Hexahydro-*closo*-hexaborate as a Ligand in Coordination Compounds: Syntheses and Crystal Structures of $[M_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]$ (M = Cu, Au)

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By reaction of $(PPh_3)_3CuCl$ and PPh_3AuCl with $[B_6H_6]^{2-}$ in organic media, dinuclear complexes are formed containing the hexaborate as a bridging ligand coordinated to the metal centers by opposite B_3 facets of the B_6 cluster in a trihapto mode. This is verified by single-crystal X-ray structural analysis of the isotypical ($Pa\bar{3}$) compounds $[Cu_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]$ (**1**) and $[Au_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]$ (**2**) which showed the metal centers to be very close to the B_3 plane [1.92 (**1**), 2.10 (**2**) Å]. The ^{11}B NMR spectra of the two compounds feature doublets, at $\delta = -15.32$ in **1** and at -11.51 in **2**, which are significantly shifted downfield in comparison to $[B_6H_6]^{2-}$ ($\delta = -17.2$).

In recent years many derivatives of the smallest and moderately stable hexahydro-*closo*-borate $[B_6H_6]^{2-}$ have been synthesized. However, only a few examples have been published in which the dianion is coordinated to metal centers. Single-crystal X-ray structural analysis of $Pb(bipy)B_6H_6$[1] has revealed that the environment of the central lead ion is formed by the bidentate bipy molecule, one *closo*-$[B_6H_6]^{2-}$ anion coordinated via a facet (Pb–B: 2.79–2.93 Å) and by two more distant $[B_6H_6]^{2-}$ anions coordinated via edges (Pb–B: 3.17–3.39 Å). In the structure of the recently described $(PPh_4)[Hg(\eta^3\text{-}B_6H_6)Ph]$[2], the mercury (II) cation is coordinated by the hexaborate anion in an η^3 fashion with the short distance to the B_3 plane being 2.17 Å.

We now report the synthesis of the new type of coordination compounds $[M_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]$ (M = Cu, Au). By X-ray diffraction analysis, it has been confirmed that the hexaborate functions as a bridging ligand, coordinated to the metal centers with two opposite B_3 facets in a symmetrical η^3 fashion. The new compounds have been further characterized by ^{11}B-NMR investigations.

Results and Discussion

Reaction of $(Bu_4N)_2[B_6H_6]$ with $(PPh_3)_3CuCl$ in an organic medium led to **1**, which was isolated as an off-white solid soluble in dichloromethane and acetonitrile.

$$(Bu_4N)_2[B_6H_6] + 2\,(PPh_3)_3CuCl \rightarrow [Cu_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]\ (\mathbf{1}) + 4\,PPh_3 + 2\,(Bu_4N)Cl$$

Analogously, treatment of $(Bu_4N)_2[B_6H_6]$ with PPh_3AuCl afforded **2**.

$$(Bu_4N)_2[B_6H_6] + 2\,PPh_3AuCl \rightarrow [Au_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]\ (\mathbf{2}) + 2\,(Bu_4N)Cl$$

The initially colourless solution turned yellow-brown and **2** was purified by column chromatography. The off-white solid was found to be soluble in dichloromethane, air-sensitive and thermally unstable. By slow diffusion of pentane and petroleum ether into solutions of **1** and **2** in dichloromethane, single crystals suitable for X-ray structure determinations were obtained. Both complexes are isotypical, crystallizing in the space group $Pa\bar{3}$ with similar cell parameters and with the expected increase in cell volume on going from **1** to **2** (4796.9 and 4956.5 Å^3, respectively). The crystal data parameters are summarized in Table 1. The representative molecular structure of the copper complex (**1**), with atom labelling, is shown in Figure 1, while Figure 2 depicts the molecular packing.

Figure 1. ORTEP[21] plot of the molecular structure of **1** in the crystal (50% probability thermal ellipsoids), **1**, M = Cu, **2**, M = Au; symmetry operations used to generate equivalent atoms: #1 $-z+1, x-1/2, -y+1/2$; #2 $y+1/2, -z+1/2, -x+1$; #3 $-y+3/2, z+1/2, x-1$; #4 $z+1, -x+3/2, y-1/2$

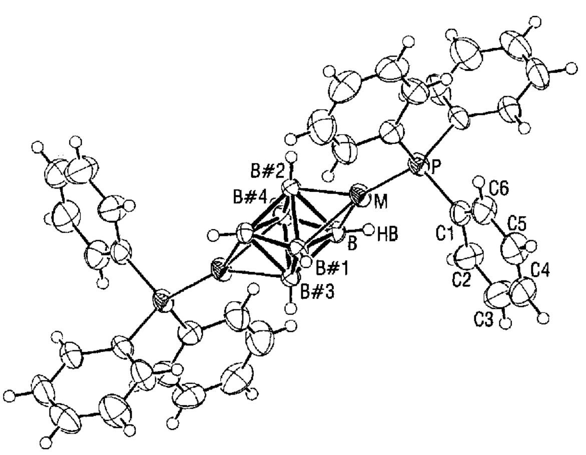

Figure 2. Molecular packing of **1** (for clarity with C1, C2 and C6 of the phenyl rings)

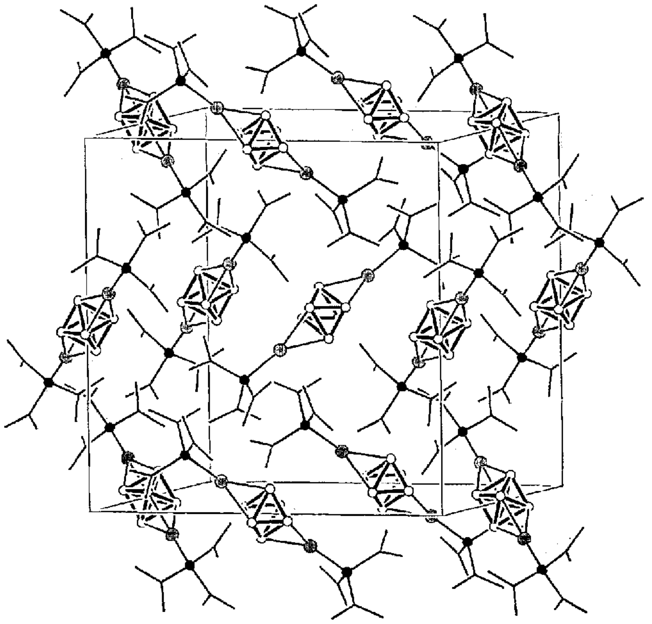

Table 1. Crystal data and refinement details for compounds **1** and **2**

compound	1	2
Formula	$C_{36}H_{36}B_6Cu_2P_2$	$C_{36}H_{36}Au_2B_6P_2$
Mol. mass	722.52	989.40
Cryst. system	cubic	cubic
Space group	$Pa\bar{3}$	$Pa\bar{3}$
a [Å]	16.865(5)	17.050(5)
V [Å^3]	4796.9	4956.5
Z	4	4
$d_{calcd.}$ [g cm^{-3}]	1.000	1.326
μ [mm^{-1}]	0.972	5.996
F(000)	1480	1880
T [K]	293	293
2σ [°]	4 - 50	4 - 50
Refl. collect.	4180	4339
Refl. indep.	1404	1456
Parameter	75	72
R1	0.0565	0.0419
wR2	0.2296	0.1252
GOF	1.379	1.171

Table 2. Selected bond lengths [Å] and bond angles [°] of **1** and **2**

	M = Cu	M = Au
M-P	2.170(3)	2.249(3)
M-B	2.178(6)	2.346(8)
M-HB	2.26(7)	2.646(10)
P-C1	1.815(7)	1.805(9)
B-B#1	1.787(12)	1.808(14)
B-B#3	1.683(11)	1.671(13)
B-HB	0.87(7)	1.028(13)
P-M-B	151.7(2)	153.6(2)
B-M-B#1	48.4(3)	45.3(3)
P-M-HB	129(2)	130.9(2)
B-M-HB	22(2)	22.7(3)
B#1-M-HB	68(2)	64.2(3)
C1-P-M	112.5(2)	111.4(3)
B#1-B-B#2	60	60
B#3-B-B#1	57.9(3)	57.2(3)
B#3-B-B#4	64.1(5)	65.5(6)
B#4-B-B#2	57.9(3)	57.2(3)
M-B-HB	84(5)	95.3(7)

In both complexes the metal atoms display a strongly distorted tetrahedral environment of three boron atoms and one phosphorus atom. The angles B−Cu−B 48.4° and P−Cu−B 151.7° in **1** and B−Au−B 45.3° and P−Au−B 153.6° in **2** represent the major deviations from tetrahedral geometry. The bond lengths within the $MPPh_3$ groups of both compounds are comparable and fall in the normal range (Table 2).

The copper atom lies only 1.92 Å above the B_3 facet. Thus, the Cu−H distances in **1** of 2.26 Å are longer than the short Cu−B distances 2.178 Å, similar to the situation in $[Cu(\eta^2\text{-}B_5H_8)(PPh_3)]$ with values of 2.33−2.76 and 2.22 Å, respectively[3]. In contrast, compounds with Cu−H−B bridges display substantially shorter Cu−H bond lengths than Cu−B distances, as has been observed in $[Cu(BH_4)(PPh_3)_2]$ with 2.02 and 2.18 Å[4] and in $[Cu(B_3H_8)(PPh_3)_2]$ with 1.84 and 2.30 Å[5], respectively. In $[(PPh_3)_2Cu_2B_{10}H_{10}]\cdot CHCl_3$, the $[B_{10}H_{10}]^{2-}$ dianion acts as a bidentate chelate linked to Cu(I) via two hydrogen bridges with Cu−H distances of 1.86 Å ($H_{equatorial}$) and 2.08 Å (H_{axial}), and a Cu−B distance of 2.30 Å[6]. Comparably short **M−B** bonds to those in **1** were also found for **2**. To date, there have been no reports on the coordination of gold compounds with *closo*-borates but there have been some with *nido*-borates. In $\{5,6\text{-}\mu\text{-}[AuP(C_6H_4Me\text{-}2)_3]\text{-}nido\text{-}B_{10}H_{13}\}$[7] the average Au−B distance of 2.29 Å is close to the Au−B distance of 2.346 Å found in **2**. Thus, the gold atom in **2** lies only 2.10 Å above the B_3 facet and, analogous to the situation in the copper complex **1**, the Au−B distances are shorter than the Au−H distances of 2.646 Å. The influence of the metal atoms on the geometry of the boron clusters is shown by an expansion of the metal-bonded facets, the B−B distances in which are about 6% longer than those between neighbouring boron atoms belonging to the opposite facets.

The ^{11}B-NMR spectra of the two complexes exhibit only one doublet in each case, indicating the magnetic equivalence of all B nuclei. As a result of coordination to metal centers a downfield shift and a concomitant decrease of the coupling constant $^1J_{BH}$ is observed: $\delta = -15.32$ [128 Hz] (**1**), $\delta = -11.51$ [114 Hz] (**2**), compared to $\delta = -17.2$ [145 Hz] in the free $[B_6H_7]^-$ ion.

The IR and Raman spectra of **1** and **2** show strong bands from the triphenylphosphine group such that the assignment of modes in the framework area below 1100 cm^{-1} is not possible. The BH stretching vibrations, observed for $(Bu_4N)_2[B_6H_6]$ at $\tilde{\nu} = 2414$ cm^{-1}[8], are shifted to higher energy, appearing as strong but broad IR bands for **1** at $\tilde{\nu} = 2445$ cm^{-1}, and for **2** at $\tilde{\nu} = 2473$ cm^{-1}. The protonated $[B_6H_7]^-$ anion exhibits ν(BH) bands in the region of 2530 cm^{-1}[8].

At first glance the formation and stability of the reported metal complexes with hexaborate anions as ligands seems somewhat surprising. However, calculations on the electronic structure of B_6 clusters using an Electron Localization Function (ELF)[9] have revealed that there is a maximum of electron density above the octahedral facets. Therefore, in substitution reactions, electrophilic attack in these areas has been discussed[10,11]. The basic character of the $[B_6H_6]^{2-}$ ion is evident from its easy protonation to give $[B_6H_7]^-$. The additional proton, which is delocalized over the whole structure of the anion at ambient temperature, becomes fixed above a facet on cooling below the coalescence temperature of −80 °C[12]. This is also found in protonated monosubstituted derivatives of the type $[B_6H_6X]^-$, X = Cl, Br, I, alkyl[13–15]. The decomposition of $[B_6H_7]^-$ in acidic solution (pH < 6) may be explained by a second protonation step, yielding the hypothetical $[B_6H_8]$ which is unstable due to excessive withdrawal of electron density from the B_6 skeleton by the two very "hard" H^+ ions. However, as is demonstrated in **1** and **2**, $[B_6H_6]^{2-}$ may be coordinated to two formally singly-charged metal ions, which, unlike H^+ are soft Lewis acids. The different polarization of the 4-center, 2-electron bonds by the metal centers is evident from the ^{11}B-NMR and IR spectra. Due to the deshielding of the ^{11}B nuclei increasing from the copper to the gold complex, the aforementioned downfield shift is observed.

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Experimental Section

All reactions were carried out in dried solvents. The hexahydro-*closo*-hexaborate was prepared by a standard procedure[8,16]. – ^{11}B NMR: Bruker AM 400 (128.38 MHz) with $BF_3 \cdot OEt_2$ as external standard. – IR: Matson Genesis FT-IR. – Raman: IFS 66 FT Bruker. – Column chromatography: silica gel 230–400 mesh.

$[Cu_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]$ (**1**): By reaction of 0.2 g (0.36 mmol) $(Bu_4N)_2[B_6H_6]$ dissolved in 20 ml ethanol with 0.62 g (0.7 mmol) $(PPh_3)_3CuCl$ dissolved in 20 ml chloroform $[Cu_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]$ was precipitated. The residue was filtered off, washed quickly with acetonitrile and purified by column chromatography (eluent: dichloromethane), yielding 0.15 g (60%) of **1** as a colourless solid. – ^{11}B NMR (CD_2Cl_2): δ = −15.32 (d, J_{BH} = 128 Hz). – IR (KBr): $\tilde{\nu}$ = 3070–3003, 2953, 2917, 2868 (CH), 2445 (BH), 1479–617 (PPh_3, BB), 526, 503, 432 cm^{-1}. – Ra: 3055, 2964, 2906, 1586, 1573, 1186, 1159, 1098, 1029, 1001, 958, 686, 618, 253.

$[Au_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)(PPh_3)_2]$ (**2**): Following the procedure described above for **1**, but using 0.35 g (0.7 mmol) of PPh_3AuCl, yielded 0.14 g (40%) of colourless **2**. – ^{11}B NMR (CD_2Cl_2): δ = −11.51 (d, J_{BH} = 114 Hz). – IR (KBr): $\tilde{\nu}$ = 3071–3004, 2954, 2867 (CH), 2473 (BH), 1480–619 (PPh_3, BB), 532, 507, 439 cm^{-1}. – Ra: 3055, 1587, 1575, 1184, 1161, 1103, 1029, 1001, 962, 768, 700, 256, 182.

Crystal Structure Determinations: The intensity data were collected with an Enraf-Nonius CAD4 four circle diffractometer (Mo-K_α radiation, graphite monochromator) and Lorentz and polarization corrections were applied[17]. The structures were solved using direct methods (SHELXS-86[18]) and refined by full-matrix least-squares techniques based on F^2 (SHELXL-93[19]). The crystallographic calculations were performed using the program XANADU[20]. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms of the cluster were refined isotropically, whereas the hydrogen atoms of the triphenylphosphine ligands were placed on calculated positions with d_{CH} = 0.98 Å. Selected bond lengths and bond angles are presented in Table 2. Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405868 (**1**) and -405869 (**2**).

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