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Inorganica Chimica Acta 358 (2005) 3967–3973

Inorganica Chimica Acta

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Insertion reactions of organic anhydrides and the Cu(I) alkoxide [CuO^{t}Bu]

Christopher E. Anson, Robert Langer, Lukasz Ponikiewski, Alexander Rothenberger *

Institut für Anorganische Chemie, Universität Karlsruhe, Engesser Straße 15, Geb. 30.45, D-76131 Karlsruhe, Germany
Institut für Nanotechnologie, Forschungszentrum Karlsruhe GmbH, Postfach 3640, 76021 Karlsruhe, Germany

Received 23 May 2005; accepted 13 June 2005
Available online 9 August 2005

Abstract

The synthesis and structural characterization of the copper salts [Cu_8(benzoate)$_8$(THF)$_6$] (**1**), [$Cu_2\{(CO_2)_2C_6H_2(Boc)_2\}dppm_2]_2$ (**2**) and [$Cu_2\{(CO_2)_2C_{10}H_4(Boc)_2\}dppm_2]_2$ (**3**) [Boc = *tert*-butoxycarbonyl, dppm = 1,2-bis(diphenylphosphino)methane] prove that cyclic organic anhydrides and dianhydrides readily insert into the Cu–O bond of [CuO^{t}Bu] forming carboxylate ligands with ester functionalities in the ligand periphery. [Mn_3(*o*-Boc-benzoate)$_6$(DME)$_2$] (**4**) (DME = 1,2-dimethoxyethane) was synthesized by the metathesis reaction of [Cu(I)(*o*-Boc-benzoate)] with $MnCl_2$.

Keywords: Metal alkoxide; Anhydride; Insertion reactions

1. Introduction

The interest in the synthesis of inorganic/organic hybrid materials is driven by possible applications as storage devices for gases, as matrices for catalytic transformations and for a variety of other purposes [1,2]. It is desirable to develop synthetic routes for molecular complexes suitable for any of these applications that allow to incorporate specific metal atoms into organic frameworks with functional groups, e.g., carboxylates, sulfonates, and phosphonates, and at the same time generate a variety of organic ligands. A contribution to this field is the exploration of insertion reactions of organic anhydrides into the metal–O bond of late transition metal alkoxides. This reaction allows a range of transition metals to be incorporated and at the same time to modify the organic ligand by selecting different alkoxy groups and organic anhydrides. This type of reaction has successfully been applied by Bergman and coworkers [3,4] to late transition metal alkoxide complexes and we have recently extended those investigations to copper alkoxides. Reactions of organic anhydrides with [CuO^{t}Bu] produce Cu(I) and Cu(II) carboxylate complexes and complement well-established synthetic procedures to these species [5–7]. Challenges in this area now include the application of the alkoxide–anhydride insertion reaction to a range of organic anhydrides and to develop synthetic methods allowing the incorporation of a variety of metal atoms before the properties of the metal organic frameworks can be investigated. As a contribution to this area, we wish to report here the recent progress made, including the synthesis and structure of unusually solvated Cu(I)benzoate, reactions of [CuO^{t}Bu] with organic dianhydrides and a metathesis reaction which should be widely applicable in future.

2. Experimental

General remarks. All operations were carried out in an atmosphere of purified argon. Solvents were dried

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[*] Corresponding author. Tel.: +49 0 721 6082849; fax: +49 0 721 6088440.
E-mail address: rothenberger@chemie.uni-karlsruhe.de (A. Rothenberger).

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doi:10.1016/j.ica.2005.06.061

over sodium/benzophenone. Organic anhydrides were recrystallized from diethylether. Chemicals were purchased from Aldrich. $[CuO^tBu]$ was prepared according to a published procedure [8]. Yields given were optimized by repeated crystallization and concentration of the mother liquor. The uniform composition of isolated products was confirmed by unit-cell determination of different batches of crystals.

1. To a solution of 0.14 g of (1.00 mmol) $[CuO^tBu]$ in 10 mL THF was added a solution of 0.27 g (1.00 mmol) benzoic acid anhydride in 5 mL of THF. The yellow solution was heated to reflux for 5 min. A colour change to pale green occurred. Storage of the reaction mixture at −40 °C for 4 days produced pale yellow crystals of $[Cu_8(benzoate)_8(THF)_6]$ **1**. Yield 0.19 g, 78%. Crystals of **1** were extremely sensitive to air and elevated temperatures preventing further analytical investigations and were selected under perfluoroether oil. Within approximately 10 s, the crystal was mounted and placed under the cryosystem of the diffractometer.

2. To a solution of 0.14 g of (1.00 mmol) $[CuO^tBu]$ in toluene (5 mL) was added a solution of 0.11 g (0.50 mmol) pyromellitic anhydride in toluene (10 mL). The resulting yellow solution was briefly heated to reflux and then a solution of 0.40 g (1.00 mmol) dppm in toluene (5 mL) was added. The solution was stirred for 2 h at room temperature. After filtration the solvent was reduced to approximately 3 mL. Addition of THF (3 mL) to the concentrated solution and storage at −40 °C for 2 days produced colourless crystals of $[Cu_2\{(CO_2)_2C_6H_2(Boc)_2\}dppm_2]_2$ **2** (11 molecules of THF as lattice-bound solvent), which slowly decomposed at room temperature upon the loss of lattice-bound solvent. Yield 0.58 g, 68%; m.p. 232 °C; *Anal.* Calc. for $C_{136}H_{128}Cu_4O_{16}P_8$ (excluding lattice-bound THF): C, 64.8; H, 5.1. Found: C, 65.3; H, 5.4%. IR (KBr) $\tilde{\nu} =$ 1718, 1591, (COO), 1433 (P–Ph), 735, 692 (C–H ar.) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 161.975 MHz, 85%H_3PO_4) −8.2 br. s, −12 br. s (PPh_2); ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) 7.7–6.9 (m, 22H ar.), 3.8 (m, 4H, THF), 3.2 (br. m, 2H, $Ph_2PC\mathbf{H_2}PPh_2$), 1.9 (m, 4H, THF), 1.4 (s, 18H, O^tBu); $^{13}C\{H\}$ NMR (400 MHz, $CDCl_3$, 25 °C, TMS) 175.7, 161.9 (COO, COO^tBu), 132.9–128.7 (C ar.), 68.1 (s, O–C, THF), 31.0 (s, CH_2CH_2O, THF), 28.1 (CH_3–C); the methylene group of dppm and the quarternary C atom of *tert*-butoxy groups could not be identified in the ^{13}C NMR.

3. To a solution of 0.12 g (0.50 mmol) 1,4,5,8-naphthyldianhydride in DME (5 mL) was added a solution of 0.14 g (1.00 mmol) $[CuO^tBu]$ in DME (5 mL). The resulting yellow solution was heated to reflux for 1 h and a colour change to orange was observed. Then, a solution of 0.40 g (1.00 mmol) dppm in DME (10 mL) was added. A colour change from orange to yellow was observed. The solution was stirred for 1 h and filtered. After filtration the solvent was reduced to approximately 5 mL and the reaction was stored at room temperature for one week producing colourless crystals of $[Cu_2\{(CO_2)_2C_{10}H_4(Boc)_2\}dppm_2]_2$ **3** (5 molecules of

Table 1
Details of the X-ray data collection and refinements

Compound	1	2	3	4
Formula	$C_{80}H_{88}Cu_8O_{22}$	$C_{180}H_{216}Cu_4O_{27}P_8$	$C_{164}H_{182}Cu_4O_{26}P_8$	$C_{84}H_{108}Mn_3O_{30}$
Formula weight	1909.82	3313.45	3071.02	1762.52
T (K)	200(2)	150(2)	150(2)	203(2)
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.0525(15)	14.286(3)	12.996(3)	10.4668(12)
b (Å)	12.1080(11)	22.927(5)	17.257(4)	15.1254(18)
c (Å)	15.0812(16)	28.716(6)	20.513(4)	16.0495(19)
α (°)	105.406(9)	90	108.73(3)	117.332(13)
β (°)	109.102(11)	98.54(3)	93.92(3)	91.311(14)
γ (°)	101.474(9)	90	90.18(3)	96.124(14)
V (Å^3)	1903.6(4)	9301(3)	4345.1(15)	2236.9(5)
Z	1	2	1	1
ρ_{calc} (g/cm^3)	1.666	1.183	1.174	1.308
μ (mm^{-1})	2.266	0.582	0.618	0.495
$F(000)$	976	3496	1610	927
2θ Range (°)	7.54–63.26	2.86–54.18	3.9–50.0	4.64–51.72
Reflections collected	15332	50971	13309	14075
Unique data	10702	20213	10398	8035
R_{int}	0.0707	0.0753	0.0744	0.0524
Parameters	993	871	856	530
wR_2 (all data)	0.1799	0.2137	0.2735	0.1332
S (Goodness-of-fit)	0.988	0.962	1.015	1.033
R_1 [$I > 2\sigma(I)$]	0.0722	0.0687	0.0867	0.0495
Peak, hole (e Å^{-3})	0.966, −0.756	0.843, −0.626	1.096, −0.615	0.389, −0.465

disordered DME as lattice-bound solvent). Yield 0.55 g, 70%; m.p. 185 °C; *Anal.* Calc. for $C_{156}H_{162}Cu_4O_{22}P_8$ (three lattice-bound DME molecules per complex remained after isolation under reduced pressure): C, 64.8; H, 5.6. Found: C, 64.5; H, 5.3%. IR (KBr) $\tilde{\nu} = 1712$, 1593 (COO), 1434 (P–Ph), 735, 691 (C–H ar.) cm^{-1}.

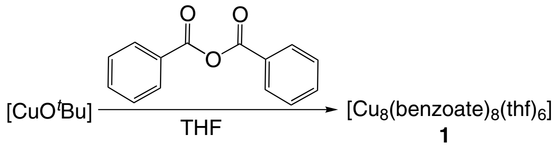
4. To a solution of 0.06 (0.50 mmol) $MnCl_2$ in 10 mL THF was added a solution of 0.15 g (1.00 mmol) phthalic acid anhydride. A solution of 0.14 g (1.00 mmol) [CuO^tBu] in 10 mL THF was added. The mixture was heated to reflux for 4 h and filtered. The pink solution was dried under reduced pressure and the solid residue was dissolved in 3 mL DME. After two days purple crystals of **4** were obtained. Yield 0.25 g, 89%; m.p. 135 °C; *Anal.* Calc. for $C_{80}H_{98}Mn_3O_{28}$: C, 57.4; H, 5.9. Found: C, 56.5; H, 5.9%. IR (KBr) $\tilde{\nu} = 1717$, 1608, 1589, 1406, 1306, 1255 (COO) cm^{-1}.

2.1. X-ray crystallographic study

Data were collected on a Stoe Stadi v equipped with a Kmw150 CCD detector (**1**), a Stoe Ipds II (**2**, **3**) and a Stoe Ipds I diffractometer connected to a Schneider rotary anode X-ray generator (**4**) using graphite-monochromated Mo Kα radiation ($v = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the shelxtl program package [9]. Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. Disordered components (lattice-bound solvent) were refined with isotropic thermal parameters. The structure of **1** is acentric, space group $P\bar{1}$, and a correction for racemic twinning was made. Several atoms of the THF ligands had anisotropic temperature factors that indicated the presence of disorder. No attempt was made to model this, in order to maintain an adequate data:parameter ratio, given the space group $P\bar{1}$ (see Table 1).

3. Results and discussion

As part of a wider study of reactions between organic anhydrides and [CuO^tBu], the simple model reaction of [CuO^tBu] with benzoic acid anhydride was carried out in THF. During storage of the reaction at room temperature, a disproportionation reaction occurred producing elemental copper, Cu(II)benzoate and *tert*-butylbenzoate. Storage of the reaction at −40 °C, however, produced the extremely air-sensitive, solvated Cu(I)benzoate **1** (Scheme 1, Fig. 1).



Scheme 1. Synthesis of **1**.

In the solid state **1**, exhibits a remarkable acentric structure consisting of two copper(I) benzoate tetramers held together by μ^2-bridging THF molecules. The bonding parameters and coordination geometries around the Cu centres in each tetrameric copper(I) carboxylate unit are similar to those observed in [$Cu_4(O_2CCF_3)_4$] [5]. **1** represents one of the very few crystallographically characterized ether-solvated Cu(I) carboxylates [10,11]. O(THF)–Cu distances are in the range Cu(8)–O(25) 2.370(13) – Cu(2)–O(23) 2.824(11) Å. Under reduced pressure THF is readily released resulting in amorphous Cu(I)benzoate.

This initial result and the reported synthesis of [$Cu_2(CO_2C_2H_2\text{-Boc})_2 \cdot$ dppm]$_2$ show that insertion reactions of organic anhydrides and [CuO^tBu] result in Cu(I) complexes if the reactions are either kept at low temperature or performed in the presence of phosphine donors [4]. In a first attempt to construct more complex aggregates via this synthetic route, reactions of dianhydrides and [CuO^tBu] were investigated.

The reactions of solutions [CuO^tBu] with pyromellitic anhydride and the anhydride of naphthalene-1,4,5,8-tetracarboxylic acid in organic solvents at ca. 70 °C produce colourless insoluble solids. In the presence of the tertiary phosphine dppm (dppm = bis-diphenylphosphinomethane), these reactions afforded the phosphine-stabilized copper salts of 4,6-bis-Boc-isophthalic acid **2** and 5,8-bis-Boc-naphthyl-1,4-dicarboxylic acid **3** in good yields (Scheme 2).

Initially, an infrared study of both compounds indicated the formation of the diester–dicarboxylate/phosphine complexes. This was verified for **2** by an NMR study. Solid samples of **3**, however, are insoluble once isolated and the molecular structures of **2** and **3** were finally determined by X-ray crystallography. In the solid state, **2** consists of two [$Cu_2(dppm)_2$] units [Cu(1)···Cu(2) 2.93(1), Cu–P av. 2.25 Å] held together by a bidentate carboxylato group [Cu(1)–O(1) 2.142(3), Cu(2)–O(2) 1.980(3) Å] (Fig. 2).

In addition to the O(carboxylate) and two P(dppm) donor centres around each copper atom, Cu(1) is coordinated by O(7) of the monodentate carboxylate group in the generated dicarboxylato ligand, resulting in a distorted tetrahedral coordination environment for Cu(1) and a trigonal planar ligand arrangement around Cu(2). An increase of the coordination number at Cu(2) is hindered by the ^{t}Bu group at O(3). Examples for three-coordinated Cu atoms in Cu(I) dicarboxylates are found in Cu(I) perfluorosuccinate, copper(I) glutarate and in the ion separated complex [Cu(OAc)(BF_4)(dppm)$_2$] [12–14]. Three- and four-coordinated Cu atoms

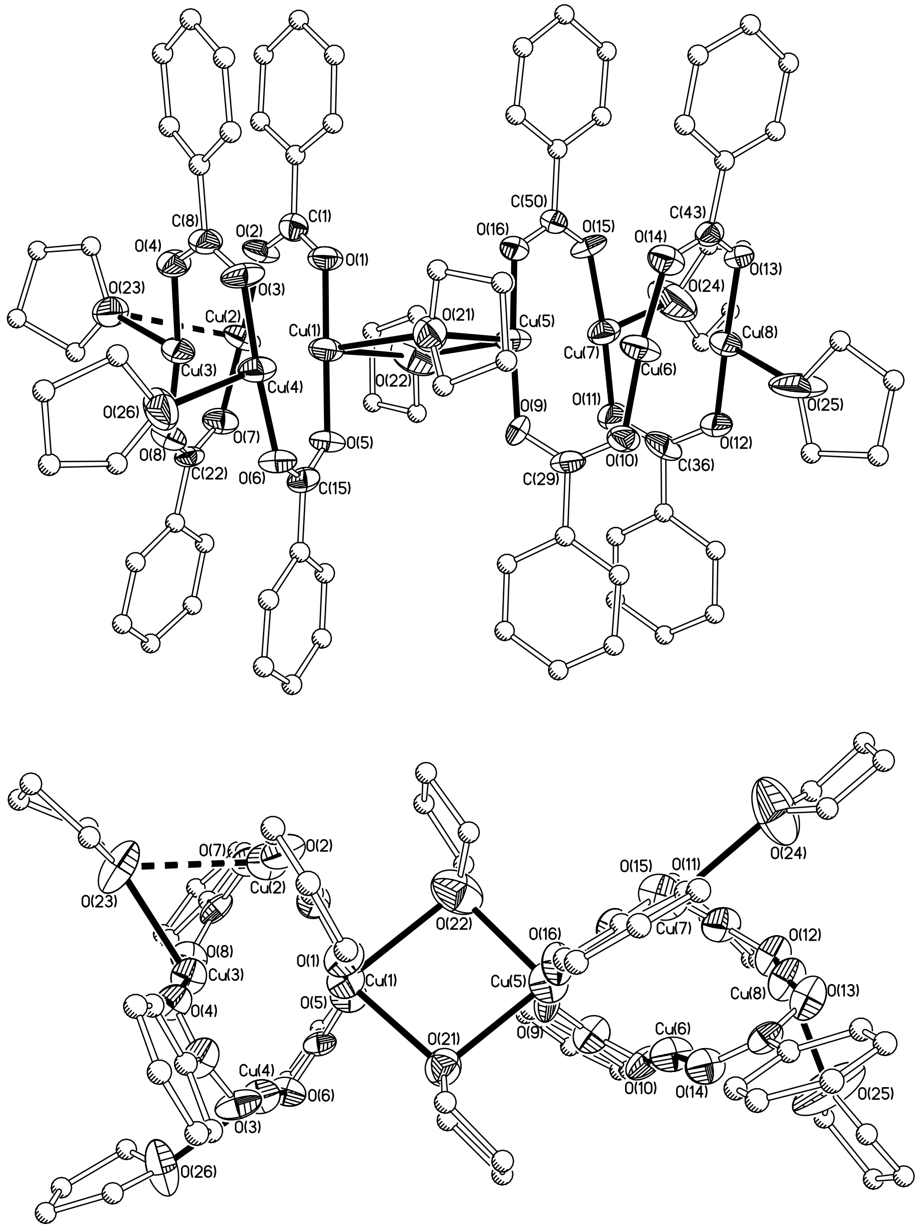
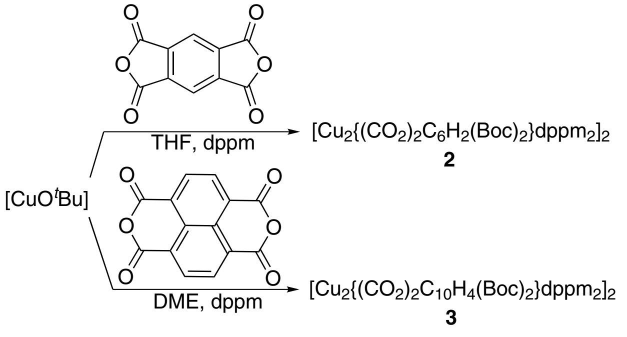


Fig. 1. Molecular structure of **1** in the solid state (view from the side and top; ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu–O(carboxylate) Cu(2)–O(7) 1.845(9), Cu(5)–O(16) 1.891(9), Cu–O(μ^2-THF) Cu(1)–O(21) 2.528(10) and Cu(1)–O(22) 2.751(13), Cu–O(THF) Cu(8)–O(25) 2.370(13), Cu(2)–O(23) 2.824(11); Cu(1)–O(21)–Cu(5) 98.0(3), Cu(1)–O(22)–Cu(5) 94.3(4).



Scheme 2. Synthesis of **2** and **3**.

are observed in the complex $[Cu_2(PhCOO)_2(dppm)_2]$ (all with similar Cu–O and Cu–P bond lengths and angles to those found in **2**) [15]. The monodentate carboxylate group is in plane with the benzene ring, whereas the bidentate carboxylate group is slightly twisted meeting the steric requirements of the $[Cu(dppm)]_2$ units in **2**. One O–C–benzene ring torsion angle of the ester groups in **2** is ca. 85.05° and larger than torsion angles observed in the sterically crowded ester hexa-Boc-benzene (O–C–benzene ring 71.6–80.7°) [16].

The molecular structure of **3** in the solid state consists of two $[Cu(dppm)]_2$ units bridged by two 1,4-dicarboxy-

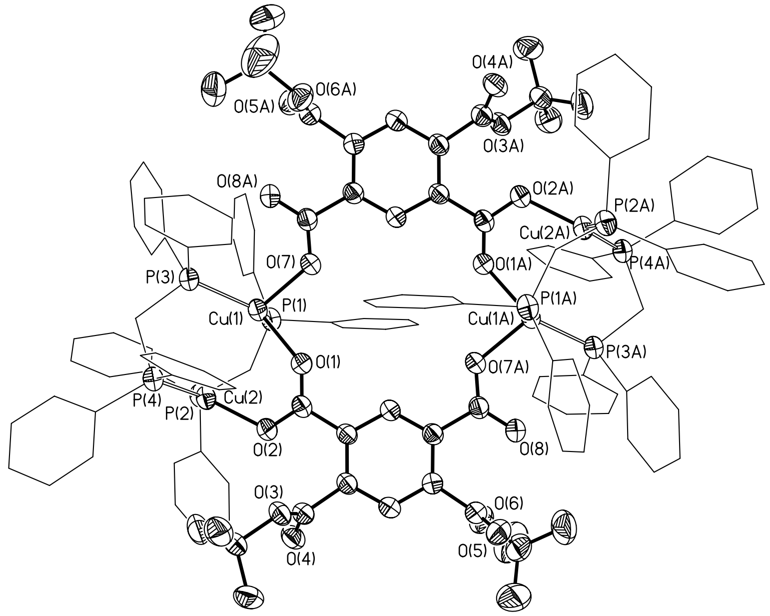


Fig. 2. Molecular structure of **2** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(7) 2.059(3), Cu(1)–O(1) 2.142(3), Cu(1)–P(3) 2.2534(11), Cu(1)–P(1) 2.3061(13), Cu(1)···Cu(2) 2.9251(11), Cu(2)–O(2) 1.980(3), Cu(2)–P(4) 2.2087(12), Cu(2)–P(2) 2.2415(13); O(7)–Cu(1)–O(1) 85.49(10), O(7)–Cu(1)–P(3) 107.12(8), O(1)–Cu(1)–P(3) 129.27(8), O(7)–Cu(1)–P(1) 101.86(9), O(1)–Cu(1)–P(1) 101.70(8), P(3)–Cu(1)–P(1) 122.02(4), O(7)–Cu(1)–Cu(2) 157.33(8), O(1)–Cu(1)–Cu(2) 72.20(7), O(2)–Cu(2)–P(4) 126.33(9), O(2)–Cu(2)–P(2) 102.89(9), P(4)–Cu(2)–P(2) 130.28(4).

late ligands in a centrosymmetric cyclic arrangement (Fig. 3).

The carboxylate ligands are monodentate resulting in four three-coordinate Cu(I) centres. The Cu···Cu distance in **3** [Cu(1)···Cu(2A) 3.1193(18) Å] is slightly larger than the corresponding distance observed in **2** [Cu(1)···Cu(2) 2.9251(11) Å]. All the carboxylate groups in **3** are slightly twisted out of the plane defined by the naphthalene rings and all copper atoms Cu(1,2) are part of the macrocyclic arrangement. Presumably, the 1,3-dicarboxylato ligand in **1** favours a smaller macrocyclic arrangement in which Cu(2) is coordinated in the periphery of the molecule rather than being involved in ring formation. Bond lengths and angles of Cu atoms in **3** are similar to

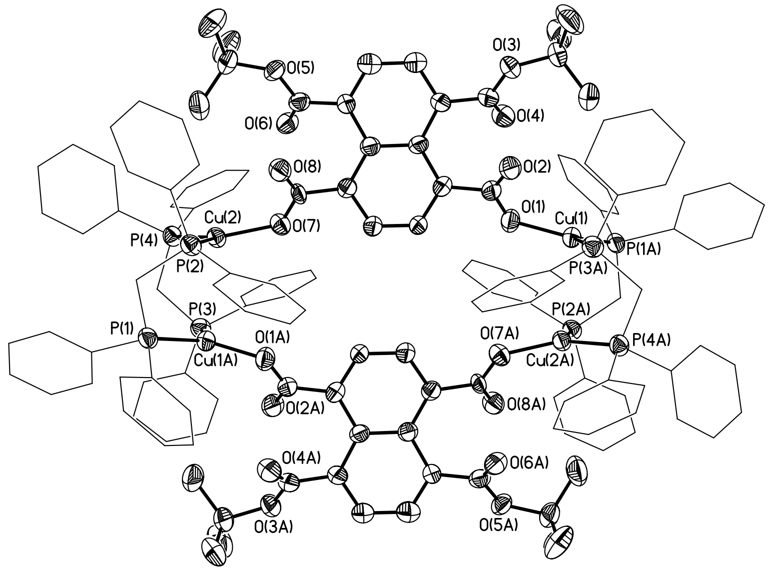


Fig. 3. Molecular structure of **3** in the solid-state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)···Cu(2A) 3.1193(18), Cu(1)–O(1) 1.947(6), Cu(1)–P(1A) 2.249(3), Cu(1)–P(3A) 2.246(3), Cu(2)–O(7) 1.983(7), Cu(2)–P(4) 2.242(2), Cu(2)–P(2) 2.254(3); O(1)–Cu(1)–P(1A) 117.2(2), O(1)–Cu(1)–P(3A) 116.7(2), P(1A)–Cu(1)–P(3A) 126.03(10) O(7)–Cu(2)–P(4) 118.4(2), O(7)–Cu(2)–P(2) 117.4(2), P(4)–Cu(2)–P(2) 123.82(10).

those observed in **2** and can be compared with corresponding values reported for Cu complexes in the literature [12–14]. The insertion reactions with the two organic dianhydrides and [CuO^{t}Bu] gave rise to the Cu(I) salts of 4,6-bis-Boc-isophthalic acid **2** and 5,8-bis-Boc-naphthyl-1,4-dicarboxylic acid **3** as the major products in these reactions (formed in yields of ca. 70% by fractionated crystallization) and the only products which could be obtained in pure form. It is assumed that byproducts in these reactions do not crystallize easily and that there might be a entropic preference for the formation of the ring architectures found in **2** and **3**.

The reactions of [CuO^{t}Bu] with dianhydrides represent a first step in our efforts to synthesize more complicated systems and indicate that the synthetic route chosen should be applicable to a variety of organic dianhydrides or polyanhydrides. Dianhydrides were so far mainly used as building blocks in condensation reactions with a variety of amines giving rise to supramolecular assemblies [17,18]. Also, hydrothermal syntheses with dianhydrides producing a range of transition metal complexes containing tetracarboxylato anions are reported [19].

Besides the extension of the synthetic route to dianhydrides, an initial aim of our investigation has also been the incorporation of other metal atoms than Cu into new complexes. This was achieved by metathesis reactions of a Cu(I) complex with transition metal salts. The first result of these efforts represents the metathesis reaction of [Cu(I)(*o*-Boc-benzoate)], obtained by the reaction of [CuO^{t}Bu] with phthalic acid anhydride, with $MnCl_2$ (Scheme 3, Fig. 4).

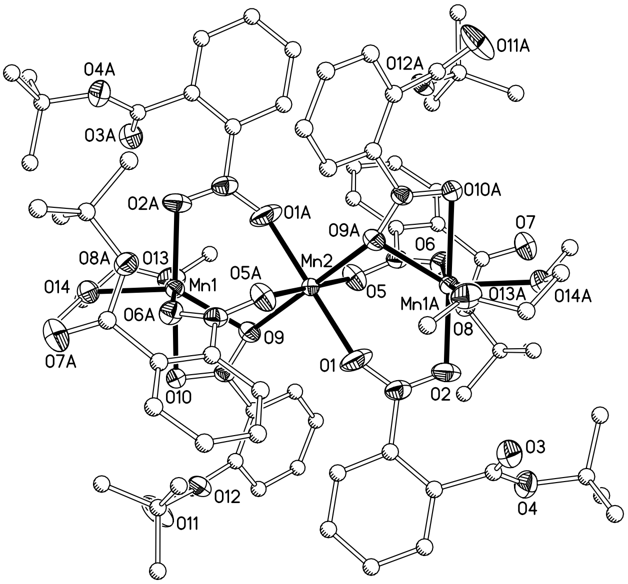
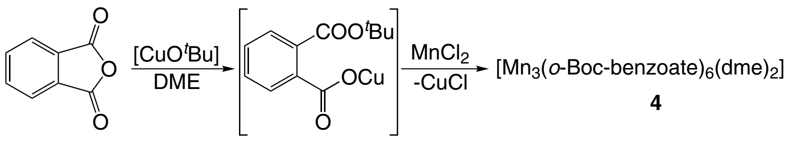


Fig. 4. Molecular structure of **4** in the solid-state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Mn–O(carboxylate) Mn(1)–O(6A) 2.090(2), Mn(1)–O(10) 2.366(2), Mn–O(DME) Mn(1)–O(14) 2.215(2) and Mn(1)–O(13) 2.285(2); O–Mn–O(*trans*) O(9)–Mn(1)–O(14) 138.83(8), O(6A)–Mn(1)–O(13) 169.73(8), O(2A)–Mn(1)–O(10) 164.12(9), O(5)–Mn(2)–O(5A) 180.00(10), O(1)–Mn(2)–O(1A) 180.000(1), O(9A)–Mn(2)–O(9) 180.000(1), O–Mn–O(*cis*) O(9)–Mn(1)–O(10) 57.06(7), O(2A)–Mn(1)–O(9) 118.50(9), O(1)–Mn(2)–O(9A) 86.29(9), O(1)–Mn(2)–O(9) 93.71(9).

[Mn_3(*o*-Boc-benzoate)$_6$(DME)$_2$] **4** is produced in good yield. The solid-state structure of **4** consists of a typical centrosymmetric arrangement of three octahedrally coordinated Mn atoms [20]. The Mn atoms are bridged by the carboxylate groups of the generated *o*-Boc-benzoato ligand with two DME ligands completing the coordination sphere of the terminal Mn atoms. Initially formed CuCl is insoluble in DME and was filtered off. Analogous reactions were also performed with $NiCl_2$, $CoBr_2$, and $FeBr_2$, giving isostructural complexes to **4**. The metathesis reactions involving Cu(I) complexes have proven to be a useful alternative to those of commonly employed alkali metal complexes. In contrast to alkali metal halides, all Cu(I) halides are insoluble in ethereal solvents. A different synthetic route to **4** represents the alcoholysis of phthalic acid anhydride with *tert*-butanol and the successive treatment with a mixture of $MnCl_2$/NEt_3.

4. Conclusions

The insertion reactions of organic anhydrides and [CuO^{t}Bu] produce Cu(I) carboxylate complexes when performed at low temperature or in the presence of tertiary phosphine ligands. This synthetic route is applicable to dianhydrides. Metathesis reactions of Cu(I) complexes obtained in these reactions with transition metal halides offer access to a large number of compounds, which will subsequently be tested for potential applications once their structural chemistry is further developed. A combinatorial approach to these compounds currently investigated is the alcoholysis of organic anhydrides and subsequent metallation by reactions with transition metal halides.



Scheme 3. Synthesis of **4** via a metathesis reaction of an intermediate Cu(I) complex.

5. Supplementary material

CCDC Nos. 271634–271637 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax: (internat.) +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

We thank Prof. Fenske for his support as well as the DFG (Center for Functional Nanostructures) and the Forschungszentrum Karlsruhe (A.R.) for funding.

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