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Novel Silver Cobaltacarborane Complexes with a Linearly Bridging Halide

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Great attention has been paid to halide coordination chemistry, not only because it constitutes the fundamentals of inorganic chemistry, but because the versatile coordination abilities of halides can be used to construct many interesting polynuclear complexes, which include halide-bridged inorganic polymers,[1] halide-capped metal clusters,[2,3] halide-templated polynuclear assemblies,[3,4] and anionic guests.[5] The structural versatility of halides mainly originates from their coordinating abilities of adopting a bridging bond between two or more metal atoms, as well as a terminal bond. Moreover, a halide bridging bond angle is so flexible that thermodynamic stability can be endowed with proper geometry, which conceptually varies from acute to right, obtuse, and linear.

In spite of innumerable reports on molecular metal halides, examples of the linearly bridging fashion are very scarce. The reason for the rarity of the linear M–X–M arrangement can be easily explained by the VSEPR (Valence Shell Electron Pair Repulsion) concept. The linear M–X–M formation has only been achieved by adopting a macrocyclic chelate ligand, which is structurally demanding, so that the VSEPR repulsions among lone-pair electrons on the halide atom could be overcome.[6]

In the synthetic exploration of new cobaltacarboranes, we found an unexpected ionic product comprising a cation with a linear Ag–X–Ag arrangement. At first, we attempted a reaction between $Tl_2C_2B_9H_{11}$ and $CoCl_2(PPh_3)_2$, mimicking the previously reported preparation of a nickellacarborane, [3,3-$(PPh_3)_2$–3,1,2–$NiC_2B_9H_{11}$].[7] We found that a new cobalt complex of dicarbollide was generated, but no more information could be obtained. Treatment of the product mixture with $AgBr(PPh_3)_3$ afforded a cationic $[L_3Ag–X–AgL_3]^+$ (L = triphenylphosphine) with **CoSAN** as a counterion (**CoSAN** = [3,3-*commo*-3,1,2-$Co(C_2B_9H_{11})_2$]).

Although linear Ag–X–Ag could be achieved, the reaction result was not well reproducible, nor was its mechanism reasonable. Hence, we directed the preparation of the linear complexes in a rationalized synthetic manner, as depicted in the following reaction equation:

$$Cs{\cdot}\mathbf{CoSAN} + 2\ MX(PPh_3)_3 \rightarrow \mathbf{CoSAN}{\cdot}[(Ph_3P)_3M–X–M(PPh_3)_3] + CsX$$

where M = Cu, Ag, and X = Cl, Br. $CuX(PPh_3)_3$ was incorporated as isolated forms that were purchased (for X = Cl) or prepared (for X = Br),[8] since adduct formation was not available at room temperature for Cu, whereas $AgX(PPh_3)_3$ was generated *in situ* from 1:3 stoichiometric reactions between AgX and PPh_3 in dichloromethane. Solutions of these group 11 sources were reacted by addition to a slurry of Cs·**CoSAN** in dichloromethane.[9]

In the case of the reaction system of $CuX(PPh_3)_3$/Cs·**CoSAN**, the result was always the same, in that only a cationic homoleptic phosphine complex was produced, regardless of the choice of X and of the use of molar ratios such as 1:1 and 1:2 between the reactants. The ^{1}H NMR spectrum of the recrystallized product shows that the integral ratio of phenyl C–*H* peaks and carboranyl C–*H* of the **CoSAN** is 45:4, suggesting that the product has a stoichiometric formula of **CoSAN**·[$Cu(PPh_3)_3$] (**CoSAN**·**1**). (see Figure S1 in supporting material). Several efforts afforded only irregular shaped crystals, with quality far from suitable for X-ray structure determination, so the unusual 3-coordinate structure could not be assured in the solid state.

Different results were obtained in the case of silver. Crystalline yellow-orange solids were obtained from 2:1 reactions of $AgX(PPh_3)_3$ and Cs·**CoSAN**. The observation of a 1:3 (= 2:6) ratio between the C_2B_9 cage and PPh_3 ligand in the ^{1}H NMR spectra (see Figures S2 and S3 in the supporting materials) coincided with the expected chemical formula of **CoSAN**·[$(Ph_3P)_3Ag–X–Ag(PPh_3)_3$] (**CoSAN**·**3a**, X = Cl; **CoSAN**·**3b**, X = Br).[10,11] Variation of the reaction molar ratio to 1:1 between Cs·**CoSAN** and $AgBr(PPh_3)_3$ resulted in the formation of the monometallic **CoSAN**·[$Ag(PPh_3)_4$] (**CoSAN**·**2**). This result was confirmed by the 1:2 (= 2:4) ratio between the C_2B_9 cage and PPh_3 in the ^{1}H NMR spectrum of the solution of the recrystallized product (see Figure S4 in the supporting material). This result differs from that with copper in the number of coordinated phosphines. However, the formulation coincides with Tolman's prediction that $[AgL_3]^+$ is unstable and $[AgL_4]^+$ is preferred for L = PPh_3 according to the cone angle concept.[12] Hence, the use of a molar ratio between silver and **CoSAN** determines which of monometallic or dimetallic cationic species will be produced, implying no preferential formation of dimetallic **3** over that of monomtallic **2**, or *vice versa*.

The solid-state molecular structures of compounds

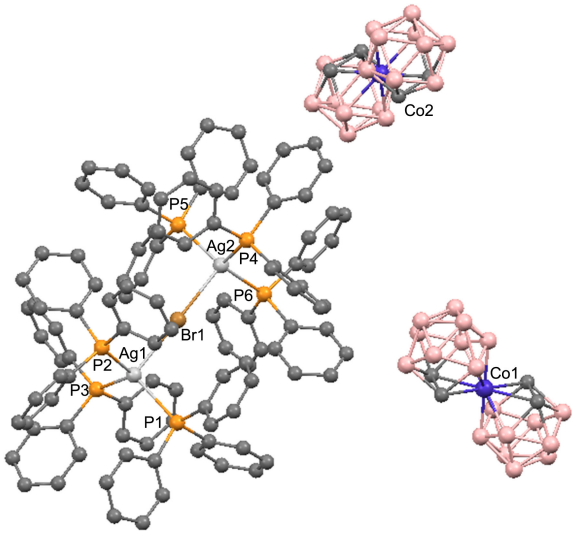

Figure 1. Crystal structure of **CoSAN·3a** showing the selected atom-numbering.

CoSAN·3a and **CoSAN·3b** were characterized by single-crystal X-ray diffraction study.[13] Both **CoSAN·3a** and **CoSAN·3b** crystallized in space groups $P\bar{1}$, and their structures were essentially iso-structural and featured ionic compounds, which consist of cationic $[(Ph_3P)_3Ag–X–Ag(PPh_3)_3]$ and a **CoSAN** anion. In the cations, three PPh_3 groups coordinated to one silver atom are staggered to those of the other, and the phenyl rings are oriented in such a way that the cations have pseudo-S_6 symmetry. Ag–X–Ag shows almost perfect linearity with angles of 178.88(3) and 178.32 (2)° for X = Cl and Br, respectively. The Ag–X distances were 2.785 (X = Cl) and 2.833 Å (X = Br), which are longer than those found in bent bridges such as Ag–X's in $[Ag_2X_2(PPh_3)_3]·2CHC1_3$.[14] The result poses the first examples of a linear bridging halide without the assistance of a sterically demanding and robust macrocyclic chelate ligand.

Supporting Information. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-943856 (**CoSAN·3a**) and 943857 (**CoSAN·3b**)). These data can be obtained free of charge *via* http:// www.ccdc.cam.ac.uk/conts/retrieving.html.

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10. **CoSAN·3a** (yield: 72%) IR (KBr, cm^{-1}): ν(B–H) = 2540 (br, vs). ^{1}H NMR ($CDCl_3$) δ 4.05 (s, 4H), 7.30-7.36 (m, 18H), 7.08-7.15 (m, 72H), 5.28 (s, solvated CH_2Cl_2), 1.24-1.32 (m, solvated pentane), 0.87 (t, solvated pentane). Anal. Calcd. for $C_{112}H_{112}ClAg_2B_{18}CoP_6CH_2Cl_2$: C, 60.76; H, 5.14; Found: C, 61.20; H, 4.94.
11. **CoSAN·3b** (yield: 12%) IR (KBr, cm^{-1}): ν(B–H) = 2558 (br, vs). ^{1}H NMR ($CDCl_3$) δ 4.04 (s, 4H), 7.30-7.36 (m, 18H), 7.10-7.20 (m, 72H), 5.28 (s, solvated CH_2Cl_2), 1.24-1.32 (m, solvated pentane), 0.87 (t, solvated pentane). Anal. Calcd. for $C_{112}H_{112}BrAg_2B_{18}CoP_6$: C, 61.34; H, 5.15; Found: C, 61.91; H, 4.94.
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13. Crystal data: **CoSAN·3a**, M = 2148.54, triclinic, space group $P\bar{1}$, a = 14.6071(2) Å, b = 14.6304(2) Å, c = 28.9886(5) Å, α = 88.5820 (10)°, β = 86.7080(10)°, γ = 88.9870(10)°, V = 6182.15(16) $Å^3$, Z = 2, d_{calc} = 1.154 g/cm^3, F(000) = 2204, 30609 unique, 1268 parameters, R_1 = 0.0459, wR_2 = 0.1402 (22316, I > 2σ(I)), GOF = 1.020, Crystal data for **CoSAN·3b**, M= 2193.00, triclinic, space group $P\bar{1}$, a = 14.4360(5) Å, b = 14.4603(5) Å, c = 28.5483(10) Å, α = 85.678(2)°, β = 88.149(2)°, γ = 88.687(2)°, V = 5938.1(4) $Å^3$, Z = 2, d_{calc} = 1.227 g/cm^3, F(000) = 2240, 20715 unique, 1264 parameters, R_1 = 0.0665, wR_2 = 0.2250 (17767, I > 2σ(I)), GOF = 0.999, Data were collected on a Bruker Apex II-CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full matrix least squares based on F^2 using SHELXL 97.
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