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A ^{11}B NMR Study of the *closo*-Hydridorhodacarborane $3,3\text{-}[(C_2H_5)_3P]_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$ Prepared in Situ from $3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$

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A complete assignment of the ^{11}B NMR spectrum (111.8 MHz) of $3,3\text{-}[(C_2H_5)_3P]_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$ (Ia) is proposed on the basis of ^{11}B NMR data obtained from specifically deuterated derivatives of I and from $3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}9,12\text{-}Br_2\text{-}3,1,2\text{-}RhC_2B_9H_9$ and $6\text{-}Ph\text{-}3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{10}$. The ^{11}B NMR of $3,3\text{-}[(C_2H_5)_3P]_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$ in tetrahydrofuran consists of five resonances of relative intensity 1:1:2:2:3 (reading upfield) which are assigned to B(10), B(8), B(9,12), B(4,7), B(6), and B(5,11), respectively.

Introduction

The first metallocarborane catalyst for the hydrogenation and isomerization of olefins, $3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H,3,1,2\text{-}RhC_2B_9H_{11}$ (I),[1] also catalyzes the exchange of terminal boron–hydrogen bonds for deuterium in the presence of D_2.[2,3] These exchanges were found to proceed for a wide variety of carborane and metallocarborane substrates, and, during these exchanges, deuteration also occurs at B–H vertices in I. For determination of the specificity for self-deuteration of I, the ^{11}B NMR study presented herein was undertaken. Our goal was to completely assign the ^{11}B NMR spectrum of I and relate this information to a mechanism for the B–H/D exchange catalyzed by I and other metallocarboranes.

The solid-state structure of I has been determined by a single-crystal X-ray diffraction study[4] and found to be that of a regular icosahedron with the rhodium vertex symmetrically bonded to the pentagonal face of the dicarbollide ligand. For reasons discussed below, the ^{11}B NMR spectrum of I consists of broad, poorly resolved resonances.[1] With the discovery[5] that substitution of triethylphosphine ligands for the triphenylphosphine ligands in I is accompanied by a marked improvement in the ^{11}B NMR spectrum of the derived complex $3,3\text{-}[(C_2H_5)_3P]_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$ (Ia), it became feasible to attempt an assignment of the spectrum.

An assignment of the ^{11}B NMR spectrum of the $1,2\text{-}C_2B_9H_{12}^-$ ion has been reported by Hawthorne et al.[6,7] and others.[8] The ^{11}B NMR spectrum of $(C_2B_9H_{11})_2Co^-$ has been assigned by Todd and co-workers.[8] The present study provides a complete assignment of the ^{11}B spectrum of Ia. Details of the mechanism for the B–H/D exchange catalyzed by I will be reported at a later date.

Results and Discussion

While ^{11}B NMR spectroscopy has found widespread application in the chemistry of boron hydrides, metalloboranes, and metallocarboranes, the ^{11}B NMR spectra of metallocarboranes with bulky dissociable ligands have proven somewhat less amenable to analysis. Broad resonances are often observed for these complexes, especially for those which contain two metal-bound triphenylphosphine ligands. It was determined however that substitution of triethylphosphine for triphenylphosphine in I greatly improved the ^{11}B NMR spectrum of the derived complex. The 111.8-MHz ^{11}B NMR spectrum of I and $3,3\text{-}[(C_2H_5)_3P]_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$ (Ia) in tetrahydrofuran (THF) solution are presented in Figure 1 for comparison. The numbering system employed throughout this paper is presented in the right side of Figure 1.[6]

This dramatic difference between the ^{11}B NMR spectra of I and Ia is most probably due to changes in the rate of molecular tumbling for these two species in solution. The longitudinal relaxation times (T_1) are relatively short for boron nuclei due to the quadrupole moment of both ^{10}B and ^{11}B.[9] The presence of bulky triphenylphosphine ligands in I apparently increases the molecular correlation time. This should lead to effective quadrupolar relaxation and thus to broad ^{11}B NMR resonances for I. In contrast, the presence of the less bulky triethylphosphine ligands in complex Ia could afford an increase in the rate of tumbling (corresponding to decrease in the molecular correlation time). This would provide an increase in T_1, resulting in diminished ^{11}B NMR line widths.[10,11]

The ^{11}B NMR spectrum of Ia in THF solution indicates the presence of a mirror plane (the spectrum contains 5 resonances of relative area 1:1:2:2:3 reading upfield); this is indicative of a higher degree of symmetry for Ia in solution than is observed for I in the solid state.[4] This increase in symmetry is accounted for by a rapid rotation of the $Rh(L)_2(H)$ vertex in Ia about the center of the pentagonal face of the dicarbollide ligand.[12]

The mirror symmetry indicated for Ia would lead ideally to the observation of six resonances in the ^{11}B NMR spectrum of relative intensity 1:1:1:2:2:2. The presence of the weight three resonance observed for Ia is attributed to coincidental overlap of the resonance for a unique boron (B(6), B(8), or B(10)) with the resonance due to one of the symmetry-equivalent pairs (B(4,7), B(5,11), or B(9,12)) (vide infra).

It was determined during the course of this study that samples of I in THF solution, when treated with excess triethylphosphine, gave ^{11}B NMR spectra identical with those

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(1) T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 4674 (1974).

(2) E. L. Hoel and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 4676 (1974).

(3) E. L. Hoel, M. Talebinasab-Savari, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **99**, 4356 (1977).

(4) G. E. Hardy, K. P. Callahan, C. E. Strouse, and M. F. Hawthorne, *Acta Crystallogr., Sect. B*, **32**, 264 (1976).

(5) The complex $3,3\text{-}[(C_2H_5)_3P]_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$ was first synthesized and completely characterized by R. T. Baker of these laboratories.

(6) For continuity, an older numbering system is used to describe the position of substitution in $7,8\text{-}C_2B_9H_{12}^-$ (referred to as $1,2\text{-}C_2B_9H_{12}^-$ in this paper). Under this system, the numerical prefix, which assigns the position of substitution, is the same for both the $C_2B_9H_{12}^-$ derivatives and the respective derivatives of I.

(7) D. V. Howe, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, *Inorg. Chem.*, **10**, 2516 (1971).

(8) A. R. Siedle, G. M. Bodner, and L. J. Todd, *J. Organomet. Chem.*, **33**, 137 (1971).

(9) S. G. Shore, in "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, 1975, p 95.

(10) E. D. Becker, "High Resolution NMR", Academic Press, New York, 1969, p 206.

(11) This explanation has been offered to account for the broad ^{11}B NMR resonances found in metalloboranes which contain bulky arylphosphines: J. D. Kennedy and J. Staves, *Z. Naturforsch., B*, **34**, 808 (1979); E. L. Muetterties, *Rev. Pure Appl. Chem.*, **29**, 585 (1972).

(12) T. B. Marder, R. T. Baker, J. A. Long, and J. A. Doi, to be submitted for publication.

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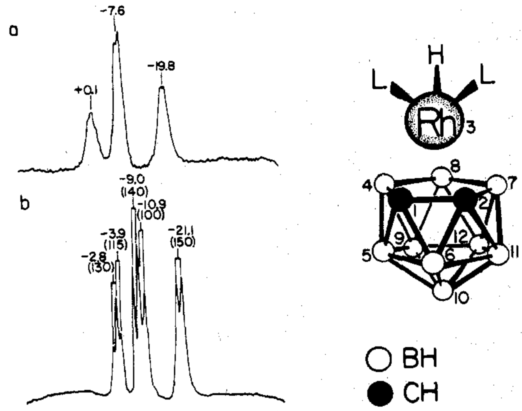

Figure 1. 111.8-MHz ^{11}B NMR spectra of 3,3-L_2-3-H-3,1,2-$RhC_2B_9H_{11}$: (a) L = PPh_3 (I); (b) L = $P(C_2H_5)_3$ (Ia).

which are observed for complex Ia in the same solvent. The hydridorhodacarboranes in this study were prepared and characterized as the bis(triphenylphosphine) complexes. The ^{11}B NMR spectra reported here are for the bis(triethylphosphine) complexes prepared in situ.

4,5,6,7,11-D_5-1,2-$C_2B_9H_7^-$ was prepared by base degradation of 3,4,5,6,7,11-D_6-1,2-$C_2B_{10}H_6$ according to a literature procedure.[13] 6-Ph-$C_2B_9H_{11}^-$ was prepared analogously from 6-Ph-$C_2B_{10}H_{11}$.[14] 9,12-Br_2-1,2-$C_2B_9H_{10}^-$ was prepared by base degradation of 9,12-Br_2-1,2-$C_2B_{10}H_{10}$.[15] All monoanions were isolated as the tetramethylammonium salts and were dried over P_2O_5 in vacuo. (μ,4,7,8,9,12-D_6-1,2-$C_2B_9H_6^-$) was prepared from K^+(1,2-$C_2B_9H_{12}^-$) in 6 M DCl/D_2O (6 days, 25 °C).[7] The ^{11}B NMR spectrum of this species revealed partial exchange had also occurred at B(5,11); only B(10) and B(6) retained complete coupling to terminal hydrogen indicating these sites had not undergone exchange.

The derivatives of I were prepared from the appropriate 1,2-$C_2B_9H_{12}^-$ derivative and $(Ph_3P)_3RhCl$ in refluxing ethanol according to a procedure developed in this laboratory[2] (eq 1).

$$C_2B_9H_{12}^- + (Ph_3P)_3RhCl \xrightarrow[C_2H_5OH]{} (Ph_3P)_2(H)RhC_2B_9H_{11} + Ph_3P + Cl^- \quad (1)$$

Typically, the reactions were complete after 10–15 min, at which time the hydridorhodacarboranes were isolated by Schlenk filtration, washed with ethanol, and dried in vacuo.

No detectable scrambling of the deuterium label was observed in these experiments. This is due to both the short reaction times and the presence of triphenylphosphine (a product of reaction I) which has been shown to effectively inhibit the B–H/D exchange catalyzed by I.[2,3] It is of note that I prepared from bridge-deuterated 1,2-$C_2B_9H_{11}D^-$ was found to contain only Rh–D ($\nu_{Rh\text{-}D}$ at 1520 cm^{-1}) with no trace of Rh–H detectable by IR (eq 2). This conclusively establishes that the hydride in I results from the oxidative addition of the bridging hydrogen in 1,2-$C_2B_9H_{12}^-$.

$$(\mu\text{-D})\text{-}1,2\text{-}C_2B_9H_{11}^- + (Ph_3P)_3RhCl \xrightarrow[C_2H_5OH]{} (Ph_3P)_2(D)RhC_2B_9H_{11} \quad (2)$$

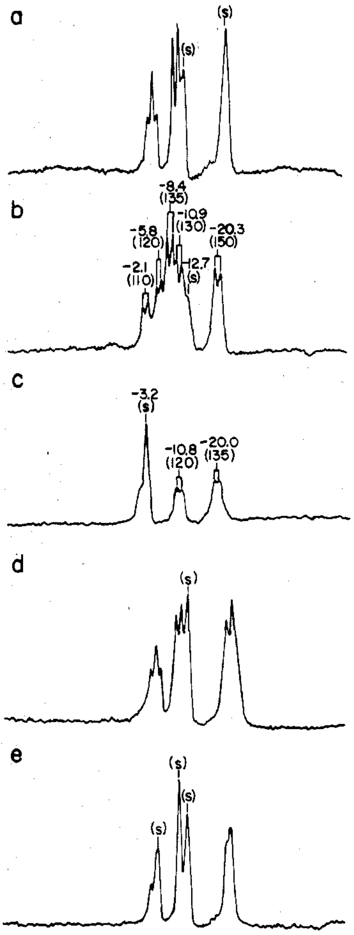

Figure 2. 111.8-MHz ^{11}B NMR spectra of (a) 4,5,6,7,11-D_5-(Ia), (b) 6-Ph-(Ia), (c) 9,12-Br_2-(Ia), (d) 3,4,7-D_3-(Ia), and (e) 6,10-H_2-(Ia).

The 111.8-MHz ^{11}B NMR spectrum of Ia in tetrahydrofuran, prepared (in situ) from 4,5,6,7,11-D_5-(I), is shown in Figure 2a. Only the resonances at −2.8, −3.9, and −9.0 ppm exhibit coupling to terminal hydrogens. The resonance of weight two at −9.0 ppm must therefore be due to the symmetry-equivalent pair of boron atoms B(9,12). The resonance at −2.8 and −3.9 ppm must be due to B(8) and B(10) (indefinite order). The lack of B–H coupling in the weight three resonance at −21.0 ppm indicates this must contain the resonance for the remaining unique boron atom B(6).

This assignment is supported by the ^{11}B NMR spectrum of 6-Ph-(Ia) prepared (in situ) from 6-Ph-(I) in tetrahydrofuran solution (Figure 2b). Replacement of a phenyl group for hydrogen on boron causes the area 3 resonance at −20.3 ppm to decrease to an area of 2. The resonance due to B(6) is shifted downfield and appears as a singlet at −12.7 ppm.

The assignment of B(9,12) is supported by the ^{11}B NMR spectrum in THF of 9,12-Br_2-(Ia) prepared (in situ) from 9,12-Br_2-(I) (Figure 2c). The borons due to B(9,12) appear as a singlet at −3.2 ppm. Substitution of Br for terminal hydrogen on boron is generally accompanied by a shift to lower field of the ^{11}B NMR resonance due to the substituted boron.[16] The resonances which remain unassigned in the spectrum of 9,12-Br_2-(Ia) exhibit chemical shifts nearly identical with those observed for Ia suggesting that the resonance at −9.0 ppm in the spectrum of Ia has moved to lower field in the spectrum of 9,12-Br_2-(Ia).

The ^{11}B NMR spectrum of Ia in THF prepared (in situ) from 3,4,7-D_3-(I) is shown in Figure 2d. The resonance of area two at −11.0 ppm appears as a singlet and is thus assigned to B(4,7). The resonance due to the remaining symmetry-

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(13) We are grateful to Dr. E. L. Hoel for the sample of 3,4,5,6,7,11-D_6-1,2-$C_2B_{10}H_6$ which was prepared from (μ_4,5,6,7,8,9,10-D_{10})$B_{10}H_4$ (J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 1804 (1962)) according to the procedure of L. J. Todd, *Inorg. Synth.*, **11**, 19 (1968).

(14) M. F. Hawthorne and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 896 (1968).

(15) H. D. Smith, T. Knowles, and H. A. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

(16) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds", W. A. Benjamin, New York, 1969, pp 407–8.

equivalent pair of borons, B(5,11), must therefore occur at −21.1 ppm.

Only the resonances due to B(8) and B(10) (which occur at low field) remain to be assigned. The ^{11}B NMR spectrum of 6,10-H_2-(Ia) in THF prepared in situ from 6,10-H_2-(I) is shown in Figure 2e. Only the resonance at −2.8 retains coupling to terminal hydrogen. The resonance due to B(6) has previously been shown to occur at −21.0 ppm (vide supra), and therefore the resonance at −2.8 ppm is assigned to B(10). The remaining resonance at −3.9 ppm is assigned to B(8) by elimination.

It is of interest to compare the present assignment with that of the analogous metallocarborane $(C_2B_9H_{11})_2Co^-$.[8] The assignments (reading upfield) are B(10), B(8), B(9,12), B(4,7), B(6), and B(5,11) for Ia and B(8), B(10), B(9,12), B(4,7), B(5,11), and B(6) for $(C_2B_9H_{11})_2Co^-$. All resonances in the ^{11}B NMR of Ia are found at higher field than those observed for $(C_2B_9H_{11})_2Co^-$ with the exception of B(6). Overall, however, the two spectra appear quite similar. The different assignment for B(8) and B(10) for two such similar spectra should serve as a caution against assigning ^{11}B NMR resonances by comparison to "similar" species.

Experimental Section

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer. ^{11}B NMR (111.8 MHz) were obtained in the Fourier-transform mode on an instrument designed and constructed by Professor F. A. L. Anet of this department.

Materials. All solvents were reagent grade and, except where otherwise noted, were distilled under argon from the appropriate drying agent immediately prior to use. Ethanol (absolute) was saturated with nitrogen but otherwise used without further purification. Tetrahydrofuran and diethyl ether (Mallinckrodt) were dried over alumina and distilled from potassium. $(Ph_3P)_3RhCl$ was prepared from $RhCl_3\cdot 3H_2O$ (Matthey-Bishop) according to a procedure in the literature.[17] $K^+(1,2\text{-}C_2B_9H_{12}^-)$ was prepared according to the literature[18] and stored in a nitrogen-filled glovebox. DCl (20% in D_2O, 99+ atom % D, Alfa-Ventron) was diluted immediately prior to use with D_2O in a nitrogen-filled glovebag.

$(CH_3)_4N^+(\mu,4,7\text{-}D_3\text{-}1,2\text{-}C_2B_9H_9^-)$. $K^+(1,2\text{-}C_2B_9H_{12}^-)$ (1.0 g, 5.8 mmol) was weighed in the drybox into a 100-mL round-bottom flask equipped with a side arm and stopcock. The flask was sealed with a gas-inlet tube equipped with a stopcock, transferred to the bench, and fitted to a nitrogen line. D_2O (1 M in DCl, 15 mL) was syringed into the flask, and the flask was shaken to achieve a homogeneous solution. The flask was then sealed under a positive pressure of N_2. After 3 days a sample of the solution was obtained with a syringe and transferred to a nitrogen-filled NMR tube. The ^{11}B NMR of this sample revealed complete deuteration at B(4,7) and the B–H–B bridge.

An additional 20 mL of D_2O was added to the flask, followed by $(CH_3)_4NCl$ (0.73 g, 6.7 mmol) in 5 mL of D_2O. The precipitate which formed was isolated by Schlenk filtration, washed with three 10-mL portions of D_2O and dried at 80 °C over P_2O_5 in vacuo. A ^{11}B NMR spectrum of the product was obtained in CH_3CN.

Preparation of NMR Samples of I and Derivatives of I. *Caution*! $(C_2H_5)_3P$ is toxic: gloves should be worn, and these operations should be performed in an efficient fume hood.

The sample of I (15–20 mg) was added to a 5-mm NMR tube which was then fitted with a rubber septum and purged with N_2 utilizing two syringe needles. After 5 min, tetrahydrofuran (0.8 mL) was added to the sample with a syringe. Immediately thereafter, $(C_2H_5)_3P$ (0.15 mL) was added with a syringe. The needles were removed and the sample was shaken to dissolve the metallocarborane. ^{11}B NMR spectra of the samples so prepared were recorded after a period of 45 min to allow for complete phosphine exchange.

Acknowledgment. We thank the Office of Naval Research and the National Science Foundation (Grant No. CHE-78-05679) for partial support of this work.

Registry No. I, 53687-46-0; 4,5,6,7,11-D_5-(I), 73274-24-5; 6-Ph-(I), 73246-77-2; 9,12-Br_2-(I), 73274-25-6; 3,4,7-D_3-(I), 73246-78-3; 6,10-H_2-(I), 73246-81-8; Ia, 73246-82-9; 4,5,6,7,11-D_5-(Ia), 73261-74-2; 6-Ph-(Ia), 73246-83-0; 9,12-Br_2-(Ia), 73274-26-7; 3,4,7-D_3-(Ia), 73246-79-4; 6,10-H_2-(Ia), 73246-80-7; $(CH_3)_4N^+(\mu,4,7\text{-}D_3)\text{-}1,2\text{-}C_2B_9H_9^-$, 73396-33-5; $K^+(1,2\text{-}C_2B_9H_{12}^-)$, 12304-72-2.

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(17) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

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