

Copper(I) Chloride Complexes of 1,2-Bis(disubstituted phosphino)-1,2-dicarba-*closo*-dodecaboranes and Crystal Structure of Chloro-[1,2-bis(diethoxyphosphino)-1,2-dicarba-*closo*-dodecaborane]triphenylphosphinecopper(I)

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Three copper(I) chloride complexes of 1,2-bis(disubstituted phosphino)-1,2-dicarba-*closo*-dodecaboranes, viz. [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)], [CuCl{1,2-[P(Et)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)] and [CuCl{1,2-[P(ⁱPr)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)], were synthesised, and the crystal structure of the first was determined. [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)] crystallizes in the monoclinic system, space group *P*2₁/*c*, with *a* = 18.597(3), *b* = 10.897(6), *c* = 20.677(5) Å, β = 112.91(2)°, *Z* = 4, *R* = 0.051, *wR* = 0.060. The structure consists of discrete molecules. The copper(I) atom is coordinated in distorted tetrahedral arrangement to two phosphorus atoms attached to the carborane cage, the phosphorus atom of PPh₃ and one chloride ion.

Metal complexes containing external chains connected via two sulfur atoms to the 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1–) moiety have been studied in detail by our group.^{1,2} The carborane cage exhibits various coordination modes in these complexes, but *S,S'* coordination is preferred. In the presence of a nucleophile the corresponding dithio *closo* derivatives tend to modify themselves via partial degradation (removal of the boron atom adjacent to the two carbon atoms), giving rise to negatively charged, strongly coordinating 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1–) ligands. Thus we have obtained *nido*-carborane complexes in the reaction of thioether-*closo*-carboranes with transition-metal complexes [MCl(PPh₃)₂] (M = Cu, Ag) in the presence of ethanol.² In these complexes the carborane cages are bidentately coordinated to the metal ions through the sulfur atoms.

It was of interest to us to establish also the coordination capability of the 1,2-diphosphorus-substituted 1,2-dicarba-*closo*-dodecaborane moiety, and whether the 1,2-diphosphorus-substituted *closo* cage is stable towards complex formation in the presence of ethanol, or whether

it undergoes a partial degradation, as in the reaction of [CuCl(PPh₃)₂] with dithio-substituted *closo*-carboranes. Here we wish to report the preparation and characterization of complexes formed by reactions of [CuCl(PPh₃)₂] with 1,2-bis(diethoxyphosphino)-, 1,2-bis(diethylphosphino)- and 1,2-bis(diisopropylphosphino)-substituted 1,2-dicarba-*closo*-dodecaboranes.

Experimental

Synthesis. Before use, 1,2-dicarba-*closo*-dodecaborane obtained from a commercial source was sublimed under high vacuum. 1,2-Bis(diethylphosphino)-1,2-dicarba-*closo*-dodecaborane(12)³ {1,2-[P(Et)₂]₂-1,2-C₂B₁₀H₁₀}, 1,2-bis(diethoxyphosphino)-1,2-dicarba-*closo*-dodecaborane(12) {1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀} and 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane(12)⁴ {1,2-[P(ⁱPr)₂]₂-1,2-C₂B₁₀H₁₀} were prepared from *o*-carborane according to the literature. A 1.6 M solution of *n*-butyllithium in hexane from Fluka was used as received. [CuCl(PPh₃)₂] was synthesised according to the literature.⁵ Ethanol was reagent grade. All solvents were deoxygenated, and all reactions were carried out under a dinitrogen atmosphere. Elemental

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analyses were performed with a Perkin-Elmer 240-B microanalyser. IR spectra (KBr disc) were recorded on a Nicolet 710-FT spectrophotometer, and $^1\text{H-NMR}$, $^{11}\text{B-NMR}$ and $^{31}\text{P-NMR}$ spectra were obtained with a Bruker AM 400WB or AC 250WB instrument.

Preparation and characterization of $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{OEt})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$. To a hot ethanol solution (50 ml) containing 130 mg (0.338 mmol) of $1,2\text{-}[\text{P}(\text{OEt})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ was added $[\text{CuCl}(\text{PPh}_3)_2]$ (211 mg, 0.338 mmol) and the mixture was refluxed for 3 h under dinitrogen. After concentration to 10 ml the solution was stored at 4°C and white crystals were obtained. The crystals were filtered, washed with cold ethanol, and dried in vacuum to yield an analytically pure solid $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{OEt})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$. Yield 225 mg, 89%. FTIR (KBr): $\nu/\text{cm}^{-1}=2618, 2571$ (B-H). $^1\text{H-FTNMR}$ (250 MHz, CDCl_3 , 25°C , TMS): $\delta=0.82$ and 1.37 (m, 12, CH_3), $3.40, 3.63$ and 4.56 (m, 8, CH_2), $7.53\text{--}7.23$ (m, 15, $\text{C}_{\text{aryl-H}}$). $^{11}\text{B-FTNMR}$ (128 MHz, CDCl_3 , 25°C , $\text{BF}_3\cdot\text{Et}_2\text{O}$): $\delta=-1.7$ [d, $^1J(\text{B,H})=114$ Hz, 2B], -5.3 (2B), -11.8 and -13.8 (6B). $^{31}\text{P-FTNMR}$ (101 MHz, CDCl_3 , 25°C , H_3PO_4): $d=125.75$ (br), 4.10 (s). Anal. calcd. for $\text{C}_{28}\text{H}_{45}\text{B}_{10}\text{ClO}_4\text{P}_3\text{Cu}$: C, 45.10; H, 6.08%. Found: C, 45.54; H, 5.71%. White crystals suitable for X-ray analysis were grown from ethanol at 4°C .

Preparation and characterization of $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{Et})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$. To a hot ethanol solution (15 ml) containing 50 mg (0.156 mmol) of $1,2\text{-}[\text{P}(\text{Et})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ was added $[\text{CuCl}(\text{PPh}_3)_2]$ (97 mg, 0.156 mmol). After refluxing for 2 h, the solvent was evaporated and dichloromethane (5 ml) and hexane (3 ml) were added. Upon evaporation of the solution at -10°C , yellow crystals were separated. These were filtered, washed with a mixture of dichloromethane and hexane (1:3, v/v), and dried in vacuum to yield an analytically pure solid $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{Et})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$. Yield 65 mg (61%). FTIR (KBr): $\nu/\text{cm}^{-1}=2624, 2592, 2570, 2554$ (B-H). $^1\text{H-FTNMR}$ (400 MHz, CDCl_3 , 25°C , TMS): $\delta=1.83$ and 1.44 (m, 12, CH_3), 2.31 and 2.08 (m, 8, CH_2), $7.65\text{--}7.38$ (m, 15, $\text{C}_{\text{aryl-H}}$). $^{11}\text{B-FTNMR}$ (128 MHz, CDCl_3 , 25°C , $\text{BF}_3\cdot\text{Et}_2\text{O}$): $\delta=-1.0$ [d, $^1J(\text{B,H})=125$ Hz, 2B], -4.1 (2B), -10.7 (6B). $^{31}\text{P-FTNMR}$ (101 MHz, CDCl_3 , 25°C , H_3PO_4): $d=13.09$ (br), 6.60 (br). Anal. calcd. for $\text{C}_{28}\text{H}_{45}\text{B}_{10}\text{ClP}_3\text{Cu}$: C, 49.33; H, 6.65%. Found: C, 49.54; H, 6.74%.

Preparation and characterization of $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{iPr})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$. To a hot ethanol solution (10 ml) containing 66 mg (0.175 mmol) of $1,2\text{-}[\text{P}(\text{iPr})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ was added $[\text{CuCl}(\text{PPh}_3)_2]$ (109 mg, 0.175 mmol), and the mixture was refluxed for 3 h under dinitrogen. The warm mixture was filtered, and the orange solid obtained was washed with warm ethanol. Recrystallization in dichloromethane/heptane

(3:1, v/v) yielded a microcrystalline orange solid. This was filtered, washed with dichloromethane/heptane (1:3, v/v) and dried in vacuum to yield an analytically pure solid $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{iPr})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$. Yield 50 mg, 61%. FTIR (KBr): $\nu/\text{cm}^{-1}=2630, 2619, 2602, 2558$ (B-H). $^1\text{H-FTNMR}$ (250 MHz, CDCl_3 , 25°C , TMS): $\delta=1.51\text{--}1.21$ (m, 12, CH_3), 2.36 (m, 8, CH). $^{11}\text{B-FTNMR}$ (128 MHz, CDCl_3 , 25°C , $\text{BF}_3\cdot\text{Et}_2\text{O}$): $\delta=-0.2$ (d, $^1J(\text{B,H})=145$ Hz, 2B), -3.8 (d, $^1J(\text{B,H})=122$ Hz, 2B), -10.6 (6B). $^{31}\text{P-FTNMR}$ (101 MHz, CDCl_3 , 25°C , H_3PO_4): $\delta=23.33$ (s, $\text{P}(\text{Pr}_2)$). Anal. calcd. for $\text{C}_{14}\text{H}_{38}\text{B}_{10}\text{ClP}_2\text{Cu}$: C, 35.36; H, 8.06%. Found: C, 34.60; H, 7.77%.

X-Ray crystallography. Crystal data and details of the data collection and structure refinement of $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{OEt})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$ are summarized in Table 1. The structure was solved by direct methods⁶ and successive Fourier syntheses.⁷ Refinement was performed with full-matrix least-squares methods,

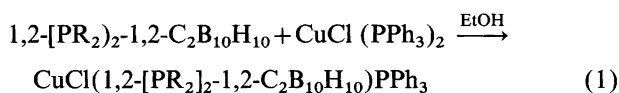
Table 1. Crystal data, data collection and structure refinement for $[\text{CuCl}\{1,2\text{-}[\text{P}(\text{OEt})_2]_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$.

Crystal data	
$\text{C}_{28}\text{H}_{45}\text{B}_{10}\text{ClCuO}_4\text{P}_3$	MoK α
$M_r=745.68$	$\lambda=0.71069\text{ \AA}$
Monoclinic	$\mu=0.789\text{ mm}^{-1}$
$P2_1/c$ (No. 14)	
Lattice parameters from 25 reflections	
$a=18.597$ (3) \AA	$\theta=12.8\text{--}16.9^\circ$
$b=10.897$ (6) \AA	$T=296\text{ K}$
$c=20.677$ (5) \AA	Colourless, bar
$\beta=112.91$ (2) $^\circ$	$0.20 \times 0.22 \times 0.32\text{ mm}$
$V=3859$ (4) \AA^3	
$Z=4$	
$D_x=1.283\text{ Mg m}^{-3}$	
Data collection	
Rigaku AFC-5S four-circle diffractometer	$\omega\text{-}2\theta$ scan
Absorption correction: empirical, psi-scans	$T_{\text{min}}=0.95, T_{\text{max}}=1.00$
8260 measured reflections	$R_{\text{int}}=0.026$
8007 unique reflections	$\Theta_{\text{max}}=26^\circ$
3669 observed reflections, criterion $I > 3\sigma(I)$	3 standard reflections, frequency 150 reflections, variation 0.5%
$h_{\text{min}}=-13$	$h_{\text{max}}=13$
$k_{\text{min}}=0$	$k_{\text{max}}=22$
$l_{\text{min}}=0$	$l_{\text{max}}=17$
Refinement	
x, y, z of H(B) atoms refined	Refinement on F
H(C) at calculated positions, with C-H=0.95 \AA	454 parameters
	3669 reflections in refinements
$R=0.051$	$w=1/\sigma^2(F)$
$wR=0.060$	$\Delta\rho_{\text{min}}=-0.36\text{ e \AA}^{-3}$
$S=1.82$	$\Delta\rho_{\text{max}}=0.42\text{ e \AA}^{-3}$
$(\Delta/\sigma)_{\text{max}}=0.05$	Atomic scattering factors included in the program
Extinction correction: none	

non-hydrogen atoms anisotropic, H(B) hydrogen atoms isotropic and H(C) hydrogen atoms in calculated positions with fixed thermal displacement parameters (1.2 times B_{eq} of the carrying atom). The ethyl moieties are not well defined: thermal displacement parameters of some atoms are great and bond parameters are highly inaccurate. Thus the ethyl groups do not allow any detailed discussion. All calculations were carried out with TEXSAN crystallographic software⁸ using a Vaxstation 3520 computer. Neutral atomic scattering factors were those included in the program. The figure was drawn with ORTEP.⁹

Results and discussion

As has been described earlier,² the reaction of thioether-*closo*-carboranes with transition-metal complexes $[MCl(PPh_3)_2]$ in ethanol yields the derivated *nido* species. We wanted to know if a similar partial degradation reaction would take place with the similar alkylphosphino-*closo*-carboranes. To do so, the reaction of 1,2-[P(Et)₂]₂-1,2-C₂B₁₀H₁₀, 1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀ and 1,2-[P(ⁱPr)₂]₂-1,2-C₂B₁₀H₁₀ with $[CuCl(PPh_3)_2]$, 1:1 ratio, in ethanol was conducted in similar conditions to these utilized earlier for the dithio compounds. The reaction is schematically written in eqn. (1). Contrary to the case of thioether-*closo*-carborane no partial degradation was found.



Spectral data of the three compounds clearly indicate the presence of the *closo*-carborane cage. The IR spectra show B–H stretching absorptions in the region from 2554 to 2624 cm⁻¹, which are indicative of *closo* species (lower values, close to 2540 cm⁻¹ are encountered for *nido* species). This interpretation is further supported by the lack of the absorption attributable to B–H–B bonding at –2.5 ppm in the ¹H-NMR spectrum and by the ¹¹B-NMR pattern, 2:2:6, between 0 and –12 ppm characteristic of *closo*-C₂B₁₀ derivatives. Thus no *closo* to *nido* degradation took place during the complex formation. The interpretation that, in each case, the *closo*-carborane cage is coordinated bidentately through the phosphorus atoms to copper(I) is supported by the ³¹P-NMR and ¹¹B-NMR spectra. The ¹¹B-NMR pattern, 2:2:6, shows the own symmetry for a *closo* cluster C₂B₁₀ coordinated to the metal as a bidentate ligand. The ³¹P-NMR spectra agree with a bidentate coordination: there are two broad signals in the spectra of $[CuCl\{1,2-[P(OEt)_2]_2-1,2-C_2B_{10}H_{10}\}(PPh_3)]$ and $[CuCl\{1,2-[P(Et)_2]_2-1,2-C_2B_{10}H_{10}\}(PPh_3)]$, and one signal in the spectrum of $[CuCl\{1,2-[P(ⁱPr)_2]_2-1,2-C_2B_{10}H_{10}\}]$.

To confirm unambiguously the existence of *closo*-structures in the complexes and to obtain detailed structural information, crystal structure analysis of the complex $[CuCl\{1,2-[P(OEt)_2]_2-1,2-C_2B_{10}H_{10}\}(PPh_3)]$ was

carried out by X-ray diffraction. A view of the molecule is shown in Fig. 1. Atomic coordinates are given in Table 2, and selected bond lengths and angles in Table 3.

The copper(I) atom is coordinated in distorted tetrahedral geometry to two phosphorus atoms attached to the *closo*-carborane cage, the phosphorus atom of the PPh₃ group and a chloride ion. The Cu(1)–P(1) and Cu(1)–P(2) distances are equal [2.247(2) and 2.245(2) Å], and the values compare very well with the average distance 2.250(3) Å reported for 1,2-bis(dimethylphosphine)ethane (=dmpe) complex $[Cu(dmpe)_2][Cu\{Co(CO)_4\}_2]$,¹⁰ but they are slightly shorter than the corresponding values of the chelating dmpe ligand in $[Cu(dmpe)_2](BF_4)_2$ ¹¹ [2.289(1) and 2.293(1) Å], and also shorter than those in $[Cu(cis-Ph_2CH=CHPPh_2)_2]PF_6$, where the distances are in the range 2.276(2)–2.289(2) Å.¹²

The Cu–P(PPh₃) distance of 2.287(2) Å in $[CuCl\{1,2-[P(OEt)_2]_2-1,2-C_2B_{10}H_{10}\}(PPh_3)]$ lies in the normal range, being significantly longer than in $[Cu\{7,8-\mu-(SCH_2CH_2OCH_2CH_2OCH_2CH_2S)-7,8-C_2B_9H_{10}\}(PPh_3)]^2$ [2.199(4) Å] but slightly shorter than in $[Cu\{7,8-\mu-(SCH_2CH_2S)-7,8-C_2B_9H_{10}\}(PPh_3)_2]$ [2.302(3) and 2.303(3) Å].¹³

The coordination sphere of copper(I) is distorted tetrahedral, as mentioned above, and the angles deviate considerably from the value of the ideal tetrahedral angle. The distortions arise in part from the restricted bite angle of the bis(diphosphino) ligand, the P(1)–Cu(1)–P(2) angle being 93.27(7)° and the inter-ligand angles ranging from 106.81(8) to 118.09(8)°. In $[RuCl_2\{1,2-[P(OEt)_2]_2-1,2-C_2B_{10}H_{10}\}]$ ¹⁴ the bite angle is much smaller, 86.42(2)°, and the smaller value is at least partly a consequence of the longer M–P distance. The bite angles in $[Cu(dmpe)_2][Cu\{Co(CO)_4\}_2]$ ¹⁰ and $[Cu(dmpe)_2](BF_4)_2$ ¹¹ are near 90° [90.9(1)° and 89.2(1)°,

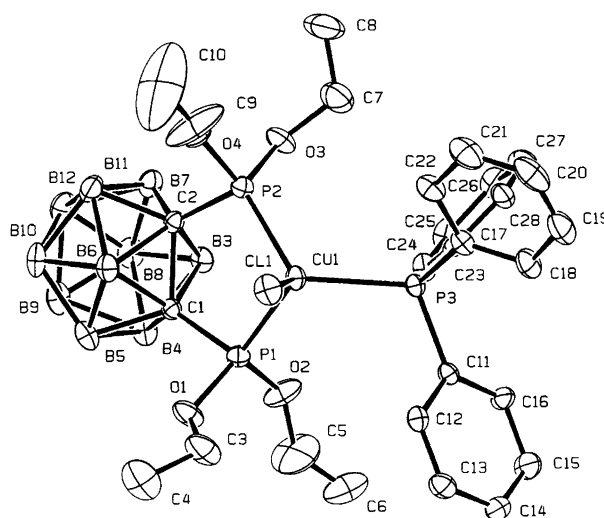


Fig. 1. ORTEP plot of $[CuCl\{1,2-[P(OEt)_2]_2-1,2-C_2B_{10}H_{10}\}(PPh_3)]$. Displacement ellipsoids are shown at 20% probability levels. H atoms are omitted for clarity.

Table 2. Non-hydrogen coordinates and equivalent isotropic displacement parameters (in Å²) for [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)].

Atom	x	y	z	B _{eq} ^a
Cu(1)	0.79659(4)	1.00699(7)	-0.00014(4)	3.43(3)
Cl(1)	0.9174(1)	0.9269(2)	0.0610(1)	5.26(9)
P(1)	0.7571(1)	0.9703(2)	-0.1158(1)	3.49(7)
P(2)	0.7002(1)	0.8944(2)	0.0097(1)	3.70(8)
P(3)	0.8029(1)	1.2108(2)	0.02798(9)	3.14(7)
O(1)	0.8074(3)	0.9029(5)	-0.1504(2)	5.7(3)
O(2)	0.7151(3)	1.0811(5)	-0.1668(3)	7.2(3)
O(3)	0.6246(3)	0.9569(5)	0.0148(3)	5.8(3)
O(4)	0.7138(3)	0.7793(5)	0.0588(3)	6.1(3)
C(1)	0.6751(3)	0.8562(5)	-0.1419(3)	3.0(3)
C(2)	0.6465(3)	0.8178(5)	-0.0765(3)	3.1(3)
C(3)	0.8900(5)	0.921(1)	-0.1265(5)	8.0(5)
C(4)	0.9269(5)	0.823(1)	-0.1470(6)	9.5(6)
C(5)	0.725(1)	1.137(1)	-0.2157(9)	18(1)
C(6)	0.7207(7)	1.243(1)	-0.2380(6)	10.9(7)
C(7)	0.6281(6)	1.026(1)	0.0725(5)	8.0(5)
C(8)	0.6059(7)	0.969(1)	0.1223(6)	10.6(7)
C(9)	0.7840(8)	0.749(1)	0.1117(9)	15(1)
C(10)	0.794(1)	0.665(2)	0.147(1)	30(2)
C(11)	0.8474(4)	1.3046(6)	-0.0186(3)	3.2(3)
C(12)	0.9128(4)	1.2586(6)	-0.0267(4)	4.0(3)
C(13)	0.9535(4)	1.3267(8)	-0.0577(4)	4.9(4)
C(14)	0.9271(5)	1.4423(8)	-0.0823(4)	5.3(4)
C(15)	0.8621(5)	1.4895(8)	-0.0765(5)	5.8(4)
C(16)	0.8220(4)	1.4201(6)	-0.0448(4)	4.3(3)
C(17)	0.8617(4)	1.2453(7)	0.1200(3)	3.8(3)
C(18)	0.8982(5)	1.3572(8)	0.1412(4)	5.4(4)
C(19)	0.9410(6)	1.378(1)	0.2119(6)	7.1(5)
C(20)	0.9489(6)	1.292(1)	0.2603(5)	7.6(6)
C(21)	0.9135(7)	1.181(1)	0.2404(5)	7.4(6)
C(22)	0.8700(4)	1.1563(8)	0.1691(4)	4.9(4)
C(23)	0.7079(4)	1.2829(5)	0.0119(3)	3.1(3)
C(24)	0.6486(4)	1.2671(7)	-0.0534(4)	4.4(3)
C(25)	0.5739(4)	1.3097(7)	-0.0668(5)	5.5(4)
C(26)	0.5574(5)	1.3649(8)	-0.0146(5)	5.7(4)
C(27)	0.6151(5)	1.3822(8)	0.0496(5)	5.7(4)
C(28)	0.6909(6)	1.3424(9)	0.0629(4)	4.9(4)
B(3)	0.5871(4)	0.9079(8)	-0.1443(4)	3.8(3)
B(4)	0.5980(5)	0.8504(8)	-0.2205(4)	4.2(4)
B(5)	0.6681(5)	0.7315(9)	-0.1935(5)	4.7(4)
B(6)	0.6991(5)	0.7151(8)	-0.1027(5)	4.1(4)
B(7)	0.5487(5)	0.7872(8)	-0.1101(5)	4.6(4)
B(8)	0.5186(5)	0.8050(9)	-0.2010(5)	5.0(4)
B(9)	0.5667(5)	0.6955(9)	-0.2314(5)	5.3(4)
B(10)	0.6309(6)	0.6137(9)	-0.1582(6)	5.7(4)
B(11)	0.6183(6)	0.6674(8)	-0.0844(5)	4.9(4)
B(12)	0.5380(5)	0.659(1)	-0.1624(6)	5.5(4)

$$^a B_{eq} = (4/3) \sum_i \sum_j b_{ij}^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

respectively], and the values are largely imposed by the geometry of the five-membered ring. For comparison, in [Cu{7,8- μ -(SCH₂CH₂S)-7,8-C₂B₉H₁₀}(PPh₃)₂], which incorporates a short and clearly strained exocyclic S,S'-connected string, the S-Cu-S bite angle is as small as 76.1(1)°.¹³

In [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)] the C(cage)-C(cage)-P angle values of 114.0(4) and 115.8(4)° are ca. 10° smaller than the P(1)-C(1)-B(4), P(1)-C(1)-B(5), P(2)-C(2)-B(7), P(2)-C(2)-B(11) angles, indicating that the phosphorus atoms are moved

towards each other from their expected positions. This trend has also been observed for other 1,2-diphosphorus-substituted *o*-carborane complexes: in [RuCl₂{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}]¹⁴ the P-C(cage)-C(cage) angles are 113.2(2) and 114.1(2)°, and in [Au{1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀}(PPh₃)]⁺ the values are 116.5(3) and 116.4(3)°.¹⁵ Comparing these values with the values 112.9(2) and 112.3(1)° observed for the free ligand 1,2-[P(ⁱPr)₂]₂-1,2-C₂B₁₀H₁₀,¹⁶ one can conclude that the bidentate coordination of a metal opens the angles only slightly.

The bulkiness of the PPh₃ ligand and orientations of the phenyl groups in [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)] have a clear effect on the geometry of the molecule: the P(2)-Cu(1)-P(3) angle is ca. 4° more opened than the P(1)-Cu(1)-P(3) angle, and the Cu-P-O angles are opened and the O-P-C(cage) angles are closed compared with the ideal tetrahedral-angle. These distortions partly cause the dissimilarity of the angles around phosphorus atoms of the bis(diphosphino) ligand, where the angles vary from 96.9(3) to 124.4(2)° for P(1) and from 95.5(3) to 124.2(2)° for P(2).

In [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)] the torsion angle P(1)-C(1)-C(2)-P(2) is 0.1(5)°, being equal to the value 0.3(2)° obtained for [RuCl₂{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}]¹⁴ and thus indicating strict planarity of the group of the four atoms. Planarity is typical for P-C(cage)-C(cage)-P and S-C(cage)-C(cage)-S groups in 1,2-bis(diphosphorus-substituted)-1,2-dicarba-*closo*-dodecaboranes and 7,8-dithio-substituted 7,8-dicarba-*nido*-undecaborates(-1), respectively, when coordinated through both sulfur or both phosphorus atoms to a metal.^{1,2,13} In [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}(PPh₃)] the metal occupies 0.169(5) Å out of the plane of the other four atoms and thus the five-membered chelate ring adopts an envelope conformation. In [Au{1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀}(PPh₃)]⁺¹⁵ the metal ion is 0.59 Å out of the plane, and in [RuCl₂{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}]¹⁴ the corresponding distance is 0.434 Å. These variable distances indicate flexibility of the five-membered chelate ring. Considerable flexibility for the corresponding chelate ring has also been reported for 7,8-dithio-substituted 7,8-dicarba-*nido*-dodecaborate complexes. In recent papers^{1,17} we have reported variable dihedral angle values for the planes through S-C-C-S and S-M-S groups in 7,8-dithio-substituted 7,8-dicarba-*nido*-undecaborate complexes, and noted that the value of the angle is a function of the length of the external S,S'-connected chain.

As expected, the geometry of the Cu-dmpe chelate rings differs considerably from than that in the compared carborane complexes. The P-C-C-P torsion angle values are 44(1)* and -46(1)*° in [Cu(dmpe)₂][Cu{Co(CO)₄}]₂,¹⁰ and 54.8(2)° in [Cu(dmpe)]₂-

* The values were derived from the reported coordinates, although recalculations indicated slight inaccuracies in both the cell parameters and/or coordinates and estimated standard deviations.

Table 3. Selected bond lengths (in Å) and angles (in °) for [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀} (PPh₃)].

Cu(1)–Cl(1)	2.280(2)	P(2)–O(3)	1.603(5)
Cu(1)–P(1)	2.247(2)	P(2)–O(4)	1.572(5)
Cu(1)–P(2)	2.245(2)	P(2)–C(2)	1.867(6)
Cu(1)–P(3)	2.287(2)	P(3)–C(11)	1.812(6)
P(1)–O(1)	1.566(5)	P(3)–C(17)	1.828(7)
P(1)–O(2)	1.593(5)	P(3)–C(23)	1.841(6)
P(1)–C(1)	1.876(6)	C(1)–C(2)	1.688(8)
Cl(1)–Cu(1)–P(1)	111.44(8)	O(4)–P(2)–C(2)	98.7(2)
Cl(1)–Cu(1)–P(2)	112.94(8)	Cu(1)–P(3)–C(11)	113.6(2)
Cl(1)–Cu(1)–P(3)	106.81(8)	Cu(1)–P(3)–C(17)	114.5(2)
P(1)–Cu(1)–P(2)	93.27(7)	Cu(1)–P(3)–C(23)	114.7(2)
P(1)–Cu(1)–P(3)	113.99(7)	C(11)–P(3)–C(17)	103.1(3)
P(2)–Cu(1)–P(3)	118.09(8)	C(11)–P(3)–C(23)	105.6(3)
Cu(1)–P(1)–O(1)	124.4(2)	C(17)–P(3)–C(23)	104.1(3)
Cu(1)–P(1)–O(2)	116.2(2)	P(1)–C(1)–C(2)	114.0(4)
Cu(1)–P(1)–C(1)	108.5(2)	P(1)–C(1)–B(3)	116.8(4)
O(1)–P(1)–O(2)	106.2(3)	P(1)–C(1)–B(4)	126.0(5)
O(1)–P(1)–C(1)	96.9(3)	P(1)–C(1)–B(5)	124.5(5)
O(2)–P(1)–C(1)	100.3(3)	P(1)–C(1)–B(6)	115.2(4)
Cu(1)–P(2)–O(3)	121.7(2)	P(2)–C(2)–C(1)	115.8(4)
Cu(1)–P(2)–O(4)	124.2(2)	P(2)–C(2)–B(3)	117.4(4)
Cu(1)–P(2)–C(2)	107.9(2)	P(2)–C(2)–B(6)	115.9(4)
O(3)–P(2)–O(4)	102.7(3)	P(2)–C(2)–B(7)	124.4(5)
O(3)–P(2)–C(2)	95.5(3)	P(2)–C(2)–B(11)	123.4(5)
P(1)–C(1)–C(2)–P(2)	0.1(5)		

(BF₄)₂,¹¹ revealing *gauche* conformation for the five-membered chelate rings. In the free ligand 1,2-[P(ⁱPr)₂]₂-1,2-C₂B₁₀H₁₀,¹⁶ the P–C(cage)–C(cage)–P torsion angle of 12.1(2)° indicates non-planarity for these atoms.¹⁶ This non-planarity probably originates from repulsion between the carborane cluster and the bulky cluster carbon substituents. In contrast, in the *nido* ligand 7,8-(PPh₂)₂-7,8-C₂B₉H₁₀(1–), these four atoms are planar, the torsion angle being only –1.3(6)°.⁴

As a rule, the C(1)–C(2) bond lengths in 1,2-disubstituted 1,2-dicarba-*closo*-dodecaboranes vary considerably with the substituents. In recent papers^{16,18} we have given an explanation to the lengthening and proposed empirical equations for calculating the distances. In [CuCl{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀} (PPh₃)] the C(1)–C(2) distance of 1.688(8) Å is in the expected range: it is equal for the value of the 1,2-disilicon-substituted *o*-carborane, 1,1'-Si(CH₃)₂-2,2'-Si(CH₃)₂-1,2-C₂B₁₀H₁₀,¹⁹ but it is longer than the distance in [RuCl₂{1,2-[P(OEt)₂]₂-1,2-C₂B₁₀H₁₀}] [1.659(3) Å]¹⁴ and shorter than that in [Au{1,2-(PPh₂)₂-1,2-C₂B₁₀H₁₀} (PPh₃)]⁺ [1.743(6) Å].¹⁵ In the free ligand 1,2-[P(ⁱPr)₂]₂-1,2-C₂B₁₀H₁₀, the distance is 1.719(3) Å.¹⁶

Conclusions

As indicated in the introduction, thioether bonded to *closo*-carborane ligands tends to remove a formal B⁺, rendering the ligand anionic upon complexation. The nucleophile needed for this in most cases has been a protic solvent. No partial degradation was observed when a non-nucleophilic solvent was used.²⁰ However, degradation does not always occur in the presence of a

nucleophile, as has been shown in this paper. Though ethanol was used as solvent, no partial degradation took place. To understand this, two factors need to be considered: the monocationic charge of the copper ion and the R groups in the –PR₂ units (R = Et, ⁱPr, OEt).

The charge of the metal ion evidently plays an important role in the partial degradation process. Up to now, partial degradation has occurred with almost all dipositively charged transition metal ions studied. Formally, the process *closo* (neutral) to *nido* (anionic) can be viewed as a way to compensate the positive charge of the cation, and a dicharged cation has a greater potential than a monocharged one. On the other hand, one step in the partial degradation process must be electron exchange between the cage and the metal, because otherwise the participation of the metal in the process would not be necessary.

It is thought that the electron density flux must follow the direction M→cage. However, since the phosphines are relatively basic this flow is reversed and consequently the partial degradation is not facilitated. Furthermore, we may consider that partial degradation of an arylcarboranylphosphine is facilitated because the negative charge of the anion can be delocalized further into the aryl groups.

In conclusion, our data suggest that partial degradation is favoured when (i) the transition metal is in a +2 oxidation state or higher, (ii) the phosphines are arylcarboranylphosphines, which are easily converted to *nido* species. With an arylcarboranylphosphine as the phosphine and the transition metal in a +1 oxidation state, the partial degradation process may or may not take place depending on other factors such as metal crowd-

edness. In general, partial degradation will not take place with a metal ion in the +1 oxidation state and an alkylcarboranylphosphine as the phosphine.

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