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Synthesis and Crystal Structure of the Gold-Carborane Anion $[11\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]^-$

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Introduction

Recent studies with salts of the anions $[10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}R_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9]^-$ (R = Me, H)[2] prompted us to prepare related complex salts in which an $Au(PPh_3)$ fragment is associated with a *nido*-C_2B_{10} cage system. The groups $Au(PPh_3)^+$ and H^+ are isolobal, and thus an anionic complex $[Me_2C_2B_{10}H_{10}Au(PPh_3)]^-$ would be related to the 12-vertex *nido*-species $[Me_2C_2B_{10}H_{11}]^-$, first prepared by Hawthorne and coworkers[3a] and shown to exist in two isomeric forms. Upon reduction of *closo*-1,2-Me_2-1,2-$C_2B_{10}H_{10}$ with sodium, followed by protonation, a kinetically unstable isomer $[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{11}]^-$ is initially produced, which rearranges into a thermodynamically stable species $[7\text{-}Me\text{-}9,10\text{-}\{\mu\text{-}C(H)Me\}\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]^-$ (see **A** and **B**, respectively, in Scheme I).[3b] It was, therefore, of interest to establish whether an anion of composition $[Me_2C_2B_{10}H_{10}Au(PPh_3)]^-$ could be obtained, whether it existed in more than one isomeric form, and if there were any structural relationships with **A** or **B**.

Results

Treatment of a tetrahydrofuran solution of $Na_2[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]$ with $[AuCl(PPh_3)]$, followed by addition of $[NEt_4]Cl$, afforded $[NEt_4][11\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]$ (**1a**) in high yield. The $[N(CH_2Ph)Et_3]^+$ salt **1b** was similarly obtained, and the structure of the anion of this salt is shown in Figure 1. Selected internuclear distances and angles are listed in Table I. The *endo*-attachment of the $Au(PPh_3)$ fragment to three boron atoms [Au–B(4) = 2.408(7), Au–B(5) = 2.247(7), Au–B(6) = 2.508(7) Å] in the open hexagonal face of the 12-vertex carborane cage is similar to the bonding of the (triphenylphosphine)gold group to the pentagonal open faces of the 11-vertex cages in $[N(CH_2Ph)Me_3][10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}nido\text{-}7,8\text{-}C_2B_9H_{11}]$[4] and $[5,10\text{-}exo\text{-}\{Rh(PPh_3)_2\}\text{-}5,10\text{-}(\mu\text{-}H)_2\text{-}10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}Me_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_7]$.[2b] In the cage face itself, the 7,9-carbon atoms C(1) and C(3) sit below and above (Figure 1) the plane defined by B(2)B(4)B(5)B(6) at distances of 0.31 and 0.23 Å, respectively. Such staggering of the carbon atoms below and above this B_4 unit is observed in the anion $[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{11}]^-$ (0.31 and 0.32 Å, respectively).[3b] Within the *nido*-C_2B_{10} cage of **1b**, there are two relatively long boron–boron connectivities [B(2)···B(7) = 1.99(1) and B(6)···B(7) = 2.002(9) Å] so that two faces of the polyhedron are essentially quadrilateral as opposed to triangular. Distortions of this type are a common feature of cages involving C_2B_{10} groups, and several examples have been discussed elsewhere.[3b,5–8] Interestingly, the anion $[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{11}]^-$ has only one quadrilateral face with a long B···B diagonal [2.093(8) Å][3b] whereas **1b** has two.

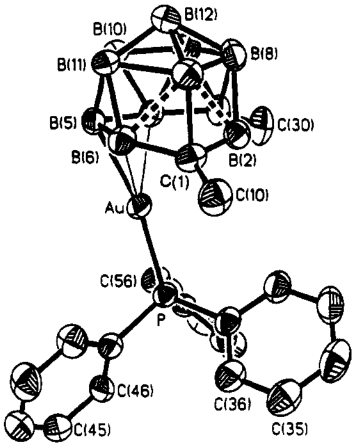

Figure 1. Molecular structure of the anion of the salt **1b**, $[11\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]^-$, showing the crystallographic labeling scheme. The thermal ellipsoids are drawn at 40% probability. All terminal hydrogens have been omitted for clarity.

Despite the isolobal relationship[9] existing between H^+ and $[Au(PPh_3)]^+$, the structures of the anions $[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{11}]^-$ and $[11\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]^-$, both derived from $[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]^{2-}$, differ as indicated in Scheme I. In the gold species, the $Au(PPh_3)$ moiety is attached primarily to the boron in the hexagonal ring which lies in the β-site with respect to the two carbons and it is also weakly linked to the two α-borons on either side. In $[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{11}]^-$ the proton bridges two adjacent boron atoms α and β, respectively, to a carbon in the open face. When η^6-coordinated to metal centers, the anion $[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]^{2-}$ displays facile dynamic behavior. One mechanism involves movement of the CMe groups, which can flip synchronously from one side of the facial B_4 plane to the other, but the dynamic process generally ceases on the NMR time scale at some temperature between 0 and –80 °C. This fluxionality is especially facile for **1a**, as revealed by the apparent equivalence of the CMe groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra at –80 °C, the lowest temperature studied.

The salts **1** do not rearrange, even after refluxing their solutions in tetrahydrofuran for 12 h. Thus no evidence for an isomer **D** was obtained, in contrast with the ready conversion of **A** into **B**. Evidently in the anions of **1**, the gold–β-boron σ-bond [Au–B(5)], supported by the weaker gold–α-boron bonds [Au–B(4) and Au–B(6)], are sufficiently strong to prevent rearrangement from occurring.

Experimental Section

The NMR measurements were made on a CD_2Cl_2 solution, using a Bruker AMX360 spectrometer. Chemical shifts (δ) are in ppm and coupling constants (*J*) are in Hz. All solvents were dried prior to use, and syntheses were carried out under nitrogen by employing the usual Schlenk tube techniques.

Synthesis of $[NEt_4][11\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]$. A THF (15 mL) solution containing *closo*-$Me_2C_2B_{10}H_{10}$ (0.08 g, 0.45 mmol) and naphthalene (*ca.* 0.02 g) was treated with small pieces of

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Scheme I

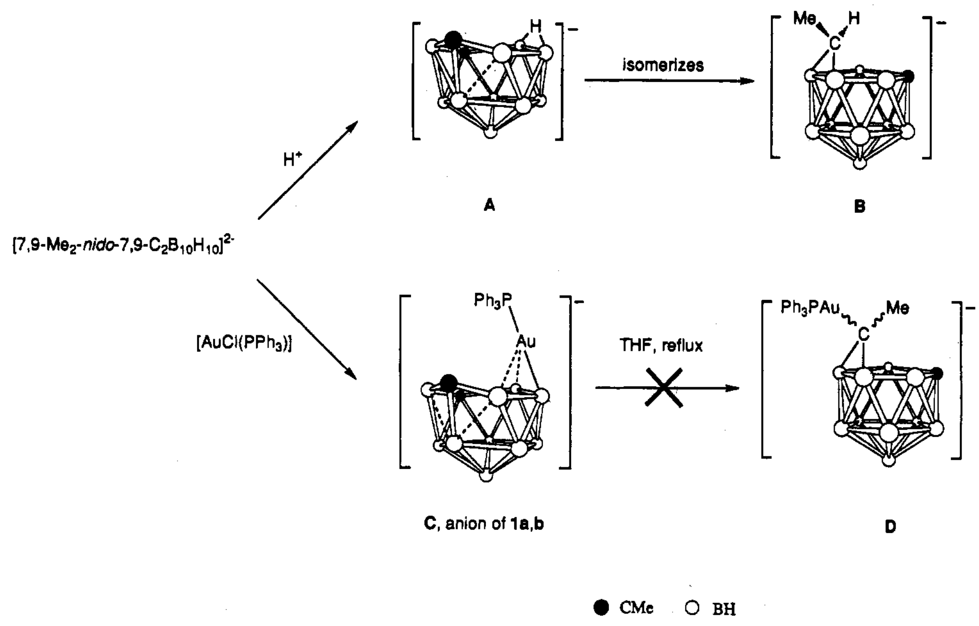

Table I. Selected Internuclear Distances (Å) and Angles (deg) for $[N(CH_2Ph)Et_3][11\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]$ (**1b**)

Au–P	2.253(2)	Au–B(4)	2.408(7)	Au–B(5)	2.247(7)	Au–B(6)	2.508(7)
C(1)–B(2)	1.502(9)	C(1)–B(6)	1.530(8)	C(1)–B(7)	1.78(1)	C(1)–C(10)	1.52(1)
B(2)–C(3)	1.69(1)	B(2)···B(7)	1.99(1)	B(2)–B(8)	1.84(1)	B(2)–H(2)	1.14(6)
C(3)–B(4)	1.676(8)	C(3)–B(8)	1.67(1)	C(3)–B(9)	1.67(1)	C(3)–C(30)	1.527(9)
B(4)–B(5)	1.854(9)	B(4)–B(9)	1.79(1)	B(4)–B(10)	1.79(1)	B(4)–H(4)	1.15(7)
B(5)–B(6)	1.84(1)	B(5)–B(10)	1.75(1)	B(5)–B(11)	1.753(9)	B(5)–H(5)	1.07(6)
B(6)···B(7)	2.002(9)	B(6)–B(11)	1.79(1)	B(6)–H(6)	1.15(7)	B(7)–B(8)	1.89(1)
B(7)–B(11)	1.906(9)	B(7)–B(12)	1.81(1)	B(7)–H(7)	1.19(7)	B(8)–B(9)	1.72(1)
B(8)–B(12)	1.72(1)	B(8)–H(8)	1.12(6)	B(9)–B(10)	1.738(9)	B(9)–B(12)	1.76(1)
B(9)–H(9)	0.99(7)	B(10)–B(11)	1.75(1)	B(10)–B(12)	1.79(1)	B(10)–H(10)	1.04(7)
B(11)–B(12)	1.74(1)	B(11)–H(11)	1.04(7)	B(12)–H(12)	1.09(7)		

P–Au–B(4)	140.6(2)	P–Au–B(5)	168.5(2)	B(4)–Au–B(5)	46.8(2)
P–Au–B(6)	136.7(2)	B(4)–Au–B(6)	77.1(2)	B(5)–Au–B(6)	45.2(2)
Au–B(4)–C(3)	91.7(4)	Au–B(4)–B(5)	62.0(3)	Au–B(4)–B(9)	140.5(4)
Au–B(4)–B(10)	118.4(4)	Au–B(4)–H(4)	106(4)	Au–B(5)–B(4)	71.2(3)
Au–B(5)–B(6)	74.9(3)	Au–B(5)–B(10)	129.5(4)	Au–B(5)–B(11)	129.2(4)
Au–B(5)–H(5)	97(4)	Au–B(6)–C(1)	77.0(3)	Au–B(6)–B(5)	59.9(3)
Au–B(6)–B(7)	114.5(4)	Au–B(6)–B(11)	113.6(4)	Au–B(6)–H(6)	114(3)

Table II. Crystallographic Data[a] for **1b**

molecular formula	$C_{35}H_{53}AuB_{10}NP$	$F(000)$	828
fw	823.8	μ(Mo Kα)/cm^{-1}	38.7
cryst system	triclinic	T, K	293
space group	$P\bar{1}$	data collcn limits, 2θ, deg	5–55
a, Å	9.583(4)	no. of data collcd (excl stds)	7358
b, Å	10.586(3)	no. of unique data	6819
c, Å	19.565(6)	no. of obsd data used	5574
α, deg	95.03(3)	criterion for data (n) used [$F_o \geq n\sigma(F_o)$]	5
β, deg	98.90(3)	no. of params refined	463
γ, deg	96.97(3)	R (R_w)[b]	0.035 (0.036)
V, Å^3	1935(1)	goodness-of-fit	1.27
Z	2	final electron density diff features (max, min.), e Å^{-3}	0.78, –1.08
d_{calc}, g/cm^3	1.41		

[a] Data collected on a Siemens R3m/V four-circle diffractometer operating in the Wyckoff ω-scan mode; graphite-monochromated Mo Kα X-radiation, $\lambda = 0.710\,73$ Å. Refinement was by full-matrix least squares with a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.0005|F_o|^2]$; $\sigma^2(F_o)$ is the variance in F_o due to counting statistics; g was chosen so as to minimize variation in $\sum w(|F_o| - |F_c|)^2$ with $|F_o|$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$.

sodium (0.02 g, 0.93 mmol), which had been washed with *n*-hexane (2 × 10 mL). The mixture was stirred for 1 h in order to generate $Na_2[7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]$ *in situ*.[3a] A THF (15 mL) solution of the compound $[AuCl(PPh_3)]$ (0.20 g, 0.40 mmol) was added to the mixture, and stirring was continued for 1 h. Addition of $[NEt_4]Cl$ (0.07 g, 0.40 mmol), with further stirring (1 h), led to the precipitation of NaCl. Solvent was removed *in vacuo*, the residue was taken up in CH_2Cl_2 (30 mL), and the mixture was filtered through a Celite pad (3 cm). Removal of solvent *in vacuo* and crystallization of the residue from CH_2Cl_2–Et_2O (12 mL, 1:5) gave mauve *microcrystals* of $[NEt_4][11\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,9\text{-}Me_2\text{-}nido\text{-}7,9\text{-}C_2B_{10}H_{10}]$ (**1a**) (0.26 g, 85%). Anal. Calcd for $C_{30}H_{51}AuB_{10}NP$: C, 47.3; H, 6.8; N, 1.8. Found: C, 46.8; H, 6.8; N, 1.9. NMR: ^{1}H, δ 1.27 [t, 12 H, CH_2*Me*, J(HH) 6], 1.95 (s, 6 H, CMe), 3.18 [q, 8 H, C*H*$_2$Me, J(HH) 6], 7.42–7.58 (m, 15 H, Ph); ^{13}C{^{1}H}, δ 134.4 [d, C^2(Ph), J(PC) 14], 132.6 [d, C^1(Ph), J(PC) 51], 131.1 [s, C^4(Ph)], 129.1 [d, C^3(Ph), J(PC) 10], 99.2 (br, *C*Me), 53.1 (*C*H$_2$Me), 31.7 (C*Me*), 7.8 (CH$_2$*Me*); ^{31}P{^{1}H}, δ 40.8 (m, vbr); ^{11}B{^{1}H}, δ 8.6 (br, 1 B), –1.1 (br, 2 B), –1.7 (br, 1 B), –8.7 (br, 2 B), –13.0 (br, 1 B), –16.8 (br, 3 B).

The synthesis of **1b** was carried out in a similar manner using $[N(CH_2Ph)Et_3]Cl$.

Table III. Atomic Positional Parameters (Fractional Coordinates × 10^4) and Equivalent Isotropic Thermal Parameters U_{eq} ($Å^2 \times 10^3$) for Compound **1b**, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	U_{eq}[a]	atom	*x*	*y*	*z*	U_{eq}[a]
Au	2004(1)	1915(1)	2663(1)	51(1)	C(32)	2548(8)	3124(6)	4541(3)	66(2)
P	1317(2)	1057(1)	3592(1)	46(1)	C(33)	2601(9)	4048(7)	5090(4)	81(3)
C(1)	2153(6)	4420(5)	2736(3)	49(2)	C(34)	1420(10)	4136(7)	5405(4)	86(3)
B(2)	3706(8)	4511(6)	3037(3)	51(2)	C(35)	185(9)	3311(6)	5180(4)	73(3)
C(3)	4805(6)	3530(6)	2751(3)	52(2)	C(36)	133(7)	2371(6)	4635(3)	61(2)
B(4)	4088(7)	2339(6)	2128(3)	47(2)	C(41)	−483(6)	216(5)	3402(3)	48(2)
B(5)	2331(7)	2487(6)	1614(3)	46(2)	C(42)	−1500(7)	729(7)	2946(3)	65(2)
B(6)	1490(8)	3783(6)	2006(3)	49(2)	C(43)	−2866(7)	125(8)	2782(4)	78(3)
B(7)	3097(8)	5227(6)	2147(4)	55(2)	C(44)	−3272(7)	−984(8)	3056(4)	78(3)
B(8)	4998(8)	4975(7)	2466(4)	59(2)	C(45)	−2300(8)	−1489(7)	3501(3)	72(3)
B(9)	5336(8)	3645(7)	1985(4)	57(3)	C(46)	−892(6)	−881(6)	3677(3)	55(2)
B(10)	3910(7)	3055(7)	1327(3)	50(2)	C(51)	2371(6)	−85(5)	3984(3)	48(2)
B(11)	2554(7)	4020(6)	1339(3)	48(2)	C(52)	2639(7)	−153(6)	4690(3)	60(2)
B(12)	4318(8)	4740(7)	1590(4)	61(3)	C(53)	3402(8)	−1085(8)	4964(4)	78(3)
C(10)	1218(7)	5146(6)	3146(3)	68(2)	C(54)	3870(8)	−1951(7)	4532(5)	81(3)
C(30)	5910(8)	3225(7)	3342(4)	77(3)	C(55)	3624(8)	−1887(7)	3827(5)	80(3)
C(31)	1309(7)	2260(5)	4312(3)	52(2)	C(56)	2905(7)	−960(6)	3552(3)	64(2)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystallography. Mauve prismatic crystals of **1b** were grown by diffusion of diethyl ether into a CH_2Cl_2 solution of the salt. The crystal used for data collection (dimensions 0.25 × 0.50 × 0.55 mm) was mounted in a sealed glass capillary under nitrogen. The cell parameters were determined by a least-squares fit of 25 reflections in the range of $14.90 \leq 2\theta \leq 27.79°$ located in a random search of the reciprocal lattice. Data collection and reduction information are given in Table II. Three standard reflections were measured every 97 reflections during data collection and these showed no significant decay. The data were corrected for Lorentz and polarization effects and an empirical absorption correction[10] based on a series of ψ-scans was also applied. The structure was solved by conventional heavy-atom methods, and successive difference Fourier syntheses were used to locate all non-hydrogen atoms.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Methyl, methylene, and phenyl hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with fixed isotropic thermal parameters (U_{iso} = 0.08 $Å^2$). The cage B–H hydrogen atoms were located in final electron density difference maps and their positions refined with fixed isotropic thermal parameters (U_{iso} = 0.08 $Å^2$). All computations were performed on a DEC μ-Vax II computer with the SHELXTL system of programs.[10] Scattering factors with corrections for anomalous dispersion were taken from ref 11 and atom parameters (x, y, z, U_{eq}'s) are listed in Table III.

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Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and complete bond distances and angles (13 pages). Ordering information is given on any current masthead page.

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