

exchange of terminal {BH} groups in boranes, carboranes, and metalloboranes,¹⁹ as well as the hydrosilylation of ketones.²⁰ In THF solution (55°, 10⁻² M I or II), 1.6 mmol of acetophenone was quantitatively hydrosilylated (2.0 mmol of diphenylsilane used) in ~17 hr as determined by ¹H nmr spectroscopy of the hydrosilylated product.

We have successfully expanded this chemistry to include the iridium congeners and are presently exploring the catalytic capabilities of these complexes. Several rhodium complexes from aryl- and alkyl-substituted [C₂B₉H₁₂]⁻ anions have been synthesized and have also proved to be hydrogenation catalysts. Intriguing reactions of ruthenium complexes with carborane anions have also been discovered, and the characterization and catalytic properties of the products are currently under investigation in these laboratories.

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Transition Metal Catalyzed Exchange of Deuterium Gas with Terminal Boron-Hydrogen Bonds in Carboranes, Metallocarboranes, and Other Boron Compounds

Sir:

Deuterated boron hydrides may be prepared by synthesis from B₂D₆¹⁻³ or by deuterium exchange on a boron hydride employing B₂D₆,^{2,3} D₂O,^{1,4} DCl catalyzed by AlCl₃,⁵ or DCl catalyzed by dioxane⁵ as the deuterium sources. Deuterated carboranes and metallocarboranes have only been prepared from deuterated decaboranes.^{6,7} We wish to report that a number of group VIII hydrogenation catalysts will effect the exchange of deuterium gas with terminal B-H bonds in a wide variety of boron compounds, including carboranes, metallocarboranes, and boron hydrides.

We recently reported the first example of oxidative addition of a B-H bond to a transition metal.⁷ The

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reaction was an "ortho" metallation in an L₃IrCl complex where L was the carboranylphosphine 1-(PMe₂)-1,2-C₂B₁₀H₁₁ (I), a reaction analogous to well-known ortho metallations in arylphosphine complexes.⁸

In the presence of catalytic amounts of (PPh₃)₃-RuHCl, an effective catalyst for the specific ortho deuteration of triphenylphosphine,⁹ I has been found to exchange hydrogen atoms for deuterium gas at boron atoms but not at carbon atoms. A mechanism involving exchange only *via* an "ortho" metallated, complexed carboranylphosphine could introduce a maximum of four deuterium atoms into I. However, mass spectral analysis of the product revealed species with more than four deuterium atoms per molecule, ruling out intramolecular exchange on the carboranylphosphine as the sole mechanism of deuterium incorporation. Subsequent experiments have revealed that a wide variety of noncomplexing boron compounds undergo similar catalytic exchange.

In a typical procedure, 1 mmol of the substrate and 0.05 mmol of the catalyst were stirred under N₂ in 20 ml of toluene at temperatures from 65 to 100° while deuterium gas was bubbled through the solution at a rate of about 3 ml/min. Table I lists the results for a

Table I. Preliminary Results of Selected Catalytic Deuterations

Substrate	Catalyst	Conditions ^a (days)	Av no. of D in product ^b
1,2-C ₂ B ₁₀ H ₁₂	(PPh ₃) ₃ RuHCl	3	8
	III	1 (65°)	10
1,7-C ₂ B ₁₀ H ₁₂	(PPh ₃) ₃ RuHCl	3	8
1,12-C ₂ B ₁₀ H ₁₂	III	1	10
1,6-C ₂ B ₈ H ₁₀	(PPh ₃) ₃ RuHCl	1	8
3-(η -C ₃ H ₅)-3,1,2-C ₂ B ₉ H ₁₁	(PPh ₃) ₃ RuHCl	3	5
CoC ₂ B ₉ H ₁₁	III	1	6
1-(η -C ₃ H ₅)-1,2,4-C ₂ B ₉ H ₁₀	(PPh ₃) ₃ RuHCl	1 (80°)	6
B ₁₀ H ₁₄	(PPh ₃) ₃ RuHCl ^c	3	3
	III ^c	1	6
(Me ₂ NH) ₂ [B ₁₀ H ₁₀] ²⁻	(PPh ₃) ₃ (CH ₃ CN)RuHCl	3 (80° in CH ₃ CN)	2
Me ₃ NBH ₃	(PPh ₃) ₃ RuHCl ^c	1	3

^a Except where noted, reactions were at 100° with 1 mmol of substrate + 0.05 mmol of catalyst in 20 ml of toluene with D₂ bubbling at ~3 ml/min. ^b Estimated from ir, ¹¹B nmr, and mass spectra. ^c Reaction with catalyst was noted.

number of substrates with two of the more effective catalysts found. The preliminary results of a comparison of different catalysts with 1,2-C₂B₁₀H₁₂ as the constant substrate are presented in Table II.

Examples of both homogeneous and heterogeneous active catalysts have been found, although the homogeneous catalysts are much more effective and selective. The most active catalysts are two metallocarboranes discovered in these laboratories,¹⁰ 3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₁₁ (II) and 2,2-(PPh₃)₂-2-H-2,1,7-RhC₂B₉H₁₁ (III), solutions of which have also been found to catalyze homogeneous hydrogenation, hydrosilylation, and alkene isomerization.¹⁰ Compounds II and III effect

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Table II. Comparison of Selected Catalysts with 1,2-C₂B₁₀H₁₂ as Substrate

System	Catalyst	Conditions ^a	Av. no. of D in product ^b
1	10% Pd on C (1 g)	3 days, 100°	2
2	(PPh ₃) ₃ RhCl ^c	18 hr, 80°	2
3	(PPh ₃) ₃ RuHCl	18 hr, 80°	5
4	(PPh ₃) ₃ RuHCl	3 days, 100°	8
5	II	1 day, 65°	10
6	III	1 day, 65°	10

^a Except where noted, reactions were with 1 mmol of 1,2-C₂B₁₀H₁₂ and 0.05 mmol of catalyst in 20 ml of toluene with D₂ bubbling at ~3 ml/min. ^b Estimated from ir, ¹¹B nmr, and mass spectra. ^c Formed nearly insoluble dimer and slowly decomposed under these conditions.

deuteration of 1,2-C₂B₁₀H₁₂ at least one order of magnitude faster than any other catalyst so far examined.

The results obtained with the catalytic systems described in Table II provide an example of the relative activity and selectivity exhibited by these catalysts with a variety of substrates. The order of rates of deuterium incorporation at the four chemically nonequivalent sets of sites in 1,2-C₂B₁₀H₁₂ was followed by 80.5-MHz ¹¹B nmr spectroscopy. With increasing deuterium exchange at a site represented by a given resonance, the doublet due to hydrogen coupling collapsed smoothly to a singlet.

The deuterated carboranes produced by system 1 in Table II had a ¹¹B nmr spectrum which showed a small degree of collapse at all four resonances, indicating little if any selectivity with this catalyst. System 2 produced a deuterated carborane with a ¹¹B nmr spectrum which exhibited considerable collapse of the resonance assigned to B(3,6),¹¹ slight collapse of that assigned to B(4,5,7,11), and no significant change in the B(8,10) and B(9,12) resonances. The ¹¹B nmr spectrum of the product of system 3 consisted of an unsymmetrical singlet for B(3,6) and B(4,5,7,11), and slightly collapsed doublets for B(8,10) and B(9,12). Under the more vigorous conditions of system 4, (PPh₃)₃RuHCl produced deuterated carborane with a ¹¹B nmr spectrum consisting of a sharp singlet for B(3,6) and B(4,5,7,11), a broad singlet for B(8,10), and a poorly resolved doublet for B(9,12). Systems 5 and 6 produced carboranes which were more than 95% deuterated.

None of these catalysts caused exchange at the carbon atoms of 1,2-C₂B₁₀H₁₂¹² (no C-D stretching absorptions in the ir spectra of the deuterated carboranes) and no exchange was observed for the bridge hydrogens of B₁₀H₁₄ (no B-D bridge absorptions in the ir spectrum of deuterated decaboranes). Although (PPh₃)₃RhCl rapidly forms the nearly insoluble dimer¹³ at the required temperatures, and slowly decomposes, (PPh₃)₃RuHCl, II, and III can all be recovered from some of the catalytic solutions.¹⁴

(11) The assignment of the ¹¹B nmr spectrum of 1,2-C₂B₁₀H₁₂ is that of J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Amer. Chem. Soc.*, **88**, 628 (1966).

(12) However, Raney nickel and D₂ effect slow exchange at carbon and none at boron, while Co(CN)₅D³⁻ + D₂ + D₂O is very effective for specific exchange at carbon.

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(14) Under the reaction conditions, these three catalysts undergo self-deuteration, (PPh₃)₃RuHCl forms [(2,6-D₂C₆H₃)₃P]₃RuDCl,⁹ and the metallocarboranes are extensively deuterated in the cage and hydride but not in the triphenylphosphine ligands.

The observed order of rates of deuteration at available sites on 1,2-C₂B₁₀H₁₂, B(3,6) > B(4,5,7,11) > B(8,10) > B(9,12), is the reverse of that established for electrophilic substitution¹⁵ and is therefore the order which might be expected for nucleophilic substitution. The pattern of substitution found for 1,7-C₂B₁₀H₁₂ [B(2,3), B(5,12), B(4,6,8,11) > B(9,10)]¹⁶ and B₁₀H₁₄ [B(6,9) > B(5,7,8,10) > B(2,4), B(1,3)] is also in accord with expected patterns of nucleophilic substitution.^{15,19}

The correlation of the pattern of reactivity for these deuteration with patterns of nucleophilic substitution is in accord with a mechanism involving oxidative addition of a transition metal complex to a terminal B-H bond.²⁰ The nucleophilic character of transition metal complexes in ortho metallation and other oxidative additions has been discussed.^{8,21} Further studies with other substrates and catalysts, including detailed kinetic and mechanistic investigations, are in progress.

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(16) This observation is based on the latest interpretation of the ¹¹B nmr spectrum of 1,7-C₂B₁₀H₁₂¹⁷ and lends further support to it. The assignment of Stanko, *et al.*,¹⁸ appears to be in error.

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Electronic Excitation Transfer in Polymers. I. Demonstration of Singlet-Singlet, Triplet-Singlet, and Triplet-Triplet Transfer in a Polystyrene Matrix Studied by a Chemiexcitation Method. Evidence for Forbidden and for Allowed Long Range Mechanisms

Sir:

Energy transfer processes which occur in solid polymeric systems are of interest from the standpoint of elucidation of energy transfer mechanisms¹ and design of strategies both to inhibit polymer photodegradation and to control the biodegradation of polymers.^{2,3} During the last decade, a number of reports concerning

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