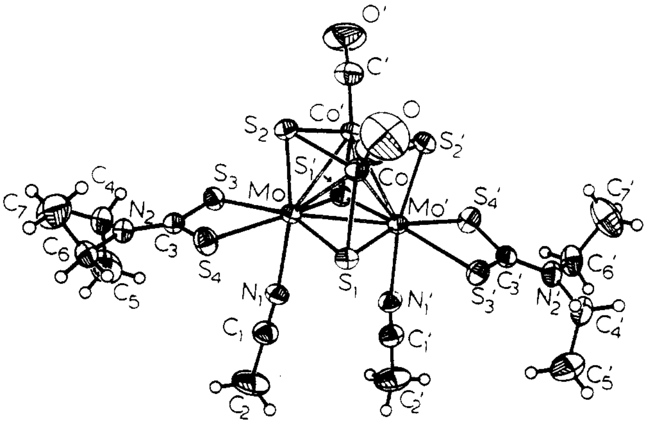

Figure 1. ORTEP drawing of $Co_2Mo_2(\mu_3\text{-}S)_4(S_2CNEt_2)(CO)_2(CH_3CN)_2$, **2**.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for $Mo_2Co_2S_4(CO)_2(CH_3CN)_2(S_2CNEt_2)_2$

	Bond Lengths		
Mo–Mo′	2.788 (1)	Co–S_1	2.184 (1)
Co–Co′	2.533 (1)	Co–S_2	2.197 (1)
Mo–Co	2.680 (1)	Co–S_2'	2.200 (1)
Mo–Co′	2.671 (1)	Mo–N_1	2.238 (2)
Mo–S_1	2.359 (1)	Co–C	1.753 (4)
Mo–S_1'	2.364 (1)	Mo–S_3	2.518 (1)
Mo–S_2	2.316 (1)	Mo–S_4	2.528 (1)
	Bond Angles		
Mo′MoCo	58.44 (1)	S_1MoS_1'	106.86 (3)
CoMoCo′	56.50 (1)	S_3MoS_4	69.82 (3)
Mo′CoMo	62.81 (1)	N_1MoS_3	78.85 (7)
Co′CoMo	61.58 (1)	N_1MoS_2	167.92 (7)
S_1CoS_2	109.20 (3)	MoS_1Mo'	72.36 (2)
S_1CoC	112.4 (1)	CoCO	176.9 (3)
S_2CoS_2'	105.94 (3)	MoN_1C_1	171.2 (3)

gous tungsten complex **3**[11] is prepared via the latter route starting from $W_2S_4(S_2CNEt_2)_2$.[12]

A single-crystal X-ray diffraction study was carried out on **2**.[13,14] The structure is illustrated in the figure, and selected bond distances and angles are given in the table. The molecule contains a $Co_2Mo_2(\mu_3\text{-}S)_4$ core. The four metal atoms are joined by six metal–metal bonds forming an approximate tetrahedron of C_{2v} symmetry. Each triangular face of the tetrahedron is capped by a sulfur atom to form the overall "thiocubane" core. Each cobalt atom is further bonded to a single terminal CO. The coordination environment about the cobalt atoms (discounting the M–M bonds) is very nearly tetrahedral. Each molybdenum atom is bound to two dithiocarbamate sulfur atoms and to the nitrogen of an acetonitrile molecule, in addition to three capping μ_3-S atoms. The coordination environment about the molybdenum is distorted octahedral. The molecule resides on a crystallographic C_2 axis which bisects the Mo′–Mo′ and Co–Co′ bonds.

The parent $Mo_2S_4(S_2CNEt_2)_2$ moiety appears as an essentially intact unit in the cluster, with the Mo–Mo′ bond length decreased very slightly from 2.817[15] to 2.788 Å. The Mo–S–Mo′ bridge angles and bond lengths have changed little. However, the dihedral angle between the MoS_1S_1' and $Mo'S_1S_1'$ planes has opened up from 147.9° to 164.4°, and the initially terminal Mo=S bonds have elongated from 2.09 to 2.312 Å as their role changes to a bridging μ_3 mode, wherein the sulfur atoms are bound to two cobalt atoms as well as to the original Mo center. The binding of two acetonitrile molecules raises the overall cluster electron count to 60 electrons, the predicted number for a stable M_4 tetrahedral cluster with six M–M bonds.[16]

The present complexes provide an interesting model for the promotion effect of cobalt in Co—Mo catalysts. When the Co fragments bind to the terminal Mo=S groups, open sites on the Mo centers are produced; i.e., the parent $Mo_2S_4(S_2CNEt_2)_2$ shows no tendency to bind CH_3CN, but the dicobalt adduct (thiocubane) clearly binds two CH_3CN ligands. Presumably, the weakened Mo–S bonding along the z axis makes the d_{z^2}, d_{xz}, and d_{yz} orbitals of molybdenum more available as acceptor orbitals, leading to binding of acetonitrile at the sixth coordination site. Thus, the sites trans to Mo–S are analogous to vancancies on Mo whose affinity for ligands may be enhanced by the presence of cobalt.

Acknowledgment. We wish to thank Dr. C. S. Day of Crystalytics Co. for carrying out the single-crystal diffraction study and Dr. D. Van Engen of the Analytical Division of Exxon Research and Engineering Co. for completion of the powder diffraction experiments.

Supplementary Material Available: Crystallography details, including tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and structure factors (26 pages). Ordering information is given on any current masthead page.

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(11) IR spectra of **3** (KBr pellet): 1961 (s), 1938 (s), 1505 (s), 1456 (w), 1436 (m), 1358 (w), 1300 (w), 1273 (m), 1209 (m), 1147 (m), 1095 (w), 1075 (m), 915 (w), 847 (w), 783 (w), 521 (m), 394 (w), 368 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{26}N_4O_2S_8Co_2W_2$: C, 18.33; H, 2.50; N, 5.34; S, 24.46; W, 35.07. Found: C, 18.03; H, 2.49; N, 5.27; S, 23.64; W, 35.27. X-ray powder diffraction experiments ($6 \le 2\theta \le 62°$, Cu radiation, manual Phillips diffractometer) indicate **2** and **3** are isomorphous, based on relative intensities and d spacings of diffraction peaks [**2** (powder data), a = 21.220 (3) Å, b = 10.666 (2) Å, c = 13.600 (2) Å, β = 99.52 (1)°; **3** (powder data), a = 21.08 (5) Å, b = 10.56 (3) Å, c = 13.54 (3) Å, β = 99.53 (7)°].

(12) Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.*, in press.

(13) The complete structure determination was carried out by Dr. C. S. Day of Crystalytics Co., P. O. Box 82286, Lincoln, NB 68501.

(14) Crystal data: space group $C2/c—C_{2h}^6$ (No. 15),[17] with a = 21.248 (5) Å, b = 10.682 (3) Å, c = 13.617 (4) Å, β = 99.53 (2)°, V = 3048 (1) $Å^3$, and Z = 4. The structure was solved by using direct methods and Fourier difference techniques. R_F = 0.027 and R_{wF} = 0.026 for 2896 independent reflections with $I > 3.0\sigma(I)$ and $3° < 2\theta < 55°$ (Mo K_α radiation). Anisotropic thermal prameters were utilized for all non-hydrogen atoms.

(15) Hunecke, J. T.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3698–3699.

(16) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305–5315.

(17) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. 1.

(18) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

An α-Lithio Boronic Ester from an α-Trimethylstannyl Boronic Ester

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Received May 20, 1985

Summary: Pinacol (1-chloroethyl)boronate (**1a**) and lithiotrimethylstannane have yielded pinacol [1-(trimethyl-

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[1] On leave from the University of Ulster at Coleraine, Aug-Dec, 1984.

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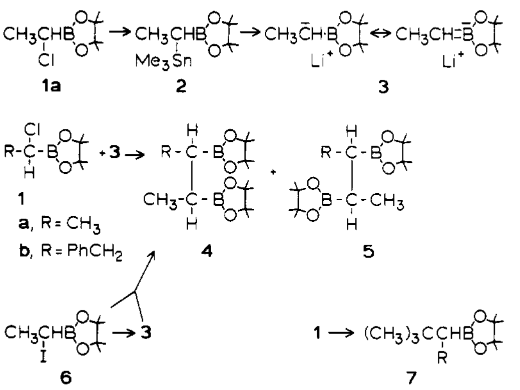
stannyl)ethyl]boronate (2), which with methyllithium at −100 °C yields pinacol 1-lithioethylboronate (3). Capture of 3 by (α-haloalkyl)boronic esters results in carbon–carbon bond formation. Generation of 3 from pinacol (1-iodoethyl)boronate with *tert*-butyllithium is followed by rapid reaction with the remaining (1-iodoethyl)boronate.

Carbanions stabilized by a single neighboring boron atom have been generated by deprotonation of the methyl group of 9-methyl-9-borabicyclo[3.3.1]nonane[2] or *B*-methyl-*B*,*B*-dimesitylborane.[3] Attempts to prepare a carbanion stabilized by a single boronic ester group in this manner have failed, though deprotonation of methylenediboronic esters has proved feasible, and observed borylcarbanion properties correlated by simple molecular orbital calculations suggest that mono(dialkoxyboryl)carbanions should be less basic than benzylic anions.[4] Bis(dialkoxyboryl)carbanions are also easily generated by abstraction of a boryl group from tris(dialkoxyboryl)methanes,[5] but attempts to deborylate *gem*-bis(dialkoxyboryl)alkanes have failed.[4,6] Desilylation of α-trimethylsilyl boronic esters by fluoride and a proton source or benzaldehyde has been demonstrated,[7] but the intermediacy of the carbanion was not proved and the synthetic utility appeared limited.

We have now found that pinacol (1-lithioethyl)boronate (**3**) can be generated from pinacol [1-(trimethylstannyl)ethyl]boronate (**2**) and methyllithium at −100 °C. Reaction of **3** with α-chloro boronic esters (**1**)[8] yields the diastereomeric coupling products **4** and **5**. Borate complex formation and rearrangement[9] is the probable route. This coupling is of potential value in designing convergent chiral syntheses based on recently developed boronic ester chemistry.[10] Its major limitation is the expected failure to preserve configuration at the carbanionic carbon, though the α-chloride should be displaced with inversion. In accord with expectation, though not full proof, pinacol (*S*)-(1-chloroethyl)boronate (**1a**) was prepared by transesterification of the (*R*,*R*)-2,3-butanediol ester[11] and reacted with (trimethylstannyl)lithium to form **2**, which was converted to **3** and coupled with (*S*)-**1a** to yield a dextrorotatory ~1:1 mixture of **4a** and **5a**.[12,13]

Acetophenone with **3** (−100 °C, then 25 °C) yielded ~1:1 (*Z*)- and (*E*)-2-phenyl-2-butene, based on NMR evidence.[14] There is ample precedent for such Wittig condensations



in borylcarbanion chemistry.[4,5] Attempted methylation of **3** with methyl iodide was unsuccessful.

Generation of **3** was also achieved by reaction of pinacol (1-iodoethyl)boronate (**6**)[12,15] with *tert*-butyllithium (or lithium (dimethylamino)naphthalenide) at −100 °C. However, even when **6** was added to excess *tert*-butyllithium, the only product (84–91%) was the **4a**/**5a** mixture from coupling of **3** with **6**. The abstraction of iodine from **6** is an unprecedented reaction for an α-halo boronic ester. The α-chloro boronic esters **1** were shown to react with *tert*-butyllithium in the normal manner[8] to form the α-*tert*-butyl substitution products: **7a**, bp 61–62 °C (4 torr) (78%);[12] **7b**, bp 83 °C (0.2 torr) (85%), but contained ~15% of an isomer, perhaps the O-migration product.[12]

Experimental Data. Pinacol (1-chloroethyl)boronate (**1a**), bp 48–52 °C (2 torr), was prepared from pinacol (dichloromethyl)boronate[16] and methyllithium by the procedure described for related compounds.[11,17] A solution of 17.34 g (91 mmol) of **1a** in ~75 mL of THF was cooled to −78 °C, and 91 mmol of titrated 0.4 M (trimethylstannyl)lithium (from trimethyltin chloride and lithium chips[18]) in THF was added dropwise over 45 min. The mixture was left at 25 °C overnight and refluxed 5 h to complete the reaction, during which time a white precipitate was produced. The pinacol [1-(trimethylstannyl)ethyl]boronate was distilled, bp 75–78 °C (3 torr); 21.2 g (73%).[19]

To prepare pinacol (1-lithioethyl)boronate (**3**), a solution of 2.07 g (6.5 mmol) of **2** in 50 mL of THF was stirred at −100 °C (95% ethanol/liquid nitrogen slush bath), 4.14 mL (6.5 mmol) of 1.57 M methyllithium in ether was added dropwise down the side of the flask over a period of 15 min, and the solution was stirred 30 min more at −100 °C. A solution of 1.239 g (6.5 mmol) of pinacol (1-chloroethyl)boronate (**1a**) in 1 mL of THF was added down the side of the flask, and the mixture was allowed to warm to 25 °C overnight. The THF codistilled (vacuum) with tetramethyltin, *m*/*e* 180 with isotopic satellites. The residue was treated with water and petroleum ether, and the or-

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(2) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854–6856.

(3) Wilson, J. W. *J. Organomet. Chem.* **1980**, *186*, 297–300.

(4) Matteson, D. S.; Moody, R. J. *Organometallics* **1982**, *1*, 20–28.

(5) (a) Castle, R. B.; Matteson, D. S. *J. Organomet. Chem.* **1969**, *20*, 19–28. (b) Matteson, D. S.; Thomas, J. R. *J. Organomet. Chem.* **1970**, *24*, 263–271. (c) Matteson, D. S.; Jesthi, P. K. *J. Organomet. Chem.* **1976**, *110*, 25–37. (d) Matteson, D. S.; Moody, R. J. *J. Org. Chem.* **1980**, *45*, 1091–1095.

(6) Moody, R. J.; Matteson, D. S. *J. Organomet. Chem.* **1978**, *152*, 265–270.

(7) Tsai, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236–341.

(8) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 1529–1535.

(9) Matteson, D. S.; Mah, R. W. H. *J. Am. Chem. Soc.* **1963**, *85*, 2599–2603.

(10) (a) Matteson, D. S.; Ray, R.; Rocks, R. R.; Tsai, D. J. S. *Organometallics* **1983**, *2*, 1536–1543. (b) Matteson, D. S.; Sadhu, K. M. *J. Am. Chem. Soc.* **1983**, *105*, 2077–2078.

(11) Sadhu, K. M.; Matteson, D. S.; Hurst, G. D.; Kurosky, J. M. *Organometallics* **1984**, *3*, 804–806.

(12) New compounds were fully characterized by NMR and elemental analyses (except **7a**, exact mass). Data for **1b** and **2** are included here.[19,20]

(13) Solution used for ^{13}C NMR: α_{546} +0.34°. The specific rotation of **5a** is not known. The ~90% ee of **1a** was confirmed by transesterification with (+)-pinanediol.[11] **2** was not checked.

(14) 90-MHz ^{1}H NMR: δ 1.6, 1.8 (d's, 3, CH_3), 2.0 (s, 3, CH_3), 5.55, 5.85 (q's, 1 C═CH), with small long-range couplings, 7.25 (m, 5 C_6H_5), 1.2 (pinacol borate impurity). Compare data for 1-phenylpropenes: Dewar, M. J. S.; Fahey, R. C. *J. Am. Chem. Soc.* **1963**, *85*, 3645–3648.

(15) From **1a** and sodium iodide in acetone, bp 61–62 °C (1.7 torr).

(16) Wuts, P. G. M.; Thompson, P. A. *J. Organomet. Chem.* **1982**, *234*, 137–141.

(17) Characterization of **1a**: Matteson, D. S.; Sadhu, K. M.; Peterson, M. L., manuscript in preparation.

(18) Nöth, H.; Schwerthöffer, R. *Chem. Ber.* **1981**, *114*, 3056–3062. Based on procedure by: Tomborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 181–184.

(19) 200-MHz ^{1}H NMR: δ 0.114 (s, with Sn satellites, J = 48.3 and 49.5 Hz, 9, $SnCH_3$), 0.696 (q, J = 7.4 Hz, 3, $CHCH_3$), 1.213 (d, J = 7.2 Hz, 1, $BCHCH_3$), 1.222 (s, 12, $OC(CH_3)_2$). 50.3-MHz ^{13}C NMR: δ −10.17 (with Sn satellites, J = 307 and 322 Hz, $SnCH_3$), 1.5 (br, BCHSn), 10.94 (CCH_3), 24.88, 24.99 ($OC(CH_3)_2$), 82.34 ($OC(CH_3)_2$). the proton-coupled spectrum yielded J_{C-H} values: $SnCH_3$ (q) 128.2, $CHCH_3$ (q of d's) 126.3, 3.3, $C(CH_3)_2$ (q of overlapping q's) 125.8, ~5, $OCCH_3$ (m) ~3.5 Hz. Anal. Calcd for $C_{11}H_{25}BO_2Sn$: C, 41.44; H, 7.90; B, 3.39; Sn, 37.23. Found: C, 41.26; H, 7.84; B, 3.49; Sn, 36.95.

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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Received June 26, 1985

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; α = 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.

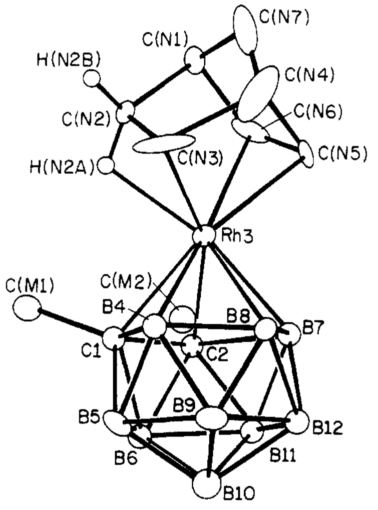
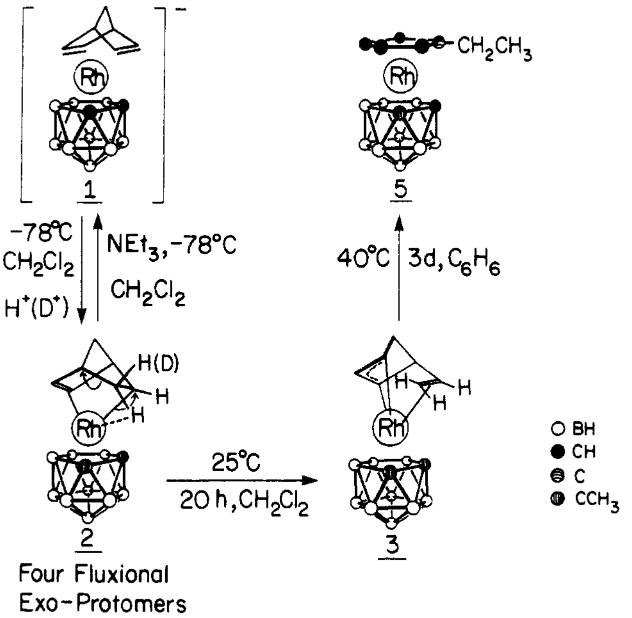


Figure 1. Molecular structure of the unstable intermediate **2**. Hydrogen atoms, except for those on C(N2), have been omitted for clarity. Selected bond lengths (Å): Rh···C(N2) = 2.36 (1); Rh–H(N2A) = 1.9 (3); Rh–C(N3) = 2.08 (1); Rh···C(N4) = 2.73 (2); Rh–C(N5) = 2.14 (1); Rh–C(N6) = 2.27 (1); Rh–C1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

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