Journal of

The Chemical Society,

Chemical Communications

NUMBER 18/1980

Precursor of an Extraordinarily Reactive Homogeneous Hydrogenation Catalyst. Synthesis, *X*-Ray Crystal Structure, and Reactions of [*closo*-1,3-μ-(η^2-3,4-CH_2 : $CHCH_2CH_2$)-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$]

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Summary The synthesis, *X*-ray crystal structure, and reactions of the catalyst precursor, the title compound (**1**), and the initial rates of some alkene hydrogenations catalysed by (**1**) are reported.

In our studies of alkene reduction catalysed by [*closo*-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$],[1] we have noted that the rate of hydrogenation is inversely proportional to the concentration of added triphenylphosphine. This observation suggests that reversible triphenylphosphine dissociation is an important equilibrium which precedes the rate-determining step of the hydrogenation sequence. The ease with which the parent catalyst could be modified through synthesis led us to explore the possibility of obtaining enhanced hydrogenation rates by replacing one of the triphenylphosphine ligands with a chelated η^2-3,4-butenyl side-chain attached to one of the dicarbollide ligand carbon atoms. The resulting rhodacarbaborane (**1**), [*closo*-1,3-μ-(η^2-3,4-CH_2=$CHCH_2CH_2$)-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$], might well undergo irreversible hydrogenation of the alkenyl side-chain under the conditions for alkene hydrogenation to produce an open co-ordination site on rhodium[2] resulting in a marked rate acceleration in the hydrogenation of alkenes. Complex (**1**) is among the most active homogeneous hydrogenation catalysts reported to date (*vide infra*), demonstrating this effect. In addition (**1**) is to our knowledge the first rhodium complex of the relatively rare hydrido-alkene class of complexes[3,4] to be isolated and structurally characterized.

When a methanol solution of [$RhCl(PPh_3)_3$] and a 20% molar excess of Cs^+[7-butenyl-7,8-$C_2B_9H_{11}$]$^-$ [5] were heated to reflux under nitrogen for 3 h a yellow microcrystalline precipitate was obtained in 90% yield† which was recrystallized from CH_2Cl_2–ethanol under an inert atmosphere (m.p. 170—173 °C, decomp.). Elemental analysis and n.m.r. and i.r. spectra supported the proposed formula for (**1**).

Crystal data: (**1**), monoclinic, space group $P2_1/c$; a = 16·494(4), b = 11·193(2), c = 17·006(3) Å, β = 122·49(1)°, U = 2648·22(95) Å^3, D_c = 1·386 g cm^{-3}, D_m = 1·229 g cm^{-3} (flotation in aqueous KI). *X*-Ray intensity data were collected by the θ—2θ scan technique with Mo-K_α radiation (graphite monochromator) on a Syntex $P\bar{1}$ automated diffractometer equipped with a scintillation counter and pulse height analyser. Of a total of 3840 reflections examined, 2336 had $I > 3\sigma(I)$ and were used in the structure determination. The data were corrected for absorption, Lorentz, and polarization effects. The structure was solved by using heavy-atom methods and refined by full-matrix least-squares techniques, converging at R = 0·044 and R_w = 0·048.‡ The molecular structure of (**1**) is shown in the Figure together with significant bond distances

† Yield based on rhodium consumed.

‡ 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.

and angles The rhodium atom is symmetrically bound to the pentagonal face of the dicarbollide ligand The vinyl unit of the butenyl group is bound to the rhodium in such a fashion that the C=C bond is nearly parallel to the pentagonal face of the dicarbollide ligand

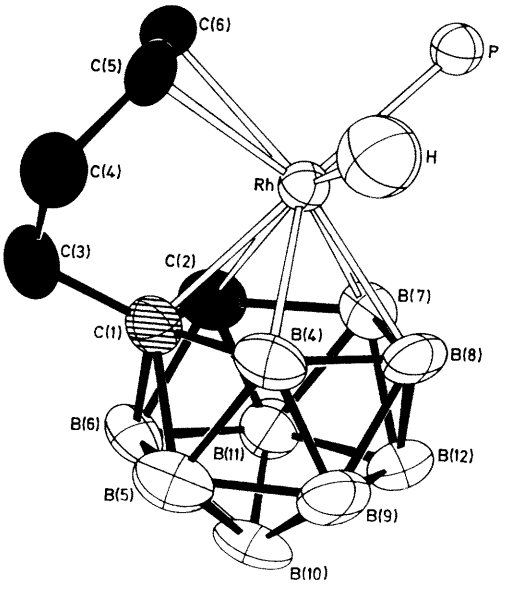

FIGURE Molecular structure of (**1**) (the phenyl rings on phosphorus and all hydrogens except the rhodium hydride have been omitted for clarity) Distances from Rh to the attached atoms are H 1 65(3), C(1) 2 211(8) C(2) 2 266(8), B(4) 2 217(9), B(7) 2 220(9), B(8) 2 217(9), C(5) 2 276(8), C(6) 2 242(8), P 2 291(2) Å Some significant angles are C(5)–Rh–C(6) 35 2(3), C(5)–Rh–H 82(2), H–Rh–P 74(3), C(6)–Rh–P 87 2(2)°

A tetrahydrofuran (THF) solution of (**1**) ($1{\cdot}8 \times 10^{-4}$ M) and trimethylvinylsilane (0 13 M) displayed an initial rate of $2\,4 \times 10^{-1}$ mol s^{-1}/(mol Rh) for the reduction of the alkene when exposed to hydrogen [$p(H_2)$ 705 mmHg] at 0 °C A THF solution of [$RhCl(PPh_3)_3$] under the same conditions exhibited an initial rate of $7{\cdot}8 \times 10^{-3}$ mol s^{-1}/(mol Rh), 30 times slower than the rate exhibited by (**1**) A THF solution of (**1**) under the same conditions as described above displayed an initial rate of 8·9 mol s^{-1}/(mol Rh) in the reduction of 3,3-dimethylbut-1-ene A CH_2Cl_2 solution of $[Ir(cod)PPr^i_3(py)]^+PF_6^-$ ($5{\cdot}0 \times 10^{-4}$ M) (py = pyridine) and 3,3-dimethylbut-1-ene (0 5 M) displayed an initial rate of 2·3 mol s^{-1}/(mol Ir) when exposed to hydrogen [$p(H_2)$ 600 mmHg] at 0 °C [4] The compound $[Ir(cod)PPr^i_3(py)]^+PF_6^-$, apparently the most active previously reported homogeneous hydrogenation catalyst, must be used in CH_2Cl_2 owing to the need for a non-co-ordinating polar solvent Complex (**1**), on the other hand, has been found to be effective as a homogeneous hydrogenation catalyst in THF, *o*-dichlorobenzene, benzene, and toluene

When 1 mmol of (**1**) in THF was exposed to hydrogen while in the presence of 2·4 mmol of triphenylphosphine, the solution took up 1 mmol of hydrogen Solvent removal *in vacuo* followed by column chromatography (silica gel, CH_2Cl_2–hexane eluant under nitrogen) gave an orange compound which was recrystallized from CH_2Cl_2–heptane in 90% yield This compound was shown to be [*closo*-1-butyl-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{10}$], on the basis of elemental analysis and i r and n m r spectra, thus demonstrating the facile hydrogenation of the alkenyl side-chain, it was identical to the product obtained from [$RhCl(PPh_3)_3$] and Cs^+[7-butyl-7,8-$C_2B_9H_{11}$]$^-$ [6] in methanol and was also found to be an effective hydrogenation catalyst

When 1 mmol of (**1**) in THF was exposed to hydrogen in the absence of triphenylphosphine the solution rapidly took up 1 mmol of hydrogen with the hydrogenation of the butenyl side-chain and then slowly evolved 0 5 mmol of hydrogen Solvent removal and column chromatography as described above gave an air-sensitive dark purple compound which we suggest is a dimer similar to $[PPh_3RhC_2B_9H_{11}]_2$ [7]

The authors thank Dr R T Baker for his help with the ^{1}H n m r spectra and catalytic screening, Dr B A Katz for his help with the crystal structure, the National Science Foundation for the purchase of the Bruker WP-200 n m r spectrometer and the Syntex Diffractometer, and the National Science Foundation and the Office of Naval Research for partial support

(*Received, 2nd May* 1980, *Com* 464)

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