Organometallic gold complexes of carborane. Theoretical comparative analysis of *ortho*, *meta*, and *para* derivatives and luminescence studies[†]

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Received 21st November 2008, Accepted 18th February 2009 First published as an Advance Article on the web 26th March 2009 DOI: 10.1039/b820803d

The synthesis and X-ray analysis of complexes $[(\mu-1,12-C_2B_{10}H_{10}){Au(PPh_3)}_2]$ and $[(\mu-1,2-C_2B_{10}H_{10})-{Au(PMe_3)}_2]$ have provided the experimental data needed to analyse two points. The first point is the use of these data to carry out a computational study with the aim of comparing the electronic structures and relative stabilities of the organometallic isomers $[(\mu-1,n-C_2B_{10}H_{10}){Au(PR_3)}_2]$ (n = 2, 7, 12; R = Ph, Me) with those of the parent carborane clusters *ortho-*, *meta-* and *para-*carborane and the influence of the monophosphine substituents. The second point is focused in the influence of the steric demand of the monophosphine in the presence or not of aurophilic interactions in the *ortho* derivatives $[(\mu-1,2-C_2B_{10}H_{10}){Au(PR_3)}_2]$ (R = Me, Ph). The photoluminescent behaviour of both the carboranes and the organometallic complexes is presented.

Introduction

Closo-carboranes are rigid three-dimensional aromatic electron withdrawing species in the sequence ortho > meta > para.¹⁻⁴ They exhibit great chemical, electrochemical and thermal stabilities which make them attractive as building blocks for the synthesis of a great variety of species. Upon deprotonation of the carbon atoms highly nucleophilic carbanions are afforded. Thus, organogold complexes with σ Au–C bonds have been reported⁵ for ortho- and meta-carborane with stoichiometries $[(\mu-1,n-1)]$ $C_2B_{10}H_{10}$ {Au(PR₃)}₂[*n* = 2 or 7], [(1-R-2-C_2B_{10}H_{10})(AuL)][R = C_5NH_4 ; L = PPh₃. R = MeOCH₂, Ph, Si^tBuMe₂; L = PR₃, AsPh₃. $R = Me; L = AsPh_3$, PPN[Au(1-Si^tBuMe_2-2-C_2B_{10}H_{10})_2] and $[(1,2-C_2B_{10}H_{11}){Au(PPh_3)}]$, the crystal structures of some of them have been characterized, as well as that of the bis-ortho-carborane compound $[\{\mu - (H_{10}B_{10}C_2 - C_2B_{10}H_{10})\}\{Au(PPh_3)\}_2]$. These studies reveal that the latter displays an aurophillic interaction between the two gold centres, whereas in the *ortho*-derivative [$\{\mu$ - $(C_2B_{10}H_{10})$ {Au(PPh₃)}₂] the gold \cdots gold distance is too long to be considered as an aurophilic interaction.

It is noticeable the lack of similar organogold complexes derived from *para*-carborane. Nevertheless, the orientation of the carbon atoms in *para*-carborane has attracted the attention of chemists. *Para*-carborane allows the synthesis of rod-like molecules and electronic transmission via the para-carborane cage has been described. Thus it has been used as a building block in calamitic molecules in which the effect of the carborane rings on the mesogenic properties has been analysed.^{6,7} As a consequence the synthesis and study of para-carborane complexes, which are almost unexplored compared with the widely studied orthocarborane coordination compounds, has increased. The electronic transmission via the para-carborane cage has been described in the cobalt systems⁸ [{ $Co_2C_2(SiMe_3)(CO)_4(dppm)$ }₂(1,12- $C_2B_{10}H_{10}$] and in luminescent iron complexes which contain the unit $[1-\{\eta^5 CpFe(CO)_{2}$ -1,12- $C_{2}B_{10}H_{10}$]⁻. Few organometallic complexes of para-carborane have been structurally characterized which include the dinuclear $[1,12-{Fe(\eta^5-Cp)(CO)_2}_2(1,12-C_2B_{10}H_{10})]$ and mononuclear $[1-{Fe(\eta^5-Cp)(CO)(PPh_3)}-(1,12-C_2B_{10}H_{11})]$ iron complexes,^{9,10} the mercury derivatives $[Hg(1-Ph-12-C_2B_{10}H_{10})_2]$, [HgCl(1-Ph-12-C₂B₁₀H₁₀)(2,2'-bipyridyl)] and the result of the reaction of the former of these mercury complexes with 2,2'bypiridyl and 2,2'-bypirimidyl.¹¹ No organometallic gold derivatives of the para isomer have been described as far as we know and complexes with C-functionalized carborane ligands from this isomer are scarcely represented. These include gold derivatives with the 1,12-(HC=C)₂-1,12-C₂ $B_{10}H_{10}$, and 1,12-(PPh₂)₂-1,12-C₂B₁₀H₁₀ ligands.^{12,13} Among them, only the crystal structures of $[\{\mu-1, 12-(C \equiv C)_2 - 1, 12 - C_2 B_{10} H_{10}\} \{Au \{P(4-OMeC_6 H_4)_3\}\}_2]$ and PPN[Au{1,12-(C=CH)₂-1,12-C₂ $B_{10}H_{10}$ }] have been reported.

Our aim in this work is to carry out a theoretical comparative analysis of organogold complexes of the *ortho-*, *meta*, and *para* isomers. With this purpose we have synthesised and structurally characterized the first organometallic gold derivative of *para*-carborane whose data also allows comparison between the organogold $[(\mu-1,n-C_2B_{10}H_{10}){Au(PPh_3)}_2]$ (n = 2, 7, 12) and the corresponding carborane isomers. The dinuclear $[(\mu-1,2-C_2B_{10}H_{10}){Au(PMe_3)}_2]$ has also been synthesised and its crystal structure elucidated in order to compare the modification of the stability of the carborane gold complexes with the monophosphine substituents and the influence of the steric demands of the

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[†] Electronic supplementary information (ESI) available: optimized geometries of the gold complexes $[(\mu-1, n-C_2B_{10}H_{10}){Au(PPh_3)}_2]$, with $n = \{2, 7, 12\}$ and the frontier orbitals in complexes $[(\mu-1, n-C_2B_{10}H_{10}){Au(PPh_3)}_2]$, with $n = \{2, 7\}$. CCDC reference numbers 710441 & 710442. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820803d

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monophosphine in the presence or not of aurophilic interactions in the *ortho*-derivatives. Photoluminescent steady-state studies have been carried out both for the carborane isomers and the organometallic complexes.

Experimental and computational methodologies

Instrumentation. C, H, N and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on Bruker ARX 400 spectrometers in CDCl₃. Chemical shifts are cited relative to SiMe₄ (¹H, external), and 85% H₃PO₄ (³¹P, external). Steady-state photoluminescence spectra were recorded with a Jobin-Yvon Horiba fluorolog FL-3-11 spectrometer using band pathways of 3 nm for both excitation and emission. The solid samples were prepared by mixing the compounds with silica gel.

Starting materials. The starting materials $[AuCl(PPh_3)]^{14}$ and $[AuCl(PMe_3)]^{15}$ were prepared according to published procedures. All other reagents are commercially available. Reaction solvents were reagent grade and were distilled from the appropriate drying agents under argon prior to use.

Synthesis of $[(\mu-1, 12-C_2B_{10}H_{10}){Au(PPh_3)}_2](1)$

To a solution of *para*-carborane (28.8 mg, 0.2 mmol) in diethyl ether at 0 °C, under an argon atmosphere, ⁿBuLi (hexane solution 1,6 M, 0.38 mL, 0.6 mmol) was added and the mixture was stirred for one hour. The solution was warmed to room temperature and [AuCl(PPh₃)] (172 mg, 0.35 mmol) was added. The suspension was stirred for 90 min and the remaining solid filtered over Celite. The filtrate was evaporated (*ca.* 5 mL). Addition of n-hexane (*ca.* 10 mL) afforded a white solid. Yield 137.4 mg (74%). Analytical data, Found: C 43.15, H 3.75; Calculated for $C_{38}H_{40}Au_2B_{10}P_2$: C 43.05, H 3.70. ³¹P {¹H} NMR: 38.0 ppm (s); ¹H NMR: 1–3 ppm (m, br, 10H, BH); 7.3-7.6 (m, br, 30H, Ph).

Synthesis of $[(\mu-1,2-C_2B_{10}H_{10}){Au(PMe_3)}_2]$ (2)

In a similar procedure to that described for **1** "BuLi (hexane solution 1,6 M, 0.38 mL, 0.6 mmol) was added to a solution of *ortho*-carborane (28.8 mg, 0.2 mmol) in tetrahydrofuran at 0 °C under an argon atmosphere and the mixture was stirred for 2.5 h. The solution was warmed to room temperature and [AuCl(PMe₃)] (107.8 mg, 0.35 mmol) was added. The suspension was stirred for two days and the remaining solid filtered over Celite. The filtrate was evaporated (*ca.* 5 mL). Addition of n-hexane (*ca.* 10 mL) afforded 54 mg of a yellow–orange solid which contains a mixture of three different compounds from which **2** represents \approx 64% (based on integration of ¹H NMR resonances). Spectroscopic data for **2**: ³¹P {¹H} NMR: 0.0 ppm (s); ¹H NMR: 1–3 ppm (m, br, BH), 1.48 ppm [J(PH) = 10 Hz, Me]. Other NMR resonances: ³¹P{¹H}–1.4 (s); ¹H 1.73 [t, J(PH) = 4 Hz)], (\approx 18%) and ³¹P{¹H} 4.3 ppm (s); ¹H 1.58 [d, J(PH = 10 Hz)] (\approx 18%).

X-Ray studies

Crystals of complexes 1 and 2 were obtained by addition of n-hexane to a solution of the compounds in dichloromethane (1) or $CDCl_3$ (2). Data were recorded on a Xcalibur Oxford Diffraction diffractometer. The crystals were mounted in an inert oil on glass

 Table 1
 Details of data collection and structure refinement for 1 and 2

Compound	1	2
Formula	$C_{38}H_{40}Au_2B_{10}P_2$	$C_8H_{28}Au_2B_{10}P_2$
M _r	1060.67	688.28
Habit	colourless plate	colourless prism
Crystal size (mm)	$0.33 \times 0.10 \times 0.06$	$0.16 \times 0.15 \times 0.09$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
Cell constants:		
a (Å)	8.1035(16)	16.807(3)
b (Å)	11.757(2)	13.648(3)
c (Å)	20.581(4)	18.454(4))
β (°)	97.18(3)	102.73(3)
$V(Å^3)$	1945.4(7)	4128.7(14)
Ζ	2	8
$D_{\rm x} ({\rm Mg}{\rm m}^{-3})$	1.811	2.215
$\mu (mm^{-1})$	7.644	14.338
F(000)	1012	2512
T (°C)	-100(2)	-100(2)
$2\theta_{\text{max}}$	52.0	52.0
No. of refl.:		
measured	28940	61066
independent	3803	4049
Transmissions	0.66-0.19	0.36-0.21
$R_{\rm int}$	0.031	0.028
Parameters	235	205
Restraints	9	0
$wR(F^2, \text{ all Refl.})$	0.058	0.042
$R(F, >4\sigma(F))$	0.023	0.020
S	1.16	1.14
max. $\Delta \rho$ (e Å ⁻³)	1.35	1.02

fibers and transferred to the cold gas stream of the diffractometer. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073$) in ω scans. An absorption correction with the program SADABS¹⁶ based on multiple scans was used. The structures were solved by direct methods (1) or the heavy atom method (2) and refined on F^2 using the program SHELXL-97.¹⁷ All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Details of data collection and refinement are shown in Table 1. The residual electron density peaks are near one of the gold atoms in both cases.

Computational method

All density functional calculations were performed with the suite of programs Gaussian03¹⁸ with the Hartree–Fock/DFT hybrid functional B3LYP method.¹⁹ Effective core pseudopotentials and their associated double- ζ basis sets, known as LANL2DZ, were used for Au.²⁰ The basis set 6–31G* was used for all other atoms.²¹

As regards to geometry optimizations, we started off with the geometries from the crystal structures^{22,23} and reached energy minima for the *ortho-*, *meta-* and *para-*carborane complexes [(μ -1,n-C₂B₁₀H₁₀){Au(PPh₃)}₂], with n = 2, 7, and 12 respectively. All geometries correspond to energy minima characterized by vibrational analysis.

Results and discussion

Preparation and crystal sctructure of $[(\mu-1,12-C_2B_{10}H_{10})-{Au(PPh_3)}_2]$ (1) and $[(\mu-1,2-C_2B_{10}H_{10}){Au(PMe_3)}_2]$ (2)

Reaction of $Li_2(1,12-C_2B_{10}H_{10})$ with [AuCl(PPh₃)] in Et₂O in molar ratio 1:2 affords the dinuclear compound [(μ -1,12-C₂B₁₀H₁₀)-

 $\{Au(PPh_3)\}_2$ (1). Complex $[(\mu-1,2-C_2B_{10}H_{10})\{Au(PMe_3)\}_2$ (2) may be prepared from $[Li_2(1,2-C_2B_{10}H_{10})]$ and $[AuCl(PMe_3)]$ in Et₂O or THF as solvents. Reaction times are longer than for the para-carborane derivative (1). Compound 2 is not isolated as a pure compound, it represents the majority product of a mixture of three species. ¹H NMR studies of the crystals of 2 (see below) has lead to spectral identification of the complex (see Experimental). In the ${}^{31}P{}^{1}H$ NMR spectrum of 1 the two equivalent phosphorus appear as a broad signal at $\delta = 38$ ppm, at a very similar field to that found for $[(\mu-1,n-C_2B_{10}H_{10}){Au(PPh_3)}_2][\delta = 38.5 (n = 2)$ or 40.5 (n = 7)]. The resonance corresponding to compound 2 is observed at much higher field (0.0 ppm). The ¹H NMR spectra of 1 and 2 show a very broad resonance corresponding to the BH hydrogen atoms between 1 and 3 ppm, one multiplet corresponding to the phenyl hydrogen atoms between 7 and 8 ppm for 1 and that corresponding to the presence of the methyl groups at 1.48 ppm in 2. No signal corresponding to the presence of unsubstituted carborane is found in these spectra.

The structures of **1** and **2** (Figs. 1 and 2) show the expected icosahedral cage for the C_2B_{10} unit having a linear coordination for gold atoms that display a slightly distorted geometry with



Fig. 1 Molecular structure of $[(\mu-1,12-C_2B_{10}H_{10}){Au(PPh_3)}_2]$ (1). Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level.



Fig. 2 Molecular structure of $[(\mu-1,2-C_2B_{10}H_{10}){Au(PMe_3)}_2]$ (2). Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level.

C–Au–P angles of 175.75(10)° (1) which are in between those found in the *ortho* [178.9(4)°, 174.2(4)°] and *meta* [179.3(2)°, 174.1(2)°] complexes with PPh₃ as monophosphine, and are similar to that found in **2** [175.87(11)°, 175.76(10)°]. Au–P and Au–C distances found in **1** and **2** compare well with those found in the analogous complexes with the *ortho*-, or *meta*-carborane isomers [(μ -1,n-C₂B₁₀H₁₀){Au(PPh₃)}₂] (n = 2, 7; see Table 2). Interestingly, the steric effects do not govern the presence of aurophilic interactions which are absent in both **2** and in [(μ -1,2-C₂B₁₀H₁₀){Au(PPh₃)}₂] despite the difference of the phosphine substituents.

Luminescence studies

Steady-state photoluminescence studies of the three isomers of carborane as well as the *ortho* and *para* derivatives have been carried out. The three carborane isomers are weakly luminescent in the solid state, both at room temperature and 77 K (table 3).

Table 2 Bond distances in the different isomers $[(\mu-1,n-C_2B_{10}H_{10})\{Au(PPh_3)\}_2]$: *ortho-*, *meta-* and *para-* [n = 2, 7, and 12 (1)] and $[(\mu-1,2-C_2B_{10}H_{10})\{Au(PMe_3)\}_2]$ (2)

	Experimental values (Å)					
Distance	Ortho ^a with PPh ₃	<i>Ortho</i> with PMe ₃	Meta ^b with PPh ₃	Para with PPh ₃		
C–C ^c	1.71(2)	1.693(5)		_		
C–Au	2.055(14) 2.033(15)	2.049(4) 2.068(4)	2.054(7) 2.047(7)	2.058(4)		
Au–P	2.270(4) 2.273(5)	2.2623(12) 2.2731(10)	2.265(2) 2.271(2)	2.2738(10)		
Au · · · Au	3.567(1)	3.5223(7)	6.14	_		
	Computed values (Å)					
	PPh ₃	PMe ₃				
Distance	ortho	meta	para	ortho	meta	para
C····C	1.687	_	_	1.686	_	_
C–Au	2.077	2.078	2.078	2.076	2.078	2.079
Au–P	2.378	2.380	2.384	2.366	2.368	2.368
Au · · · Au	3.762	—	—	3.799	_	—

^a Data from reference 22. ^b Data from reference 23. ^c For carborane carbon atoms.

 Table 3
 Emission maxima (nm) for the three carborane isomers and their organogold complexes in the solid state

Compound	Room T	77 K
Ortho-carborane	356	354
Meta-carborane	380	390
Para-carborane	345	320
$[(\mu-1,2-C_2B_{10}H_{10}){Au(PPh_3)}_2]$	368, 500	399, 500
$[(\mu-1,2-C_2B_{10}H_{10})]$ Au(PMe ₃)]	391, 500	403, 516
$[(\mu-1,7-C_2B_{10}H_{10})]$ Au(PPh ₃)]	394, 527	396, 513
$[(\mu-1, 12-C_2B_{10}H_{10}){Au(PPh_3)}_2]$	367, 506	389, 555

They display emissions between 345 and 390 nm (table 3). The corresponding excitation maxima appear between 285 and 310 nm. Luminescence studies of *ortho*-carborane have been reported²⁴ which for this isomer describe a weak emission at 395 nm at room temperature as well as a structured emission at 410 nm both in the solid state at 77 K and in ethanol frozen solutions. We have observed emission near 390 nm for the three carborane isomers. The band at lower energies has not been observed by us, although we have seen a very weak shoulder (whose tail goes on almost until 500 nm) in the band described above upon excitation near 260 nm. Upon excitation at lower energies the intensity of the shoulder decreases and even or almost disappears and the emission near 390 nm is always present.

The organometallic derivatives display two emission bands (Table 3) whose maxima appear at about 380 and 520 nm. Emission at higher energies resembles that of the unsubstituted carboranes and we propose for this band an intraligand (IL-carborane) origin. The relative intensity of both emissions depends on the excitation wavelength. The high energy band always displays very low intensity and even disappears. The spectra shown in Fig. 3 have been recorded with an excitation wavelength of 300 nm. Metal to ligand charge transitions (MLCT) could be responsible for these emissions near 520 nm.



Fig. 3 Emission spectra of the organogold complexes $[(\mu-1,n-C_2B_{10}H_{10})-{Au(PR_3)}_2]$ (n = 2 (R = Ph, Me), 7 (R = Ph), 12 (R = Ph). Excitation wavelength 310 nm.

Computational studies of $[(\mu-1,n-C_2B_{10}H_{10}){Au(PPh_3)}_2]$, n = 2, 7, and 12

In Fig. 4 we display the optimized geometry of the *para*-complex $[(\mu-1,12-C_2B_{10}H_{10}){Au(PPh_3)}_2]$. Comparison of exper-

Compound	ortho	meta	para
$[(1,n-C_2B_{10}H_{12})]$ $[(1,n-C_2B_{10}H_{12})]$	+19.7	+3.4	0.0
$[(1,n-C_2B_{10}H_{10})\{Au(PMe_3)\}_2]$	+11.7 +13.6	+0.4 +0.5	0.0



Fig. 4 Main parameters for the optimized geometry of complex $[(\mu-1,12-C_2B_{10}H_{10}){Au(PPh_3)}_2]$. *C_i* symmetry point-group.

imental and computed distances show good agreement. Similar results have been obtained for the *ortho-* and *meta-*complexes $[(\mu-1,n-C_2B_{10}H_{10}){Au(PPh_3)}_2]$ (n = 2, 7). The ESI† contains the atomic coordinates for the optimized geometries.

The relative stability of the three isomers for three families of complexes: (i) the unsubstituted carboranes, (ii) disubstituted with two "AuPPh₃" fragments and (iii) disubstituted with two "AuPMe₃" fragments, have been analysed and are presented in Table 4. Among each family of complexes the relative stability shows the same order: $para \ge meta > ortho$. These studies are in agreement with the previously reported theoretical studies for the carborane isomers [1b,c]. The organometallic gold complexes show in all cases higher stabilities than the corresponding parent carboranes. This stabilization may arise from the fact that the gold-phosphine fragment can provide more electron density to the carborane carbon atoms, compared with hydrogen. A different analysis can be carried out in order to compare those species which contain the same carborane isomer. These data suggest that coordination of the "Au(PPh₃)" fragment leads to more stable complexes than the coordination of "Au(PMe₃)" with higher differences found for the ortho isomers. The electronic properties of PPh₃, compared with PMe₃ (balance between σ -donor/ π -acceptor character) could be responsible for these differences. Furthermore, the crystallographic data for the ortho-carborane gold complexes show the absence of aurophilic interactions that could contribute to the stability of these compounds. Consequently, steric factors do not play a great influence, either on the stability of the compounds or in the presence of gold \cdots gold contacts.

Fig. 5 displays some frontier orbitals for the *para* complex $[(\mu-1,12-C_2B_{10}H_{10}){Au(PPh_3)}_2]$, whereas the ESI† contains the plots for the respective frontier orbitals of the *ortho-* and *meta-* complexes. The four higher occupied molecular orbitals are responsible for Au–P and Au–C bonds: two of the latter are displayed in Fig. 5a and Fig. 5b, corresponding to symmetric and antisymmetric combinations of their localized bonds. We should



Fig. 5 Selected molecular orbitals for optimized complex $[(\mu-1,12-C_2B_{10}H_{10}){Au(PPh_3)}_2]$: (a) HOMO-3; (b) HOMO; and (c) LUMO. Orbital function isovalue = 0.02.

highlight the contribution from the cage boron atoms on the symmetric orbital (HOMO), which delocalizes electron density onto the carborane cage. A similar situation applies for the *meta*-and *ortho*-complexes.

The LUMO of the *para*-complex is shown in Fig. 5c, whose wave function amplitude leads to the conclusion that a nucleophilic attack should be directed mainly towards the carborane cage. Thus, the nucleophilic/electrophilic character of these complexes lie mainly onto the {P-Au-carborane-Au-P} central part and the *exo* phenyl groups respectively, with the exception of the *para*-complex, the latter having the LUMO or more accessible orbital for surplus electrons along the whole skeleton of the complex (see ESI†).

Electronic charges are purely formal and can be obtained through different population analyses. Since natural population analysis (NPA) shows a more "realistic" scheme as compared to the Mulliken charges, we have only included here the NPA analysis, although the same trends can be observed in the Mulliken population analysis (see ESI[†]). Table 5 gathers the natural bond order (NBO) charges for the *ortho-*, *meta-* and *para-*complexes

Table 5 NPA charges (in electrons) in *ortho-*, *meta-*, and *para-*carborane, and the corresponding complexes $[(\mu-1, n-C_2B_{10}H_{10})Z_2]$ (n = 2, 7, 12), with Z = H or AuPPh₃ fragment

	ortho		
	H	AuPPh ₃	AuPMe ₃
С	-0.548	-0.719	-0.714
\mathbf{B}^{A}	0.147	0.140	0.145
\mathbf{B}^{B}	-0.012	-0.016	-0.011
BC	-0.181	-0.178	-0.176
\mathbf{B}^{D}	-0.154	-0.153	-0.151
Au	_	0.355	0.292
P	—	1.006	0.970
	meta		
	H	AuPPh ₃	AuPMe ₃
С	-0.708	-0.871	-0.869
BA	0.147	0.142	0.145
Вв	-0.014	-0.015	-0.011
B ^C	0.010	0.007	0.010
\mathbf{B}^{D}	-0.181	-0.178	-0.176
Au		0.351	0.298
P	—	1.003	0.969
	para		
	Н	AuPPh ₃	AuPMe ₃
c	-0.696	-0.855	-0.859
В	-0.013	0.015	-0.010
Au		0.348	0.295
Р		1.003	0.972

together with the same charges of the parent carboranes for comparative purposes.



For *ortho*- and *meta*-C₂B₁₀H₁₂ isomers, the charges on the boron atoms depend on their positions as compared to the charges on the carbon atoms, with variations ranging up to 0.33, whereas the charges on boron atoms for *para*-C₂B₁₀H₁₂ are equal due to the symmetry of the cluster. However, the *para*- and *meta*-C₂B₁₀H₁₂ isomers have similar charges on carbon atoms: ~ -0.71, with a lower change on the carbon (-0.55) for the *ortho*-C₂B₁₀H₁₂ isomer; the latter can be attributed to the relative stability found in these molecules (Table 2). These variations are also transferred to the related complexes when H is substituted by Au(PR₃), an indication that the electronic structure of the isomers for each molecular species can be transferred between each other: [H \leftrightarrow Au(PR₃)]. Finally, an important increase of negative charge of ~ -0.2 is observed for carbon atoms in organogold complexes, whereas charges on boron atoms remain almost unchanged.

The NPA charges on Au atoms are 0.35 and 0.29 for all isomers having R = Ph and Me, respectively, whereas the charge on P has about 1.0. These data support the changes in the donor nature of

the phosphine ligands. These values for triphenylphospine can be compared with those computed on the experimental geometries of [AuCl(PPh₃)]²⁵ and [AuPh(PPh₃)]²⁶ with the same theoretical model: The NPA charges on P are 1.05 and 1.00, respectively, as is expected for a gold(I)–phosphine fragment. However, the NPA charges on Au, 0.19 and 0.17 respectively, have a decrease of *ca.* 0.2e as compared to the carborane complexes. Hence, the increase of the polarity in the X–Au(PPh₃) bonds can be related to the electron-deficiency nature of carborane boxes (as reflected in the HOMO orbital plot, see Fig. 5b and ESI†) together with the electron withdrawing role of the cages in the [(μ -1,n-C₂B₁₀H₁₀){Au(PPh₃)}₂] (n = 2, 7, 12) complexes, as compared to well known compounds, such as [AuX(PPh₃)] (X = Cl, Ph).

Conclusions

The ortho-carborane compound $[(\mu-1,2-C_2B_{10}H_{10}){Au(PMe_3)}_2]$ and the first organogold derivative of *para*-carborane [(μ -1,12- $C_2B_{10}H_{10}$ {Au(PPh₃)}₂ have been synthesised and their crystal structures elucidated. These studies have provided the basis for a comparative study for the three isomeric species ortho-, meta- and para-carborane having AuPR₃ groups bonded to the carbon cage atoms or hydrogen atoms, $[(1,n-C_2B_{10}H_{10})Z_2], (Z = H, AuPPh_3;$ AuPMe₃, n = 2, 7, 12), in an attempt to analyze the electronic structure and the relative stabilities of the three complexes as compared to their carborane parent compounds, as well as the influence of the phosphine substituents. The three carboranes, and the organogold complexes are emissive. The parent carboranes display a weak band at about 390 nm. The organogold derivatives display, in addition to this band, a more intense one at lower energies (at about 520 nm). The band at higher energies can be tentatively assigned to IL transitions, whereas that at lower energies could arise from MLCT transitions.

An interesting future direction that could be followed is related to the self-assembling of carborane moieties which could lead to the synthesis of the as yet unknown crystal structure of the gold carborane trimer shown in Fig. 6b, whose optimized

Fig. 6 (a) Experimental structure of the methylated mercuracarborane trimer.²⁶ (b) Optimized geometry of the yet unknown gold carborane derivative trimer (same theoretical level as used in this work, see main text).

geometry (Fig. 6a) is compared with that of the analogous mercuracarborane derivative described by Hawthorne *et al.*²⁷

Acknowledgements

We thank the Ministerio de Educacion y Ciencia No. CTQ2007-67273-C02-01 and MAT2006-13646-C03-02 for financial support.

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