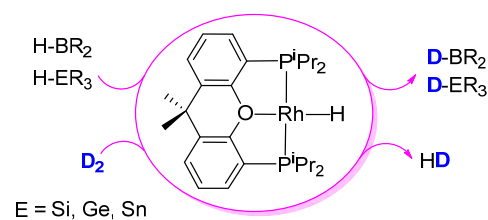


A General Rhodium Catalyst for the Deuteration of Boranes and Hydrides of the Group 14 Elements

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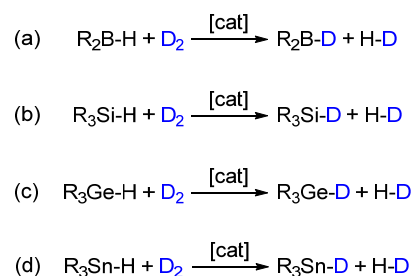
ABSTRACT: Pinacolborane, catecholborane, triethylsilane, triphenylsilane, dimethylphenylsilane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, triethylgermane, triphenylgermane, and triphenylstannane deuterated at the heteroatom position have been catalytically prepared in 50-70% isolated yield, through H/D exchange between the D₂ molecule and the respective boranes and hydrides of the group 14 elements, in the presence of the rhodium(I)-monohydride catalyst precursor RhH{κ³-P,O,P-[xant(PⁱPr₂)₂]} (xant(PⁱPr₂)₂ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene).

Additions of B-H and E-H bonds of boranes (R₂BH) and hydrides of the group 14 elements (R₃EH; E = Si, Ge, Sn) to unsaturated organic molecules, the so called reactions of hydroboration,¹ hydrosilylation,² hydrogermylation,³ and hydrostannation,⁴ are powerful tools in the modern organic synthesis, which allow the access to a great number of handy synthetic intermediates. The use of isotopically-labeled reagents for these reactions is of paramount importance from two different points of view: they provide relevant mechanistic information,⁵ which is necessary for a rational improvement of the reactions, and generate products bearing heavy isotopes with a slower metabolism,⁶ facilitating lower pharmaceutical doses. Unfortunately, deuterated-boranes, -silanes, -germanes, and -stannanes are very expensive and the required one is not always commercially available. As a consequence, they are prepared by graduate students and postdoctoral researchers in the majority of the academic laboratories of organic chemistry, including organometallics.

Preparation of such reagents by multistep procedures may be even more expensive than the commercial products, given the loss of yield in each step and the time required. So, catalytic one-pot synthesis promoted by transition metals is an attractive alternative. Benzene-*d*₆,⁷ D₂O,⁸ and D₂ are usual sources of deuterium. The use of the former requires that the catalyst activates C-D bonds, whereas the utility of the second one needs of stable metal species toward the hydrolysis. So, only D₂ has general applicability. Thus, reactions shown in Scheme 1 are the most clean and straightforward method to prepare these classes of deuterated compounds. Catalysts are also specific for each type of reagent. Some complexes of iron,⁹ cobalt,¹⁰ rhodium,¹¹ and iridium¹² stabilized by P,N,P- and

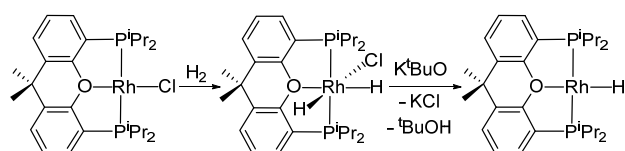
N,N,N-pincer and chelate-diphosphines and NHC ligands have shown to be efficient for the exchange in boranes (a). Deuterated pinacolborane (pinBD) has been also synthesized in high yield, by deuteration of B₂pin₂, in the presence of iron and cobalt precursors.^{9,10b} Catalysts for the deuteration of silanes (b) include ruthenium-polyhydrides,¹³ half-sandwich rhodium(III) derivatives,¹⁴ iridium(III)-NHC compounds,¹⁵ and platinum(0)-phosphine species.¹⁶ As far as we know, catalysts for the reactions with germanes (c) and stannanes (d) have not been reported so far. This specificity forces us to prepare or to buy a particular catalyst for the preparation of each class of deuterated reagent that is desired. In this note, we report and recommend the use of the square-planar complex RhH{κ³-P,O,P-[xant(PⁱPr₂)₂]} (xant(PⁱPr₂)₂ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) as catalyst precursor, which is efficient for the four reactions of Scheme 1, working under very mild conditions and with low catalyst loading.

Scheme 1. Reactions with Deuterium



This complex is a notable example of stable late-transition-metal unsaturated monohydride.¹⁷ It catalyzes the direct borylation of arenes,¹⁸ the decyanative borylation of nitriles,¹⁹ the dehydrogenation of ammonia borane,²⁰ the dehydropolymerization of amine boranes,²¹ and the hydroboration of diphenylacetylene.²² Furthermore, it participates in the catalytic cycle of dehydrogenative borylation-hydroborylation of bis(alkyl)alkynes.²³ So far, a handicap for its use was the preparation procedure, which afforded moderated yield. In order to solve this issue and to give it a more general use, we have significantly improved its preparation. Now, it is simple (see Experimental Section), little time is needed, and takes place in high yield (90%) in spite of involving two steps. It starts from the chloride derivative $\text{RhCl}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$, which is almost quantitatively transformed into the dihydride-rhodium(III) complex $\text{RhH}_2\text{Cl}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ by oxidative addition of H_2 in pentane. The dechlorination of the latter with KO^tBu also in pentane yields the monohydride (Scheme 2).

Scheme 2 Preparation of $\text{RhH}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$



The catalysis was carried out at room temperature, under 1.14 bar of D_2 , in diethyl ether as solvent, with concentrations of substrate and catalyst of 0.36 M and 3.6×10^{-3} M, respectively. Under these conditions, the boranes pinacolborane and catecholborane; the silanes triethylsilane, triphenylsilane, dimethylphenylsilane and 1,1,1,3,5,5,5-heptamethyltrisiloxane; and the germanes triethylgermane and triphenylgermane were transformed in the respective species monodeuterated at the element with conversions higher than 95%, in all cases, after 6 h (Table 1). The stannane triphenylstannane was also converted into the monodeuterated counterpart. However, in this case, the reaction had to be performed in the absence of light and in the presence of 5 mol% of hydroquinone, to prevent the formation of the radical $\text{Ph}_3\text{Sn}\cdot$. The latter dimerizes to afford $\text{Ph}_3\text{Sn-SnPh}_3$, which is a usual impurity of the reagent. The deuterated compounds were isolated in 50-70% yield after purification and were characterized by NMR spectroscopy. The purification of the deuterated triphenylsilane, triphenylgermane, and triphenylstannane was performed by column chromatography on silica gel, whereas the remaining compounds were distilled in a Kugelrohr glass oven.

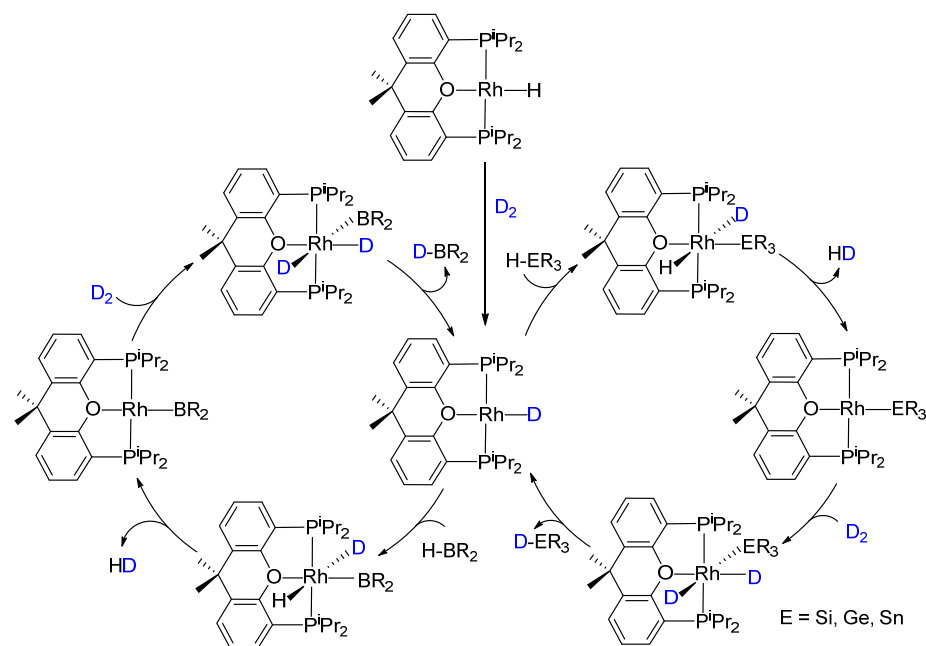
Table 1. H/D Isotopic Exchange of Boranes, Silanes, Germanes, and Stannanes Catalyzed by $\text{RhH}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$.^a

Product	Deuterium incorporation	Isolated yield
pinB-D	>95%	65%
catB-D	>95%	47%
$\text{Et}_3\text{Si-D}$	>95%	72%
$\text{Ph}_3\text{Si-D}$	>95%	78%
$\text{PhMe}_2\text{Si-D}$	>95%	68%
$(\text{Me}_3\text{SiO})_2\text{MeSi-D}$	>95%	70%
$\text{Et}_3\text{Ge-D}$	>95%	58%
$\text{Ph}_3\text{Ge-D}$	>95%	72%
$\text{Ph}_3\text{Sn-D}$	>95%	81%

^a Reactions were carried out in diethyl ether (5 mL) in a 160 mL screw cap Schlenk flask under 1.14 bar of D_2 . The deuteration of HSnPh_3 was performed in the presence of hydroquinone (5 mol%) and in the absence of light. To ensure full deuteration two D_2 loadings are used. Deuterium incorporation based on integration of ^1H NMR spectra.

The deuteration can be rationalized according to Scheme 3. Under D_2 atmosphere complex $\text{RhH}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ undergoes H/D exchange to afford the deuteride counterpart $\text{RhD}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$, which is the true catalyst of the reactions. This species oxidatively adds the B-H or E-H bond of the substrates, along the O-Rh-H axis with the electropositive element on the oxygen atom of the diphosphine, to afford the respective rhodium(III) derivatives $\text{RhHD}(\text{BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ and $\text{RhHD}(\text{ER}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$. This is strongly supported by the reactions of $\text{RhH}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ with pinacolborane (pinBH), catecholborane (catBH), triethylsilane (Et_3SiH), and triphenylsilane (Ph_3SiH).²⁴ As is well known, there is a marked diagonal relationship between the elements of rows 2 and 3, which is particularly pronounced for boron and silicon and evident in the chemistry of the platinum group metals.²⁵ In accordance with it, the square-planar monohydride reacts with the four compounds of the same manner, to give the related *trans*-dihydrides $\text{RhH}_2(\text{BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ ($\text{BR}_2 = \text{Bpin}$, Bcat) and $\text{RhH}_2(\text{SiR}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ ($\text{SiR}_3 = \text{SiEt}_3$, SiPh_3).²⁴ The ether-diphosphine $\text{xant(P}^i\text{Pr}_2)_2$ is flexible and the ether function displays hemilabile character. As results, transitory and stable species bearing the ligand coordinated in fashions $\kappa^3\text{-mer}$,²⁶ $\kappa^3\text{-fac}$,²⁷ $\kappa^2\text{-cis}$,²⁸ and $\kappa^2\text{-trans}$ ²⁹ are known. This coordinating versatility allows it a fast interconversion between the different coordination modes. Thus, it adapts to the requirements of the participating intermediates of the catalytic cycles, for which is able of performing the necessary geometrical transformations on the metal coordination sphere to allowing reactions initially forbidden. As proof of this ability, complexes $\text{RhH}_2(\text{BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ and $\text{RhH}_2(\text{SiR}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ undergo reductive elimination of H_2 , to

Scheme 3. Deuteration Mechanism



give the respective square-planar boryl- and silyl-derivatives $\text{Rh}(\text{BR}_2)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ and $\text{Rh}(\text{SiR}_3)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ in spite of the *trans* disposition of the hydride ligands and the concerted nature of the elimination.²⁴ Under the catalytic conditions, the square-planar boryl complexes and the $\text{Rh}(\text{ER}_3)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ counterparts can be similarly formed by reductive elimination of HD from $\text{RhHD}(\text{BR}_2)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ and $\text{RhHD}(\text{ER}_3)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$. In this way, the subsequent oxidative addition of D_2 to the metal center of these square-planar species, now along the O-Rh-B or O-Rh-E axis, could give the *cis*-dideuteride intermediates $\text{RhD}_2(\text{BR}_2)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ and $\text{RhD}_2(\text{ER}_3)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$, which should yield the wished R_2BD and R_3ED products through the respective reductive eliminations, regenerating the catalyst.

The behavior of the catalyst during the deuteration of Et_3SiH was followed by $^31\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure S30). In accordance with Scheme 3, the hydride-deuteride-rhodium(III) complex $\text{RhHD}(\text{SiEt}_3)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ ($\delta_{31\text{P}}$, 61.8; $\delta_{1\text{H}}$, -5.87; $\delta_{2\text{H}}$, -5.9) is the key species of the catalysis. It is rapidly formed and the unique detected species while Et_3SiH is present in the solution. Once the deuteration is completed the deuteride-rhodium(I) catalyst is quantitatively regenerated. These observations confirm the cycle proposed on the basis of the previously mentioned stoichiometric reactions and points out the reductive elimination of H-D from $\text{RhHD}(\text{SiEt}_3)\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ as the rate determining step of the catalysis.

In conclusion, the rhodium(I)-monohydride $\text{RhH}\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ is an efficient catalyst precursor to perform the H/D exchange between the D_2 molecule and the heteroatom-H bond of boranes and hydrides of the group 14 elements. The deuterated products are obtained in high yields and deuterium incorporation at the wished position higher than 95%. The preparation of this precursor is simple, little time is needed, and takes place in very high yield.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with exclusion of air using Schlenk-tube techniques or in a drybox. Pentane and diethyl ether were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^1H , ^2H , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, Bruker Avance 400 MHz or Bruker Avance 500 MHz instruments at 25 °C. Chemical shifts (expressed in ppm) are referenced to residual solvent peaks (^1H , ^2H , ^{13}C), $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B), or SiMe_4 (^{29}Si). High-resolution electrospray (HRMS) and MALDI-TOF mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer and a Bruker Autoflex III, MALDITOF/TOF equipped with a DCTB matrix, respectively. $\text{RhH}_2\text{Cl}\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ was prepared as reported previously.¹⁷

Improved Method of Synthesis of $\text{RhH}\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$. A suspension of $\text{RhH}_2\text{Cl}\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (1000 mg, 1.71 mmol) in pentane (30 mL) was treated with K^tBuO (250 mg, 2.23 mmol). The resulting mixture was stirred at room temperature for 12 h, and during this time the gradual darkening of the color was observed. The resulting suspension was extracted with pentane (5 x 30 mL) and filtered through a porous frit to remove the potassium salts, getting a very dark solution, that was dried to vacuum to afford a very dark solid. Yield: 850 mg (91%). NMR data agree with those reported previously.¹⁷

General Procedure for the Deuteration Experiments. In an argon-filled glovebox a screw cap Schlenk flask (volume ~ 160 mL) was charged with $\text{RhH}\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (10 mg, 0.018 mmol), the corresponding substrate (1.83 mmol) and diethyl ether (5 mL). The resulting solution was freeze-pump-thaw degassed and filled with D_2 (0.14 bar over the atmospheric pressure) while immersed in liquid N_2 . The solution was thawed and stirred for 3 hours at room temperature. Then, the flask atmosphere was removed and it was charged

again with 1.14 bar of D₂. After 3 additional hours, the deuterium atmosphere was replaced by argon and two different purification methods were used: flash chromatography over silica gel using diethyl ether as eluent (DSiPh₃, DGePh₃ and DSnPh₃) or by evaporation to dryness and vacuum distillation (DBpin, DBcat, DSiEt₃, DSiMe₂Ph, DSiMe(OSiMe₃)₂, and DGeEt₃). The deuteration of HSnPh₃ was performed following the general procedure but in the presence of hydroquinone (0.09 mmol) and in the absence of light.

Pinacolborane-d₁. Colorless liquid. Yield: 153 mg (65%). NMR Spectra (Figures S1-S3): ¹H NMR (300.13 MHz, C₆D₆): δ 1.00 (s, 12H). ²H NMR (46.07 MHz, C₆H₆): δ 4.25 (broad s, $\nu_{1/2} = 67$ Hz). ¹¹B NMR (96.29 MHz, C₆D₆): δ 28.3 (broad t, $J_{B-D} = 20.4$ Hz). NMR data agree with those reported previously.³⁰

Catecholborane-d₁. Colorless liquid. Yield: 104 mg (47%). NMR Spectra (Figures S4-S6): ¹H NMR (300.13 MHz, C₆D₆): δ 6.97 (dd, $J_{H-H} = 5.7$ Hz, $J_{H-H} = 3.3$ Hz, 2H), 6.75 (dd, $J_{H-H} = 6.0$ Hz, $J_{H-H} = 3.6$ Hz, 2H). ²H NMR (46.07 MHz, C₆H₆): δ 4.38 (broad s, $\nu_{1/2} = 60$ Hz). ¹¹B NMR (96.29 MHz, C₆D₆): δ 28.6 (broad s). NMR data agree with those reported previously.³¹

Triethylsilane-d₁. Colorless liquid. Yield: 155 mg (72%). NMR Spectra (Figures S7-S9): ¹H NMR (300.13 MHz, C₆D₆): δ 0.97 (t, $J = 7.8$ Hz, 9H), 0.53 (q, $J = 7.8$ Hz, 6H). ²H NMR (61.42 MHz, C₆H₆): δ 3.9 (s). ²⁹Si{¹H} NMR (59.63 MHz, C₆D₆): δ -0.1 (t, $J_{Si-D} = 27.4$ Hz). NMR data agree with those reported previously.^{7d}

Triphenylsilane-d₁. White solid. Yield: 373 mg (78%). NMR Spectra (Figures S10-S12): ¹H NMR (300.13 MHz, C₆D₆): δ 7.70 (m, 6H), 7.30 (m, 9H). ²H NMR (61.42 MHz, C₆H₆): δ 5.7 (s). ²⁹Si{¹H} NMR (59.63 MHz, C₆H₆): δ -18.7 (t, $J_{Si-D} = 30.0$ Hz). NMR data agree with those reported previously.^{13b}

Dimethylphenylsilane-d₁. Colorless liquid. Yield: 171 mg (68%). NMR Spectra (Figures S13-S15): ¹H NMR (300.13 MHz, C₆D₆): δ 7.44 (m, 2H), 7.17 (m, 3H), 0.18 (s, 6H). ²H NMR (61.42 MHz, C₆H₆): δ 4.6 (s). ²⁹Si{¹H} NMR (59.63 MHz, C₆D₆): δ -17.8 (t, $J_{Si-D} = 28.9$ Hz). NMR data agree with those reported previously.^{7d}

1,1,1,3,5,5,5-Heptamethyltrisiloxane-d₁. Colorless liquid. Yield: 286 mg (70%). NMR Spectra (Figures S16-S18): ¹H NMR (300.13 MHz, C₆D₆): δ 0.15 (s, 21H). ²H NMR (61.42 MHz, C₆H₆): δ 5.0 (s). ²⁹Si{¹H} NMR (59.63 MHz, C₆D₆): δ 3.6 (s), -42.0 (t, $J_{Si-D} = 36.0$ Hz). NMR data agree with those reported previously.^{7d}

Triethylgermane-d₁.³² Colorless liquid. Yield: 170 mg (58%). NMR Spectra (Figures S19-S20-S21): ¹H NMR (300.13 MHz, C₆D₆): δ 1.11 (t, $J = 7.5$ Hz), 0.87 (q, $J = 7.8$ Hz, 6H). ²H NMR (61.42 MHz, C₆H₆): δ 3.9 (s). ¹³C{¹H} NMR (75.47 MHz, C₆D₆): δ 9.4, 8.4. HRMS (Figure S22, electrospray, m/z): calcd for C₆H₁₅Ge [M - D]⁺, 161.0381; found, 161.0367.

Triphenylgermane-d₁.³² White solid. Yield: 403 mg (72%). NMR Spectra (Figures S23-S24-S25): ¹H (300.13 MHz, C₆D₆): δ 7.50 (m, 6H), 7.14 (m, 9H). ²H NMR (61.42 MHz, C₆H₆): δ 5.9 (s). ¹³C{¹H} NMR (75.47 MHz, C₆D₆): δ 151.2, 135.6, 129.5, 128.8. MALDI-TOF (m/z): calcd for C₁₈H₁₅Ge [M - D]⁺, 305.038; found, 304.968.

Triphenylstannane-d₁.³² Oily white solid. Yield: 521 mg (81%). NMR Spectra (Figures S26-S27-S28): ¹H (300.13 MHz, C₆D₆): δ 7.60 (m, 6H), 7.10 (m, 9H). ²H NMR (61.42 MHz, C₆D₆): δ 6.9 (s with tin satellites, $J_{119Sn-D} = 319$ Hz,

$J_{117Sn-D} = 303$ Hz). ¹³C{¹H} NMR (75.47 MHz, C₆D₆): δ 137.7, 137.3, 129.4, 129.0. HRMS (Figure S29, electrospray, m/z): calcd for C₁₈H₁₅Sn [M - D]⁺, 351.0193; found, 351.0175.

NMR Spectroscopic Study of the Catalytic Deuteration of Triethylsilane. In the glovebox, two J Young NMR tubes were charged with a solution of RhH{κ³-P,O,P-[xant(PⁱPr₂)₂]} (10 mg, 0.02 mmol), triethylsilane (30 μL, 0.2 mmol) in diethyl ether (0.40 mL) or diethyl ether-*d*₁₀ (0.40 mL), respectively. The argon atmosphere was replaced by a deuterium atmosphere (1.14 bar) and ³¹P{¹H}, ¹H, and ²H NMR spectra were recorded periodically.

Gram-Scale Preparation of Triphenylsilane-d₁. In an argon-filled glovebox a screw cap Schlenk flask (volume ~ 160 mL) was charged with RhH{κ³-P,O,P-[xant(PⁱPr₂)₂]} (54.6 mg, 0.1 mmol), HSiPh₃ (2.604 g, 10 mmol) and diethyl ether (27.5 mL). The resulting solution was freeze-pump-thaw degassed and filled with D₂ (0.14 bar over the atmospheric pressure) while immersed in liquid N₂. The solution was thawed and stirred for 1 hour at room temperature. After this time, the flask atmosphere was removed and it was charged again with 1.14 bar of D₂. This procedure was repeated each hour, up to four times. Then the deuterium atmosphere was replaced by argon and triphenylsilane-*d*₁ was purified by flash chromatography over silica gel using diethyl ether as eluent. Isolated yield: 2.28 g (87%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR spectra, selected HRMS (PDF).

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) See for example: (a) Chong, C. C.; Kinjo, R. Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide. *ACS Catal.* **2015**, *5*, 3238-3259. (b) Obligacion, J. V.; Chirik, P. J. Earth-abundant transition metal catalysts for alkene hydrosilylation and hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15-34. (c) Shegavi, M. L.; Bose, S. K. Recent advances in the catalytic hydroboration of carbonyl compounds. *Catal. Sci. Technol.* **2019**, *9*, 3307-3336.
- (2) See for example: (a) *Hydrosilylation: A Comprehensive Review on Recent Advances*; Marciniak, B., Ed.; Springer: Berlin, **2009**. (b) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. *ACS Catal.* **2016**, *6*, 290-300 (c) Du, X.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. *ACS Catal.* **2017**, *7*, 1227-1243. (d) Iglesias, M.; Fernández-Alvarez, F. J.; Oro, L. A. Non-classical hydrosilane mediated reduc-

tions promoted by transition metal complexes. *Coord. Chem. Rev.* **2019**, *386*, 240-266.

(3) See for example: (a) Esteruelas, M. A.; Martín, M.; Oro, L. A. The π -(Hydroxyalkenyl)germane Complexes $\text{Rh}(\text{acac})\{\eta^2\text{-}(E)\text{-Et}_3\text{GeCH}=\text{CHC}(\text{OH})\text{R}_2\}(\text{PCy}_3)$ (R = Me, Ph) as Intermediates in the Hydrogermylation of Alkynols Catalyzed by $\text{Rh}(\text{acac})(\text{cyclooctene})(\text{PCy}_3)$. *Organometallics* **1999**, *18*, 2267-2270. (b) Matsuda, T.; Kadowaki, S.; Yamaguchi, Y.; Murakami, M. Ruthenium-Catalyzed *trans*-Hydrogermylation of Alkynes: Formation of 2,5-Disubstituted Germales through Double *trans*-Hydrogermylation of 1,3-Diynes. *Org. Lett.* **2010**, *12*, 1056-1058. (c) Itazaki, M.; Kamitani, M.; Nakazawa, H. *Trans*-selective hydrogermylation of alkynes promoted by methyliron and bis(germyl)hydridoiron complexes as a catalyst precursor. *Chem. Commun.* **2011**, *47*, 7854-7856. (d) Meißner, G.; Kretschmar, K.; Braun, T.; Kemnitz, E. Consecutive Transformations of Tetrafluoropropenes: Hydrogermylation and Catalytic C-F Activation Steps at a Lewis Acidic Aluminum Fluoride. *Angew. Chem. Int. Ed.* **2017**, *56*, 16338-16341. (e) Liang, H.; Ji, Y.-X.; Wang, R.-H.; Zhang, Z.-H.; Zhang, B. Visible-Light-Initiated Manganese-Catalyzed *E*-Selective Hydrosilylation and Hydrogermylation of Alkynes. *Org. Lett.* **2019**, *21*, 2750-2754.

(4) See for example: (a) Yoshida, H. Stannylation Reactions under Base Metal Catalysis: Some Recent Advances. *Synthesis* **2016**, *48*, 2540-2552. (b) Alami, M.; Hamze, A.; Provot, O. Hydrostannylation of Alkynes. *ACS Catal.* **2019**, *9*, 3437-3466.

(5) (a) Gómez-Gallego, M.; Sierra, M. A. Kinetic Isotope Effects in the Study of Organometallic Reaction Mechanisms. *Chem. Rev.* **2011**, *111*, 4857-4963. (b) Simmons, E. M.; Hartwig, J. F. On the Interpretation of Deuterium Kinetic Isotope Effects in C-H Bond Functionalizations by Transition-Metal Complexes. *Angew. Chem. Int. Ed.* **2012**, *51*, 3066-3072. (c) Maji, A.; Guin, S.; Feng, S.; Dahiya, A.; Singh, V. K.; Liu, P.; Maiti, D. Experimental and Computational Exploration of *para*-Selective Silylation with a Hydrogen-Bonded Template. *Angew. Chem. Int. Ed.* **2017**, *56*, 14903-14907. (d) Bag, S.; Petzold, M.; Sur, A.; Bhowmick, S.; Werz, D. B.; Maiti, D. Palladium-Catalyzed Selective *meta*-C-H Deuteration of Arenes: Reaction Design and Applications. *Chem. Eur. J.* **2019**, *25*, 9433-9437.

(6) *Synthesis and Application of Isotopically Labeled Compounds*; Pleiss, U.; Voges, R.; Eds. John Wiley: Chichester, New York, **2001**, vol. 7.

(7) (a) Kakizawa, T.; Kawano, Y.; Shimoi, M. H-D Exchange Reaction of Borane-Lewis Base Adducts by Rhenium Polyhydride Complexes. *Chem. Lett.* **1999**, 869-870. (b) Iluc, V. M.; Fedorov, A.; Grubbs, R. H. H/D Exchange Processes Catalyzed by an Iridium-Pincer Complex. *Organometallics* **2012**, *31*, 39-41. (c) Schmidt, D.; Zell, T.; Schaub, T.; Radius, U. Si-H bond activation at $\{(\text{NHC})_2\text{Ni}^0\}$ leading to hydrido silyl and bis(silyl) complexes: a versatile tool for catalytic Si-H/D exchange, acceptorless dehydrogenative coupling of hydrosilanes, and hydrogenation of disilanes to hydrosilanes. *Dalton Trans.* **2014**, *43*, 10816-10827. (d) Komuro, T.; Osawa, T.; Suzuki, R.; Mochizuki, D.; Higashi, H.; Tobita, H. Silyl-pyridine-amine pincer-ligated iridium complexes for catalytic silane deuteration via room temperature C-D bond activation of benzene- d_6 . *Chem. Commun.* **2019**, *55*, 957-960.

(8) Zhou, R.; Li, J.; Cheo, H. W.; Chua, R.; Zhan, G.; Hou, Z.; Wu, J. Visible-light-mediated deuteration of silanes with deuterium oxide. *Chem. Sci.* **2019**, *10*, 7340-7344.

(9) Cummins, A. W. M.; Li, S.; Willcox, D. R.; Muilu, T.; Docherty, J. H.; Thomas, S. P. Synthesis of DBPin using Earth-abundant metal catalysis. *Tetrahedron* **2020**, *76*, 131084.

(10) (a) Obligacion, J. V.; Chirik, P. J. Bis(imino)pyridine Cobalt-Catalyzed Alkene Isomerization-Hydroboration: A Strategy for Remote Hydrofunctionalization with Terminal Selectivity. *J. Am. Chem. Soc.* **2013**, *135*, 19107-19110. (b) Qiao, L.; Zhang, L.; Liu, G.; Huang, Z. A highly efficient cobalt-catalyzed deuterogenolysis of diboron: Synthesis of deuterated pinacolborane and vinylboronates. *Tetrahedron* **2019**, *75*, 4138-4142.

(11) Colebatch, A. L.; Hawkey Gilder, B. W.; Whittell, G. R.; Ouldroyd, N. L.; Manners, I.; Weller, A. S. A General, Rhodium-Catalyzed, Synthesis of Deuterated Boranes and *N*-Methyl Polyaminoboranes. *Chem. Eur. J.* **2018**, *24*, 5450-5455.

(12) Nelson, D. J.; Egbert, J. D.; Nolan, S. P. Deuteration of boranes: catalysed versus non-catalysed Processes. *Dalton Trans.* **2013**, *42*, 4105-4109.

(13) (a) Ayed, T.; Barthelat, J.-C.; Tangour, B.; Pradère, C.; Donnadieu, B.; Grellier, M.; Sabo-Etienne, S. Structure and Bonding in a Disilazane Ruthenium Complex. Catalytic Selective Deuteration of Disilazane. *Organometallics* **2005**, *24*, 3824-3826. (b) Smart, K. A.; Mothes-Martin, E.; Annaka, T.; Grellier, M.; Sabo-Etienne, S. Silane Deuteration Catalyzed by Ruthenium Bis(dihydrogen) Complexes or Simple Metal Salts. *Adv. Synth. Catal.* **2014**, *356*, 759-764.

(14) (a) Campos, J.; Esqueda, A. C.; López-Serrano, J.; Sánchez, L.; Cossio, F. P.; de Cozar, A.; Álvarez, E.; Maya, C.; Carmona, E., A Cationic Rh(III) Complex That Efficiently Catalyzes Hydrogen Isotope Exchange in Hydrosilanes. *J. Am. Chem. Soc.* **2010**, *132*, 16765-16767. (b) Rubio, M.; Campos, J.; Carmona, E. Rhodium-Catalyzed, Efficient Deutero- and Tritiosilylation of Carbonyl Compounds from Hydrosilanes and Deuterium or Tritium. *Org. Lett.* **2011**, *13*, 5236-5239. (c) Campos, J.; Rubio, M.; Esqueda, A. C.; Carmona, E. Large-scale preparation and labelling reactions of deuterated silanes. *J. Label Compd. Radiopharm.* **2012**, *55*, 29-38. (d) Espada, M. F.; Esqueda, A. C.; Campos, J.; Rubio, M.; López-Serrano, J.; Álvarez, E.; Maya, C.; Carmona, E. Cationic $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Rh}^{\text{III}}$ Complexes with Metalated Aryl Phosphines Featuring η^4 -Phosphorus plus Pseudo-Allylic Coordination. *Organometallics* **2018**, *37*, 11-21.

(15) (a) Fortman, G. C.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. Catalytic deuteration of silanes mediated by N-heterocyclic carbene-Ir(III) complexes. *Chem. Commun.* **2011**, *47*, 9723-9725. (b) Egbert, J. D.; Nolan, S. P. Tandem deuteration/hydrosilylation reactions catalyzed by a rhodium carbene complex under solvent-free conditions. *Chem. Commun.* **2012**, *48*, 2794-2796.

(16) Kratish, Y.; Bravo-Zhivotovskii, D.; Apeloig, Y. Convenient Synthesis of Deuteriosilanes by Direct H/D Exchange Mediated by Easily Accessible Pt(0) Complexes. *ACS Omega* **2017**, *2*, 372-376.

(17) Esteruelas, M. A.; Oliván, M.; Vélez, A. Xantphos-Type Complexes of Group 9: Rhodium versus Iridium. *Inorg. Chem.* **2013**, *52*, 5339-5349.

(18) Esteruelas, M. A.; Oliván, M.; Vélez, A. POP-Rhodium-Promoted C-H and B-H Bond Activation and C-B Bond Formation. *Organometallics* **2015**, *34*, 1911-1924.

(19) Esteruelas, M. A.; Oliván, M.; Vélez, A. Conclusive Evidence on the Mechanism of the Rhodium-Mediated Decyanative Borylation. *J. Am. Chem. Soc.* **2015**, *137*, 12321-12329.

(20) Esteruelas, M. A.; Nolis, P.; Oliván, M.; Oñate, E.; Vallribera, A.; Vélez, A. Ammonia Borane Dehydrogenation Promoted by a Pincer-Square-Planar Rhodium(I) Monohydride: A Stepwise Hydrogen Transfer from the Substrate to the Catalyst. *Inorg. Chem.* **2016**, *55*, 7176-7181.

(21) Adams, G. M.; Colebatch, A. L.; Skornia, J. T.; McKay, A. I.; Johnson, H. C.; Lloyd-Jones, G. C.; Macgregor, S. A.; Beattie, N. A.; Weller, A. S. Dehydropolymerization of $\text{H}_3\text{B}\cdot\text{NMe}_2$ To Form Polyaminoboranes Using $[\text{Rh}(\text{Xantphos-alkyl})]$ Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 1481-1495.

(22) Curto, S. G.; Esteruelas, M. A.; Oliván, M.; Oñate, E. Insertion of Diphenylacetylene into Rh-Hydride and Rh-Boryl Bonds: Influence of the Boryl on the Behavior of the β -Borylalkenyl Ligand. *Organometallics* **2019**, *38*, 4183-4192.

(23) Curto, S. G.; Esteruelas, M. A.; Oliván, M.; Oñate, E. Rhodium-Mediated Dehydrogenative Borylation-Hydroborylation of Bis(alkyl)alkynes: Intermediates and Mechanism. *Organometallics* **2019**, *38*, 2062-2074.

(24) Esteruelas, M. A.; Oliván, M.; Vélez, A. POP-Pincer Silyl Complexes of Group 9: Rhodium versus Iridium. *Inorg. Chem.* **2013**, *52*, 12108-12119.

(25) Buil, M. L.; Esteruelas, M. A.; Fernández, I.; Izquierdo, S.; Oñate, E. Cationic Dihydride Boryl and Dihydride Silyl Osmium(IV) NHC Complexes: A Marked Diagonal Relationship. *Organometallics* **2013**, *32*, 2744-2752.

(26) Esteruelas, M. A.; Fernández, I.; Martínez, A.; Oliván, M.; Oñate, E.; Vélez, A. Iridium-Promoted B-B Bond Activation: Preparation and X-ray Diffraction Analysis of a *mer*-Tris(boryl) Complex. *Inorg. Chem.* **2019**, *58*, 4712-4717; and references therein.

(27) Esteruelas, M. A.; García-Yebra, C.; Martín, J.; Oñate, E. *mer, fac*, and Bidentate Coordination of an Alkyl-POP Ligand in the Chemistry of Nonclassical Osmium Hydrides. *Inorg. Chem.* **2017**, *56*, 676-683.

(28) Antiñolo, A.; Esteruelas, M. A.; García-Yebra, C.; Martín, J.; Oñate, E.; Ramos, A. Reactions of an Osmium(IV)-Hydroxo Complex with Amino-Boranes: Formation of Boroxide Derivatives. *Organometallics* **2019**, *38*, 310-318.

(29) (a) Bakhmutov, V. I.; Bozoglian, F.; Gómez, K.; González, G.; Grushin, V. V.; Macgregor, S. A.; Martin, E.; Miloserdov, F. E.; Novikov, M. A.; Panetier, J. A.; Romashov, L. V. CF₃-Ph Reductive Elimination from [(Xantphos)Pd(CF₃)(Ph)]. *Organometallics* **2012**, *31*, 1315-1328. (b) Jover, J.; Miloserdov, F. M.; Benet-Buchholz, J.; Grushin, V. V.; Maseras, F. On the Feasibility of Nickel-Catalyzed

Trifluoromethylation of Aryl Halides. *Organometallics* **2014**, *33*, 6531-6543.

(30) Wu, J. Y.; Moreau, M.; Ritter, T. Iron-Catalyzed 1,4-Hydroboration of 1,3-Dienes. *J. Am. Chem. Soc.* **2009**, *131*, 12915-12917.

(31) Brown, J. M.; Lloyd-Jones, G. C. Vinylborane Formation in Rhodium-Catalyzed Hydroboration of Vinylarenes. Mechanism versus Borane Structure and Relationship to Silylation. *J. Am. Chem. Soc.* **1994**, *116*, 866-878

(32) Although Et₃GeD (CAS registry number 13314-60-6), Ph₃GeD (CAS registry number 2816-42-4) and Ph₃SnD (CAS registry number 6181-00-6) are known, no NMR data have been reported for them.