ELSEVIER

Journal of Organometallic Chemistry 651 (2002) 34–43

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and reactivity of the rhodium monocarbollide complexes [1-NH=CMe$_2$-2-Cl-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] and [1-NH$_3$-2-Cl-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$]

Jason A. Kautz, Denis A. Kissounko, Natalia S. Kissounko, F. Gordon A. Stone *

Department of Chemistry and Biochemistry, Baylor University, Waco, TX 76798-7348, USA

Received 5 December 2001; received in revised form 28 January 2002; accepted 29 January 2002

Abstract

The carborane 7-NH=CMe$_2$-*nido*-7-CB$_{10}$H$_{12}$ reacts with [RhCl(PPh$_3$)$_3$] in toluene at reflux temperatures to give the charge-compensated 16-electron Rh(III) complex [1-NH=CMe$_2$-2-Cl-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] (**1**) in good yield. The structure of this product was established by X-ray diffraction (XRD). Upon methanolysis **1** affords [1-NH$_3$-2-Cl-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] (**2**), also a 16-electron charge-compensated Rh(III) complex. Some reactions of **2** were investigated. At room temperature, in the presence of Na$_2$CO$_3$, it reacts with acetic, methacrylic, and crotonic anhydrides to give the complexes [1,2-μ-{NHC(R)=O}-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] [R = Me (**3**), CMe=CH$_2$ (**4a**), and (*E*)-CH=CHMe (**4b**)], respectively. Benzoyl bromide with **2** and Na$_2$CO$_3$ yields [1,2-μ-{NHC(Ph)=O}-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] (**5**). An XRD study of **4a** established that the acyl group is coordinated to the rhodium through the oxygen. In the crystal molecules lie pair-wise linked by a B–H⇀Rh bridge so that in one molecule the rhodium atom has a 16-electron valence shell and in the other an 18-electron configuration. However, in solution NMR studies reveal that only monomeric molecules occur. With CNBu^t in the presence of Na$_2$CO$_3$, compound **2** affords [1-NH$_2$-2,2-(CNBu^t)$_2$-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] (**7**), the structure of which was determined by XRD. The NMR parameters of the new compounds are reported and discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Carborane; Rhodacarboranes; Amino-substituents

---

1. Introduction

Although transition metal complexes containing C-amine substituted monocarbollide ligands were first reported in 1967 [1,2], until recently there were few metallacarboranes known in which the metal is coordinated by [7-NR$_3$-*nido*-7-CB$_{10}$H$_{10}$]$^{2-}$ or [7-NR$_2$-*nido*-7-CB$_{10}$H$_{10}$]$^{3-}$ (R = H or alkyl groups). This is surprising since these two ligands are isolobal with the species [7,8-R$_2$-*nido*-7,8-C$_2$B$_9$H$_9$]$^{2-}$ and [*nido*-7-CB$_{10}$H$_{11}$]$^{3-}$, respectively, and numerous metallacarboranes containing these groups have been reported and their chemistry explored [3].

It has recently become evident that the direct reaction between a low valent transition metal complex and a C-amine carborane 7-NR$_3$-*nido*-7-CB$_{10}$H$_{12}$, or an anion derived from the latter by treatment with base, provides a convenient route to various C-amine monocarbollide complexes. Thus the reagents 7-NR$_3$-*nido*-7-CB$_{10}$H$_{12}$ (NR$_3$ = NMe$_3$, NH$_2$Bu^t, NMe$_2$Bu^t) all react with [Ru$_3$(CO)$_{12}$] in toluene at reflux temperatures to yield the cluster compounds [1-NR$_3$-2,2-(CO)$_2$-7,11-(μ-H)$_2$-2,7,11-{Ru$_2$(CO)$_6$}-*closo*-2,1-RuCB$_{10}$H$_8$] [4]. A related osmium compound has been obtained using a similar procedure [5]. In these tri-ruthenium and -osmium species the [7-NR$_3$-*nido*-7-CB$_{10}$H$_{10}$]$^{2-}$ groups ligate one metal center in the usual pentahapto manner but coordinate to the other two metal atoms via exopolyhedral B–H⇀Ru(Os) bridge bonds. Thus the cage formally functions as a ten-electron donor to the metal triangle. In contrast a mononuclear anionic metal complex [1,2-μ-NHBu^t-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^-$ is obtained from the reaction between Li[7-NHBu^t-*nido*-7-CB$_{10}$H$_{12}$] and [Mo(CO)$_3$(NCMe)$_3$] in refluxing NCMe. In this product the exopolyhedral NHBu^t group forms an intra-molecular bridge between the

---

* Corresponding author. Tel.: +1-254-710-4427; fax: +1-254-710-2403.

E-mail address: gordon-stone@baylor.edu (F.G.A. Stone).

PII: S0022-328X(02)01218-4

cage-carbon and the molybdenum so that the [7-NHBu^t-*nido*-7-$CB_{10}H_{10}$]$^{3-}$ group formally donates eight electrons to a single metal center [6].

Significant variations in the nature of the products are also observed in reactions between [$RhCl(PPh_3)_3$] and the C-amine *nido*-carboranes 7-NR_3-*nido*-7-$CB_{10}H_{12}$, depending on experimental conditions and the different substituents R. Several years ago it was shown that in methanolic KOH solution, the carborane 7-NH_3-*nido*-7-$CB_{10}H_{12}$ reacts with [$RhCl(PPh_3)_3$] to give [1-NH_2-2,2-$(PPh_3)_2$-2-H-*closo*-2,1-$RhCB_{10}H_{10}$]$^-$, which is converted in refluxing methanol to dimeric [2,2′-μ-H-{1,2′-μ-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$}$_2$]$^-$ [7]. In contrast, the carborane 7-NMe_3-*nido*-7-$CB_{10}H_{12}$ in refluxing methanol with the same rhodium reagent yields primarily 18-electron [1-NMe_3-2,7-$(PPh_3)_2$-2-H-2-Cl-*closo*-2,1-$RhCB_{10}H_9$], along with the 16-electron complex [1-NMe_3-2-PPh_3-2-Cl-*closo*-2,1-$RhCB_{10}H_{10}$] [8]. Moreover, 7-NH_2Bu^t-*nido*-7-$CB_{10}H_{12}$ reacts with [$RhX(PPh_3)_3$] (X = Cl or Br) in refluxing toluene to give 16-electron compounds [1-NH_2Bu^t-2-PPh_3-2-X-*closo*-2,1-$RhCB_{10}H_{10}$] as the only products [9].

Employment in these syntheses of C-amine *nido*-carboranes where the N atom carries a functional group is of particular interest because the exopolyhedral amine groups can in some circumstances interact with the metal center in an intra- or inter-molecular fashion [6,7]. Moreover, the presence of a functional group allows for the possibility of derivatization. Herein we describe studies of the reaction between [$RhCl(PPh_3)_3$] and the carborane 7-NH=CMe_2-*nido*-7-$CB_{10}H_{12}$, which is readily obtained from 7-NH_3-*nido*-7-$CB_{10}H_{12}$ [10].

2. Experimental

2.1. General considerations

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk-line techniques. Solvents were stored over and distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40–60 °C. NMR spectra were recorded at the following frequencies, ^1H, 360.1; ^{13}C, 90.6; ^{11}B, 115.5; and ^{31}P, 145.8 MHz. The compounds 7-NH=CMe_2-*nido*-7-$CB_{10}H_{12}$ [10] and [$RhCl(PPh_3)_3$] [11] were prepared according to the literature. Maleic anhydride was distilled prior to use. All other reagents were used as supplied.

2.2. Synthesis of [1-NH=CMe_2-2-Cl-2-PPh_3-closo-2,1-$RhCB_{10}H_{10}$]

A mixture of [$RhCl(PPh_3)_3$] (0.234 g, 0.25 mmol) and 7-NH=CMe_2-*nido*-7-$CB_{10}H_{12}$ (0.047 g, 0.25 mmol) was refluxed in toluene (20 ml) for 3 h. Solvent was removed in vacuo, and the oily residue was washed three times with Et_2O–petroleum ether (10 ml, 2:1) to remove excess PPh_3. The resulting powder was then extracted with a mixture of toluene–petroleum ether (5:1) through a Celite plug until the washings were almost colorless. The combined extracts were concentrated to ca. 5 ml and layered with 50 ml of petroleum ether to afford upon slow diffusion at room temperature (r.t.) red crystals of [1-NH=CMe_2-2-Cl-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**1**) (0.130 g).

2.3. Synthesis of [1-NH_3-2-Cl-2-PPh_3-closo-2,1-$RhCB_{10}H_{10}$]

Compound **1** (0.050 g, 0.08 mmol) was dissolved in a mixture of CH_2Cl_2 (10 ml) and MeOH (10 ml) and the reactants stirred overnight. The solution was evaporated to dryness and the residue was crystallized from CH_2Cl_2 layered with petroleum ether to give [1-NH_3-2-Cl-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**2**) (0.035 g) as red crystals.

2.4. Reactions of **2** with carboxylic acid anhydrides and benzoyl bromide

1. Compound **2** (0.05 g 0.09 mmol) in CH_2Cl_2 (20 ml) was treated with $(MeCO)_2O$ (9 μl, 0.09 mmol) and Na_2CO_3 (0.10 g) and the mixture stirred overnight. After filtration through a Celite plug, solvent was removed in vacuo. The residue was taken up in CH_2Cl_2–toluene (5:1, ca. 5 ml) and layered with petroleum ether, which upon slow diffusion at −20 °C afforded brown microcrystals of [1,2-μ-{NHC(Me)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**3**) (0.046 g).
2. Following the same procedure, reaction between **2** (0.10 g, 0.18 mmol) and $(CH_2{=}C(Me)CO)_2O$ (29 μl, 0.19 mmol) gave brown crystals of [1,2-μ-{NHC(CMe=CH_2)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**4a**) (0.08 g).
3. Similarly, **2** (0.080 g, 0.15 mmol) and [(*E*)-CHMe=CHCO]$_2$O (23 μl, 0.15 mmol) afforded brown crystals of [1,2-μ-{NHC[(*E*)-CH=CHMe]=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**4b**) (0.07 g).
4. Reaction between **2** (0.050 g, 0.09 mmol) and PhCOBr (10.8 μl, 0.09 mmol) gave brown crystals of [1,2-μ-{NHC(Ph)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**5**) (0.048 g).

2.5. Reactions of **2** and **3** with CNBu^t

1. Complex **3** (0.083 g, 0.15 mmol) was dissolved in CH_2Cl_2 (20 ml) and CNBu^t (50 μl, 0.45 mmol) was added. After stirring overnight the reaction mixture was concentrated to ca. 2 ml. Petroleum ether (ca.

30 ml) was added, and the yellow precipitate obtained was recovered by filtration and washed with petroleum ether (2 × 10 ml). Crystallization at − 20 °C from CH_2Cl_2 layered with petroleum ether yielded yellow microcrystals of a compound formulated as [1-NHC(Me)=O-2,2-$(CNBu^t)_2$-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**6**) (0.103 g) on the basis of spectroscopic evidence discussed below.

2. Compound **2** (0.015 g, 0.03 mmol) in CH_2Cl_2 (20 ml) at − 78 °C was treated with dried Na_2CO_3 (0.10 g), and $CNBu^t$ (6 μl, 0.06 mmol). The mixture was slowly warmed to r.t., and stirred for 2 h. After filtration, solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2–toluene (5:1, ca. 5 ml) and the solution layered with petroleum ether. Slow diffusion at ca. − 20 °C afforded yellow crystals of [1-NH_2-2,2-$(CNBu^t)_2$-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**7**) (0.01 g).

2.6. Reaction of **2** with $B(C_6F_5)_3$

Complex **2** (0.025 g, 0.05 mmol), dissolved in CH_2Cl_2 (20 ml), was treated with Na_2CO_3 (0.10 g) and $B(C_6F_5)_3$ (0.024 g, 0.05 mmol). After stirring overnight, the reaction mixture was filtered and the solvent was removed in vacuo. The residue was taken up in CH_2Cl_2–THF (5:1, ca. 5 ml) and the mixture layered with petroleum ether, which upon slow diffusion at − 20 °C afforded brown crystals of [{1,2′-μ-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$}$_2$] (**8**) (0.011 g).

2.7. Crystal structure determination and refinement

Crystals of **1** and **7** were grown by slow diffusion of petroleum ether into solutions of the compounds in CH_2Cl_2–toluene (7:1); crystals of **4a** were grown by slow diffusion of heptane into a CH_2Cl_2 solution. A summary of appropriate crystallographic parameters is given in Table 4.

Intensity data were measured on either a Siemens SMART CCD (**1**) or an Enraf–Nonius CAD4 (**4a** and **7**) diffractometer using Mo–K_α X-radiation ($\lambda = 0.71073$ Å). Data for **1** were integrated using SAINT [12] and corrected for absorption using the program SADABS [13]. Data for **4a** and **7** were corrected for Lorentz, polarization, and absorption affects, the last with numerical corrections based on the measurements of the various crystal faces.

The structures were solved by direct methods. Successive difference Fourier syntheses were employed to locate all non-hydrogen atoms using SHELXTL version 5.03 [13]. Refinements were made by full-matrix least-squares on all F^2 data using SHELXL-97 [14]. Anisotropic thermal parameters were included for all non-hydrogen atoms. For all structures, cage-carbon atoms were assigned by comparison of the bond lengths to adjacent boron atoms in conjunction with the magnitudes of their isotropic thermal parameters. All hydrogen atoms, except those directly bonded to nitrogen, were included in calculated positions and allowed to ride on their parent boron or carbon atoms with fixed isotropic thermal parameters [$U_{iso}(H) = 1.2U_{iso}$(parent), or $U_{iso}(H) = 1.5U_{iso}(C)$ for methyl hydrogens]. The amine hydrogen atoms in all three structures were located in difference Fourier maps; their positional parameters were allowed to refine with fixed isotropic thermal parameters, $U_{iso}(H) = 1.2U_{iso}(N)$.

The asymmetric unit of compound **1** contains two independent rhodacarborane molecules plus one-half molecule of toluene as solvent. The toluene molecule was disordered over an inversion center with site occupancies for the carbon atoms fixed at 100 and 50%

Table 1
Analytical and physical data

Compound [a]	Color	Yield (%)	Anal. (%) [b]		
			C	H	N
1, [1-NH=CMe_2-2-Cl-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Red	89	45.1 (44.9)	5.5 (5.5)	2.3 (2.4)
2, [1-NH_3-2-Cl-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Red	75	48.3 (48.8) [c]	5.8 (5.7)	2.2 (2.2)
3, [1,2-μ-{NHC(Me)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Brown	91	43.5 (43.3) [d]	5.2 (5.1)	2.7 (2.4)
4a, [1,2-μ-{NHC(CMe=CH_2)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Brown	76	47.6 (47.7)	5.5 (5.4)	2.5 (2.4)
4b, [1,2-μ-{NHC[(*E*)-CH=CHMe]=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Brown	83	47.4 (47.7)	5.5 (5.4)	2.5 (2.4)
5, [1,2-μ-{NHC(Ph)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$]	Brown	85	47.9 (48.4) [d]	5.5 (4.9)	2.5 (2.1)
7, [1-NH_2-2,2-$(CNBu^t)_2$-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] [e]	Yellow	51	51.1 (51.4)	7.0 (6.7)	6.3 (6.2)
8, [{1,2′-μ-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$}$_2$]	Red–brown	44	44.8 (44.6)	5.6 (5.3)	2.7 (2.7)

[a] In the IR spectra of all the compounds were observed a broad medium-intensity band at ca. 2550 cm^{-1} due to B–H absorptions, and a weak band at ca. 3450 cm^{-1} due to N–H absorptions.

[b] Calculated values are given in parentheses.

[c] Crystallizes with one molecule of toluene.

[d] Crystallizes with 0.5 molecule of CH_2Cl_2.

[e] ν_{max}(NC) 2182 and 2198 cm^{-1} in CH_2Cl_2.

Table 2
^{1}H and ^{13}C-NMR data

Compound	^{1}H (δ) [a]	^{13}C (δ) [b]
1	2.57, 2.79 (s × 2, 3H × 2, CMe$_2$), 7.43–7.69 (m, 15H, Ph), 12.64 (br s, 1H, NH)	23.3, 28.8 (C*Me* × 2), 77.6 [br d, *J*(RhC) = 63, cage C], 129.3–136.2 (Ph), 190.0 (*C*Me$_2$)
2	7.47–7.55 (m, 15H, Ph), 7.77 (br s, 3H, NH$_3$)	68.7 [br d, *J*(RhC) = 54, cage C], 130.2–136.7 (Ph)
3	2.16 (s, 3H, Me), 7.08–7.66 (m, 16H, Ph, NH)	21.1 (Me), 90.3 [br d, *J*(RhC) = 63, cage C], 129.3–134.5 (Ph), 183.5 (C=O)
4a	1.92 (s, 3H, Me), 5.60 [br s, 1H, =CH (*trans* to Me)], 5.87 [br s, 1H, =CH (*cis* to Me)], 7.06 (br s, 1H, NH), 7.17–7.45 (m, 15H, Ph)	23.9 (Me), 90.4 (br, cage C), 127.7 (=CH$_2$), 129.2–134.5 (Ph), 134.7 (=*C*Me), 179.7 (C=O)
4b	1.90 (s, 3H, Me), 5.95 [d, 1H, *J*(HH) = 18, =C*H*Me], 6.84 (m, 1H, =C(H)CO, 7.05 (br s, 1H, NH), 7.17–7.47 (m, 15H, Ph)	18.5 (Me), 90.4 (br, cage C), 125.6 (=*C*HMe), 129.2–134.5 (Ph), 148.8 *C*(H)C=O, 177.4 (C=O)
5	6.93–7.69 (m, 22H, Ph, NH$_2$)	90.3 [br d, *J*(RhC) = 68, cage C], 128.4–134.4 (Ph), 179.0 (C=O)
7 [c]	1.28 (s, 18H, Bu^t), 7.44–7.60 (m, 15H, Ph)	29.7 (C*Me*$_3$), 58.7 (*C*Me$_3$), 96.3 (br, cage C), 128.6–134.7 (Ph), 139.2 (br, *C*NBu^t)
8	3.78 (br s, 4H, NH$_2$), 6.93–7.69 (m, 30H, Ph)	85.1 [br d, *J*(RhC) = 40, cage C], 128.3–134.4 (Ph)

Chemical shifts (δ) in ppm, coupling constants (*J*) in Hertz, measurements at ambient temperatures in CD$_2$Cl$_2$.

[a] Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. -1 to $+3$.

[b] ^{1}H-decoupled chemical shifts are positive to high frequency of SiMe$_4$.

[c] NH$_2$ protons not observed.

where appropriate; no hydrogens were included. Significant residual electron density peaks (< 2.0 e Å^{-3}) were found near the Rh centres, most likely due to an inability to correct completely for X-ray absorption effects on poorly formed crystals.

Both CNBu^t groups in complex **7** were disordered over two positions by a slight bend in the C–N≡C bond angles. Major and minor components were refined in parts with occupancies of 0.555/0.445 and 0.718/0.282 for groups C(3)–C(6) and C(8)–C(11), respectively. Also, one of the phenyl rings of the triphenylphosphine ligand was disordered by a 46.3° rotation through the C(41)–C(44) C_2 axis. Major and minor components were refined in parts with respective occupancies of 0.508 and 0.492. Due to the weak nature and insufficient number of intensity data, members of each respective disordered group were refined with equivalent anisotropic displacement parameters in an effort to ensure a reasonable data to parameter ratio (ca. 11.5:1). Furthermore, many geometric parameters were restrained by use of the SHELXL-97 DFIX card in order to preserve reasonable geometric environments around the atoms in the disordered moieties. These restraints include, N–C(Bu^t), 1.45(2) and C–C(Bu^t), 1.53(2) Å. Both amine hydrogens were restrained to N–H 0.95(2) Å. All calculations were carried out on Dell PC computers.

3. Results and discussion

In toluene at reflux temperatures [RhCl(PPh$_3$)$_3$] undergoes an oxidative addition reaction with 7-NH=CMe$_2$-*nido*-7-CB$_{10}$H$_{12}$ to give the charge-compensated 16-electron Rh(III) complex [1-NH=CMe$_2$-2-Cl-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] (**1**) in good yield (Scheme 1). Data characterizing **1** are summarized in Tables 1–3. However, in order to establish fully the molecular structure of this product an X-ray diffraction (XRD) study was carried out. One of two independent rhodacarborane molecules in the unit cell is shown in Fig. 1, and selected bond distances and angles for both

Table 3
^{11}B and ^{31}P-NMR data

Compound	^{11}B (δ) [a]	^{31}P (δ)[b]
1	9.6 (3B), 6.3 (2B), −5.2 (1B), −15.2 (4B)	33.7 [d, *J*(RhP) = 172]
2	10.4 (1B), 9.2 (2B), 7.3 (2B), −7.5 (1B), −15.0 (4B)	33.1 [d, *J*(RhP) = 162]
3	19.9 (2B), 9.1 (3B), −8.5 (1B), −12.5 (2B), −16.8 (2B)	26.3 [d, *J*(RhP) = 164]
4a	19.7 (2B), 9.2 (3B), −8.4 (1B), −12.3 (2B), −16.8 (2B)	24.3 [d, *J*(RhP) = 160]
4b	19.9 (2B), 9.1 (3B), −8.5 (1B), −12.3 (2B), −16.7 (2B)	26.3 [d, *J*(RhP) = 156]
5	19.9 (2B), 9.3 (3B), −8.2 (1B), −12.2 (2B), −16.6 (2B)	26.6 [d, *J*(RhP) = 162]
7	12.3 (1B), 1.8 (2B), 0.7 (2B), −10.1 (1B), −11.1 (2B), −12.6 (2B)	31.5 [d, *J*(RhP) = 94]
8	11.2 (3B), 6.1 (2B), −8.0 (1B), −12.5 (2B), −15.2 (2B)	30.2 [d, *J*(RhP) = 156]

Chemical shifts (δ) in ppm, coupling constants (*J*) in Hertz, measurements at ambient temperatures in CD$_2$Cl$_2$.

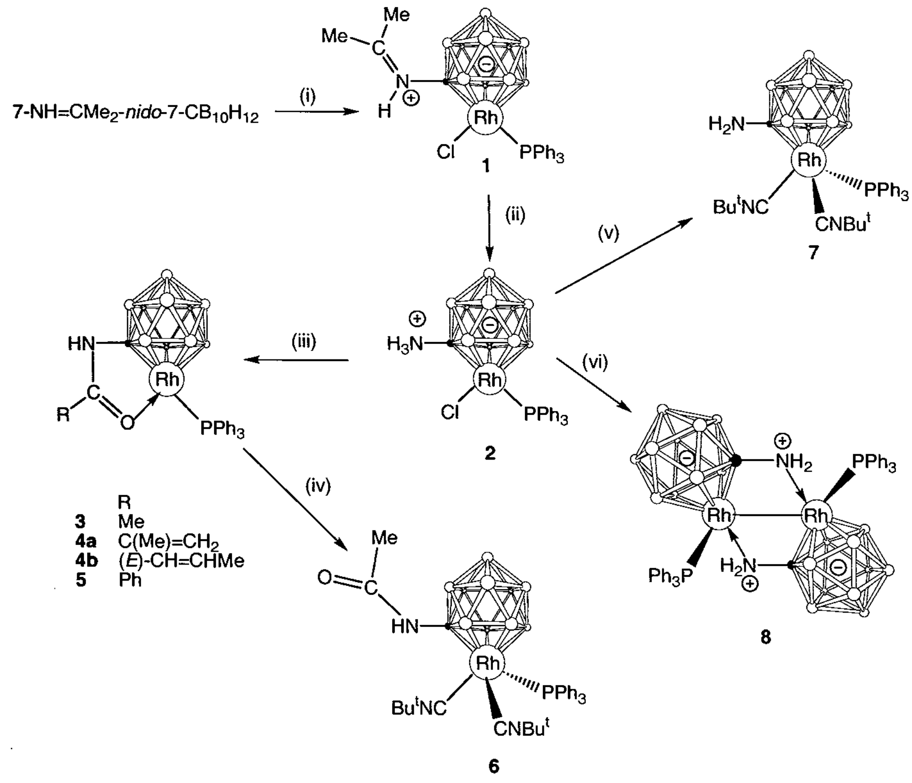
[a] ^{1}H-decoupled chemical shifts are positive to high frequency of BF$_3$·OEt$_2$ (external). Broadness of some peaks makes assignment of their relative intensities uncertain in some spectra.

[b] ^{1}H-decoupled chemical shifts are positive to high frequency of 85% H$_3$PO$_4$ (external).

Table 4
Crystallographic data for compounds **1**·1/4 toluene, **4a** and **7**

	1·1/4 toluene	**4a**	**7**
Formula	$C_{23.75}H_{34}B_{10}ClNPRh$	$C_{46}H_{62}B_{20}N_2O_2P_2Rh_2$	$C_{29}H_{45}B_{10}N_3PRh$
M	610.95	1158.94	677.66
Crystal color, habit	Red plates	Red plates	Yellow prisms
Crystal dimensions (mm)	0.40 × 0.20 × 0.10	0.49 × 0.41 × 0.09	0.45 × 0.40 × 0.32
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	10.152(8)	11.3438(13)	10.704(2)
b (Å)	12.120(14)	18.541(2)	15.8598(14)
c (Å)	24.57(3)	25.927(3)	21.249(3)
α (°)	95.81(8)		
β (°)	98.49(9)	95.285(9)	103.720(11)
γ (°)	95.01(10)		
Z	4	4	4
V (Å^3)	2958(5)	5430(1)	3504.2(8)
D_{calc} (g cm^{-3})	1.372	1.425	1.284
μ(Mo–K$_\alpha$) (mm^{-1})	0.738	0.711	0.558
T (K)	173	173	293
θ range (°)	1.69–25.00	1.58–24.00	1.62–22.56
Reflections measured	25187	8743	6165
Independent reflections	10357	8210	4622
R_{int}	0.0558	0.0354	0.0985
wR_2 (all data), R_1 [a]	0.1551, 0.0587	0.0993, 0.0416	0.1441, 0.0655

[a] $wR_2=[\Sigma\{w(F_o{}^2-F_c{}^2)^2\}/\Sigma w(F_o{}^2)^2]^{1/2}$; $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ with $F_o>4\sigma(F_o)$.



Scheme 1. (i) $[RhCl(PPh_3)_3]$ in toluene at reflux; (ii) MeOH; (iii) $(MeCO)_2O$, $[CH_2{=}C(Me)CO]_2O$, $(MeCH{=}CHCO)_2$ or PhCOBr with Na_2CO_3; (iv) $CNBu^t$ (v) $CNBu^t$ and Na_2CO_3; (vi) $B(C_6F_5)_3$ and Na_2CO_3.

molecules are listed in Table 5. The rhodium atom is coordinated on one side by the groups PPh_3 and Cl, and on the other by the open face of a zwitterionic 7-NH=CMe$_2$-*nido*-7-$CB_{10}H_{10}$ moiety in a pentahapto manner. Overall the structure of **1** is very similar to that of [1-NH$_2$Bu^t-2-Br-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$], the product isolated by reacting [RhBr(PPh$_3$)$_3$] with 7-NH$_2$Bu^t-*nido*-7-CB$_{10}$H$_{12}$ [9].

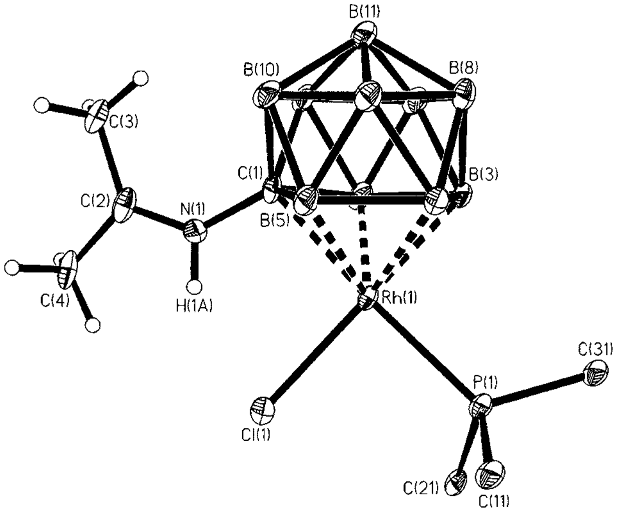


Fig. 1. Structure of [1-NH=CMe$_2$-2-Cl-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] (**1**) showing the crystallographic labeling scheme. Thermal ellipsoids are shown at the 40% probability level for the structures. Also in all Figures hydrogen atoms are omitted for clarity, with the exception of those on the pendant groups.

The NMR data for **1** (Tables 2 and 3) are in accord with the structure found by the X-ray analysis. Thus there are resonances for the two non-equivalent Me groups at δ 2.57 and 2.79 (^{1}H), and 23.3 and 28.8 (^{13}C{^{1}H}), respectively. The ^{1}H-NMR resonance for the NH proton was seen at relatively low field (δ 12.64, in CD$_2$Cl$_2$). This is at a considerably lower chemical shift than that measured [δ 7.37, in (CD$_3$)$_2$CO] for the corresponding proton in 7-NH=CMe$_2$-*nido*-7-CB$_{10}$H$_{12}$ [10], indicating that in **1** the N–H group is acidic in character. Interestingly this protonic character was indicated by the X-ray study which revealed an apparent intramolecular N–H···Cl interaction with average N···Cl and Cl···H distances of 2.99(2) and 2.22(4) Å, respectively, and with an N–H···Cl angle of 152°. A similar feature is present in the molecule [1-{NH(CH$_2$CH=CHMe)$_2$}-2-X-2-PPh$_3$-*closo*-2,1-RhCB$_{10}$H$_{10}$] (X = Br or Cl) which has parameters, N···Br(Cl) = 3.074(6) and Br(Cl)···H = 1.92(7) Å with N–H···Br(Cl) = 150°. This species had a disordered structure with two different halogens in the single-crystal [15].

A significant feature of the structure of **1** is the absence of η^2-coordination between the C=N bond and the metal atom which, if present, would give this Rh(III) species an 18-electron configuration. For **1** the C=N bond distance [1.298(7) Å (molecule **1**)] is very similar to the corresponding distance [1.301(10) Å] found in [7-(*E*)-NMe=CHMe-2,2,2-(CO)$_3$-*closo*-2,1-FeCB$_{10}$H$_{10}$] [16]. With di- or monocarbollide metal complexes we have previously observed that if exopolyhedral C=C groups are attached to boron atoms in the

Table 5
Selected interatomic distances (Å) and angles (°) for **1**

Molecule 1					
Bond lengths					
Rh(1)–B(2)	2.125(7)	Rh(1)–B(5)	2.143(7)	Rh(1)–B(4)	2.155(7)
Rh(1)–B(3)	2.177(7)	Rh(1)–C(1)	2.242(6)	Rh(1)–P(1)	2.336(3)
Rh(1)–Cl(1)	2.366(3)	C(1)–N(1)	1.448(7)	N(1)–C(2)	1.298(7)
N(1)–H(1A)	0.87(2)	N(1)···Cl(1)	3.005(6)	H(1A)···Cl(1)	2.25(4)
Bond angles					
B(2)–Rh(1)–P(1)	129.1(2)	B(5)–Rh(1)–P(1)	133.5(2)	B(4)–Rh(1)–P(1)	93.4(2)
B(3)–Rh(1)–P(1)	92.2(2)	C(1)–Rh(1)–P(1)	175.0(2)	B(2)–Rh(1)–Cl(1)	118.0(2)
B(5)–Rh(1)–Cl(1)	103.9(2)	B(4)–Rh(1)–Cl(1)	145.9(2)	B(3)–Rh(1)–Cl(1)	165.1(2)
C(1)–Rh(1)–Cl(1)	95.0(2)	P(1)–Rh(1)–Cl(1)	89.92(11)	N(1)–C(1)–B(6)	120.4(5)
N(1)–C(1)–B(10)	121.3(5)	N(1)–C(1)–B(5)	119.0(5)	N(1)–C(1)–B(2)	117.5(5)
N(1)–C(1)–Rh(1)	105.2(4)	C(2)–N(1)–C(1)	134.6(5)	N(1)–H(1A)···Cl(1)	144(5)
Molecule 2					
Bond lengths					
Rh(2)–B(22)	2.120(7)	Rh(2)–B(25)	2.139(7)	Rh(2)–B(24)	2.170(7)
Rh(2)–B(23)	2.192(7)	Rh(2)–C(21A)	2.235(6)	Rh(2)–P(2)	2.343(3)
Rh(2)–Cl(2)	2.380(3)	C(21A)–N(2)	1.453(7)	N(2)–C(5)	1.281(8)
N(2)–H(2A)	0.90(2)	N(2)···Cl(2)	2.973(6)	H(2A)···Cl(2)	2.18(4)
Bond angles					
B(22)–Rh(2)–P(2)	130.6(2)	B(25)–Rh(2)–P(2)	132.1(2)	B(24)–Rh(2)–P(2)	92.9(2)
B(23)–Rh(2)–P(2)	93.1(2)	C(21A)–Rh(2)–P(2)	175.64(14)	B(22)–Rh(2)–Cl(2)	117.1(2)
B(25)–Rh(2)–Cl(2)	103.2(2)	B(24)–Rh(2)–Cl(2)	146.2(2)	B(23)–Rh(2)–Cl(2)	164.1(2)
C(21A)–Rh(2)–Cl(2)	93.8(2)	P(2)–Rh(2)–Cl(2)	90.52(11)	N(2)–C(21A)–B(26)	119.9(5)
N(2)–C(21A)–B(30)	120.7(5)	N(2)–C(21A)–B(25)	118.6(5)	N(2)–C(21A)–B(22)	118.4(5)
N(2)–C(21A)–Rh(2)	105.9(4)	C(5)–N(2)–C(21A)	134.5(5)	N(2)–H(2A)···Cl(2)	147(5)

$\overline{\mathrm{CBBBB}}$ or $\overline{\mathrm{CCBBB}}$ rings ligating metal atoms they have a propensity to η^2-coordinate to the metal centers [16,17]. Although our knowledge of metallacarborane complexes with cage-pendant C=N groups is at present somewhat limited, it is noteworthy that the compound [7-(*E*)-NMe=CHMe-2,2,2-$(CO)_3$-*closo*-2,1-$FeCB_{10}H_{10}$] does not eliminate a CO molecule to allow coordination of the C=N group to iron. Moreover, in the monocarbollide iron complex [7-(*E*)-NMe=CHMe-2:6-η^2:σ-{(*E*)-CH=CHBu^t}-2,2-$(CO)_2$-*closo*-2,1-$FeCB_{10}H_9$], which has both CH=CHBu^t and NMe=CHMe groups attached to borons in the metal-coordinated $\overline{\mathrm{CBBBB}}$ ring, it is the C=C bond rather than the C=N which η^2-bonds to the iron atom [16]. Thus the non-coordination of the C=N bond to rhodium in **1** is perhaps not surprising. However, lack of an η^2-C=N link to the metal center may be inhibited by the presence of the intramolecular N–H···Cl interaction referred to above.

It has been reported that the dicarbollide rhodacarborane [3-Cl-3,3-$(PPh_2Me)_2$-*closo*-3,1,2-$RhC_2B_9H_{11}$] reacts with Ag[SbF_6] in acetonitrile to afford the cationic complex [3-NCMe-3,3-$(PPh_2Me)_2$-*closo*-3,1,2-$RhC_2B_9H_{11}$][SbF_6] [18]. It was thus anticipated that by treating **1** with Ag[BF_4] or Tl[PF_6] in the presence of donor molecules L (tertiary phosphines or alkynes) we might obtain $[BF_4]^-$ and $[PF_6]^-$ salts of cationic species [1-NH=CMe_2-2-PPh_3-2-L-*closo*-2,1-$RhCB_{10}H_{10}]^+$ with carbon-appended $[–NH=CMe_2]^+$ groups. However, we were unable to isolate any pure products from these reactions.

The acidity of the NH proton in **1**, indicated by the ^{1}H-NMR, suggested that it might be deprotonated by basic reagents to afford an anion [1-N=CMe_2-2-Cl-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}]^-$ which would subsequently react to yield a variety of products upon treatment with electrophiles. However, we were unable to characterize any identifiable species by this procedure, We believe this to be due to the ready hydrolysis of the intermediate anion, and that of compound **1** itself. This observation suggested that treatment of **1** with MeOH in CH_2Cl_2 at room temperature would afford the complex [1-NH_3-2-Cl-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**2**), not obtainable by other routes, and this proved to be so. In a somewhat related reaction we have recently reported that traces of water hydrolyze the iminium group in [7-(*E*)-NMe=CHMe-2,2,2-$(CO)_3$-*closo*-2,1-$FeCB_{10}H_{10}$] to give [7-NH_2Me-2,2,2-$(CO)_3$-*closo*-2,1-$FeCB_{10}H_{10}$] [16].

Compound **2** was fully characterized by the data given in Tables 1–3. The $^{11}B\{^1H\}$-NMR spectrum displays a very similar pattern to that of **1**, and both the ^{1}H and $^{13}C\{^1H\}$-NMR spectra reveal the absence of Me groups. In the ^{1}H-NMR spectrum the NH_3 group resonates at δ 7.77, but the signal is partially obscured by the protons of the PPh_3 ligand. Unlike **1**, complex **2** is relatively moisture stable and can be handled in air, thus making it a suitable candidate to study the reactivity of a metallacarborane with an exopolyhedral NH_3 group.

In CH_2Cl_2 compound **2**, in the presence of Na_2CO_3 as a mild deprotonating agent, reacts with acetic, methacrylic, and crotonic anhydrides at room temperature to give the complexes [1,2-μ-{NHC(R)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] [R = Me (**3**), CMe=CH_2 (**4a**), and (*E*)-CH=CHMe (**4b**)]. Benzoyl bromide reacts with **2** in a similar manner to yield [1,2-μ-{NHC(Ph)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**5**). The ^{1}H-and $^{13}C\{^1H\}$-NMR spectra of the four complexes showed the expected signals for the NHC(R)=O groups (Table 2). In the ^{1}H-NMR spectrum of **4b** the magnitude of the *J*(HH) coupling (18 Hz) for the C*H*=C*H*Me protons indicates that they are in a transoid arrangement. The $^{11}B\{^1H\}$-NMR spectra of each species displayed five peaks of relative intensity 2:3:1:2:2, consistent with a molecular mirror plane. In their IR spectra none of the compounds showed a band at ca. 1650 cm^{-1} characteristic for a NHC(R)=O group. Since the $^{13}C\{^1H\}$-NMR spectra revealed diagnostic resonances for the acyl fragment at δ 183.5 (**3**), 179.7 (**4a**), 177.4 (**4b**) and 179.0 (**5**) it seemed likely that this group was coordinated to the rhodium atom. However, it was only after an XRD study of **4a** that it became evident that this was indeed the case.

In the crystal, molecules of **4a** exist in an arrangement of two neutral rhodacarborane subunits as shown in Fig. 2. Selected bond distances and angles are listed in Table 6. The two crystallographically unique monomers are joined by an agostic interaction between one of the B–H vertices in the non-coordinating B_5 belt

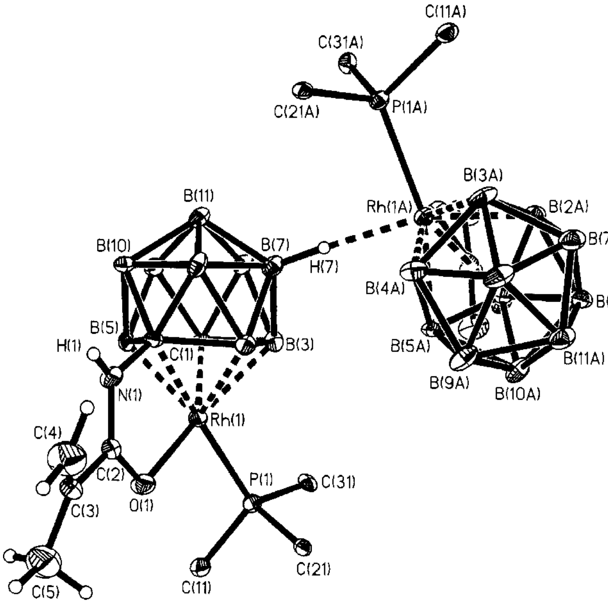


Fig. 2. Structure of [1,2-μ-{NHC(CMe=CH_2)=O}-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**4a**) showing the crystallographic labeling scheme.

of the carborane cage and the metal center of the adjacent molecule. In one molecule the atom Rh(1) (Rh(III), d^6) has a 16-electron configuration, formally acquiring two-electrons from the PPh_3 ligand and eight-electrons ($6\pi + 2\sigma$) from a $[7\text{-}\{NHC(CMe{=}CH_2){=}O\}\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]^{3-}$ unit. The other metal atom Rh(1A) acquires an 18 electron valence shell by acquisition of an additional two-electrons via the B(7)–H(7)⇀Rh(1A) bridge. The position of H(7) was located and refined [B(7)–H(7) 1.12(2), Rh(1A)–H(7) 2.13(3), Rh(1A)···B(7) 3.190(6) Å; B(7)–H(7)–Rh(1A) 157(4)°]. The Rh–H separation is somewhat longer than those involving the B–H⇀Rh bridges in the dimeric molecule $[(3\text{-}PPh_3\text{-}closo\text{-}3,1,2\text{-}RhC_2B_9H_{11})_2]$ [1.78(6) Å] [19], in accord with a weaker bridge system in **4a**. Indeed the Rh–H and Rh···B separations in **4a** are on the order of 0.4 and 0.8 Å longer, respectively, than typical B–H⇀Rh bonds found in several molecules having such groups recorded in the Cambridge Crystallographic Data Centre [20]. In this regard, the interunit B–H⇀Rh interaction in **4a** appears to be intermediate between a regular two-electron three-centre covalent bond and a longer-range intermolecular electrostatic interaction. It is not surprising, therefore, that there was no evidence from the ^1H or $^{11}B\{^1H\}$-NMR spectra for agostic B–H⇀Rh bonding in **4a** in solution. Nor were there signals for non-equivalent PPh_3 ligands in the $^{31}P\{^1H\}$ spectrum, which the asymmetry would require in a dimeric structure. The Rh(1)–O(1) [2.133(3) Å] and Rh(1A)–O(1A) [2.171(3) Å] bond lengths in **4a** are comparable with that [2.185(8) Å] found in $[1\text{-}Me\text{-}3\text{-}\{CH_2CH_2C({=}O)\text{-}OBu^n\}\text{-}3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ [21] where the rhodium is ligated by an oxygen atom in the ring system $\mathrm{RhCH_2CH_2C({=}O)OBu^n}$.

Since in solutions the complexes **3**–**5** are not associated and, therefore, remain 16-electron molecules it seemed likely that reactions with donor ligands might occur allowing the rhodium to acquire an 18-electron valence shell. To minimize steric effects the rod-like donor $CNBu^t$ was chosen. After treatment of **3** in CH_2Cl_2 with two equivalents of $CNBu^t$, spectroscopic examination of the mixture revealed that reaction was incomplete. It was evident that one component of this mixture was a species in which the acyl group was no longer coordinated to the rhodium. Thus in the IR spectrum there was a band diagnostic for a non-coordinated amido C=O group at 1691 cm^{-1} with two additional bands corresponding to $CNBu^t$ ligands at 2202 and 2183 cm^{-1}. In the $^{31}P\{^1H\}$-NMR spectrum there was a resonance at δ 37.6 [$J(RhP) = 108$ Hz]. This coupling constant is significantly smaller than those generally observed with 16-electron rhodium complexes (ca. 150–170 Hz). The data suggested the formation of a complex $[1\text{-}NHC(Me){=}O\text{-}Me\text{-}2,2\text{-}(CNBu^t)_2\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}RhCB_{10}H_{10}]$ (**6**). To force the reaction to go to completion the synthesis was repeated using three equivalents of $CNBu^t$. After removal of solvent a solid product was obtained. However, repeated crystallization failed to yield a sample of **6** which gave a satisfactory microanalysis, probably due to partial ligand dissociation. Nevertheless the nature of the compound was strongly indicated by the spectroscopic properties. The $^{13}C\{^1H\}$-NMR spectrum of the crystals in CD_2Cl_2 showed a resonance for the uncoordinated C=O group at δ 165.2, a chemical shift in the range for such groups in amides [22]. The corresponding signal for the ligating acyl carbon in **3** occurs at δ 183.5. Peaks for the *Me*C(=O), C*Me*$_3$ and *C*Me$_3$ nuclei appear at δ 22.6,

Table 6
Selected interatomic distances (Å) and angles (°) for **4a**

Bond lengths					
Rh(1)–B(2)	2.093(5)	Rh(1)–B(5)	2.108(6)	Rh(1)–C(1)	2.118(5)
Rh(1)–O(1)	2.133(3)	Rh(1)–B(3)	2.175(6)	Rh(1)–B(4)	2.186(5)
Rh(1)–P(1)	2.3445(13)	C(1)–N(1)	1.448(6)	B(7)–H(7)	1.12(2)
N(1)–C(2)	1.329(7)	C(2)–O(1)	1.264(6)	C(2)–C(3)	1.473(7)
C(3)–C(4)	1.335(8)	C(3)–C(5)	1.448(8)	Rh(1A)–B(2A)	2.098(6)
Rh(1A)–H(7)	2.13(3)	Rh(1A)–C(1A)	2.140(5)	Rh(1A)–O(1A)	2.171(3)
Rh(1A)–B(3A)	2.177(6)	Rh(1A)–B(5A)	2.186(5)	Rh(1A)–B(4A)	2.187(6)
Rh(1A)–P(1A)	2.3537(13)	C(1A)–N(1A)	1.453(6)	N(1A)–C(2A)	1.322(6)
C(2A)–O(1A)	1.248(6)	C(3A)–C(5A)	1.488(8)	C(2A)–C(3A)	1.498(7)
C(3A)–C(4A)	1.313(8)				
Bond angles					
C(1)–Rh(1)–O(1)	80.6(2)	C(1)–Rh(1)–P(1)	172.89(14)	O(1)–Rh(1)–P(1)	96.83(10)
C(2)–N(1)–C(1)	122.1(4)	O(1)–C(2)–N(1)	120.6(5)	O(1)–C(2)–C(3)	119.5(5)
C(2)–O(1)–Rh(1)	111.7(3)	C(5)–C(3)–C(2)	115.6(5)	C(4)–C(3)–C(2)	119.1(5)
C(4)–C(3)–C(5)	125.2(6)	H(7)–Rh(1A)–O(1A)	78.5(12)	C(1A)–Rh(1A)–O(1A)	79.5(2)
H(7)–Rh(1A)–P(1A)	83.2(12)	C(1A)–Rh(1A)–P(1A)	156.33(13)	O(1A)–Rh(1A)–P(1A)	96.76(9)
C(2A)–N(1A)–C(1A)	121.6(4)	O(1A)–C(2A)–N(1A)	122.3(5)	O(1A)–C(2A)–C(3A)	118.1(5)
C(2A)–O(1A)–Rh(1A)	110.4(3)	C(5A)–C(3A)–C(2A)	115.3(5)	C(4A)–C(3A)–C(2A)	119.9(5)
C(4A)–C(3A)–C(5A)	124.5(5)				

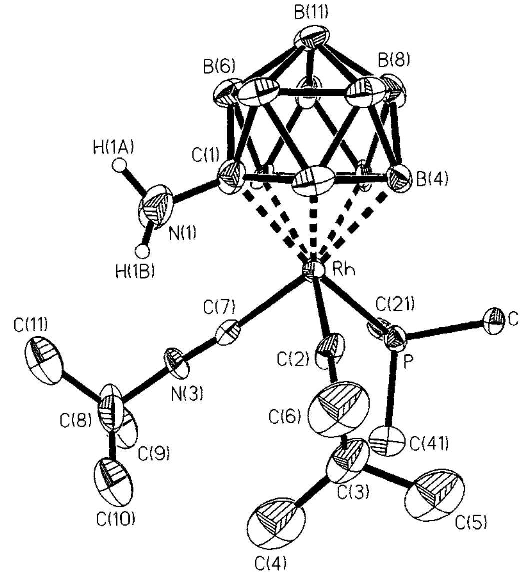


Fig. 3. Structure of [1-NH_2-2,2-($CNBu^t$)$_2$-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**7**) showing the crystallographic labeling scheme.

29.6 and 58.6, respectively, and that for the cage-carbon at δ 84.0. The $^{11}B\{^1H\}$-NMR spectrum of **6** displays a pattern typical for an 18-electron monocarbollide rhodium species with six broad overlapping peaks at δ 11.6 (1B), 1.2 (3B), − 1.8 (1B), − 7.8 (1B), − 11.2 (2B), − 13.9 (1B) and − 14.4 (1B).

The reaction between **2** and $CNBu^t$ in CH_2Cl_2, in the presence of Na_2CO_3, was next investigated. The product formed was [1-NH_2-2,2-($CNBu^t$)$_2$-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] (**7**), characterised by the data in Tables 1–3. The IR spectrum showed C≡N absorptions at 2198 and 2182 cm^{-1}. A single-crystal XRD study was carried out. The molecule is shown in Fig. 3 and selected structural parameters are listed in Table 7.

The structure closely resembles that of [1-$NHBu^t$-2,2-($CNBu^t$)$_2$-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$] [9] differing only by replacement of the $NHBu^t$ group in the latter by an NH_2 moiety in **7**. A signal for the NH_2 group, which would be broad, was not observed in the ^1H-NMR spectrum. Evidently **7** is formed by elimination of HCl from **2** with addition of two $CNBu^t$ molecules to the metal center so that the complex has an 18-electron configuration. Despite the presence of the primary NH_2 group, compound **7** appeared to possess low reactivity. Unlike **2** it did not react with acetic anhydride.

Finally it was found that if **2** in CH_2Cl_2 was treated with $B(C_6F_5)_3$ in the presence of Na_2CO_3 a brown microcrystalline product could be isolated. We tentatively formulate this compound as a dimer [{1,2′-μ-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$}$_2$] (**8**) resulting from the deprotonation of **2** by Na_2CO_3 and removal of Cl^- by the boron reagent. The reaction does not proceed in the absence of either Na_2CO_3 or $B(C_6F_5)_3$. Unfortunately, despite repeated attempts, crystals of **8** of sufficient size for an X-ray crystallographic analysis were unobtainable, but microanalytical and NMR data are given in Tables 1–3. Additional evidence for the formulation of **8** was provided by a FAB mass spectrum. The latter showed an envelope in the molecular ion region centered at $m/z = 1023.105$ (2%) ($[M+H]^+$; calc. for $^{12}C_{38}{}^1H_{55}{}^{10}B_4{}^{11}B_{16}{}^{14}N_2{}^{31}P_2{}^{103}Rh_2$, 1023.387) and another set of peaks centered at $m/z = 511.165$ (5%) corresponding to the monomer 1-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$ ($[M/2]^+$; calc. for $^{12}C_{19}{}^1H_{27}{}^{10}B_2{}^{11}B_8{}^{14}N^{31}P^{103}Rh$, 511.195). The proposed structure is akin to that of the dimeric anionic species [2,2′-μ-H-{1,2′-μ-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$}$_2$]$^-$ [7].

4. Conclusion

The results show that complex **1** can be obtained in high yield from [$RhCl(PPh_3)_3$] and 7-NH=CMe_2-*nido*-7-$CB_{10}H_{12}$, and that **1** is a convenient precursor for

Table 7
Selected internuclear distances (Å) and angles (°) for **7**

Bond lengths					
Rh–C(7)	1.991(10)	Rh–C(2)	2.030(8)	Rh–B(2)	2.194(8)
Rh–B(3)	2.214(9)	Rh–B(5)	2.235(10)	Rh–C(1)	2.236(9)
Rh–B(4)	2.243(10)	Rh–P	2.340(2)	C(1)–N(1)	1.421(11)
C(2)–N(2)	1.134(9)	C(7)–N(3)	1.139(11)		
Bond angles					
C(7)–Rh–C(2)	88.7(4)	C(7)–Rh–B(2)	87.0(4)	C(2)–Rh–B(2)	156.3(3)
C(7)–Rh–B(3)	125.6(4)	C(2)–Rh–B(3)	144.6(4)	C(7)–Rh–B(5)	127.4(4)
C(2)–Rh–B(5)	83.2(4)	C(7)–Rh–C(1)	90.6(3)	C(2)–Rh–C(1)	109.9(3)
C(7)–Rh–B(4)	168.8(3)	C(2)–Rh–B(4)	99.6(4)	C(7)–Rh–P	90.7(3)
C(2)–Rh–P	88.9(3)	B(2)–Rh–P	114.5(3)	B(3)–Rh–P	82.8(3)
B(5)–Rh–P	140.6(3)	C(1)–Rh–P	161.2(2)	B(4)–Rh–P	96.8(3)
N(1)–C(1)–B(10)	115.5(8)	N(1)–C(1)–B(6)	115.6(8)	N(1)–C(1)–B(5)	122.3(8)
N(1)–C(1)–B(2)	120.7(8)	N(1)–C(1)–Rh	111.3(6)	N(2)–C(2)–Rh	177.2(8)
N(3)–C(7)–Rh	174.6(9)				

$[1\text{-}NH_3\text{-}2\text{-}Cl\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}RhCB_{10}H_{10}]$ (**2**) via methanolysis under mild conditions. Treatment of **2** with a mild base such as Na_2CO_3 we suggest leads to the formation of an anionic intermediate $[1\text{-}NH_2\text{-}2\text{-}Cl\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}RhCB_{10}H_{10}]^-$. The nitrogen center of the latter then attacks an electrophilic sp^2 carbon center in a carboxylic anhydride or benzoyl bromide to give the corresponding 16-electron amido derivatives **3**–**5**. The amido groups in these products are intramolecularly coordinated to rhodium *via* oxygen. Direct nucleophilic attack by $CNBu^t$ at the rhodium atom of **2** affords the bis(isocyanide) derivative **7**. Both reactions are accompanied by elimination of HCl.

5. Supplementary material

Atomic coordinates, a complete listing of bond lengths and angles, and the thermal parameters for **1**, **4a** and **7** have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 175014, 175015 and 175016. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Street, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Robert A. Welch Foundation for support (Grant AA-1201) and Dr John C. Jeffery, School of Chemistry, Bristol University, UK for access to the Siemens SMART CCD area-detector three-circle diffractometer for the measurements on molecule **1**.

References

[1] D.E. Hyatt, J.L. Little, F.R. Scholer, L.J. Todd, J. Am. Chem. Soc. 89 (1967) 3342.
[2] W.H. Knoth, J. Am. Chem. Soc. 89 (1967) 3342.
[3] R.N. Grimes, in: G. Wilkinson, E.W. Abel, F.G.A. Stone, (Eds.) Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982; Vol. 1, section 5.5. R.N. Grimes, in: Comprehensive Organometallic Chemistry II; E.W. Abel, F.G.A. Stone, G. Wilkinson, (Eds.), Pergamon Press: Oxford, 1995; Vol. 1 (Housecroft, C.E., Ed.), Chapter 9. R.N. Grimes, Coord. Chem. Rev. 200–202 (2000) 773.
[4] V.N. Lebedev, D.F. Mullica, E.L. Sappenfield, F.G.A. Stone, Organometallics 15 (1996) 1669.
[5] V.N. Lebedev, D.F. Mullica, E.L. Sappenfield, F.G.A. Stone, J. Organomet. Chem. 536–537 (1997) 537.
[6] S. Du, J.A. Kautz, T.D. McGrath, F.G.A. Stone, Inorg. Chem. 40 (2001) 6563.
[7] J.A. Walker, C.A. O'Con, L. Zheng, C.B. Knobler, M.F. Hawthorne, J. Chem. Soc. Chem. Commun. (1983) 803.
[8] I.T. Chizhevsky, I.V. Pisareva, P.V. Petrovskii, V.I. Bregadze, F.M. Dolgushin, A.I. Yanovsky, Y.T. Struchkov, M.F. Hawthorne, Inorg. Chem. 35 (1996) 1386.
[9] J.C. Jeffery, V.N. Lebedev, F.G.A. Stone, Inorg. Chem. 35 (1996) 2967.
[10] T. Jelinek, J. Plesek, S. Hermanek, B. Stibr, Collect. Czech. Chem. Commun. 50 (1985) 1376.
[11] J.A. Osborn, G. Wilkinson, Inorg. Synth. 10 (1967) 67.
[12] Siemens X-ray Instruments, Madison, WI, 1997.
[13] SHELXTL version 5.03, Bruker AXS, Madison. WI, 1995.
[14] SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany, 1997.
[15] I.T. Chizhevsky, I.V. Pisareva, P.V. Petrovskii, V.I. Bregadze, A.I. Yanovsky, Y.T. Struchkov, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 32 (1993) 3393.
[16] A. Franken, S. Du, P.A. Jelliss, J.A. Kautz, F.G.A. Stone, Organometallics 20 (2001) 1597.
[17] S. Anderson, D.F. Mullica, E.L. Sappenfield, F.G.A. Stone, Organometallics 15 (1996) 1676.
[18] G. Ferguson, J. Pollock, P.A. McEneaney, D.P. O'Connell, T.R. Spalding, J.F. Gallagher, R. Maciás, J.D. Kennedy, Chem. Commun. (1996) 679.
[19] P.E. Behnken, T.B. Marder, R.T. Baker, C.B. Knobler, M.R. Thompson, M.F. Hawthorne, J. Am. Chem. Soc. 107 (1985) 932.
[20] The United Kingdom Chemical Database Service, D.A. Fletcher, R.F. McMeeking, D.J. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746.
[21] R.T. Baker, M.S. Delaney, R.E. King, C.B. Knobler, J.A. Long, T.B. Marder, T.E. Paxson, R.G. Teller, M.F. Hawthorne, J. Am. Chem. Soc. 106 (1984) 2965.
[22] R.M. Silverstein, F.X. Webster, Spectrometric Identification of Organic Molecules, sixth edn, Wiley, New York, 1998, p. 248.