

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-(PPh₂Me)₂-3,1,2-closo-RhC₂B₉H₁₁][SbF₆] **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 particular¹ 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*-MC₂B₉ 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-(SMe₂)-7,8-*nido*-C₂B₉H₁₀}[–],⁴ {10-(py)-7,9-*nido*-C₂B₉H₁₀}[–],⁵ {9-(PPh₃)-7-*nido*-TeB₁₀H₉}[–],² and {10-(PPh₃)-7,8-*nido*-As₂B₉H₈}[–].³ Apparently, the only reported cationic MC₂B₉ compound which does not have a charge-compensated ligand is [3-(η⁵-C₅H₅)-3,1,2-*closo*-NiC₂B₉H₁₁]⁺.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 rhodadicarborane complex [3-(MeCN)-3,3-(PPh₂Me)₂-3,1,2-*closo*-RhC₂B₉H₁₁][SbF₆] **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-{η²-SC(H)NPh}-3-(PPh₃)-3,1,2-*closo*-RhC₂B₉H₁₁] **2** and is shown in Scheme 1. Compound **2** is afforded in excellent yield from the microwave-assisted reaction between [3,3-(PPh₃)₂-3-H-3,1,2-*closo*-RhC₂B₉H₁₁]⁷ and PhNCS.[†]

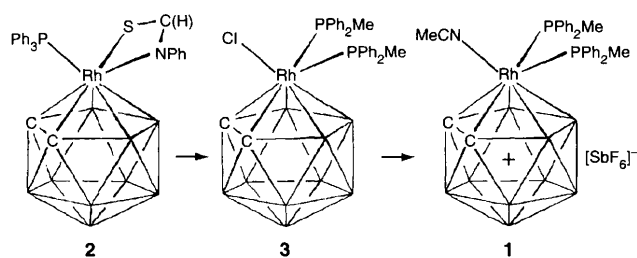
The formation of the chloro complex [3,3-(PPh₂Me)₂-3-Cl-3,1,2-*closo*-RhC₂B₉H₁₁] **3** occurs by reaction of **3** with solvent CH₂Cl₂ in the presence of an excess of PPh₂Me, and has so far

been most efficient when photo-assisted,⁸ the overall yield of **3** from the rhodadicarborane reagent [3,3-(PPh₃)₂-3-H-3,1,2-*closo*-RhC₂B₉H₁₁] 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 η² to η¹. We are currently attempting to isolate a species intermediate between compounds **2** and **3**. Note that complexes analogous to **3**, but with the phosphines PPhMe₂ or PPh₃,^{7,8} have been prepared previously in excellent yields from the reactions between [3,3-(L)₂-3-H-3,1,2-*closo*-RhC₂B₉H₁₁] and CH₂Cl₂ (L = PPhMe₂) or CHCl₃–aqueous HCl mixtures (L = PPh₃).

The reaction between **3** and Ag[SbF₆] in toluene/acetonitrile at room temp. for 12 h afforded a single major product [3-(MeCN)-3,3-(PPh₂Me)₂-3,1,2-*closo*-RhC₂B₉H₁₁][SbF₆] **1**.[†] Recrystallisation from CH₂Cl₂–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 ¹¹B chemical shifts for equivalent sites are all within 2 ppm of each other apart from the ¹¹B(8) sites which are *trans* to the MeCN or Cl[–] ligands. The difference in ¹¹B(8) shifts is still very small at 3 ppm. The ¹H 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_(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



Scheme 1

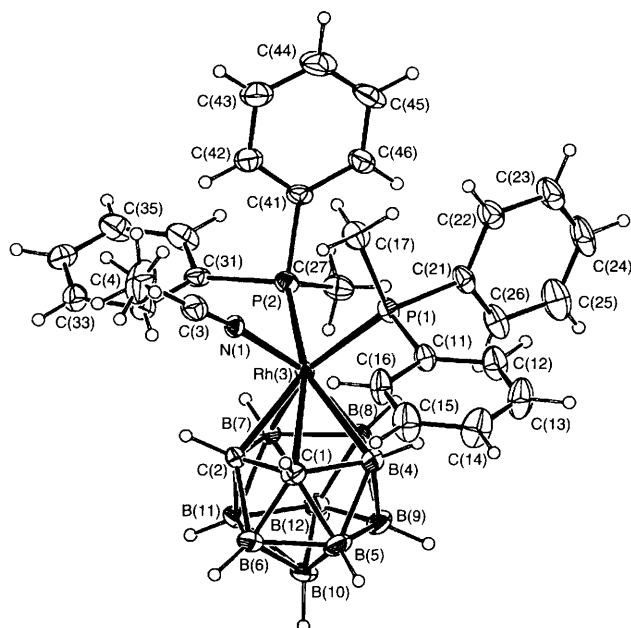


Fig. 1 An ORTEP view of the cation in **1** with the atom numbering scheme. For clarity, the non-cluster carbon and hydrogen atoms are drawn as small spheres of an arbitrary size. Selected interatomic distances (Å) and angles (°): Rh(3)–N(1) 2.108(3), Rh(3)–C(1) 2.209(4), Rh(3)–C(2) 2.196(4), Rh(3)–B(4) 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).

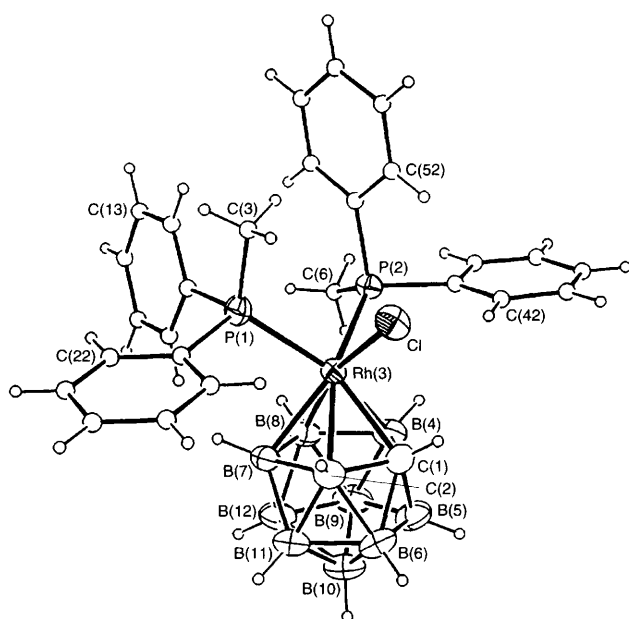


Fig. 2 An ORTEP view of **3** with the atom numbering scheme. For clarity, the non-cluster carbon and hydrogen atoms are drawn as small spheres of an arbitrary size. Selected interatomic distances (Å) and angles (°): Rh(3)–Cl 2.4205(8), Rh(3)–C(1) 2.208(3), Rh(3)–C(2) 2.205(3), Rh(3)–B(4) 2.254(4), Rh(3)–B(7) 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-(PPh₂Me)₃-3,1,2-*closo*-RhC₂B₉H₁₁][SbF₆] **1** is very similar to that in the neutral compound [3,3-(PPh₂Me)₂-3-Cl-3,1,2-*closo*-RhC₂B₉H₁₁] **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-{η²-SC(H)NPh}-3-(PPh₃)-*closo*-3,1,2-RhC₂B₉H₁₁] **2**. A mixture of [3,3-(PPh₃)₂-3-H-*closo*-3,1,2-RhC₂B₉H₁₁]⁷ (0.32 g, 0.427 mmol), CH₂Cl₂ (20 cm³) 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 (CH₂Cl₂–hexane, 3:2). The single product, *R_f* = 0.80, was recrystallised from CH₂Cl₂ to afford orange crystals of [3-{η²-SC(H)NPh}-3-(PPh₃)-3,1,2-*closo*-RhC₂B₉H₁₁] **2** (0.247 g, 95.5%). IR: ν_{max}/cm^{−1} 2590m(sh), 2560vs(sh), 2540vs, 2530vs(sh) (BH). ¹¹B and ¹H NMR data for **2** (CDCl₃, 294–298 K): {ordered as: assignment δ(¹¹B) [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, δ(¹H) CH(1,2) +4.12 and +4.32; SC(H)NPh +8.84; and δ(¹³C) SC(H)NPh +180.9; and (at 219 K) δ(³¹P), ppm relative to −40.480730 MHz (nominally 85% aq. H₃PO₄), +42.7, ¹J(¹⁰³Rh–³¹P) 154 Hz.

[3,3-(PMePh₂)₂-3-Cl-3,1,2-*closo*-RhC₂B₉H₁₁] **3**. To a solution of [3-{η²-SC(H)NPh}-3-(PPh₃)-*closo*-3,1,2-RhC₂B₉H₁₁] **2** (0.050 g, 0.079 mmol) in CH₂Cl₂ (20 cm³) was added PMePh₂ (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 (CH₂Cl₂–hexane, 3:2). A single compound was extracted into CH₂Cl₂ and recrystallised from CH₂Cl₂–hexane (3:2) as orange block crystals of [3,3-(PMePh₂)₂-3-Cl-3,1,2-*closo*-RhC₂B₉H₁₁] **3** (0.051 g, 96.2%). IR: ν_{max}/cm^{−1} 2604s, 2585m, 2571s, 2552vs, 2534m(sh), 2524vs (BH). ¹¹B and ¹H NMR data for **3** (CDCl₃, 294–298 K): {ordered as: assignment δ(¹¹B) [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]; δ(¹H) CH(1,2) +3.64; δ(¹H)PMe +1.62, *N*(³¹P–¹H) 10.5 Hz (*cisoid* [AX₃]₂ coupling pattern). Additionally (at 219 K) δ(³¹P) +19.1, ¹J(¹⁰³Rh–³¹P) 129 Hz.

[3-(MeCN)-3,3-(PMePh₂)₂-*closo*-3,1,2-RhC₂B₉H₁₁][SbF₆] **1**. A suspension of Ag[SbF₆] (0.128 g, 0.372 mmol) in toluene (4 cm³) was added to a solution of [3,3-(PMePh₂)₂-3-Cl-3,1,2-*closo*-RhC₂B₉H₁₁] **3** (0.050 g, 0.074 mmol) in MeCN (10 cm³). The orange solution was stirred at room temp. for 12 h. The solvent was removed under reduced pressure. Preparative TLC (CH₂Cl₂–hexane–MeCN, 9:9:2) produced one major component, *R_f* = 0.1. Recrystallisation from CH₂Cl₂–MeCN (4:1) afforded yellow crystals of [3-(MeCN)-3,3-(PMePh₂)₂-*closo*-3,1,2-RhC₂B₉H₁₁][SbF₆] **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). ¹¹B and ¹H NMR data for **1** (CD₂Cl₂, 294–298 K) {ordered as: assignment δ(¹¹B) [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, δ(¹H)CH(1,2) +3.06, (CH₃CN) +2.61, (PMe) +1.63, *N*(³¹P–¹H) 10.1 ± 0.5 Hz (*cisoid* [AX₃]₂ coupling pattern). δ(³¹P) (CD₂Cl₂, 233 K) +22.3, ¹J(¹⁰³Rh–³¹P) 124.5 Hz.

‡ Crystal data for **1**: C₃₀H₄₀B₉F₆NP₂RhSb, *M* = 912.52, monoclinic, *P*2₁/*n*, *a* = 12.959(2), *b* = 15.885(2), *c* = 18.694(2) Å, β = 98.57(2)°, *U* = 3805.3(10) Å³, *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, $\beta = 99.81(4)^\circ$, $U = 3215.1(3)$ Å³, $Z = 4$, $D_c = 1.39$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.7093$ Å, $\mu(\text{Mo-K}\alpha) = 7.0$ 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-K α 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 NRCVAX¹¹ and SHELXL¹² 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 ORTEP¹³ 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.

References

- 1 M. F. Hawthorne, *J. Organomet. Chem.*, 1975, **100**, 97; R. N. Grimes, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 1.
- 2 J. P. Sheehan, T. R. Spalding, G. Ferguson, J. F. Gallagher, B. Kaitner and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1993, 35; G. Ferguson, J. F. Gallagher, J. P. Sheehan, T. R. Spalding, J. D. Kennedy and R. Macías, *J. Chem. Soc., Dalton Trans.*, 1993, 3147.
- 3 G. Ferguson, Li Yiwei, T. R. Spalding and J. C. Patterson, *Acta Crystallogr. Sect. C*, 1995, **51**, 1498.
- 4 N. L. Douek and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1993, 1917.
- 5 H. C. Kang, S. S. Lee, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1991, **30**, 2024.
- 6 R. J. Wilson, L. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1969, **91**, 758.
- 7 R. T. Baker, M. S. Delaney, R. E. King, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxson, R. G. Teller and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2965.
- 8 A. R. Siedle, *J. Organomet. Chem.*, 1975, **90**, 249.
- 9 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, in *Structure Correlation*, ed. H.-B. Burgi and J. D. Dunitz, VCH, Weinheim, 1994, vol. 2, appendix A.
- 10 D. R. Baghurst, R. C. B. Copley, H. Fleischer, D. M. P. Mingos, G. O. Kyd, L. J. Yellowlees, A. J. Welch, T. R. Spalding and D. O'Connell, *J. Organomet. Chem.*, 1993, **447**, C14.
- 11 E. J. Gabe, Y. LePage, J. P. Charland, F. J. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.
- 12 G. M. Sheldrick, SHELXL, a program for refinement of crystal structures, University of Göttingen, 1993.
- 13 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.
- 14 A. L. Spek, Molecular Graphics program, University of Utrecht, 1994.

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