# Reactions of Coinage Metal Salts with a Mixed Sulfonic/Carboxylic Acid Anhydride

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Dedicated to Professor Dieter Fenske on the Occasion of his 65<sup>th</sup> Birthday

**Abstract.** The synthesis and structures of four new compounds are reported.  $[Cu_2(2-sba)(dppm)_2]$  (1),  $[Ag_4(2-sba)_2(PPh_3)_4]$  (2),  $[Ag_2(2-sbaH)_2(PPh_3)_4]$  (3),  $[Ag(2-sbaH)(PPh_3)_3]$  (4) (2-sbaH<sub>2</sub> = 2-sulfobenzoic acid) were prepared by treatment of 2-sulfobenzoic

# Introduction

Mixed sulfonic/carboxylic acid derivatives have received a lot of attention as ingredients for microemulsions containing micelles as novel reaction containers [1, 2]. It has been demonstrated, that in these micelles, nanoscale particles can be formed with favourable size distribution [1, 2]. Recently, sulfonated carboxylic acids have also been used in an effort to generate porous coordination polymers [3-5]. In addition to metal phosphonate-based metalorganic frameworks, similar compounds containing metal sulfonates as building blocks are likely to emerge [6]. More commonly, sulfonic/carboxylic acid derivatives, e.g., 2-sulfobenzoic acid anhydride are used as reagents in stereoselective synthesis [7, 8] and only recently the 1-step dichlorination of 2-sulfobenzoic acid anhydride by PCl<sub>5</sub> has been reported [9]. To the best of our knowledge, however, no reactions between metal salts and compounds containing the structural fragment  $-SO_2-O-C(O)-$  have been reported. The investigation to be presented here adds on to previously reported work of reactions between perthio- and perselenophosphonic acid anhydrides [10-16] and describes reactions of 2-sulfobenzoic acid anhydride with coinage metal salts.

### **Results and Discussion**

When the late transition metal salts CuOtBu and  $AgO_2CMe$  are treated with 2-sulfobenzoic acid anhydride and tertiary phosphines the complexes 1-4 were obtained.

acid anhydride with metal salts under anhydrous conditions (1, 2) and in the presence of water (3, 4).

**Keywords:** Copper; Silver; Metal carboxylates; Metal alkoxides; Crystal structures; Mixed anhydrides



Scheme 1 Synthesis of 1-4 (MX = CuOtBu, AgO<sub>2</sub>CMe; 2-sbaH<sub>2</sub> = 2-sulfobenzoic acid; dppm = 1,2-*Bis*-diphenylphospinomethane). Possibly, traces of water were present in reactions leading to the formation of 3 and 4.

As a common theme of the reactions, the ring-opening of the acid anhydride was observed producing coinage metal complexes of the  $[2-sba]^{2-}$  and  $[2-sbaH]^-$  anions  $(2-sbaH_2 = 2-sulfobenzoic acid)$ . In the case of 1, the complex formed consists of the  $[2-sba]^{2-}$  anion which coordinates two Cu<sup>+</sup> ions. In the presence of the auxiliary ligand dppm crystals of 1 were obtained (Fig. 1, scheme 1). In the solid state Cu(1) is four-coordinated by the  $[2-sbaH]^-$  anion in chelating mode via O atoms of the sulfonato/carboxylato group and P(1,3) of two bridging dppm ligands. Cu(2) is surrounded by P(2,3) and  $\mu$ -O(4).

The reaction bears a remarkable resemblance to earlier investigations where di-*tert*-butylether was identified unequivocally as the leaving group in reactions of CuO*t*Bu with the perthiophosphonic acid anhydride  $[ArP(S)(\mu-S)]_2$ (Ar = 4-anisyl) [12]. **1** represents the first mixed sulfonate/ carboxylate salt obtained under anhydrous conditions. The new reaction presented here may offer a very convenient route to novel metal complexes and it is currently probed if solvent can be excluded entirely.

In order to probe the broader applicability of the concept to open up mixed sulfonic/carboxylic acid anhydrides by generating volatile leaving groups, a number of metal carboxylates were treated with 2-sulfobenzoic acid anhydride. In the case of AgO<sub>2</sub>CMe this resulted in the formation of



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Figure 1 Molecular structure of 1 in the solid state.

Selected bond lengths /Å and angles /°: S(1)-O(1) 1.447(3), S(1)-O(2) 1.450(3), S(1)-O(3) 1.463(3), Cu(1)-O(3) 2.085(3), Cu(1)-O(4) 2.130(3), Cu(1)-P(1) 2.2251(12), Cu(1)-P(3) 2.2457(13), Cu(2)-P(2) 2.2359(13), Cu(2)-P(4) 2.2263(13), Cu(2)-O(4) 2.025(3), O(3)-Cu(1)-O(4) 91.84(11), O(3)-Cu(1)-P(1) 116.36(9), O(4)-Cu(1)-P(1) 102.33(10), O(3)-Cu(1)-P(3) 110.349(9), O(4)-Cu(1)-P(3) 110.15(9), P(1)-Cu(1)-P(3) 126.98(5), O(4)-Cu(2)-P(4) 105.52(10), O(4)-Cu(2)-P(2) 107.84(10), P(4)-Cu(2)-P(2) 145.56(5).

**2** (Fig. 2, scheme 1). As volatile leaving group acetic acid anhydride was formed (verified by  $^{13}$ C NMR of the mother liquor; scheme 2).

$$2 \underbrace{\bigcirc}_{0} + 4 \operatorname{AgOAc} \xrightarrow{\operatorname{PPh_3}}_{\operatorname{CH_2Cl_2}} \operatorname{[Ag_4(2-sba)_2(PPh_3)_4]} + 2\operatorname{Ac_2O}}_{\mathbf{2}}$$

Scheme 2 Detailed synthesis of 2  $(2-sbaH_2 = 2-sulfobenzoic acid)$ .

In the solid state 2 exists as a centrosymmetric dimer of  $[Ag_2(2-sba)(PPh_3)_2]$  units held together by  $\mu_2$ -O(4) and  $\mu_3$ -O(1). Ag-O and Ag-P distances found in 2 are similar to distances found in related phosphine-stabilised Ag<sup>I</sup> sulfonates [17-22]. Despite the clear-cut synthesis of 2 correct elemental analysis could not be obtained indicating that there are several metal complexes formed with different ratios phosphine: Ag. Only 2, however, could be characterized by X-ray crystallography. The multidentate nature of the  $[2-sba]^{2-}$  anion promises a rich coordination chemistry of mixed sulfonate/carbolxylate ligands in future. Here the preparation of 1 and 2 illustrates a new synthetic route to these species. The fact that a metal alkoxide or a metal carboxylate can generate a volatile leaving group (ether or anhydride), when treated with a mixed sulfonic/carboxylic acid anhydride, indicates a potentially broader applicability of the synthetic concept (the formation of di-tert-butylether or acetic anhydride is believed to represent the thermodynamic driving force for the reactions).

Hydrolysis of 2-sulfobenzoic acid anhydride, treatment with AgO<sub>2</sub>CMe and crystallization under different con-



Figure 2 Molecular structure of 2 (phenyl groups of triphenylphosphine ligands are omitted; symmetry operation (A) -x+1, -y+1, -z+1).

Selected bond lengths /Å and angles /°: S(1)-O(1) 1.493(3), S(1)-O(2) 1.445(2), S(1)-O(3) 1.451(3), Ag(1)-O(1) 2.444(2), Ag(1)-O(4) 2.268(3), Ag(1)-O(1A) 2.580(3), Ag(2)-O(4A) 2.167(2), Ag(2)-O(1) 2.491(3), Ag(1)-P(1) 2.3518(12), Ag(2)-P(2) 2.3390(11), O(4)-Ag(1)-P(1) 143.02(7), O(4)-Ag(1)-O(1) 80.99(9), P(1)-Ag(1)-O(1) 126.37(7), O(4)-Ag(1)-O(1A) 130.80(7), O(1)-Ag(1)-O(1A) 80.46(9), O(4A)-Ag(2)-P(2) 155.17(6), O(4A)-Ag(2)-O(1) 75.39(9), P(2)-Ag(2)-O(1) 126.64(6).

ditions gave rise to **3** and **4**. In the solid state **3** exists as a dimer of two  $[Ag(2-sbaH)(PPh_3)_2]$  units (Fig. 3). The two units are connected by two moderate hydrogen bonds between O(5) and O(2A) and between symmetry-related O atoms (distance O(5)···O(2A) 2.624(3) Å) [23]. In the <sup>1</sup>H NMR spectrum a resonance for hydrogen-bonded protons was observed at 14 ppm and in the crystal structure hydrogen atoms were fixed in calculated positions.



Figure 3 Molecular structure of 3 (phenyl groups of triphenylphosphine ligands are omitted; symmetry operation (A) -x+1, -y+1, -z+1).

Selected bond lengths /Å and angles /°: S(1)-O(1) 1.466(2), S(1)-O(2) 1.467(2), S(1)-O(3) 1.447(2), Ag(1)-O(1) 2.373(2), Ag(1)-O(4) 2.524(2), Ag(1)-P(1) 2.4464(7), Ag(1)-P(2) 2.4387(7),  $O(5)\cdots O(2A) 2.624(3)$ , O(1)-Ag(1)-P(2) 125.17(6), O(1)-Ag(1)-P(1) 95.20(5), P(2)-Ag(1)-P(1) 127.45(2), O(1)-Ag(1)-O(4) 88.84(7), P(2)-Ag(1)-O(4) 93.33(5), P(1)-Ag(1)-O(4) 122.51(6).



**Figure 4** Molecular structure of **4** (phenyl groups of triphenyl-phosphine ligands are omitted).

Selected bond lengths /Å and angles /°: S(1)-O(3) 1.473(10), S(1)-O(4) 1.443(10), S(1)-O(5) 1.447(9), Ag(1)-P(1) 2.543(2), Ag(1)-P(2) 2.563(2), Ag(1)-P(3) 2.546(3), Ag(1)-O(1) 2.559(11), O(3) $\cdots$ O(2) 2.491(13), P(1)-Ag(1)-P(3) 115.46(9), P(1)-Ag(1)-O(1) 99.4(2), P(1)-Ag(1)-P(2) 117.25(6), P(3)-Ag(1)-O(1) 117.5(2), P(3)-Ag(1)-P(2) 113.63(9), O(1)-Ag(1)-P(2) 90.3(2).

The Ag atom in **3** is chelated by an O atom of the sulfonato and carboxyl group. Coordination of two PPh<sub>3</sub> ligands completes the distorted tetrahedral coordination sphere of Ag(1). A slightly modified work-up produced **4** in moderate yield. In contrast to **3** intramolecular strong hydrogenbonding is observed in **4** (distance O(3)...O(2) 2.491(13) Å). O(1) of the carboxylato ligand and P atoms of three PPh<sub>3</sub> ligands are coordinated to Ag(1) in distorted tetrahedral arrangement.

Future work will attempt to extend the investigations to other metals and in particular to make use of mixed sulfonic/carboxylic acid anhydrides as novel building blocks for coordination polymers.

# **Experimental Section**

All operations were carried out in an atmosphere of purified dinitrogen. Solvents were dried over appropriate drying agents and freshly distilled. CuOtBu was synthesized according to a published procedure [24].

1: A mixture of 184 mg (1.00 mmol) 2-sulfobenzoic acid cyclic anhydride and 136 mg (1.00 mmol) CuOtBu was dissolved in 12 mL toluene (or DME). The yellow solution was heated for 5 minutes under reflux. A solution of 385 mg (1.0 mmol) dppm in 5 mL toluene was added and the mixture stirred for 2 h. Toluene (or DME) was removed under reduced pressure. Addition of  $CH_2Cl_2$  (4 mL) and pentane (5 mL) at room temperature and storage of the solution for four days produced colorless crystals of 1. 0.3 g, yield 53 %; mp 160 °C (decomposition); Found: C, 60.79; H, 4.27 %.  $2C_{57}H_{48}Cu_2O_5P_4S \cdot CH_2Cl_2$  requires C, 60.66; H, 4.34 %.

**IR** (KBr): v(CH) 3051 s, 2917 m, v(COO) 1615 s, 1486 s, v(C-H of PPh) 1434 s, v(S-O) 1360 s, v(S-O) 1167 s, 1008 s, 848 s, 608 s cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta = 8.36-7.77$  (4H, m, ArH), 7.1~7.5 (40H, m, ArH), 5.34 (s, *CH*<sub>2</sub>*Cl*<sub>2</sub>), 3.16 (4H, br, *CH*<sub>2</sub>); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, 25 °C, 65 % H<sub>3</sub>PO<sub>4</sub>)  $\delta = -9.8$ .

**2**: A mixture of 184 mg (1.0 mmol) 2-sulfobenzoic acid cyclic anhydride and 167 mg (1.0 mmol) AgO<sub>2</sub>CMe was dissolved in 4 mL

toluene (the experiment was also performed using  $D_6$ -benzene in order to confirm the formation of acetic anhydride). The cloudy solution was stirred for 3 hours, and then 524 mg (2.0 mmol) PPh<sub>3</sub> was added. The resulted colorless solution was stirred for overnight and  $D_6$ -Benzene was removed. Addition of CH<sub>2</sub>Cl<sub>2</sub> (8 mL) and pentane (13 mL) at room temperature for one week produced colorless crystal **2**. 0.28 g, yield 60 %; mp 218 °C; despite repeated attempts, correct elemental analysis could not be obtained indicating that possibly byproducts with different phosphine:Ag ratio are formed.

IR (KBr): v(CH) 3055 s, v(CO) 1662 s, 1477 s, v(C-H of PPh) 1434 s, v(S-O) 1327 s, v(S-O) 1158 s, 973 s, 844 m, 745 s cm  $^{-1}$ .

**3**: A mixture of 184 mg (1.00 mmol) 2-sulfobenzoic acid cyclic anhydride and 167 mg (1.00 mmol)  $AgO_2CMe$  was dissolved in 8 mL THF and 1 mL of a standard solution of water in THF (1 mol/L). The cloudy solution was stirred for 5 hours, and then 524 mg (2.00 mmol) PPh<sub>3</sub> was added. The colorless solution was stirred 12 h. Storage of the solution at room temperature for one week produced colorless crystals of **3**. 0.51 g, yield 61 %; mp 120 °C; Found: C, 62.01; H, 4.55 %. C<sub>43</sub>H<sub>35</sub>AgO<sub>5</sub>P<sub>2</sub>S requires C, 61.95; H, 4.23 %.

**IR** (KBr): v(CH) 3059 s, 2981 s, v(OH) 2623 m, v(CO) 1705 s, 1478 s, v(C-H of PPh) 1438 s, v(S-O) 1367 s, v(S-O) 1167 s, 1017 s, 899 s, 749 s cm<sup>-1</sup>; <sup>1</sup>H **NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 14.16 (1H, s, br, OH), 7.98-7.82 (4H, m, ArH), 7.3~7.5 (30H, m, ArH), 5.33 (2H, s, *CH*<sub>2</sub>*Cl*<sub>2</sub>); <sup>31</sup>P **NMR** (162 MHz, CDCl<sub>3</sub>, 25 °C, 65 % H<sub>3</sub>PO<sub>4</sub>)  $\delta$  = 11.6.

**4**: The preparation follows the procedure described for **3**. Addition of  $CH_2Cl_2$  (5 mL) and pentane (9 mL) at room temperature followed by storage of the reaction mixture for three days produced colorless crystals of **4**. 0.53 g, yield 67 %; mp 130 °C; Found: C, 62.93; H, 4.23 %.  $C_{61}H_{50}AgO_5P_3S \cdot CH_2Cl_2$  requires C, 63.03; H, 4.44 %.

**IR** (KBr): v(ArH) 3056 s, v(OH) 2604 m, v(CO) 1702 s, 1658 s, 1481 s, v(C-H of PPh) 1434 s, v(S-O) 1376 s, v(S-O) 1163 s, 1001 s, 746 s cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 14.40 (1H, s, OH), 8.00-7.85 (4H, m, ArH), 7.3~7.4 (45H, m, ArH), 5.33 (2H, s, *CH*<sub>2</sub>*Cl*<sub>2</sub>); <sup>31</sup>**P NMR** (162 MHz, CDCl<sub>3</sub>, 25 °C, 65 % H<sub>3</sub>PO<sub>4</sub>)  $\delta$  = 10.9.

# X-ray Crystallographic Study

Data for 1-4 were collected on STOE (IPDS II and STADI IV) diffractometers using graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  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 [25]. Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. Disordered components were refined with isotropic thermal parameters. A summary of crystal data and refinement parameters is given in table 1.

CCDC nos. 649058-649061 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].

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Compound	1	2	3	4
Formula	C <sub>60</sub> H <sub>54</sub> Cl <sub>6</sub> Cu <sub>2</sub> O <sub>5</sub> P <sub>4</sub> S	$C_{86}H_{68}Ag_4O_{10}P_4S_2$	C47H43AgO6P2S	C <sub>61</sub> H <sub>50</sub> AgO <sub>5</sub> P <sub>3</sub> S
Formula weight	1350.75	1880.88	905.68	1095.85
T/K	200(2)	150(2)	100(2)	150(2)
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	P21/c	$P\overline{1}$	$P\overline{1}$	Pbca
alÅ	12.861(3)	12.064(2)	12.4353(6)	19.729(4)
b/Å	20.043(4)	13.310(3)	13.0267(7)	20.415(4)
c/Å	23.815(5)	13.901(3)	14.4157(8)	24.949(5)
$\alpha /^{\circ}$	~ /	69.52(3)	81.829(4)	
βl°	100.65(3)	69.15(3)	87.077(4)	
ν/°		66.99(3)	61.620(4)	
V/Å <sup>3</sup>	6033(2)	1861.5(6)	2033.33(19)	10049(3)
Ζ	4	1	2	8
$\mu/\mathrm{mm}^{-1}$	1.159	1.241	0.676	0.591
F(000)	2760	944	932	4512
Reflections collected	12873	13046	16183	12962
Unique data	10218	7555	8248	6343
R <sub>int</sub>	0.0188	0.0666	0.0389	0.0738
Parameters	703	478	515	227
$w\mathbf{R}_2$ (all data)	0.1766	0.1374	0.1166	0.2138
$R_1 [I > 2\sigma(I)]$	0.0514	0.0477	0.0382	0.0723

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

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