

Tetrakis[(triphenylphosphine)gold(i)](tricyclohexylphosphine)boronium Tetrafluoroborate, a Novel Boron-centred Gold Cluster

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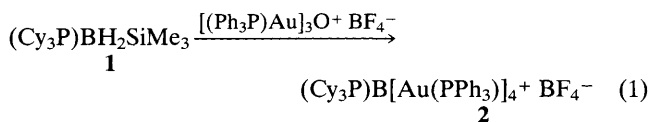
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Treatment of tricyclohexylphosphine(trimethylsilyl)borane with tris[(triphenylphosphine)gold(i)]oxonium tetrafluoroborate [in tetrahydrofuran (thf) at -78°C] affords moderate yields of the title compound $[(\text{Cy}_3\text{P})\text{B}(\text{AuPPh}_3)_4]^+ \text{BF}_4^-$, the cation of which features pentacoordinate boron atoms in the centre of a (pseudo) square pyramid with the Cy_3P ligand in the apical position (Cy = cyclohexyl).

The discovery of novel carbon-, nitrogen-, phosphorus- and arsenic-centred gold(I) clusters with hypercoordinate main group elements¹⁻³ has prompted us to attempt the synthesis of analogous boron-centred species. Just like the hexacoordinate carbon clusters had been originally predicted by molecular orbital theory,⁴ more recent calculations including relativistic effects⁵⁻⁷ suggested very strongly that the isoelectronic boron compounds should also be available as stable cationic clusters.

Although *e.g.* borohydride reduction of gold salts is a very important process for preparing highly coloured gold colloids for the glass and ceramics industry, very little is known about the inclusion of boron atoms or boron hydride units into small gold cluster particles. A literature survey shows that only a limited number of boron-centred mixed-metal clusters containing gold have been well characterized,⁸ mainly together with iron as the second component. Gold-boron bonds have also been shown to be present in gold-substituted carbaboranes.⁹⁻¹² Until very recently, there appeared to be no suitable starting material available for the preparation of a homoleptic cluster $[(\text{R}_3\text{P})\text{Au}]_6\text{B}^+$, isoelectronic⁵ with $[(\text{R}_3\text{P})\text{Au}]_6\text{C}^{2+}$. However, in a report by Imamoto and Hikosaka¹³ a method for the silylation of phosphineboranes was disclosed, the products of which now open up a new pathway.

Tricyclohexylphosphine(trimethylsilyl)borane **1**,[†] was reacted with tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate¹⁴ in thf at -78°C [eqn. (1)]. A yellow crystalline product (**2**, dec. temp. 150°C) was obtained from the reaction mixture in almost 60% yield through precipitation with pentane and recrystallisation from dichloromethane. The compound is air-stable, soluble in polar organic solvents, and readily characterized by analytical and spectroscopic data.



The mass spectra of **2** (FAB) show the cation $(\text{Cy}_3\text{P})\text{B}[\text{Au}(\text{PPh}_3)_4]^+$ at $m/z = 2127.5$ (37%), together with ions of lower mass readily identified as fragments of this species. In the ³¹P NMR spectra of solutions in dichloromethane (25°C) there are two broad resonances which represent

an A_4B pattern, with the doublet for the Ph_3P ligands at δ 42.9, and a quintet for the Cy_3P group at δ 58.0 ($J_{\text{P,P}} = 65 \text{ Hz}$). The ¹¹B NMR spectrum shows the sharp signal of the anion at $\delta -4$ ($J_{\text{B,F}} = 1 \text{ Hz}$) and a broad resonance for the cluster-centring boron atom at $\delta 12.2$. In corroboration of the ³¹P data, line multiplicities and intensities of the ¹H and ¹³C NMR spectra indicate the presence of four equivalent Ph_3P groups and one Cy_3P group.[†] In the IR spectrum of compound **2** no absorptions are observed in the B-H stretching region.

Details of the structure of the cation of **2** have been determined by a single crystal X-ray diffraction study.[‡] The cation has no crystallographic symmetry, but the symmetry of the $\text{PB}(\text{AuP})_4$ skeleton is close to point group C_{4v} (Fig. 1). The four gold atoms are arranged in a slightly distorted and folded square [alternating Au-Au-Au angles of $86.59(1)$, $92.68(2)$, $87.52(2)$ and $91.92(2)^\circ$], which is capped by the boron atom

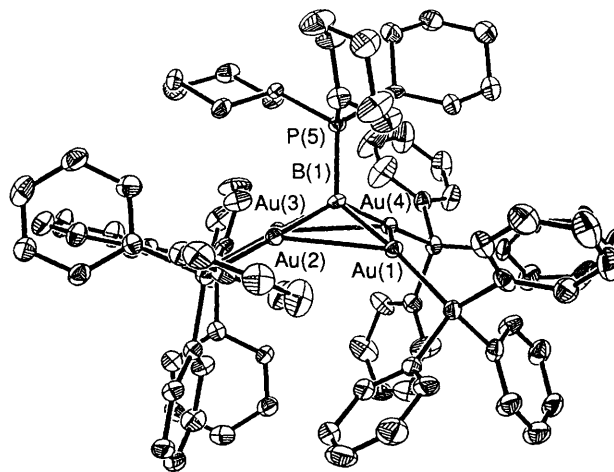


Fig. 1 Structure of the cation $(\text{Cy}_3\text{P})\text{B}[\text{Au}(\text{PPh}_3)_4]^+$ in compound **2** (ORTEP) with atomic numbering scheme. Hydrogen atoms are omitted for clarity.

[‡] Crystal and structure solution data for $2 \cdot \text{H}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot \text{C}_{90}\text{H}_{93}\text{Au}_4\text{B}_2\text{F}_4\text{P}_5 \cdot \text{H}_2\text{O} \cdot \text{C}_{10.5}\text{HCl}$, M_r 2275.57, $a = 49.038(6)$, $b = 14.376(1)$, $c = 27.960(5) \text{ \AA}$, $\beta = 101.01(1)^\circ$, space group $\text{C}2/c$ (No. 15 Int. Tables), $V = 18521.7 \text{ \AA}^3$, $Z = 8$, $D_c = 1.632 \text{ g cm}^{-3}$, $T = -65^\circ\text{C}$; $\mu(\text{Mo-K}\alpha) = 64.8 \text{ cm}^{-1}$, $\lambda(\text{Mo-K}\alpha) = 0.70169 \text{ cm}^{-1}$, CAD4 diffractometer, 21423 reflections measured, 20197 unique, and 10712 observed [$F_0 \geq 4.0\sigma(F_0)$]; Lorentz, polarisation and absorption corrections [DIFABS]¹⁵ applied. Structure solution by direct methods [SHELXS-86],¹⁶ with missing non-hydrogen atoms located by successive difference Fourier syntheses [CRYSTALS];¹⁷ hydrogens included in fixed idealized positions, the counterion and the solvate molecules refined with isotropic thermal parameters using a split model for BF_4^- , with fluorine sites half occupied (SOF 0.5). Refinement of 948 parameters in six blocks converged at $R = 0.045$ ($R_w = 0.047$) using the weighting scheme of Prince.¹⁸ Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[†] The preparation of $(\text{Cy}_3\text{P})\text{BH}_2\text{SiMe}_3$ **1** followed the disclosed procedure.¹³ The product (0.30 g, 0.82 mmol) in thf (10 ml) is treated with $[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}^+ \text{BF}_4^-$ (480 mg, 0.32 mmol) in thf (15 ml) at -78°C and allowed to react for 2 d with stirring at 20°C . The volume of the reaction mixture is reduced to 10 ml in a vacuum and pentane is added to precipitate the product **2**, orange crystals (from dichloromethane), yield 310 mg (58%), dec. temp. 150°C ; satisfactory elemental analysis]. ¹H NMR (CD_2Cl_2): δ 0.98–2.40 (m, 33H, Cy), 7.10–7.50 (m, 60H, Ph). ¹H/¹³C NMR (CD_2Cl_2): δ 26.6 (s, C4, Cy), 28.3 (d, $J_{\text{P,C}} = 5.8 \text{ Hz}$, C2, Cy), 30.0 (s, C3, Cy), 40.3 (d, $J_{\text{P,C}} = 74.9 \text{ Hz}$, C1, Cy); 129.1 (‘t’, AXX' , $J = 4.7 \text{ Hz}$, C3, Ph), 130.8 (s, C4, Ph), 133.2 (‘d’, AXX' , $J = 54 \text{ Hz}$, C1, Ph), 134.4 (‘t’, AXX' , $J = 7.4 \text{ Hz}$, C2, Ph).

bearing an apical Cy_3P ligand. The B–Au–P angles are all close to linear, with Au–P distances in the expected range (2.30 Å). The Au–B distances [2.16(1)–2.19(1) Å] are much shorter than those found in the known boron-centred bimetallic clusters (ca. 2.30 Å),⁸ and all Au–B–Au angles (with neighbouring gold atoms) are close to 81°, which leads to remarkably short basal Au···Au contacts [2.7982(5), 2.8240(5), 2.8303(5) and 2.8401(5) Å].

As for isoelectronic $\text{RC}(\text{AuL})_4^+$ species³ the bonding in the novel $[\text{L}'\text{B}(\text{AuL})_4]^+$ cluster ($\text{L}' = \text{Cy}_3\text{P}$, $\text{L} = \text{Ph}_3\text{P}$) can be accounted for by a simplified molecular orbital diagram with local C_{4v} symmetry for $\text{P}'\text{B}(\text{AuP})_4$. With a localized apical P–B single bond [from $\text{P}'(\text{sp}^3)$ and $\text{B}(\text{sp})$ hybrids] and four localized Au–P bonds [from $\text{Au}(\text{sp})$ and $\text{P}(\text{sp}^3)$ hybrids], the electron-deficient BAu_4 unit is left with three bonding MOs which are filled with the remainder six core electrons. The electron count is best represented by the components $[\text{L}'\text{-B:}]^{3-}$ and four times $[\text{LAu}]^+$. This simple picture is neglecting contributions from the $\text{Au}[(6s^2)5d^{10}]$ cores, for which relativistic calculations are mandatory. Previous theoretical studies of homoleptic polyhedral gold clusters of carbon, nitrogen and boron have shown^{5,6} that these contributions are highly significant, and similar conclusions are probably valid for the title cluster. Pertinent theoretical work is in progress, and experiments aiming at the preparation of the $\text{B}(\text{AuL})_6^+$ clusters are continued.

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