/7), 98.7 (C1/2) ppm.

Synthesis of [CuBr(cyclooctyne)]$_2$ (5b). Cyclooctyne (6.0 g, 55.5 mmol) was added to 6.04 g (42.1 mmol) of copper(I) bromide in 100 mL of tetrahydrofuran. The suspension was stirred at 20 °C. Within 1 h an almost clear solution was formed. After filtration the solvent was removed under vacuum and the residue crystallized from 160 mL of hot cyclopentane. Yield: 10.48 g (99%) of product was obtained as colorless

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(12) Brantin, K.; Hakansson, M.; Jagner, S. *J. Organomet. Chem.* **1994**, *474*, 229. Hakansson, M.; Wettström, K.; Jagner, S. *J. Organomet. Chem.* **1991**, *421*, 347.

(13) (a) Brandsma, L.; Verkruijsse, H. D. *Synthesis* **1978**, 290. (b) Krebs, A.; Kimling, H. *Tetrahedron Lett.* **1970**, 761; *Liebigs Ann. Chem.* **1974**, 2074.

crystals. Mp: 120 °C. Solubility: good in tetrahydrofuran, chloroform and acetonitrile, less good in *n*-hexane and cyclopentane. Anal. Calcd for $C_{16}H_{24}Cu_2Br_2$ (503.27): C, 38.19; H, 4.81. Found: C, 39.23; H, 4.87. Molecular mass: 537 (in chloroform), 255 (in acetonitrile). IR (Nujol): ν(C≡C) 2050 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.71 (m, CH_2, C5/6), 1.87 (m, CH_2, C4/7), 2.45 (m, CH_2, C3/8) ppm. ^{13}C NMR ($CDCl_3$): δ 24.7 (C3/8), 29.2 (C5/6), 32.8 (C4/7), 99.5 (C1/2) ppm.

Synthesis of [CuI(cyclooctyne)]$_2$ (5c). Cyclooctyne (2.2 g, 20.3 mmol) was added to 2.93 g (15.4 mmol) of copper(I) iodide in 100 mL of tetrahydrofuran. The suspension was stirred at 20 °C. An almost clear solution quickly formed. After filtration the solvent was removed under vacuum and the residue crystallized from 85 mL of hot cyclopentane. Yield: 2.9 g (63%) of product was obtained as colorless crystals. Mp: 134 °C. Solubility: good in tetrahydrofuran, chloroform, and acetonitrile, less good in *n*-hexane and cyclopentane. Anal. Calcd for $C_{16}H_{24}Cu_2I_2$ (597.26): C, 32.18; H, 4.05. Found: C, 32.68; H, 4.13. Molecular mass: 578 (in chloroform), 299 (in acetonitrile). IR (Nujol): ν(C≡C) 2061 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.67 (m, CH_2, C5/6), 1.85 (m, CH_2, C4/7), 2.43 (m, CH_2, C3/8) ppm. ^{13}C NMR ($CDCl_3$) δ 26.8 (C3/8), 29.3 (C5/6), 33.2 (C4/7), 100.9 (C1/2) ppm.

Synthesis of [CuCl(cyclooctyne)$_2$] (7a). Cyclooctyne (0.55 g, 5.1 mmol) was added to 0.35 g (0.85 mmol) of [(cyclooctyne)-CuCl]$_2$ (**5a**) in 30 mL of tetrahydrofuran. The solution was stirred at 20 °C for 2 h. Almost the whole solvent was removed under vacuum and the residue dissolved in 30 mL of cyclopentane. Cooling to 7 °C (over 15 h) gave 0.30 g (56%) of product in the form of colorless needles. Mp: 103 °C. Solubility: good in tetrahydrofuran and chloroform, moderate in *n*-hexane and cyclopentane. Anal. Calcd for $C_{16}H_{24}CuCl$ (315.36): C, 60.94; H, 7.67. Found: C, 59.26; H, 7.23. Molecular mass: 254 (in chloroform). IR (Nujol): ν(C≡C) 2073 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.69 (m, CH_2, C5/6), 1.90 (m, CH_2, C4/7), 2.48 (m, CH_2, C3/8) ppm. ^{13}C NMR ($CDCl_3$): δ 24.0 (C3/8), 29.2 (C5/6), 33.2 (C4/7), 97.2 (C1/2) ppm.

Synthesis of [CuBr(cyclooctyne)$_2$] (7b). Cyclooctyne (2.0 g, 18.5 mmol) was added to a warm solution of 3.02 g (6.00 mmol) [(cyclooctyne)CuBr]$_2$ (**5b**) in 100 mL of cyclopentane. A white voluminous precipitate was formed. About 50% of the solvent was removed under vacuum. Filtration afforded 3.58 g (83%) of product in the form of a colorless powder. Mp: 115 °C. Solubility: good in tetrahydrofuran and chloroform, moderate in *n*-hexane and cyclopentane. Anal. Calcd for $C_{16}H_{24}CuBr$ (359.82): C, 53.41; H, 6.72. Found: C, 53.62; H, 6.76. Molecular mass: 326 (in chloroform). IR (Nujol): ν(C≡C) 2076 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.68 (m, CH_2, C5/6), 1.90 (m, CH_2, C4/7), 2.47 (m, CH_2, C3/8) ppm. ^{13}C NMR ($CDCl_3$): δ 25.2 (C3/8), 29.6 (C5/6), 33.7 (C4/7), 98.2 (C1/2) ppm.

Synthesis of [CuI(cyclooctyne)$_2$] (7c). Cyclooctyne (0.17 g, 1.76 mmol) was added to a solution of 0.31 g (0.52 mmol) of [(cyclooctyne)CuI]$_2$ (**5c**) in 15 mL of cyclopentane. A white voluminous precipitate was formed after a short time. About 50% of the solvent was removed under vacuum. Filtration afforded 0.27 g (64%) of product in the form of a colorless powder. Mp: 106 °C. Solubility: good in tetrahydrofuran and chloroform, moderate in *n*-hexane and cyclopentane. Anal. Calcd for $C_{16}H_{24}CuI$ (406.81): C, 47.24; H, 5.95. Found: C, 47.01; H, 6.16. Molecular mass: 335 (in chloroform). IR (Nujol): ν(C≡C) 2072 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.69 (m, CH_2, C5/6), 1.91 (m, CH_2, C4/7), 2.50 (m, CH_2, C3/8) ppm. ^{13}C NMR ($CDCl_3$): δ 25.4 (C3/8), 28.4 (C5/6), 32.7 (C4/7), 98.4 (C1/2) ppm.

Synthesis of [(cyclooctyne)CuBr$_2$Cu(S-alkyne)] (9). 3,3,6,6-Tetramethyl-1-thia-4-cycloheptyne (S-alkyne; 0.251 mL, 1.49 mmol) was added to a suspension of 0.75 g (1.49 mmol) of [(cyclooctyne)CuBr]$_2$ (**5b**) in 20 mL of tetrahydrofuran. After the mixture was stirred for 20 h, the solvent was reduced under vacuum to 5 mL. The remaining solution was layered with 10 mL of cyclopentane. Cooling to 7 °C (during 15 h) gave 0.62 g (74%) of product in the form of slightly brown blocks. Mp: 180 °C dec. Solubility: good in tetrahydrofuran, chloroform, acetonitrile, and toluene, less good in *n*-hexane and cyclopentane. Anal. Calcd for $C_{18}H_{28}Cu_2Br_2S$ (563.39): C, 38.38; H, 5.01. Found: C, 38.43; H, 5.00. Molecular mass: 604 (in chloroform). IR (Nujol): ν(C≡C) 2078, 2003, 1981 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.27 (s, CH_3, S-alkyne), 1.68 (m, CH_2, C5/6, cyclooctyne), 1.87 (m, CH_2, C4/7, cyclooctyne), 2.45 (m, CH_2, C3/8, cyclooctyne), 2.92 (s, SCH_2, S-alkyne) ppm. ^{13}C NMR (CD_2Cl_2): δ 24.7 (C3/8, cyclooctyne), 26.7 (CH_3, S-alkyne), 29.2 (C5/6, cyclooctyne), 32.5 (C4/7, cyclooctyne), 36.3 (CCH_3, S-alkyne), 52.6 (SCH_2, S-alkyne), 99.4 (C≡C, cyclooctyne), 110.0 (C≡C, S-alkyne) ppm.

X-ray Crystallography. The structures of all compounds were determined from single-crystal X-ray data. Crystals were grown by cooling solutions of the compounds in cyclopentane (in the case of **9**, in tetrahydrofuran/cyclopentane). The diffractometers used and the crystallographic data are given in Tables 2, 4, and 6. All structures were solved by direct methods.[14] The structures were refined by the least-squares method based on F^2 with all reflections.[15]All non-hydrogen atoms were refined anisotropically; the hydrogens were placed in calculated positions. The structure plots have been made using the plot part of the SHELXTL PLUS program system.[16]

In the chloro and iodo compounds **5a**,**c** the molecule is located exactly on an inversion center of the space group $P\bar{1}$. Thus, the asymmetric unit is built up only by half of the molecule. In the case of the bromo complex **5b** the inversion center of the space group $P2_1/c$ does not fully coincide with the symmetry center of the molecule (the crystallographic inversion center and the chemical symmetry center of the dimeric molecule are 0.246 Å apart). Thus, the structure is disordered and a whole molecule of **5b** with a site occupation factor of 0.5 for every atom was chosen as the asymmetric unit. Chemically identical bonds were given the same length by applying restraints. In principle it is also possible to refine the structure of **5b** in the space groups *Pc*, *P*2$_1$, or $P\bar{1}$ using the twin option of the SHELXL program, but this treatment led to worse *R* values. In the structures of **5c** and **7a** there is disorder for the carbon atoms C3, C4, C5, C6, and C7 (CH_2 carbons not bound to the C≡C triple bond). In **5c** two sites with site occupancy factors (sof) of 0.647 and 0.353 were refined; in **7a** two sites with sof = 0.814 and 0.186 were refined.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (grant Be 760/8-3) and the Fonds der Chemischen Industrie of Germany for financial support of this work.

Supporting Information Available: Crystallographic data for compounds **5a**–**c**, **7a**–**c**, and **9**, including tables of crystal data, atomic coordinates, bond distances and bond angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Also, the crystal structures have been deposited at the Cambridge Crystallographic Data Centre. The following deposition numbers were allocated: **5a**, CCDC-138855; **5b**, CCDC-138856; **5c**, CCDC-138857; **7a**, CCDC-138858; **7b**, CCDC-138859; **7c**, CCDC-138860; **9**, CCDC-138861.

OM000079G

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[15] Sheldrick, G. M. SHELXL-97: Program for the Refining of Crystal Structures; Göttingen, Germany, 1997.

[16] Sheldrick, G. M. SHELXTL-PLUS: Structure Determination Software Programs; Göttingen, Germany, 1988.

[17] (a) Spek, A. L. DIFABS, Part of the Program PLATON-95. *Acta Crystallogr., Sect. A* **1990**, C34. (b) Walker, N.; Stuart, D. DIFABS, An Empirical Method for Correcting Diffractometer Data for Absorption Effects. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

[18] Sheldrick, G. M. SADABS, Program for Area Detector Absorption Corrections; Göttingen, Germany, 1996.