Inorganica Chimica Acta, *129* (1987) 107–114

Copper(I) Complexes with Unsaturated Nitrogen Ligands. Part III.* Copper(I) Diazadiene Complexes with Carbon Monoxide, Olefins and Acetylenes

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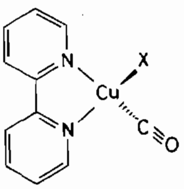
(Received October 27, 1986)

Abstract

Diazadienes, R–N=CR′–CR′=N–R, a versatile chelating ligand system similar to 2,2′-bipyridine or 1,10-phenanthroline, readily form 1:1 complexes with copper(I) trifluorsulfonate. By the addition of small organic ligands like carbon monoxide, ethylene or other olefins, and alkynes twenty-four new compounds of stoichiometry (diazadiene)Cu(L)O_3SCF_3 are obtained. Even the very electron-poor acetylene dicarboxylic acid esters can be coordinated to copper(I). The crystal and molecular structures of one cyclohexene complex (**6**) and one carbonyl complex (**9**) have been determined by X-ray diffraction techniques. (**6**: monoclinic, space group *Cc*, a = 17.1181(58), b = 12.8755(54), c = 17.2138(77) Å, β = 108.060(33)°, Z = 4; final R = 0.076, R_w = 0.054. **9**: orthorhombic, space group $P2_12_12_1$, a = 11.2226(18), b = 12.0142(30), c = 18.4974(34) Å, Z = 4; final R = 0.057, R_w = 0.036). Both structures indicate a tendency of copper(I) to adopt trigonal planar coordination geometry, this tendency being more pronounced in the olefin complex. There is still some interaction with one oxygen atom of the triflate anion. Most complexes dissociate in dilute solution, while in concentrated solutions it was possible to obtain ^{1}H NMR spectra and in some cases even ^{13}C NMR spectra, which show an averaged C_{2v} symmetry. It was not possible by NMR to distinguish between dissociation and non-rigidity processes.

Introduction

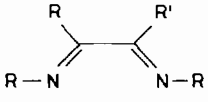
Recently we reinvestigated the coordination chemistry of 2,2′-bipyridine copper(I) chloride and bromide with carbon monoxide [1], for which a five coordinate copper atom had been reported [2]. We could unequivocally establish their structures **I** and **II**. They show a distorted tetrahedral coordination geometry, which has similarly been reported for the majority of other copper(I) carbonyl, olefin and acetylene complexes (with nitrogen containing ligands) [3, 4], although few examples are known, in which copper has trigonal coordination geometry [5] or tetragonal pyramidal coordination geometry involving coordination number five [6, 7].



I, X = Cl
II, X = Br

In complexes with tridentate N-donor ligands the formation of tetrahedral cationic copper carbonyls is found [8], while in the presence of bidentate donors the anions seem to play an important role. Thus halide ions, if present, typically appear in the coordination sphere [9] and even with the 'non-coordinating' anion $[B(C_6H_5)_4]^-$ the η^2-coordination of one aromatic ring is observed [10].

In recent papers Thompson *et al.* reported on the interaction of small molecules (CO, C_2H_4, C_3H_6 and C_2H_2) with Cu(I) and bidentate N-donors in the presence of $[ClO_4]^-$ and $[BF_4]^-$ [11, 12]. They showed that with carbon monoxide there is still some interaction of the anion with copper while with the unsaturated hydrocarbons strictly trigonal coordination occurs, leaving these anions uncoordinated.



III

Our general interest in the coordination chemistry of the versatile ligands of the 1,4-diaza-1,3-diene

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*For Part II see ref. 1.

0020-1693/87/$3.50

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(dad) type (**III**) has led us to investigate their interaction with copper(I) in the presence of carbon monoxide, alkenes and alkynes. We report here on the preparation and crystal structure determination of (dad)copper(I)-trifluoromethanesulfonates and these unsaturated molecules.

Experimental

All syntheses were performed under an inert atmosphere with Schlenk equipment. All solvents were dried and distilled under nitrogen before use. $CuO_3SCF_3 \cdot 0.5C_6H_6$ was prepared from Cu_2O and $HOSO_2CF_3$ (1:1 molar ratio) in benzene with separation of water by azeotropic distillation. Dad ligands were prepared according to literature procedures [13, 14]. 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.

General Procedures for the Preparation of (dad)Cu-(L)(O_3SCF_3)

Copper(I)trifluoromethanesulfonate benzene solvate $CuO_3SCF_3 \cdot 0.5C_6H_6$ (0.5 g, 2 mmol) and the dad ligand (2 mmol) were stirred in 10 ml of hexane and 20 ml of dichloromethane for 10 min under a nitrogen atmosphere. Then the nitrogen was replaced by ethylene (=L) and the reaction mixture was rapidly stirred for about 30 min. Precipitation by addition of hexane (50 ml) afforded orange or red products. They were collected by filtration and dried in a vacuum.

The above procedure with the following changes was used to prepare the carbonyl complexes: reduction of the initial solvent volume to 5 ml of hexane and 10 ml of dichloromethane; replacement of nitrogen by carbon monoxide and use of 20 ml of hexane for precipitation. The yellow or orange products were filtered under a slight carbon monoxide pressure, dried with a stream of carbon monoxide and stored under carbon monoxide.

A procedure similar to that for ethylene complexes was also used for the other alkene and alkyne complexes: instead of replacing nitrogen by ethylene, the liquid alkene/alkyne was added (cyclohexene 50 mmol; butynediyldiacetate, dimethoxybutyne 20 mmol; acetylenedimethylcarboxylate 3 mmol).

Ethylene Complexes

(Ethylene)[diacetylbis(3,5-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (1)

IR (cm^{-1}): 1650, 1610, 1590 (C=N). ^{1}H NMR (ppm): 7.20(H4$_{ar}$); 6.83(H2$_{ar}$); 4.31(CH$_2$=CH$_2$); 2.27(CH$_3$). ^{13}C NMR (ppm): 171.4(C=N); 147.0(C–N), 139.4, 128.4, 118.3(C$_{ar}$); 88.2(C=C); 21.3, 18.8(CH$_3$).

(Ethylene)[glyoxalbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (2)

IR (cm^{-1}): 1635, 1585 (C=N). ^{1}H NMR (ppm): 8.25(s, CH=N); 7.19(H$_{ar}$); 4.5(s, CH$_2$=CH$_2$); 2.92-(sept., CH, ^3J = 6.75 Hz); 1.15(d, CH$_3$). ^{13}C NMR (ppm): 162.5(C=N); 144.6(C–N); 138.8, 127.8, 124.1(C$_{ar}$); 95.8(C=C); 28.5(CH); 23.8(CH$_3$).

(Ethylene)[diacetylbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(II) (3)

IR (cm^{-1}): 1640, 1585 (C=N). ^{1}H NMR (ppm): 7.22(H$_{ar}$); 4.13(s, CH$_2$=CH$_2$); 2.75(sept., CH, ^3J = 6.75 Hz); 2.38(s, CH$_3$–C=N); 1.18, 1.15(d, CH$_3$). ^{13}C NMR (ppm): 171.8(C=N); 141.4(C–N); 137.8, 127.7, 124.4(C$_{ar}$); 89.7(C=C); 29.0(CH); 23.7, 23.2(CH$_3$); 19.5(CH$_3$–C=N).

Cyclohexene Complexes

(Cyclohexene)[diacetylbis(3,5-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (4)

IR (cm^{-1}): 1645, 1595 (C=N). ^{1}H NMR (ppm): 6.83(H4); 6.61(H2); 5.26(CH=CH); 2.28(s, CH$_3$, 12H); 2.22(s, CH$_3$, 6H); 1.69, 1.45(CH$_2$, 8H).

(Cyclohexene)[diacetylbis(2,6-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (5)

IR (cm^{-1}): 1645, 1600 (C=N). ^{1}H NMR (ppm): 7.07(H$_{ar}$); 5.11(CH=CH); 2.33(s, CH$_3$–C=N); 2.09-(CH$_3$); 1.59, 1.54(CH$_2$).

(Cyclohexene)[glyoxalbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (6)

IR (cm^{-1}): 1635, 1590 (C=N). ^{1}H NMR (ppm): 8.60(CH=N); 7.25(H$_{ar}$); 5.46(CH=CH); 2.92(sept., CH(CH$_3$)$_2$); 1.85, 1.53(CH$_2$, 4H); 1.22(d, CH$_3$).

(Cyclohexene)[diacetylbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (7)

IR (cm^{-1}): 1640, 1583 (C=N). ^{1}H NMR (ppm): 7.22(H$_{ar}$); 5.16(CH=CH); 2.72(sept., CH, ^3J = 6.75 Hz); 2.39(s, CH$_3$–C=N); 1.61, 1.46(CH$_2$, 4H); 1.18, 1.15(d, CH$_3$). ^{13}C NMR (ppm): 174.0(C=N); 141.5-(C–N); 137.7, 127.5, 125.3(C$_{ar}$); 110.9(C=C); 29.1(CH); 25.1, 22.4(CH$_2$); 23.5, 19.5(CH$_3$).

(Cyclohexene)(diacetylbis(4-methylphenylimine)]-trifluoromethanesulfonatocopper(I) (8)

IR (cm^{-1}): 1635, 1580 (C=N). ^{1}H NMR (ppm): 7.15(d, H$_{ar}$); 6.94(d, H$_{ar}$); 5.23(CH=CH); 2.30, 2.25(s, CH$_3$); 1.63, 1.39(CH$_2$, 4H).

Carbonyl Complexes

(Carbonyl)glyoxalbis(2,4-dimethylpentyl-3-imine)]trifluoromethanesulfonatocopper(I) (9)

IR (cm^{-1}): 2108(CO); 1653, 1638, 1582(C=N). ^{1}H NMR (ppm): 7.76(s, CH=N); 2.50(t, CH–N);

1.98(CH); 0.80(d, CH_3, $^3J = 6.7$ Hz); 0.78(d, CH_3, $^3J = 6.8$ Hz). ^{13}C NMR (ppm): 170.4(CO); 158.0(C=N); 120.5(q, CF_3, $^1J = 320$ Hz); 83.7(C–N); 29.5(C–$(CH_3)_2$); 20.0, 18.4(CH_3).

(Carbonyl)[diacetylbis(3,5-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (10)

IR (cm^{-1}): 2105(CO); 1640, 1603, 1592(C=N). ^{13}C NMR (ppm): 171.8(CO); 168.9(C=N); 147.1, 139.5, 128.5, 118.3(C_{ar}); 21.3, 18.6(CH_3).

(Carbonyl)[diacetylbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (11)

IR (cm^{-1}): 2093(CO); 1640, 1580(C=N). ^{13}C NMR (ppm): 169.6(CO); 159.9(C=N); 144.3, 139.0, 127.9, 124.1(C_{ar}); 120.1(q, CF_3, $^1J = 302$ Hz); 28.3, 24.0(CH_3).

The following analogous carbonyl complexes were only characterised by elemental analyses and IR (cm^{-1}): (**12**) 2102(CO); 1592(C=N). (**13**) 2105(CO); 1637, 1590(C=N). (**14**) 2103(CO); 1645, 1587(C=N). (**15**) 2101(CO); 1638, 1584(C=N).

Alkyne Complexes

(3-Hexyne)[diacetylbis(3,5-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (16)

IR (cm^{-1}): 2053, 2020(C≡C); 1654, 1603, 1589(C=N). ^1H NMR (ppm): 6.90(H_p); 6.78(H_o); 2.41(s, CH_3, 6H); 2.33(s, CH_3, 12H); 1.90(q, CH_2, $^3J = 7.3$ Hz); 0.90(t, CH_3). ^{13}C NMR (ppm): 173.6(C=N); 147.2(C–N); 139.7, 128.3, 117.9(C_{ar}); 89.6(C≡C); 21.2(CH_3–C=N); 18.8(CH_3); 14.7(CH_2–CH_3); 14.3(CH_3–CH_2).

(3-Hexyne)[diacetylbis(2,6-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (17)

IR (cm^{-1}): 2045, 2015(C≡C); 1648, 1600(C=N). ^1H NMR (ppm): 7.29(H_{ar}); 2.44(s, CH_3, 6H); 2.18(s, CH_3, 12H); 1.69(q, CH_2, $^3J = 7.2$ Hz); 0.81(t, CH_3). ^{13}C NMR (ppm): 174.3(C=N); 141.9(C–N); 127.0, 125.5, 125.0(C_{ar}); 89.8(C≡C), 16.7(CH_3–C=N); 16.1(CH_3); 12.7(CH_2–CH_3); 12.2(CH_3–CH_2).

(3-Hexyne)[glyoxalbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (18)

IR (cm^{-1}): 2040(C≡C); 1665, 1580(C=N). ^1H NMR (ppm): 8.84(s, CH=N); 7.27(H_{ar}); 2.98(sept., CH); 1.83(q, CH_2, $^3J = 7.5$ Hz); 1.25(d, CH_3, $^3J = 6.8$ Hz); 0.90(t, CH_3). ^{13}C NMR (ppm): 166.8(C=N); 143.7(C–N); 138.0, 128.3, 124.0(C_{ar}); 91.2(C≡C); 28.8(CH_3–C=N); 23.1(CH_3); 15.0(CH_2–CH_3); 14.3(CH_3–CH_2).

(2-Butyne-1,4-diyldiacetate)[diacetylbis(2,6-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (19)

IR (cm^{-1}): 2025(C≡C); 1740(CO); 1640, 1598(C=N). ^1H NMR (ppm): 7.09(H_{ar}); 4.15(s, CH_2); 2.40(s, CH_3, 6H; 2.15(s, CH_3, 12H); 1.93(s, CH_3–COO). ^{13}C NMR (ppm): 175.4(C=N); 167.7(C=O); 141.6(C–N); 127.1, 125.7, 125.4(C_{ar}); 87.4(C≡C); 50.0 (CH_2); 18.4(CH_3–CH_2); 16.8(CH_3–C=N); 16.1(CH_3).

(2-Butyne-1,4-diyldiacetate)[glyoxalbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (20)

IR (cm^{-1}): 2060(C≡C); 1753(C=O); 1643, 1585(C=N). ^1H NMR (ppm): 8.68(s, CH=N); 7.27(H_{ar}); 4.40(s, CH_2); 3.00(sept., CH, $^3J = 6.75$ Hz); 1.96(s, CH_3–COO); 1.24(d, CH_3). ^{13}C NMR (ppm): 177.2(C=N); 169.5(C=O); 141.5(C–N); 137.6, 128.3, 124.7(C_{ar}); 91.3(C≡C); 51.8(CH_2); 28.9(CH); 23.2(CH_3); 20.4(CH_3–COO).

(2-Butyne-1,4-diyldiacetate)[diacetylbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (21)

IR (cm^{-1}): 2013(C≡C); 1750(CO); 1646, 1600(C=N). ^1H NMR (ppm): 7.25(H_{ar}); 3.90(s, CH_2); 2.82(sept., CH); 2.52(s, CH_3–C=N); 1.88(s, CH_3–COO); 1.22, 1.16(d, CH_3, $^3J = 6.75$ Hz).

(1,4-Dimethoxy-2-butyne)[diacetylbis(2,6-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (22)

IR (cm^{-1}): 2040(C≡C); 1640, 1593(C=N). ^1H NMR (ppm): 7.09(H_{ar}); 3.55(s, CH_2); 3.00(s, CH_3–O); 2.38(s, CH_3–C=N); 2.13(s, CH_3, 12H). ^{13}C NMR (ppm): 177.1(C=N); 144.0(C–N); 128.9, 127.7, 127.1(C_{ar}); 92.5(C≡C); 60.8(CH_2–O); 57.9(CH_3–O); 18.7(CH_3–C=N); 18.1(CH_3).

(1,4-Dimethoxy-2-butyne)[diacetylbis(2,6-diisopropylphenylimine)]trifluoromethanesulfonatocopper(I) (23)

IR (cm^{-1}): 1980(C≡C); 1645, 1605, 1585(C=N). ^1H NMR (ppm): 7.27(H_{ar}); 3.43(s, CH_2); 3.02(s, CH_3–O); 2.81(sept., CH, $^3J = 6.75$ Hz); 1.22, 1.14(d, CH_3).

(Acetylenedimethylcarboxylate)[diacetylbis(2,6-dimethylphenylimine)]trifluoromethanesulfonatocopper(I) (24)

IR (cm^{-1}): 1995(C≡C); 1720(C=O); 1642, 1600(C=N). ^1H NMR (CD_3COCD_3, ppm): 7.25(H_{ar}); 3.38(s, CH_3–O); 2.54(s, CH_3–C=N); 2.25(s, CH_3).

X-ray Crystallographic Measurements

Crystals of **6**/**9** suitable for diffraction studies were obtained by cooling a warm saturated solution in a 1:1 mixture of CH_2Cl_2/hexane, containing either excess of cyclohexene (**6**) or working under an atmosphere of carbon monoxide (**9**).

The crystals chosen were encapsulated in a glass capillary under a nitrogen atmosphere. They were placed on a SYNTEX $P2_1$ four circle diffractometer

TABLE I. Crystallographic Data for (dad)Cu(c-hexen)(O_3SCF_3) (6) and (dad)Cu(CO)(O_3SCF_3) (9)

	6	9
Formula	$C_{33}H_{46}CuF_3N_2O_3S$	$C_{18}H_{32}CuF_3N_2O_4S$
Molecular weight	671.34	493.06
Crystal system	monoclinic	orthorhombic
Space group	*Cc*	$P2_12_12_1$
a (Å)	17.1181(58)	11.2226(18)
b (Å)	12.8755(54)	12.0142(30)
c (Å)	17.2138(77)	18.4974(34)
β (°)	108.060(33)	–
V (Å^3)	3607.1(26)	2494.0(9)
Z	4	4
D_{calc} (g/cm^3)	1.236	1.313
Crystal size (mm^3)	0.4 × 0.3 × 0.2	0.5 × 0.4 × 0.6
μ (cm^{-1})	7.07	10.01
2*θ* range (°)	2–45	3–60
h/*k*/*l* range	0/0/0–20/16/20	0/0/0–15/16/26
No. reflections measured	2365	4111
No. reflections used	1402 ($I \geqslant 3\sigma(I)$)	2562 ($I \geqslant 2\sigma(I)$)
No. variables refined	165	295
R	0.076	0.057
R_w	0.054 ($w = 3.7185$)	0.036 ($w = 2.2604$)
Max. e/Å^3	0.4	0.7
Max. shift/e.s.d.	0.5	0.23

using graphite-monochromated Mo K*α* radiation (λ = 0.70926 Å), which was used for all crystallographic measurements. Cell parameters were obtained and refined on the basis of 16 (6) or 25 (9) computer centered reflections chosen from diverse regions of 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. 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.

Both structures were solved by direct methods [15] and subsequent difference-Fourier synthesis [16]. Refinement by full-matrix least squares progressed to the reported *R* values (Table I), the function minimised was: $[\Sigma w(F_o - F_c)^2/\sigma_{(F_o)}{}^2][\Sigma w \times F_o{}^2/\sigma_{(F_o)}{}^2]^{-1}$. The plots (Figs. 1 and 2) were drawn with the SCHAKAL program [19].

Results and Discussion

Synthesis and Properties

The preparation of the copper(I) complexes (dad)-Cu(L)(O_3SCF_3) is outlined in eqn. (1). Reaction of copper(I) triflate with the ligands dad and L in tetrahydrofuran or dichloromethane at room temperature leads to solutions of the corresponding complexes, which can be precipitated by addition of hexane.

$$Cu(O_3SCF_3)\cdot 0.5C_6H_6 + dad + L \xrightarrow{-0.5C_6H_6} (dad)Cu(L)(O_3SCF_3) \quad (1)$$

1–**24**

	dad	RN=CR′–CR′=NR	L
	R′	R	
1	CH_3	C_6H_3–3,5$(CH_3)_2$	ethylene
2	H	C_6H_3–2,6(i-C_3H_7)$_2$	ethylene
3	CH_3	C_6H_3–2,6(i-C_3H_7)$_2$	ethylene
4	CH_3	C_6H_3–3,5$(CH_3)_2$	c-hexene
5	CH_3	C_6H_3–2,6$(CH_3)_2$	c-hexene
6	H	C_6H_3–2,6(i-C_3H_7)$_2$	c-hexene
7	CH_3	C_6H_3–2,6(i-C_3H_7)$_2$	c-hexene
8	CH_3	C_6H_4–4(CH_3)	c-hexene
9	H	$CH(CH(CH_3)_2)_2$	CO
10	CH_3	C_6H_3–3,5$(CH_3)_2$	CO
11	CH_3	C_6H_3–2,6(i-C_3H_7)$_2$	CO
12	H	C_6H_4–4(CH_3)	CO
13	H	C_6H_3–2,6$(CH_3)_2$	CO
14	CH_3	C_6H_3–2,6$(CH_3)_2$	CO
15	H	C_6H_3–2,6(i-C_3H_7)$_2$	CO
16	CH_3	C_6H_3–3,5$(CH_3)_2$	3-hexyne
17	CH_3	C_6H_3–2,6$(CH_3)_2$	3-hexyne
18	H	C_6H_3–2,6(i-C_3H_7)$_2$	3-hexyne
19	CH_3	C_6H_3–2,6$(CH_3)_2$	$(CH_3COOCH_2C\equiv)_2$
20	H	C_6H_3–2,6(i-C_3H_7)$_2$	$(CH_3COOCH_2C\equiv)_2$
21	CH_3	C_6H_3–2,6(i-C_3H_7)$_2$	$(CH_3COOCH_2C\equiv)_2$
22	CH_3	C_6H_3–2,6$(CH_3)_2$	$(CH_3OCH_2C\equiv)_2$
23	CH_3	C_6H_3–2,6(i-C_3H_7)$_2$	$(CH_3OCH_2C\equiv)_2$
24	CH_3	C_6H_3–2,6$(CH_3)_2$	$(CH_3OOCC\equiv)_2$

Because of the dissociation equilibria of L a variable excess of this ligand is necessary to obtain good yields. In particular some of the carbonyl complexes are so unstable that they have to be handled and stored under an atmosphere of carbon monoxide. Decarbonylation may otherwise occur even in the solid state [1]. The complexes are yellow to red microcrystalline materials, which are slightly sensitive to air. Dilute solutions do not contain much of the undissociated complexes. Thus in most cases electronic spectra cannot be recorded for the pure compounds, while NMR spectra in concentrated solutions can be obtained. The NMR data always show an averaged C_{2v} symmetry for the dad ligands, which probably gives a much too simple picture of the coordination geometry around copper.

Crystal Structures of (dad)Cu(c-hexene)(O_3SCF_3) (6) and (dad)Cu(CO)(O_3SCF_3) 9

The structures of one olefin complex **6** and one carbonyl complex **9** were determined by X-ray diffraction methods. Crystallographic data are collected in Table I, positional parameters in Table II. Figures 1 and 2 show a molecule of complex **6** and **9** respectively. Important bond lengths and angles of both structures are given in Table III.

TABLE II. Positional and Thermal Parameters (with e.s.d.s)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
(dad)Cu(c-hexene) (O_3SCF_3) (6)				
Cu	0.0000(0)	0.7871(2)	0.0000(0)	0.074(2)
S	0.0828(4)	0.0633(5)	0.3432(4)	0.094(8)
F1	0.6181(9)	0.2544(12)	−0.2042(9)	0.190(7)[a]
F2	0.6418(8)	0.3791(10)	−0.2741(8)	0.149(5)[a]
F3	0.7196(11)	0.3459(13)	−0.1559(10)	0.192(7)[a]
O1	0.5853(7)	0.3872(10)	−0.0805(8)	0.091(4)[a]
O2	0.6244(9)	0.5330(12)	−0.1546(8)	0.130(5)[a]
O3	0.5017(9)	0.4319(10)	−0.2154(8)	0.128(5)[a]
N1	0.4474(8)	0.3997(10)	0.0490(7)	0.063(4)[a]
N2	0.5846(7)	0.2874(11)	0.1203(7)	0.065(4)[a]
C0	0.6420(15)	0.3504(20)	−0.2007(14)	0.170(12)[a]
C1	0.4905(10)	0.4176(13)	0.1256(9)	0.069(5)[a]
C2	0.5657(10)	0.3611(12)	0.1628(10)	0.068(5)[a]
C11	0.3736(6)	0.4533(10)	0.0201(7)	0.061(5)[a]
C12	0.3009(6)	0.4142(10)	0.0278(7)	0.078(6)[a]
C13	0.2268(6)	0.4648(10)	−0.0061(7)	0.112(7)[a]
C14	0.2254(6)	0.5581(10)	−0.0477(7)	0.109(7)[a]
C15	0.2981(6)	0.5990(10)	−0.0554(7)	0.105(7)[a]
C16	0.3722(6)	0.5466(10)	−0.0215(7)	0.079(6)[a]
C21	0.6556(6)	0.2276(9)	0.1541(7)	0.072(5)[a]
C22	0.7314(6)	0.2584(9)	0.1474(7)	0.078(6)[a]
C23	0.8010(6)	0.1975(9)	0.1816(7)	0.096(6)[a]
C24	0.7948(6)	0.1057(9)	0.2223(7)	0.099(7)[a]
C25	0.7190(6)	0.0748(9)	0.2289(7)	0.095(7)[a]
C26	0.6494(6)	0.1358(9)	0.1948(7)	0.080(6)[a]
C31	0.4344(11)	0.2273(16)	−0.1077(10)	0.091(6)[a]
C32	0.5021(12)	0.1694(13)	−0.0803(10)	0.087(6)[a]
C33	0.5052(14)	0.0581(15)	−0.0403(13)	0.137(9)[a]
C34	0.4183(15)	0.0172(18)	−0.0624(18)	0.191(12)[a]
C35	0.3506(15)	0.0880(17)	−0.0678(15)	0.179(11)[a]
C36	0.3469(11)	0.1879(15)	−0.1166(11)	0.112(8)[a]
C120	0.2982(11)	0.3109(13)	0.0701(10)	0.097(7)[a]
C121	0.3114(15)	0.3204(17)	0.1586(11)	0.137(9)[a]
C122	0.2227(11)	0.2445(16)	0.0325(12)	0.142(9)[a]
C160	0.4492(11)	0.5936(15)	−0.0296(11)	0.109(7)[a]
C161	0.4870(12)	0.6725(15)	0.0356(10)	0.132(9)[a]
C162	0.4474(15)	0.6426(20)	−0.1095(13)	0.201(12)[a]
C220	0.7417(12)	0.3616(12)	0.1087(11)	0.096(6)[a]
C221	0.7927(13)	0.3535(17)	0.0545(13)	0.162(10)[a]
C222	0.7730(13)	0.4502(15)	0.1670(12)	0.142(9)[a]

(continued)

TABLE I. *(continued)*

Atom	x/a	y/b	z/c	U_{eq}
C260	0.5670(11)	0.1043(15)	0.2000(12)	0.120(8)[a]
C261	0.5540(14)	−0.0127(15)	0.1961(13)	0.153(10)[a]
C262	0.5561(13)	0.1381(16)	0.2799(12)	0.156(10)[a]
(dad)Cu(CO)(O_3SCF_3) (9)				
Cu	0.0704(1)	−0.0118(1)	0.0203(1)	0.055(1)
S	0.3284(1)	0.0185(2)	0.0953(1)	0.061(2)
F1	0.4898(4)	−0.0165(4)	−0.0039(2)	0.131(6)
F2	0.3938(4)	−0.1629(3)	0.0269(3)	0.127(6)
F3	0.5287(4)	−0.0933(4)	0.0966(3)	0.132(7)
O0	0.0618(6)	−0.2339(4)	0.0858(3)	0.110(7)
O1	0.2502(3)	0.0466(3)	0.0349(2)	0.062(4)
O2	0.3963(4)	0.1110(4)	0.1228(2)	0.086(6)
O3	0.2752(4)	−0.0534(4)	0.1485(2)	0.099(6)
N1	−0.0182(4)	0.1382(4)	0.0412(2)	0.055(5)
N2	0.0367(4)	0.0372(4)	−0.0850(2)	0.055(5)
C000	0.4432(8)	−0.0692(7)	0.0506(5)	0.102(11)
C0	0.0609(7)	−0.1491(5)	0.0615(3)	0.071(7)
C1	−0.0358(5)	0.1898(4)	−0.0178(3)	0.061(6)
C2	−0.0122(6)	0.1342(5)	−0.0859(3)	0.063(7)
C10	−0.0550(6)	0.1920(5)	0.1091(3)	0.063(7)
C11	−0.1693(7)	0.1339(6)	0.1375(4)	0.087(9)
C12	0.0506(6)	0.1981(6)	0.1610(3)	0.078(8)
C20	0.0467(5)	−0.0243(5)	−0.1547(3)	0.058(6)
C21	−0.0433(6)	−0.1210(5)	−0.1524(3)	0.072(8)
C22	0.1771(6)	−0.0586(5)	−0.1695(3)	0.070(8)
C111	−0.1477(8)	0.0110(7)	0.1618(5)	0.131(12)
C112	−0.2717(6)	0.1415(7)	0.0832(4)	0.106(11)
C121	0.0151(8)	0.2341(7)	0.2377(4)	0.114(11)
C122	0.1440(7)	0.2766(6)	0.1302(4)	0.106(11)
C211	−0.1736(7)	−0.0800(7)	−0.1407(4)	0.116(12)
C212	−0.0397(7)	−0.1919(6)	−0.2218(3)	0.104(10)
C221	0.2602(6)	0.0427(5)	−0.1671(4)	0.090(9)
C222	0.2250(7)	−0.1484(6)	−0.1203(3)	0.085(9)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $U(\text{eq}) = 1/3(U_{11} + U_{22} + U_{33})$.

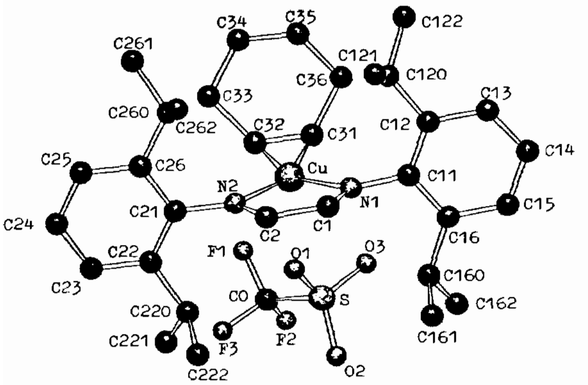

Fig. 1. SCHAKAL plot of (dad)Cu(c-hexene)(O_3SCF_3) (6) with numbering scheme.

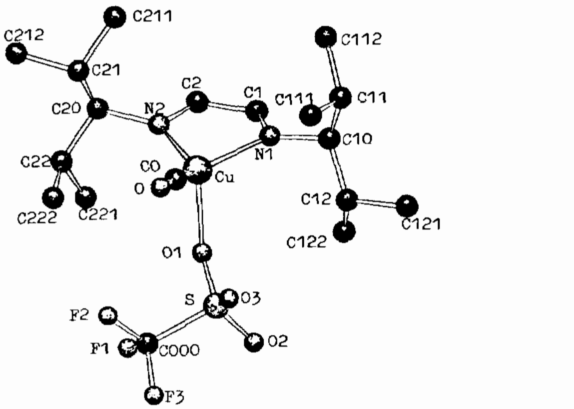

Fig. 2. SCHAKAL plot of (dad)Cu(CO)(O_3SCF_3) (9) with numbering scheme.

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

(dad)Cu(c-hexene)(O_3SCF_3) (**6**)

Cu–N1 2.02(1), Cu–N2 2.13(1), N1–C1 1.32(2), N2–C2 1.30(2), C1–C2 1.44(2), Cu–C31 2.00(2), Cu–C32 2.06(2), C31–C32 1.34(3), Cu–O1 2.64(1).
N1–Cu–N2 81.4(5), C31–Cu–C32 38.4(7), C31/C32[a]–Cu–O1 97.9(7).

(dad)Cu(CO)(O_3SCF_3) (**9**)

Cu–N1 2.094(5), Cu–N2 2.070(4), N1–C1 1.27(1), N2–C2 1.29(1), C1–C2 1.45(1), Cu–CO 1.820(6), CO–O 1.11(1), Cu–O1 2.153(4).
N1–Cu–N2 80.9(2), O1–CuCO 129.9(2), Cu–CO–O 176.1(7).

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[a]Atom 1/atom 2 means the midpoint of the line through the two atoms.

Both structures roughly correspond to each other in the overall geometry around the metal, indicating a transition from coordination number four to three. The interaction between copper and the triflate ion is still quite remarkable in the carbonyl complex **9** (Cu–O1 = 2.15 Å) as compared to **6** (Cu–O1 = 2.64 Å). This agrees well with a smaller angle between the (dad)Cu plane and the CO group (149.9°) as compared to the corresponding angle (168.2°) in the almost trigonal planar complex **6**. In copper(I) complexes with *N,N*-chelating ligands, the interactions of the small ligand molecules CO, C_2H_4 and C_2H_2 with the anions $[ClO_4]^-$ and $[BF_4]^-$ are even smaller, as was recently shown by Thompson *et al.* [11, 17]. In their structural examples the carbonyl complex, too, shows a slightly more pronounced interaction with the anion. Floriani *et al.* describe a Cu(CO) complex with substantial bonding of copper to a $[B(C_6H_5)_4]^-$ anion [10]. Although steric reasons might be invoked to account for these slight differences, since olefins are more bulky than carbonyl ligands, it is probably the higher donor capacity of the former ligands, which is important. The first gas phase ionization potentials of carbon monoxide (14.0 eV) and ethylene (10.5 eV) differ already by 3.5 eV [18]. This difference is even greater for alkyl substituted olefins and carbon monoxide.

The olefinic double bond in **6** is parallel to the copper/dad chelate plane. This arrangement of olefinic ligands seems to be typical for d^{10} complexes, although deviations occur and the rotational barriers for Ni(0) complexes are low [20]. As back-donation is generally not regarded to be important for Cu(I) in comparison to Ni(0), the conformational stability of the olefinic ligands should even be less. Unfortunately we could not yet distinguish by NMR dissociation from non-rigidity processes for **6**.

For the carbonyl complex **9**, which is by far the most stable of the CO complexes reported here, and the complexes **10** and **11**, ^{13}C NMR signals could be recorded successfully (δ = 169.7–171.8 ppm). They are in agreement with one value reported earlier [21]. There was no indication for the formation of dicarbonyl complexes in solution [12] (see also ref. 22)* nor for bis(alkene) or bis(alkyne) complexes.

Supplementary Material

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD – 52152, the names of the authors, and the journal citation.

References

1 L. Stamp, H. tom Dieck and J. Kopf, *Inorg. Chem.*, submitted for publication.
2 S. Kitagawa and M. Munakata, *Inorg. Chem.*, *20*, 2261 (1981).
3 M. Pasquali, C. Floriani and H. Gaetani-Manfredotti, *Inorg. Chem.*, *20*, 3382 (1981).
4 M. R. Churchill, B. G. DeBoer, F. J. Rotella, O. M. Abu Salah and M. I. Bruce, *Inorg. Chem.*, *14*, 2051 (1975).
5 J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, *105*, 3522 (1983).
6 R. R. Gagne, J. L. Allison, R. S. Gall and C. A. Koval, *J. Am. Chem. Soc.*, *99*, 7170 (1977).
7 M. W. McCool, R. E. Marsh, D. M. Ingle and R. R. Gagne, *Acta Crystallogr., Sect. B*, *37*, 935 (1981).
8 R. R. Gagne, R. P. Kreh, J. A. Dodge, R. E. Marsh and M. McCool, *Inorg. Chem.*, *21*, 254 (1982).
9 M. Pasquali, G. Marini and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 937 (1979).
10 M. Pasquali, C. Floriani and H. Gaetani-Manfredotti, *Inorg. Chem.*, *19*, 1191 (1980).
11 J. S. Thompson and J. F. Whitney, *Inorg. Chem.*, *23*, 2813 (1984).
12 J. S. Thompson and M. Swiatek, *Inorg. Chem.*, *24*, 110 (1985).
13 J. M. Kliegman and R. K. Barnes, *Tetrahedron*, *26*, 2555 (1970).
14 H. tom Dieck, K.-D. Franz and W. Majunke, *Z. Naturforsch., Teil B*, *30*, 972 (1975).
15 G. M. Sheldrick, 'SHELXS-84', a computer program for the automatic solution of crystal structures, University of Göttingen, 1984.
16 G. M. Sheldrick, 'SHELX76', programs for crystal structure determination, University of Cambridge, 1976.

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*The formation of dicarbonyls is reported without structural or spectroscopic proof.

17 J. S. Thompson and J. F. Whitney, *Acta Crystallogr., Sect. C, 40,* 756 (1984).

18 D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, 'Molecular Photo Electron Spectroscopy', Wiley, London, 1970.

19 E. Keller, 'SCHAKAL', a FORTRAN program for the graphic representation of molecules, *Chemie Unserer Zeit, 14,* 56 (1980).

20 P. W. Jolly, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), 'Comprehensive Organometallic Chemistry', Vol. 6, Pergamon, New York, 1982.

21 R. L. Geerts, J. C. Hoffman, K. Folting, T. H. Lemmen and K. G. Caulton, *J. Am. Chem. Soc., 105,* 3503 (1983).

22 S. Kitagawa, M. Munakata and N. Miyaji, *Inorg. Chem., 21,* 3842 (1982).