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Partial Degradation of the New *exo*-Heterodisubstituted Carborane Derivatives with d^{10} Transition Metal Ions (Cu, Au)

Francesc Teixidor,[†] Rajae Benakki,[†] Clara Viñas,*,[†] Raikko Kivekäs,[‡] and Reijo Sillanpää[§]

Institut de Ciència de Materials de Barcelona, Universitat
Autonoma de Barcelona, E-08193 Bellaterra, Spain,
Department of Chemistry, University of Helsinki, Box 55,
Helsinki, FIN-00014, Finland, and Department of Chemistry,
University of Turku, Turku FIN-20500, Finland

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Introduction

The influence of substitution at the cluster carbon atoms in metallacarboranes by electron rich elements has been of interest to us. Recent results have shown that reaction of electron rich d^{10} metal ions Cu(I), Ag(I), and Au(I) with *exo*-dithiocarboranes, $[1,2\text{-}\mu\text{-(SRS)-}1,2\text{-}C_2B_{10}H_{10}]$,[1] and *exo*-diphosphinocarboranes, $[1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$,[2] in degassed ethanol leads to partial degradation (removal of the carbon's adjacent boron atom) of the *closo* species. Neutral complexes with the formula $[M(7,8\text{-}\mu\text{-(SRS)-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$ and $[M(7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$ (M = Cu(I), Ag(I), Au(I)) were obtained, respectively. In these examples, partial degradation of *closo* to *nido* took place and the metal is coordinated through two sulfur or two phosphorus atoms. There are some examples with Hg(II) and Ag(I), where interaction between the metal and the C_2B_3 open face has taken place. It has been mainly found with dithiocarboranes of the type $[1,2\text{-}\mu\text{-}(SCH_2S)\text{-}1,2\text{-}C_2B_{10}H_{10}]$.[3] In contrast, no reaction has taken place between *exo*-monothiocarboranes $[1\text{-SR-}2\text{-R}'\text{-}1,2\text{-}C_2B_{10}H_{10}]$ or *exo*-monophosphinocarboranes $[1\text{-}PR_2\text{-}2\text{-R}'\text{-}1,2\text{-}C_2B_{10}H_{10}]$ with d^{10} , Au(I), and Cu(I) transition metal complexes. In these cases the free carborane was recovered. Thus, although complexes of dithio and diphosphino[1,2] carboranes with d^{10} transition metals have been reported, there is no previous report of complexes incorporating the anionic heterodisustituted ligands $[7\text{-}PR_2\text{-}8\text{-SR-}7,8\text{-}C_2B_9H_{10}]^{-}$.

To know more on the influence of electron rich elements bonded to the carborane cluster, we have studied the reactions of the new *closo exo*-heterodisubstituted carborane derivatives $1\text{-SR-}2\text{-}PPh_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with $[MCl(PPh_3)_n]$ (M = Cu, n = 2; M = Au, n = 1) in ethanol. Our aim in this study is to have an "in situ" comparison of the reactivity of C−SR and C−PPh_2 by reaction with metal complexes.

Experimental Section

Materials and Methods. Commercial *o*-carborane was sublimed under high vacuum at 0.01 mmHg prior to use. $1\text{-SR-}1,2\text{-}C_2B_{10}H_{11}$ and $1\text{-SR-}2\text{-}PPh_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = Et, Bz) were synthesized according to the literature.[4,5] A 1.6 M solution of *n*-butyllithium in *n*-hexane was used as purchased. $[AuCl(PPh_3)]$ [6] and $[CuCl(PPh_3)_2]$ [7] were synthesized as described elsewhere. All organic compounds and inorganic salts were analytical reagent grade and were used as received. The solvents were reagent grade. All reactions were carried out under a dinitrogen atmosphere by using Schlenck techniques. Microanalyses were performed by using a Perkin-Elmer 240B microanalyzer. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), ^{11}B NMR (96.29 MHz), and $^{31}P\{^1H\}$ NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shift values for ^1H NMR spectra were referenced to an internal standard of $SiMe_4$ in deuterated solvents. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. Chemical shift values for $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4.

Synthesis of $[Au(7\text{-}PPh_2\text{-}8\text{-SEt-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$. $[AuCl(PPh_3)]$ (127.4 mg, 0.26 mmol) was added to a solution of $1\text{-}PPh_2\text{-}2\text{-SEt-}1,2\text{-}C_2B_{10}H_{10}$ (100.0 mg, 0.26 mmol) in deoxygenated ethanol (10 mL). The yellow mixture was refluxed for 1 h 30 min. The resulting white-brown solid was then filtered off, washed with hot ethanol (5 mL) and diethyl ether (5 mL), and dried in a vacuum line to yield 172.0 mg, (0.21 mmol, 80%). Anal. Calcd for $C_{34}H_{40}AuB_9P_2S$: C, 48.79; H, 4.82; S, 3.83. Found: C, 49.20; H, 4.83; S, 3.51. FTIR (cm^{-1}): ν (B−H) 2541. $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ −2.3 (s br, 1H, B*H*B), 0.6 (t, J(HH) = 7, 3H, CH_3), 1.8 (m, 1H, CH_2), 2.7 (m, 1H, CH_2), 7.6 (m, 23 H, Ph), 8.3 (2H, q(1:1:1:1), J = 8.2, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.2 (s, CH_3), 33.0 (s, SCH_2), 54.0 (s, $BC_{cluster}$), 59.0 (s, $BC_{cluster}$), 128.2−135.2 (Ph). ^{11}B NMR ($CDCl_3$): δ −6.3 (2B), −9.6 (2B), −17.3 (1B), −21.1 (2B), −31.1 (1B), −35.3 (d, J(BH) = 72, 1B). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.3 (d, J(PP) = 308, PPh_3), 53.3 (d, J(PP) = 308, PPh_2).

Synthesis of $[Au\ (7\text{-}PPh_2\text{-}8\text{-SBz-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$. The procedure is as before using $1\text{-}PPh_2\text{-}2\text{-SBz-}1,2\text{-}C_2B_{10}H_{10}$ and $[AuClPPh_3]$ in a 0.11 mmol scale, yield 50.0 mg, (0.06 mmol, 50%). Recrystallization from chloroform/*n*-hexane (1:1) gave yellow crystals. Anal. Calcd for $C_{39}H_{42}AuB_9P_2S{\cdot}CHCl_3$: C, 47.01; H, 4.24; S, 3.14. Found: C, 47.02; H, 4.31; S, 3.34. FTIR (cm^{-1}): ν(B−H) 2537, 2516. $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ −2.2 (s br, 1H, B*H*B), 3.1 (d, J(HH) = 11, 1H, CH_2), 4.2 (d, J(HH) = 11, 1H, CH_2), 6.6−7.0 (m, 28H, Ph), 8.2 (2H, q(1:1:1:1), J = 11.2, Ph). ^{11}B NMR ($CDCl_3$): δ −6.2 (2B), −9.8 (2B), −17.3 (2B), −21.0 (1B), −31.1 (1B), −34.5 (d, J(BH) = 72, 1B). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.2 (d, J(PP) = 307, PPh_3), 52.9 (d, J(PP) = 307, PPh_2).

Synthesis of $[Cu(7\text{-}PPh_2\text{-}8\text{-SEt-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$. $[CuCl(PPh_3)_2]$ (49.2 mg, 0.08 mmol) was added to a solution of $1\text{-}PPh_2\text{-}2\text{-SEt-}1,2\text{-}C_2B_{10}H_{10}$ (30.0 mg, 0.08 mmol) in deoxygenated ethanol (5 mL). The mixture was refluxed for 2 h. The solution was then concentrated in a vacuum to 2 mL and cooled (0 °C). The solid was filtered, and the filtrate was evaporated at the vacuum to yield a white solid, 17.0 mg (0.024 mmol, 30%). Anal. Calcd for $C_{34}H_{40}CuB_9P_2S$: C, 58.05; H, 5.73; S, 4.56. Found: C, 57.82; H, 5.42; S, 4.11. FTIR (cm^{-1}): ν(B−H) 2537. $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ −2.3 (s br, 1H, B*H*B), 1.2 (m, 3H, CH_3), 2.5 (m, 1H, S−CH_2), 2.8 (m, 1H, S−CH_2), 7.3−7.5 (m, 23 H, Ph), 8.0 (q(1:1:1:1), J = 7, 2H,, Ph); $^{31}P\{^1H\}$, δ −2.7 (s br, 1P), 16.4 (s br, 1P). ^{11}B NMR (acetone-d_6): δ −8.4 (2B), −13.2 (1B), −14.5 (2B), −16.9 (2B), −30.9 (d, J(BH) = 114, 1B), −34.4 (d, J(BH) = 138, 1B).

Synthesis of $[Cu\ (7\text{-}PPh_2\text{-}8\text{-SBz-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$. $[CuCl(PPh_3)_2]$ (69.2 mg, 0.11 mmol) was added to a solution of $1\text{-}PPh_2\text{-}2\text{-SBz-}1,2\text{-}C_2B_{10}H_{10}$ (50.0 mg, 0.11 mmol) in deoxygenated ethanol (6

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* To whom correspondence should be addressed. Fax: Int code + (93) 5805729. E-mail. Clara@icmab.es.

[†] Universitat Autonoma de Barcelona.

[‡] University of Helsinki.

[§] University of Turku.

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Table 1. Crystallographic Data and Structure Refinement for $[Au(7\text{-}PPh_2\text{-}8\text{-}SBz\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]\cdot CHCl_3$ and $[Cu(7\text{-}PPh_2\text{-}8\text{-}SBz\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]\cdot {}^1/_2CH_2Cl_2$

empirical formula	$C_{40}H_{43}AuB_9Cl_3P_2S$	$C_{39.5}H_{43}B_9ClCuP_2S$
fw	1018.35	808.02
T, °C	21	21
λ, Å	0.710 69	0.710 69
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	14.652(4)	10.338(5)
b, Å	14.747(3)	17.057(17)
c, Å	12.618(2)	23.739(2)
α, deg	109.091(14)	90
β, deg	100.965(17)	96.043(15)
γ, deg	111.454(15)	90
V, Å^3	2244.3(8)	4163(5)
Z	2	4
D_{calcd}, g cm^{-3}	1.507	1.289
μ, cm^{-1}	36.03	7.45
F(000)	1008	1668
independent reflns	7909	6963
params	535	517
goodness-of-fit on F^2	1.035	0.976
R1^a [$I > 2\sigma(I)$]	0.0354	0.0710
wR2^b [$I > 2\sigma(I)$]	0.072	0.1200
large diff peak/hole, e Å^{-3}	0.662 and −0.659	0.366 and −0.341

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

mL). The mixture was refluxed for 3 h and then the solvent was evaporated. The resulting residue was treated with dichloromethane/*n*-hexane (1:1) and cooled (0 °C), yielding 38.4 mg (0.05 mmol, 45%) of a white solid; yellow crystals were obtained from dichloromethane/*n*-hexane. Anal. Calcd for $C_{39}H_{42}CuB_9P_2S\cdot{}^1/_2CH_2Cl_2$: C, 58.70; H, 5.32; S, 3.96. Found: C, 58.43; H, 5.20; S, 3.65. FTIR (cm^{-1}): ν (B−H) 2537. $^1H\{^{11}B\}$ NMR (acetone-d_6): δ −2.3 (s br, 1H, B*H*B), 3.9 (d, J(HH) = 12, 1H, CH_2), 4.3 (d, J(HH) = 12, 1H, CH_2), 6.7−7.2 (m, 30H, Ph). ^{11}B NMR (acetone-d_6): δ −7.0 (1B), −8.8 (2B), −12.1 (1B), −14.7 (d, J(BH) = 132, 3B), −30.9 (d, J(BH) = 141, 1B), −34.5 (d, J(BH) = 159, 1B).

X-ray Studies. Single-crystal data collections for $[Au(7\text{-}PPh_2\text{-}8\text{-}SBz\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$ and $[Cu(7\text{-}PPh_2\text{-}8\text{-}SBz\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$ were performed at room temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo Kα radiation. For both compounds, the unit cell parameters were determined by least-squares refinement of 25 (17 for $[Cu(7\text{-}PPh_2\text{-}8\text{-}SBz\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$ carefully centered reflections. The data were collected by the $\omega-2\theta$ technique to a maximum 2θ value of 50°. Both data were corrected for Lorentz and polarization effects, and for absorption (ψ scans). The structures were solved by direct methods, and full-matrix least-squares refinements on F^2 were performed by using the SHELXS-86 program.[8] Non-hydrogen atoms were refined with anisotropic displacement parameters and BH hydrogens with isotropic displacement parameter. The rest of the hydrogen atoms were included in the calculations at fixed distances from their host atoms (riding model). Crystallographic data and refinement for the compounds are presented in Table 1, and selected bond distances and angles, in Tables 2 and 3.

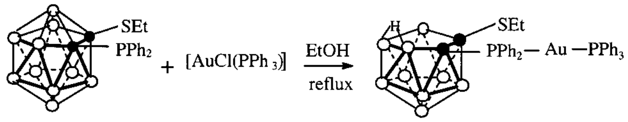
Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Au(7\text{-}PPh_2\text{-}8\text{-}SBz\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3]\cdot CHCl_3$

Au−P(1)	2.3186(13)	P(2)−C(24)	1.823(5)
Au−P(2)	2.3051(13)	P(1)−C(7)	1.826(5)
S−C(8)	1.799(5)	P(1)−C(12)	1.832(5)
S−C(42)	1.817(6)	P(1)−C(18)	1.816(5)
P(1)−C(30)	1.811(5)	C(7)−C(8)	1.600(6)
P(2)−Au−P(1)	173.28(5)	C(30)−P(2)−C(24)	105.7(2)
C(18)−P(1)−C(7)	106.5(2)	C(36)−P(2)−C(24)	107.0(2)
C(18)−P(1)−C(12)	107.1(2)	C(18)−P(1)−Au	114.87(17)
C(8)−S−C(42)	102.2(2)	C(24)−P(2)−Au	111.36(17)
C(7)−P(1)−C(12)	107.1(2)	C(30)−P(2)−Au	118.42(17)
C(7)−P(1)−C(18)	106.5(2)	C(36)−P(2)−Au	108.23(16)
C(12)−P(1)−C(18)	107.1(2)	C(8)−C(7)−B(11)	112.9(4)
C(7)−P(1)−Au	113.67(15)	C(8)−C(7)−B(2)	111.1(4)
C(12)−P(1)−Au	107.15(17)	C(8)−C(7)−P(1)	117.7(3)
C(30)−P(2)−C(36)	105.5(2)	C(7)−C(8)−S	120.5(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(7\text{-}PPh_2\text{-}8\text{-}SBz\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]\cdot{}^1/_2CH_2Cl_2$

Cu−P(1)	2.257(2)	P(1)−C(12)	1.811(7)
Cu−P(2)	2.222(2)	P(1)−C(18)	1.826(7)
Cu−S	2.302(2)	P(2)−C(24)	1.813(7)
Cu···Cl	2.999(4)	P(2)−C(36)	1.820(9)
S−C(8)	1.821(6)	P(2)−C(30)	1.837(7)
S−C(42)	1.836(7)	C(7)−C(8)	1.594(8)
P(1)−C(7)	1.834(6)		
P(1)−Cu−P(2)	134.38(8)	C(7)−P(1)−C(18)	106.7(3)
P(1)−Cu−S	92.04(7)	C(12)−P(1)−C(18)	106.4(3)
P(2)−Cu−S	129.17(8)	C(7)−P(1)−Cu	106.4(2)
P(1)−Cu···Cl	103.73(9)	C(12)−P(1)−Cu	103.6(2)
P(2)−C···Cl	90.02(9)	C(18)−P(1)−Cu	126.7(2)
S−Cu···Cl	98.56(11)	C(24)−P(2)−Cu	115.6(3)
C(8)−S−C(42)	104.2(3)	C(36)−P(2)−Cu	113.5(3)
C(8)−S−Cu	104.6(2)	C(30)−P(2)−Cu	112.3(2)
C(42)−S−Cu	106.8(3)	C(8)−C(7)−P(1)	115.8(4)
C(7)−P(1)−C(12)	105.2(3)	C(7)−C(8)−S	119.1(4)

Scheme 1. Partial Degradation by Complexation of $[Au(7\text{-}PPh_2\text{-}8\text{-}SEt\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$



Results and Discussion

The $1\text{-}PPh_2\text{-}2\text{-}SR\text{-}1,2\text{-}C_2B_{10}H_{10}$ *closo* compounds have two nonequivalent coordinating sites, $C-PPh_2$ and $C-SR$. The coordination capacity concomitant with the partial degradation of the cluster cage in electron rich homodisubstituted ligands from C_2B_{10} to $[C_2B_9]^-$ has been proven. Furthermore it has been found that the metal driven partial degradation of the *closo* cluster does not take place for monosubstituted $C-PPh_2$ or $C-SR$ compounds.[9] As a consequence it was not known whether these *closo* heterodisubstituted compounds would deboronate to the nido $[C_2B_9]^-$ species, hence reverting to good coordinating ligands or, on the contrary, would remain passive, maintaining the *closo* structure. On the other hand the non-equivalency of the substituents permitted to distinguish the coordinating capacity of one substituent vs the other, a fact that had not been proven when homodisubstituted ligands had been used.

To learn about this last possibility, a complex fragment usually requiring only one coordinating site was chosen. This would permit one to distinguish both coordinating sites and to know whether dicoordination was necessary to deboronate the cluster to produce the *nido* species. The complex $[AuCl(PPh_3)]$ was chosen as the source of the $[Au(PPh_3)]^+$ fragment.

Reaction of $[AuCl(PPh_3)]$ with $1\text{-}PPh_2\text{-}2\text{-}SEt\text{-}1,2\text{-}C_2B_{10}H_{10}$ in ethanol at reflux in 1:1 molar ratio yielded a complex of formula $[Au(7\text{-}PPh_2\text{-}8\text{-}SEt\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)]$ (see Scheme 1). The IR spectrum of the complex shows the B−H stretching absorption at 2541 cm^{-1}, which is indicative of *nido* species. This interpretation is further supported by the ^1H NMR, with the presence of the absorption at −2.3 ppm attributed to the B−H−B bond. The $^{11}B\{^1H\}$ NMR pattern (1:4:1:1:1:1) in the range −6 to −35 ppm agrees with a *nido* $[C_2B_9]^-$ derivative.

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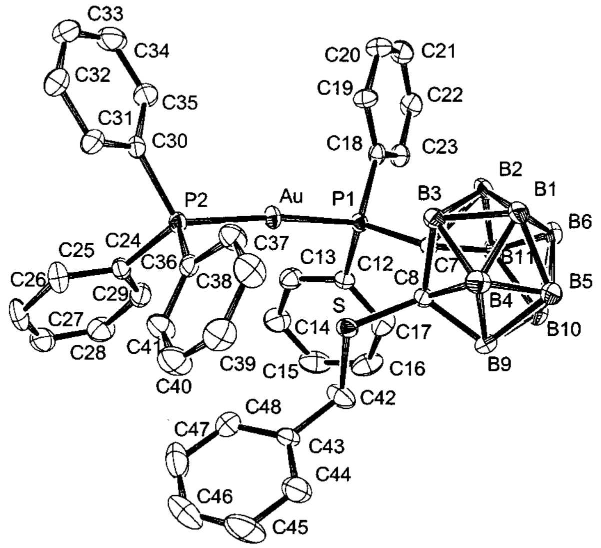
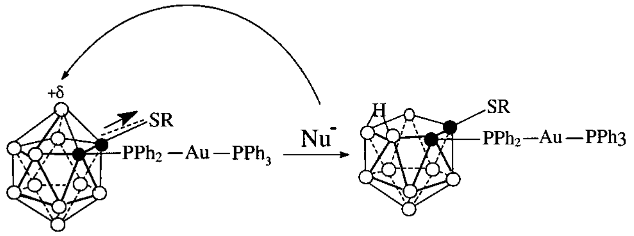


Figure 1. ORTEP plot of [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$CHCl_3$, showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

In addition, the $^{31}P\{^1H\}$ NMR spectra displayed two sets of doublets, indicating two different phosphorus atoms in the molecule. One doublet is centered at $\delta = 41.7$ ppm ($^2J(PP) = 308$ Hz), which can be assigned to PPh_3, while the other one is at $\delta = 54.7$ ppm ($^2J(PP) = 308$ Hz), which is assigned to the C_c−PPh_2 group.[10] The J value indicates a trans disposition of the phosphorus atoms.[11] The $^2J(PP)$ coupling proves that the moiety C−PPh_2 is coordinated to Au(I); however, no indication from the spectroscopic data is available about the participation of the C−SEt moiety on coordination to Au(I). To ascertain this, crystals of [Au(7-PPh_2-8-SEt-7,8-$C_2B_9H_{10}$)(PPh_3)] were needed; however, they were elusive in our hands. Therefore, a reaction in comparable conditions was carried on between the similar but bulkier *closo* ligand 1-PPh_2-2-SBz-1,2-$C_2B_{10}H_{10}$ and [AuCl(PPh_3)]. As a result, the gold complex [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)] was obtained. The spectroscopic data were consistent with those obtained for [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]. Crystals suitable for X-ray analysis were obtained from chloroform/*n*-hexane (1:1). The X-ray crystal structure of [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)], shown in Figure 1, clearly confirmed the *nido* nature of the resulting gold complex and the ligand's monodentate behavior toward Au(I) with the nonparticipation of C−SR in bonding.

As mentioned earlier, metal driven partial degradation had been found for C−SR and C−PPh_2 homodisubstituted *closo* compounds but not for monosubstituted ones. These reactions with heterodisubstituted C−SR and C−PPh_2 have brought relevant new data. Unlike the monosubstituted *closo* compounds these heterodisubstituted have produced partial degradation upon coordination to Au(I), in spite of the fact that only monocoordination has taken place. This supports our actual interpretation that the sulfur atoms of the C−SR group pulls electron density off the cage. Thus, although C−SR does not participate in bonding, its electron withdrawing capacity favors removal of B(3), the carbon's adjacent boron atom, upon C−PPh_2 coordination to metal (see Scheme 2). This shall be the main difference between 1-SR-2-PPh_2-1,2-$C_2B_{10}H_{10}$ and 1-Me-2-PPh_2-1,2-$C_2B_{10}H_{10}$ when the first one deboronates to produce the $[C_2B_9]^-$ *nido* species while the second one does not. This explanation is in contradiction with an earlier one produced by our group which had interpreted the metal driven partial degradation of homodisubstituted compounds in terms of the transfer of electron density from the metal to the cluster through the C−S-M or C−P-M bonds. It was hypothesized that a pseudoreduction of the carborane cluster was taking place, leading to opening of the carborane cluster and further nucleophilic attack. This explanation had already been abandoned upon measurements of the redox $E°$ value in metallacarboranes containing C−S bonds.[12]

Scheme 2. Proposed Mechanism for the Partial Degradation of [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)] during the Complexation Process with [AuCl(PPh_3)] in Ethanol



For comparative purposes the reaction with a similar monovalent fragment requiring a higher coordination number was performed. The trigonal [CuCl(PPh_3)$_2$] complex was used as a source of the "[Cu(PPh_3)$_2$]$^+$" or "[Cu(PPh_3)]$^+$" synthons. The reaction of 1-PPh_2-2-SEt-1,2-$C_2B_{10}H_{10}$ with [CuCl(PPh_3)$_2$] was carried out in the same conditions as those described for the Au(I) complexes to yield [Cu(7-PPh_2-8-SEt-7,8-$C_2B_9H_{10}$)(PPh_3)]. The partial degradation of *closo* to a *nido* cluster was clearly proven by the spectroscopic data. The appearance in the ^1H NMR of a resonance at −2.3 ppm attributed to the endohedral open face hydrogen, the $^{11}B\{^1H\}$ NMR pattern 2:1:2:2:1:1 in the range −7 to −35 ppm, and the IR ν(B−H) frequency at 2537 cm^{-1} are clear indications of the *nido* formation. Similarly to the [Au(7-PPh_2-8-SEt-7,8-$C_2B_9H_{10}$)(PPh_3)] complex, the $^{31}P\{^1H\}$ NMR of [Cu(7-PPh_2-8-SEt-7,8-$C_2B_9H_{10}$)(PPh_3)] showed two broad resonances at −2.7 and +16.4 ppm, which prove the presence of two nonequivalent phosphine groups in the molecule. Again no information could be obtained from the spectroscopic data about the participation of C−SR in bonding to metal, and as with [Cu(7-PPh_2-8-SEt-7,8-$C_2B_9H_{10}$)(PPh_3)] no adequate crystals were obtained. The reaction, in the same conditions, with R = Bz provided the complex [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]. The spectroscopic data of both [Cu(7-PPh_2-8-SEt-7,8-$C_2B_9H_{10}$)(PPh_3)] and [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)] were comparable. Recrystallization in dichloromethane/*n*-hexane gave adequate crystals to solve the crystal structure (Figure 2).

Crystal Structures of [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)] and [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]. The X-ray crystal structure analyses of the original 1-PPh_2-2-SBz-1,2-$C_2B_{10}H_{10}$ complexes of Au(I) and Cu(I) clearly confirmed the deboronation of the *closo* cluster to the *nido* species in both complexes and the nonparticipation of C−SR on bonding in the gold one. In [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$CHCl_3$

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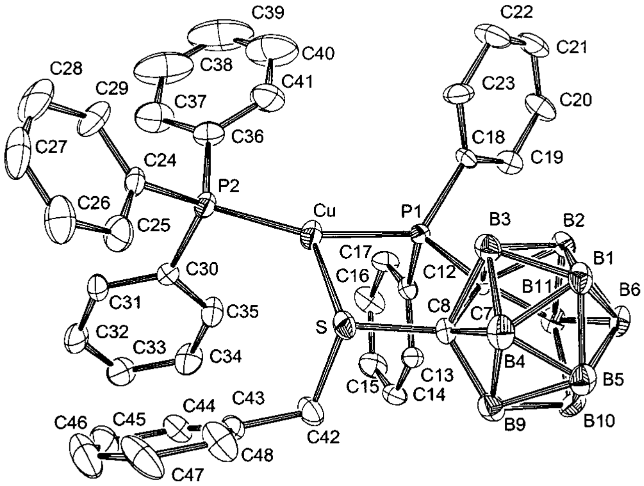

Figure 2. ORTEP plot of [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·CH_2Cl_2, showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

(Figure 1), the carborane ligand behaves monodentately toward the Au(I) cation and the metal is almost linearly (173.29(5)°) coordinated to two P atoms.

In [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$^1/_2CH_2Cl_2$ (Figure 2) the carborane ligand coordinates bidentately to Cu(I) via S and P atoms. The third coordination position is occupied by the P atom from the PPh_3 ancillary ligand. The Cl atom of dichloromethane is at a distance of 2.999(4) Å from the tricoordinated Cu(I), suggesting a very weak dipole−dipole interaction between the atoms. This assumption is supported by the fact that Cu is moved by 0.263(2) Å away from the plane of the tricoordinated atoms toward the Cl atom. Since the disordered dichloromethane molecules are across inversion centers, they seem to keep two neighbor complex units together, thus forming dimeric units.

In both compounds, the C(7)−C(8) distance is quite similar, being 1.600(6) Å for the Au derivative and 1.594(8) Å for the Cu derivative. The P−C(7)−C(8)−S moieties do not deviate much from planarity, the corresponding torsion angles being 2.4(5) and −5.1(7)° for [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$CHCl_3$ and [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$^1/_2CH_2Cl_2$, respectively.

The largest difference in bond angles between the two complexes arises from different coordination modes of the carborane ligand. When changing Au(I) to Cu(I), and going from monodentate P to bidentate S,P coordination, the metal must move toward the S atom in [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$^1/_2CH_2Cl_2$, and thus the C(7)−P(1)−M angle decreases from 113.67(15)° in [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$CHCl_3$ to 106.4(2)° in [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]·$^1/_2CH_2Cl_2$, thus opening C(18)−P(1)−M from 114.87(17) to 126.7(2)°. This phenomenon implies distortions in the ligand bond angles, especially around the P1 atom (see Tables 2 and 3). The small difference of the C(8)−C(7)−P(1) bond angles, 117.7(3)° for the Au complex and 115.8(4)° for the Cu complex, is a consequence of the bidentate ligand coordination in the Cu complex.

Conclusion

These heterodisubstituted 1-PPh_2-2-SR-1,2-$C_2B_{10}H_{10}$ ligands are able to coordinate to copper and gold with concomitant deboronation to produce the *nido* species [7-PPh_2-8-SR-7,8-$C_2B_9H_{10}$]$^-$. The two coordinating moieties C−PPh_2 and C−SR are not equivalent, as has been demonstrated upon reaction to Au(I), where the C−PPh_2 moiety is more reactive. Contrarily to the monosubstituted *closo* species which do not undergo metal driven partial degradation, these heterodisubstituted *closo* species do. This is so although monocoordination has taken place in front of Au(I), which is attributed to the strong electron-pulling capacity of the C−SR fragment. With metals requiring a higher coordination number than 2, as with Cu(I), both C−PPh_2 and C−SR moieties coordinate to metal and deboronation takes place.

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Supporting Information Available: Tables of X-ray of experimental details, hydrogen atom positional parameters and thermal parameters, anistropic thermal parameters, and interatomic distances and angles for [Au(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)] and [Cu(7-PPh_2-8-SBz-7,8-$C_2B_9H_{10}$)(PPh_3)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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