An air-stable, cationic metallacarborane without a charge-compensated carborane ligand

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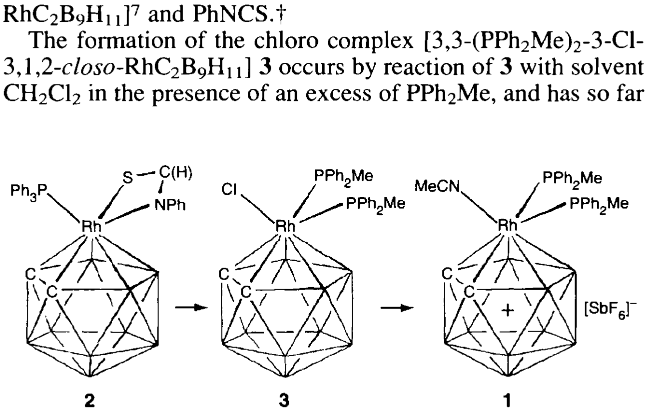
The first air-stable, cationic rhodadicarborane complex, [3-(MeCN)-3,3-(PPh$_2$Me)$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$][SbF$_6$] 1, which does not contain a 'charge-compensated' carborane ligand is synthesised and structurally characterised by X-ray crystallography and spectroscopic techniques (IR and NMR).

Although research into transition-element derivatives of heteroboranes in general and carboranes in particular[1] has been extremely fruitful over the past thirty years, remarkably few cationic compounds have been isolated.[2–4] This is true even for the most common structural type, *i.e.* that based on the twelve-vertex *closo*-MC$_2$B$_9$ cage. Furthermore, essentially all of the cationic species which have been reported have contained 'charge-compensated' ligands,[5] *i.e.* heteroborane ligands with a two-electron substituent (L) such as a phosphine, amine, ether or thioether attached to a boron atom as a B–L unit in place of {B–H}$^-$ so that the boron–ligand site can be regarded as zwitterionic with the positive charge localised at the ligand. Reported charge-compensated ligands have included {9-(SMe$_2$)-7,8-*nido*-C$_2$B$_9$H$_{10}$}$^-$,[4] {10-(py)-7,9-*nido*-C$_2$B$_9$H$_{10}$}$^-$,[5] {9-(PPh$_3$)-7-*nido*-TeB$_{10}$H$_9$}$^-$,[2] and {10-(PPh$_3$)-7,8-*nido*-As$_2$B$_9$H$_8$}$^-$.[3] Apparently, the only reported cationic MC$_2$B$_9$ compound which does not have a charge-compensated ligand is [3-(η^5-C$_5$H$_5$)-3,1,2-*closo*-NiC$_2$B$_9$H$_{11}$]$^+$.[6] However, this compound was generated electrochemically and its isolation and structural characterisation were not reported.

In continuation of our study of cationic metallaheteroboranes[2,3] we now report the synthesis and structural characterisation of a cationic rhodadicarbaborane complex [3-(MeCN)-3,3-(PPh$_2$Me)$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$][SBF$_6$] **1** which does *not* contain any charge-compensating unit on the carborane ligand. The reaction sequence used to synthesise **1** starts from the thioformamido complex [3-{η^2-SC(H)NPh}-3-(PPh$_3$)-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$] **2** and is shown in Scheme 1. Compound **2** is afforded in excellent yield from the microwave-assisted reaction between [3,3-(PPh$_3$)$_2$-3-H-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$][7] and PhNCS.†

The formation of the chloro complex [3,3-(PPh$_2$Me)$_2$-3-Cl-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$] **3** occurs by reaction of **3** with solvent CH$_2$Cl$_2$ in the presence of an excess of PPh$_2$Me, and has so far been most efficient when photo-assisted,[8] the overall yield of **3** from the rhodadicarbaborane reagent [3,3-(PPh$_3$)$_2$-3-H-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$] being 90%.† It seems probable that the conversion of **2** into **3** could progress *via* a complex in which one of the donor atoms of the thioformamido ligand has been displaced by a phosphine ligand and the Rh–{SC(H)NPh} interaction is consequently reduced from η^2 to η^1. We are currently attempting to isolate a species intermediate between compounds **2** and **3**. Note that complexes analogous to **3**, but with the phosphines PPhMe$_2$[7] or PPh$_3$,[7,8] have been prepared previously in excellent yields from the reactions between [3,3-(L)$_2$-3-H-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$] and CH$_2$Cl$_2$ (L = PPhMe$_2$) or CHCl$_3$–aqueous HCl mixtures (L = PPh$_3$).



Scheme 1

The reaction between **3** and Ag[SbF$_6$] in toluene/acetonitrile at room temp. for 12 h afforded a single major product [3-(MeCN)-3,3-(PPh$_2$Me)$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_{11}$][SbF$_6$] **1**.† Recrystallisation from CH$_2$Cl$_2$–MeCN solution gave yellow crystals of **1** in 15% yield. Compounds **1** and **3** were initially characterised with NMR spectroscopy† and subsequently with X-ray crystallography.‡ Both exhibit very similar NMR characteristics and cluster geometries. The cluster NMR shielding patterns of the cationic cluster **1** and the neutral chloride compound **3** are very similar. The ^{11}B chemical shifts for equivalent sites are all within 2 ppm of each other apart from the ^{11}B(8) sites which are *trans* to the MeCN or Cl$^-$ ligands. The difference in ^{11}B(8) shifts is still very small at 3 ppm. The ^{1}H shielding patterns are also very similar indeed, with differences at BH sites all being < 0.17 ppm. The CH(1,2) sites are somewhat more differentially shielded, by 0.3 ppm, perhaps due to the different anisotropies of the immediately adjacent Cl$^-$ and MeCN ligands.

The structure of **1**, Fig. 1, is directly related to **3**, Fig. 2, with the acetonitrile molecule replacing the chlorine atom. The ranges of cage interatomic distances are remarkably similar in **1** and **3**. The Rh–C distances in **1** are 2.209(4) and 2.196(4) Å compared with 2.205(3) and 2.208(3) Å in **3**. The C(1)–C(2) distance in **1** is 1.631(5) Å compared with 1.618(5) Å in **3**. The ranges of C–B and B–B distances in **1** are 1.685(6)–1.718(6) and 1.750(7)–1.831(6) Å respectively which are very similar to those in **3**. The three Rh–B distances in **1**, 2.236(4), 2.242(4) and 2.246(4) Å, fall within the narrow range of Rh–B distances in **3**, *i.e.* 2.223(4)–2.254(4) Å. The *exo*-cage Rh–P distances in both **1** and **3** are significantly different at Rh–P(1) 2.3771(11) and Rh–P(2) 2.3498(10) Å for **1**, and 2.3500(9) and 2.3414(9) Å for **3**, respectively. The Rh–Cl distance is 2.4205(8) Å in **3**. In the rhodium–acetonitrile region of **1**, the Rh–N distance of 2.108(3) Å is slightly shorter than the value of 2.139 Å which has been calculated as the mean for Rh–N$_{\text{(nitrile)}}$ distances in general. The N(1)–C(3) and C(3)–C(4) distances, 1.130(4) and 1.453(4) Å respectively, are typical of N≡C and C–C bonds in acetonitrile complexes.[9]

In conclusion, we have demonstrated that it is possible to isolate stable cationic metallaheteroboranes which do not contain charge-compensated ligands. The geometrical cage

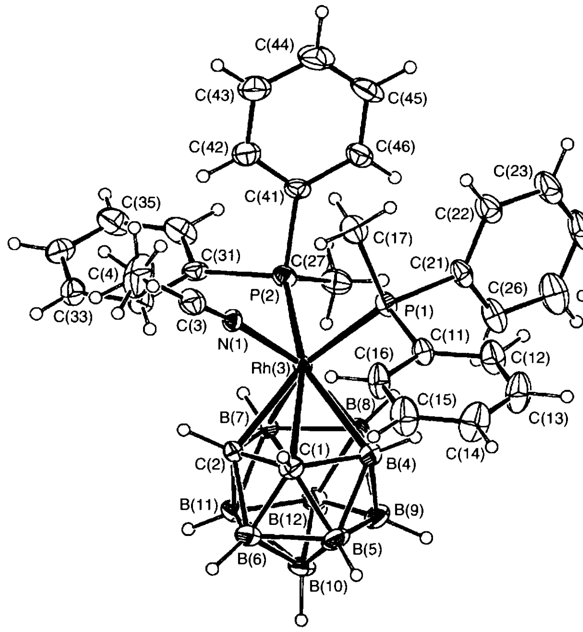


Fig. 1 An ORTEP view of the cation in **1** with the atom numbering scheme. For clarity, the non-cluster carbon and hydrogen atoms are drawn as small spheres of an arbitrary size. Selected interatomic distances (Å) and angles (°): Rh(3)–N(1) 2.108(3), Rh(3)–C(1) 2.209(4), Rh(3)–C(2) 2.196(4), Rh(3)–B(4) 2.236(4), Rh(3)–B(7) 2.246(4), Rh(3)–B(8) 2.242(4), Rh(3)–P(1) 2.3771(11), Rh(3)–P(2) 2.3498(10), C(1)–C(2) 1.631(5), N(1)–C(3) 1.130(4), C(3)–C(4) 1.453(4), C–B distances range from C(2)–B(7) 1.685(6) to C(1)–B(6) 1.718(6) and B–B distances from B(6)–B(11) 1.750(7) to B(7)–B(8) 1.831(6); C(3)–N(1)–Rh(3) 174.1(3), N(1)–C(3)–C(4) 178.4(5), N(1)–Rh(3)–P(1) 85.62(9), N(1)–Rh(3)–P(2) 90.43(9), P(1)–Rh(3)–P(2) 94.27(4), N(1)–Rh(3)–C(1) 93.94(13), N(1)–Rh(3)–C(2) 89.56(13).

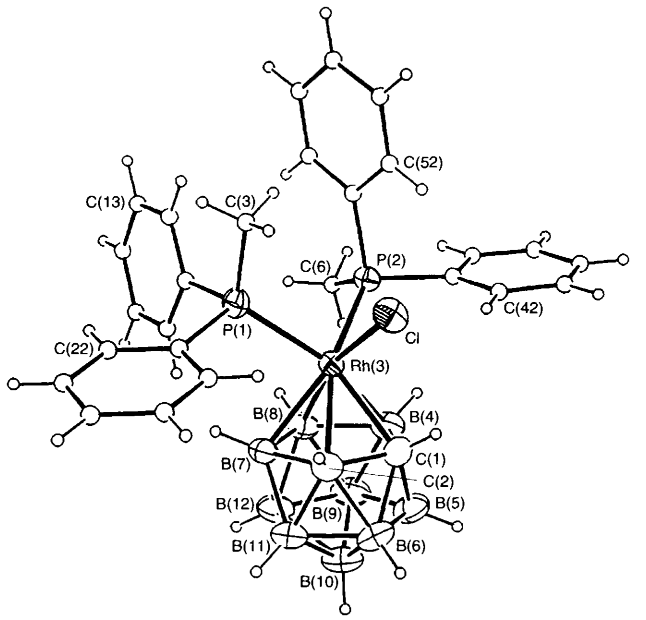


Fig. 2 An ORTEP view of **3** with the atom numbering scheme. For clarity, the non-cluster carbon and hydrogen atoms are drawn as small spheres of an arbitrary size. Selected interatomic distances (Å) and angles (°): Rh(3)–Cl 2.4205(8), Rh(3)–C(1) 2.208(3), Rh(3)–C(2) 2.205(3), Rh(3)–B(4) 2.254(4), Rh(3)–B(7) 2.223(4), Rh(3)–B(8) 2.244(4), Rh(3)–P(1) 2.3500(9), Rh(3)–P(2) 2.3414(9), C(1)–C(2) 1.618(5), C–B distances range from C(1)–B(5) 1.690(6) to C(1)–B(6) 1.733(6) and B–B distances from B(6)–B(11) 1.748(7) to B(4)–B(8) 1.825(6); Cl–Rh(3)–P(1) 87.67(3), Cl–Rh(3)–P(2) 92.00(3), P(1)–Rh(3)–P(2) 92.68(3), Cl–Rh(3)–C(1) 87.03(9), Cl–Rh(3)–C(2) 91.90(9).

structure of the cation in [3-(MeCN)-3,3-$(PPh_2Me)_3$-3,1,2-*closo*-$RhC_2B_9H_{11}$][SbF_6] **1** is very similar to that in the neutral compound [3,3-$(PPh_2Me)_2$-3-Cl-3,1,2-*closo*-$RhC_2B_9H_{11}$] **3** and the similarity of the cluster NMR shielding patterns are indicative of closely similar electronic structures with no significant differences in localisation of charge density. Our results therefore concur with a description of the cage bonding which suggests delocalisation of the positive charge over all the cage atoms rather than localisation on any particular atom or unit. We are presently investigating the reaction chemistry of **1** and analogous compounds with other eleven-atom heteroborane ligands.

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Footnotes

† [3-{η^2-SC(H)NPh}-3-(PPh_3)-*closo*-3,1,2-$RhC_2B_9H_{11}$] **2**. A mixture of [3,3-$(PPh_3)_2$-3-H-*closo*-3,1,2-$RhC_2B_9H_{11}$][7] (0.32 g, 0.427 mmol), CH_2Cl_2 (20 cm^3) and PhNCS (0.058 g, 0.427 mmol) was introduced into a glass microwave reaction vessel.[10] The mixture was subjected to microwave irradiation (650 W) for 5 min. The maximum pressure obtained during the reaction was *ca.* 10 atm. The resultant orange solution was concentrated under reduced pressure and subjected to preparative TLC (CH_2Cl_2–hexane, 3 : 2). The single product, R_f = 0.80, was recrystallised from CH_2Cl_2 to afford orange crystals of [3-{η^2-SC(H)NPh}-3-(PPh_3)-3,1,2-*closo*-$RhC_2B_9H_{11}$] **2** (0.247 g, 95.5%) IR: ν_{max}/cm^{-1} 2590m(sh), 2560vs(sh), 2540vs, 2530vs(sh) (BH). ^{11}B and ^1H NMR data for **2** ($CDCl_3$, 294–298 K): {ordered as: assignment $\delta(^{11}B)$ [δ^1H]} B(10) +7.4 [+3.80], B(8) +4.1 [+2.82], B(4,7) −4.8 [+2.64] and −6.9 [+2.39], B(9,12) −3.4 [+2.29] and −8.0 [+2.00], B(5,11) −12.1 [+2.01] and −15.6 [+1.78], B(6) −23.1 [+1.67]; additionally, $\delta(^1H)$ CH(1,2) +4.12 and +4.32; SC(*H*)NPh +8.84; and $\delta(^{13}C)$ *S*C(H)NPh +180.9; and (at 219 K) $\delta(^{31}P)$, ppm relative to −40.480730 MHz (nominally 85% aq. H_3PO_4), +42.7, $^1J(^{103}Rh–^{31}P)$ 154 Hz.

[3,3-$(PMePh_2)_2$-3-Cl-3,1,2-*closo*-$RhC_2B_9H_{11}$] **3**. To a solution of [3-{η^2-SC(H)NPh}-3-(PPh_3)-*closo*-3,1,2-$RhC_2B_9H_{11}$] **2** (0.050 g, 0.079 mmol) in CH_2Cl_2 (20 cm^3) was added $PMePh_2$ (0.158 g, 0.79 mmol). The mixture was heated at reflux for 48 h while being irradiated with a 60 W tungsten filament lamp placed 8 cm from the reaction flask. The orange solution produced was concentrated under reduced pressure and subjected to preparative TLC (CH_2Cl_2–hexane, 3 : 2). A single compound was extracted into CH_2Cl_2 and recrystallised from CH_2Cl_2–hexane (3 : 2) as orange block crystals of [3,3-$(PMePh_2)_2$-3-Cl-3,1,2-*closo*-$RhC_2B_9H_{11}$] **3** (0.051 g, 96.2%). IR: ν_{max}/cm^{-1} 2604s, 2585m, 2571s, 2552vs, 2534m(sh), 2524vs (BH). ^{11}B and ^1H NMR data for **3** ($CDCl_3$, 294–298 K): {ordered as: assignment $\delta(^{11}B)$ [δ^1H]} B(8) +8.8 [+3.74], B(10) −0.4 [+1.84], B(4,7) −2.6 [+2.83], B(9,12) −4.9 [+2.17], B(5,11) −17.2 [+1.49], B(6) −17.7 [+2.05]; $\delta(^1H)$ CH(1,2) +3.64; $\delta(^1H)$PMe +1.62, $N(^{31}P–^1H)$ 10.5 Hz (*cisoid* $[AX_3]_2$ coupling pattern). Additionally (at 219 K) $\delta(^{31}P)$ +19.1, $^1J(^{103}Rh–^{31}P)$ 129 Hz.

[3-(MeCN)-3,3-$(PMePh_2)_2$-*closo*-3,1,2-$RhC_2B_9H_{11}$][SbF_6] **1**. A suspension of Ag[SbF_6] (0.128 g, 0.372 mmol) in toluene (4 cm^3) was added to a solution of [3,3-$(PMePh_2)$-3-Cl-3,1,2-*closo*-$RhC_2B_9H_{11}$] **3** (0.050 g, 0.074 mmol) in MeCN (10 cm^3). The orange solution was stirred at room temp. for 12 h. The solvent was removed under reduced pressure. Preparative TLC (CH_2Cl_2–hexane–MeCN, 9 : 9 : 2) produced one major component, R_f = 0.1. Recrystallisation from CH_2Cl_2–MeCN (4 : 1) afforded yellow crystals of [3-(MeCN)-3,3-$(PMePh_2)_2$-*closo*-3,1,2-$RhC_2B_9H_{11}$][SbF_6] **1** (0.010 g, 14.8%). IR: ν_{max}/cm^{-1} 2620vs(sh)(BH), 2607w(sh)(BH), 2592s(BH), 2575vs(BH), 2565s(sh)(BH), 2544m(BH), 2308vs(CN), 2280vs(CN). ^{11}B and ^1H NMR data for **1** (CD_2Cl_2, 294–298 K) {ordered as: assignment $\delta(^{11}B)$ [δ^1H]} B(10) +11.8 [+3.87], B(8) +0.5 [+1.91], B(9,12), −3.3 [+2.25], B(4,7) *ca.* −3.3 [+2.81], B(5,11) −15.3 [+1.66], B(6) −18.0 [+2.06]; additionally, $\delta(^1H)$CH(1,2) +3.06, (CH_3CN) +2.61, (PMe) +1.63, $N(^{31}P–^1H)$ 10.1 ±0.5 Hz (*cisoid* $[AX_3]_2$ coupling pattern). $\delta(^{31}P)$ (CD_2Cl_2, 233 K) +22.3, $^1J(^{103}Rh–^{31}P)$ 124.5 Hz.

‡ *Crystal data* for **1**: $C_{30}H_{40}B_9F_6NP_2RhSb$, M = 912.52, monoclinic, $P2_1/n$, a = 12.959(2), b = 15.885(2), c = 18.694(2) Å, β = 98.57(2)°, U = 3805.3(10) $Å^3$, Z = 4, D_c = 1.593 g cm^{-3}, λ(Mo-Kα) = 0.7093 Å, μ(Mo-Kα) = 1.281 mm^{-1}, $F(000)$ = 1808, T = 294 K, R = 0.0354, R_w (SHELXL, F^2) = 0.0730 for 5102 observed reflections.

For **3**: $C_{28}H_{37}B_9ClP_2Rh$, M = 671.19, monoclinic, $P2_1/n$, a = 10.6861(5), b = 16.1880(12), c = 18.8621(10) Å, β = 99.81(4)°, U = 3215.1(3) Å^3, Z = 4, D_c = 1.39 g cm^{-3}, λ(Mo-Kα) = 0.7093 Å, μ(Mo-Kα) = 7.0 mm^{-1}, F(000) = 1368, T = 294 K, R = 0.031, R_w (NRCVAX, F) = 0.034 for 4450 observed reflections.

Structure solution of **1** and **3**: For both structures, data were collected using an Enraf-Nonius CAD4 diffractometer to a maximum theta of 27° for **1** and to 30° for **3**, using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz, polarization and absorption effects. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations using the NRCVAX[11] and SHELXL[12] programs for **1** and NRCVAX for **3** on a Silicon Graphics 4D-35 work station. For **1** and **3** all H atoms were visible in difference maps and were allowed for as riding atoms. The acetonitrile H atoms in **1** were disordered and were allowed for by 0.5 occupancy sites. Diagrams were prepared with the aid of ORTEP[13] and PLATON.[14] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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