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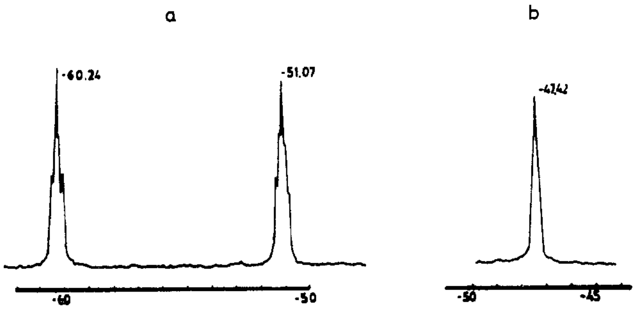

Figure 5. $^{31}P\{^1H\}$ NMR spectra of (a) $[Au_6(P(C_6H_5)_2(CH_2)_3P(C_6H_5)_2)_4](NO_3)_2$ and (b) $Au_4L_4I_2$.

of four Au atoms is present and I atoms bridge over two opposite edges[5] (see Figure 4). In both clusters there are almost linear P–Au–Au–P moieties with very short Au–Au bond lengths (2.65 and 2.63 Å) as compared to the other Au–Au distances (2.80–2.92 Å). In accord with its structure the Mössbauer spectrum of $Au_4L_4I_2$ shows only one quadrupole pair. The Mössbauer parameters are given in Table IV compared with data of P-connected Au sites in some Au cluster compounds. Quadrupole splittings and isomer shifts are in rather narrow ranges. Neither the presence or absence of a central gold nor the connection to one or two phosphines gives clearly distinct data. So the conclusion that we formulated earlier[13,14] about the ratio of radial to tangential interactions seems to be in doubt with regard to the present data.

The $^{31}P\{^1H\}$ NMR spectrum of $[Au_6(dppp)_4]^{2+}$ in CD_2Cl_2 solution shows two sets of quintets of equal intensity, positioned at −51.07 and −60.24 ppm (downfield relative to TMP) with a coupling of 5.0 ± 0.2 Hz (see Figure 5). The spectrum is in agreement with the presence of two magnetically inequivalent sets of four P atoms, coupled via the Au skeleton. No additional coupling via the propylene bridge could be detected. The $^{31}P\{^1H\}$ NMR spectrum of $[Au_4L_4I_2$ shows one singlet at −47.4 ppm (see Figure 4).

Except for the spectrum of $[Au_5(Ph_2PCH_2PPh_2)_3(Ph_2PCHPPh_2)]^{2+}$, which is rather complex,[6,7] the spectra of all other gold clusters containing monodentate phosphine and even $[Au_{11}(dppp)_5]^{3+}$ show one singlet.[11] The solid-state spectrum of $[Au_9L_8](NO_3)_3$ has two lines of about equal intensities[15] in accordance with the two crystallographically distinct sets of four P atoms. No P–P coupling could, however, be detected. The presence of one singlet in the solution spectra finds its best explanation in a fast intramolecular equilibration of the P sites, a process that is less probable for the more rigid $[Au_5(Ph_2PCH_2PPh_2)_3(Ph_2PCHPPh_2)]^{2+}$ and $[Au_6(dppp)_4]^{2+}$ clusters.

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Registry No. $[Au_6[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_4](NO_3)_2{\cdot}xCH_2Cl_2$, 83060-80-4; $[Au_9L_8](NO_3)_3$, 37336-35-9; $Au_4L_4I_2$, 78519-63-8; Au, 7440-57-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Dinuclear Copper(I) Benzoato Complexes Containing Acetylenes: Synthesis, Structure, and Reactivity with Molecular Hydrogen

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Cuprous carboxylato species are considered the first well-documented examples of complexes involved in homogeneous catalyzed hydrogenation.[2a] In spite of this, the reactivity of copper(I) carboxylato derivatives with unsaturated substrates which potentially can undergo hydrogenation is very poorly explored. We can mention that copper(I) promotes the activation of the H_2 molecule by heterolytic splitting,[2b] which would be highly interesting for the hydrogenation of molecules containing oxygen atoms, like CO and CO_2. A further interest in copper(I) carboxylato derivatives comes from the fact that a bimetallic unit seems to survive in their reactions with various σ ligands.[3] This observation was further confirmed by the result obtained in the reaction of copper(I) acetate with olefins, although no structural evidence supports this hypothesis.[4] Very recently, however, it was found that the reaction of copper(I) benzoate with carbon monoxide led, in the presence of ancillary ligands, to the isolation of the first dicopper(I) unit containing a bridging carbonyl.[5]

The present report concerns the reactivity of copper(I) benzoate with disubstituted acetylenes leading to the isolation and structural identification of dinuclear copper(I) acetylene complexes. The fact that copper(I) has a rich chemistry with acetylenes notwithstanding,[6-8] we are dealing with the first model complexes having a disubstituted acetylene coordinated to a low-nuclearity copper(I) system.

Experimental Section

Owing to the air sensitivity of the complexes, all operations were carried out in a dry oxygen-free nitrogen atmosphere, with use of standard Schlenk techniques. Solvents were purified and dried by standard methods. Acetylenes were recrystallized or distilled before use. A modified procedure was used for the preparation of $[Cu(PhCO_2)]_4$.[5,9] IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

Reaction of Diphenylacetylene with Copper(I) Benzoate. Copper(I) benzoate (0.53 g, 0.72 mmol) was added to a methanolic solution (20 mL) of Ph_2C_2 (0.52 g, 2.92 mmol). A microcrystalline white solid immediately formed (0.70 g, 66.1%), while the mother solution cooled at 0 °C gave crystals suitable for the X-ray analysis. Both precipitates were shown to be the same compound. Anal. Calcd for $[Cu(PhCO_2)(Ph_2C_2)]_2$, $C_{42}H_{30}O_4Cu_2$: C, 69.52; H, 4.14. Found: C,

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Table I. Summary of Crystal Data and Intensity Data Collection[a]

A. Crystal Parameters

formula: $C_{42}H_{30}Cu_2O_4$	$a = 17.161$ (2) Å
cryst syst: monoclinic	$b = 19.083$ (3) Å
space group: $P2_1/c$ (C_{2h}^5, No. 14)	$c = 21.658$ (3) Å
$Z = 8$	$\alpha = 90°$
fw: 25.8	$\beta = 92.83$ (1)°
$D_{calcd} = 1.361$ g cm^{-3}	$\gamma = 90°$

B. Collection of Intensity Data

diffractometer	Siemens AED
radiation	Ni-filtered Cu Kα ($\lambda = 1.541\,78$ Å)
scan type	$\theta/2\theta$
scan speed	3-12 ° θ/min
scan width	$(\theta - 0.5°)-[\theta + (0.5 + \Delta\theta)]$[b]
reflecns measd	$\pm hkl$
2θ range	6-120°
std reflecn	(391) measd every 50 data; no significant decay
unique total data	10 536
unique obsd data ($I > 2\sigma$)	3974
abs coeff	17.6 cm^{-1}
cryst dimens	0.25 × 0.20 × 0.55 mm
no. of variables	361

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the Cu K$\bar{\alpha}$ components of 30 reflections with θ = 20-40°. [b] $\Delta\theta = ((\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda) \tan\theta$.

69.05; H, 4.08. The IR spectrum (Nujol) shows strong, wide bands centered at 1410 and 1560 cm^{-1} for the benzoato group, while the C≡C stretching frequency of the metal-bonded Ph_2C_2 falls at 1980 cm^{-1}. Extensive decomposition of the starting copper(I) benzoate was observed when the reaction was carried out in tetrahydrofuran.

Reaction of Copper(I) Benzoate with Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (0.615 g, 4.33 mmol) was added to a methanolic solution (30 mL) of copper(I) benzoate (0.926 g, 1.25 mmol). The resulting solution became red, and a yellow solid formed (0.40 g, 28%). Further solid was recovered from the mother solution. Anal. Calcd for $[Cu(PhCO_2)(Me_2O_4C_4)]_2$ (II), $Cu_2C_{26}H_{22}O_{12}$: C, 47.78; H, 3.37. Found: C, 48.01; H, 3.15. The IR spectrum shows an unshifted carbonyl band at 1730 cm^{-1} for the ester group and two bands centered at 1375 and 1540 cm^{-1} for the benzoato ligand.

Reaction of Complex II with Molecular Hydrogen. Complex II (0.175 g, 0.24 mmol) absorbed in methanol 0.34 mmol of hydrogen (P_{H_2} = 1 atm, T = 16 °C). The absorption of H_2 carried out in the presence of quinoline was significantly lower. Moreover, the hydrogenation of II (1.27 g) was carried out in the presence of an excess of Ph_2C_2 (6.20 g) at 50 °C and with P_{H_2} = 100 atm. Even under these conditions the conversion of Ph_2C_2 into 1,2-diphenylethane (0.45 g) is not catalytic. Formation of some copper metal was observed.

Collection and Reduction of X-ray Data. The crystal selected for study was mounted in a glass capillary and sealed under nitrogen. Preliminary investigations using rotation and Weissenberg photographs showed monoclinic ($2/m$) symmetry with systematic absences consistent with the space group $P2_1/c$. Crystal data and details of the parameters associated with data collection are given in Table I.

Data were collected at room temperature on a single-crystal diffractometer. The θ–2θ scan method was used with individual profile analysis.[10] The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by Wilson's method.[11] No correction for absorption was applied.

Solution and Refinement of the Structure. Initial coordinates for the four independent copper atoms were determined by direct methods (MULTAN).[12] The remaining non-hydrogen atoms were found by standard Fourier methods. Refinement[13] was by isotropic full-matrix least-squares methods to R = 11.6%, followed by anisotropic refinement of all atoms except those involving phenyl rings down to R_F = 8.2% (R_{wF} = 9.1%). During the entire refinement the phenyl rings were treated as rigid bodies having D_{6h} symmetry. No attempts were made to locate hydrogen atoms. The function minimized during the least-squares refinement was $\sum w|\Delta F|^2$. The weighting scheme used was $w = k/[\sigma^2(F_o) + |g|(F_o^2)]$; k is redetermined after each structure factor calculation by fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|(F_o^2)]/k$. The value of g was that giving the smallest variation of the mean value of $w(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o. In the final refinement no parameter shifted by more than 0.3 times its standard deviation, the values for k and g were 0.7439 and 0.002, respectively, and the goodness of fit was 1.61. The NO/NV ratio was 3974:361 = 11.0:1. A final difference Fourier synthesis showed no enexpected features with no peaks higher than 0.50 e Å^{-3}. Anomalous scattering corrections were included in all structure factor calculations. Scattering factors for neutral atoms were taken from ref 14 for Cu and from ref 15 for O and C.

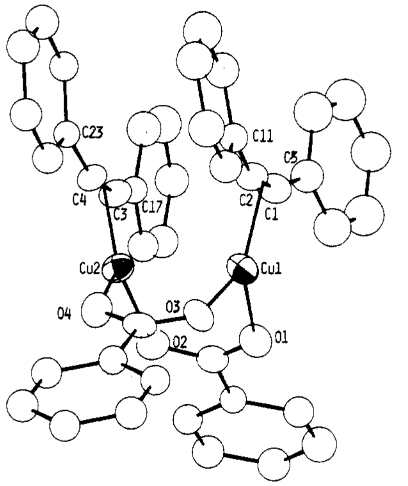
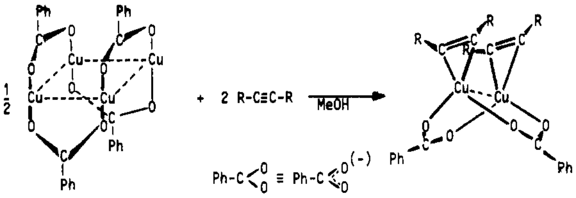


Figure 1. ORTEP drawing of molecule 1, one of the two crystallographically independent molecules in complex II. Thermal ellipsoids are drawn at the 30% probability level.

Final atomic coordinates are listed in Table II, and thermal parameters are given in Table SI.[16]

Results and Discussion

Disubstituted acetylenes R—C≡C—R (R = Ph, CO_2Me) break down the tetrameric structure of copper(I) benzoate, giving the dimetallic unit shown in eq 1, where each copper(I)



(1)

I

II, R = Ph
III, R = CO_2Me

bonds a carbon–carbon triple bond and the two coppers are bridged by two benzoato groups. Reaction 1 must be carried out in methanol; other solvents, like tetrahydrofuran, decompose the starting copper(I) benzoate. IR spectra show in both complexes the same features with significant bands due to the asymmetric (1500–1600-cm^{-1} region) and to the symmetric (1400-cm^{-1} region) stretching vibrations of the carboxylato

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Table II. Fractional Atomic Coordinates ×10⁴ [a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu11	4821 (1)	2278 (1)	8579 (1)	Cu21	1341 (1)	2495 (1)	3047 (1)
Cu12	6058 (1)	2274 (1)	7796 (1)	Cu22	85 (1)	2482 (1)	3807 (1)
O11	5424 (7)	1508 (6)	8992 (5)	O21	520 (6)	2394 (4)	2405 (4)
O12	6374 (6)	1457 (5)	8319 (5)	O22	−498 (6)	2421 (5)	3010 (4)
O13	4318 (6)	1774 (5)	7895 (5)	O23	1377 (5)	1514 (4)	3308 (5)
O14	5292 (6)	1824 (5)	7235 (4)	O24	382 (6)	1497 (4)	3923 (4)
C11	5055 (9)	3143 (8)	9014 (7)	C21	1783 (7)	3438 (6)	3113 (6)
C12	4575 (8)	3269 (7)	8558 (7)	C22	2149 (7)	3069 (6)	3481 (6)
C13	6705 (9)	3073 (7)	8045 (7)	C23	124 (8)	3453 (6)	4145 (6)
C14	6281 (9)	3241 (7)	7605 (7)	C24	456 (7)	3055 (6)	4500 (6)
C15	5529 (6)	3280 (8)	9570 (4)	C25	1522 (6)	4091 (4)	2811 (4)
C16	5771 (6)	2727 (8)	9955 (4)	C26	1893 (6)	4709 (4)	3005 (4)
C17	6225 (6)	2860 (8)	10494 (4)	C27	1662 (6)	5349 (4)	2742 (4)
C18	6435 (6)	3546 (8)	10650 (4)	C28	1060 (6)	5370 (4)	2286 (4)
C19	6192 (6)	4100 (8)	10265 (4)	C29	689 (6)	4751 (4)	2092 (4)
C110	5739 (6)	3966 (8)	9725 (4)	C210	920 (6)	4112 (4)	2354 (4)
C111	4100 (6)	3686 (6)	8149 (4)	C211	2703 (5)	2894 (5)	3987 (3)
C112	4253 (6)	4400 (6)	8086 (4)	C212	2681 (5)	2259 (5)	4306 (3)
C113	3796 (6)	4805 (6)	7673 (4)	C213	3192 (5)	2141 (5)	4816 (3)
C114	3184 (6)	4496 (6)	7322 (4)	C214	3725 (5)	2659 (5)	5008 (3)
C115	3031 (6)	3782 (6)	7385 (4)	C215	3747 (5)	3294 (5)	4689 (3)
C116	3489 (6)	3377 (6)	7798 (4)	C216	3236 (5)	3411 (5)	4179 (3)
C117	7325 (5)	3113 (6)	8517 (4)	C217	−178 (5)	4077 (4)	3880 (4)
C118	7666 (5)	2508 (6)	8772 (4)	C218	104 (5)	4705 (4)	4133 (4)
C119	8257 (5)	2562 (6)	9236 (4)	C219	−149 (5)	5343 (4)	3880 (4)
C120	8507 (5)	3221 (6)	9444 (4)	C220	−684 (5)	5353 (4)	3374 (4)
C121	8166 (5)	3825 (6)	9189 (4)	C221	−966 (5)	4725 (4)	3121 (4)
C122	7575 (5)	3771 (6)	8726 (4)	C222	−713 (5)	4086 (4)	3374 (4)
C123	5871 (5)	3709 (5)	7148 (4)	C223	949 (5)	2812 (5)	5045 (3)
C124	6026 (5)	4426 (5)	7181 (4)	C224	928 (5)	2127 (5)	5268 (3)
C125	5636 (5)	4887 (5)	6772 (4)	C225	1383 (5)	1939 (5)	5794 (3)
C126	5091 (5)	4629 (5)	6329 (4)	C226	1859 (5)	2437 (5)	6096 (3)
C127	4936 (5)	3912 (5)	6296 (4)	C227	1880 (5)	3125 (5)	5872 (3)
C128	5326 (5)	3452 (5)	6706 (4)	C228	1425 (5)	3310 (5)	5347 (3)
C129	6090 (12)	1306 (8)	8830 (8)	C229	−204 (10)	2360 (6)	2503 (7)
C130	6582 (5)	874 (4)	9271 (4)	C230	−758 (5)	2265 (4)	1945 (3)
C131	7325 (5)	658 (4)	9116 (4)	C231	−1561 (5)	2265 (4)	2022 (3)
C132	7812 (5)	314 (4)	9553 (4)	C232	−2078 (5)	2148 (4)	1516 (3)
C133	7556 (5)	186 (4)	10145 (4)	C233	−1792 (5)	2032 (4)	931 (3)
C134	6813 (5)	402 (4)	10300 (4)	C234	−989 (5)	2032 (4)	854 (3)
C135	6326 (5)	747 (4)	9863 (4)	C235	−472 (5)	2149 (4)	1361 (3)
C136	4601 (10)	1666 (7)	7388 (7)	C236	930 (9)	1228 (6)	3663 (7)
C137	4100 (6)	1288 (4)	6887 (4)	C237	1081 (6)	476 (4)	3810 (4)
C138	4408 (6)	1144 (4)	6315 (4)	C238	605 (6)	105 (4)	4199 (4)
C139	3958 (6)	789 (4)	5861 (4)	C239	715 (6)	−614 (4)	4284 (4)
C140	3200 (6)	579 (4)	5979 (4)	C240	1302 (6)	−961 (4)	3980 (4)
C141	2892 (6)	723 (4)	6550 (4)	C241	1778 (6)	−589 (4)	3591 (4)
C142	3342 (6)	1077 (4)	7004 (4)	C242	1668 (6)	129 (4)	3506 (4)

[a] The first digits in the labels of the atoms indicate the molecule.

group,[17] while the $C\equiv C$ stretching vibration, which is usually very weak in copper(I) complexes,[8,18] was identified at 1980 cm^{-1} for complex II only. The bands due to the ester groups ($R = CO_2Me$) (complex (III)) are practically unchanged after complexation. The structure of II determined by an X-ray analysis has many interesting features. Figure 1 shows an ORTEP[19] diagram of one (molecule 1) of the two independent dimers (molecules 1 and 2) forming the crystals of complex II. Bond distances and angles are reported in Table III. Two benzoate groups bridge the two metal atoms in both crystallographically independent dimers. The $C\equiv C$ unit completes the trigonal-planar geometry around each copper. The diphenylacetylene molecules are not planar as a consequence of small rotations around the $C-C_{Ph}$ bond (maximum torsion angle 28 (5)°). However, their mean planes in each dimer are practically parallel (Figure 2), the dihedral angle being 4.5 and 9.3° in dimers 1 and 2, respectively. The planes defined by Cu1, Cu2, O13, O14 and Cu1, Cu2, O11, O12 are nearly orthogonal, the angle between being 101.1° in molecule 1, while the corresponding value for molecule 2 is 99.7°. The $[Cu_2(PhCO_2)_2]$ moieties maintain the structural characteristics they have in the original tetrameric copper(I) benzoate,[20] like the Cu···Cu proximity (Table (III)), but the Cu–O bond distances are significantly longer (mean value 1.957 (1) vs. 1.839 (6) Å), and by consequence the C–O bond distances are shorter (mean value 1.252 (10) vs. 1.27 (1) Å). Cu–C bond distances (mean value 1.953 (9) Å) are found in the same range observed for other multinuclear π-acetylido copper(I) complexes (Table IV). The following features of the Ph_2C_2 ligand are of primary importance: $C\equiv C$ bond length (mean value 1.224 (18) Å); C–C–Ph deformation angle (mean value 158.5 (7)°). The C–C bond length in acetylenes bonded to copper(I) is usually shorter than found for more basic metals, and consequently the deformation angle C–C–Ph has a higher value (Table IV). This is in agreement with a poor back-donation by copper(I). The IR spectrum of complex II shows

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Table III. Interatomic Distances (Å) and Angles (Deg)

	molecule 1	molecule 2		molecule 1	molecule 2
Cu1–O1	1.985 (11)	1.940 (10)	Cu2–O2	1.987 (10)	1.955 (9)
Cu1–O3	1.933 (10)	1.956 (8)	Cu2–O4	1.945 (10)	1.961 (8)
Cu1–C1	1.933 (15)	1.955 (12)	Cu2–C3	1.947 (14)	1.992 (12)
Cu1–C2	1.938 (14)	1.969 (12)	Cu2–C4	1.934 (14)	1.939 (12)
Cu1–A^a	1.827 (15)	1.867 (12)	Cu2–B^a	1.843 (14)	1.872 (12)
Cu1···Cu2	2.782 (3)	2.776 (3)			
O1–C29	1.271 (23)	1.272 (20)	O3–C36	1.240 (19)	1.239 (18)
O2–C29	1.264 (21)	1.236 (18)	O4–C36	1.283 (20)	1.232 (18)
C29–C30	1.492 (19)	1.511 (17)	C36–C37	1.531 (18)	1.490 (14)
C1–C2	1.277 (21)	1.215 (17)	C3–C4	1.213 (21)	1.204 (17)
C1–C5	1.443 (17)	1.467 (14)	C3–C17	1.441 (17)	1.410 (14)
C2–C11	1.418 (17)	1.454 (14)	C4–C23	1.484 (17)	1.493 (14)
C1–Cu1–C2	38.5 (6)	36.0 (5)	C3–Cu2–C4	36.4 (6)	35.6 (5)
O3–Cu1–C2	112.3 (5)	112.5 (5)	O4–Cu2–C4	115.0 (5)	111.6 (5)
O3–Cu1–C1	150.7 (6)	148.6 (5)	O4–Cu2–C3	151.3 (5)	147.2 (5)
O1–Cu1–C2	147.3 (6)	150.1 (4)	O2–Cu2–C4	145.0 (6)	148.3 (5)
O1–Cu1–C1	108.8 (6)	114.2 (4)	O2–Cu2–C3	108.7 (6)	112.7 (5)
O1–Cu1–O3	100.4 (4)	97.1 (3)	O2–Cu2–O4	99.6 (4)	100.0 (4)
O3–Cu1–A*	131.5 (6)	130.5 (5)	O4–Cu2–B^a	133.2 (5)	129.7 (5)
O1–Cu1–A*	128.0 (6)	132.2 (4)	O2–Cu2–B^a	126.8 (6)	130.3 (5)
O1–C29–O2	124.3 (16)	126.0 (14)	O3–C36–O4	126.7 (13)	127.6 (11)
O2–C29–C30	117.1 (15)	117.0 (13)	O4–C36–C37	114.9 (12)	115.6 (12)
O1–C29–C30	118.6 (15)	117.0 (13)	O3–C36–C37	118.4 (13)	116.8 (12)
Cu1–C1–C2	70.9 (9)	72.6 (8)	Cu2–C3–C4	71.2 (9)	69.8 (8)
Cu1–C2–C1	70.5 (9)	71.4 (8)	Cu2–C4–C3	72.4 (9)	74.6 (9)
Cu1–C1–C5	131.0 (11)	129.8 (8)	Cu2–C3–C17	129.0 (9)	129.1 (9)
Cu1–C2–C11	132.8 (10)	130.6 (8)	Cu2–C4–C23	128.7 (9)	126.1 (8)
C1–C2–C11	156.6 (14)	157.7 (12)	C3–C4–C23	158.3 (14)	159.0 (12)
C2–C1–C5	157.9 (15)	157.1 (12)	C4–C3–C17	159.5 (14)	161.1 (13)

[a] A and B are the midpoints of C1–C2 and C3–C4, respectively.

Table IV. C≡C and Cu–C Bond Lengths and Deformation Angles in Selected Diphenylacetylene and π-Acetylidocopper(I) Complexes

complex	C≡C bond, Å	Cu–C bond, Å	C≡C–A angle, deg	ref
$[Pt(C_2Ph_2)(PPh_3)_2]$	1.32 (9)		140	23a
$[Ni(C_2Ph_2)(CN\text{-}t\text{-}Bu)_2]$	1.28 (2)		149	23b
$[Nb(Cp)(C_2Ph_2)_2(CO)]$	1.35 (2)		138	23c
$[Nb(Cp)(C_2Ph_2)(C_4Ph_4)(CO)]$	1.26 (4)		142	23d
$[W(C_2Ph_2)_3(CO)]$	1.30		140	23e
$[W(Cp)Ph(C_2Ph_2)O]$	1.29 (3)		143.5 (4)	23f
$[Pt(C_2Ph_2)_2]$	1.280 (6)		153	23g
$[Ti(Cp)_2(C_2Ph_2)(CO)]$	1.285 (10)		138.8 (7) 145.8 (7)	23h
$[Cu_4Ir_2(C_2Ph)_8(PPh_3)_2]$	$1.226\ (37)_{av}$	$1.986\ (70)_{av}$ $2.185\ (42)_{av}$	$164.7\ (38)_{av}$	24a
$[Cu(C_2Ph)ClRu(Cp)(PPh_3)_2]$	1.25 (1)	2.01 (1) 2.04 (1)	165.0 (10)	24b
$[Cu(C_2Ph)ClFe(Cp)(CO)_2]$	1.234 (13)	2.016 (12) 2.003 (10)	162 (1)	24c
$[Cu(C_2Ph)(PMe_3)]$	1.237 (22)	2.085 (14) 2.061 (16)	153 (15)	24d
$[Cu(C_2Ph_2)(PhCO_2)]_2$	$1.224\ (18)_{av}$	$1.953\ (9)_{av}$	$158.5\ (7)_{av}$	*a*

[a] Present work.

a weak band at about 1980 cm^{-1}, as expected on the basis of the structural parameters cited above.[8,18] The close spectroscopic similarities between II and III allow us to propose the same dimeric structure for III. This is further supported by the IR spectrum showing that the ester groups are not involved in any kind of interaction with the metal. Another interesting feature of the reported structure concerns the close proximity and the mutual orientation of the two diphenylacetylene units (Figure 2), each of them independently anchored to a metal of the bimetallic unit. The distances between corresponding acetylenic carbon atoms C1···C3 and C2···C4 (Figure 2) are 3.61 (2) and 3.66 (2) Å in molecule 1 and 3.73 (2) and 3.71 (2) Å in molecule 2. The two diphenylacetylene molecules have the appropriate geometry for a metal-promoted conversion to a tetraphenylcyclobutadiene ligand. A structural model having two close C–C unsaturated units would have some relevance in photochemical copper(I)-promoted reactions of unsaturated substrates.[21]

Complex II absorbs H_2 at atmospheric pressure and room temperature, and the reaction is stoichiometric even when the hydrogenation is carried out with an excess of diphenylacetylene in more drastic conditions, at 100 atm and 50 °C. 1,2-Diphenylethane is the only hydrogenation product formed. It could be interesting to note that the hydrogenation of *p*-benzoquinone promoted by copper(I) carboxylato derivatives

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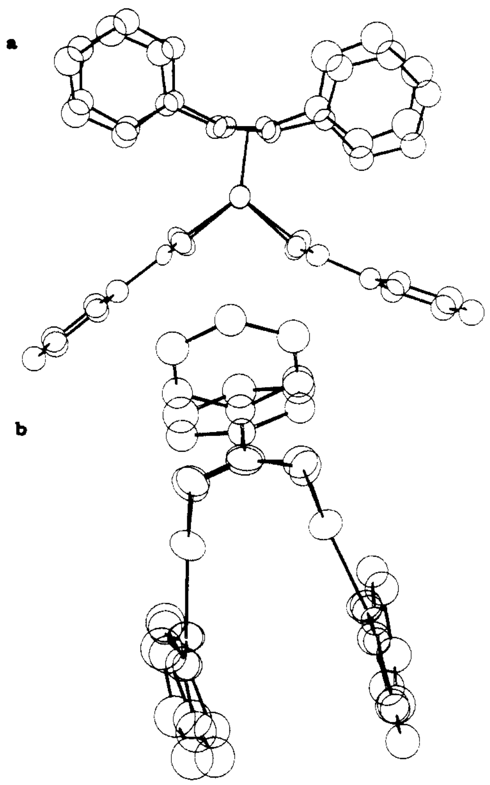

Figure 2. Projection of molecule 1 of complex II directly down (a) the Cu–Cu vector and (b) the C1≡C2 triple bond.

was carried out into the presence of a nitrogen base, since the formation of the corresponding carboxylic acids inhibited the reaction.[2] This is justified by the fact that the hydrogenation promoted by copper(I) is usually viewed as the consequence of the heterolytic splitting of the H_2 molecule. This process is enhanced by the presence of a basic substance, which plays a fundamental role in copper-based hydrogenation systems. In the absence of any added base, the oxygen atoms of the benzoato group can act as basic sites, benzoic acid being formed in many hydrogenation reactions of copper(I) benzoato complexes.[22]

In spite of this, the absorption of H_2 by complex II in the presence of quinoline decreases rather than increases. This unexpected result can be ascribed to a difference in the mechanism of hydrogenation of such different substrates. Molecules like *p*-benzoquinone may involve the oxidation of copper(I) to copper(II), so that the function of molecular hydrogen is to reduce the oxidation state of the metal acting as primary reducing agent of the organic molecule. Such a mechanism is unlikely in case of substrates like acetylenes, which do not cause the oxidation of the metal.

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Registry No. II, 82808-26-2; III, 82808-27-3; $Cu(PhCO_2)$, 14604-51-4; PhC≡CPh, 501-65-5; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and Table SI, listing anisotropic and isotropic thermal parameters (17 pages). Ordering information is given on any current masthead page.

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Chromium(IV)-Induced Carbon–Carbon Bond Scission

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Induced electron-transfer reactions, in which a Co^{III}-bound organic ligand suffers a net two-electron oxidation initiated by an external oxidant such as Ce(IV), yielding a carbon radical intermediate, have been studied in detail by Taube and co-workers.[1] The cation radical formed subsequently undergoes an intramolecular second one-electron transfer, resulting in the reduction at the Co(III) center without altering the carbon skeleton of the ligand, except in case of Co^{III}-bound oxalato.[2] The extension of this work to Ce(IV) oxidation of Co(III) complexes of the α-hydroxy acids lactic, mandelic, and benzilic acids[3] showed no evidence for partition of the intermediate, even when the Ce(IV):Co(III) ratio taken exceeded 20:1, and the results are consistent with a mechanism in which electron transfers to the oxidants and C–C fission are synchoronous or nearly so.

The present note concerns the highly reactive oxidant Cr(IV), which is known to resemble Ce(IV) in reactivity.[4] We are interested in the oxidation of lactic, mandelic, benzilic, 2-hydroxy-2-ethylbutyric and 2-hydroxy-2-methylbutyric acid complexes of $(H_3N)_5Co^{III}$ in aqueous perchlorate. Though the oxidation of alcohols[5,6] and of aliphatic and aromatic aldehydes[7] by Cr(IV), generated by the reaction of Cr(VI) and V(IV),[8] has been extensively studied, this appears to be the first time this system has been employed for an induced electron-transfer reaction involving Co(III) complexes, with ligands in which the reaction centers are separated by a saturated fragment and should necessarily involve the breakage of a carbon–carbon bond.

Experimental Section

Vanadium(IV) perchlorate solution was prepared by the method of Espenson[8] using vanadyl sulfate (Alfa Product) and barium perchlorate (Alfa). Solutions of VO_2ClO_4 were prepared by dissolving V_2O_5 in 1 M $HClO_4$ overnight. Potassium dichromate (AR) was used

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