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Alkynyl Gold(I) Rigid-Rod Molecules from 1,12-Bis(ethynyl)-1,12-dicarba-*closo*-dodecaborane(12)

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Reactions of 1,12-bis(ethynyl)-1,12-dicarba-*closo*-dodecaborane(12), 1,12-$(HC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ (diethynylcarborane, $decH_2$), with gold complexes of type [Au(acac)L] (acac = acetylacetonate) gave the neutral digold complexes $[(AuL)_2(\mu\text{-dec})]$ [L = PPh_3 (**1**), $P(C_6H_4\text{-}OMe\text{-}4)_3$ (**2**), $C(NH^tBu)(NEt_2)$ (**3**)]. The neutral complex $[(AuCN^tBu)_2(\mu\text{-dec})]$ (**5**) was obtained by adding ^tBuNC to the complex $[Au_2(\mu\text{-dec})]_n$ (**4**) resulting from the reaction of $decH_2$ with $[AuCl(SMe_2)]$ and NEt_3. The anionic complex PPN$[Au(decH)_2]$ (**6**) (PPN = $Ph_3P{=}N{=}PPh_3$) was isolated from its mixture with $(PPN)_2[\{Au(decH)\}_2(\mu\text{-dec})]$ (**7**) by reacting PPN$[Au(acac)_2]$ and $decH_2$ in 1:4 molar ratio. The rigid-rod structures of the digold compound **2**·CH_2Cl_2 and the salt **6**·$CHCl_3$ were determined by X-ray crystallography.

Introduction

Together with the linearity of the C≡C bond in alkynyl ligands, the preference of gold(I) for linear dicoordination makes alkynylgold(I) compounds attractive candidates for the design of linear-chain metal-containing polymers with extended electronic conjugation along the backbone.[1−6] Among the many alkynylgold(I) compounds described, some show liquid crystalline properties[7] or nonlinear-optical behavior.[8,9] In addition, some alkynylgold(I) derivatives belong to a new class of luminophores with interesting photophysical and photochemical properties.[10]

Since 1,4-bis(ethynyl)benzene is a widely used precursor in the syntheses of many rigid-rod metal complexes,[2,3,11] the recently reported[12] compound 1,12-bis(ethynyl)-1,12-dicarba-*closo*-dodecaborane(12) (diethynylcarborane, $decH_2$) may be considered as a precursor for the same purpose. Monoethynyl *ortho*- and *meta*-carboranes have been shown to form alkynylmetals with the acetylenic hydrogen replaced by metals.[13] As the robust cage in *para*-carborane has a 5-fold symmetry through the axis of the cage carbons and the hydrogens at the cage carbons are easily substituted, there has been substantial interest in the *para*-carborane unit $-CB_{10}H_{10}C-$ as a linker/building block for rigid-rods,[14] liquid crystals,[15] and materials with large hyperpolarizabilities.[16] Recent studies of various *para*-carborane derivatives show evidence of electronic transmission via the *para*-carborane cage.[17]

Here we describe the syntheses of new rigid-rod alkynylgold(I) derivatives from 1,12-bis(ethynyl)-1,12-

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dicarba-*closo*-dodecaborane(12). The crystal structures of two rigid-rod molecules containing two metal centers and a $-C\equiv C-CB_{10}H_{10}C-C\equiv C-$ carborane linker or a gold center with two $-C\equiv C-CB_{10}H_{10}C-C\equiv CH$ groups are also discussed.

Experimental Section

^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions with a Varian Unity 300 at room temperature. Chemical shifts are referenced to $BF_3{\cdot}Et_2O$ (^{11}B), H_3PO_4 (^{31}P), or TMS (^1H, ^{13}C). The gold complexes [Au(acac)L],[18,19] [AuCl(SMe$_2$)],[20] PPN[Au(acac)$_2$][18] (acacH = acetylacetone, PPN = $Ph_3P{=}N{=}PPh_3$), and decH$_2$[12] were prepared as described in the literature.

Synthesis of [(AuPPh$_3$)$_2$(*μ*-dec)] (1). To a solution of decH$_2$ (20 mg, 0.1 mmol) in degassed CH_2Cl_2 (5 mL) was added [Au(acac)PPh$_3$] (114 mg, 0.2 mmol). The resulting light suspension was stirred for 5 h and filtered through Celite. The pale yellow solution was concentrated under reduced pressure (to ca. 1 mL). By addition of Et_2O (20 mL) a white microcrystalline solid was obtained, which was filtered off, washed with Et_2O (5 mL), and air-dried. Yield: 32 mg (29%). Mp: 258 °C (dec). Anal. Calcd for $C_{42}H_{40}Au_2B_{10}P_2$: C, 45.50; H, 3.64. Found: C, 45.62; H, 3.75. IR (cm^{-1}): ν(BH) 2666 (s), 2614 (s), ν(C≡C) 2146 (w). $^1H\{^{11}B\}$ NMR: δ 7.42 (m, 30 H, Ph), 2.55 (s, 10 H, BH). $^{13}C\{^1H\}$ NMR: δ 134.2 (d, $^2J_{CP}$ = 14 Hz, *o*-CH), 131.5 (d, $^4J_{CP}$ = 2 Hz, *p*-CH), 129.6 (d, $^1J_{CP}$ = 56 Hz, *i*-C), 129.1 (d, $^3J_{CP}$ = 11 Hz, *m*-CH), 121.8 (s, *C*≡CAu), 100.0 (d, $^2J_{CP}$ = 31 Hz, CAu). $^{31}P\{^1H\}$ NMR: δ 42.25 (s). ^{11}B NMR: δ −11.4 (d, J_{BH} = 165 Hz).

Synthesis of [{AuP(C$_6$H$_4$OMe-4)$_3$}$_2$(*μ*-dec)] (2). To a solution of decH$_2$ (20 mg, 0.1 mmol) in acetone (15 mL) was added[Au(acac)P(C$_6$H$_4$OMe-4)$_3$] (149 mg, 0.23 mmol), and the mixture was stirred for 4.25 h and filtered through Celite. The solution was concentrated under vacuum (to ca. 1 mL), and Et_2O (10 mL) was added to precipitate a white microcrystalline solid, which was filtered off and air-dried. Yield: 87.5 mg (64%). Mp: 232 °C (dec). Anal. Calcd for $C_{48}H_{52}Au_2B_{10}O_6P_2$: C, 44.73; H, 4.07. Found: C, 44.46; H, 4.08. IR (cm^{-1}): ν(BH) 2614 (s), ν(C≡C) 2132 (w). $^1H\{^{11}B\}$ NMR: δ 7.32, 6.90 (AA′BB′, 24 H, C_6H_4), 3.81 (s, 18 H, Me), 2.54 (s, 10 H, BH). $^{13}C\{^1H\}$ NMR: δ 162.1 (s, *p*-C), 135.6 (d, $^2J_{CP}$ = 15 Hz, *o*-CH), 124.2 (s, *C*≡CAu), 121.3 (d, $^1J_{CP}$ = 60 Hz, *i*-C), 114.6 (d, $^3J_{CP}$ = 13 Hz, *m*-CH), 100.0 (d, $^2J_{CP}$ = 33 Hz, CAu), 66.6 (s, C cage), 55.4 (s, Me). $^{31}P\{^1H\}$ NMR: δ 38.61 (s). ^{11}B NMR: δ −11.3 (d, J_{BH} = 161 Hz). Crystals of **2**·2CH$_2$Cl$_2$ suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a CH_2Cl_2 solution of **2**.

Synthesis of [{Au{C(NH^{t}Bu)(NEt$_2$)}}$_2$(*μ*-dec)] (3). To a solution of [Au(acac){C(NH^{t}Bu)(NEt$_2$)}] (183 mg, 0.4 mmol) in degassed acetone (10 mL) was added a solution of decH$_2$ (25 mg, 0.13 mmol) in the same solvent (10 mL). The mixture was stirred for 9.25 h and filtered through Celite, and the solution was concentrated under reduced pressure to dryness. The residue was then stirred with Et_2O (30 mL), filtered off, washed with Et_2O (5 mL), and recrystallized from CH_2Cl_2/Et_2O to give a white powder. Yield: 19 mg (16%). Mp: 164 °C (dec). Anal. Calcd for $C_{24}H_{50}N_4B_{10}Au_2$: C, 32.14; H, 5.62; N, 6.25. Found: C, 31.68; H, 5.41; N, 5.95. IR (cm^{-1}): ν(NH) 3368 (s), ν(BH) 2657 (s), 2606 (s), ν(C≡C) 2128 (s). $^1H\{^{11}B\}$ NMR δ 5.74 (s, 2 H, NH), 3.92 (q, 4 H, $^3J_{HH}$ = 7 Hz, CH$_2$), 3.18 (q, 4 H, $^3J_{HH}$ = 7 Hz, CH$_2$), 2.52 (s, 10 H, BH), 1.54 (s, 18 H, ^{t}Bu), 1.21 (t, 6 H, $^3J_{HH}$ = 7 Hz, CH$_2$*Me*), 1.13 (t, 6 H, $^3J_{HH}$ = 7 Hz, CH$_2$*Me*). ^{11}B NMR: δ −11.4 (d, J_{BH} = 168 Hz).

[(AuCN^{t}Bu)$_2$(*μ*-dec)] (5). To a solution of decH$_2$ (21 mg, 0.11 mmol) in degassed CH_2Cl_2 (6 mL) were added [AuCl(SMe$_2$)] (65 mg, 0.22 mmol) and NEt$_3$ (0.061 mL, 0.44 mmol). No changes were observed after 1.5 h of stirring. The solution was concentrated to dryness, the residue was stirred with acetone (0.5 mL) and water (10 mL), the resulting suspension was filtered, and the pale yellow solid was washed with water (8 mL) and air-dried. The color of this solid, presumed to be the polymer [Au$_2$(*μ*-dec)]$_n$ (**4**), slowly darkened, suggesting that decomposition to metallic gold was taking place. The dried solid was suspended in CH_2Cl_2 (3 mL), and ^{t}BuNC (0.1 mL, 0.89 mmol) was added. A pale yellow solution immediately formed, which was stirred for 2.5 h and then filtered through a short column of Celite. The solution was concentrated under reduced pressure (to ca. 1 mL), and Et_2O (5 mL) was added to give a white microcrystalline solid. This solid was filtered off, washed with Et_2O (2 × 5 mL), and air-dried. Yield: 30 mg (36%). Mp 162 °C. Anal. Calcd for $C_{16}H_{28}Au_2B_{10}N_2$: C, 25.61; H, 3.76; N, 3.73. Found: C, 26.03; H, 3.86; N, 3.77. IR (cm^{-1}): ν(BH) 2618 (s), ν(N≡C) 2234 (s), ν(C≡C) 2140 (w). $^1H\{^{11}B\}$ NMR: δ 2.47 (s, 10 H, BH), 1.51 (s, 18 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 112.6 (*C*≡CAu), 99.4 (CAu), 66.2 (C cage), 58.6 (*C*Me), 29.8 (Me). ^{11}B NMR: δ −11.5 (d, J_{BH} = 166 Hz).

Synthesis of PPN[Au(decH)$_2$] (6). To a solution of decH$_2$ (0.039 g, 0.2 mmol) in degassed CH_2Cl_2 (5 mL) was added a solution of PPN[Au(acac)$_2$] (0.048 g, 0.05 mmol) in the same solvent (10 mL). The mixture was stirred for 8 h and filtered through Celite. The solution was then concentrated to dryness under reduced pressure, giving a residue, which was stirred with *n*-hexane (15 mL), filtered off, washed with *n*-hexane (10 mL), and finally air-dried to give a white microcrystalline solid shown by NMR to be a mixture of **6** and (PPN)$_2$[{Au(decH)}$_2$(*μ*-dec)] (**7**) [41 mg, 71% yield; **6**/**7** = 80/20; mp 176 °C]. Anal. Calcd for $C_{48}H_{52}AuB_{20}NP_2$: C, 51.56; H, 4.69; N, 1.25. Found: C, 50.60; H, 5.04; N, 1.09. IR (cm^{-1}): ν(CH) 3302 (w), 3238 (s), ν(BH) 2616 (s); ν(C≡C) 2114 (s). PPN: 1581 (m), 1320−1220 (s,br), 544 (s), 527 (s), 491 (s). Slow evaporation of a solution of the above-mentioned mixture in chloroform gave very small crystals identified by X-ray crystallography as the anionic complex **6**·CHCl$_3$. Attempts to purify the minor complex **7** by recrystallization have not proved successful, and it was characterized by NMR and FAB-MS as a mixture with **6**.

Complex 6. $^1H\{^{11}B\}$ NMR: δ 7.45−7.76 (m, 30 H, PPN), 2.43 (s, 10 H, BH), 2.27 (s, 10 H, BH), 1.96 (s, 2 H, C≡CH) ppm. $^{31}P\{^1H\}$ NMR: δ 21.71 (s). ^{11}B NMR: δ −11.2 (d, J_{BH} = 158 Hz, 10 B), −12.5 (d, J_{BH} = 158 Hz, 10 B). $^{13}C\{^1H\}$ NMR:

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Table 1. Crystal Data and Structure Refinements for 2·CH_2Cl_2 and 6·$CHCl_3$

	2·CH_2Cl_2	**6**·$CHCl_3$
formula	$C_{50}H_{56}Au_2B_{10}Cl_4O_6P_2$	$C_{49}H_{53}AuB_{20}Cl_3NP_2$
fw	1458.72	1237.38
T (K)	173(2)	100(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/c$
a (Å)	13.2942(9)	22.9998(15)
b (Å)	12.0671(13)	14.5902(10)
c (Å)	19.2784(13)	17.1371(11)
α (deg)	90	90
β (deg)	105.662(5)	91.6690(10)
γ (deg)	90	90
V (Å^3)	2977.9(4)	5748.3(7)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.627	1.430
μ (mm^{-1})	5.199	2.791
F(000)	1420	2456
cryst size (mm^3)	0.42 × 0.40 × 0.26	0.18 × 0.07 × 0.05
θ range for data collection (deg)	3.04 to 25.00	1.65 to 26.37
index ranges	$-15 \le h \le 2$ $0 \le k \le 14$ $-22 \le l \le 22$	$25 \le h \le 28$ $-18 \le k \le 15$ $-21 \le l \le 21$
no. of reflns collected	5979	33 615
no. of ind reflns	5239 [R(int) = 0.0220]	11 702 [R(int) = 0.0772]
completeness to θ	(=25.00°) 99.8%	(=26.00°) 99.7%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
abs correction	psi-scans	
max. and min. transmn	0.901 and 0.470	
no. of data/restraints/params	5239/7/342	11702/72/682
goodness-of-fit on F^2	0.919	0.953
$R(F)^a$	0.0306	0.0613
$R_w(F^2)^b$	0.0704	0.1515
$\Delta\rho$ (e Å^{-3})	1.029 and −0.833	4.194 and −1.400

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $F > 2\sigma(F)$. [b] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

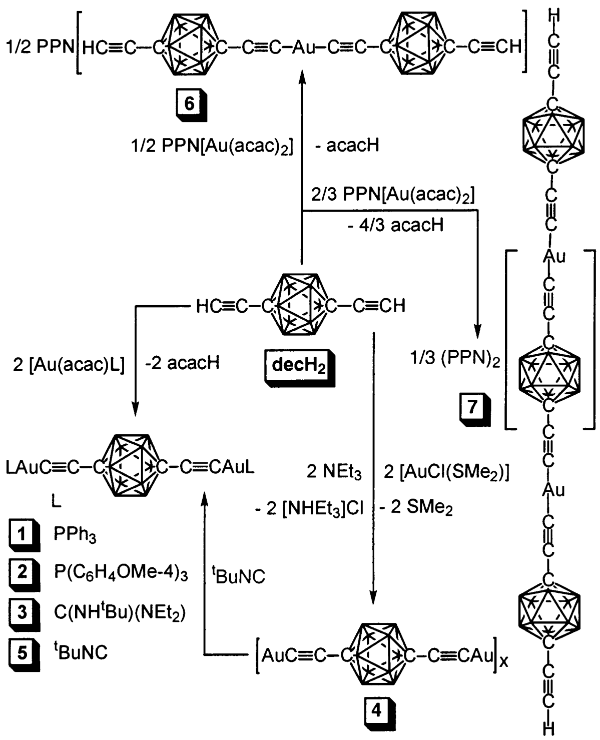
δ 134.0 (m, *p*−CH), 132.2 (m, *m*-CH), 129.7 (m, *o*-CH), 127.0 (m, *ipso*-C), 117.06 (*C*≡CAu), 97.84 (CAu), 66.8 (C cage) ppm. MS (FAB$^-$): *m*/*z* 580 (M$^-$, 100).

Complex 7 (in 1:4 mixture with **6**). $^1H\{^{11}B\}$ NMR: δ 2.32 (s, BH) ppm. ^{11}B NMR: δ −12.0 ppm. Other peaks corresponding to **7** are presumed hidden in peaks assigned to **6**. MS (FAB$^-$): *m*/*z* 968 (MH$^-$, 6).

Crystallography. Crystal data and refinement details are presented in Table 1. Crystals were mounted on glass fibers and transferred to the cold gas stream of the diffractometer (**2**·CH_2Cl_2 Siemens P4 and **6**·$CHCl_3$ Bruker Smart APEX). Data were recorded with Mo Kα radiation (λ = 0.71073 Å) in ω-scan mode. Absorption corrections were applied to **2**·CH_2Cl_2 on the basis of Ψ-scans.

Structures were solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using a riding model. *Special features of refinement*: In compound **2**·CH_2Cl_2, the solvent molecules (CH_2Cl_2) in the crystal are disordered over two sites (ca. 73:27). In compound **6**·$CHCl_3$, the residual electron density near the gold atoms is high. To solve this problem, different crystals were measured. Despite very careful measurements, the large difference peak remains. Because absorption corrections (multiscan with SADABS or face-indexing) or no correction at all does not have any effect, it is probably a genuine disorder effect. In this compound the solvent molecules ($CHCl_3$) in the crystal are disordered over two sites (ca. 56:44).

Scheme 1



Results and Discussion

Synthesis. A summary of the reactions carried out in this study is depicted in Scheme 1. Reactions of the carborane, decH_2, with (acetylacetonato)gold(I) complexes, [Au(acac)L], gave the neutral digold compounds [$(AuL)_2(\mu$-dec)] where L is a phosphine, PPh_3 (**1**) or $P(C_6H_4OMe-4)_3$ (**2**), or a carbene, $C(NH^tBu)(NEt_2)$ (**3**). These are new examples of the synthetic utility of (acetylacetonato)gold(I) complexes, which have been shown to be versatile and efficient reagents for the synthesis of a variety of coordination and organometallic complexes.[9,21−23]

The reaction in CH_2Cl_2 between decH_2 and [AuCl(SMe_2)], in the presence of an excess of NEt_3 (1:2:4), led to a solution that, after concentrating to dryness and washing successively with acetone and water, gave a pale yellow solid, which in view of its insolubility and reactivity (see below) we believe to be $[Au_2(\mu\text{-dec})]_n$ (**4**), similar to the stable polymeric complexes [AuC≡C(R)C≡CAu]$_x$ [R = $C_6H_4C_6H_4$-4,4′, ($C_6H_2Me_2$-2,5)-4,[11] C_6H_4-1,3, (C_6HMe_3-2,4,6)-1,3, and (C_6Me_4-2,3,5,6)-1,4], which we have previously prepared[24] by the same method. In these polymers, the dicoordination at gold must be

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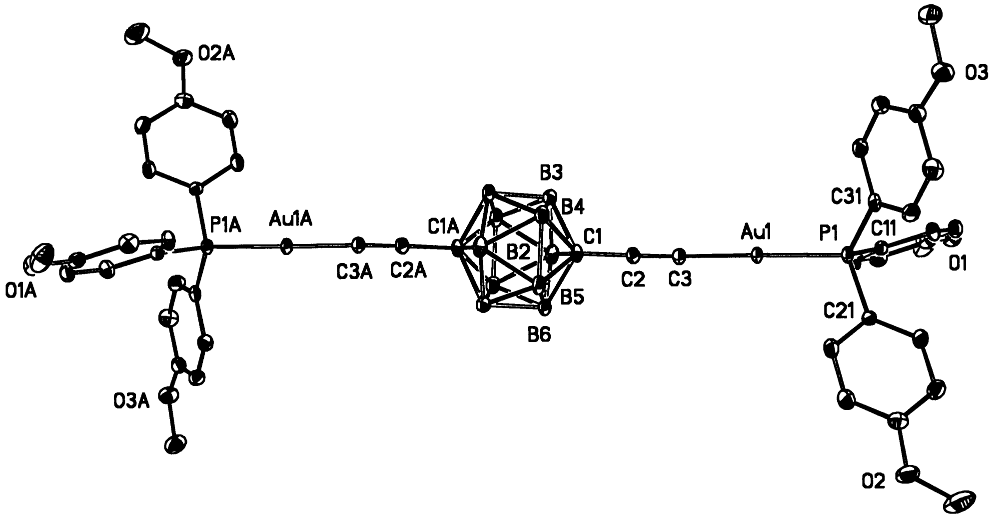

Figure 1. Crystal structure of **2**·$2CH_2Cl_2$ (30% thermal ellipsoids). Hydrogen atoms and solvent molecules are omitted. Selected distances (Å) and angles (deg): Au1−C3 2.007(5), Au1−P1 2.2743(14), C2−C3 1.181(7), C1−C2 1.455(7), average C−P 1.811(5), av C−B 1.715(8), av B−B(tropical) 1.777(10), av B−B(meridianal) 1.758(9), C1···C1A 3.112, Au1···Au1A 12.36, C1−C2−C3 170.0(6), C2−C3−Au1 174.3(15), C3−Au1−P 179.26(15).

completed by π (C≡C) → Au interactions which are separated by strong donors such as phosphine or isocyanide ligands. On the basis of the recent isolation by us[25] of some $[(AuNHEt_2)_2\{(C{\equiv}C)_2\text{-}\mu\text{-R}\}]$ complexes (R = different arylene radicals) we suggest that the solution initially formed in the reaction of $decH_2$ with $[AuCl(SMe_2)]$ and NEt_3 is likely to contain the neutral complex $[(AuNEt_3)_2(\mu\text{-dec})]$, which would be stable only in the presence of an excess of NEt_3. When the excess is removed by concentration to dryness and washing, $[(AuNEt_3)_2(\mu\text{-dec})]$ transforms into the insoluble polymer since π (C≡C) → Au bonds would replace the labile Et_3N → Au ones. The byproduct $NHEt_3Cl$ is separated by washing with water. In view of the surprisingly poor stability of $[Au_2(\mu\text{-dec})]_n$ (**4**) we decided not to characterize it but to suspend it in CH_2Cl_2 and treat it with a 4:1 excess of ^tBuNC. The suspension immediately dissolved, and $[(AuCN^tBu)_2(\mu\text{-dec})]$ (**5**) was obtained from the solution.

We have reported the syntheses of some anionic alkynylgold(I) complexes from the reactions of the salt $PPN[Au(acac)_2]$ with alkynes.[21,26] In the reaction of $PPN[Au(acac)_2]$ with $decH_2$ designed to give $PPN[Au(decH)_2]$ (**6**), we decided to use an excess of the dialkyne (4:1) over the 2:1 stoichiometric ratio in order to avoid the formation of the polymer $(PPN)_n[Au(\mu\text{-dec})]_n$. However, although the desired complex **6** was obtained in good yield (71%), its NMR spectra showed the presence of a second product (ca. 20%, identified as $(PPN)_2[\{Au(decH)\}_2(\mu\text{-dec})]$ (**7**) by NMR and FAB mass spectroscopy) that we could not separate. By slow evaporation of a solution of the mixture in $CHCl_3$, a small amount of crystals formed. Many of these poor-quality crystals were subjected to X-ray crystallography and the identity of **6** was confirmed. Despite repeated recrystallization, complex **7** could not be isolated pure.

In an attempt to obtain pure **6**, we used a $decH_2$/$PPN[Au(acac)_2]$ 6:1 molar ratio, but in this case, the NMR of the isolated product showed the presence of not only both components of the previous mixture but also ca. 10% of $decH_2$.

Crystal Structure of the Rigid-Rod Compounds 2·$2CH_2Cl_2$ and 6·$CHCl_3$. The crystal structure of **2**·$2CH_2Cl_2$ (Figure 1) has an inversion center at the center of the carborane cage. Both in **2**·$2CH_2Cl_2$ and in **6**·$CHCl_3$ (Figures 2, 3) the coordination environment of the gold centers is, as usual, almost linear [**2**, C(3)−Au(1)−P 179.26(15)°; **6**, 178.3(3)°]. Additionally, the anion $[Au(decH)_2]^-$ in **6** is very long [C(6)−C(16) 20.51 Å] and almost linear since the segments C(6)−Au and Au−C(16) form an angle of 174.9°. Despite the greater *trans*-influence of the C-donor with respect to P-donor ligands, the Au−C bond distances [**2**, Au(1)−C(3) 2.007(5); **6**, Au(1)−C(3) 1.999(7), Au(1)−C(13) 2.002(7) Å] are all similar.

In both complexes, the C≡C bond distances [**2**, 1.181(7); **6**, 1.188(10), 1.166(9) Å)] are similar to those found in $decH_2$ [1.179(3), 1.180(3) Å][12] and $dec(SiMe_3)_2$ [1.193(3) Å].[27] However, the average C−B and tropical B−B bond lengths [**2**, 1.715(8) and 1.777(10) Å, respectively; **6**, 1.714(11) and 1.778(13) Å, respectively] in the C_2B_{10} cages of **2** and **6** differ from the cages in the reported structures [1.726(3) and 1.793(3) Å, respectively for $decH_2$,[12] or 1.726(2) and 1.789(2) Å, respectively, for $dec(SiMe_3)_2$[27]]. These differences are likely due to the less accurate data obtained for **2**·$2CH_2Cl_2$ and **6**·$CHCl_3$, rather than to the gold substituents, as the thermal motion in *para*-carboranes mostly takes the form of rotation around the cage C···cage···C axis [**2**, C(1)···C(1A) (Figure 1); **6**, C(1)···C(4) and C(11)···C(14) (Figure 2), and the resulting systematic error is largest for the tropical B−B bonds.[12]

In **2**·CH_2Cl_2 there are no intermolecular contacts between gold atoms and the gold-phosphine fragments display geometric parameters similar to those in other

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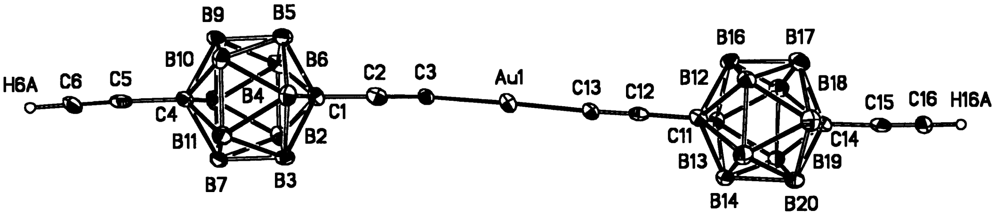

Figure 2. Crystal structure of the anion in **6**·$CHCl_3$ (30% thermal ellipsoids). Solvent molecules, hydrogen atoms, except C≡CH, and the cation are omitted. Selected distances (Å) and angles (deg): Au(1)−C(3) 1.999(7), Au(1)−C(13) 2.002 (7), C(1)−C(2) 1.461(10), C(11)−C(12) 1.472(10), C(2)−C(3) 1.188(10), C(12)−C(13) 1.166(9), average C−B 1.714(11), av B−B(tropical) 1.778(13), av B−B(meridianal) 1.764(13), C(6)···C(16), 20.51, C(3)−Au(1)−C(13) 178.3(3), torsion angle Au-(1)−C(6)//Au(1)−C(16) 174.9.

$P(C_6H_4OMe\text{-}4)_3$ complexes containing linearly dicoordinated gold(I).[19,28] Although many dimetal complexes with the 1,4-bis(ethynyl)benzene bridge have been prepared, only three crystal structures of these compounds are reported in the literature,[2,29] and one is of a digold compound, namely, $Me_3PAuC{\equiv}CC_6H_2Me_2C{\equiv}CAuPMe_3$.[22] Comparison of its structure with that of complex **2** revealed the bond distances along the P−Au−C−C−C rod to be similar. The average Au−Au distance of 12.06 Å in the structure of the *para*-phenylene complex is shorter than in the structure of **2**·$2CH_2Cl_2$ by 0.30 Å, as expected from the bigger carborane unit in the latter. The structure of compound **2** contains the longest rigid Au−Au distance yet reported for a digold compound.

The packing diagram of **6**·$CHCl_3$ displays self-assembling of the $[Au(decH)_2]^-$ anions through two C≡C−H···Au and one C≡C−H···π(C≡C) intermolecular hydrogen bonding (Figure 3), while no Au···Au aurophilic contacts are observed. The data involving the H···Au interaction are not very reliable because of the residual electron density found at gold, but the C···Au [C(6AA)···Au(1) 3.53 Å, C(16B)···Au(1) 3.72 Å], H(16H)···M (M = midpoint of the π-system; 2.67 Å; the ethynyl C−H distance is normalized to 1.08 Å), and C(16B)···M (3.51 Å) distances and the C(16B)−H(16B)···M (134.3°) angle point to the existence of hydrogen bonds that justify the formation of the observed infinite sheet of anions (Figure 4). There are many examples of C−H···Au (C···Au: 3.0−3.9 Å) and C≡C−H···π(C≡C) hydrogen bonding (H···M 2.3−2.8 Å, C···M 3.4−3.9 Å, C−H···M 123.3−177.5°),[30] although only one complex with a C≡C−H···π(C≡C−Au) hydrogen bond has been reported.[33] 1,4-Bis(ethynyl)benzene shows C≡C−H···π(C≡C) hydrogen bonds (H···M 2.596 Å, C···M 3.67 Å, C−H···M 174.8°) that give a packing similar to that in **6**·$CHCl_3$.[31] Despite the existence of many complexes containing intermolecular C−H···Au interactions, just a few papers have reported such contacts,[5,22,32,33] and only one corresponds to an ethynyl C≡C−H···Au interaction with a C···Au distance of 3.99 Å.[32]

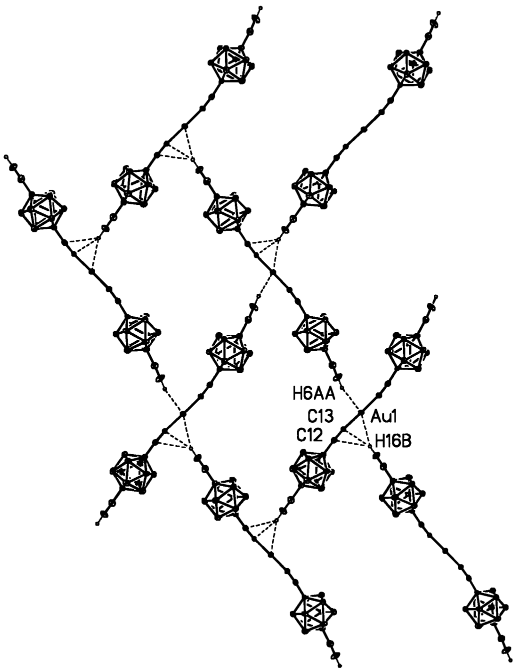

Figure 3. Packing diagram of the anions of **6**·$CHCl_3$ showing the C≡C−H···Au and C≡C−H···π(C≡C) intermolecular hydrogen bonding.

NMR and IR Spectroscopy. The ^{11}B and $^1H\{^{11}B$ broad-band decoupled} NMR spectra of complexes show one or two (in the case of **6**) doublets at frequencies similar to those reported for the starting carborane and its $SiMe_3$ derivative.[12] In **6**, the $^1H\{^{11}B$ selective} spectrum indicates the BH peak at 2.43 ppm to correspond to the borons at −11.2 ppm. Because the $\delta(^1H\{^{11}B\})$ of $decH_2$ (2.49 ppm) is similar to that at 2.43 ppm in **6**, the peak at 2.27 ppm in this complex could be assigned to the protons facing the gold atom. Consequently, the greater shielding of these protons [and that of their B nuclei, resonating also at higher field (−12.5 ppm)] indicates that the negative charge is located around the gold atom. A sharp peak at 1.96 ppm in the proton spectrum of **6** is assigned to the acetylenic hydrogens.

The inequivalence of the Et groups and the presence of only one NH and ^tBu resonances in the proton spectrum of **3** are indicative of the multiple character of the C−NEt_2 bond in the carbene ligand and the free rotation around the C−NH^tBu one.

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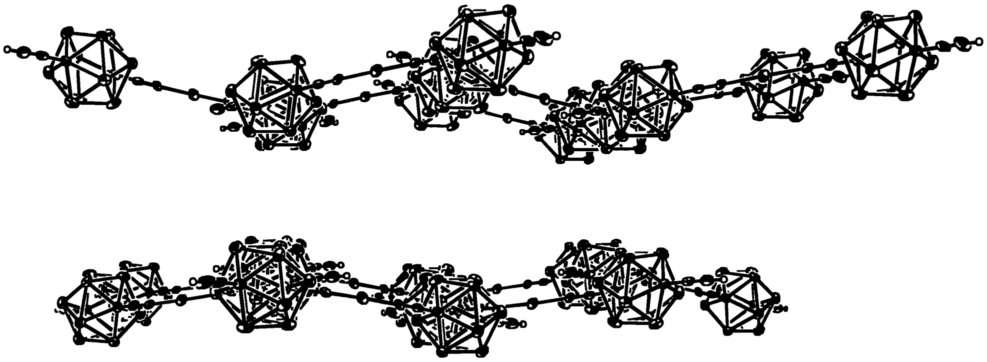

Figure 4. Layers of anions in **6**·$CHCl_3$

The $^{13}C\{^1H\}$ NMR spectra of **3** could not be measured even after prolonged accumulation due to its low solubility. In the remaining neutral complexes, the $^{13}C-Au$ resonance (99.4−100 ppm) is highfield shifted with respect to those in **6** (97.84 ppm) in support of the above assignments. The resonance due to the cage carbons is observed in the $^{13}C\{^1H\}$ spectra of these complexes toward 66 ppm, but this peak is not observed in the spectrum of **1**, as well as one of the two peaks expected for **6**. Regarding the C≡CAu moiety, we have tentatively assigned the carbon bound to gold (α-C) at higher field with respect to the β-C due to the coupling of the former with ^{31}P observed in **1** and **2**.

The IR spectra of all these complexes show bands characteristic of the fragments they contain. Thus, in the spectra of **1**−**3**, **5**, and **6** the bands in the regions 2606−2666 and 2114−2146 are respectively due to the B−H and C≡C stretching modes in the carborane fragment. Additionally, the spectra show bands due to N−H (**3**, 3368 cm^{-1}), C≡N (**5**, 2234 cm^{-1}), C−H (**6**, 3238, 3302 cm^{-1}), and PPN (**6**, 1581, 1320−1220, 544, 527, 491 cm^{-1}).

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Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2**·CH_2Cl_2 and **6**·$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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