Synthesis and Characterization of Seven-co-ordinate Hydrido-complexes of Ruthenium with Carbaborane: *X*-Ray Diffraction Study of 2,1,7-[$(PPh_3)_2RuH_2C_2B_9H_{11}$]

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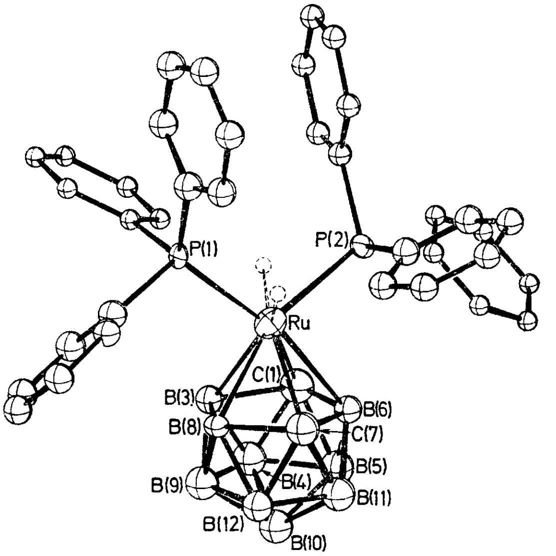
Summary Oxidative additions of 7,8- and 7,9-$C_2B_9H_{12}^-$ to [$(PPh_3)_3RuHCl$] have yielded novel dihydrido-ruthenium complexes 3,1,2- and 2,1,7-[$(PPh_3)_2RuH_2C_2B_9H_{11}$] respectively; the latter's structure has been confirmed by *X*-ray diffraction study and it has been found reversibly to eliminate its hydride ligands as H_2 upon heating *in vacuo.*

We report the preparation of two new ruthenium complexes *via* oxidative addition of the carbaborane monoanion[1] $C_2B_9H_{12}^-$ to [$(PPh_3)_3RuHCl$].

An apparently light-blue crystalline complex (I) is obtained when 7,9-$C_2B_9H_{12}^-$ is heated under reflux with [$(PPh_3)_3RuHCl$]·PhMe in ethanol. Its i.r. spectrum shows a doublet at ν 2025 cm^{-1} (Ru–H). The ^{1}H n.m.r. spectrum clearly exhibits a 1:2:1 triplet at τ 16·9 (J_{P-H} 28·8 Hz), the 80·5 Hz ^{11}B n.m.r. spectrum is broad with doublets at τ −1·2, 7·6, 13·1, and 18·3 p.p.m. relative to BF_3–OEt_2 (rel. area 1 : 3 : 4 : 1), and the ^{31}P n.m.r. spectrum indicates one singlet (τ −34·5 p.p.m. from 85% H_3PO_4, ^{1}H decoupled). Elemental analyses further support the formulation of (I) as 2,1,7-[$(PPh_3)_2RuH_2C_2B_9H_{11}$]; formally a 7-co-ordinate Ru^{IV} complex.



FIGURE

To confirm the *closo*-structure and the arrangement of the ligands, a single crystal *X*-ray diffraction study has been carried out using light-blue crystals of (I) grown from *p*-dioxan.

Crystal data: $M = 1024{\cdot}47$ {calc. for [$(PPh_3)_2RuH_2C_2B_9H_{11}$]·$3C_4H_8O_2$}, monoclinic, space group *Cc*, $a = 24{\cdot}01(1)$, $b = 13{\cdot}523(2)$, $c = 19{\cdot}344(5)$ Å; $\beta = 123{\cdot}32(3)$°, $U = 5250(3)$ Å^3, $Z = 4$; $D_c = 1{\cdot}296$, $D_m = 1{\cdot}29(3)$ (flotation) g cm^{-3}; *R* is currently 0·098 for 1982 reflections above background (Syntex $P\bar{1}$ four-circle diffractometer, Mo-K_α *X*-radiation, $\lambda = 0{\cdot}71069$ Å).

The result (Figure) confirms the structure of (I). The Ru atom is symmetrically bonded to all five atoms of the carbaborane open face; distances range from 2·22(2) to 2·32(2) Å. The two PPh_3 ligands are almost exactly related by a 2-fold axis through Ru and B(10). Rh–P distances are 2·342(4) and 2·301(4) Å; the difference is probably due only to packing interaction.[2] The P(1)–Ru–P(2) angle is 101·1(2)°. While the two hydrides remain to be located, their positions can be inferred to be that lying symmetrically between the PPh_3 groups.

On exposure to H_2, (I) turns grayish-white, but its spectral and analytical properties are unchanged. Hence traces of a blue impurity must be responsible for the colour of (I) On heating *in vacuo* to 160 °C (I) gives a dark-blue complex (II) with the loss of 1 equiv. of H_2. The spectra of (II) give no evidence for any hydride in the complex. Its ^{11}B n.m.r. spectrum shows broad doublets centred at τ −3·0, 0·0, 5·2, 10·9, and 22·1 p.p.m. (rel. area 1 : 1 : 2 : 2 : 3) and its ^{31}P n.m.r. spectrum consists of one singlet at τ −60·8 p.p.m. (^{1}H decoupled). Compound (II) is therefore postulated to be 2,1,7-[$(PPh_3)_2RuC_2B_9H_{11}$]; formally a 16-electron Ru^{II} complex. It readily reacts with H_2 at ambient temperature to regenerate (I).

Both (I) and (II) react with CO in CH_2Cl_2 solution (room temperature) or in the solid state (60—80 °C) to give 2,1,7-[$(PPh_3)_2RuCOC_2B_9H_{11}$]. They also react with HCl to give [$(PPh_3)_2RuCl_2C_2B_9H_{11}$].

Reaction of the isomeric carbaborane 7,8-$C_2B_9H_{12}^-$ with [$(PPh_3)_3RuHCl$]·PhMe gives a colourless complex (III) formulated as 3,1,2-[$(PPh_3)_2RuH_2C_2B_9H_{11}$], ν 2040 cm^{-1} (Ru–H). Its ^{1}H n.m.r. spectrum shows a 1 : 2 : 1 hydride resonance at τ 16·3 (J_{P-H} 28 Hz) and its ^{11}B n.m.r. spectrum contains resonances at τ −13·9, −4·6, and 5·4 p.p.m. (2 : 5 : 2). Unlike (I), heating (II) *in vacuo* results in irreversible loss of H_2. It does, however, react readily with CO and HCl to give analogous derivatives.

Solutions of complexes (I) and (II) have been shown to be active in catalytic hydrogenation of olefins. This is currently being investigated further.

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