The formation of *nido* $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ from *closo* $1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = Ph, Et, ^{i}Pr or OEt): a process enhanced by complexation

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Abstract

To gain insight into the mutual influence of an electron-rich element directly connected to the carborane cage, the coordination behavior of phosphorus atoms directly bonded to the cage has been studied. The reactivity of bisphosphines $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Ph, Et, ^{i}Pr or OEt) has been investigated. These new chelating ligands exhibit some similarities to the much used 1,2-diphenylphos-phinoethane (diphos), such as the spacing between the two phosphorus atoms, and their five-membered ring chelating ability, but there are notable differences, and dissimilar ligating properties are expected. The differences are mainly due to the incorporated carborane cluster and can be summarized as follows: (1) the ligand is anionic, (2) the phosphorus atoms lie in an eclipsed conformation and (3) B(3)–H coordination to the metal is possible. To study the partial degradation of the *closo* clusters to the *nido* clusters enhanced by complexation, several metal complexes were treated with the *closo* ligands in ethanol. The crystal structures of $[AuCl_2 \{7,8\text{-}(P(^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}]$ and $[RuCl_2\{7,8\text{-}(P(^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ have been determined.

Keywords: Carboranes; Anionic; Phosphines; Degradation

1. Introduction

exo-Dithiocarborane ligands, derivatives of 7,8-dicarba-*nido*-undecaborate(1-) show a coordinating [1,2] ability distinctly different from that of common organic dithioethers. This has been attributed to the influence of electron-rich elements directly connected to the carborane cage. To gain further insight into this effect we are engaged in a study of the influence of the carborane cage on the coordinating behavior of phosphorus atoms directly bonded to the cage. With this in mind we are currently investigating the behavior of 7,8-bis(diphenyl-phosphino)-7,8-dicarba-*nido*-undecaborate(1-) "[7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}]^-$" (nph$^-$) compounds, and other *nido*-carboranyldiphosphines such as "[7,8-$(PEt_2)_2$-7,8-$C_2B_9H_{10}]^-$" (net$^-$), "[7,8-$(P^iPr_2)_2$-7,8-$C_2B_9H_{10}]^-$" (nip$^-$) and "[7,8-$(P\{OEt\}_2)_2$-7,8-$C_2B_9H_{10}]^-$" (neo$^-$). The ligands are denoted as follows: cR denotes the moiety 1,2-diphosphine-1,2-di-

carba-*closo*-dodecaborane and nR$^-$ the moiety 7,8-diphosphine-7,8-dicarba-*nido*-undecaborate; R (= Ph, Et, ^{i}Pr or OEt) refers to the organic substituents on each phosphorus atom. Table 1 presents a list of the ligands. Although complexes of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane "[1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}]$" (cph) with transition metals such as nickel(II) [3], cobalt(II) [4], gold(I) [5], platinum(II) [6], palladium(II) [7], chromium, molybdenum, tungsten, iron [8] and manganese [9] have been reported, the only report dealing with the anion nph$^-$ is that in our recent paper [10]. This new chelating ligand, nph$^-$, exhibits some similarities to the much used 1,2-diphenylphosphinoethane (diphos) in respect of the spacing between the two phosphorus atoms and in their ability to form their five-membered chelate rings. However, there are also significant differences, and some dissimilarities in ligating properties are to be expected. These differences are mainly attributable to the effects of the incorporated carborane cluster, and these can be summarized as follows: (i) the ligand is anionic, (ii) the phosphorus atoms are fixed by the geometry of the cluster in an

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Table 1

Carbaborane ligands with their abbreviation and the complexes obtained

cph	$1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$
nph$^-$	$[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$
cet	$1,2\text{-}(PEt_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$
net$^-$	$[7,8\text{-}(PEt_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$
cip	$1,2\text{-}(P^iPr_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$
nip$^-$	$[7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$
ceo	$1,2\text{-}(P\{OEt\}_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$
neo$^-$	$[7,8\text{-}(P\{OEt\}_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$
cdc	$1,1';2,2'\text{-}(PPh)_2\text{-}1,1';2,2'\text{-}(C_2B_{10}H_{10})_2$
ndc^{2-}	$[7,7';8,8'\text{-}(PPh)_2\text{-}7,7';8,8'\text{-}(C_2B_9H_{10})_2]^{2-}$
	[CuCl(cph)]
	[CuCl(cph)(PPh$_3$)]
	[Ag(nph)(PPh$_3$)]
	[Ag(nph)]$_n$
	[Ag(nph)(bipy)]
	[Au(nph)(PPh$_3$)]
	[AuCl$_2$(nph)]
	[Hg(nph)$_2$]
	[RhCl(cph)(PPh$_3$)]
	[Rh(nph)(CO)(PPh$_3$)]
	[RhCl(nph)$_2$]
	[RuCO(nph)$_2$]
	[Au(net)(PPh$_3$)]
	[AuCl$_2$(net)]
	[Au(nip)(PPh$_3$)]
	[AuCl$_2$(nip)]
	[Au(neo)(PPh$_3$)]
	[Au$_2$(ndc)(PPh$_3$)$_2$]
	[RuCl$_2$(cet)$_2$]
	[RuCl$_2$(ceo)$_2$]

eclipsed conformation, whereas diphos in its complexes adopts the more relaxed *gauche* conformation and (iii) interaction involving B(3)–H coordination to the metal is possible, as observed in 7,8-dithio-7,8-dicarba-*nido*-undecaborate (1-) derivatives [11,12]. In order to throw further light on the partial degradation of the *closo* clusters to the *nido* clusters induced by complexation, several metal complexes were treated with cR ligands in ethanol. The results are described below, together with the molecular structures of [AuCl$_2$(nip)] and [RuCl$_2$(ceo)$_2$], two of the complexes formed.

2. Results and discussion

The basic geometries of diphos and nR$^-$ when they are coordinated to metals are shown in Fig. 1, A and B. Fig. 1, C and D, shows the planes containing the two carbon atoms and the metal, for diphos and nR$^-$ respectively. In the case of diphos (Fig. 1, C) the P atoms are in an above-the-plane and below-the-plane P disposition, but only in an above-the-plane P disposition in the case of nR$^-$ (Fig. 1, D). Consequently, the energy required to reach planarity is smaller in C than in D, and the latter should be much less mobile. On the

contrary, the arrangement shown in Fig. 1, B, allows proximity between B(3)–H and M, and so B(3)–H...M interaction would be facilitated by the restricted mobility of the C$_2$P$_2$M moiety. Furthermore, the anionic nature of nR$^-$, where the charge can be considered to be confined to the carborane cluster, allows the metal ion to be surrounded by an extra soft neutral ligand, e.g. MX(P–P)L by M(nR)LL'. These properties should lend a versatile behavior of the nR$^-$ ligand.

The reaction of cR with alkoxide ion [13] does not give the expected new nR$^-$ species but instead yields 7,8-dicarba-*nido*-undecaborate(-1) by C–P cleavage and removal of one boron atom.

In order to establish the conditions leading to formation of nR$^-$ we have investigated the reactions of cR with several transition metal complexes in ethanol, which seems to be the appropriate solvent for the degradation process. By 'partial degradation' we refer to the removal of one formally B$^+$ fragment from the *closo* species (C$_2$B$_{10}$ cluster) to yield the *nido* species (C$_2$B$_9^-$ cluster).

The partial degradation procedure was first observed for the reaction of "electron-rich" d^{10} metal ions (Cu(I), Ag(I) and Au(I)) with 1',2'-(1,10-dithio-4,7-dioxadecane)-1',2'-dicarba-*closo*-dodecaborane in degassed ethanol, and this resulted in partial degradation of the *closo* compound [14].

The reaction of cph with AgNO$_3$, with or without PPh$_3$, in ethanol, yields white compounds with the stoichiometries [Ag(nph) (PPh$_3$)] and [Ag(nph)]$_n$ respectively, as shown in the following equation for the reaction with AgNO$_3$ and PPh$_3$:

cph + AgNO$_3$ + PPh$_3$

$$\xrightarrow[\text{N}_2]{\text{ethanol}} [Ag(nph)(PPh_3)] + \text{others} \qquad (1)$$
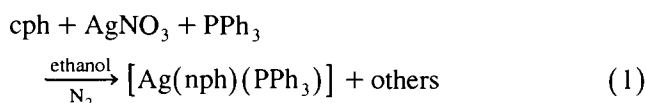
The appearance of the signal from the hydrogen bridge at $\delta \approx -2.1$ ppm in the ^{1}H NMR spectrum and the 2:3:2:1:1 pattern of the ^{11}B NMR spectrum in the range between -8 and -37 ppm indicates that the original *closo* cluster of the ligand is not retained upon
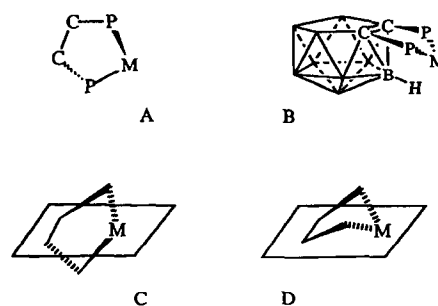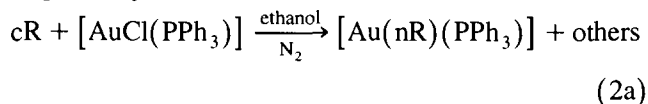

Fig. 1. The essential aspects of the geometries of diphos and nR$^-$, when coordinated to a metal.

coordination, and that partial degradation has taken place. The resonance at $\delta \approx -2.1$ ppm provides information about the charge on the cluster, and indeed about the presence or absence of the open-face hydrogen bridge. The lack of any resonances at higher fields than -2.1 ppm in the ^1H NMR spectrum rules out any B(3)–H $\rightarrow$ M interaction [12,15]. Thus we suggest that the metal atom is coordinated by the two phosphorus atoms of nph$^-$ and by PPh$_3$, the positive charge on the metal being compensated by the negative charge on the cluster. In order to study the influence of the coordinating ability of nph$^-$, a similar reaction was carried out with bipy instead of PPh$_3$, since bipy, as a bidentate chelating ligand, could compete with one of the phosphorus atoms of nph$^-$. The outcome was analogous to that found for PPh$_3$ and yellowish stable solids were obtained with good yields. The ^1H NMR and ^{11}B NMR chemical shifts are again as expected for the *nido* ligand nph$^-$, indicating that degradation has taken place.
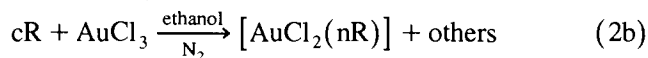
The reaction of cph in ethanol with [CuCl(PPh$_3$)$_2$] in a 1:1 molar ratio of ligand to metal [10] with [AuCl(PPh$_3$)], [RhCl(CO)(PPh$_3$)$_2$], [RuClH(CO)(PPh$_3$)$_3$] and AuCl$_3 \cdot n$H$_2$O, and in a 2:1 ratio with RhCl$_3 \cdot n$H$_2$O, AuCl$_3 \cdot n$H$_2$O and Hg(NO$_3$)$_2$ yielded complexes in which partial degradation had taken place, as was evident from the ^{11}B NMR and ^1H NMR data.

This procedure for partial degradation of arylic *closo* carboranyldiphosphines can be extended to alkyl or alkoxy species. Thus reaction of cR (R = Ph, Et, ^{i}Pr or OEt) with [AuCl(PPh$_3$)] or AuCl$_3 \cdot n$H$_2$O in ethanol

yields the compounds [Au(nR)(PPh$_3$)] and [AuCl$_2$(nR)] respectively:

$$cR + [AuCl(PPh_3)] \xrightarrow[\text{N}_2]{\text{ethanol}} [Au(nR)(PPh_3)] + \text{others}$$

$$(2a)$$

(R = Ph, Et, ^{i}Pr or OEt)

$$cR + AuCl_3 \xrightarrow[\text{N}_2]{\text{ethanol}} [AuCl_2(nR)] + \text{others} \qquad (2b)$$

(R = Ph, Et or ^{i}Pr).

When the starting *closo* ligand is cdc, the reaction with [AuCl(PPh$_3$)] in ethanol yields [Au$_2$(ndc)(PPh$_3$)$_2$], which is a degraded double-cluster species in which the ligand bridges the two gold atoms:

$$cdc + 2[AuCl(PPh_3)] \xrightarrow[\text{N}_2]{\text{ethanol}} [Au_2(ndc)(PPh_3)_2]$$

$$+ \text{others} \qquad (3)$$
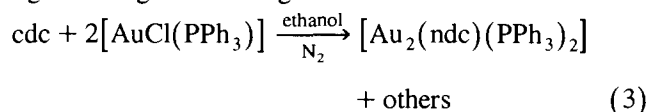
In all cases the appearance of a signal from the B–H–B bridge in the ^1H NMR spectrum at approximately -2.5 ppm and the 2:3:2:1:1 pattern of the ^{11}B NMR spectrum in the range between -6 and -35 ppm indicates that the *closo* cluster structure has not been retained and that partial degradation has taken place. The absence of any resonance at higher fields than -3.00 ppm in the ^1H NMR spectrum rules out any B(3)–H $\rightarrow$ M interaction.

When ethanol was used as solvent, partial degradation of the cluster took place. To examine influence of the solvent, we carried out the reaction of cph with

Table 2
Crystallographic data for [AuCl$_2$(nip)] (1) and [RuCl$_2$(ceo)$_2$] (2)

	1	2
Formula	C$_{14}$H$_{38}$AuB$_9$Cl$_2$P$_2$	Cu$_{20}$H$_{10}$B$_{20}$Cl$_2$P$_4$O$_8$Ru
Formula weight	633.56	470.38
Crystal habit	Yellow prism	Yellow prism
Crystal size (mm)	0.12 × 0.18 × 0.20	0.20 × 0.36 × 0.38
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	8.139(1)	10.040(2)
b (Å)	20.482(2)	13.077(2)
c (Å)	15.398(1)	17.024(2)
β (°)	105.30(1)	90.81(1)
V (Å^3)	2475.8(6)	2235(1)
Z	4	2
T (K)	294	294
λ (Å)	0.71069	0.71069
ρ_{calc} (g cm^{-3})	1.699	1.398
μ (cm^{-1})	62.70	6.43
Transmission	0.55–1.00	0.89–1.15
R (F_o) [a]	0.032	0.027
R_w (F_o) [b]	0.035	0.037

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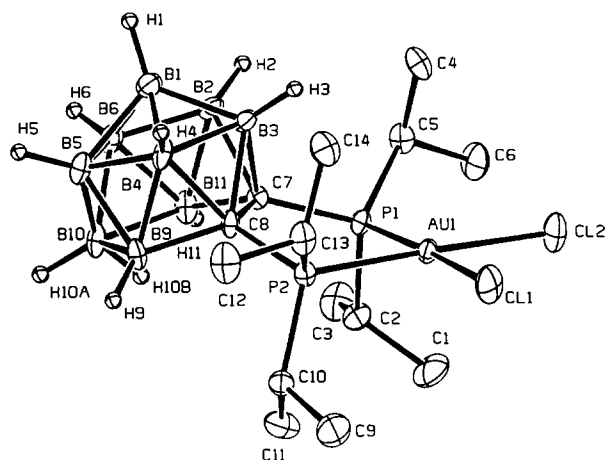[b] $R_w(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Fig. 2. Simplified ORTEP plot of [AuCl$_2$(nip)]. Thermal ellipsoids are shown at 30% probability levels, except for H atoms which are drawn with an isotropic displacement parameter of 1.0.

[CuCl(PPh$_3$)$_2$] in CHCl$_3$. Under those conditions no partial degradation took place and the cluster retained the *closo* structure. Furthermore, both the nature of the metal and that of the ligands that it bears greatly influence the reaction path. As an example, the reaction of cph with CuCl$_2$ or [RhCl(PPh$_3$)$_3$] in a 1 : 1 molar ratio in ethanol does not involve partial degradation but yields [CuCl(cph)] and [RhCl(cph)(PPh$_3$)]. In these cases there is no resonance in the ^{1}H NMR spectrum at approximately − 2.5 ppm, and the pattern (4 : 6 or

Table 3
Positional parameters and B_{eq} for [AuCl$_2$(nip)] (1)

Atom	x	y	z	B_{eq} (Å^2)
Au(1)	− 0.12691(3)	0.91504(1)	0.82606(2)	1.97(1)
Cl(1)	− 0.2408(3)	0.8738(1)	0.9387(1)	4.0(1)
Cl(2)	− 0.3282(3)	0.9994(1)	0.8034(2)	4.0(1)
P(1)	0.0007(2)	0.9540(1)	0.7177(1)	1.89(7)
P(2)	0.0711(2)	0.8314(1)	0.8547(1)	2.04(7)
C(1)	0.105(1)	1.0595(5)	0.8381(7)	4.9(5)
C(2)	0.158(1)	1.0182(4)	0.7674(5)	2.7(3)
C(3)	0.213(1)	1.0625(4)	0.6988(7)	4.4(4)
C(4)	− 0.296(1)	0.9412(4)	0.5736(6)	3.3(4)
C(5)	− 0.147(1)	0.9861(4)	0.6137(5)	2.6(3)
C(6)	− 0.210(1)	1.0560(4)	0.6215(6)	3.9(4)
C(7)	0.1204(8)	0.8854(3)	0.6890(5)	1.7(3)
C(8)	0.1564(8)	0.8262(3)	0.7567(5)	1.8(3)
C(9)	0.197(1)	0.8461(5)	1.0429(6)	4.9(5)
C(10)	0.248(1)	0.8483(4)	0.9542(5)	2.8(3)
C(11)	0.340(1)	0.9118(5)	0.9466(6)	4.1(4)
C(12)	0.113(1)	0.7011(4)	0.9123(6)	3.9(4)
C(13)	− 0.021(1)	0.7546(4)	0.8815(5)	2.9(3)
C(14)	− 0.178(1)	0.7312(4)	0.8099(6)	3.6(4)
B(1)	0.123(1)	0.7754(5)	0.5877(6)	2.6(4)
B(2)	0.092(1)	0.8594(5)	0.5777(6)	2.3(3)
B(3)	0.007(1)	0.8145(4)	0.6541(6)	2.1(3)
B(4)	0.156(1)	0.7525(4)	0.7002(6)	2.5(4)
B(5)	0.336(1)	0.7613(5)	0.6596(6)	2.7(4)
B(6)	0.294(1)	0.8290(5)	0.5818(6)	2.7(4)
B(9)	0.344(1)	0.7917(5)	0.7672(7)	2.6(4)
B(10)	0.440(1)	0.8362(5)	0.6874(7)	2.8(4)
B(11)	0.279(1)	0.8991(4)	0.6449(7)	2.5(4)

^{a} $B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j \beta_{ij} a_i \cdot a_j$.

Table 4
Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for [AuCl$_2$(nip)] (1)

Interatomic distances

Au(1)–Cl(1)	2.331(2)	P(2)–C(10)	1.836(8)
Au(1)–Cl(2)	2.344(2)	P(2)–C(13)	1.835(8)
Au(1)–P(1)	2.327(2)	C(1)–C(2)	1.53(1)
Au(1)–P(2)	2.313(2)	C(2)–C(3)	1.54(1)
P(1)–C(2)	1.852(8)	C(4)–C(5)	1.52(1)
P(1)–C(5)	1.850(8)	C(5)–C(6)	1.54(1)
P(1)–C(7)	1.830(7)	C(7)–C(8)	1.575(9)
P(2)–C(8)	1.823(7)		

Interatomic angles

|			
Cl(1)–Au(1)–Cl(2)	88.78(8)	Au(1)–P(2)–C(10)	111.8(3)
Cl(1)–Au(1)–P(1)	176.98(7)	Au(1)–P(2)–C(13)	111.9(2)
Cl(1)–Au(1)–P(2)	89.07(7)	C(8)–P(2)–C(10)	108.5(3)
Cl(2)–Au(1)–P(1)	93.82(7)	C(8)–P(2)–C(13)	113.7(3)
Cl(2)–Au(1)–P(2)	177.59(7)	C(10)–P(2)–C(13)	104.4(4)
P(1)–Au(1)–P(2)	88.30(6)	P(1)–C(2)–C(1)	113.2(6)
Au(1)–P(1)–C(2)	109.7(3)	P(1)–C(2)–C(3)	115.3(6)
Au(1)–P(1)–C(5)	115.6(2)	C(1)–C(2)–C(3)	110.5(7)
Au(1)–P(1)–C(7)	106.0(2)	P(1)–C(5)–C(4)	113.8(5)
C(2)–P(1)–C(5)	108.9(4)	P(1)–C(5)–C(6)	114.7(6)
C(2)–P(1)–C(7)	107.0(3)	C(4)–C(5)–C(6)	110.5(7)
C(5)–P(1)–C(7)	109.3(3)	P(1)–C(7)–C(8)	116.7(4)
Au(1)–P(2)–C(8)	106.5(2)	P(2)–C(8)–C(7)	117.2(5)
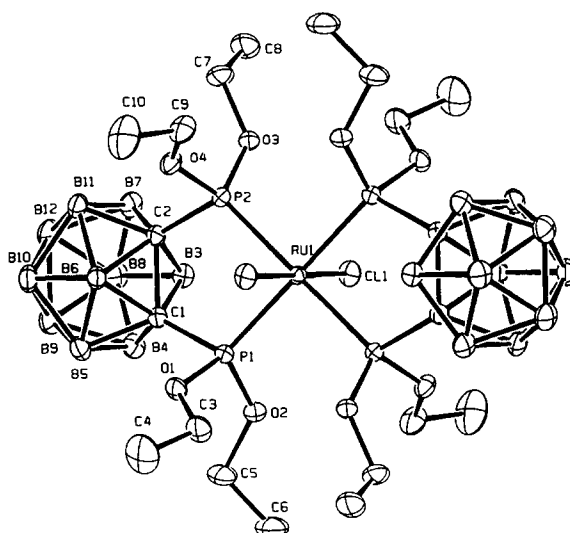
Fig. 3. Simplified ORTEP plot of [RuCl$_2$(ceo)$_2$]. Thermal ellipsoids are shown at 30% probability levels, except for H atoms which are drawn with an isotropic displacement parameter of 1.0.

2:2:6) of the ^{11}B NMR spectrum in the range between 0 and −11 ppm indicates that the *closo* cluster nature has been retained. The compound [RhCl(cph)(PPh$_3$)] was previously synthesized [16] in benzene; in that case the retention of the cph *closo* structure was expected because the solvent was non-protic and non-nucleophilic.

The reactions of cet or ceo with [RuCl$_2$(PPh$_3$)$_3$] in ethanol in a 2:1 molar ratio also take place without partial degradation, as evidenced by the ^{11}B NMR and ^{1}H NMR spectra, yielding [RuCl$_2$(cet)$_2$] and [RuCl$_2$(ceo)$_2$] respectively.

The X-ray crystal structure of [AuCl$_2$(nip)] (**1**) clearly

Table 5
Positional parameters and B_{eq} [a] for [RuCl$_2$(ceo)$_2$] (**2**)

Atom	x	y	z	B_{eq} (Å^2)
Ru(1)	0	0	0	1.79(1)
Cl(1)	0.20478(6)	0.09823(5)	0.00553(4)	3.01(3)
P(1)	−0.06700(6)	0.06273(5)	0.12077(4)	2.13(3)
P(2)	0.09559(6)	−0.13422(5)	0.06967(4)	2.14(3)
O(1)	−0.2115(2)	0.0416(2)	0.1545(1)	2.88(8)
O(2)	−0.0423(2)	0.1819(1)	0.1339(1)	3.11(9)
O(3)	0.2449(2)	−0.1589(1)	0.0467(1)	3.13(9)
O(4)	0.0262(2)	−0.2417(1)	0.0824(1)	3.12(9)
C(1)	0.0240(2)	−0.0020(2)	0.2053(1)	2.2(1)
C(2)	0.1083(2)	−0.1050(2)	0.1783(1)	2.2(1)
C(3)	−0.3332(3)	0.0777(3)	0.1151(2)	4.0(1)
C(4)	−0.4468(4)	0.0480(4)	0.1613(3)	7.8(3)
C(5)	−0.1009(4)	0.2448(3)	0.1964(2)	4.5(2)
C(6)	−0.1225(4)	0.3488(3)	0.1670(2)	5.1(2)
C(7)	0.3126(3)	−0.2568(2)	0.0581(2)	3.9(1)
C(8)	0.4597(3)	−0.2400(3)	0.0551(2)	4.9(2)
C(9)	−0.0319(4)	−0.3106(2)	0.0251(2)	4.2(2)
C(10)	−0.1384(5)	−0.3685(4)	0.0623(3)	8.1(3)
B(3)	0.1950(3)	0.0042(3)	0.2023(2)	2.6(1)
B(4)	0.1049(3)	0.0596(3)	0.2802(2)	3.0(1)
B(5)	−0.0393(3)	−0.0167(3)	0.2970(2)	3.1(1)
B(6)	−0.0372(3)	−0.1209(2)	0.2297(2)	2.6(1)
B(7)	0.2498(3)	−0.1190(3)	0.2340(2)	3.1(1)
B(8)	0.2480(4)	−0.0153(3)	0.3011(2)	3.5(2)
B(9)	0.1036(4)	−0.0287(3)	0.3605(2)	3.7(2)
B(10)	0.0164(4)	−0.1396(3)	0.3279(2)	3.4(2)
B(11)	0.1080(4)	−0.1957(3)	0.2506(2)	3.1(1)
B(12)	0.1934(4)	−0.1389(3)	0.3313(2)	3.7(2)

[a] $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} a_i \cdot a_j$.

confirms the *nido* nature of the cage in this Au(III) complex. The crystal data are presented in Table 2 and the structure of **1** is shown in Fig. 2. The atomic coordinates are given in Table 3 and selected bond parameters in Table 4. In the complex the Au(III) cation is bonded to the two phosphorus atoms of the bidentate *nido* carborane cage and to two chloride ions in a square planar arrangement. The Au–P bond lengths are 2.327(2) and 2.313(2) Å. The Au–Cl bonds are 2.331(2) and 2.344(2) Å. The P–Au–P bite angle is 88.30(6)° and all other angle values deviate by at most 4° from the values for ideal square planar coordination.

The torsion angle of P(1)–C(7)–C(8)–P(2) is 1.4(7)°, which means that these atoms are nearly in the same plane, and Au(1) lies 0.601 Å out of that plane, indicating an envelope conformation for the five-membered ring. The P(1)–C(7)–C(8) and P(2)–C(8)–C(7) angles are 116.7(4) and 117.2(5)° respectively. In a related free ligand [N(CH$_3$)$_4$][7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$], the P–C(cage)–C(cage) angles are 116.5(9) and 113.4(9)° [17]. The similarity of the angles in the complex and free ligand indicate that the metal ion does not have any significant effect on the structure of the boron cage.

The X-ray diffraction study of *trans*-[RuCl$_2$(ceo)$_2$] (**2**) confirms that the *closo* structure of the complex has been retained. The complex has a centrosymmetric octahedral structure (Fig. 3) with Ru(II) on the crystallographic inversion center. The Cl atoms are in a *trans* disposition. The atomic coordinates are given in Table 5 and the selected bond lengths and angles in Table 6.

The lengths of the Ru–P bonds are 2.3219(7) and 2.3187(7) Å and that of the Ru–Cl bond is 2.4251(7) Å. These values are close to the corresponding values for *trans*-[RuCl$_2$(depe)$_2$] [18] (depe = 1,2-bis(diethylphosphino)ethane). The P(1)–Ru(1)–P(2) bite angles are 86.42(2)° and 83.40(4)° for **2** and *trans*-[RuCl$_2$(depe)$_2$] respectively. The other octahedral angles in **2** are close to the ideal values. The torsion angle P(1)–C(1)–C(2)–P(2) is 0.3(2)°, indicating the planarity of this fragment. The Ru(II) cation lies 0.434 Å out of this plane, pointing to an envelope conformation for the five-membered chelate ring. In *trans*-[RuCl$_2$(depe)$_2$] the relevant torsion angle is 51.2(5)°.

The P(1)–C(1)–C(2) and P(2)–C(2)–C(1) angles are 113.2(2) and 114.1(2)° respectively. In a related free ligand, 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecarborane, the corresponding values are 112.9(2) and 112.3(1)° [19]. These values show that there is little constraint on these angles. On the contrary, in the Au(I)' complex [Au(cph)(PPh$_3$)]ClO$_4$, the P(1)–C(1)–C(2) and P(2)–C(2)–C(1) angles are 116.3(3) and 116.4(3)° respectively [5b] indicating that Au(I) has a greater effect on the bonding parameters of the *closo* cage than does Ru(II).

We conclude that the diphosphine *closo* derivatives, which are neutral diphosphines, undergo structural modification upon coordination. We attribute this to transfer of electron density from the metal to the cage by P–M coordination (Fig. 4), which causes a pseudoreduction of the cluster, leading to opening of the cage. In such a

Table 6
Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for [RuCl$_2$(ceo)$_2$] (**2**)

| *Interatomic distances*			
Ru(1)–Cl(1)	2.4251(7)	P(2)–C(2)	1.891(3)
P(1)–O(1)	1.592(2)	O(1)–C(3)	1.463(3)
P(1)–O(2)	1.594(2)	O(2)–C(5)	1.474(4)
P(1)–C(1)	1.893(3)	O(3)–C(7)	1.462(3)
P(2)–O(3)	1.588(2)	O(4)–C(9)	1.445(4)
P(2)–O(4)	1.585(2)	C(1)–C(2)	1.659(3)
Interatomic angles			
Cl(1)–Ru(1)–Cl(1^I)	180.00	O(1)–P(1)–C(1)	94.7(1)
Cl(1)–Ru(1)–P(1)	91.98(3)	O(2)–P(1)–C(1)	105.0(1)
Cl(1)–Ru(1)–P(1^I)	88.02(3)	Ru(1)–P(2)–O(3)	114.38(7)
Cl(1)–Ru(1)–P(2)	92.10(3)	Ru(1)–P(2)–O(4)	124.17(8)
Cl(1)–Ru(1)–P(2^I)	87.90(3)	Ru(1)–P(2)–C(2)	111.64(8)
P(1)–Ru(1)–P(1^I)	180.00	O(3)–P(2)–O(4)	105.8(1)
P(1)–Ru(1)–P(2)	86.42(2)	O(3)–P(2)–C(2)	103.4(1)
P(1)–Ru(1)–P(2^I)	93.58(2)	O(4)–P(2)–C(2)	94.0(1)
P(2)–Ru(1)–P(2^I)	180.00	P(1)–O(1)–C(3)	122.6(2)
Ru(1)–P(1)–O(1)	122.33(8)	P(1)–O(2)–C(5)	125.7(2)
Ru(1)–P(1)–O(2)	115.05(8)	P(2)–O(3)–C(7)	125.7(2)
Ru(1)–P(1)–C(1)	111.88(8)	P(1)–C(1)–C(2)	113.2(2)
O(1)–P(1)–O(2)	105.0(1)	P(2)–C(2)–C(1)	114.1(2)

Symmetry code: I = −x, −y, −z.

R = Ph, Et, iPr, OEt
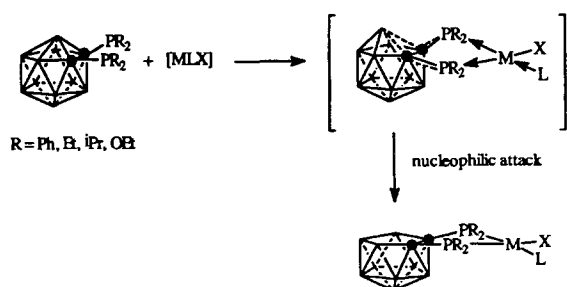
Fig. 4. Proposed mechanism for the partial degradation of 1,2-diphos-phine-o-carborane derivatives in the complexation with the transition metal species [MLX] (M = Cu(I), Ag(I), Au(I,III), Hg(II), Rh(I,III) or Ru(II); L = solvent, PPh$_3$, or CO; X = Cl or NO$_3$).

situation the apical boron atom, which would be the less strongly coordinated, is susceptible to nucleophilic attack and partial cluster opening takes place. Ethanol is a suitable nucleophile to bring about this partial degradation. In general, the nR$^-$ ligand is almost always formed when cR (R = aryl or alkyl) reacts with an electron-rich transition metal complex in ethanol. However, there are certain exceptions, as mentioned for reaction of cph with CuCl$_2$ and [RhCl(PPh$_3$)$_3$] and for cR (R = Et or OEt) with [RuCl$_2$(PPh$_3$)$_3$]. This procedure for bringing about partial degradation is less suitable for carboranyldiphosphines without aryl groups. The absence of a mesomeric effect in such cases leads to a lower ability to delocalize the electron density, and so partial degradation, which is essentially a cluster pseudoreduction, is less likely.

Possibly neutralization of the positive charge on the metal by the negative charge on the generated anionic diphosphines provides a driving force for the cluster degradation.

3. Experimental section

3.1. General methods

1,2-Dicarba-closo-dodecaborane (commercial) was sublimed under high vacuum prior to use. The 1,2-bis(diphenylphosphino), 1,2-bis(diethylphosphino), 1,2-bis(diisopropylphosphino) and 1,2-bis(dietoxyphosphite)-1,2-dicarba-closo-dodecarborane and 1,1';2,2'-(PPh$_2$)$_2$-1,1';2,2'-(C$_2$B$_{10}$H$_{10}$)$_2$ were prepared from 1,2-dicarba-closo-dodecaborane by standard methods [17]. A 1.6 M solution of n-butyllithium in hexane (Fluka) was used as purchased. [CuCl(PPh$_3$)$_2$] [20], [AuCl(PPh$_3$)] [21], [RhCl(PPh$_3$)$_3$] [22], [RhCl(CO)-(PPh$_3$)$_2$] [23], [RuClH(CO) (PPh$_3$)$_3$] [24] and [RuCl$_2$-(PPh$_3$)$_3$] [25] were made as described elsewhere.

All organic compounds and inorganic salts were either Fluka or Aldrich analytical reagent grade and were used as supplied. The solvents were reagent grade. All reactions were carried out under dinitrogen by

use of Schlenk techniques. Microanalyses were performed in our analytical laboratory with a Perkin–Elmer 240B microanalyser. The IR spectra were recorded with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H NMR, ^{11}B NMR and ^{31}P NMR were recorded on a Bruker AM 400WB or AC 250WB instrument.

3.2. Preparation of [CuCl(cph)]

After addition of CuCl$_2$ · 2H$_2$O (42 mg, 0.250 mmol) to a refluxing solution of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (125 mg, 0.250 mmol) in deoxygenated ethanol (30 cm^3) the mixture was refluxed for 4 h. The yellow solid formed was then filtered off, washed with hot ethanol and dried in vacuum. Recrystallization from chloroform–hexane gave yellow microcrystals (107 mg, (71%)). Anal. Found: C, 50.45; H, 4.95. C$_{26}$H$_{30}$B$_{10}$P$_2$-ClCu calc.: C, 51.06; H, 4.94%. IR (KBr): v 2655, 2592, 2576, 2548 (B–H) cm^{-1}. ^{1}H NMR CDCl$_3$, (400 MHz, 25°C, tetramethylsilane (TMS)): δ 8.11–8.08, 7.32–7.19 (m, C$_{aryl}$–H) ppm. ^{11}B NMR (CD$_2$Cl$_2$, 128 MHz, 25°C, BF$_3$·Et$_2$O): δ −0.3 (2B), −6.3 (2B), −9.9 (6B) ppm. ^{31}P NMR (Cl$_3$CH, 162 MHz, 25°C, H$_3$PO$_4$): δ −9.07 (s) ppm.

A similar procedure but starting from CuCl$_2$ · 2H$_2$O (15 mg, 0.090 mmol), and {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (90 mg, 0.179 mmol) (i.e. in a 1:2 ratio) in deoxygenated ethanol (25 cm^3), and with 3 h refluxing yielded yellow microcrystals of [CuCl(cph)] (45 mg (83%)) with analytical and ^{1}H, ^{11}B and ^{31}P NMR spectral data identical with those described above.

3.3. Preparation of [CuCl(cph) (PPh$_3$)]

After addition of CuCl(PPh$_3$)$_2$ (124 mg, 0.189 mmol) to a solution of {1,2-[PPh$_2$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (100 mg, 0.198 mmol) in deoxygenated chloroform (15 cm^3), the yellow solution was refluxed for 6 h. The solution was then concentrated to about 10 cm^3 and cooled (0°C), to the yellow microcrystals which were filtered off, washed with cold chloroform:diethyl ether (1:3) and dried in vacuum to afford a 70 mg yield (41%). Anal. Found: C, 60.34; H, 5.22. C$_{44}$H$_{45}$B$_{10}$P$_3$ClCu calc.: C, 60.48; H, 5.19%. Fourier transform (FT) IR (KBr): v(B–H) 2597, 2588, 2578, 2563, 2553 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 400 MHz, 25°C, TMS): δ 7.20–7.35, 8.00 (m, C$_{aryl}$–H) ppm. ^{11}B FTNMR (CD$_2$Cl$_2$, 128 MHz, 25°C, BF$_3$·Et$_2$O): δ −0.7 (2B), −5.0 (2B), −9.8 (6B) ppm. ^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ −2.29 (br), 12.66 (br) ppm.

3.4. Preparation of [Ag(nph)(PPh$_3$)]

{1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (150 mg, 0.300 mmol) was added, with protection from light to a solution of AgNO$_3$ (51 mg, 0.300 mmol) and PPh$_3$ (78 mg, 0.300

mmol) in deoxygenated ethanol (40 cm^3). The mixture was refluxed for 4.5 h and the formed solids were then filtered off, washed with hot ethanol and dried in vacuum to afford 219 mg of ochre-colored microcrystals (84%). Anal. Found: C, 59.55; H, 5.34. $C_{44}H_{45}B_9P_3Ag$ calc.: C, 60.61; H, 5.20%. FTIR (KBr): $v(B–H)$ 2572, 2539, 2528, 2512, 2500, 2477 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 400 MHz, 25°C, TMS): δ −2.1 (br, 1H, BHB), 7.05–7.62 (m, 35H, C_{aryl}–H) ppm. ^{11}B FTNMR (CDCL$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −8.7 (2B), −13.5 (3B), −18.0 (2B), −31.5 (1B), −36.2 (d, $^1J(B,H)$ = 131 Hz, 1B) ppm. ^{31}P FTNMR (Cl$_3$CH, 101 MHz, 25°C, H$_3$PO$_4$): δ 23.00 (d, $^1J(Ag,P)$ = 257 Hz) ppm.

3.5. Preparation of [Ag(nph)]$_3$

A solution of AgNO$_3$ (17 mg, 0.190 mmol) in methanol (5 cm^3) was added with protection from light to a slurry of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (60 mg, 0.100 mmol) in deoxygenated methanol (10 cm^3). The mixture, still protected from light, was stirred at room temperature for 6 h and the brown solid formed was filtered off, washed with methanol and dried in vacuum. Recrystallization from acetonitrile–propanol gave white microcrystals (37 mg (61%)). Anal. Found: C, 50.79; H, 5.25. $C_{26}H_{30}B_9P_2Ag$ calc.: C, 51.23; H, 4.96%. FTIR (KBr): $v(B–H)$ 2584, 2534 cm^{-1}. ^{1}H FTNMR (CD$_3$CN, 400 MHz, 25°C, TMS): δ −2.1 (br, 1H, BHB), 7.21, 7.34–7.42, 7.63 (m, 20H, C_{aryl}–H) ppm. ^{11}B FTNMR (CH$_3$CN, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −8.2 (d, $^1J(B,H)$ = 132 Hz, 2B), −13.3 (d, $^1J(B,H)$ = 135 Hz, 3B), −17.3 (2B), −31.3 (d, $^1J(B,H)$ = 122 Hz, 1B), −35.8 (d, $^1J(B,H)$ = 141 Hz, 1B) ppm. ^{31}P FTNMR (CH$_3$CN, 162 MHz, 25°C, H$_3$PO$_4$): δ 20.40 (d, $^1J(P–Ag)$ = 244 Hz) ppm.

3.6. Preparation of [Ag(nph)(bipy)]

A mixture of AgNO$_3$ (34 mg, 0.199 mmol) and 2,2'-bipyridine (31 mg, 0.199 mmol) was added to a slurry of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (100 mg, 0.199 mmol) in deoxygenated ethanol (30 cm^3). The mixture was protected from the light and stirred at room temperature for 15 h. The dark-brown solid formed was filtered off, washed with ethanol and dried in vacuum. Recrystallization from dichloromethane–heptane gave a yellow crystals (108 mg (71%)). Anal. Found: C, 55.53; H, 5.38; N, 3.11. $C_{36}H_{38}B_9P_2N_2Ag$ calc.: C, 56.46; H, 5.00.; N, 3.66%. IR (KBr): $v(B–H)$ 2572, 2528; v(bipy) 1592, 1573, 1471, 759 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 25°C, TMS): δ −2.0 (br, 1H, BHB), 7.17–7.37, 7.55, 77.68, 8.03, 8.23, 8.52 (m, 28H, C_{aryl}–H) ppm. ^{11}B NMR (CH$_2$Cl$_2$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −9.1 (d, $^1J(B,H)$ = 110 Hz, 2B), −11.2 (d, $^1J(B,H)$ =

122 Hz, 3B), −14.0 (2B), −32.1 (d, $^1J(B,H)$ = 131 Hz, 1B), −36.6 (d, $^1J(B,H)$ = 139 Hz, 1B) ppm. ^{31}P NMR (CH$_2$Cl$_2$, 162 MHz, 25°C, H$_3$PO$_4$): δ 15.53 (d, $^1J(P–Ag)$ = 182 Hz) ppm.

3.7. Preparation of [Au(nph)(PPh$_3$)]

[AuCl(PPh$_3$)] (98 mg, 0.198 mmol) was added to a slurry of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (60 mg, 0.198 mmol) in deoxygenated ethanol (50 cm^3). The yellow mixture was refluxed for 3 h and the formed solid was then filtered off, washed with hot ethanol and dried in vacuum to afford yellow microcrystals (100 mg (58%)). Anal. Found: C, 54.64; H, 4.90. $C_{44}H_{45}B_9P_3Au$ calc.: C, 54.99; H, 4.72%. IR (KBr): $v(B–H)$ 2574, 2539, 2519 ppm. ^{1}H NMR (acetone-d_6, 400 MHz, 25°C, TMS): δ −2.0 (br, 1H, BHB), 7.24–7.33, 7.45–7.59, 7.68–7.69 (m, 35H, C_{aryl}–H) ppm. ^{11}B NMR (CHCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −7.8 (2B), −12.9 (d, $^1J(B,H)$ = 86 Hz, 3B), −16.9 (2B), −29.5 (1B), −34.9 (d, $^1J(B,H)$ = 155 Hz, 1B) ppm. ^{31}P NMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 45.51 (t, $^1J(P,P)$ = 128 Hz), 62.90 (d, $^1J(P,P)$ = 128 Hz) ppm.

3.8. Preparation of [AuCl$_2$(nph)]

AuCl$_3$ · nH$_2$O (50% Au) (157 mg, 0.398 mmol) was added to a refluxing solution of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (100 mg, 0.199 mmol) in deoxygenated ethanol (25 cm^3). The slurry was refluxed for 5 h and then the solids formed was filtered off, washed with hot ethanol and dried in vacuum to afford 120 mg (78%) of yellow crystal. Anal. Found: C, 40.37; H, 4.34. $C_{26}H_{30}B_9P_2Cl_2Au$ calc.: C, 40.58; H, 3.93%. IR (KBr): $v(B–H)$ 2598, 2581, 2576, 2535, 2530 cm^{-1}. ^{1}H NMR (acetone-d_6, 400 MHz, 25°C, TMS): δ −1.90 (br, 1H, BHB), 7.32, 7.65–7.78, 8.27–8.30 (m, 20H, C_{aryl}–H) ppm. ^{11}B NMR (CHCl$_3$, 128 MHz, 25°C, BF · Et$_2$O): δ −8.7 (2B), −12.0 (d, $^1J(B,H)$ = 16 Hz, 3B), −14.9 (2B), −25.8 (1B), −34.2 (d, $^1J(B,H)$ = 154 Hz, 1B) ppm. ^{31}P NMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 96.1 (s) ppm.

When the carborane : Au(III) ratio was 1 : 1 and the conditions otherwise the same, the same product was obtained but it had to be recrystallized and the yield was only 55%. Thus AuCl$_3$–nH$_2$O (50% Au) (47 mg, 0.119 mmol) was added to a refluxing solution of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (60 mg, 0.119 mmol) in deoxygenated ethanol (15 cm^3). The slurry was refluxed for 3 h and then the dark-brown solid formed was filtered off and washed with hot ethanol. It was then recrystallized in dichloromethane (15 cm^3)–heptane (5 cm^3) to give a yellow solid (50 mg (55%)), with properties identical with those above.

3.9. Preparation of (Hg(nph)$_2$)

Hg(NO$_3$)$_2$–H$_2$O (51 mg, 0.150 mmol) was added to a refluxing solution of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (150 mg, 0.300 mmol) in deoxygenated ethanol (40 cm^3). The slurry was refluxed for 5 hours and the solid then filtered off, washed with hot ethanol and dried in vacuum to afford 50 mg of a white product. The colourless filtrate was cooled (0°C) to yield a further 45 mg (53%). Anal. Found: C, 51.90; H, 5.18. C$_{52}$H$_{60}$B$_{18}$P$_4$Hg calc.: C, 51.87; H, 5.02%. IR (KBr): v(B–H) 2616, 2585, 2540, 2533 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C, TMS): δ – 2.32 (br, 2H, BHB), 6.77–7.74 (m, 40H, C$_{aryl}$–H) ppm. ^{11}B NMR (CHCl$_3$, 128 MHz, 25°C, BF$_3$·Et$_2$O): δ –7.0 (4B), –11.7 (6B), –15.4 (4B), –29.1 (2B), –33.9 (d, ^1J(B,H) = 100 Hz, 2B) ppm. ^{31}P NMR (CH$_2$Cl$_2$, 101 MHz, 25°C, H$_3$PO$_4$): δ 37.22 (dd, ^1J(P,P) = 12 Hz, ^1J(P,Hg) = 103 Hz) ppm.

3.10. Preparation of [RhCl(cph)(PPh$_3$)]

[RhCl(PPh$_3$)$_3$] (92 mg, 0.099 mmol) was added to a refluxing solution of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (50 mg, 0.099 mmol) in deoxygenated ethanol (15 cm^3). The brown slurry was refluxed for 4 h and the formed solid was then filtered off, washed with hot ethanol and dried in vacuum to afford yellow product (47 mg (52%)). Anal. Found: C, 56.84; H, 5.10. C$_{44}$H$_{45}$B$_{10}$P$_3$ClRh calc.: C, 57.87; H, 4.97%. IR (KBr): v(B–H) 2658, 2645, 2638, 2621, 2612, 2600, 2559, 2542 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C, TMS): δ 7.00–7.52, 8.35–8.22 (m, C$_{aryl}$–H) ppm. ^{11}B NMR (CHCl$_3$, 128 MHz, 25°C, BF$_3$·Et$_2$O): δ –3.7 (d, ^1J(B,H) = 115 Hz, 4B), –11.0 (6B) ppm. ^{31}P NMR' (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 29.21 (two dd, ^1J(P,P) = 34 Hz, ^1J(P,P) = 130 Hz, ^1J(P,Rh) = 361 Hz), 87.62 (two dd, ^1J(P,P) = 38 Hz, ^1J(P,Rh) = 152 Hz, ^1J(Rh,P) = 361 Hz), 101.10 (dt, ^1J(P,P) = 35 Hz, ^1J(P,Rh) = 199 Hz) ppm.

3.11. Preparation of [Rh(nph)(CO)(PPh$_3$)]

[RhCl(CO)(PPh$_3$)$_2$] (113 mg, 0.119 mmol) was added to a refluxing solution of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (60 mg, 0.119 mmol) in deoxygenated ethanol (20 cm^3). The orange slurry was refluxed for 2 h and then the solids were filtered off, washed with hot ethanol and dried in vacuum to afford yellow product (75 mg (55%)). Anal. Found: C, 58.37; H, 4.99. C$_{45}$H$_{45}$B$_9$P$_3$ORh calc.: C, 60.39; H, 5.07%. IR (KBr): v(B–H) 2582, 2538, 2524; v(Co) 2032, 2014 (cm^{-1}). ^{1}H NMR (acetone-d_6, 400 MHz, 25°C, TMS): δ –2.5 (br, 1H, BHB), 6.93, 7.18–7.33, 7.64 (m, 35H, C$_{aryl}$–H) ppm. ^{11}B NMR (CH$_2$Cl$_2$, 128 MHz, 25°C, BF$_3$·Et$_2$O): δ –10.5 (1B), –13.2 (2B), –15.0 (2B), –17.9 (2B), –31.5 (1B), –39.5 (1B) ppm.

3.12. Preparation of [RhCl(nph)$_2$]

A solution of RhCl$_3$·nH$_2$O (49.14%) (36 mg, 0.149 mmol) in acetone (2 cm^3) was added to a refluxing solution of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (150 mg, 0.298 mmol) in deoxygenated ethanol (25 cm^3). The mixture was refluxed for 5 h and the formed solids were then filtered off and washed with hot ethanol. The brown solid was discarded, the filtrate was evaporated to dryness and the residue was dissolved in acetone (10 cm^3). Addition of ethyl ether followed by cooling (0°C) caused a yellow solid to separate, and then was filtered off, washed with diethyl ether and dried in vacuum to yield 110 mg (65%) of product. Anal. Found: C, 52.88; H, 5.44. C$_{52}$H$_{60}$B$_{18}$P$_4$ClRh calc.: C, 54.70; H, 5.30%. IR (KBr): v(B–H) 2631, 2578, 2537, 2525, 2522 cm^{-1}. ^{1}H NMR (acetone-d_6, 400 MHz, 25°C, TMS): δ –2.2 (br, 2H, BHB), 6.70–6.76, 7.03–7.12, 7.32–7.40 (m, 40H, C$_{aryl}$–H) ppm. ^{11}B NMR (acetone, 128 MHz, 25°C, BF$_3$·Et$_2$O): δ –8.6 (4B), –14.5 (10B), –27.9 (2B), –33.8 (d, ^1J(B,H) = 131 Hz, 2B), –11.0 (6B) ppm. ^{31}P NMR (acetone 162 MHz, 25°C, H$_3$PO$_4$): δ 82.28 (d, ^1J(P,Rh) = 139 Hz) ppm.

3.13. Preparation of [Ru(CO)(nph)$_2$]

[RuClH(CO)(PPh$_3$)$_3$] (190 mg, 0.199 mmol) was added to a slurry of {1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (100 mg, 0.199 mmol) in deoxygenated ethanol (50 cm^3). The mixture was stirred for 12 h at room temperature and then refluxed for 3 h. The formed solids were filtered off and washed with hot ethanol. The insoluble solid was discarded and the filtrate evaporated to dryness. The residue was dissolved in the minimum amount of chloroform. Addition of hexane and cooling (0°C) led to separation of an ochre solid, which was filtered off, washed with hexane and dried in vacuum to yield 52 mg (45%). Anal. Found: C, 58.32; H, 5.34. C$_{53}$H$_{60}$B$_{18}$P$_4$ORu calc.: C, 56.20; H, 5.34%. IR (KBr): v(B–H) 2535; v(CO) 2004, 1971 cm^{-1}. ^{1}H NMR (acetone-d_6, 400 MHz, 25°C, TMS): δ –2.1 (br, 2H, BHB), 6.87–7.73 (m, 40H, C$_{aryl}$–H) ppm. ^{11}B NMR (acetone-CH$_2$Cl$_2$, 128 MHz, 25°C, BF$_3$–Et$_2$O): δ –8.6 (4B), –14.0 (10B), –28.2 (2B), –34.3 (d, ^1J(B,H) = 115 Hz, 2B) ppm. ^{31}P NMR (CD$_2$Cl$_2$, 101 MHz, 25°C, H$_3$PO$_4$): δ = 32.7 (s) ppm.

3.14. Preparation of [Au(net)(PPh$_3$)]

To 30 cm^3 of hot deoxygenated ethanol containing {1,2-(PEt$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (87 mg, 0.273 mmol) was added a mixture of [AuCl (PPh$_3$)] (154 mg, 0.273 mmol) and PPh$_3$ (75 mg, 0.273 mmol). The mixture was refluxed for 2 h and the yellow solid formed was filtered off from the warm solution, then washed with warm ethanol and dried in vacuum, to yield 107 mg of

yellow microcrystals (51%). Anal. Found: C, 43.33; H, 5.87. $C_{28}H_{45}B_9P_3Au$ calc.: C, 43.74; H, 5.90%. FTIR (KBr): v(B–H) 2557, 2519 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 250 MHz, 25°C, TMS): δ −2.5 (br, 1, BHB), 0.91–1.08 (m, 12, CH$_3$), 2.01–2.11 (m, 8, CH$_2$), 7.47 (m, 15, C$_{aryl}$–H) ppm. ^{11}B FTNMR (CDCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −9.3 (d, ^1J(B,H) = 123 Hz, 2B), −14.3 (3B), −18.6 (2B), −29.6 (1B), −33.7 (d, ^1J(B,H) = 140 Hz, 1B) ppm. ^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 46.05 (br), 64.62, (s) ppm.

3.15. Preparation of [AuCl$_2$(net)]

To 15 cm^3 of hot deoxygenated ethanol containing {1,2-(PEt$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (95 mg, 0.297 mmol) was added AuCl$_3$ · nH$_2$O (50% Au) (117 mg, 0.297 mmol). The mixture was refluxed for 3 h and the yellow solid then filtered off from the warm solution. It was washed with warm ethanol and dried in vacuum to yield 100 mg of yellow microcrystals (59%). Anal. Found: C, 21.14; H, 5.49. $C_{10}H_{30}B_9P_2Cl_2Au$ calc.: C, 20.80; H, 5.24%. FTIR (KBr): v(B–H) 2591, 2568, 2558, 2534 cm^{-1}. ^{1}H FTNMR (CD$_2$Cl$_2$, 250 MHz, 25°C, TMS): δ −2.5 (br, 1H, BHB), 1.30–1.53 (m, 12H, CH$_3$), 1.91–1.97 and 2.26–2.72 (m, 8H, CH$_2$) ppm. ^{11}B FTNMR (CD$_2$Cl$_2$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −7.4 (d, ^1J(B,H) = 142 Hz, 2B), −12.9 (d, ^1J(B,H) = 148 Hz, 3B), −16.5 (d, ^1J(B,H) = 145 Hz, 2B), −24.6 (d, ^1J(B,H) = 146 Hz, 1B), −30.8 (d, ^1J(B,H) = 149 Hz, 1B) ppm. ^{31}P FT-NMR (CD$_2$Cl$_2$, 101 MHz, 25°C, H$_3$PO$_4$): δ 118.69 (s) ppm.

3.16. Preparation of [Au(nip) (PPh$_3$)]

To 15 cm^3 of hot deoxygenated ethanol containing {1,2-(P^{i}Pr$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (100 mg, 0.266 mmol) was added [AuCl(PPh$_3$)] (150 mg, 0.266 mmol). The mixture was refluxed for 2 h and the yellow solid filtered off from the warm mixture. It was washed with warm ethanol and dried in vacuum, to yield 170 mg of a microcrystalline yellow solid (78%). Anal. Found: C, 46.23; H, 6.15. $C_{32}H_{53}B_9P_3Au$ calc.: C, 46.59; H, 6.48%. FTIR (KBr): v(B–H) 2583, 2574, 2547, 2528 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 250 MHz, 25°C, TMS): δ −2.7 (br, 1H, BHB), 1.07–1.19 (m, 24H, CH$_3$), 2.21–2.30 (m, 2H, CH), 2.79–2.84 (m, 2H, CH), 7.43–7.51 (m, 15H, C$_{aryl}$–H) ppm. ^{11}B FTNMR (CDCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −8.0 (d, ^1J(B,H) = 118 Hz, 2B), −14.2 (d, ^1J(B,H) = 131 Hz, 3B), −18.9 (2B), −29.6 (1B), −32.4 (d, ^1J(B,H) = 127 Hz, 1B) ppm. ^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 44.51 (t, ^2J(P,P) = 128 Hz, P^{i}Pr$_2$), 85.62 (d, ^2J(P,P) = 128 Hz, PPh$_3$) ppm.

3.17. Preparation of [AuCl$_2$(nip)]

To 15 cm^3 of hot deoxygenated ethanol containing {1,2-(P^{i}Pr$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (60 mg, 0.159 mmol) was added AuCl$_3$ · nH$_2$O (50% Au) (125 mg, 0.318 mmol). The mixture was refluxed for 2 h and the brown solid then filtered off from the warm solution. It was washed with warm ethanol and dried in vacuum. Recrystallization from dichloromethane–hexane gave yellow crystals, which were filtered off, washed with a mixture of dichloromethane : hexane (1 : 3) and dried in vacuum to yield 55 mg (75%). When a carborane : Au(III) ratio of 1 : 1 was used, with the reaction conditions otherwise the same, the same product was obtained but with a yield of only 50%. Anal. Found: C, 26.06; H, 5.86. $C_{14}H_{38}B_9P_2Cl_2Au$ calc.: C, 26.54; H, 6.05%. FTIR (KBr): v(B–H) 2620, 2605, 2595, 2552, 2521 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 250 MHz, 25°C, TMS): δ −2.8 (br, 1H, BHB), 1.50–1.67 (m, 24H, CH$_3$), 3.16–3.26 (m, 2H, CH), 3.53–3.60 (m, 2H, CH) ppm. ^{11}B FTNMR (CDCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −8.8 (d, ^1J(B,H) = 141 Hz, 2B), −14.2 (d, ^1J(B,H) = 154 Hz, 3B), −18.0 (d, ^1J(B,H) = 123 Hz, 2B), −26.4 (d, ^1J(B,H) = 110 Hz, 1B), −31.5 (d, ^1J(B,H) = 150 Hz, 1B) ppm. ^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 127 (s) ppm.

A yellow crystal suitable for the X-Ray study was grown from a dichloromethane : heptane solution (3 : 1) after partial evaporation of the solvent.

3.18. Preparation of [Au(neo)(PPh$_2$)]

To 10 cm^3 of hot deoxygenated ethanol containing {1,2-(P{OEt}$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (58 mg, 0.151 mmol) was added [AuCl(PPh$_3$)] (85 mg, 0.151 mmol). The mixture was refluxed for 2 h and then allowed to cool. The white solid that separated was filtered off, washed with cold ethanol and dried in vacuum to yield 65 mg (52%) of product Anal. Found: C, 39.43; H, 5.39. $C_{28}H_{45}B_9O_4P_3Au$ calc.: C, 40.28; H, 5.43%. FTIR (KBr): v(B–H) 2539 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 250 MHz, 25°C, TMS): δ −2.5 (br, 1H, BHB), 1.32–1.43 (m, 12H, CH$_3$), 4.12–4.20 (m, 8H, CH$_2$), 7.49–7.58 (m, 15H, C$_{aryl}$–H) ppm. ^{11}B FTNMR (CDCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −6.3 (2B), −10.6 and −13.2 (3B), −18.5 and −21.6 (2B), −31.3 (1B), −35.1 (1B) ppm. ^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 136.41 (d, ^2J(P,P) = 49 Hz, P(OEt)$_2$), 157.87 (dd, ^2J(P,P) = 49, 402 Hz, PPh$_3$) ppm.

3.19. Preparation of [Au$_2$(ndc)(PPh$_3$)$_2$]

To 20 cm^3 of hot deoxygenated ethanol containing 1,1′;2,2′-(PPh)$_2$-1,1′;2,2′-(C$_2$B$_{10}$H$_{10}$)$_2$ (70 mg, 0.140

mmol) was added [AuCl(PPh$_3$)] (158 mg, 0.281 mmol). The mixture was refluxed, for 2 h and the ivory solid was then filtered off from the warm mixture washed with warm ethanol and dried in vacuum to yield 135 mg (69%). Anal. Found: C, 43.63; H, 4.29. C$_{52}$H$_{60}$B$_{18}$P$_4$Au$_2$ calc: C, 44.69; H, 4.33%. FTIR (KBr): v(B–H) 2541, 2529 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 250 MHz, 25°C, TMS): δ −2.2 and −2.5 (br, 2H, BHB), 6.96–7.70, 7.45–7.75 and 7.89–8.15 (m, 40H, C$_{aryl}$–H) ppm. ^{11}B FTNMR (CDCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −6.8 (6B), −9.8 (2B), −15.3 (6B), −29.4 and −32.6 (2B) ppm. ^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 40.32 (d, ^2J(P,P) = 30 Hz, PPh), 43.76 (d, ^2J(P,P) = 30 Hz, PPh$_3$) ppm.

3.20. Preparation of [RuCl$_2$(cet)$_2$]

To 20 cm^3 of hot deoxygenated ethanol containing {1,2-(PEt$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (40 mg, 0.125 mmol) was added [RuCl$_2$(PPh$_3$)$_3$](60 mg, 0.063 mmol). The brown mixture was refluxed for 2 h and the yellow solution was evaporated to dryness. The residue was dissolved in dichloromethane (3 cm^3), and heptane was added to precipitate yellow microcrystals which were filtered off, washed with dichloromethane:heptane (1:4) and dried in vacuum to yield 24 mg (47%) of product. Anal. Found: C, 29.56; H, 6.89. C$_{20}$H$_{60}$B$_{20}$P$_4$Cl$_2$Ru calc.: C, 29.56; H, 7.44%. FTIR (KBr): v(B–H) 2630, 2620, 2572 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 400 MHz, 25°C, TMS): δ 1.14–1.25 (m, 12H, CH$_3$), 2.16–2.25 and 2.66–2.75 (m, 8H, CH$_2$) ppm. ^{11}B FTNMR (CDCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −3.3 (4B), −11.4 (6B) ppm. ^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 63.71 (s, PEt$_2$) ppm.

3.21. Preparation of [RuCl$_2$(ceo)$_2$]

To 15 cm^3 of hot deoxygenated ethanol containing {1,2-(P{OEt}$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$} (200 mg, 0.520 mmol) was added [RuCl$_2$(PPh$_3$)$_3$] (249 mg, 0.260 mmol). The brown mixture was refluxed for 2 hours and the resulting yellow slurry was filtered while warm, the solid collected was washed with hot ethanol and dried in vacuum to yield 60 mg (25%) of product. The yellow filtrate was evaporated to dryness and the residue dissolved in dichloromethane (5 cm^3). Addition of heptane (3 cm^3) led to separation of yellow microcrystals, which were filtered off, washed with dichloromethane:heptane (1:4) and dried in vacuum to yield a further 55 mg (total, 47%). Anal. Found: C, 25.97; H, 6.17. C$_{20}$H$_{60}$B$_{20}$P$_4$O$_8$Cl$_2$ calc.: C, 25.53; H, 6.43%. FTIR (KBr): v(B–H) 2576, 2568, 2558, 2547 cm^{-1}. ^{1}H FTNMR (CDCl$_3$, 400 MHz, 25°C, TMS): δ 1.31–1.36 (t, ^2J(H,H) = 7 Hz, 12H, CH$_3$), 4.40–4.55 (m, 8H, CH$_2$) ppm. ^{11}B FTNMR (CDCl$_3$, 128 MHz, 25°C, BF$_3$ · Et$_2$O): δ −2.5 and −4.4 (4B), −11.7 (6B) ppm.

^{31}P FTNMR (CDCl$_3$, 101 MHz, 25°C, H$_3$PO$_4$): δ 159.07 (s, P(OEt)$_2$) ppm.

A yellow crystal suitable for X-ray analysis was grown from a dichloromethane:heptane solution (3:1) after partial evaporation of the solvent.

3.22. X-ray structure determination of [AuCl$_3$(nip)] (1)

Single-crystal data collection was performed with a Rigaku AFC5S diffractometer using monochromatized Mo Kα radiation (λ = 0.710 69 Å). The scan mode was ω–2θ. The unit-cell parameters were determined by least-squares refinements of 25 carefully centered reflections (29° < 2θ < 42°). The data obtained were corrected for Lorentz and polarization effects and for dispersion. A correction for empirical absorption (ψ scan) was applied. A total of 5356 reflections were collected (2θ_{max} = 52°), 4994 of which were unique (R_{int} = 0.085). Of those, 3271 were considered as observed in terms of the criterion $I > 3\sigma(I)$. The three check reflections monitored after every 150 reflections showed no decay.

The structure was solved by direct methods using MITHRIL [26]. Least-squares refinements and all subsequent calculations were performed using TEXSAN [27], a crystallographic software package, which minimizes the function $\Sigma w(\Delta F)^2$ where $w = 1/\sigma^2(F_0)$. Refinement of all non-hydrogen atoms anisotropic and BH hydrogen atoms with the fixed displacement factor (1.2 × that of the host atom) (other hydrogen atoms included in calculated positions with fixed isotropic displacement factors) reduced the R value to 0.032 (R_w = 0.035) for 283 parameters. Neutral atomic scattering factors were those included in the program. Structures were plotted with ORTEP [28].

3.23. X-ray structure determination of [RuCl$_2$(ceo)$_2$] (2)

Data collection was performed as for 1. The unit-cell parameters were determined by least-squares refinements of 23 carefully centered reflections (44° < 2θ < 50°). The data obtained were corrected for Lorentz and polarization effects and for dispersion. A correction for absorption (DIFFABS [28]) was applied. A total of 4852 reflections were collected (2θ_{max} = 52°), giving 4586 unique reflections (R_{int} = 0.014). Of those, 3556 were considered as observed in terms of the criterion $I > 3\sigma(I)$. The three check reflections monitored after every 150 reflections showed no decay.

The structure was solved and refined as 1. Refinement reduced the R value to 0.027 (R_w = 0.037) for 280 parameters.

3.24. Supplementary data

For both **1** and **2**, tables of hydrogen atom coordinates and thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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