Cluster Compounds

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Tetrahedral Gold(I) Clusters with Carba-*closo*-dodecaboranylethynido Ligands: [{12-($R_3PAu)_2C{\equiv}C$-*closo*-1-$CB_{11}H_{11}\}_2$]**

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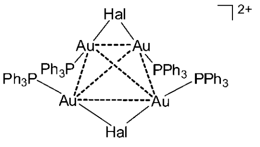
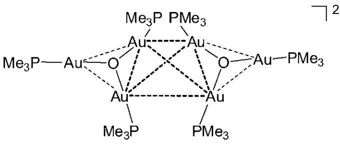
The increasing interest in the supramolecular chemistry of gold(I) compounds is a result of the unusual, for example optical properties, of these substances that are a result of inter- and intramolecular aurophilic interactions.[1–4] In turn, the self-assembly is often based on the intermolecular gold–gold interactions.[2,5] Salts of the tetranuclear bis(triphenylphosphane gold(I))halonium dications **A**[6,7] that contain four gold atoms in a distorted tetrahedral arrangement with four relatively short intermolecular Au···Au distances and two longer intramolecular Au···Au distances are unusual compounds of this type, which are only stable in the solid state. The bis(trigoldoxonium) dication **B**[8] and the bis(tetraauriomethane) complex **C**[9] are the only other examples with a similar arrangement. Similar to **A**, complexes **B** and **C** were only observed in the solid state and they dissociate in solution because of electrostatic repulsion.[7] A series of other tetranuclear gold(I) clusters that consist of two dinuclear gold(I) complexes in which the four gold atoms lie at the corners of a distorted square[10–12] is known, for example $\{[(Ph_3PAu)_2SCH_2Ph]_2\}^{2+}$ (**D**).[10]

An important class of building blocks for supramolecular gold(I) compounds are Au^I alkynyl complexes. Coinage-metal clusters can be prepared through the π-coordination of the alkynes to coinage-metal ions in combination with metallophilic interactions.[13,14] Only a limited number of such coinage-metal clusters that solely consist of gold(I) cations with ethynido/alkyne ligands have been described.[15–17] Herein we report distorted tetrahedral Au^I_4 clusters with carboranylethynido ligands. These clusters are formed by self-assembly of two dinuclear gold(I) complexes and they are present in the solid sate and for the first time in solution, as well.



Hal = Cl, Br, I **A**



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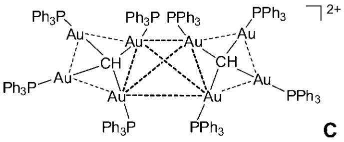

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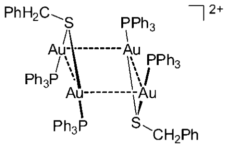
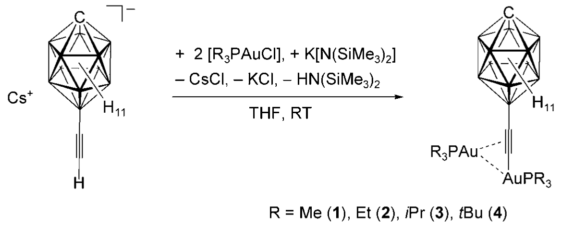


D

Cesium ethynylcarba-*closo*-dodecaborate[18,19] reacts with $[R_3PAuCl]$ and potassium bis(trimethylsilyl)amide in THF to give the neutral dinuclear gold(I) complexes [12-$(R_3PAu)_2$-$C{\equiv}C$-*closo*-1-$CB_{11}H_{11}$] (R = Me (**1**), Et (**2**), *i*Pr (**3**), *t*Bu (**4**)) in 63–95 % yield and which are thermally stable up to 220 °C (**1**; Scheme 1).



Scheme 1. Synthesis of **1**–**4**.

The dinuclear complexes **1**–**4** can alternatively be synthesized with KOH in ethanol but in lower yields. Neither in the course of these syntheses nor during the aqueous workup was the addition of water to the C≡C bond observed. In contrast, the formation of tetranuclear gold(I) clusters containing μ_4-methylydine ligands was rationalized by the reaction of dinuclear ethynidogold(I) complexes, which were formed as intermediates, with water under weakly basic conditions.[20]

The addition of only one equivalent of $[R_3PAuCl]$ in the reaction depicted in Scheme 1 still results in the formation of the dinuclear complexes **1**–**4** as main products and not anionic mononuclear gold(I) complexes [12-$R_3PAuC{\equiv}C$-*closo*-1-$CB_{11}H_{11}]^-$. These anionic species are however accessible from salts with weakly coordinating cations, as exemplified by the synthesis of [nBu$_4$N][12-$Me_3PAuC{\equiv}C$-*closo*-1-$CB_{11}H_{11}$] in Scheme 2. Probably, the use of weakly coordinating cations avoids salt elimination reactions.[21]

The easy formation of the complexes **1**–**4** and their high chemical as well as thermal stabilities is due to the properties

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$$[nBu_4N][12\text{-}HC{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}] \xrightarrow[\text{THF, RT}]{\substack{+\ [Me_3PAuCl],\ +\ [nBu_4N]OH \\ -\ H_2O,\ -\ [nBu_4N]Cl}} [nBu_4N][12\text{-}Me_3PAuC{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$$

Scheme 2. Synthesis of $[nBu_4N][12\text{-}Me_3PAuC{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$.

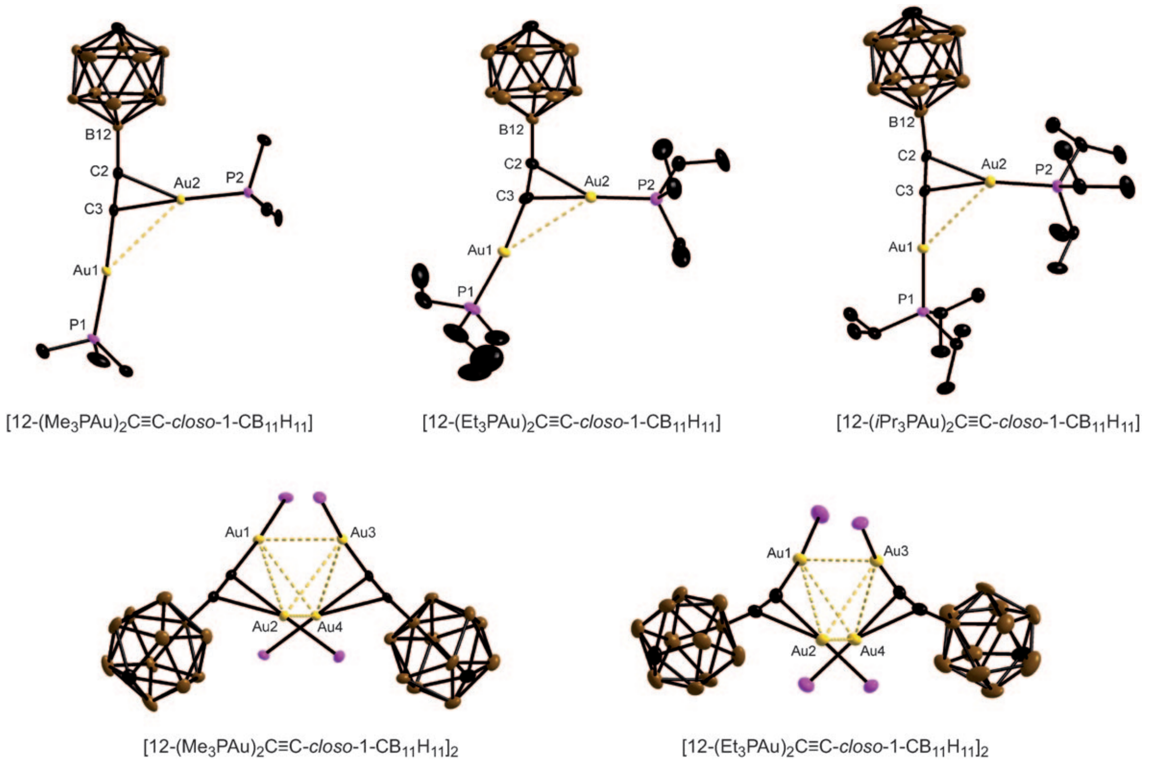
of the ethynido ligand $[12\text{-}C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^{2-}$ which has an electron-rich C≡C group. Its electron richness is a result of the bonding to boron in the anionic and thus relatively electron-rich cluster.

In the complexes **1**–**3**, one of the R_3PAu fragments is σ- and the second is π-coordinated to the ethynido ligand (Figure 1).[22] Only a few related gold(I) complexes with two Au^I centers that are coordinated to a single ethynido ligand[13,15,17] have been structurally characterized, to date, and only one complex with two phosphane–gold(I) fragments is known: $[(tBu_3PAu)_2C{\equiv}CtBu][SbF_6]$.[17] This is surprising because dinuclear phosphane–gold(I) complexes analogous to **1**–**4** are probably key-intermediates in the Au^I-catalyzed cycloisomerization of 1,5-allenynes[23] and dinuclear gold(I) complexes play an important role in Au^I-catalyzed reactions of alkynes.[24]

The coordination of a second Me_3PAu fragment in **1** results in a longer and hence weaker C≡C bond than in $[12\text{-}Me_3PAuC{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ in agreement with data derived from ab initio and DFT calculations (Supporting Information Tables S7 and S9). In the IR spectra, the C≡C stretch of 1988 cm^{-1} for **1** and 2081 cm^{-1} for the anionic complex support this trend. The π-coordination is not symmetric in the structures of **1**–**3** because the Au^I fragment is shifted towards the terminal C atom of the ligand.

The complexes with the Me_3P and Et_3P ligands (**1** and **2**) are dimers in the solid state (Figure 1) whereas compound **3** with the sterically more demanding iPr_3P ligand is monomeric. The four Au atoms in $\mathbf{1}_2$ and $\mathbf{2}_2$ are connected by aurophilic interactions to form Au^I_4 clusters with a distorted tetrahedral geometry. Au^I_4 clusters coordinated by ethynido ligands had not been reported, to date. The only similar Au^I_4 clusters are the cationic complexes **A**, **B**, and **C** that are stabilized by different types of ligands.

The dimerization of **1** and **2** is based on four intermolecular Au⋯Au contacts in the range 3.0437(4)–3.1533(6) Å (Table 1). The intramolecular Au⋯Au distances of approximately 3.41 Å for $\mathbf{1}_2$ and 3.58 Å for $\mathbf{2}_2$ are indicative for weak aurophilic interactions.[4] The reason for the considerably shorter intramolecular d(Au⋯Au) of 3.2880(5) Å in **3** than in $\mathbf{1}_2$ and $\mathbf{2}_2$ is that the bonding situation is less-crowded in the monomeric **3** than in the dimeric species. The $[\{R_3PAu\}_4(C{\equiv}C)_2]$ core in $\mathbf{2}_2$ is more strained than in $\mathbf{1}_2$ because of the increased steric demand of the Et_3P ligands. This effect is evident from larger bond angles in $\mathbf{2}_2$ than $\mathbf{1}_2$, for example ∡(C≡C−Au) 168.1(11) ($\mathbf{2}_2$) and 177.1(5)° ($\mathbf{1}_2$; Supporting Information, Table S7), and longer intermolecular Au⋯Au distances.



$[12\text{-}(Me_3PAu)_2C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ $[12\text{-}(Et_3PAu)_2C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ $[12\text{-}(iPr_3PAu)_2C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$

$[12\text{-}(Me_3PAu)_2C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]_2$ $[12\text{-}(Et_3PAu)_2C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]_2$

Figure 1. One of the two independent dinuclear gold(I) complexes **1** (left, top) and **2** (center, top), respectively, and the dinuclear Au^I complex **3** (right, top) as well as the tetranuclear gold(I) cluster $\mathbf{1}_2$ (left, bottom) and $\mathbf{2}_2$ (right, bottom) in the crystal structures. (C atoms of the phosphane ligands in $\mathbf{1}_2$ and $\mathbf{2}_2$ and all the H atoms are omitted for clarity.)

Table 1: Experimental Au···Au distances in **1**$_2$, **2**$_2$, and **3**.

Complex	Au···Au$_{\mathrm{intra}}$ [Å] Au$_\sigma$···Au$_\pi$	Au···Au$_{\mathrm{inter}}$ [Å] Au$_\sigma$···Au$_\sigma$	 Au$_\sigma$···Au$_\pi$	 Au$_\pi$···Au$_\pi$
1$_2$	3.4120(4)	3.0913(4)	3.0437(4)	3.1240(4)
	3.4177(4)		3.0782(5)	
2$_2$	3.5650(7)	3.0730(9)	3.1048(9)	3.1533(6)
	3.5986(9)		3.1423(8)	
3	3.2880(5)	–	–	–

Whether the tetranuclear gold(I) clusters **1**$_2$ and **2**$_2$ dissociate in solution or not was studied by ^{1}H DOSY NMR spectroscopy[25] in [D$_6$]DMSO, (CD$_3$)$_2$CO, and CD$_2$Cl$_2$.[26] The intermolecular dimerization in solution by aurophilic interactions was rarely observed,[1] hence, only one similar DOSY NMR study on gold(I) complexes has been reported.[12] The comparison of the hydrodynamic radii at 25 °C to radii estimated from structural data shows that in solution the complexes **3** and **4** are monomeric and the cluster **1**$_2$ remains dimeric (Supporting Information, Tables S2–S4). In contrast, for **2**, an equilibrium with its dimer **2**$_2$ is found. At 25 °C the equilibrium is shifted approximately to two thirds and at 75 °C practically completely to the monomeric, dinuclear complex **2** (Supporting Information, Table S5). Even at 75 °C **1**$_2$ does not dissociate into **1**. The increased steric strain of the $\mathrm{Au^I_4}$ cluster in **2**$_2$ compared to **1**$_2$, which is evident from structural data, is also displayed by the equilibrium between **2**$_2$ and **2** in solution.

In the ^{31}P{^{1}H} NMR spectra of the dinuclear gold(I) complexes **3** and **4** only one signal is observed in the range of −80 to 100 °C. Hence, the respective gold(I) fragments undergo a fast intramolecular exchange at the ethynido ligand. Similarly, for the tetranuclear gold(I) cluster **1**$_2$ a single ^{31}P{^{1}H} NMR signal is detected. In contrast, the ^{31}P{^{1}H} NMR spectrum of **2**/**2**$_2$ consists at low temperatures of two signals; at $\delta = 23.6$ ppm the signal of **2**$_2$ and at $\delta = 32.9$ ppm the signal of **2**. At higher temperatures the signals coalesce (Figure 2). The analysis of the intensities of the signals of **2** and **2**$_2$ in the range of −50 to 30 °C yielded an enthalpy for the dimerization of $-(37\pm5)$ kJ mol^{-1} and a free enthalpy at 25 °C of $-(12\pm5)$ kJ mol^{-1}.

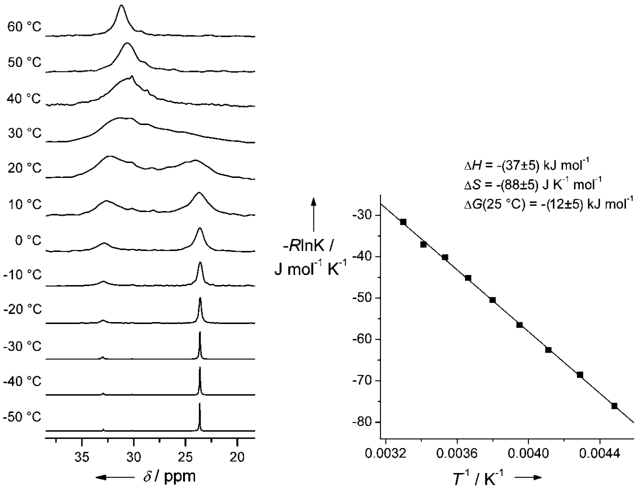


Figure 2. Temperature-dependant ^{31}P{^{1}H} NMR spectra of **2**/**2**$_2$ in [D$_8$]THF and van't Hoff plot ($R = 0.9995$) of the dimerization of **2**.

The dimerization of **1** to yield the tetrahedral $\mathrm{Au^I_4}$ cluster **1**$_2$ was studied by ab initio and DFT methods.[26] The aurophilic interactions between the two monomers in **1**$_2$ are slightly overestimated by (RI)-MP2 calculations, as evident from short Au···Au distances (Supporting Information, Table S8). The bond parameters derived from DFT calculations with the (RI)-Slater-Dirac, (RI)-TPSS, and TPSSh functional are in better agreement with the experimental bond parameters whereas, as expected,[4] (RI)-BP86 and B3LYP calculations result in Au···Au distances that are too long. The energy of dimerization is −208.3 kJ mol^{-1} at the (RI)-MP2 level of theory and −181.3 kJ mol^{-1} using the (RI)-Slater–Dirac functional (both corrected for BSSE[26]) and under consideration of solvent effects for DMSO (COSMO[26]) −186.0 and −96.4 kJ mol^{-1}, respectively. These energies underline the differences between **1**$_2$ and the dicationic tetrahedral $\mathrm{Au^I_4}$ clusters **A**, **B**, and **C**: As a result of Coulomb repulsion **A**, **B**, and **C** have positive energies of dimerization according to ab initio and DFT calculations[27] and they are only present as monomers in solution.[6–9]

In the ^{13}C NMR spectrum both signals of the ^{13}C nuclei of the C≡C unit in the tetranuclear gold(I) cluster **1**$_2$ are split into triplets because of the coupling to two equivalent ^{31}P nuclei of the Me$_3$PAu fragments that are coordinated to the alkynyl group (Supporting Information, Figure S1 and Table S9). The coupling to the ^{11}B nucleus of the antipodal boron atom results in a further splitting of the signals into quartets with lines of equal intensities. $^2J(^{31}\mathrm{P},^{13}\mathrm{C})$ in **1**$_2$ (67.3 Hz) is slightly less than half the $^2J(^{31}\mathrm{P},^{13}\mathrm{C})$ in [12-Me$_3$PAuC≡C-*closo*-1-CB$_{11}$H$_{11}$]$^-$ (142.3 Hz). The chemical shifts and the $^nJ(^{13}\mathrm{C},^{11}\mathrm{B})$ couplings of the C≡C group in **1**$_2$, [12-Me$_3$PAu-C≡C-*closo*-1-CB$_{11}$H$_{11}$]$^-$, and [12-HC≡C-*closo*-1-CB$_{11}$H$_{11}$]$^-$ are also different, which reflects the different bonding situations (Supporting Information, Table S9).

The tetranuclear gold(I) clusters **1**$_2$ and **2**$_2$ are stable in the solid sate as well as in solution as a result of the coordination of the electron-rich ethynido ligand [12-C≡C-*closo*-1-CB$_{11}$H$_{11}$]$^{2-}$. This stability reveals a new and unexpected facet of dinuclear gold(I) ethynido complexes, species that have rarely been studied to date. These and related tetrahedral $\mathrm{Au^I_4}$ clusters are promising novel building blocks for supramolecular networks with bridging diethynido ligands. Currently, we are studying the optical properties of complexes **1**–**4**.

Experimental Section

1$_2$: Cs[12-HC≡C-*closo*-1-CB$_{11}$H$_{11}$] (145 mg, 0.49 mmol) was dissolved in THF (10 mL) under an Ar atmosphere. Successively solutions of K[N(SiMe$_3$)$_2$] in DME (1 M, 0.5 mL, 0.50 mmol) and of [Me$_3$PAuCl] (300 mg, 0.97 mmol) in THF (10 mL) were added. The reaction mixture was stirred for 1 h. Water (50 mL) was added and the THF was removed under reduced pressure resulting in the formation of a white precipitate of **1**$_2$ that was collected by filtration and dried in a vacuum. Yield 333 mg (95 %). $T_{\mathrm{decomp.}} = 220$ °C (DSC). ^{1}H{^{11}B} NMR (400 MHz, CD$_3$CN): $\delta = 2.39$ (sextet, $^3J(^1\mathrm{H},^1\mathrm{H}) = 3.4$ Hz, 1 H; CH$_{\mathrm{cluster}}$), 1.72 (s, 5 H, BH), 1.65 (s, 5 H, BH), 1.62 ppm (d, $^2J(^{31}\mathrm{P},^1\mathrm{H}) = 11.1$ Hz, 18 H; CH$_3$). ^{13}C{^{1}H} NMR (400 MHz, [D$_8$]THF): $\delta = 130.2$ (qt, $^1J(^{13}\mathrm{C},^{11}\mathrm{B}) = 89.4$ Hz, $^3J(^{31}\mathrm{P},^{13}\mathrm{C}) = 12.1$ Hz, 1 C; *B*C≡C), 128.8 (tq, $^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 67.3$ Hz, $^2J(^{13}\mathrm{C},^{11}\mathrm{B}) = 12.7$ Hz, 1 C; BC≡*C*), 50.9

(s, 1C; $C_{cluster}$), 16.6 ppm (d, $^1J(^{31}P,^{13}C) = 38.0$ Hz, 6C; CH_3). ^{11}B NMR (128 MHz, [D_8]THF): $\delta = -8.7$ (s, 1B; B12), -12.2 (d, $^1J(^{11}B,^1H) = 144.0$ Hz, 5B; B7–11), -16.3 ppm (d, $^1J(^{11}B,^1H) = 153.4$ Hz, 5B; B2–6). $^{31}P\{^1H\}$ NMR (162 MHz, [D_8]THF): $\delta = -10.39$ ppm (s, 2P). Raman: $\tilde{\nu} = 1988$ cm^{-1} (vs, $\nu(C{\equiv}C)$). Elemental analysis (%) calcd for $C_{18}H_{58}Au_4B_{22}P_4$: C 15.18, H 4.10; found: C 15.20, H 3.82.

The analogous digold(I) complexes $\mathbf{2}_2$, **3**, and **4** were synthesized as described for $\mathbf{1}_2$.

$\mathbf{2}_2$: Yield 309 mg (90%). $T_{decomp.} = 195$ °C (DSC). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): $\delta = 2.38$ (sextet, $^3J(^1H,^1H) = 3.4$ Hz, 1H; $CH_{cluster}$), 1.91 (dq, $^2J(^{31}P,^1H) = 10.1$ Hz, $^3J(^1H,^1H) = 7.6$ Hz, 12H; CH_2), 1.72 (s, 5H, BH), 1.65 (s, 5H, BH), 1.18 ppm (td, $^3J(^{31}P,^1H) = 18.7$ Hz, $^3J(^1H,^1H) = 7.6$ Hz, 18H; CH_3). ^{11}B NMR (128 MHz, CD_3CN): $\delta = -8.9$ (s, 1B; B12), -12.3 (d, $^1J(^{11}B,^1H) = 138.7$ Hz, 5B; B7–11), -16.3 ppm (d, $^1J(^{11}B,^1H) = 150.4$ Hz, 5B; B2–6). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): $\delta = 34.5$ ppm (s, br, 2P). Raman: $\tilde{\nu} = 1985$ cm^{-1} (vs, $\nu(C{\equiv}C)$). Elemental analysis (%) calcd for $C_{30}H_{82}Au_4B_{22}P_4$: C 22.63, H 5.19; found: C 22.81, H 5.19.

3: Yield 106 mg (63%). $T_{decomp.} = 190$ °C (DSC). $^1H\{^{11}B\}$ NMR (400 MHz, $(CD_3)_2CO$): $\delta = 2.49$ (d of septets, $^2J(^{31}P,^1H) = 9.0$ Hz, $^3J(^1H,^1H) = 7.2$ Hz, 6H; CH), 2.31 (sextet, $^3J(^1H,^1H) = 3.2$ Hz, 1H; $CH_{cluster}$), 1.86 (s, 5H, BH), 1.71 (s, 5H, BH), 1.35 ppm (dd, $^3J(^{31}P,^1H) = 16.1$ Hz, $^3J(^1H,^1H) = 7.1$ Hz, 36H; CH_3). ^{11}B NMR (128 MHz, $(CD_3)_2CO$): $\delta = -8.9$ (s, 1B; B12), -12.2 (d, $^1J(^{11}B,^1H) = 137.9$ Hz, 5B; B7–11), -16.4 ppm (d, $^1J(^{11}B,^1H) = 150.5$ Hz, 5B; B2–6). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): $\delta = 66.58$ ppm (s, 2P). Raman: $\tilde{\nu} = 1990$ cm^{-1} (vs, $\nu(C{\equiv}C)$). Elemental analysis (%) calcd for $C_{21}H_{53}Au_2B_{11}P_2$: C 28.65, H 6.07; found: C 28.64, H 6.15.

4: Yield 160 mg (85%). $T_{decomp} = 180$ °C (DSC). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): $\delta = 2.38$ (sextet, $^3J(^1H,^1H) = 3.3$ Hz, 1H; $CH_{cluster}$), 1.73 (s, 5H, BH), 1.65 (s, 5H, BH), 1.52 ppm (d, $^3J(^{31}P,^1H) = 13.8$ Hz, 54H; CH_3). ^{11}B NMR (128 MHz, CD_3CN): $\delta = -8.9$ (s, 1B; B12), -12.3 (d, $^1J(^{11}B,^1H) = 137.8$ Hz, 5B; B7–11), -16.3 ppm (d, $^1J(^{11}B,^1H) = 154.3$ Hz, 5B; B2–6). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): $\delta = 91.85$ ppm (s, 2P). Raman: $\tilde{\nu} = 1990$ cm^{-1} (vs, $\nu(C{\equiv}C)$). Elemental analysis (%) calcd for $C_{27}H_{65}Au_2B_{11}P_2$: C 33.62, H 6.79; found: C 33.10, H 6.94.

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Keywords: alkynyl ligands · aurophilicity · carborates · gold · metal–metal interactions

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