ganic phase was distilled. A forerun of **1a** and **2** was followed by 0.72 g (71%) of 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)butane (**4a**/**5a**); bp 81 °C (0.3 torr); *m/e* found, 310.16.[12] Similar preparation of 9.4 mmol of **3** in 25 mL of THF and reaction with an equivalent amount of pinacol (1-chloro-2-phenylethyl)boronate (**1b**)[20] yielded 58% (2.1 g) of the cross-coupling product, ~1:1 **4b** and **5b**: bp 138–140 °C (0.4 torr); 50.3-MHz ^{13}C NMR δ 18 and 28.5 (br BC peaks), others in accord with assigned structure; *m/e* found, 386.21.[12]

Acknowledgment. We thank the National Science Foundation for research Grant CHE-8400715 and the Boeing Corp. for a departmental gift in support of purchase of the Nicolet NT-200 NMR instrument.

Supplementary Material Available: NMR data and elemental analyses for new compounds **4a**–**7b** (2 pages). Ordering information is given in any current masthead page.

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(20) From pinacol (dichloromethyl)boronate[16] and benzylmagnesium chloride in the usual manner:[11] bp 109–110 °C (0.35 torr); 90-MHz ^{1}H NMR: δ 1.21 (s, 12, OC(CH$_3$)$_2$), 3.14 (m, 2, PhCH$_2$), 3.60 (m, 1 BCHCl), 7.25 (s, 5, C$_6$H$_5$), similar to related compounds;[8] 50.3-MHz ^{13}C NMR δ 24.454, 24.506 (CCH$_3$), 40.21 (PhC), 43 (br, BCCl), 84.36 (OCMe$_2$), 126.67, 128.25, 129.13, 138.23 (C$_6$H$_5$). Anal. Calcd for C$_{14}$H$_{20}$BClO$_2$: C, 63.08; H, 7.56; B, 4.06; Cl, 13.30. Found: C, 63.32; H, 7.55; B, 4.06; Cl, 12.96.

Aromatization of the Norbornadiene Ligand to an η^5-Ethylcyclopentadienyl Ligand in a Rhodacarborane via an Intermediate Which Contains an Agostic Hydrogen Atom

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Summary: Protonation of [*closo*-3,3-(η^4-bicyclo[2.2.1]hepta-2,5-diene)-1,2-(CH$_3$)$_2$-3,1,2-RhC$_2$B$_9$H$_9$]$^-$, **1**, with CF$_3$COOH in CD$_2$Cl$_2$ at −78 °C produced the isolated fluxional intermediate **2**, which exhibited an agostic hydrogen atom in an X-ray diffraction study. **2**: orthorhombic; *Pbca*; a = 14.780 (3) Å, b = 14.097 (4) Å, c = 15.342 (4) Å; Z = 8. On standing at 25 °C for 20 h, **2** is isomerized to **3**, [3-(η^2-vinyl)-3-(η^4-cyclopentenyl)-1,2-(CH$_3$)$_2$-3,1,2-RhC$_2$B$_9$H$_9$], which was characterized by X-ray diffraction. **3**: triclinic; $P\bar{1}$, a = 8.803 (4) Å, b = 7.949 (3) Å, c = 12.246 (4) Å; a = 94.69 (3)°, β = 95.16 (3)°, γ = 106.43 (3)°; Z = 2. Thermolysis of **3** at 40 °C in C$_6$H$_6$ solution affords **5**, [*closo*-3-(η^5-C$_5$H$_4$(C$_2$H$_5$))-1,2-(CH$_3$)$_2$-3,1,2-RhC$_2$B$_9$H$_9$], in nearly quantitative yield. Mechanisms are proposed.

We wish to report the reaction sequence leading to the unusual aromatization of the norbornadiene (NBD) ligand of the rhodacarborane anion[1] [*closo*-3,3-(η^4-bicyclo[2.2.1]hepta-2,5-diene)-1,2-(CH$_3$)$_2$-3,1,2-RhC$_2$B$_9$H$_9$]$^-$, **1**, to the η^5-ethylcyclopentadienyl ligand upon protonation of **1**. Both an unstable species, **2**, which contains an agostic H atom[2] and a η^2-vinyl η^3-cyclopentenyl complex, **3**, have been identified as intermediates. Both **2** (Figure 1) and **3** (Figure 2) have been structurally characterized by X-ray diffraction studies.

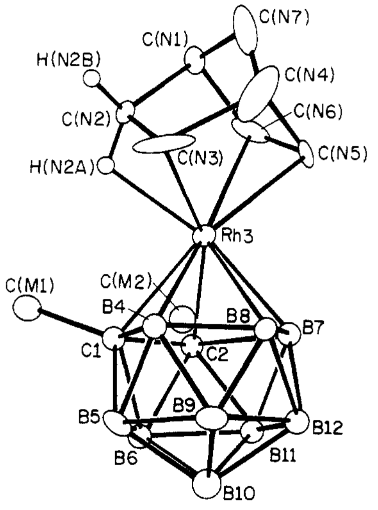
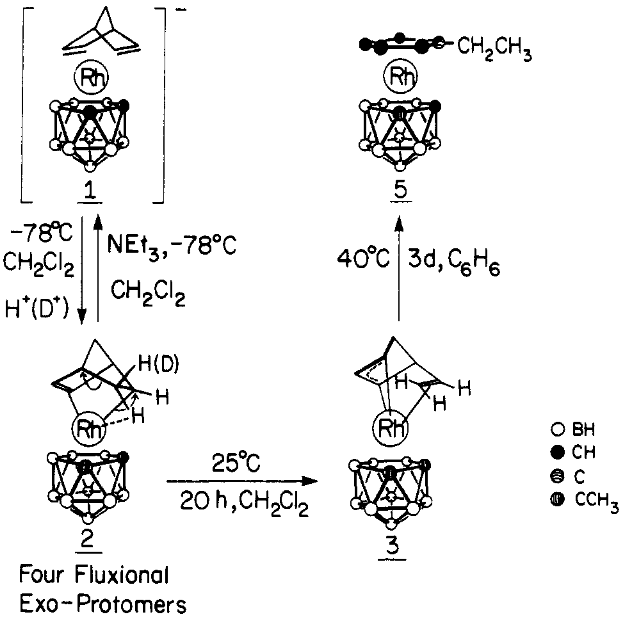


Figure 1. Molecular structure of the unstable intermediate **2**. Hydrogen atoms, except for those on C(N2), have been omitted for clarity. Selected bond lengths (Å): Rh···C(N2) = 2.36 (1); Rh–H(N2A) = 1.9 (3); Rh–C(N3) = 2.08 (1); Rh···C(N4) = 2.73 (2); Rh–C(N5) = 2.14 (1); Rh–C(N6) = 2.27 (1); Rh–C1 = 2.23 (1); Rh–C2 = 2.28 (1), Rh–B4 = 2.18 (1), Rh–B7 = 2.18 (1), Rh–B8 = 2.24 (1); angle Rh–H(N2A)–C(N2) = 108 (21)°.

Scheme I



Protonation of **1** (PPN salt) with 2 equiv of CF$_3$COOH in CD$_2$Cl$_2$ at −78 °C produced neutral and thermally unstable **2**. The −78 °C 200-MHz ^{1}H FTNMR spectrum of **2** exhibited a broad upfield triplet [−0.85 ppm (J = 10 Hz)], six equivalent carboranyl methyl ^{1}H [2.25 ppm (s)],

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(1) Analytically pure PPN salt of **1** was prepared by the reaction of Cs[*nido*-7,8-(CH$_3$)$_2$-7,8-C$_2$B$_9$H$_{10}$] with 4 equiv of sodium isopropoxide and 1 equiv of [Rh(NBD)Cl]$_2$ in 2-propanol followed by precipitation of the PPN salt by addition of PPNCl. 200-MHz ^{1}H NMR (CD$_2$Cl$_2$, 25 °C, δ); 7.71–7.45 (envelope, 30 H, phenyl C–H of PPN$^+$ cation), 3.49 (m, br, 2 H, bridgehead C–H of NBD ligand), 3.24 (q, J = 2.3 Hz, 4 H, vinylic C–H of NBD ligand), 1.89 (s, 6 H, carboranyl methyl C–H), 1.12 (t, J = 1.6 Hz, 2 H, bridging methylene C–H of NBD ligand) showing NBD to be a rapid rotor with respect to the carborane ligand.

(2) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395 and references therein.

0276-7333/85/2304-1692$01.50/0

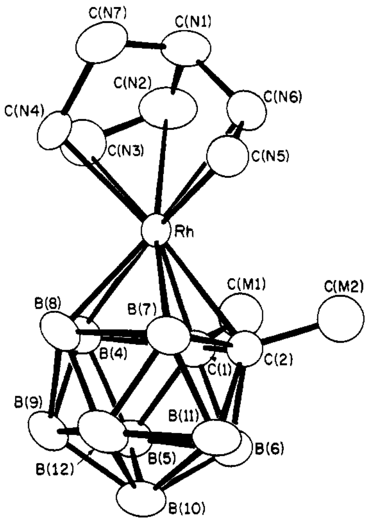

Figure 2. Molecular structure of 3. Hydrogen atoms have been omitted for clarity. The disorder-related molecule is not shown. Selected bond distances (Å): Rh–C(N2) = 2.373 (3), Rh–C(N3) = 2.144 (7), Rh–C(N4) = 2.183 (5), Rh–C(N5) = 2.280 (7), Rh–C(N6) = 2.363 (3), Rh–C1 = 2.280 (3), Rh–C2 = 2.256 (3), Rh–B4 = 2.188 (3), Rh–B7 = 2.188 (3), Rh–B8 = 2.248 (3).

broad unassigned resonances at 4.47, 3.89, and 3.09 ppm, and bridging CH_2 at 1.55 ppm. These broad resonances did not respond to ^1H decoupling, and it was concluded that 2 was fluxional and symmetrical with respect to dicarbollide CH_3 substituents on the NMR time scale. Repetition of these ^1H FTNMR experiments with CF_3COOD produced no dimunition of the upfield triplet and no apparent exchange of H by D when 2 was allowed to stand several days with 100 equiv of CF_3COOD in CD_2Cl_2 at −58 °C. Neutralization of CD_2Cl_2 solutions of 2 with triethylamine at −78 °C rapidly regenerated 1 in quantitative yield.

A low-temperature X-ray diffraction study[3] of 2 provided confirmation of the presence of a η^2,η^1-2,5-norbornenyl ligand and an agostic H atom (Figure 1) which is undoubtedly responsible for the −0.85 ppm ^1H NMR resonance. The unstable intermediate 2 consists of Rh symmetrically bound to the planar C_2B_3 face of a C_2B_9 icosahedral fragment and to a η^2,η^1-2,5-norbornenyl fragment, π-bound to C(N5)=C(N6), σ-bound to C(N3), and further bound to this ligand via H(N2A). The nearly linear projection of the bridgehead carbon atoms (C(N1), C(N7), and C(N4) on the C_2B_3 plane bisects the two carbon atoms in this plane and passes through B8, thus separating the icosahedral fragment into mirror-related halves. The exo addition of H^+ (or D^+) to 1 explains the retention of the agostic H atom resonance in the 2 produced when 1 is acidified with CF_3COOD. The precise nature of the fluxionality of 2 is not known although both intermolecular exchange and intramolecular 1,2-proton shift processes are feasible (Scheme I). The fluxional behavior observed in the present instance is quite likely analogous to that recently reported[4] with the 1,5-cyclooctadiene (COD) complex analogous to 2. In both the COD and NBD systems the bonding electron pair in the C–H bond of the agostic interaction nominally completes the complement of 18 electrons in the valence shell of the formal Rh^{3+} center.

After standing 20 h at 25 °C in CH_2Cl_2 solution, 2 is converted to 3, an isomer of 2. An X-ray diffraction study[5,6] of 3 revealed (Figure 2) the presence of a η^2-vinyl η^3-cyclopentenyl ligand in an 18-electron formal Rh^{3+} metallacarborane. The product 3 consists of Rh symmetrically bound to the planar C_2B_3 face of a C_2B_9 icosahedral fragment and to a η^2-vinyl η^3-cyclopentenyl ligand, π-bound to C(N5)=C(N6), and further bound to the allyl fragment C(N2), C(N3), and C(N4). This ligand is disordered about a noncrystallographic mirror through C(N1)–C(N7). The projection of C(N1)–C(N7) on the C_2B_3 bonding face of the icosahedron coincides with a line from B8 to the midpoint between C1 and C2. The mechanism proposed for the metal-assisted conversion of 2 to 3 is presented in Scheme I and is presumably driven by the formation of the allylic 18-electron Rh^{3+} center in 3 from the relatively unstable agostic species 2. The reactivity of 2 is remarkable when compared with the stability of the analogous $[(\eta^2,\eta^1\text{-2,5-norbornenyl})Rh(\eta\text{-}C_5H_5)]^+$ complex 4 studied by Lewis.[7] Complex 4 is stable at 25 °C for more than 24 h, contains no agostic H atom, and is not fluxional in the presence of CF_3COOH. These observations once again point up the differences between η-C_5H_5 and the corresponding dicarbollide species.

Thermolysis of 3 at 40 °C in C_6H_6 for 3 days results in the nearly quantitative formation of the (η^5-cyclopentadienyl)rhodacarborane derivative [*closo*-3-(η^5-$(C_5H_4(C_2H_5))$-1,2-$(CH_3)_2$-3,1,2-$RhC_2B_9H_9$], 5, which was unequivocally identified by high resolution mass spectra and ^1H FTNMR.[8] This aromatization reaction may be truly intramolecular since added rhodium catalyst pre-

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(3) Crystal data for 2: $C_{11}H_{24}RhB_9$; M_r = 356.5; red parallelepiped; orthorhombic; 0.1 × 0.2 × 0.6 mm, space group *Pbca*; a = 14.780 (3) Å, b = 14.097 (4) Å, c = 15.342 (4) Å; V = 3197 (1) Å^3; Z = 8; d(calcd) = 1.482 g cm^{-3}; T = 115 K. A total of 3513 unique reflections were collected of which 1963 were considered observed ($I \geq 3\sigma(I)$) and were used in subsequent calculations (UCLA Crystallographic Package and SHELX76), all of which were performed on the VAX 11/780 of the chemistry department (Syntex $P\bar{1}$ diffractometer; Mo Kα radiation; graphite monochromator; λ = 0.7107 Å, θ–2θ scan; 0 < 2θ < 54°; μ = 9.4 cm^{-1}). The structure was solved by Multan78. In the final least-squares cycle, based on F, 183 parameters were refined, including positionsl and anisotropic thermal parameters for one Rh, nins B, and nine C and positional and isotropic thermal parameters for two methyl C. Values for atomic scattering factors and anomalous scattering were taken from; "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV. Refinement is currently at R = 0.061 and R_w = 0.071. The goodness of fit is 1.91 as defined by $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ with N_o (number of observations) = 1963 and N_v (number of variables) = 183. All cage hydrogen atoms were located and included in the structure factor calculations, but not refined. No hydrogen atoms of the norbornenyl ligand other than the two on C(N2) were located. Positional parameters of agostic H(N2A) were refined, using only reflections having $(\sin\theta)/\lambda$ < 0.25 and then were included without further refinement.

(4) Speckman, D. M.; Knobler, C. B.; Hawthorne, M. F. *Organometallics*, **1985**, *4*, 426.

(5) Crystal data for 3: $C_{11}H_{24}RhB_9$: M_r = 356.5; yellow-orange parallelepiped; triclinic; space group $P\bar{1}$; a = 8.803 (4) Å, b = 7.949 (3) Å, c = 12.246 (4) Å; α = 94.69 (3)°, β = 95.16 (3)°, γ = 106.43 (3)°; V = 813.4 (6) Å^3; Z = 2; D(calcd) = 1.46 g cm^{-3}. A total of 4753 unique reflections were collected of which 4339 were considered observed ($I > 3\sigma(I)$ and were used in subsequent calculations (Syntex $P\bar{1}$ diffractometer; Mo Kα radiation; graphite monochromator; λ = 0.7107 Å; θ–2θ scan; 0 < 2θ < 60°; μ = 9.3 cm^{-1}). The structure was solved by the heavy-atom method using SHELX76. In the final least-squares cycle, based on F, 299 parameters were refined, including positional and anisotropic thermal parameters for one Rh, nine B, and eight C and positional and isotropic thermal parameters for two methyl C, four C of the disordered ligand, and nine H of the carborane icosahedron. Refinement is currently at R = 0.035 and R_w = 0.048. The goodness of fit is 1.77 (299 parameters).

(6) In the course of refinement of 3, it was discovered that the isotropic thermal parameter of one carbon atom (C(N4)) was found to be unusually high (B = ca 10 Å^2), and another peak of about 3 e Å^{-3} was found in the region of the η^2-vinyl η^3-cyclopentenyl ligand. This ligand occupies two different sites at occupancies 0.57 and 0.43 with nearly complete overlap for four of the seven atoms (C(N1), C(N2), C(N6), and C(N7)). Occupancy was constrained to total 1.0 and was refined for nonoverlapping atoms C(N4) and C(N4′) and applied without further refinement. C(N5)–C(N6) was constrained to be 1.37 Å, and C(N3)–C(N4) and C(N2)–C(N3) were constrained to be 1.42 Å. Hydrogen atoms were located on difference electron density maps. The two ligand sites are related by a noncrystallographic mirror through C(N1)–C(N7).

(7) Evans, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1971**, 1252; *J. Chem. Soc., Dalton Trans.* **1977**, 510.

cursors such as $[(PPh_3)_3RhCl]$ and $RhCl_3$ failed to affect the reaction at 25 °C. Due to a paucity of detailed information, further speculation regarding this mechanism is unwarranted at this time.

Acknowledgment. We gratefully acknowledge the Basic Science Division of the Department of Energy for the support of this research under Grant No. DE-AT03-80 ER10073.

Supplementary Material Available: Tables of atomic positions, thermal parameters, bond lengths and angles, and structure factor data for **2** and **3** (48 pages). Ordering information is given on any current masthead page.

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(8) ^1H NMR (C_6D_6, 25 °C, ppm); 4.64 (m, 2 H, cyclopentadienide C–H), 4.54 (m, 2 H, cyclopentadienide C–H), 1.97 (q, J = 7.5 Hz, 2 H, secondary C–H of ethyl group), 1.90 (s, 6 H, carboranyl methyl C–H), 0.80 (t, J = 7.5 Hz, 3 H, tertiary C–H of ethyl group). $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C, ppm): 6.15 (1), 4.12 (1), –0.33 (2), –8.28 (2), –13.36 (2), –14.87 (1). Mass spectrum: m/z $(RhC_{11}H_{24}(^{10}B)(^{11}B)_8)^+$ calcd 357.1800, obsd 357.1827.

Additions and Corrections

D. M. Roddick, M. D. Fryzuk, P. F. Seidler, G. L. Hillhouse, and J. E. Bercaw*: Halide, Hydride, Alkyl, and Dinitrogen Complexes of Bis(pentamethylcyclopentadienyl)hafnium. **1985**, *4*, 97.

In eq 12 on page 99, Cp^*_2MH has a subscript missing. The formula should read $Cp^*_2MH_2$.

On page 103, the experimental details for the preparation of $Cp^*_2HfCl_2$ (**2**) were incompletely reported. A revised preparation is given below. LiCp* was prepared by the method of Threlkel and Bercaw (*J. Organomet. Chem.* **1977**, *136*, 1). $HfCl_4$ (31.8 g, 0.099 mol) and LiCp* (31.0 g, 0.218 mol) were placed in a flask with 200 mL of xylene and refluxed under argon for 3 days. The xylene was then removed under vacuum, and the residue was suspended in 200 mL of CH_2Cl_2 and 200 mL of 4 M HCl. The CH_2Cl_2 layer was separated and the aqueous layer washed four times with 20-mL portions of CH_2Cl_2. The CH_2Cl_2 solutions were combined and dried over $MgSO_4$. Crystallization from CH_2Cl_2/petroleum ether afforded **2** in 76% yield (39.1 g).

Book Reviews

Chemical Mössbauer Spectroscopy. Edited by R. H. Herber. Plenum Press, New York, London. 1984. xiii + 378 pages. $59.50.

This book is the proceeding of a symposium entitled "Twenty-Five Years of Chemical Mössbauer Spectroscopy", held April 8–13, 1984, in St. Louis, MO, as part of the 187th national meeting of the American Chemical Society. The editor has done a remarkable job in getting this volume printed and published in less than 1 year, for a reasonable price. This was not achieved without some sacrifices however. The quality of the figures and the typescript varied considerably from chapter to chapter as might have been expected from the use of camera-ready manuscripts. Some chapters were particularly difficult to read because of the overlapping of subscripts and superscripts with the lines immediately below and above. Camera-ready copy also places the sources of errors in each chapter squarely on the individual contributors. Fortunately, except for two chapters, typographical errors are few.

Unfortunately the first chapter is the one which contains the most errors, which I hope are typographical, and this creates a poor impression. In this chapter the discussion of the origin of the isomer shift and its relation to the s electron density is confusing and that concerning the quadrupole interaction incorrect. The expression $\Delta E_Q = {}^1/_2\, e^2qQ(1 + \eta^2/3)^{1/2}$ is correctly given as the quadrupole splitting, but two lines later it is stated that the spectrum will be a Lorentzian-shaped doublet with $2\Delta E_Q$ splitting. A few lines below it is stated that when $\eta = 0$, $\Delta E_Q = e^2qQ/2$ and the quadrupole coupling constant, as defined by NQR (i.e., e^2qQ), is half the peak separation. Surely e^2qQ is twice the doublet separation. Later in this chapter ferrocene is reduced by removing an electron. These errors should have been eliminated by careful proofreading. I also found the sections listing data for many compounds very difficult to follow; these data should have been presented in tables.

The next two chapters were a pleasure to read. The first of these presents a clear summary of the phenomenon of high spin–low spin transitions and of light-induced crossover. The next, on the application of magnetic ordering phenomena, would be useful to those interested in carrying out research in this area of Mössbauer spectroscopy and particularly valuable as an aid to beginning researchers in the field. Both of these chapters, as does the chapter on organotin chemistry, emphasise the necessity of