

Synthesis, X-Ray Crystal Structure, and Reactions of [*closo*-1,3- μ -2,3- μ -{1,2- μ -(η^2 -3,4-CH₂CH₂C(Me)=CHCH₂CH₂CH₂)}-3-H-3-PPh₃-3,1,2-RhC₂B₉H₉], a Metallocarbaborane Catalyst

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

in (3).² Such a 'head to tail' dimerization of alkenes around a rhodium centre has previously been observed by Bennet.⁵

In addition to our studies¹ of alkene reduction catalysed by [*closo*-3-H-3,3-(PPh₃)₂-3,1,2-RhC₂B₉H₁₁] (2), we have modified the parent catalyst through synthesis by replacing one triphenylphosphine ligand with a chelating alkene attached to the dicarbollide ligand. We have previously reported the synthesis, structure, and reactions of [*closo*-1,3- μ -(η^2 -3,4-CH₂=CHCH₂CH₂)-3-H-3-PPh₃-3,1,2-RhC₂B₉H₁₀] (3)² and now report the synthesis, structure, and reactions of [*closo*-1,3- μ -2,3- μ -{1,2- μ -(η^2 -3,4-CH₂CH₂C(Me)=CHCH₂CH₂CH₂)}-3-H-3-PPh₃-3,1,2-RhC₂B₉H₉], (1). Complex (1) is a member of the relatively rare hydrido-alkene class of complexes^{2,3} and, to our knowledge, only the second such rhodium complex isolated and structurally characterized.²

When an ethanolic solution of [RhCl(PPh₃)₃] and a 20% molar excess of Cs[7,8-bis(butenyl)-7,8-C₂B₉H₁₀]⁴ was heated under reflux under nitrogen for 3 h, a yellow microcrystalline precipitate was obtained in 90% yield.† The product was recrystallized from CHCl₃-n-heptane or 1,2-dichloroethane-n-heptane under an inert atmosphere (m.p. 195–197 °C, decomp.). Elemental analysis and n.m.r. and i.r. spectra supported the proposed formula for (1).

Crystal data for (1): C₂₈H₃₀B₉PRh, monoclinic, space group P2₁/c; *a* = 9.834(3), *b* = 9.615(4), *c* = 39.291(12) Å, β = 98.72(2)°, *U* = 2825(1) Å³, *D_c* = 1.431 g cm⁻³, *D_m* = 1.361 g cm⁻³ (floatation in aqueous KI).‡ **X-Ray** intensity data were collected at -153 °C by the θ -2 θ scan technique with Mo-*K* α radiation (zirconium filter) on a Picker FACS 1 automated diffractometer equipped with a scintillation counter and pulse height analyser. Of a total of 3403 reflections examined, 1942 had *I* > 3 σ (*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* = 0.082 and *R_w* = 0.096, with the phenyl rings treated as rigid groups.§ The molecular structure of (1) is shown in the Figure together with significant bond distances and angles. The two butenyl side chains attached to the dicarbollide ligand have dimerized in a 'head to tail' manner and the resulting chelating alkene is bound to the rhodium in such a fashion that the C=C bond is nearly parallel to the dicarbollide ligand, bonding similar to that

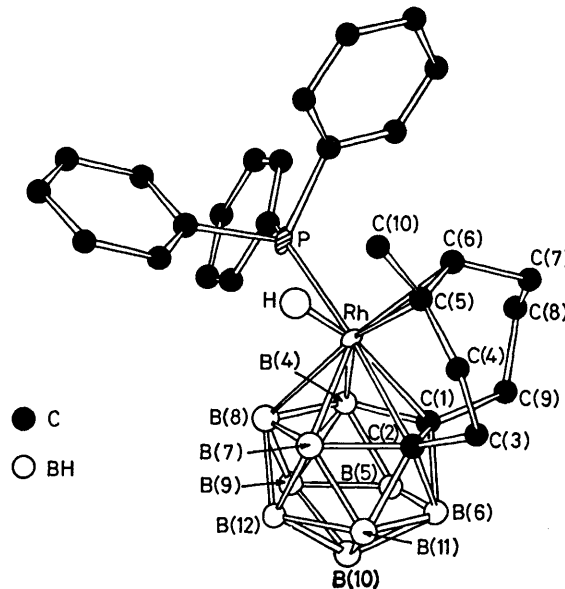


FIGURE. Molecular structure of (1); all hydrogen atoms except that bonded to rhodium have been omitted for clarity. Bond lengths from Rh to the attached atoms are: H 1.4, P 2.342(5), C(2) 2.239(17), C(1) 2.318(14), B(4) 2.235(20), B(7) 2.205(22), B(8) 2.201(21), C(5) 2.260(15), and C(6) 2.317(15); C(5)-C(6) 1.459(24) and C(5)-C(10) 1.515(23) Å. Some significant bond angles are C(5)-Rh-C(6) 37.2(6)°, C(2)-Rh-C(5) 82.2(6)°, C(1)-Rh-C(6) 93.3(6)°, H-Rh-C(5) 79°, H-Rh-C(6) 92°, H-Rh-P 52°, C(5)-Rh-P 109.8(4)°, C(6)-Rh-P 93.1(5)°, C(4)-C(5)-C(6) 123(2)°, C(4)-C(5)-C(10) 113(1)°, C(10)-C(5)-C(6) 117(2)°, C(5)-C(6)-C(7) 130(2)°, and Rh-C(6)-C(5) 116(2)°. The position of the hydrogen atom was not refined.

A tetrahydrofuran (THF) solution of (1) (2.72×10^{-3} M) displayed the following initial rates of hydrogenation of the following terminal alkenes (9.84×10^{-2} M) at 25 °C [*p*(H₂) 585 mmHg]: 1.1×10^{-3} mol s⁻¹/(mol Rh) for 3,3-dimethylbut-1-ene; 2.4×10^{-3} mol s⁻¹/(mol Rh) for trimethylvinylsilane; and 9.1×10^{-4} mol s⁻¹/(mol Rh) for *n*-butyl acrylate. Under the same conditions (2) exhibited comparable rates,⁶ while a THF solution of (3) (1.8×10^{-4} M),

† Yield based on rhodium consumed.

‡ Unit-cell dimensions were measured at -153 °C. *D_m* was measured at 25 °C.

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

one of the most reactive homogeneous hydrogenation catalysts reported to date, and the following alkenes (0.13M) displayed the following initial rates at 0 °C [$p(\text{H}_2)$ 705 mmHg]:² 2.3×10^{-1} mol s⁻¹/(mol Rh) for trimethylvinylsilane; and 8.9 mol s⁻¹/(mol Rh) for 3,3-dimethylbut-1-ene. Complex (1), unlike (3), may be recovered unchanged from THF solutions exposed to hydrogen at 25 or 40 °C, indicating that the chelating alkenyl moiety is not hydrogenated as in (3).² Complex (1) shows no enhancement in the rate of hydrogenation of alkenes over the rates displayed by (2). Complex (1) was also found to catalyse the

isomerisation of alkenes but was not active for the hydrogenation of alkynes or for the hydroformylation of alkenes.

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¹ T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1974, **96**, 4674; G. E. Hardy, K. P. Callahan, C. E. Strouse, and M. F. Hawthorne, *Acta Crystallogr., Sect. B*, 1976, **32**, 264.

² M. S. Delaney, C. B. Knobler, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1980, 849.

³ D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Am. Chem. Soc.*, 1967, **89**, 6387; J. W. Byrne, H. V. Blaser, and J. A. Osborn, *ibid.*, 1975, **97**, 3871; T. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1324; J. Evans, B. F. G. Johnson, and J. Lewis, *ibid.*, 1977, 510; H. Felkin, G. E. Morris, and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1976, 710; K. W. Muir and J. A. Ibers, *J. Organomet. Chem.*, 1969, **18**, 175; T. V. Ashworth, E. Singleton, and M. Laing, *ibid.*, 1976, **117**, C113; T. V. Ashworth, M. J. Nolte, and E. Singleton, *ibid.*, p. C73; H. Felkin, T. Khan, G. E. Morris, and R. H. Crabtree, *ibid.*, 1978, **144**, C15; G. R. Clark, P. W. Clark, A. J. Jones, M. A. Mazid, and D. R. Russell, *ibid.*, 1979, **166**, 109; H. Felkin, T. Fillebeen-Khan, G. E. Morris, and R. H. Crabtree, *ibid.*, 1979, **168**, 183; G. R. Clark, P. W. Clark, and K. Marsden, *ibid.*, 1979, **173**, 231; G. Del Piero, G. Perego, and M. Cesari, *Gazz. Chim. Ital.*, 1975, **105**, 529; R. Crabtree, *Acc. Chem. Res.*, 1979, **12**, 331.

⁴ Bis(butenyl)-*o*-carbaborane may be prepared by a method similar to the method of preparation of 4-(*o*-carbaboranyl)butene by D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, W. Schwartz, M. S. Cohen, and M. Fein, *Inorg. Chem.*, 1963, **2**, 1120, and degraded by the method of M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862.

⁵ M. A. Bennet, R. N. Johnson, and B. Tomkins, *J. Organomet. Chem.*, 1973, **54**, C48.

⁶ R. T. Baker, U.C.L.A. doctoral dissertation, 1980.