

Oxidative and Cluster Aufbau Reactions of *nido*-6-Metalladecaboranes induced by Lewis Bases such as SMe_2 : High-yield Formation of [1-($\eta^6\text{-C}_6\text{Me}_6$)-*isocloso*-1-RuB₉H₉] and the Molecular Structure of the Rh-*commo*-(*isonido*-eleven-vertex)-(*closo*-ten-vertex) *conjuncto* species [($\eta^5\text{-C}_5\text{Me}_5$)RhB₉(SMe₂)H₁₀RhB₉H₇(SMe₂)₂][†]

Evert J. Ditzel, Xavier L. R. Fontaine, Norman N. Greenwood, John D. Kennedy, and Mark Thornton-Pett
School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

The reaction of SMe_2 with [6-($\eta^6\text{-C}_6\text{Me}_6$)-*nido*-6-RuB₉H₁₃] gives an 80% yield of [1-($\eta^6\text{-C}_6\text{Me}_6$)-*isocloso*-1-RuB₉H₉], whereas reaction with the analogous [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB₉H₁₃] gives a variety of products, of which one (20%) is the novel *conjuncto* species [($\eta^5\text{-C}_5\text{Me}_5$)RhB₉(SMe₂)H₁₀RhB₉H₇(SMe₂)₂] that has a structure based on a unique *isonido*-type eleven-vertex {7',9'-Rh₂B₉} and a *closo* ten-vertex {2-RhB₉} cluster joined at a common rhodium atom.

We report first that the reaction of SMe_2 with [6-($\eta^6\text{-C}_6\text{Me}_6$)-*nido*-6-RuB₉H₁₃] [structure (1)] in refluxing toluene gives the ten-vertex *isocloso* species [1-($\eta^6\text{-C}_6\text{Me}_6$)-*isocloso*-1-RuB₉H₉] in 75–80% yield [structure (2)].[‡] There is a theoretical interest in these *isocloso*-type species,¹ and since the *nido*-6-ruthenadecaborane can be made readily in high yield (80%) from commercially available B₁₀H₁₄,² more extensive experimental examination of this type of ten-vertex *isocloso* compound is thus facilitated.

Secondly we report that, by contrast, reaction of SMe_2 with the closely related [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB₉H₁₃], a compound that may also be obtained in high yield from B₁₀H₁₄,³ takes a completely different course. Addition of SMe_2 to a

refluxing solution of the *nido*-6-rhodadecaborane in toluene, followed by chromatographic separation, yields a variety of products of which one (20%) is the brown, air-stable dirhodium *conjuncto* species [($\eta^5\text{-C}_5\text{Me}_5$)RhB₉(SMe₂)-H₁₀RhB₉H₇(SMe₂)₂] shown in Figure 1.[§] Other main pro-

[§] *Crystal data*: C₁₆H₅₀B₁₈Rh₂S₃, $M = 739.18$, orthorhombic, space group *Pbca*, $a = 1741.3(3)$, $b = 1868.8(2)$, $c = 2114.5(3)$ pm, $U = 6.883(1)$ nm³, $Z = 8$, $D_c = 1.43$ g cm⁻³, μ (Mo-K α) = 10.46 cm⁻¹. A total of 6858 reflections collected on a Nicolet P3/F diffractometer at 290 K. Data were corrected for Lorentz, polarization, and absorption. 4386 reflections were considered observed [$I < 2.0\sigma(I)$] and used to solve the structure (*via* standard heavy atom methods). The C₅Me₅ ligand was found to be disordered and was treated as two interlocking idealised groups [2/3 : 1/3 ratio; C–C(ring) = 145 pm, C–C(terminal) = 150 pm] refined with isotropic thermal parameters. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the SMe₂ groups were included in calculated positions and assigned to an overall isotropic thermal parameter while all the borane hydrogen atoms (including the 'triply' bridging one) were located in Fourier difference maps and freely refined with individual isotropic thermal parameters. A weighting scheme $w = [\sigma^2(F_0) + 0.0004(F_0)^2]^{-1}$ was used at the end of refinement. Final residuals are $R = 0.0487$ and $R_w = 0.0484$. 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.

[†] [9'-($\eta^5\text{-C}_5\text{Me}_5$)-2',3,9-(SMe₂)₃-*nido*-7',9'-dirhodaundecaborano-(7':2)-*closo*-2-rhodadecaborane].

[‡] Identified by n.m.r. spectroscopy and comparison with samples produced from other methods [M. Bown, PhD Thesis, University of Leeds, 1987 (M. Bown, X. L. R. Fontaine, N. N. Greenwood, and J. D. Kennedy, to be submitted); E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, to be submitted]; BH proton and ¹¹B n.m.r. data as follows {ordered as: position $\delta(^{11}\text{B})/\text{p.p.m.}$ { $\delta(^1\text{H})/\text{p.p.m.}$ }} BH(2,3,4) +93.2 [+8.65], BH(8,9,10) +26.8[+3.98], and BH(5,6,7) –13.5 [–0.02]; $\delta(^1\text{H})$ (C₆Me₆) +2.18 p.p.m.; CDCl₃ solution at 294–297 K.

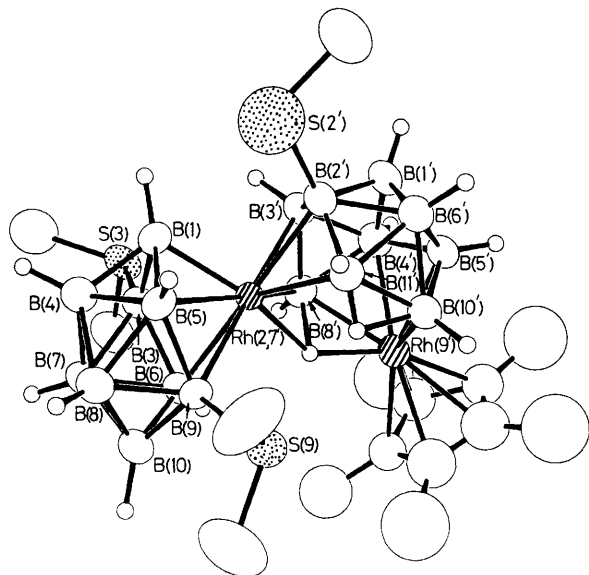
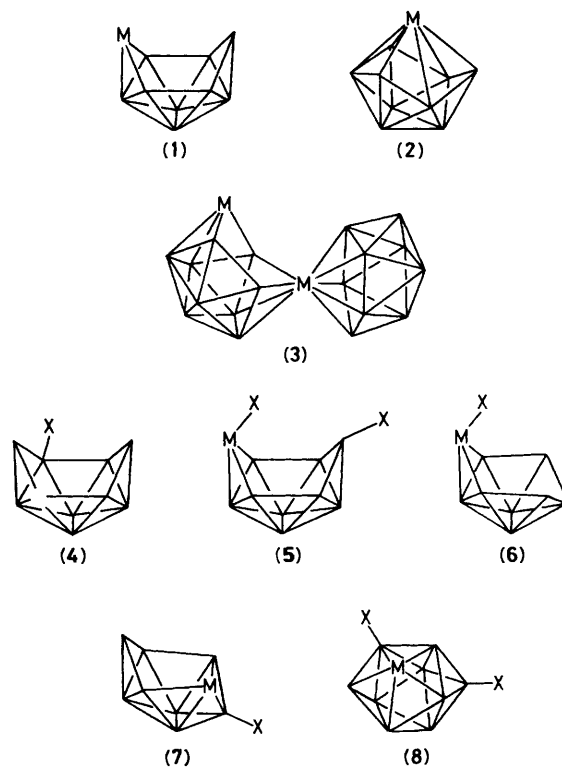


Figure 1. Molecular structure of $[(C_5Me_5)RhB_9(SMe_2)H_{10}RhB_9H_7(SMe_2)_2]$. For the purpose of clarity only the C_5Me_5 ring of 2/3 occupancy \S is shown. Selected interatomic distances are: from Rh(2,7') to Rh(9') 329.7(4), to B(1) 205.5(9), to B(3) 226.7(9), to B(6) 230.5(9), to B(9) 228.3(9), to B(2') 223.0(9), to B(3') 228.6(9), to B(8) 222.4(10), to B(11') 229.5(9), and to H(7',8',9') 205(8) pm; from Rh(9') to B(5') 220.0(10), to B(8') 218.1(11), to B(10') 228.2(11), to H(7',8',9') 160(7), to C(ring a; 2/3 occupancy) 220.7(8)—232.6(8), and to C(ring b; 1/3 occupancy) 217.7(13)—229.1(13) pm. B-B distances for the *closo* fragment 167.8(12)—182.6(14) and for the *nido* fragment 173.4(14)—182.6(14) pm. The angle between the Rh(7')B(8')B(11') and B(8')Rh(9')B(10')B(11') planes is 28°, intermediate between the corresponding angles of 21° and 53° exhibited by the true *nido* and *isonido* {PtIrB₉} and {RhIrB₉} clusters in references 7 and 8 respectively.

The triply bridging nature of the hydrogen atom at Rh(7')B(8')-Rh(9') is corroborated by n.m.r. evidence: $\delta[{}^1H(7',8',9')]$ is selectively and sharply decoupled by irradiation at $\nu[{}^{11}B(8')]$ in ${}^1H\text{-}({}^{11}B\text{selective})$ experiments, and exhibits two couplings $J({}^{103}Rh\text{-}{}^1H)$ of 13.5 and 26.9 Hz, each consistent with a magnitude expected for ${}^1J({}^{103}Rh\text{-}{}^1H)$ but not for ${}^2J({}^{103}Rh\text{-}{}^1H)$, which we have never observed in any compounds with a Rh-B- ${}^1H_\mu$ structural feature [implying ${}^2J({}^{103}Rh\text{-}{}^1H_\mu)$ typically $\leq ca. 5$ Hz].

ducts, which include two bis(dimethylsulphide)-substituted *closo*-{2-RhB₉} mono-clusters and a further brown {Rh₂B₁₈}-based species, will be reported on more fully elsewhere.

As can be seen from Figure 1 the structure of the dirhodium title compound comprises a ten-vertex *closo*-{2-RhB₉} and an eleven-vertex open {7',9'-Rh₂B₉} cluster conjoined 7' : 2 at a common rhodium atom [structure (3)]. A *conjuncto* compound with disparate metallaborane groups is, as far as we are aware, previously unreported [although metallaborane-metallacarborane and bis(metallacarborane) examples are known].⁴ More interest derives from the easy cluster aggregation under conditions that induce the $\{(\eta^6\text{-}C_6Me_6)Ru\}$



analogue to undergo simple dihydrogen loss to give $[(\eta^6\text{-}C_6Me_6)RuB_9H_9]$, and these observations may be of relevance in the development of other cluster aufbau processes to result in more condensed 'macropolyhedral' species. The easy cleavage of the Rh-(C₅Me₅) linkage, recently regarded as noteworthy,⁵ also has interesting synthetic implications.

The ten-vertex *closo*-{RhB₉} subcluster is a straightforward ten-vertex Wadlan '22-electron' bicapped square antiprism {compare $[(C_5Me_5)RhB_9H_7(PMe_2Ph)_2]$ in reference 6}, but the open-faced eleven-vertex {Rh₂B₉} subcluster is novel. Thus, although formally of Wadlan '24-electron' eleven-vertex *closo* formulation, it has an open face with two bridging hydrogen atoms. Additionally, the five-membered {Rh(7')B(8')Rh(9')B(10')B(11')} open face has a bent configuration that is intermediate between pentagonal quasi-planar exhibited by true *nido* species {compare $[(PPh_3)(Ph_2PC_6H_4)Hr(PMe_3)_2PtB_9H_{10}]$ in reference 7} and the quadrilateral configuration exhibited by the recently recognized *isonido* type of eleven-vertex compound {compare $[(C_5Me_5)_2RhIrB_9H_{11}]$ in reference 8}. In accord with this intermediacy, the unusual triply bridging hydrogen atom associated with Ru(7')B(8')Rh(9') is also intermediate between the M-H-B⁷ and M-H-M⁸ bridges characteristic of true *nido* and *isonido* types, respectively. \P

The conditions of the formation of the *conjuncto* compound are quite critical. When the reaction is carried out at room temperature, the main products are $[5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}8\text{-}10\text{-}(SMe_2)\text{-}nido\text{-}5\text{-}RhB_9H_{11}]$ (65%) and $[5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}7\text{-}(SMe_2)\text{-}nido\text{-}5\text{-}RhB_9H_{11}]$ (ca. 25%) [structure (4)], and subsequent mild thermolysis of these, in refluxing toluene, either as isolated species or admixed with their co-products, does not yield significant quantities of the *conjuncto* species. When other Lewis bases (isocyanides, phosphines, amines, etc.) are used, the products are generally substituted monometallic cluster species, often with the *nido*-5-metalladecaborane and *isocloso*-1-metalladecaborane structures (4) and (2), although

\P Proton and ${}^{11}B$ n.m.r. data as follows {ordered as $\delta({}^{11}B)/p.p.m.$ [$\delta({}^1H)/p.p.m.$ of directly bound H atoms]}: +45.7 [+5.28], +41.3 [+5.36], +18.6 [SMe₂ at +2.63, +2.56], +17.0 [+2.85], +7.8 [+2.19], ca. +5.3 [SMe₂ at +2.68, +2.38], ca. +5.1 [+4.27], ca. +5.2 [+3.46], +3.4 [+2.81], -1.3 [+3.05], -11.3 [+1.71], -13.7 [SMe₂ at +2.34, +2.28], ca. -20.6 [+0.96], ca. -20.8 [+1.24], ca. -20.9 [+1.86], -23.2 [+0.32], -28.9 [+0.37], and -30.4 [+0.05]; also $\delta({}^1H)(\mu_3\text{-}RhBRh) - 15.61$ p.p.m., ${}^1J({}^{103}Rh\text{-}{}^1H) 13.5$ and 26.9 Hz, $\delta({}^1H)(\mu_2\text{-}BB) - 0.01$ p.p.m., and $\delta({}^1H)(C_5Me_5) + 1.77$ p.p.m.; CDCl₃ solution at 294—297 K.

we have also identified products with structures (5)—(8), and additional products for which n.m.r. analysis suggests more novel structures.^{2,6,9}

We thank the S.E.R.C. for support.

Received, 21st April 1989; Com. 9/01787I

References

- 1 J. E. Crook, M. Elrington, N. N. Greenwood, J. D. Kennedy, and J. D. Woollins, *Polyhedron*, 1984, **3**, 901; N. N. Greenwood, 'Inorganic Chemistry: Toward the 21st Century' (A.C.S. Symposium Series 211), ed. M. H. Chisholm, A.C.S., Washington, 1983, 33; R. T. Baker, *ibid.*, ed. M. H. Chisholm, 1983, 346; *Inorg. Chem.*, 1986, **25**, 110; J. D. Kennedy, *ibid.*, 1986, **25**, 111; R. L. Johnston and D. M. P. Mingos, *ibid.*, 1986, **25**, 3321; K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, J. Plešek, B. Štíbr, and M. Thornton-Pett, *ibid.*, 1989, **28**, 2219.
 - 2 M. Bown, X. L. R. Fontaine, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1987, **325**, 233.
 - 3 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 547.
 - 4 See, for example, M. Creswick, I. Bernal, and G. Evrard, *Cryst. Struct. Commun.*, 1979, **8**, 839; L. Borodinsky and R. N. Grimes, *Inorg. Chem.*, 1982, **21**, 1921; L. Borodinsky, E. Sinn, and R. N. Grimes, *Inorg. Chem.*, 1982, **21**, 1928.
 - 5 M. Paneque and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1989, 105.
 - 6 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 2417.
 - 7 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1983, 949.
 - 8 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 455.
 - 9 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 2059 and 2809; K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1989, in the press; E. J. Ditzel and Zhu Sisan, unpublished observations, University of Leeds, 1988—1989.
-