Metallocarbaboranes in Catalysis. *X*-Ray Crystal and Molecular Structure of $3\text{-PPh}_3\text{-3-CO-4-C}_5\text{H}_5\text{N-3,1,2-RhC}_2\text{B}_9\text{H}_{10}$

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Summary The preparation of two rhodium carbaborane complexes which have catalytic activity, $3,3\text{-(PPh}_3)_2\text{-4-C}_5\text{H}_5\text{N-3,1,2-RhC}_2\text{B}_9\text{H}_{10}$ and its carbonyl derivative $3\text{-PPh}_3\text{-3-CO-4-C}_5\text{H}_5\text{N-3,1,2-RhC}_2\text{B}_9\text{H}_{10}$, is described; the *X*-ray crystal structure of the latter compound was also determined.

THE utility of rhodium carbaborane complexes as catalysts for industrially important processes has been demonstrated.[1–3] As part of our studies[1–5] we recently prepared $3,3\text{-(PPh}_3)_2\text{-4-C}_5\text{H}_5\text{N-3,1,2-RhC}_2\text{B}_9\text{H}_{10}$ (**1**) and its carbonyl derivative $3\text{-PPh}_3\text{-3-CO-4-C}_5\text{H}_5\text{N-3,1,2-RhC}_2\text{B}_9\text{H}_{10}$ (**2**) in order to investigate their catalytic activity. Structural parameters for either molecule are of interest owing to the paucity of data on formal Rh^{I} carbaboranes, and the renewed interest in the orientation of ML_2 fragments of d^8 metals with respect to the open face of a carbaborane anion[6–10] in metallocarbaborane complexes. We therefore undertook the structure determination of (**2**) by single crystal *X*-ray diffraction.

The parent complex (**1**) was prepared as follows. NaH and $9\text{-C}_5\text{H}_5\text{N-7,8-C}_2\text{B}_9\text{H}_{11}$[11] were stirred in tetrahydrofuran (THF) until H_2 ceased to be evolved. This solution was then immediately introduced to a THF solution of $\text{RhCl(PPh}_3)_3$ and was heated at reflux for 1 h in an inert atmosphere. The product was isolated as blue-black crystals from ethanol–THF. An i.r. spectrum of the complex showed bands due to co-ordinated phosphine and carbaborane fragments. The carbonyl adduct (**2**) is rapidly formed in high yield by passing CO through a THF solution of (**1**).

Crystal data: $\text{C}_{26}\text{H}_{30}\text{B}_9\text{NOPRh}$ (**2**), $M = 603{\cdot}7$, triclinic, space group $P\bar{1}$, $a = 10{\cdot}743(4)$, $b = 10{\cdot}339(4)$, $c = 14{\cdot}210(5)$ Å, $\alpha = 96{\cdot}11(2)$, $\beta = 79{\cdot}11(2)$, $\gamma = 115{\cdot}25(2)°$, $Z = 2$, μ (Mo-K_α) $= 7{\cdot}56\ \text{cm}^{-1}$. Data were collected on a Picker FACS-I four-circle diffractometer at −154 °C and the structure was solved by standard Patterson and Fourier techniques. Full matrix least squares refinement of all atomic positions converged to an *R* factor of 0·037 (2874 reflections).†

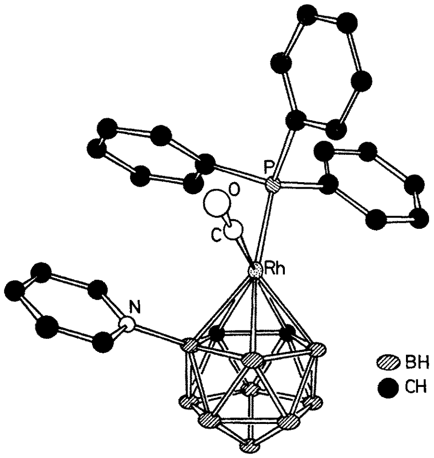

FIGURE A molecular plot of (**2**). Some pertinent distances are Rh–P 2·284(2), Rh–C(O), 1·795(6), Rh–C(cage)$_{\text{av}}$ 2·298(5), Rh–B$_{\text{av}}$ 2·263(6), B–B$_{\text{av}}$ 1·783(5), C–B$_{\text{av}}$ 1·706(22), Rh · · · N 3·144(8), and B–N 1·545(7) Å.

The structure of the molecule is illustrated in the Figure along with some pertinent interatomic distances. The most noteworthy feature of the structure is the configuration of the $\text{Rh(CO)(PPh}_3)$ fragment with respect to the carbaborane monoanion. A comparison of bond distances of the rhodium atom from the C_2B_3 face [Rh–C(av.) − Rh–B(av.) = 0·031 Å] and the small value of the slip parameter[7] ($\Delta = 0{\cdot}02$ Å) enables us to classify this structure as *closo*. Additionally the C–C bond length [1·630(7) Å]

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† 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.

TABLE

Complex	L_2 Ligand(s)	Δ/Å
3-[$C_2H_4(NMe_2)_2$]-3,1,2-$PdC_2B_9H_{11}$	$C_2H_4(NMe_2)_2$	0·52
3,3-$(PMe_3)_2$-3,1,2-$PdC_2B_9H_{11}$	$(PMe_3)_2$	0·26
(**2**)	(CO)(PPh_3)	0·02

is consistent with the non-slipped nature of this metallocarbaborane.[10] This result is in agreement with other work which has illustrated that in addition to the electronic configuration of the metal and the heteroatom nature of the cluster, the π acidity of the ML_2 ligands affects the degree of slip in metallocarbaboranes.[7,8] A comparison (Table) of slip parameters of three d^8 complexes displays this trend which is in accordance with the relative π acidity of the ligands. This trend also illustrates the effect of the $5e_1(y) - d_{yz}{}^*$ molecular orbital on the ML_2 fragment slip. As the degree of backbonding from this metal orbital increases, its energy and effect on the geometry of the complex decreases. This trend is also in accordance with the smaller d–p promotion energy of Rh relative to Pd.

The orientation of the Rh(CO)(PPh_3) unit is unexpected. Theoretical studies have shown that the most stable conformation of d^8 ML_2 fragments is parallel to a line joining the two *ortho* carbon atoms.[9] In the present structure the Rh(CO)(PPh_3) fragment is rotated by *ca.* 90° from this expected orientation. Presumably this is due to steric interactions between the ligands and pyridine ring.

The pyridine group can be regarded as an 'innocent' ligand. The boron atom bonded to this aromatic ring exhibits an average B–B distance [1·813(6) Å] which compares favourably with the average B–B distances of the other boron atoms of the C_2B_3 face [1·795(6) Å]. The distance of the ring from the Rh atom [Rh–N 3·144(8) Å] precludes any interaction and the tilt of the aromatic ring with respect to the carbaborane cage is dictated entirely by crystal packing forces, rather than electronic interactions. Presumably the pyridine ring exhibits unhindered rotation in solution.

Solutions of (**1**) and (**2**) are catalysts for the hydroformylation reaction, and are now being studied in detail.

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