The Hurtley Reaction. 1. Synthesis and Characterization of Copper(I) Benzoates Containing Reactive Ortho C–X (X = Cl, Br) Bonds and Their Reactivity toward Organocopper(I) Compounds: Crystal Structure of a Thermally Stable Trinuclear Hetero Copper(I) Cluster, Bis(benzoato)mesityltricopper(I)

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A facile, general synthesis of copper(I) carboxylates via the reaction of carboxylic acids with mesitylcopper(I) is described. The 1:1 molar reaction of pentameric mesitylcopper(I) with 2-chloro- or 2-bromobenzoic acids rapidly yields the corresponding reactive copper(I) benzoates $[Cu(\mu\text{-}O_2CC_6H_4Cl\text{-}2)]_4$ (1b) and $[Cu(\mu\text{-}O_2CC_6H_4Br\text{-}2)]_4$ (1c), which are the postulated intermediates in the Hurtley reaction. Reaction at ambient temperature of 1b, 1c, and the parent copper(I) benzoate $[Cu(\mu\text{-}O_2CC_6H_5)]_4$ (1a) with a further equivalent of mesitylcopper(I) affords the first examples of thermally stable mixed (benzoato)organocopper(I) cluster 2, viz. $[Cu_3(C_6H_2Me_3\text{-}2,4,6)(\mu\text{-}O_2CC_6H_4X\text{-}2)_2]$ (X = H, 2a; X = Cl, 2b; X = Br, 2c). An X-ray structure determination of 2a ($C_{23}H_{21}O_4Cu_3$, monoclinic, space group $C2/c$, a = 16.926 (2) Å, b = 11.781 (1) Å, c = 10.763 (1) Å, β = 94.48 (1)°, Z = 4, R_w = 0.059 using 1627 reflections) revealed the unique trinuclear geometry of these clusters. In 2a the two benzoato fragments are each bonded as four-electron donors to a pair of copper atoms (Cu–O = 1.862 (av) Å; Cu···Cu = 2.888 (2) Å) while the mesityl fragment is three-center, two-electron bonded to two copper atoms (Cu–C = 1.957 (6) Å; Cu···Cu = 2.421 (2) Å)). Corresponding reactions of benzoic acids with 4-tolylcopper(I) require lower temperatures than those with mesitylcopper(I) and yield the 4-tolyl analogues of 2, e.g. $[Cu_3(C_6H_4Me\text{-}4)(\mu\text{-}O_2CC_6H_4X\text{-}2)_2]$ (X = H, 3a; X = Br, 3c).

Introduction

There are many reports of the stoichiometric use of organocuprates and related organocopper(I) reagents for the formation of new C–C bonds.[2] However, efficient procedures for the direct formation of C–C bonds via condensation of aryl and vinyl halides with carbanions in the presence of a *catalytic* amount of copper or copper salt are relatively scarce. The mechanisms of such copper-catalyzed reactions, such as the Hurtley reaction or the Ullmann ether synthesis reaction, are in most cases, poorly understood and still a matter of considerable debate.[3]

In copper-assisted reactions the reactivity of the aryl or vinyl halides generally decreases in the series I > Br > Cl > F. Bromine derivatives combine a reasonable reactivity with an acceptable degree of side-product formation, whereas iodine derivatives in many cases give rise to increased side-production formation. The product formation with chlorine substrates is often very low while fluorine substrates are nonreactive under normal reaction conditions. An understanding and an extension of the scope of the copper-catalyzed reactions is a worthwhile goal, and, for instance, a facile substitution of chlorine atoms would be very interesting from an industrial point of view.

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(2) (a) Posner, G. H. *An Introduction to Synthesis using Organocopper Reagents*; Wiley-Interscience: New York, 1980. (b) Kauffmann, T. *Angew. Chem.* **1974**, 86, 321; *Angew. Chem., Int. Ed. Engl.* **1974**, 13, 291. (c) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A.; *Tetrahedron* **1984**, 40, 5005. (d) van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Chapter 14, Vol. 2.

(3) Lindley, J. *Tetrahedron* **1984**, 40, 1433.

**Table I. Analytical and Molecular Weight^a Data of Complexes 1, 2, and 3**

	anal. found (calcd)					
compound	C	H	X	Cu	O	mol wt $(n)^a$
[Cu(μ-O$_2$CC$_6$H$_4$Cl-2)]$_4$ (1b)	38.60 (38.37)	2.12 (1.84)	15.88 (16.17)	28.61 (29.00)	14.43 (14.60)	
[Cu(μ-O$_2$CC$_6$H$_4$Br-2)]$_4$ (1c)	32.00 (31.91)	1.90 (1.53)	30.23 (30.32)	24.35 (24.98)	11.86 (12.14)	
[Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_5$)$_2$] (2a)	50.08 (50.03)	4.04 (3.83)		34.31 (34.53)	11.53 (11.59)	470 (2.5)
[Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_4$Cl-2)$_2$] (2b)	44.31 (44.49)	3.20 (3.08)	11.09 (11.42)	30.49 (30.70)	10.11 (10.30)	534 (2.6)
[Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_4$Br-2)$_2$] (2c)	37.82 (37.09)	2.49 (2.70)	22.91 (22.51)	27.20 (26.86)	9.26 (9.02)	
[Cu$_3$(C$_6$H$_4$Me-4)(μ-O$_2$CC$_6$H$_5$)$_2$] (3a)	48.04 (48.13)	3.47 (3.27)		35.64 (36.38)	12.02 (12.21)	
[Cu$_3$(C$_6$H$_4$Me-4)(μ-O$_2$CC$_6$H$_4$Br-2)$_2$] (3c)	37.09 (36.99)	2.443 (2.22)	23.15 (23.43)	27.59 (27.96)	9.65 (9.38)	

^{a} The degree of association was measured in a concentration range of 7×10^{-3}–4×10^{-2} mol/L (concentration based on the trimeric unit).

Scheme I

proposed intermediates A[6,7]

proposed intermediates B[9]
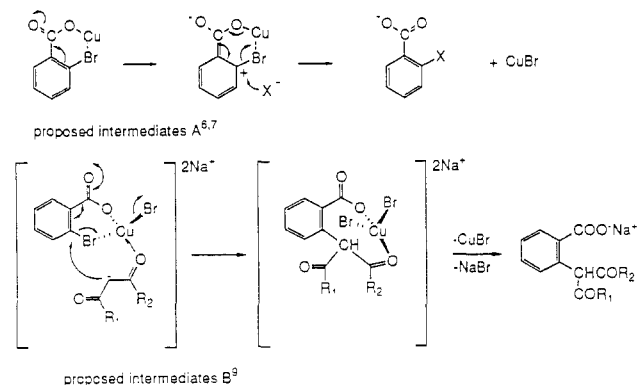
Recently we began investigations into the mechanism of the copper-catalyzed condensation reaction using 2-halobenzoic acids with sodium acetylacetonate (eq 1). The

$$(1)$$
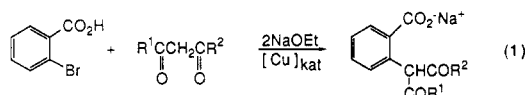
first example of such a reaction, found by Hurtley in 1929,[4] was the condensation of 2-bromobenzoic acid with resorcinol and various β-dicarbonyl compounds that proceeded smoothly in ethanol solution in the presence of sodium ethoxide and either copper powder or copper(II) acetate as catalyst. Similar copper-catalyzed substitution reactions between β-carbonyl nucleophiles and either halobenzoic acids or halopyridine carboxylic acids were used in the following decades for the formation of C–C bonds.[5]

The first attempts to describe the intermediates in these nucleophilic substitution reactions were made by Goldberg[6] and by Mayer and Fikentscher.[7] They proposed that a copper(I) carboxylate is the essential intermediate and that the polarization of the carbon–halogen bond is augmented by intramolecular coordination of the halogen to the copper(I) atom (see Scheme IA).

Later a thorough investigation of the Hurtley reaction was published by Cirigottis, Ritchie, and Taylor.[8] They found that (i) the only effective solvents are alcohols and water, (ii) the reaction is most successful with 2-bromobenzoic acids (low yields are obtained with 2-iodobenzoic acids, and no product is formed when 2-chlorobenzoic acids are used), (iii) replacement of the carboxyl group by any other functional group prevents the reaction, and (iv) a copper species (most likely copper(I)) is the essential catalyst. They also stated that the high reactivity they found for 8-bromo-1-naphthoic acid was evidence against

the type of intermediates invoked by Goldberg[6] and by Mayer and Fikentscher[7] since the required resonance structures (see Scheme IA) are not possible in this substrate.

In 1975 Bruggink and McKillop reported that when the β-dicarbonyl compound itself was used as the reaction solvent, the yield of C–C coupled products increased considerably. Furthermore, they found that the formation of side products was suppressed, and under these conditions 2-chlorobenzoic acids also were reactive.[9] On the basis of their results they proposed tetrahedrally coordinated Cu(I) intermediates (see Scheme IB).

In our investigations relating to the Hurtley reaction a stepwise approach has been chosen: (i) isolation of the postulated intermediates (copper(I) 2-halobenzoates) and (ii) the study of the reactivity of these intermediates with β-dicarbonyl compounds. The information gained in this way hopefully can be used to improve other copper-catalyzed nucleophilic aromatic halogen substitution reactions.

There is, as yet, no information about the synthesis and structure of copper(I) benzoates with a reactive carbon–halogen bond ortho to the –C(O)OCu moiety. Copper(I) benzoates without reactive carbon–halogen bonds can be synthesized by the reaction of copper(I) oxide with the corresponding benzoic acid, and the structure of tetrameric copper(I) benzoate (1a) has been elucidated (see eq 2).[10]

$$4 C_6H_5CO_2H + 2 Cu_2O \xrightarrow{-2 H_2O} \qquad (2)$$
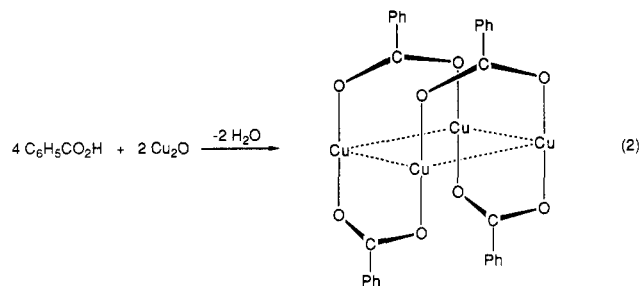
Since arylcopper(I) reagents and copper(I) benzoates are known to react with halides to form biaryls[2] (see eq 3) and aryl benzoates[11] (see eq 4), respectively, problems in the synthesis of 2-halo-substituted copper(I) benzoates are to be expected. We now report a successful facile synthesis of copper(I) 2-chlorobenzoate (1b) and copper(I) 2-bromobenzoate (1c) and describe the reactions of these new benzoates and the parent copper(I) benzoate (1a) with mesitylcopper(I) and p-tolylcopper(I). The reactions with mesitylcopper(I) give rise to isolable novel mixed (benzoato)organocopper(I) clusters, [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_4$X-2)$_2$] (X = H, 2a; X = Cl, 2b; X = Br, 2c) of which 2a has been characterized by an X-ray structure determination.

(4) Hurtley, W. R. H. *J. Chem. Soc.* **1929**, 1870.

(5) Cf. ref 18–31 in ref 9.

(6) Goldberg, A. A. *J. Chem. Soc.* **1952**, 4368.

(7) Mayer, W.; Fikentscher, R. *Chem. Ber.* **1958**, *91*, 1536.

(8) Cirigottis, K. A.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1974**, *27*, 2209.

(9) Bruggink, A.; McKillop, A. *Tetrahedron* **1975**, *31*, 2607.

(10) (a) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2463. (b) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1977**, 299.

(11) Cohen, T.; Lewin, A. H. *J. Am. Chem. Soc.* **1966**, *88*, 4521.

$$ArCu + Ar'X \rightarrow ArAr' + CuX \quad (3)$$

$$ArCO_2Cu + Ar'X \rightarrow ArCO_2Ar' + CuX \quad (4)$$

Experimental Section

General Data. All reactions were carried out under dry oxygen-free nitrogen by using standard Schlenk techniques. Solvents were carefully dried and distilled prior to use. $[Cu(\mu\text{-}O_2CC_6H_5)]_4$ (**1a**),[10a] 4-tolylcopper(I),[12] and mesitylcopper(I)[13] were synthesized according to literature procedures. Other starting compounds are commercially available (Janssen Chimica).

^{1}H NMR spectra were obtained on a Bruker AC 100 or Bruker WM 250 NMR spectrometer. IR spectra (Nujol) were recorded with a Perkin-Elmer 283 spectrophotometer. Cryoscopic molecular weight determinations were carried out in benzene under dry oxygen-free nitrogen. Elemental analyses (see Table I) were carried out by the Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

Reactions with Mesitylcopper(I). Synthesis of [Cu(μ-O₂CC₆H₄X-2)]₄ (X = Cl, 1b; X = Br, 1c). A benzene solution (40 mL) of Cu_5Mes_5 (914 mg, 5 mmol) was added in 5 min to a stirred solution of 2-halobenzoic acid (5.5 mmol, 1.1 equiv) in diethyl ether (40 mL) at room temperature. When the addition of mesitylcopper(I) was started, the solution became slightly green and a white precipitate formed within a few minutes. This precipitate was directly isolated by filtration, washed with diethyl ether (2 × 10 mL) and hexane (2 × 10 mL), and dried in vacuo. Yield 70–80% of $[Cu(\mu\text{-}O_2CC_6H_4X\text{-}2)]_4$ (X = Cl, **1b**): IR data (Nujol) ν_{asym} (CO₂) 1571 cm⁻¹, ν_{asym} (CO₂) 1402 cm⁻¹, X = Br, **1c**: IR data (Nujol) ν_{asym} (CO₂) 1570 cm⁻¹, ν_{asym} (CO₂) 1403 cm⁻¹.

General Procedure for the Synthesis of Copper(I) Carboxylates ([Cu(μ-O₂CR)]ₙ). This reaction has been carried out for R = 2-MeC₆H₄, 2,4,6-Me₃C₆H₂, 2-NO₂C₆H₄, and CH₂CN. A benzene solution (20 mL) of Cu_5Mes_5 (1828 mg, 10 mmol) was added in 20 min to a solution of 1.1 equiv of carboxylic acid, RCO₂H, in diethyl ether (20 mL) at room temperature. A white precipitate was formed directly. After 2 h this precipitate was isolated by filtration, washed with diethyl ether (2 × 10 mL) and hexane (2 × 10 mL), and dried in vacuo; Yield 80–90% of [Cu(μ-O₂CR)]ₙ.

Synthesis of [Cu₃(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₄X-2)₂] (X = H, 2a; X = Cl, 2b; X = Br, 2c). A benzene or toluene solution (30 mL) of Cu_5Mes_5 (914 mg, 5 mmol) was added in 15 min to a suspension of 1 (5 mmol) in benzene or toluene (30 mL) at room temperature. After addition of mesitylcopper(I) a clear yellow solution was obtained. When the reaction mixture was stirred for 10 min more, a pale yellow precipitate was formed. This was isolated by filtration, washed with diethyl ether (2 × 10 mL) and hexane (2 × 10 mL), and dried in vacuo. Yield 30–40% of [Cu₃(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₄X-2)₂] (X = H, **2a**): ^{1}H NMR data (in C₆D₆, TMS internal, δ, ppm) 2.07 (s, 3 H, 4-Me), 2.67 (s, 6 H, 2,6-Me), 6.70 (s, 2 H, H3 + H5, Mes), 7.05 (m, br, 3 H, H3 + H4 + H5, RCO₂ ligand), 8.05 (m, H2 + H6, RCO₂ ligand). X = Cl, **2b**: ^{1}H NMR data (in C₆D₆, room temperature, TMS internal, δ, ppm) 2.03 (s, 3 H, 4-Me), 2.53 (s, 6 H, 2,6-Me), 6.62 (s, 2 H, H3 + H5, Mes), 6.70 (m, 2 H, H4 + H5, RCO₂ ligand), 7.09 (dd, 1 H, H3, RCO₂ ligand), 7.77 (dd, H6, RCO₂ ligand). X = Br, **2c**: ^{1}H NMR data were not obtained since **2c** is insoluble in benzene and toluene.

If this reaction is carried out with a total of 15 mL of benzene or toluene (i.e., four times more concentrated), addition of mesitylcopper(I) resulted immediately in the formation of the yellow suspension and the compounds 2 can be isolated similarly but in somewhat higher yields. (70% for **2a** and 40% for **2b** and **2c**).

Crystals suitable for an X-ray structure determination of **2a** were obtained by slow distillation of pentane into the benzene filtrate from the more concentrated reaction mixture.

Larger Scale Synthesis of [Cu₃(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₅)₂] (2a). A toluene solution (30 mL) of Cu_5Mes_5 (3.654 g, 20 mmol) was added in 15 min to a suspension of **1a** (3.706 g,

20 mmol) in toluene (30 mL) at room temperature. The pale yellow suspension which immediately formed, was isolated directly by filtration, washed with toluene (2 × 10 mL) and hexane (2 × 10 mL) and dried in vacuo; yield 4.980 g (90%) of Cu₃-(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₅)₂] (**2a**).

Reactions with 4-Tolylcopper(I). Attempted Synthesis of [Cu(μ-O₂CC₆H₄X-2)]₄ (X = H 1a; X = Br, 1c). At Room Temperature. To a yellow suspension of 4-tolylcopper(I) (6 mmol) in 30 mL of toluene was slowly added the appropriate benzoic acid (6 mmol). The yellow suspension turned from green to brown within 1 h. The material isolated by filtration was not the desired pure copper(I) benzoate.

At Lower Temperature. To a yellow suspension of 4-tolylcopper(I) (6 mmol) in toluene (30 mL) cooled to −70 °C was added benzoic acid (6 mmol) or 2-bromobenzoic acid (6 mmol). The temperature was slowly raised, and the color of the reaction mixture changed slowly from yellow (at −70 °C) via red (at −40 °C) to yellow-green (at −10 °C). Filtration at 0 °C afforded a green-brown solid which was not the desired pure copper(I) benzoate.

Synthesis of [Cu(C₆H₄Me-4)(μ-O₂CC₆H₄X-2)₂] (X = H, 3a; X = Br, 3c). To a yellow suspension of 4-tolylcopper(I) (6 mmol) in toluene (30 mL) cooled to −70 °C was added 3 mmol of benzoic acid or 2-bromobenzoic acid. The temperature was slowly raised to −40 °C, and the resulting dark red suspension was filtered. The small amount of brown solid obtained proved to be unidentifiable.

The orange filtrate was recooled to −80 °C and the yellow solid deposited over a period of 2 days. This solid was isolated by filtration, washed with hexane (3 × 10 mL), and dried in vacuo, yield 20% of [Cu(C₆H₄Me-4)(μ-O₂CC₆H₄X-2)₂] (X = H, **3a**): ^{1}H NMR data (in C₆D₆, room temperature TMS internal, δ, ppm) 1.98 (s, 3 H, 4-Me), 6.87 (d, 2 H, H2 + H6, 4-tolyl), 7.76 (d, 2 H, H3 + H5, 4-tolyl), 6.84–7.10 (m, br, 3 H, H3 + H4 + H5, RCO₂ ligand), 8.01 (m, H2 + H6, RCO₂ ligand). X = Br, **3c**: ^{1}H NMR data could not be obtained since **3c** is insoluble in benzene and toluene.

Synthesis of [Cu(C₆H₄Me-4)(μ-O₂CC₆H₅)₂] Using [Cu(μ-O₂CC₆H₅)]₄. Copper(I) benzoate (1.112 g, 6 mmol) was added to a yellow suspension of 4-tolylcopper(I) (932 mg, 6 mmol) in 40 mL of toluene at −70 °C and the temperature slowly raised to 0 °C over 5 h. The yellow suspension was filtered and the solid yellow product washed with hexane (3 × 10 mL) and dried in vacuo. The filtrate (without hexane washings) was cooled to −30 °C, and after being left standing for 2 days at −30 °C a yellow solid deposited. This yellow solid was isolated by filtration, washed with hexane (3 × 10 mL), and dried in vacuo. Elemental analysis indicated both isolated solids to be [Cu₃(C₆H₄Me-4)(μ-O₂CC₆H₅)₂]

Table II. Crystal Data and Details of the Structure Determination of [Cu₃(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₅)₂] (2a)

formula	C₂₃H₂₁O₄Cu₃
mol wt	553.39
cryst system	C2/c
space group	monoclinic
a, Å	16.926 (2)
b, Å	11.781 (1)
c, Å	10.763 (1)
β, deg	94.48 (1)
V, Å³	2139.6 (6)
Z	4
D(calcd), g cm⁻³	1.71
μ(Cu Kα), cm⁻¹	36.3
transmissn factors	0.61–1.36
cryst size, mm	0.3 × 0.25 × 0.25
radiatn	Cu Kα
T, K	295
θ_{max}, deg	70
data set	$-20 \leq h \leq 20, 0 \leq k \leq 14, 0 \leq l \leq 13$
ref reflctns	1
total unique reflctns	2032
obsd data ($I > 2.5\sigma$)	1627
no. of parameters	139
weighting scheme	$\omega = 1/(1.3 + F_0 + 0.0077F_0^2)$
final R	0.059
R_w	0.094
max shift/error	0.3
min, max res dens, e Å⁻³	−0.8, +0.8

(12) Camus, A.; Marsich, N. *J. Organomet. Chem.* **1968**, *14*, 441.

(13) Tsuda, T.; Yazawa, K.; Watanabe, T.; Fujii, T.; Seagusa, T. *J. Og. Chem.* **1981**, *46*, 192.

Table III. Fractional Coordinates of the Atoms of
[Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_5$)$_2$] (2a)

	x	y	z
Cu(1)	0.05031 (2)	0.21231 (3)	0.17611 (3)
Cu(2)	0.0 (0)	0.43489 (4)	0.25 (0)
C(1)	0.1086 (1)	0.4057 (2)	0.0641 (2)
C(2)	0.1593 (1)	0.4589 (2)	-0.0262 (2)
C(3)	0.1595 (1)	0.5755 (2)	-0.0397 (2)
C(4)	0.2066 (1)	0.6240 (2)	-0.1241 (2)
C(5)	0.2521 (1)	0.5603 (2)	-0.1947 (2)
C(6)	0.2526 (1)	0.4453 (3)	-0.1811 (2)
C(7)	0.2066 (1)	0.3941 (2)	-0.0968 (2)
C(8)	0.0 (0)	0.0803 (2)	0.25 (0)
C(9)	-0.0492 (1)	0.0196 (2)	0.1611 (2)
C(10)	-0.0490 (1)	-0.0984 (2)	0.1625 (2)
C(11)	0.0 (0)	-0.1580 (2)	0.25 (0)
C(12)	-0.1021 (1)	0.0795 (2)	0.0622 (2)
C(13)	0.0 (0)	-0.2863 (3)	0.25 (0)
O(1)	0.1130 (1)	0.2982 (1)	0.0765 (1)
O(2)	0.06496 (10)	0.4670 (1)	0.1236 (2)
H(3)	0.132 (1)	0.613 (2)	0.001 (2)
H(4)	0.209 (1)	0.684 (2)	-0.120 (2)
H(5)	0.279 (2)	0.606 (3)	-0.231 (3)
H(6)	0.283 (2)	0.403 (3)	-0.228 (3)
H(7)	0.208 (1)	0.305 (2)	-0.080 (2)
H(10)	-0.087 (1)	-0.150 (2)	0.096 (2)
H(121)	-0.083 (1)	0.173 (2)	0.038 (2)
H(122)	-0.104 (2)	0.037 (2)	-0.026 (2)
H(123)	-0.169 (1)	0.086 (2)	0.083 (2)

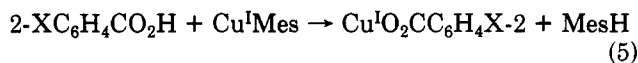(3a); Total isolated yield 631 mg (40%).

Structure Determination and Refinement of [Cu$_3$-(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_5$)$_2$] (2a). Crystal data and numerical details of the structure determination are listed in Table II. The final values of all refined atomic coordinates are listed in Table III. X-ray data were collected on a Nonius CAD4 diffractometer for a yellow transparent crystal mounted in a Lindemann glass capillary. A total of 2032 reflections with $\theta \le 70°$ were measured employing graphite-monochromatized Cu Kα radiation. A total of 405 were below the 2.5$\sigma(I)$ level and were treated as unobserved.

The asymmetric unit consists of one half of a formula unit situated at a crystallographic 2-fold axis. The two independent Cu atoms were found from an E map obtained by means of the symbolic addition program set SIMPEL.[14] The remaining non-hydrogen atoms were derived by means of the heavy-atom technique. After isotropic block-diagonal least-squares refinement an empirical absorption correction was applied.[15]

Subsequent anisotropic refinement converged to R = 0.059 for the 1627 observed reflections. The H atoms were indicated in a ΔF synthesis except those of the methyl group of C(13) which, situated on a twofold axis, necessarily exhibits rotational disorder. The H atoms were introduced at their calculated positions and were not refined. A weighting scheme was applied, and the anomalous scattering of copper was taken into account.[16]
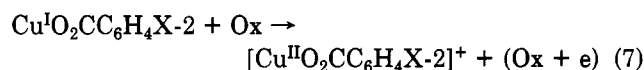
Results and Discussion

Synthesis and Characterization of [Cu(μ-O$_2$CC$_6$H$_4$X-2)]$_4$ (X = Cl, 1b; X = Br, 1c). The reaction of pentameric mesitylcopper(I) with 2-chloro- or 2-bromobenzoic acids yields instantaneously the corresponding copper(I) benzoates [Cu(μ-O$_2$CC$_6$H$_4$Cl-2)]$_4$ (1b) and [Cu(μ-O$_2$CC$_6$H$_4$Br-2)]$_4$ (1c) via an acid–base like reaction (eq 5).

$$2\text{-XC}_6\text{H}_4\text{CO}_2\text{H} + \text{Cu}^I\text{Mes} \rightarrow \text{Cu}^I\text{O}_2\text{CC}_6\text{H}_4\text{X-2} + \text{MesH} \quad (5)$$

These copper(I) benzoates which contain a reactive ortho carbon-halogen bond have to be isolated immediately after their precipitation from the reaction mixture. Attempted

isolation of 1b or 1c from the reaction mixture with mesitylcopper(I) after a reaction period of 30 min affords a slightly blue, impure product. Clearly some of the copper(I) benzoate product has undergone a valence disproportionation reaction (eq 6) or an oxidation reaction (eq 7).

$$2\text{Cu(I)} \rightarrow \text{Cu(0)} + \text{Cu(II)} \quad (6)$$

$$\text{Cu}^I\text{O}_2\text{CC}_6\text{H}_4\text{X-2} + \text{Ox} \rightarrow$$
$$[\text{Cu}^{II}\text{O}_2\text{CC}_6\text{H}_4\text{X-2}]^+ + (\text{Ox} + \text{e}) \quad (7)$$

The pure dry copper(I) benzoate compounds are white and are stable for several days when stored in the dark under a nitrogen atmosphere. When exposed to air, they slowly turn faintly blue in about 24 h. Compounds 1b and 1c are insoluble in diethyl ether as well as in aromatic and noncoordinating solvents at ambient temperature. When dissolution of 1b and 1c is attempted in coordinating solvents such as methanol or tetrahydrofuran, immediate decomposition occurs. This behavior prevented the preparation of crystals for an X-ray structural determination of these copper(I) 2-halobenzoates.

The IR spectra of 1b and 1c exhibit the same features as that of [Cu(μ-O$_2$CC$_6$H$_5$)]$_4$ (1a), and, therefore, it is likely that the geometrical structure of these new compounds is similar to that of 1a (see eq 2).[10] The copper(I) 2-halobenzoates also exhibit the same reactivity as 1a toward arylcopper(I) compounds (vide infra) and diethyl acetylenedicarboxylate, yielding novel tetrameric copper(I) alkyne benzoate complexes.[17]

It is worth noting that in this new synthesis of copper(I) benzoates there is no interference from the possible reaction of the organocopper(I) reagent or the generated copper(I) benzoate with the aryl halide present, 2-halobenzoic acid, to afford biaryls or esters,[2,11] respectively. It can, therefore, be concluded that under our reaction conditions the acid–base like reaction (eq 5) is much faster than biaryl and ester formation reactions.

It proved to be impossible to prepare the copper(I) 2-halobenzoates [Cu(μ-O$_2$CC$_6$H$_4$Cl-2)]$_4$ (1b) and [Cu(μ-O$_2$CC$_6$H$_4$Br-2)]$_4$ (1c) by the previously reported copper(I) oxide method (see eq 4). This route fails since 1b and 1c react further at the elevated temperatures at which the copper oxide/benzoic acid reaction has to be executed.[18] Instead of the desired copper(I) 2-halobenzoates it mainly yields copper(II) salts and zerovalent copper via a valence disproportionation reaction (vide supra).

General Synthesis of Copper(I) Benzoates. The reactions of mesitylcopper(I) can be extended to several other benzoic acids (2-MeC$_6$H$_4$CO$_2$H, 2,4,6-Me$_3$C$_6$H$_2$CO$_2$H, and 2-NO$_2$C$_6$H$_4$CO$_2$H) and carboxylic acids (CH$_3$CO$_2$H and CNCH$_2$CO$_2$H) and enables us to synthesize the corresponding copper(I) carboxylates in good yield. For instance, copper(I) 2-nitrobenzoate, whose synthesis via the copper(I) oxide route can be very tedious, was obtained from the reaction of mesitylcopper(I) with 2-nitrobenzoic acid in 80% yield. In this case the possible oxidation of the organocopper(I) reagent by the nitro fragment[19] does not interfere with the copper(I) benzoate formation reaction.

Reactions of mesitylcopper(I) with two other active hydrogen compounds, acetylacetone and methanol, however, were not successful. On the basis of observations

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Scheme II

$3/4$ [Cu(μ-O$_2$CC$_6$H$_5$)]$_4$ + $3/5$ [Cu(C$_6$H$_2$Me$_3$-2,4,6)]$_5$ $\rightleftharpoons$
   1a

$\rightleftharpoons$ {[Cu$_6$ (C$_6$H$_2$Me$_3$-2,4,6)$_n$ (μ-O$_2$CC$_6$H$_5$)$_{6-n}$]} $\rightleftharpoons$
       soluble reaction intermediates; n= 2,3,4

$\rightleftharpoons$ [Cu$_3$ (C$_6$H$_2$Me$_3$-2,4,6) (μ-O$_2$CC$_6$H$_5$)$_2$]
    2a

made during the synthetic procedure, we believe that the acid–base like reaction always proceeded smoothly but that the stability of the products is the limiting factor[20] preventing isolation of the pure compounds.

Synthesis of [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_4$X-2)$_2$] (X = H, 2a; X = Cl, 2b; X = Br, 2c). Further reaction of the isolated compounds 1 with another equivalent of mesitylcopper(I) affors the first examples of stable mixed (benzoato)organocopper clusters [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_4$X-2)$_2$] (X = H, **2a**; X = Cl, **2b**; X = Br, **2c**). A noteworthy aspect of this synthesis is that when the reaction mixture is dilute (see Experimental Section), all of the copper(I) benzoate starting compound is dissolved after the addition of 1 equiv of mesitylcopper(I); i.e., well-soluble intermediates are formed. The pale yellow products then deposit from this homogeneous reaction mixture after several minutes.

The measured cryoscopic molecular weights of **2a** and **2b** show that they are trimeric in benzene solution (see Table I). The attempted cryoscopic molecular weight determination of **2c** was not successful due to its insolubility. The much lower solubility of this bromo compound compared to that of the chloro analogue cannot be explained at this moment. The ^{1}H NMR data indicate a 2:1 stoichiometry between the benzoate and mesityl fragments (see Experimental Section). Together these data lead to a [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_4$X-2)$_2$] stoichiometry.

To study the soluble intermediates obtained after mixing mesitylcopper(I) with copper(I)benzoate, a completely homogeneous benzene solution of the reaction mixture of **2a** was immediately evaporated to dryness. The cryoscopic molecular weight of the yellow residue gave an apparent molecular weight of 1092; this indicates that these intermediates are most likely hexanuclear species of general formula [Cu$_6$(C$_6$H$_2$Me$_3$-2,4,6)$_n$(μ-O$_2$CC$_6$H$_5$)$_{6-n}$] (n = 2, 3, 4; see Scheme II). This result pertains to the concentration range 5×10^{-3}–5×10^{-2} mol/L (based on the hexameric unit). Interestingly, upon standing for 1 night the solution from the cryoscopic molecular weight experiment deposits a large amount of the dissolved copper(I) compound (40%) as **2a** (based on elemental and ^{1}H NMR analysis).

In summary, the trimeric reaction products 2 are formed by an interaggregate exchange reaction between pentameric mesitylcopper(I) and tetrameric copper(I) benzoate via soluble hexameric intermediates. The reason for the exclusive isolation of the trimeric compounds 2 seems to be due to their poor solubility.

The reactions of copper(I) benzoates with arylcopper(I) compounds to form mixed (benzoato)organocopper(I) compounds seem to be of a general type. When, for instance, copper(I) methylbenzoates are used in reactions with mesitylcopper(I), the mesitylbenzoate analogues of 2 are isolated.[21] Furthermore when copper(I) 3-methylbenzoate reacts with [8-(dimethylamino)naphthyl]cop-

Figure 1. ORTEP drawing of [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_5$)$_2$] showing 40% probability ellipsoids.

Table IV. Selected Bond Distances (Å) of [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_5$)$_2$] (2a)

around the copper atoms		within the ligands	
Cu(1)–O(1)	1.868 (5)	O(1)–C(1)	1.265 (8)
Cl(1)–C(8)	1.957 (6)	O(2)–C(1)	1.232 (8)
Cu(1)···Cu(1*)	2.421 (2)	C(1)–C(2)	1.493 (8)
Cl(1)···Cu(2)	2.888 (2)	C(8)–C(9)	1.427 (6)
Cu(2)–O(2)	1.855 (5)	C(9)–C(10)	1.382 (8)
		C(10)–C(11)	1.401 (7)

Table V. Selected Bond Angles (deg) of [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(μ-O$_2$CC$_6$H$_5$)$_2$] (2a)

C(8)–Cu(1)–O(1)	161.2 (2)	C(9)–C(8)–C(9*)	118.0 (6)
O(2)–Cu(2)–O(2*)	156.6 (2)	Cu(1)–O(1)–C(1)	123.9 (4)
Cu(1)–Cu(2)–Cu(1*)	49.55 (05)	O(1)–C(1)–O(2)	125.1 (6)
Cu(1)–C(8)–Cu(1)	76.4 (3)	C(1)–O(2)–Cu(2)	131.4 (4)

per(I) as the arylcopper(I) compound, a compound with a 2:1 benzoate-to-aryl ratio was isolated.[22]

However, when aliphatic carboxylates, i.e. copper(I) acetate or copper(I) cyanoacetate, instead of benzoates, were used in reactions with mesitylcopper(I), the starting carboxylates were isolated quantitatively. This is most likely due to the total insolubility in benzene of these copper(I) carboxylates which have a polymeric structure in the solid state.[23]

A noteworthy property of the reaction of copper(I) benzoates with arylcopper(I) compounds is that no spontaneous C–C coupling products of the aryl fragments are obtained. This contrasts with the reactions of copper(I) (trifluoromethyl)sulfonate with organocopper(I) compounds where in various cases (e.g. CuC$_6$H$_4$Me-4) even a catalytic amount of copper(I) (trifluoromethyl)sulfonate causes a quantitative formation of the corresponding biaryl.[24] The nonoccurrence of this C–C coupling reaction in the case copper(I) benzoate reactions with arylcopper(I) compounds probably is due to the lower electron-withdrawing capability of the benzoate fragment compared to that of the (trifluoromethyl)sulfonate ligand.[2d,24]

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Table VI. Selected Atomic and Bond Distances (Å) of Several Relevant Copper(I) Complexes

complex	Cu–O	Cu···Cu		Cu–C	ref
		benzoato-bridged	aryl-bridged		
[Cu₃(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₅)₂]	1.861 (5)ᵃ	2.888 (2)	2.421 (2)	1.957 (6)	b
[Cu(μ-O₂CC₆H₅)]₄	1.812 (13)–1.877 (14)	2.709 (6)–2.770 (5)			10b
[Cu(μ-O₂CC₆H₅)(PhC≡CPh)]₂	1.933 (10)–1.987 (10)	2.779 (3)ᵃ			29
[Cu(μ-O₂CC₆H₅)(NC₉H₇)]₂	1.944 (5)–2.107 (5)	2.638 (2)			30
[Cu₄(μ-O₂CC₆H₄Cl-2)₄(DEAD)₂]ᶜ	1.899 (4)–1.927 (3)	2.941 (2)–3.129 (3)			17
[Cu(C₆H₂Me₃-2,4,6)]₅			2.437 (8)–2.469 (9)	1.96 (2)–2.06 (2)	25
[Cu₆(C₆H₄NMe₂-2)₄(C≡CC₆H₄Me-4)₂]			2.521 (5)	1.984 (7)–2.130 (6)	27
[Cu(C₆H₄CH₂NMe₂-2)]₄			2.383ᵃ	1.97 (2)–2.16 (2)	26

ᵃ Average of two distances that do not differ significantly. ᵇ This paper. ᶜ DEAD = diethyl acetylenedicarboxylate.

Solid-State Structure of [Cu₃(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₅)₂] (2a).

The monoclinic unit cell of the crystal contains four unique discrete molecules each having two-fold crystallographic symmetry.

The unique trinuclear structure of 2a in the solid state is shown in Figure 1. Selected bond distances, bond angles, and torsion angles are listed in Tables IV and V. The structure comprises an isosceles triangle of copper atoms with the two longer edges bridged by benzoato groups and the shorter edge bridged by a mesityl group. The molecule possesses an axis of symmetry passing through unique Cu(2) and the ipso carbon atom of the mesityl group [C(8)].

Each of the two identical benzoato units is bridge bonded as a four-electron donor to a pair of copper atoms while the mesityl group is three-center, two-electron bonded to its two copper atoms. The Cu(1)–O(1) and Cu(2)–O(2) distances, 1.868 (5) and 1.855 (5) Å, respectively, are in the expected range for bridging benzoates (see Table VI). The Cu···Cu distance of the benzoato-bridged copper atoms (2.888 (2) Å) is in the expected range (see Table VI).

The Cu(1)–C(8)(mesityl) distance is 1.957 (6) Å and is comparable to the copper–carbon bond distances found in pure pentameric mesitylcopper(I) by Floriani et al.[25] The Cu···Cu distance of the mesityl-bridged copper atoms, 2.421 (2) Å, reflects the specific bridging bonding mode of electron-deficient three-center, two-electron bonded aryl groups (the range for Cu···Cu distances bridged by three-center, two-electron bonds is 2.37–2.53 Å[26,27] (see Table VI). The mesityl unit is bonded almost perpendicularly (87.5°) with respect to the Cu(1)···Cu(1*) vector, so stabilizing the Cu–C–Cu bonding (vide infra). For a more detailed discussion about the stability of the three-center, two-electron arylcopper(I) bond see ref 2d.

An interesting structural feature of 2a is the almost planar arrangement of the central ten-membered ring comprising the three copper atoms together with the bridging mesityl carbon and CO atoms (puckering factor Q = 0.26[28]). This planarity contrasts with the out of the Cu plane coordination of the benzoato unit in [Cu(μ-O₂CC₆H₅)]₄ (1a) schematically shown in eq 2.[10b] The interbond angles around the copper atoms of 161.2° (Cu(1)) and 156.6° (Cu(2)) reflect the tendency of two-coordinate copper to adopt linear hybridization.[2d]

Attempted Isolation of [Cu₃(C₆H₂Me₃-2,4,6)₂(μ-O₂CC₆H₅)].

In the 1:1 molar reaction of mesitylcopper(I) with copper(I) benzoate there should be cluster compounds

Figure 2. Molecular orbitals (MO's) involved in the three-center, two-electron copper–carbon bonding. MO I is the lowest MO which not only is bonding between C(ipso) and Cu but is also bonding between the two Cu atoms.

present with a composition different to that found in 2, for example, [Cu₃(C₆H₂Me₃-2,4,6)₂(μ-O₂CC₆H₅)] with a 1:2 benzoato to mesityl ratio. After the isolation of [Cu₃(C₆H₂Me₃-2,4,6)(μ-O₂CC₆H₅)₂] we tried to isolate such species from the mother liquor by concentrating and/or cooling these solutions. However, in all cases these solutions blackened indicating the formation of copper metal. This is a probable consequence of the known biaryl coupling reaction.[2] The reaction products were not studied in detail.

Synthesis of [Cu₃(C₆H₄Me-4)(μ-O₂CC₆H₄X-2)₂] (X = H, 3a; X = Br, 3c).

In order to yield well-defined copper(I) benzoato compounds the 1:1 molar acid–base like reaction of benzoic acids with 4-tolylcopper(I) had to be carried out at considerably lower temperatures than with mesitylcopper(I) (eq 5) to yield proper copper(I) compounds. On the basis of observations during the reactions of 4-tolylcopper(I) with benzoic acid at room temperature (starting at –70 °C, see Experimental Section) the isolation of a proper copper(I) compound was attempted at –40 °C.

The yellow compounds isolated from the filtrate were not the expected pure copper(I) carboxylates 1 but the 4-tolyl analogues of 2, i.e. [Cu₃(C₆H₄Me-4)(μ-O₂CC₆H₄X-2)₂] (X = H, 3a; X = Br, 3c; for X = Cl the reaction was not carried out). Compound 3a could also be synthesized by the interaggregate reaction of 4-tolylcopper(I) with copper(I) benzoate.

Compounds 3 were considerably less stable in solution than their mesityl analogues 2. This is most likely due to the nature of the electron-deficient three-center, two-electron bonding mode of the aryl group: the 4-tolyl species 3, which lacks ortho methyl substituents, being less stable than the mesityl compounds 2. Ortho methyl substituents, which are present in the bridging mesityl ligand of compounds 2, stabilize the electron-deficient three-center, two-electron bonding mode of aryl ligands by enhancing the contribution of MO II[27] (see Figure 2).

Conclusions

The reaction of mesitylcopper(I) with acidic compounds is a versatile synthetic procedure for new copper(I) compounds with its success limited by the thermal stability of the products. The reactions with mesitylcopper(I) are

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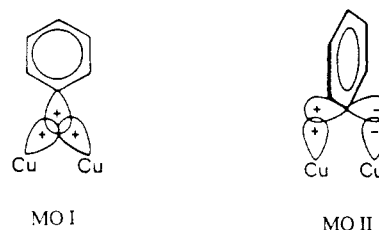
more successful than the reactions with 4-tolylcopper(I) because of the increased stability of the mixed organo-(benzoato)copper(I) intermediates in the mesityl case.

The copper(I) 2-halobenzoates (halo is Cl or Br) synthesized via this method show similar IR spectra and reactivity toward mesitylcopper(I) as copper(I) benzoate, thus forming trimeric mixed (2-halobenzoate)organocopper(I) clusters. Consequently, it is assumed that the structural features of these compounds are essentially similar. This means that the enhanced polarization of the carbon–halogen bond, by intramolecular coordination of the halogen to copper, which is proposed in the Hurtley reaction (see Scheme I), is not present in the pure copper(I) 2-halobenzoates [Cu(μ-O$_2$CC$_6$H$_4$Cl-2)]$_4$ (**1b**) and [Cu(μ-O$_2$CC$_6$H$_4$Br-2)]$_4$ (**1c**). However, under the conditions of the Hurtley reaction there are more species present than in our synthetic procedure and the temperature is considerably higher. The influence of all these factors will be discussed in a forthcoming paper.[18]

Finally, it should be emphasized that the reaction of copper(I) benzoates with arylcopper(I) compounds, which generates mixed (benzoato)organocopper(I) clusters, seems to be of a general nature.

Fluxionality of (η^2-Naphthalene)(^{i}Pr$_2$P(CH$_2$)$_n$^{i}Pr$_2$P)Ni^0 (n = 2, 3) in the Solid State and Solution As Studied by CP/MAS and 2D ^{13}C NMR Spectroscopy

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Variable-temperature one- and two-dimensional liquid-state ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra and solid-state MAS ^{31}P and CP/MAS ^{13}C NMR spectra of microcrystalline (C$_{10}$H$_8$)(dippp)Ni (**1**) and (C$_{10}$H$_8$)(dippe)Ni (**2**) (dippp = 1,3-bis(diisopropylphosphino)propane; dippe = 1,2-bis(diisopropylphosphino)ethane) confirm that the structures of these complexes in both aggregation states are identical. The arene is η^2-bonded to nickel. In both the liquid and the solid state the P$_2$Ni moiety moves between the 1,2- and 3,4-positions within one ring of the naphthalene, but this does not interchange the phosphorus atoms. In solution this process is intramolecular and has an activation barrier of less than 6 kcal/mol while high-temperature 2D chemical exchange CP/MAS experiments yield an activation energy of more than 23 kcal/mol in the solid. Two-dimensional magnetization transfer experiments on the dissolved molecules confirm that there are two further fluxional processes involving rotation and migration of the P$_2$Ni moiety around the 1,2-, 3,4-, 5,6-, and 7,8-positions of both six-membered rings. The activation barrier for the migration of the η^2-bonded P$_2$Ni moiety in the bicyclic compound is approximately 15 kcal/mol.

Introduction

Numerous simple organometallic molecules undergo fast dynamic processes in solution so rapidly even at low temperatures that the range of slow exchange cannot be reached in high-resolution ^{13}C high-field NMR spectroscopy.[1] An unambiguous structure determination is then often not possible. Even if an X-ray analysis is available for such compounds, in many cases the question remains open whether the structures in both aggregation states are identical and whether the molecules are also fluxional in the solid state.

In such situations solid-state NMR spectroscopy[2] is a particularly attractive technique. First, low-temperature studies are not restricted by the viscosity or freezing point

of a solvent. Thus a slow-exchange limit occurring at very low temperatures should be reached more readily in the solid state although under such conditions it is by no means a routine experiment to rotate air- and moisture-sensitive samples at high speeds.[3] Second, the activation barrier for a given process may become much higher in the solid state. Even if the exchange rate is so low at elevated temperatures that no line broadening is evident, recently introduced one-[4] and two-dimensional[5-7] techniques based

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