

Facile Pathway-defined Fluxional Cluster Isomerization in Ten-vertex *closo*-2,1,6-Metalladiboranes of Ruthenium and Rhodium

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Multi-element n.m.r. spectroscopy allied with deuterium labelling and single-crystal X-ray diffraction analysis reveals fluxionality within [2-(η^6 -C₆Me₆)-*closo*-2,1,6-RuC₂B₇H₉] and [2-(η^5 -C₅Me₅)-*closo*-2,1,6-RhC₂B₇H₉] (2), that is specifically defined and extremely facile.

We report an unprecedented fluxional isomerism in two new *closo* ten-vertex metalladiboranes, [2-(η^6 -C₆Me₆)-*closo*-2,1,6-RuC₂B₇H₉] (1) and [2-(η^5 -C₅Me₅)-*closo*-2,1,6-RhC₂B₇H₉] (2), that is specifically defined and extremely facile.

Reaction between [(η^6 -C₆Me₆)RuCl₂]₂, or [(η^5 -C₅Me₅)RhCl₂]₂, and [*arachno*-4,6-C₂B₇H₁₂]⁻ in CHCl₃ solution results in the formation of compound (1) (60%; unopti-

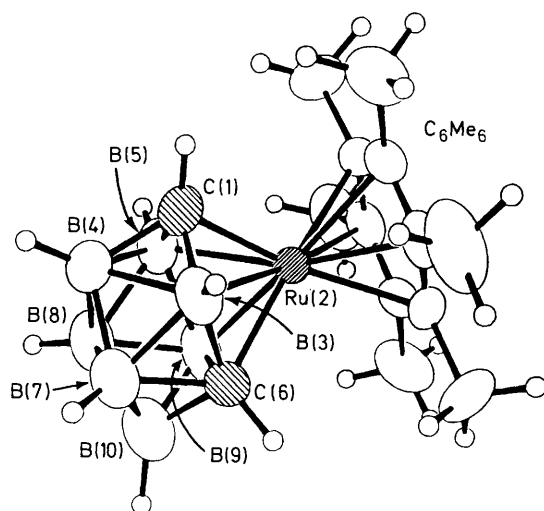
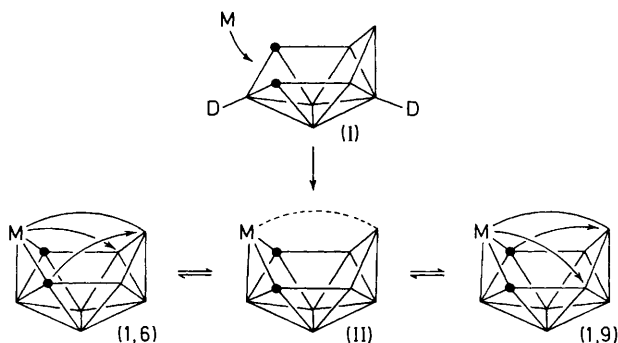


Figure 1. Drawing of the crystallographically determined molecular structure of [2-(η^6 -C₆Me₆)-*closo*-2,1,6-Ru₂C₂B₇H₉] [compound (1); actually obtained for the 3,9-dideuterated derivative]. Selected interatomic distances are as follows: Ru(2)–C(1) 205.8(6), Ru(2)–B(3) 224.6(6), Ru(2)–B(5) 227.4(6), Ru(2)–C(6) 219.8(5), Ru(2)–B(9) 219.8(6) pm. The fluxional isomerism to give the enantiomer effectively (see Scheme) involves reversible migration of C(1) to the 9-, B(3) to the 5-, B(5) to the 10-, C(6) to the 1-, B(7) to the 8-, B(8) to the 7-, B(9) to the 6-, and B(10) to the 3-position, whereas Ru(2) and B(4) remain at the 2- and 4-positions respectively.



Scheme 1

mised), or compound (2) (63%: unoptimised), respectively, as air-stable yellow crystalline solids. X-Ray diffraction analysis on the 3,9-dideuterated isotopomer of compound (1) reveals the molecular structure shown in Figure 1.[†] The cluster site electron densities, thermal parameters, *etc.*, indicate that C(6)/B(9)–B(6)/C(9) disorder is not significant, and a crystallographic inversion centre therefore dictates that both enantiomers (formally the 2,1,6- and 2,1,9-isomers) are each specifically present and ordered in the crystal.

N.m.r. spectroscopy at 294 K on compound (1) reveals a 2:1:2:1:1 ¹¹B and a 2:1:2:2:1:1 ¹H relative intensity pattern for the {C₂B₇H₉} unit,[‡] indicating fluxionality but with scrambling only within each of selected site pairs. Low temperature n.m.r. (<213 K) revealed seven separate ¹¹B and nine separate ¹H resonances for the {C₂B₇H₉} unit,[§] consistent with the solid-state structure. Intermediate temperatures showed that the exchange occurred within each of the pairs CH(1)/CH(6), BH(5)/BH(10), and BH(4)/BH(7), with coalescence temperatures giving a value for $\Delta G^{\ddagger}_{272}$ of *ca.* 45 kJ mol⁻¹. BH(3), BH(8), and BH(9) each remained in, or

[†] Crystal data for C₁₄H₂₅B₇D₂Ru, *M* = 374.11, triclinic, space group *P*1̄, *a* = 839.4(2), *b* = 935.8(2), *c* = 1259.1(3) pm, α = 77.08(2), β = 84.99(2), γ = 64.92(2)°, *U* = 0.8731(3) nm³, *Z* = 2, μ = 7.90 cm⁻¹, *F*(000) = 380. Scan widths 2.0° + α -doublet splitting, scan speeds 2.0–29.3° min⁻¹ and 4.0 < 2 θ < 50.0°. Total data collected = 3150, no. observed = 3039 [*I* > 2.0 σ (*I*)], *R* = 0.0295, *R*_w = 0.0346 (*g* = 0.0001).

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the $\omega/2\theta$ scan mode using graphite-monochromated Mo-K α radiation following a procedure described elsewhere.⁵ The data set was corrected for absorption empirically.⁶ The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares using SHELXL76.⁷ All non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms were included in calculated positions (C–H = 108 pm) and refined with an overall isotropic temperature factor while all borane hydrogen atoms were located in Fourier difference maps and freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] N.m.r. data: assignment, $\delta(^{11}\text{B})$ at 294 K [$\delta(^1\text{H})$ at 294 K]; BH(5 and 10), –3.2 [+2.46]; BH(9), –5.75 [+2.605]; BH(4 and 7), –19.6 [+1.01]; BH(8), –20.6 [+0.45]; BH(3), –23.7 [+0.73]; CH(1 and 6), – [+4.10]; C₆Me₆, – [+2.12]; CD₂Cl₂ solution.

[§] N.m.r. data: assignment, $\delta(^{11}\text{B})$ at 213 K [$\delta(^1\text{H})$ at 193 K]; BH(10), +16.5 [+4.87]; BH(4), *ca.* –6.5 [+1.81]; BH(9), *ca.* –6.5 [+2.48]; BH(8), –21.05 [+0.32]; BH(5), –24.1 [–0.22]; BH(3), –24.1 [+0.58]; BH(7), –33.7 [–0.03]; CH(1), – [+5.60]; CH(6), – [+2.39]; C₆Me₆, – [+2.04]; CD₂Cl₂ solution; $\delta(^{11}\text{B})$ and $\delta(^1\text{H})$ in p.p.m. to low field (high frequency) of BF₃(OEt₂) and SiMe₄ respectively; assignments by [¹¹B–¹H]-COSY, [¹H–¹H]-COSY, and ¹H-¹¹B(selective)} n.m.r. experiments.

was converted to, a chemically identical position throughout the fluxionality. Variable temperature n.m.r. on specifically deuteriated $[3,9\text{-D}_2\text{-}2\text{-}(\eta^6\text{-C}_6\text{Me}_6)\text{-}closo\text{-}2,1,6\text{-RuC}_2\text{B}_7\text{H}_7]$, prepared using $[3,5\text{-D}_2\text{-}arachno\text{-}4,6\text{-C}_2\text{B}_7\text{H}_{10}]^-$ (schematic structure I in Scheme 1), confirmed this and showed that any other more extensive site-scrambling did not occur on a longer time-scale. The rhodium analogue (2) was static at 294 K, but exhibited an equivalent fluxionality at higher temperatures with $\Delta G^\ddagger_{345} ca. 58 \text{ kJ mol}^{-1}$.

These results specifically eliminate the possibility of isomerisation by triangular face rotation, and define the fluxional isomerisation as occurring *via* two concerted or sequential diamond-square-diamond processes involving the Ru(2)C(1)B(5)B(9) and Ru(2)C(6)B(9)B(10) units. These four-atom units both contain ruthenium which is known^{1,2} to induce open character among adjacent faces. The process may therefore proceed *via* 'square-face' *isonido*³ intermediates, possibly linked by a transition state that approximates geometrically to a 6,9-bridged normal *nido* (schematic structure II). This last permits a ready visualisation of the isomerisation and suggests a mechanism for cluster formation (see Scheme 1).

Although numerous metalladecaborane cluster isomerisations have been reported, in no case, as far as we are aware, has the detailed mechanism of the rearrangement previously been defined. Furthermore, activation energies for reported isomerisations are high, so that temperatures above about

600 K, or ultra-violet irradiation, are generally necessary.⁴ The specifically defined and extremely facile fluxional isomerism of compounds (1) and (2) is therefore without precedent.

We thank the S.E.R.C., the British Council, and the Royal Society for support, and the University of Leeds Research Fund for an equipment grant. J. D. K. thanks Donna Kennedy for assistance with his travelling expenses.

Received, 8th March 1988; Com. 8/00942B

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