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SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF [*exo-nido*-$Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{10}Me_2)$]

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ABSTRACT

In this work, the reaction of the 16-electron species $[Rh(\eta^3\text{-}C_8H_{13})(\eta^5\text{-}C_2B_9H_9Me_2)]$ with PPh_3 was investigated and the product, [*exo-nido*-$Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{10}Me_2)$], which is in an equilibrium with the *closo* analogue was characterized by $^{31}P\{^1H\}$, ^1H, ^{13}C and ^{11}B NMR spectroscopy. A mechanism for the complex formation is suggested which is related to the previously reported reactions between the 16-electron complex and PR_3 (R = Me and Et) ligands.

INTRDUCTION

The *nido*-icosahedral cage fragments $\eta^5\text{-}C_2B_9H_9R_2$ (R = H or Me), known as carborane ligands, assigned formally a dinegative charge, are regarded as a tridentate ligand and are isolobal with the more familiar uninegative η-C_5R_5 (R = H or Me) groups of organometallic complex chemistry.[1,2] These similarities have led to the synthesis of carborane analogues of metallocenes, arenes and other known types of metal complexes.[3] The salt $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_{11})]$ was first reported by Hawthorne et al.[4] as part of an extensive study of hydrogenation reactions homogeneously catalysed by rhodocarborane complexes.[5-8] Stone and co-workers[9,10] have synthesised the salts $[NEt_4][Rh(CO)(L)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (L=CO or PPh_3)]. The salt $[NEt_4][Rh(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ was also prepared by these workers by a different method[11] to that described by Hawthorne et al.[12]

The carborane ligands are isolobal with the familiar η-C_5R_5 (R = H or Me) groups, therefore, the anionic rhodacarborane complexes will be isolobal with the species $[Fe(CO)_2(\eta\text{-}C_5R_5)]^-$ and $[M(CO)_5]^-$ (M = Mn or Re), and the latter complexes have been known as useful synthons for preparing mixed metal complexes.[13-16] Anionic rhodacarborane complexes were expected to behave in a similar manner and Stone et al. have reported several heteropolynuclear metal complexes using these anions as precursors.[9,10,17-21]

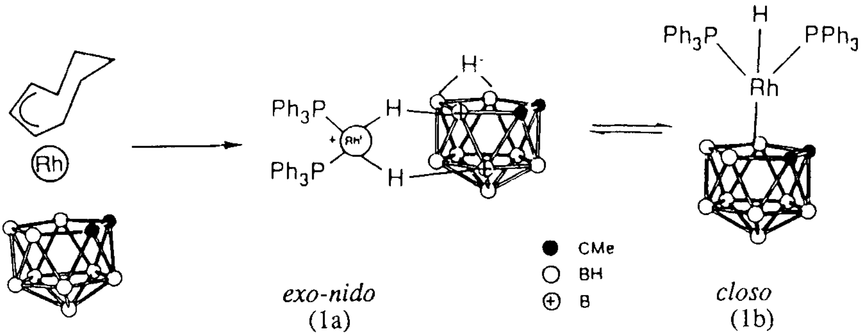
Hawthorne et al.[22] described the synthesis and reactivity of 12-vertex-*closo*-bis(triphenylphosphine)hydridorhodacarborane complexes, many of which show catalytic activity in a variety of reactions including the hydrogenation and isomerization of alkenes.

Related to the above bis(triphenylphosphine)hydridorhodacarborane compounds is $[RhH(PEt_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$[11], prepared as one of the products of the reaction of $[Rh(\eta^3\text{-}C_8H_{13})(\eta^5\text{-}C_2B_9H_9Me_2)]$[23] with PEt_3.

RESULTS AND DISCUSSION

Reaction with PPh_3

The reaction between the 16-electron compound $[Rh(\eta^3\text{-}C_8H_{13})(\eta^5\text{-}C_2B_9H_9Me_2)]$ with PPh_3 in CH_2Cl_2 at 25°C gave the *exo-nido* species



exo-nido
(1a)

closo
(1b)

Fig. 1. The Reaction of the 16-Electron Compound [$Rh(\eta^3\text{-}C_8H_{13})$ $(\eta^5\text{-}C_2B_9H_9Me_2)$] with PPh_3 and the *closo-exo-nido* Equilibrium in Solution

[*exo-nido*-$Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{10}Me_2)$] (1a) which is in an equilibrium with the *closo* species, [$RhH(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)$] (1b), in solution (Fig. 1).

Analytical, physical and $^{31}P\{^1H\}$, ^1H, ^{13}C, ^{11}B NMR data for the complex [*exo-nido*-$RhH(PPh_3)_2(\eta^5\text{-}C_2B_9H_{10}Me_2)$] are given in Table I.

NMR Spectra

The $^{31}P\text{-}\{^1H\}$-NMR data of the compound [$Rh(\eta^3\text{-}C_8H_{13}(\eta^5\text{-}C_2B_9H_9\text{-}Me_2)$] (Table I) revealed two doublets at δ 44.8 [J(RhP) = 188 Hz] and δ 43.5 [J(RhP) = 143 Hz] in the ratio of *ca.* 2:1 which is attributed to the *exo-nido* and *closo* species, respectively. The ^1H NMR data (Table I) showed a multiplet for the terminal metal hydride of (1b) at δ -9.16 and a broad resonance at *ca.* δ -2.5 which indicated the presence of a B-H-B bridge in the *exo-nido* species (1a). As mentioned above, Hawthorne et al. reported the compound [$RhH(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$] obtained from the reaction of [$RhCl(PPh_3)_3$] and [*nido*-7,8-$C_2B_9H_{12}$]$^-$ or [*nido*-7,9-$C_2B_9H_{12}$]$^-$ in absolute ethanol at reflux temperature. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of (1a) displayed a doublet at δ 39.5 [J(RhP) = 125 Hz] and the ^1H NMR

Table I. NMR Data for ($^{31}P\{^1H\}$, ^1H, ^{13}C, ^{11}B) the Complex [*exo-nido*-$Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{10}Me_2)$]

$^{31}P^{a,b,c}$	44.8 [d, RhP, *nido* J(RhP) 188] 43.5 [d, RhP, *closo* J(RhP) 143]
$^1H^{b,f}$	*-9.16 [m, 1H, RhH], *2.17 (s, 6H, Me), 2.30 (s, 6H, Me), 7.12-7.85 (m, Ph)
$^{13}C^{a,d,f}$	135.7-134.1 (Ph), 72.0 (s, *C*Me), *70.6 (s, *C*Me), *29.4 (s, C*Me*), 28.5 (s, C*Me*)
$^{11}B^{a,b,e}$	3.5 (1B), -3,5 (2B), -8.8 (1B), -11.6 (3B), -14.1 (2B)

^{a}Proton decoupled, ^{b}Chemical shifts in ppm, Coupling constants in Hz, Measurements in CD_2Cl_2 at ambient temperatures. ^{c}Chemical shifts are relative to 85% H_3PO_4 (external), ^{d}Chemical shifts are referenced versus $SiMe_4$ (0.0 ppm), ^{e}Chemical shifts are referenced versus $BF_3.Et_2O$ (external), ^{f}Peaks asterisked are due to minor isomer.

spectrum revealed a peak at δ -8.40 [J(PH) = 29 Hz, J(RhH) = 17 Hz]. It should be noted that these data are in good agreement with those obtained for the complex (1b).

Reaction with PMe_3

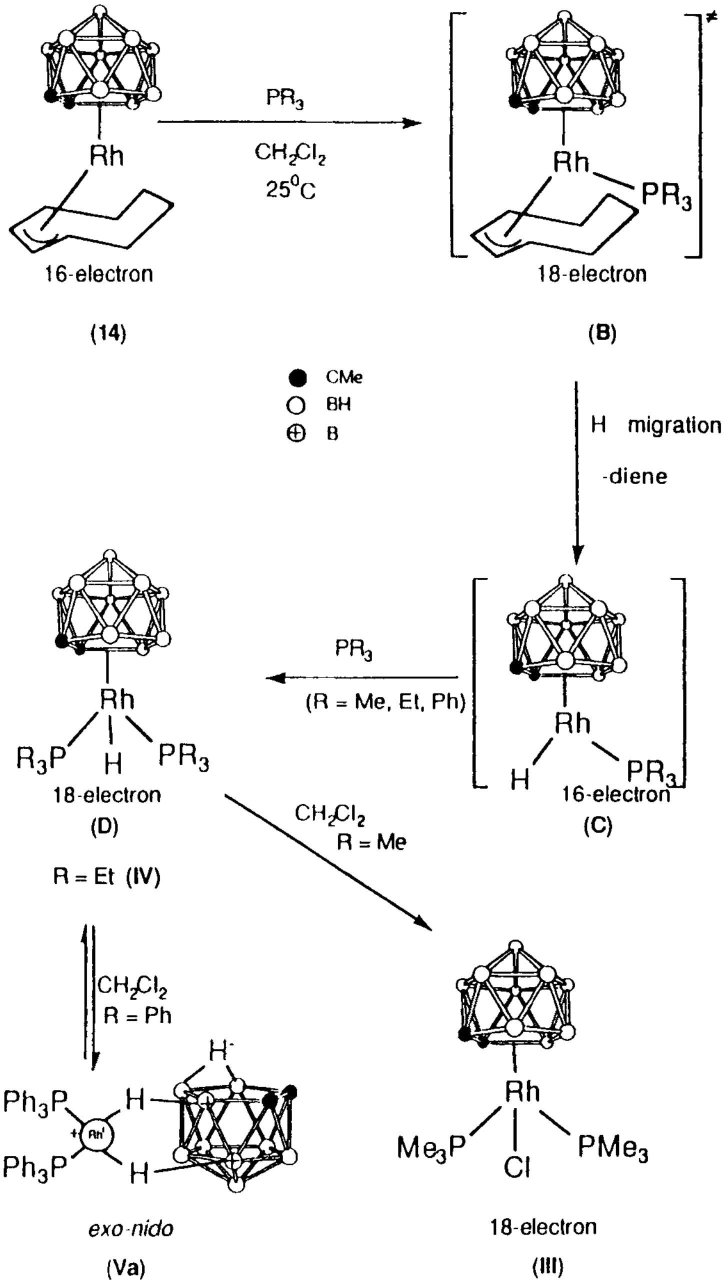
The reaction of the compound [$Rh(\eta^3\text{-}C_8H_{13})(\eta^5\text{-}C_2B_9H_9Me_2)$] with excess PMe_3 and PEt_3 has previously been investigated.[11] In the case of PMe_3, the reaction was carried out in CH_2Cl_2 at 25°C and instead of the expected product, [Rh(PMe$_3$)(η^3-C$_8$H$_{13}$)(η^5-C$_2$B$_9$H$_9$Me$_2$)], a chlorobis-(trimethylphosphine) species, formulated as [RhCl(PMe$_3$)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)], was obtained. The ^{31}P-{^{1}H} NMR spectrum of this compound revealed a doublet at δ 3.17 [J(RhP) = 125 Hz] which showed a PMe$_3$ group coordinated to rhodium. The molecular structure of the compound [RhCl-(PMe$_3$)$_2$-(η^5-C$_2$B$_9$H$_9$Me$_2$)] was fully established by a single crystal X-ray diffraction study.[11]

Reaction with PEt$_3$

The reaction between the compound [Rh(η^3-C$_8$H$_{13}$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] with excess PEt$_3$ in CH$_2$Cl$_2$ at 25°C afforded the hydrido compound [RhH-(PEt$_3$)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)]. The ^{31}P-{^{1}H} NMR spectrum displayed a doublet at δ 32.6 [J(RHP) = 135 Hz) and the ^{1}H NMR spectrum revealed a high-field resonance at δ -9.87 [t, J(PH) = 31 Hz].[11] Hawthorne et al.[22] have also obtained the compound [RhH(PEt$_3$)$_2$(η^5-C$_2$B$_9$H$_{11}$)] from the reaction of [Rh(PEt$_3$)$_3$[BF$_4$] and [*nido*-7,8-C$_2$B$_9$H$_{11}$]$^-$ in methanol.

Proposed Mechanism for the Reaction of [Rh(η^3-C$_8$H$_{13}$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] with Phosphine Ligands

Related to the reactions of the compound [Rh(η^3-C$_8$H$_{13}$)-(η^5-C$_2$B$_9$H$_9$Me$_2$)] with phosphine ligands, a mechanism can be suggested for the reaction described herein. (Scheme 1). The first step of the reaction involves the addition of the phosphine ligand to the 16-electron compound [Rh(η^3-C$_8$H$_{11}$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] to form an 18-electron intermediate (B) in which both groups η^3-C$_8$H$_{11}$ and PR$_3$ are coordinated to the rhodium metal centre. Migration of a hydride from the η^3-C$_8$H$_{13}$ ligand to rhodium and loss of cyclooctadiene would then produce the 16-electron intermediate (C) which then reacts with an additional phosphine ligand to form the 18-electron hydride complex (D). In case of PPh$_3$, a *closo-exo-nido* equilibrium is established. Examples of *closo-exo-nido* tautomers have been demonstrated and *exo-nido* rhodium species have been reported by



Scheme 1. Proposed Mechanism For The Complexes Formed by the Reaction of $[Rh(\eta^3\text{-}C_8H_{13})(\eta^5\text{-}C_2B_9H_9Me_2)]$ with PR_3 (R = Me, Et, Ph) Ligands

Hawthorne et al.[24] They prepared the compound [Rh$(PPh_3)(\eta^5$-$C_2B_9H_9$-{μ-(o-xylylene)}] by heating [RhCl$(PPh_3)_3$] with [Me_3NH][*nido*-7,8-μ-(o-xylylene)-7,8-$C_2B_9H_{10}$] in ethanol. Reaction of this compound with two equivalents of PCy_3 (Cy = cyclohexyl) exchanged one PPh_3 by PCy_3 and produced a red-orange species. The distinguishing feature associated with rhodocarboranes of this class is the presence of an $[RhL_2]^+$ (L = phosphine) moiety tightly held to a [*nido*- 7,8-$C_2B_9H_{12}]^-$ fragment through the agency of a pair of B-H—>Rh three-centre, two electron bonds. Since the carborane anion and the rhodium cation retain their formal charges in the *exo-nido* compounds, these species may be thought of as ion pairs whose Coulombic binding interaction is greatly augmented by the two *cis*-B-H—>Rh bridge bonds.

Hawthorne et al.[24] suggested a general *closo-exo-nido* equilibrium for all phosphinerhodacarboranes derived from the isomeric *nido*-$[C_2B_9H_{12}]^-$ anions and their substituted derivatives. The *closo-exo-nido* tautomerism reported was formally viewed as a reversible oxidative addition-reductive elimination equilibrium in which the 12-electron $[Rh(PPh_3)_2]^+$ moiety oxidatively adds the B-H—>B bridge system of the *nido*-carborane anion accompanied by η^5-bonding to the open face of the anion.

closo-exo-nido Tautomerism

Hawthorne et al.[24] have reported that the *exo-nido* tautomers exhibited interesting behaviour in their ^1H NMR spectra in the B-H—>B and Rh-H—>B bridging region (*ca.* δ -2 to -8) which is consistent with the broad band at δ -2.5 observed for the compound [*exo-nido*-Rh$(PPh_3)_2$-$(\eta^5$-$C_2B_9H_{10})$].

In the view of these results, interconversions between the tautomers (1a) and (1b) must be slow on the NMR time scale since peaks due to both the *closo* and *exo-nido* species were observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra.

In the reaction of [Rh$(\eta^3$-$C_8H_{11})(\eta^5$-$C_2B_9H_9Me_2)$] with PEt_3, the *closo*-hydrido complex [RhH$(PEt_3)_2(\eta^5$-$C_2B_9H_9Me_2)$] was obtained as the final product and no peaks due to *exo-nido* species were observed in any of the spectra.[11]

It was reported that[11] the reaction between the compound [Rh(η^3-C_8H_{13})(η^5-$C_2B_9H_9Me_2$)] and PMe_3 afforded the *closo* chloro compound [Rh(PMe_3)$_2$(η^5-$C_2B_9H_9Me_2$)] which was characterised by an X-ray diffraction study. It was suggested[11] that this reaction proceeds in the same way to produce the hydrido compound [RhH(PMe_3)$_2$(η^5-$C_2B_9H_9Me_2$)] which subsequently exchanges the hydride ligand for chloride in CH_2Cl_2 solution.

Hawthorne and co-workers[22] have synthesized *closo*-chlororhodacarborane complexes bearing phosphine ligands. The compound [RhCl(PPh_3)$_2$(η^5-$C_2B_9H_{11}$)] was prepared by heating the hydrido species [RhH(PPh_3)$_2$(η^5-$C_2B_9H_{11}$)] in $CHCl_3$-aqueous HCl, whereas the compound [RhCl(PMe_2Ph)(η^5-$C_2B_9H_{11}$)] was simply obtained by recrystallisation of the compound [RhH(PMe_2Ph)$_2$(η^5-$C_2B_9H_{11}$)] in CH_2Cl_2.

It was reported[22] that a bright orange crystalline complex [RhClH(PPh_3)(η^5-$C_2B_9H_{10}Ph$)] was obtained, as well as the expected chloro compound [RhCl(PPh_3)$_2$(η^5-$C_2B_9H_{10}Ph$)], when the complex [RhClH(PPh_3)(η^5-$C_2B_9H_{10}Ph$)] was recrystallised slowly by layering heptane over a CH_2Cl_2 solution of the complex.

EXPERIMENTAL

The synthesis was carried out using Schlenk-tube techniques, under a dry, oxygen-free nitrogen atmosphere. All solvents were rigourously dried before use. Light petroleum refers to the fraction of b.p. 40-60°C.

Alumina used in chromatography columns (*ca.* 20 cm in length and 3.0 cm in diameter) was BDH aluminium oxide (Brockman Activity II). The NMR spectra were recorded on JEOL JNM FX90Q, GX270 or GX400 spectrometers. The compound [Rh(η^3-C_8H_{13})(η^5-$C_2B_9H_9Me_2$)] was prepared by treating [NEt_4][Rh(cod)(η^5-$C_2B_9H_9Me_2$)] with excess HBF_4 in CH_2Cl_2 at -78°C, a method which is slightly different from the one described previously by Hawthorne et al.[23]

Preparation of the Complex [*exo-nido*-Rh$(PPh_3)_2(\eta^5$-$C_2B_9H_9Me_2)$]

The complex [Rh$(\eta^3$-$C_8H_{13})(\eta^5$-$C_2B_9H_9Me_2)$]^{23} (0.20 g, 0.53 mmol) was treated with PPh_3 (0.14 g, 0.53 mmol) in CH_2Cl_2 (15 mL) at 25°C and the mixture was stirred for *ca.* 8 h. The solvent was removed *in vacuo* and the residue was chromatographed on alumina. Elution with CH_2Cl_2-light petroleum (1:3) afforded one major orange band. Removal of solvent *in vacuo* gave a red solution. Recrystallisation from CH_2Cl_2-light petroleum (1:4) gave brick-red microcrystals of [*exo-nido* Rh$(PPh_3)_2$-$(\eta^5$-$C_2B_9H_{10}Me_2)$], m.p. 162 °C (decomp.); yield, 0.18 g (43 %).

Anal. Found: C, 58.4, H, 5.9, P, 7.6 %

Calcd. for $C_{40}H_{46}P_2B_9Rh.1/2CH_2Cl_2$: C, 58.5, H, 5.7, P, 7.5 %

M.W: 831.35

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