

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

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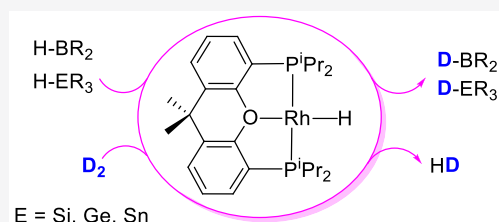


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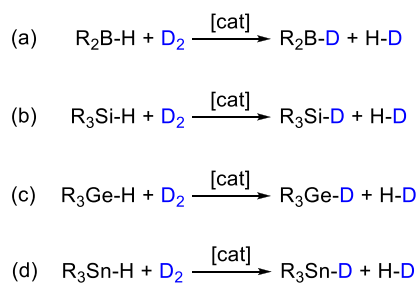
**ABSTRACT:** Pinacolborane, catecholborane, triethylsilane, triphenylsilane, dimethylphenylsilane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, triethylgermane, triphenylgermane, and triphenylstannane deuterated at the heteroatom position have been catalytically prepared in 50–70% isolated yield, through H/D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



Additions of B–H and E–H bonds of boranes (R<sub>2</sub>BH) and hydrides of the group 14 elements (R<sub>3</sub>EH; E = Si, Ge, Sn) to unsaturated organic molecules, the so-called reactions of hydroboration,<sup>1</sup> hydrosilylation,<sup>2</sup> hydrogermylation,<sup>3</sup> and hydrostannation,<sup>4</sup> are powerful tools in the modern organic synthesis, which allow 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,<sup>5</sup> which is necessary for a rational improvement of the reactions, and generate products bearing heavy isotopes with a slower metabolism,<sup>6</sup> 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*<sub>6</sub>,<sup>7</sup> D<sub>2</sub>O,<sup>8</sup> and D<sub>2</sub> 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 D<sub>2</sub> 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,<sup>9</sup> cobalt,<sup>10</sup> rhodium,<sup>11</sup> and iridium<sup>12</sup> 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 deuterogenolysis of B<sub>2</sub>pin<sub>2</sub>, in the presence of iron and cobalt precursors.<sup>9,10b</sup> Catalysts for the deuteration of

## Scheme 1. Reactions with Deuterium



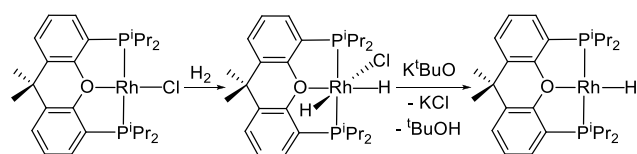
silanes (b) include ruthenium-polyhydrides,<sup>13</sup> half-sandwich rhodium(III) derivatives,<sup>14</sup> iridium(III)-NHC compounds,<sup>15</sup> and platinum(0)-phosphine species.<sup>16</sup> To our knowledge, catalysts for the reactions with germanes (c) and stannanes (d) have not been reported to date. 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{κ<sup>3</sup>-P,O,P-[xant(P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]} (xant(P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub> = 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.

This complex is a notable example of stable late-transition-metal unsaturated monohydride.<sup>17</sup> It catalyzes the direct borylation of arenes,<sup>18</sup> the decanative borylation of nitriles,<sup>19</sup> the dehydrogenation of ammonia borane,<sup>20</sup> the dehydrogenation of

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merization of amine boranes,<sup>21</sup> and the hydroboration of diphenylacetylene.<sup>22</sup> Furthermore, it participates in the catalytic cycle of dehydrogenative borylation–hydroborylation of bis(alkyl)alkynes.<sup>23</sup> So far, a handicap for its use was the preparation procedure, which afforded a moderate 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](#)) with reduced reaction time, resulting in a 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  $\text{H}_2$  in pentane. The dechlorination of the latter with  $\text{KO}^t\text{Bu}$  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  $\text{D}_2$ , in diethyl ether as solvent, with concentrations of substrate and catalyst of 0.36 M and  $3.6 \times 10^{-3}$  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.

The deuteration can be rationalized according to [Scheme 3](#). Under a  $\text{D}_2$  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 ( $\text{Et}_3\text{SiH}$ ), and triphenylsilane ( $\text{Ph}_3\text{SiH}$ ).<sup>24</sup> 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.<sup>25</sup> In accordance with it, the square-planar monohydride reacts with

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

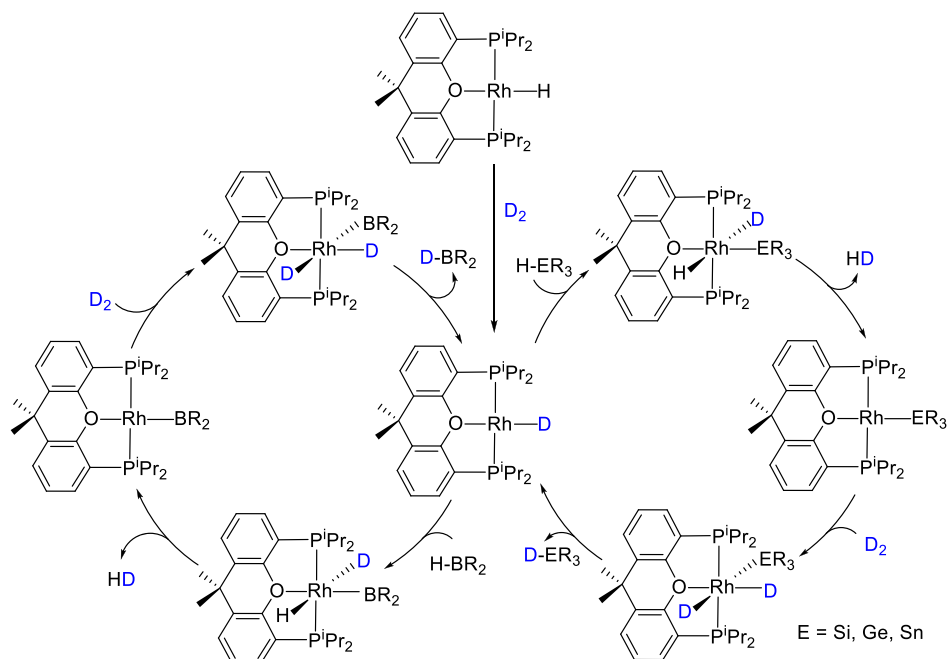
$\text{R}_2\text{B-H}$	catalyst 1 mol%	$\text{R}_2\text{B-D}$
$\text{R}_3\text{E-H}$	25 °C, 6 h $\text{D}_2$ (1.14 bar) diethyl ether	$\text{R}_3\text{E-D}$
Product	Deuterium incorporation	Isolated yield
pinB-D	>95%	65%
catB-D	>95%	47%
$\text{Et}_3\text{Si-D}$	>95%	72%
$\text{Ph}_3\text{Si-D}$	>95%	78%
$\text{PhMe}_2\text{Si-D}$	>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%

<sup>a</sup>Reactions were carried out in diethyl ether (5 mL) in a 160 mL screw cap Schlenk flask under 1.14 bar of  $\text{D}_2$ . The deuteration of  $\text{HSnPh}_3$  was performed in the presence of hydroquinone (5 mol %) and in the absence of light. To ensure full deuteration two  $\text{D}_2$  loadings are used. Deuterium incorporation based on integration of  $^1\text{H}$  NMR spectra.

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  $\text{RhH}_2(\text{SiR}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$  ( $\text{SiR}_3 = \text{SiEt}_3, \text{SiPh}_3$ ).<sup>24</sup> 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  $\kappa^3\text{-mer}$ ,<sup>26</sup>  $\kappa^3\text{-fac}$ ,<sup>27</sup>  $\kappa^2\text{-cis}$ ,<sup>28</sup> and  $\kappa^2\text{-trans}$ <sup>29</sup> 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, enabling 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  $\text{H}_2$ , to give the respective square-planar boryl- and silyl-derivatives  $\text{Rh}(\text{BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$  and  $\text{Rh}(\text{SiR}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$  in spite of the *trans* disposition of the hydride ligands and the concerted nature of the elimination.<sup>24</sup> Under the catalytic conditions, the square-planar boryl complexes and the  $\text{Rh}(\text{ER}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$  counterparts can be similarly formed by reductive elimination of HD from  $\text{RhHD}(\text{BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$  and  $\text{RhHD}(\text{ER}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ . In this way, the subsequent oxidative addition of  $\text{D}_2$  to the metal center of these square-planar species, now along the O–Rh–B or O–RhE axis, could give the *cis*-dideuteride intermediates  $\text{RhD}_2(\text{BR}_2)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$  and  $\text{RhD}_2(\text{ER}_3)\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ , which should yield the wished  $\text{R}_2\text{BD}$  and  $\text{R}_3\text{ED}$  products through the respective reductive eliminations, regenerating the catalyst.

The behavior of the catalyst during the deuteration of  $\text{Et}_3\text{SiH}$  was followed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy ([Figure](#)

Scheme 3. Deuteration Mechanism



S30). In accordance with Scheme 3, the hydride-deuteride-rhodium(III) complex  $\text{RhHD}(\text{SiEt}_3)\{\kappa^3\text{-P,O,P-[xant(PiPr}_2)_2]\}$  ( $\delta_{31\text{P}}$ , 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  $\text{Et}_3\text{SiH}$  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  $\text{RhHD}(\text{SiEt}_3)\{\kappa^3\text{-P,O,P-[xant(PiPr}_2)_2]\}$  as the rate-determining step of the catalysis.

In conclusion, the rhodium(I)-monohydride  $\text{RhH}\{\kappa^3\text{-P,O,P-[xant(PiPr}_2)_2]\}$  is an efficient catalyst precursor to perform the H/D exchange between the  $\text{D}_2$  molecule and the heteroatom–H bond of boranes and hydrides of the group 14 elements. The deuterated products are obtained in high yields, and >95% deuterium incorporation was achieved at the desired position. The preparation of this precursor is simple, with reduced reaction time, and results in very high yields.

## 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.  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , 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 ( $^1\text{H}$ ,  $^2\text{H}$ ,  $^{13}\text{C}$ ),  $\text{BF}_3\cdot\text{OEt}_2$  ( $^{11}\text{B}$ ), or  $\text{SiMe}_4$  ( $^{29}\text{Si}$ ). 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, MALDI-TOF equipped with a DCTB matrix, respectively.  $\text{RhH}_2\text{Cl}\{\kappa^3\text{-P,O,P-[xant(PiPr}_2)_2]\}$  was prepared as reported previously.<sup>17</sup>

**Improved Method of Synthesis of  $\text{RhH}\{\kappa^3\text{-P,O,P-[xant(PiPr}_2)_2]\}$ .** A suspension of  $\text{RhH}_2\text{Cl}\{\kappa^3\text{-P,O,P-[xant(PiPr}_2)_2]\}$  (1000 mg, 1.71 mmol) in pentane (30 mL) was treated with  $\text{K}^t\text{BuO}$  (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 × 30 mL) and filtered through a porous frit to remove the potassium salts, obtaining 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.<sup>17</sup>

**General Procedure for the Deuteration Experiments.** In an argon-filled glovebox a screw cap Schlenk flask (volume ~160 mL) was charged with  $\text{RhH}\{\kappa^3\text{-P,O,P-[xant(PiPr}_2)_2]\}$  (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  $\text{D}_2$  (0.14 bar over the atmospheric pressure) while immersed in liquid  $\text{N}_2$ . The solution was thawed and stirred for 3 h at room temperature. Then, the flask atmosphere was removed and it was charged again with 1.14 bar of  $\text{D}_2$ . After an additional 3 h, the deuterium atmosphere was replaced by argon and two different purification methods were used: flash chromatography over silica gel using diethyl ether as eluent ( $\text{DSiPh}_3$ ,  $\text{DGePh}_3$ , and  $\text{DSnPh}_3$ ) or by evaporation to dryness and vacuum distillation ( $\text{DBpin}$ ,  $\text{DBcat}$ ,  $\text{DSiEt}_3$ ,  $\text{DSiMe}_2\text{Ph}$ ,  $\text{DSiMe(OSiMe}_3)_2$ , and  $\text{DGeEt}_3$ ). The deuteration of  $\text{HSnPh}_3$  was performed following the general procedure but in the presence of hydroquinone (0.09 mmol) and in the absence of light.

**Pinacolborane- $d_1$ .** Colorless liquid. Yield: 153 mg (65%). NMR Spectra (Figures S1–S3):  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.00 (s, 12H).  $^2\text{H}$  NMR (46.07 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  4.25 (broad s,  $\nu_{1/2}$  = 67 Hz).  $^{11}\text{B}$  NMR (96.29 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  28.3 (broad t,  $^1J_{\text{B-D}}$  = 20.4 Hz). NMR data agree with those reported previously.<sup>30</sup>

**Catecholborane- $d_1$ .** Colorless liquid. Yield: 104 mg (47%). NMR Spectra (Figures S4–S6):  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.97 (dd,  $J_{\text{H-H}}$  = 5.7 Hz,  $J_{\text{H-H}}$  = 3.3 Hz, 2H), 6.75 (dd,  $J_{\text{H-H}}$  = 6.0 Hz,  $J_{\text{H-H}}$  = 3.6 Hz, 2H).  $^2\text{H}$  NMR (46.07 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  4.38 (broad s,  $\nu_{1/2}$  = 60 Hz).  $^{11}\text{B}$  NMR (96.29 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  28.6 (broad s). NMR data agree with those reported previously.<sup>31</sup>

**Triethylsilane- $d_1$ .** Colorless liquid. Yield: 155 mg (72%). NMR Spectra (Figures S7–S9):  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.97 (t,  $J$  = 7.8 Hz, 9H), 0.53 (q,  $J$  = 7.8 Hz, 6H).  $^2\text{H}$  NMR (61.42 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  3.9 (s).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.63 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -0.1 (t,  $^1J_{\text{Si-D}}$  = 27.4 Hz). NMR data agree with those reported previously.<sup>7d</sup>

**Triphenylsilane- $d_1$ .** White solid. Yield: 373 mg (78%). NMR Spectra (Figures S10–S12):  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.70 (m, 6H), 7.30 (m, 9H).  $^2\text{H}$  NMR (61.42 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  5.7 (s).

$^{29}\text{Si}\{^1\text{H}\}$  NMR (59.63 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  -18.7 (t,  $J_{\text{Si-D}} = 30.0$  Hz). NMR data agree with those reported previously.<sup>13b</sup>

**Dimethylphenylsilane- $d_1$ .** Colorless liquid. Yield: 171 mg (68%). NMR Spectra (Figures S13–S15):  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.44 (m, 2H), 7.17 (m, 3H), 0.18 (s, 6H).  $^2\text{H}$  NMR (61.42 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  4.6 (s).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.63 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -17.8 (t,  $J_{\text{Si-D}} = 28.9$  Hz). NMR data agree with those reported previously.<sup>7d</sup>

**1,1,1,3,5,5,5-Heptamethyltrisiloxane- $d_1$ .** Colorless liquid. Yield: 286 mg (70%). NMR Spectra (Figures S16–S18):  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.15 (s, 21H).  $^2\text{H}$  NMR (61.42 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  5.0 (s).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.63 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.6 (s), -42.0 (t,  $J_{\text{Si-D}} = 36.0$  Hz). NMR data agree with those reported previously.<sup>7d</sup>

**Triethylgermane- $d_1$ .** Colorless liquid. Yield: 170 mg (58%). NMR Spectra (Figures S19–S21):  $^1\text{H}$  NMR (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.11 (t,  $J = 7.5$  Hz), 0.87 (q,  $J = 7.8$  Hz, 6H).  $^2\text{H}$  NMR (61.42 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  3.9 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  9.4, 8.4. HRMS (Figure S22, electrospray,  $m/z$ ): calcd for  $\text{C}_6\text{H}_{15}\text{Ge}$  [ $\text{M} - \text{D}$ ] $^+$ , 161.0381; found, 161.0367.

**Triphenylgermane- $d_1$ .**<sup>32</sup> White solid. Yield: 403 mg (72%). NMR Spectra (Figures S23–S25):  $^1\text{H}$  (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.50 (m, 6H), 7.14 (m, 9H).  $^2\text{H}$  NMR (61.42 MHz,  $\text{C}_6\text{H}_6$ ):  $\delta$  5.9 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  151.2, 135.6, 129.5, 128.8. MALDI-TOF ( $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{15}\text{Ge}$  [ $\text{M} - \text{D}$ ] $^+$ , 305.038; found, 304.968.

**Triphenylstannane- $d_1$ .**<sup>32</sup> Oily white solid. Yield: 521 mg (81%). NMR Spectra (Figures S26–S28):  $^1\text{H}$  (300.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.60 (m, 6H), 7.10 (m, 9H).  $^2\text{H}$  NMR (61.42 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.9 (s with tin satellites,  $J_{119\text{Sn-D}} = 319$  Hz,  $J_{117\text{Sn-D}} = 303$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  137.7, 137.3, 129.4, 129.0. HRMS (Figure S29, electrospray,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{15}\text{Sn}$  [ $\text{M} - \text{D}$ ] $^+$ , 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  $\text{RhH}\{\kappa^3\text{-P}_2\text{O}_2\text{-P-[xant(P}^i\text{Pr}_2)_2]\}$  (10 mg, 0.02 mmol) and triethylsilane (30  $\mu\text{L}$ , 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  $^{31}\text{P}\{^1\text{H}\}$ ,  $^1\text{H}$ , and  $^2\text{H}$  NMR spectra were recorded periodically.

**Gram-Scale Preparation of Triphenylsilane- $d_1$ .** In an argon-filled glovebox a screw cap Schlenk flask (volume  $\sim 160$  mL) was charged with  $\text{RhH}\{\kappa^3\text{-P}_2\text{O}_2\text{-P-[xant(P}^i\text{Pr}_2)_2]\}$  (54.6 mg, 0.1 mmol),  $\text{HSiPh}_3$  (2.604 g, 10 mmol), and diethyl ether (27.5 mL). The resulting solution was freeze–pump–thaw degassed and filled with  $\text{D}_2$  (0.14 bar over the atmospheric pressure) while immersed in liquid  $\text{N}_2$ . The solution was thawed and stirred for 1 h at room temperature. Afterward, the flask atmosphere was removed and it was charged again with 1.14 bar of  $\text{D}_2$ . 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

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.0c01967>.

NMR spectra, selected HRMS (PDF)

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## Notes

The authors declare no competing financial interest.

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