Synthesis and Molecular Structure of [3-(PPh_3)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$], a Versatile Metallocarbaborane Reagent

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Summary The action of nitric acid or NO_2–N_2O_4 mixture on [3,3-(PPh_3)$_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] affords the nitratorhodacarbaborane [3-(PPh_3)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$] (**1**) whose structure has been determined by *X*-ray crystallography; the latter species has been shown to be a useful precursor in the synthesis of other rhodacarbaborane derivatives.

IN continuation of our studies of the chemical properties of metallocarbaborane complexes[1–4] we have found that treatment of [3,3-(PPh_3)$_2$-3-H-3,1,2-$RhC_2B_9H_{11}$][1] with excess of nitric acid in dichloromethane or NO_2–N_2O_4 in benzene, at room temperature, affords an air-stable red complex (**1**) isolated in good yield (*ca.* 70%) by column chromatography (silica gel–CH_2Cl_2) and crystallization.

The i.r. spectrum of (**1**), as a Nujol mull, showed absorptions characteristic of terminal B–H bonds and co-ordinated triphenylphosphine. The $^{31}P\{^1H\}$ n.m.r. spectrum† of (**1**) in $CDCl_3$ showed a doublet centred at +36·1 p.p.m., $J_{\text{Rh–P}}$ 168·5 Hz. The $^{11}B\{^1H\}$ n.m.r. spectrum,‡ also in $CDCl_3$, showed resonances at −25·7, −9·2, −3·1, and +11·8 p.p.m. of relative intensities 1 : 2 : 4 : 2. Also no signal attributable to a Rh–H group could be detected in the ^1H n.m.r. spectrum of (**1**).

Microanalytical data for crystalline (**1**) proved inconclusive apparently because of solvent loss; however the presence of Rh, N, P, and B in the ratio 1 : 1 : 1 : 9 was clearly indicated. In a further attempt to elucidate the nature of (**1**) we noted that (**1**) reacts with PPh_3 and either H_2 or hydrochloric acid in tetrahydrofuran (THF) solution to generate quantitatively [3,3-(PPh_3)$_2$-3-X-3,1,2-$RhC_2B_9H_{11}$] (X = H[1] or Cl,[5] respectively). Further, it has been shown that transition metal nitrato complexes can be obtained by the action of nitric acid on platinum-metal phosphine complexes.[6] Accordingly we tentatively formulated (**1**) as [3-(PPh_3)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$] in which a *closo*-rhodacarbaborane cage and a bidentate nitrato ligand acting as a three-electron donor towards rhodium are present. This formulation was subsequently confirmed by an *X*-ray crystallographic study.

Crystal data: (PPh_3)$NO_3RhC_2B_9H_{11}\cdot 3CH_2Cl_2$, $M = 814{\cdot}4$, triclinic, space group $P1$, $a = 12{\cdot}592(5)$, $b = 16{\cdot}382(8)$, $c = 17{\cdot}059(6)$ Å, $\alpha = 75{\cdot}74(4)$, $\beta = 105{\cdot}34(3)$, $\gamma = 120{\cdot}05(3)^\circ$, $Z = 2$, μ(Mo-K_α) = 7·29 cm^{-1}. Data were collected on a Picker FACS-I four circle diffractometer at room temperature with the crystal sealed in a thin-walled capillary to prevent solvent loss. The structure was solved by standard Patterson and Fourier techniques. Severe disorder in the solvent molecules has prevented a satisfactory refinement of the structure and at present the agreement factor stands at 0·123 (3497 reflections).§

The molecule is illustrated in the Figure along with some pertinent bond distances and angles. As postulated the complex consists of a rhodium atom bonded to a $C_2B_9H_{11}{}^{2-}$

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† All ^{31}P n.m.r. spectra are with reference to external D_3PO_4.

‡ All ^{11}B n.m.r. spectra are with reference to external $BF_3\cdot OEt_2$.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

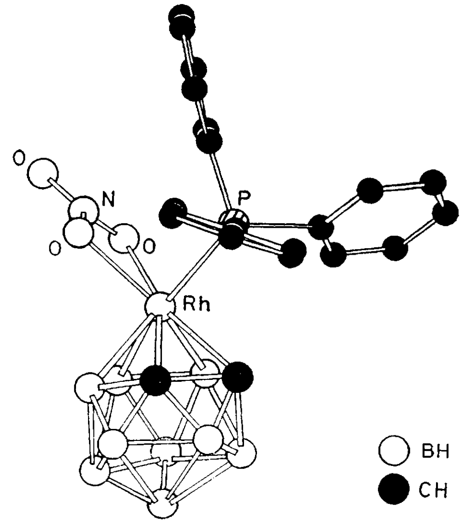

FIGURE. A molecular plot of (**1**). Some distances (averaged from two unique molecules) are: Rh–O 2·20(1), Rh–P 2·38(1), N–O 1·22(1), Rh–C 2·14(2), Rh–B 2·14(3), C–C 1·88(7), C–B 1·80(2), and B–B 1·82(2) Å.

anion, triphenylphosphine, and nitrato ligands with the *closo*-RhC$_2$B$_9$H$_{11}$ fragment in its usual distorted icosahedral geometry. The nitrato group is bound in an apparently symmetrically bidentate fashion with an average Rh–O bond length of 2·20(1) Å. This value is 0·1 Å larger than various Rh$^{\text{III}}$–O bonds in complexes containing carbonato or acetylacetonato ligands[7] but does compare favourably with Rh$^{\text{III}}$–O distances in complexes with weakly bound water molecules [2·24(1) and 2·28(1) Å].[8] The only metallocarbaborane with a metal–oxygen bond is [3,3-(PPh$_3$)$_2$-3-(HSO$_4$)-3,1,2-RhC$_2$B$_9$H$_{11}$] with an Rh–O distance of 2·245(8) Å.[9]

[3-(PPh$_3$)-3,3-(NO$_3$)-3,1,2-RhC$_2$B$_9$H$_{11}$ (**1**) has proved to be an extremely useful precursor in the synthesis of previously inaccessible rhodacarbaborane derivatives. For example (**1**) reacts with CO gas and hydrochloric acid in THF at room temperature to afford, in 85% yield, air-stable [3-(PPh$_3$)-3-(CO)-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$] (**2**) characterized by elemental analysis, and i.r. and n.m.r. spectroscopy.¶ Previous attempts in this laboratory to prepare (**2**) by direct reaction of CO with the previously documented [3,3-(PPh$_3$)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$][5] have failed.

Complex (**1**) also reacts with PPh$_3$ in diethyl ether at room temperature to give, in 81% yield, orange [3,3-(PPh$_3$)$_2$-3-(NO$_3$)-3,1,2-RhC$_2$B$_9$H$_{11}$] (**3**) characterized by elemental analysis** and i.r. and n.m.r. spectroscopy. In particular the ^{31}P{^{1}H} n.m.r. spectrum of (**3**) at room temperature in CDCl$_3$ shows, in addition to a doublet centred at +28·0 p.p.m. ($J_{\text{Rh-P}}$ 133·5 Hz) attributed to (**3**), resonances characteristic of unco-ordinated triphenylphosphine and complex (**1**). Thus (**3**) apparently exhibits behaviour in solution similar to that reported for [3,3-(PPh$_3$)$_2$-3-(HSO$_4$)-3,1,2-RhC$_2$B$_9$H$_{11}$].[9]

Finally we note that (**2**) reacts with PPh$_3$ in THF at room temperature to afford [3,3-(PPh$_3$)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$][5] in 81% yield and that (**3**) reacts with either H$_2$ or hydrochloric acid, also in THF at room temperature, to give [3,3-(PPh$_3$)$_2$-3-X-3,1,2-RhC$_2$B$_9$H$_{11}$] (X = H[1] in 79% yield, or X = Cl[5] in 90% yield, respectively).

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¶ Satisfactory analytical data were obtained for (**2**). Its i.r. spectrum, as a Nujol mull, showed ν(CO) at *ca.* 2062 cm^{-1}, and its ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ showed a doublet centred at +39·6 p.p.m, $J_{\text{Rh-P}}$ = 107·4 Hz.

** Satisfactory analytical data were obtained for (**3**).

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