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# Synthesis and Reactivity of New Niobocene Hydride-Stibine and Hydride-Stilbene Complexes. X-ray Crystal Structure of $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(trans-\eta^2-C,C-PhCH=CHPh)]$

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Supporting Information

**ABSTRACT:** The synthesis of a stable hydride triphenylstibine derivative, Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(SbPh<sub>3</sub>) (1), has been achieved through the formation of the transient coordinatively unsaturated 16-electron species [Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)] by thermolytic loss of H<sub>2</sub> from Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)<sub>3</sub> (2) followed by the coordination of a triphenylstibine ligand. Low-temperature protonation of 1 with a slight excess of CF<sub>3</sub>COOD led to the  $\eta^{2}$ -dihydrogen complex 3 as the monodeuterated H–D isotopomers of [Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>( $\eta^{2}$ -HD)(SbPh<sub>3</sub>)]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> (3-*d*<sub>1</sub>). When the temperature was increased to room temperature, complex 3 was converted into the



*transoid* dihydride  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)_2(SbPh_3)]CF_3CO_2$  (4). Surprisingly, when CF<sub>3</sub>COOH in deuterated solvents was used in the protonation process, the final  $\eta^2$ -dihydrogen product always contained a substantial amount of deuterated isotopomers. Furthermore, a new hydrido olefin niobocene complex,  $[Nb(\eta^5-(C_5H_4SiMe_3)_2(H)(trans-\eta^2-C,C-PhCH=CHPh)]$  (5), can be synthesized by elimination of the stibine ligand from 1 followed by the addition of *cis* or *trans* stilbene. Complex 5 can also be obtained by reaction of 2 in the presence of *cis* or *trans* stilbene by the thermolytic loss of H<sub>2</sub>. All of these compounds were characterized by IR and multinuclear NMR spectroscopy, and the molecular structure of 5 was determined by single-crystal X-ray diffraction.

# INTRODUCTION

Transition metal hydride derivatives are thought to be involved in a wide variety of organic transformations.<sup>1</sup> In a seminal work, Kubas and co-workers reported<sup>2</sup> a new family of hydride complexes, the dihydrogen derivatives, in which the dihydrogen molecule is coordinated to a metal center. Currently, the study of new dihydrogen transition metal complexes [ $M(\eta^2-H_2)$ ] has experienced an increase in interest, as demonstrated by the continued appearance of numerous research papers and review articles regarding topics such as the correlation of structure/ NMR spectroscopic properties,<sup>3</sup> aqueous chemistry,<sup>4</sup> H<sub>2</sub> activation processes involving transition metal complexes,<sup>5</sup> and the relevance of these compounds to H<sub>2</sub> bioconversion in hydrogenases and hydrogen storage.<sup>6,7</sup>

Protonation of metal hydride complexes is generally recognized as the most common method to prepare  $[M(\eta^2 - H_2)]$  complexes.<sup>6</sup> In this field elegant computational studies have been reported by Lledós and co-workers,<sup>8</sup> and they have elucidated the ways in which the protonation takes place between a hydride complex and an acidic species.

One of the longstanding areas of interest within our research group has concerned the preparation and spectroscopic and

theoretical characterization of  $\eta^2$ -dihydrogen complexes, namely,  $[Nb(\eta^5-C_5H_4SiMe_3)_2(HD)(L)]^+CF_3CO_2^-$  (L = phosphine, phosphite, isocyanide, or carbonyl).<sup>9</sup> All of these compounds represent good examples of elongated dihydrogen complexes, in agreement with their <sup>1</sup>H NMR-calculated H–H distances.<sup>10</sup>

Moreover, after the preparation of the first hydride-olefin niobocene  $[Nb(\eta^5-C_5H_5)_2(H)(\eta^2-C_2H_4)]$  by Tebbe and Parshall,<sup>11</sup> two alternative processes, namely, the reaction of metallocene dihalides and trihydrides (M = Nb, Ta) with various alkylmagnesium halides and olefins, respectively, have been employed to prepare this class of complex. Bercaw<sup>12</sup> and Green<sup>13</sup> and co-workers have investigated in depth the mechanism for the formation of these compounds. A few years later, several of us reported an investigation into this kind of complex that improved our understanding of the mechanistic and reactivity behavior.<sup>14</sup> Surprisingly, in all cases only  $\alpha$ -olefins have been employed, probably because Bercaw and co-

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workers<sup>12a</sup> in 1985 reported that attempts to prepare complexes of sterically demanding olefins resulted in intractable oils.

The aim of the work reported here was twofold: (i) to prepare a new hydride-niobocene derivative that incorporates  $Sb(C_6H_5)_3$  as an ancillary ligand and to study the protonation process that led to the isolation of a new example of dihydrogen-niobocene complexes and (ii) to study the synthesis of new olefin-hydride-niobocene derivatives in which the olefin has a sterically demanding character.

#### RESULTS AND DISCUSSION

Preparation of a Hydride-Stibine Niobocene Com**plex.** The complex Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(SbPh<sub>3</sub>) (1) was readily prepared in high yield (95%) by thermal treatment in THF of Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)<sub>3</sub> (2) in the presence of triphenylstibine (eq 1). In the preparation of a hydride-stibine complex, the initial step would involve the formation of the coordinatively unsaturated 16-electron species  $[Nb(\eta^5 C_5H_4SiMe_3_2(H)$  by thermolytic loss of  $H_2$  followed by coordination of the triphenylstibine ligand (see eq 1). The reaction is similar to that previously reported<sup>9</sup> for the preparation of several families of niobocene complexes, Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(L) (L =  $\pi$ -acid ligand). Complex 1 was isolated as an air-sensitive, red, oily material of spectroscopic purity, and it is, as far as we know, the first example of an organometallic niobocene complex with triphenylstibine as a ligand.<sup>15</sup> In addition, the stability of complex 1 shows an extraordinary solvent dependence; for example, at room temperature in acetone the complex evolves to an intractable mixture of products. This chemical behavior is in contrast with that found for other analogous hydride niobocene derivatives  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(L)]$  (L =  $\pi$ acid ligand) reported by us.<sup>9</sup>

$$Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(H)_{3} + SbPh_{3}$$

$$\xrightarrow{(2)}{} \xrightarrow{-H_{2}/\Delta} Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(H)(SbPh_{3})$$

$$(1)$$

$$(1)$$

Complex 1 was characterized by IR and multinuclear NMR spectroscopy. A stretching mode,  $\nu$ (Nb–H), was detected by infrared spectroscopy for this complex at ca. 1700 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum, in C<sub>6</sub>D<sub>6</sub>, shows a high-field resonance at ca. –8.08 ppm for the hydride ligand and four multiplets, corresponding to an ABCD spin system, for the cyclopentadienyl rings, a finding consistent with an asymmetrical environment for the niobium center (see Experimental Section).

Preparation and Spectroscopic Characterization of a  $\eta^2$ -Dihydrogen-Stibine Niobocene Complex. Low-temperature protonation of neutral hydride complexes to give cationic dihydrogen species was reported for the first time by Crabtree and co-workers in 1985.<sup>16</sup> Following this method, several cationic dihydrogen niobocene complexes,  $[Nb(\eta^5-C_5H_4SiMe_3)_2(\eta^2-H_2)(L)]^+$  (L = phosphine, phosphite, isocyanide), have been prepared by some of us<sup>9</sup> by protonation at low temperature of the corresponding neutral hydride niobium(III) complexes.

Complex  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(Sb(C_6H_5)_3)]$  (1) was easily protonated at low temperature to give the corresponding dihydrogen-containing complex  $[Nb(\eta^5-C_5H_4SiMe_3)_2(\eta^2-H_2)-(Sb(C_6H_5)_3)]^+$  (3), as a major isotopomer, according to eq 2.

$$Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(H)(SbPh_{3})$$

$$\xrightarrow{+CF_{3}COOH} [Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})(\eta^{2}-H_{2})(SbPh_{3})]CF_{3}COO$$
(3)
(2)

This process was carried out by addition of a slight excess of  $CF_3COOH$  to an acetone- $d_6$  solution of complex 1 at 193 K in an NMR tube.

The <sup>1</sup>H NMR spectra show a broad nonsymmetrical dihydrogen resonance at 228 K at ca. -4.7 ppm and a broad line width, which is explained by the rapid dipolar relaxation of these nuclei. It is well known that in metallocene complexes with two different substituents in the equatorial plane, namely, triphenylstibine and dihydrogen ligands, the two hydrogen atoms might appear to be chemically inequivalent if the rotation can be frozen.<sup>9</sup> Decoalescence was observed on lowering the temperature, and at 223 K two high-field resonances were present at 4.7 and 5.4 ppm. On decreasing the temperature to 193 K, the high-field resonance observed at -5.4 ppm had a 1:1:1 triplet pattern. On increasing the temperature to 273 K, the broad signal split into a singlet and a 1:1:1 triplet (see Figure 1, I).



Figure 1. Variable-temperature <sup>1</sup>H NMR spectra of 3 and  $3-d_1$  (acetone- $d_6$ ) at high field.

We assume that the protonation of 1 gives rise to complex 3 as the major isotopomer together with the monodeuterated isotopomers  $3-d_1$ .

This fact was confirmed by adding CF<sub>3</sub>COOD to an acetoned<sub>6</sub> solution of 1 at 228 K in an NMR tube. The <sup>1</sup>H NMR spectrum showed a broad resonance at ca. -4.7 ppm, and on increasing the temperature to 273 K, a 1:1:1 triplet with a coupling <sup>1</sup>J<sub>(H-D)</sub> = 20.7 Hz was observed (see Table 1); this value is consistent with the formation of an H–D bond and provides compelling evidence for the presence of a dihydrogen complex in 3<sup>2-6</sup> (see Figure 1, II). On lowering the temperature to 193 K, decoalescence of the signal was observed and the high-field <sup>1</sup>H NMR spectrum displayed two triplets (1:1:1) centered at ca.  $\delta$  -5.0 ppm, probably due to the existence of two different rotamers: *endo* 3a-d<sub>1</sub> and *exo* 3b-d<sub>1</sub> (Scheme 1). Both isotopomers show a similar <sup>1</sup>J<sub>HD</sub> coupling of

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#### Table 1

complex <sup>a</sup>	$J_{ m HD}$ (Hz)	$\stackrel{r_{\rm H-H}}{{\rm (A)}^{\scriptscriptstyle {\cal D}}}$	$\Delta G$ (kcal/mol)
(HD) gas	43.22	0.698	
$[Nb(\eta^2-HD)(CNR)]CF_3COO^{9c}$	30.0	0.919	8.4-9.1
$[{Nb}'(\eta^2-HD)(CO)]BF_4^{9d}$	26.4	0.979	
$[{Nb}(\eta^2-HD)(Sb(Ph)_3)]CF_3COO^c$	20.7	1.074	10.8
$[{Nb}(\eta^2-HD)(PHPh_2)]CF_3COO^{9b}$	18.2	1.116	11.0
$\begin{matrix} [\{\text{Nb}\}](\eta^2\text{-HD})(\text{PMePh}_2)] \\ \text{CF}_3\text{COO}^{9\text{d}} \end{matrix}$	15.0	1.169	11.0

<sup>*a*</sup>{Nb}' = Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>; {Nb} = Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>. <sup>*b*</sup>Calculated using  $r_{HH} = 1.42 - 0.0167 J_{HD}$ . <sup>*c*</sup>In this article.

ca. 20.7 Hz, in agreement with the presence of H–D molecules coordinated  $[M-(\eta^2-HD)]^9$  to the niobium center.



These rotamers are present due to the fact that the rotation of the coordinated HD molecule is frozen on the NMR time scale at this temperature.<sup>9</sup> Coalescence is reached at 228 K, and at this temperature or above, it is not possible to distinguish between the two isotopomers, because when the temperature is raised, the rotamers *endo* H **3a** and *exo* H **3b** interconvert by rotation of the HD molecule, so at 273 K a single resonance (1:1:1 triplet) is observed at ca. -5.0 ppm.

The above phenomenon allowed us to estimate the free energy of activation of the internal rotation at the coalescence temperature ( $\Delta G^{\#} = 10.8 \text{ kcal/(mol K)}$ ). Similar values have been observed previously for the related complexes<sup>9</sup> [Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>( $\eta^{2}$ -H<sub>2</sub>)(PMe<sub>2</sub>Ph)]CF<sub>3</sub>COO (6) ( $\Delta G^{\#} = 11 \text{ kcal/}$ (mol K))<sup>9d</sup> and [Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>( $\eta^{2}$ -H<sub>2</sub>)(CNR)]CF<sub>3</sub>COO (7) ( $\Delta G^{\#} = 8.29 \text{ kcal/(mol K)})$ .<sup>9c</sup> As a consequence of this relatively high barrier, rotation of the HD molecule can be blocked on the NMR time scale. The value of the <sup>1</sup>J<sub>HD</sub> coupling constant (20.7 Hz) is in excellent agreement with the presence of a stretched dihydrogen ligand (as a comparison, the <sup>1</sup>J<sub>HD</sub> value for the HD gas molecule is 43.2 Hz).<sup>17</sup> An effective method to ascertain the approximate distance between the hydrogen atoms of a dihydrogen ligand is through the <sup>1</sup>J<sub>HD</sub> value, using eq 3:<sup>17</sup>

Scheme 2

$$r_{\rm H-H} = 1.42 - 0.0167 J_{\rm HD} \tag{3}$$

In this way, it is possible to calculate a value of  $r_{H-H} = 1.074$  Å for complex 3, and this lies within the range of distances of other dihydrogen ligands calculated by this method; see Table 1.

After the low-temperature protonation of complex 1 the temperature was raised to room temperature, at which point the high-field resonance at -5.0 ppm began to disappear and a new resonance appeared at -2.22 ppm. This fact can be explained by the transformation of complex 3 into the *transoid* isomer  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)_2(Sb(C_6H_5)_3)]^+$  (4) through an irreversible process (see Scheme 2).

Complex 4 also gives rise to spectroscopic data that are consistent with a symmetrical disposition of the niobium center, with signals for an  $A_2B_2$  spin system observed in the <sup>1</sup>H NMR spectrum for the cyclopentadienyl ligands.<sup>9b</sup>

The formation of complex 4 could be considered to be the result of an oxidative addition of the coordinated dihydrogen molecule in 3 to give a *cisoid* dihydride derivative (not observed) that transforms rapidly into the thermodynamically more stable *transoid* isomer.

When the reaction between 1 and  $CF_3COOH$  in toluene was performed in a Schlenk tube, initially at low temperature and then with warming to room temperature in a slow process, the only isolated product was the *transoid* dihydride 4.

Deuterated species  $3 \cdot d_1$  was observed as a minor isotopomer when the low-temperature protonation of 1 was carried out with CF<sub>3</sub>COOH in the deuterated solvent CD<sub>3</sub>COCD<sub>3</sub>. The formation of this species could be explained by an H/D isotope exchange process. Dihydrogen metal complexes have been used as catalysts for H/D exchange between protic solvents and D<sub>2</sub> due to their Brönsted acidity and the rapid and reversible dissociation of  $H_2$ .<sup>18a</sup> In contrast, very few examples of H/D exchange between  $\eta^2$ -H<sub>2</sub> complexes and aprotic solvents have been reported, and a mechanistic interpretation has never been proposed.<sup>18b,c</sup> As mentioned above, complex 3 in CD<sub>3</sub>COCD<sub>3</sub> rapidly undergoes an H/D interchange at low temperature. The isotope exchange reactions are very fast and initially produce the monodeuterated isotopomer  $3-d_1$ , as shown by the presence of high-field resonances with H-D coupling (see above). Nevertheless, the formation of other isotopomers must also be considered, although the bideuterated isotopomer  $3-d_2$ was not studied by <sup>2</sup>H NMR spectroscopy. The exchange reaction is a fast process because it was observed even at 193 K.

It seems that different mechanisms can operate in this process. In the mechanism proposed in Scheme 3, the cationic  $\eta^2$ -H<sub>2</sub> complex regenerates the terminal hydride by protonation of the deuterated acetone solvent (*step a*), which then protonates a terminal hydride with deuterium from the terminal D to give the  $\eta^2$ -HD complex and the enol (*step b*), which quickly isomerizes to form acetone again (*step c*). Each step



Scheme 3



proposed in Scheme 3 has been observed independently in previous studies.<sup>18,19</sup>

Finally, one cannot rule out the formation of the perdeuterated isotopomer  $[Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(\eta^{2}-D_{2})-(SbPh_{3})]CF_{3}COO(3-d_{2})$  under the same reactions conditions by a second H/D isotope exchange following an analogous mechanism to that described above.

In an effort to prevent the formation of the monodeuterated isotopomer derivative, we decided to use  $CD_3CN$  as solvent in the protonation reaction at low temperature. Surprisingly, a rapid proton/deuterium exchange also took place even when working at a temperature close to the melting point of acetonitrile.

The H/D exchange in acetone- $d_6$  or acetonitrile- $d_3$  did not happen with other related niobium complexes,<sup>10</sup> and we are therefore convinced of the crucial role of the stibine ligand in this process; in this sense some precedent for deuterium exchange with a phosphine ligand in an iron dihydrogen complex has been reported.<sup>20</sup>

**Preparation of a Hydride-Olefin-Niobocene Complex, [Nb**( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(*trans-* $\eta^2$ -C,C-PhCH=CHPh)] (5). The complex [Nb( $\eta^5$ -C<sub>3</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(*trans-* $\eta^2$ -C,C-PhCH= CHPh)] (5) was readily prepared in high yield (90%) by thermal treatment in THF of Nb( $\eta^5$ -C<sub>3</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(SbPh<sub>3</sub>) (1) in the presence of *cis-* or *trans-*stilbene (Scheme 4). In the preparation of complex 5, the initial step would involve the formation of the coordinatively unsaturated 16-electron species [Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)] by thermolytic loss of SbPh<sub>3</sub> followed by coordination of the olefin present in solution. The reaction is similar to that previously described for complex 1 (*vide infra*). Complex 5 was isolated as an air-sensitive, yellowish, microcrystalline solid.

Alternatively, **5** can be formed when a THF solution of  $Nb(\eta^5-C_5H_4SiMe_3)_2(H)_3$  (2) in the presence of *cis*- or *trans*-stilbene (see Scheme 4) is warmed to 60 °C for 3 h.

This is the first example of a hydride olefin niobocene complex having been prepared by the reaction of a niobocene trihydride with a sterically demanding olefin.<sup>12–14</sup> Some years ago some of us reported the synthesis of new hydride olefin complexes, namely,  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(trans-\eta^2-C,C-ROOC-C(H)=C(H)-COOR)]$  (R = Me, <sup>t</sup>Bu) by reaction of 2 with activated alkynes such as ROOC-C=C-COOR (R = Me, <sup>t</sup>Bu) in an insertion process of the carbon–carbon triple bond into the Nb–H bond.<sup>21</sup>

Only the *trans*-isomer of complex 5 has been prepared, regardless of the olefin employed (i.e., *cis*- or *trans*-stilbene),



and therefore the reaction pathways proposed in Scheme 5 seem reasonable for this process.

It seems that two different pathways can operate in this process depending on the olefin employed. First, when cisstilbene was used, path a is suggested with the formation of the hydride olefin intermediate I, which quickly evolves with the formation of an intermediate alkylniobocene species II through insertion of the C=C moiety into the Nb-H bond. Subsequently, the probable interaction between the phenyl substituents would generate rotation through the C–C bond to generate a new, less hindered chain configuration in which the two bulky groups are as far from each other as possible (intermediate III). Finally, the favored  $\beta$ -elimination process would lead to the formation of the thermodynamically more stable trans-olefin hydride niobocene complex 5. Second, in *path b* we propose the typical trapping process of the unsaturated 16-electron hydride intermediate by a trans-stilbene compound, with the direct formation of the corresponding complex 5.

The thermal stability of complex **5** has been demonstrated. When the temperature was raised to the boiling point of the solvent, exchange of the hydride ligand with the hydrogen atoms of the olefin did not take place, in contrast with other analogous hydride-olefin-niobocene derivatives reported by some of us.<sup>14</sup> Furthermore, a particular inertness toward the insertion of several unsaturated molecules, namely, CO, CNR, and CS<sub>2</sub>, is noteworthy, even under harsh reaction conditions.<sup>22</sup> This situation is in contrast to the behavior observed previously by us for other hydride olefin niobocene complexes.<sup>14</sup>

The structural characterization of **5** was carried out by spectroscopic and X-ray diffraction studies.

The IR spectrum of **5** shows a weak, broad band at 1730 cm<sup>-1</sup> assigned to  $\nu$ (Nb–H). The <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> shows the hydride resonance at  $\delta$  –2.67 ppm. The <sup>1</sup>H and <sup>13</sup>C NMR spectra exhibit eight and 10 resonances for the proton and carbon atoms, respectively, for the two cyclopentadienyl ligands, indicating that they are not equivalent. This behavior is in agreement with the structural disposition (*vide infra*) observed for this complex, where the olefinic carbon atoms are coplanar with the niobium and hydride atoms in such a way

# Scheme 5



that their substituents (in a *trans*-disposition) are situated in a plane orthogonal to that containing the aforementioned atoms. This structural disposition leads to the presence of two resonances for the inequivalent SiMe<sub>3</sub> groups. Finally, the presence in the <sup>1</sup>H NMR spectra of AB spin systems for the olefinic protons as two doublets at 3.79 and 3.42 ppm, with a coupling constant of  ${}^{3}J_{\text{HaHb}} = 13.73$  Hz, must also be emphasized, as this is in agreement with a *trans* disposition (see Experimental Section).

Furthermore, the X-ray crystal structure of **5** was determined. The molecular structure is shown in Figure 2 along with the atom-numbering scheme. Selected bond distances and angles are listed in Table 2.

Complex 5 adopts the typical bent-metallocene structure. The environment around the Nb center shows two  $\eta^{5}$ -coordinated Cp' ligands, one  $\eta^{2}$ -coordinated stilbene molecule, and a hydride ligand. The distances between the metal atom and the centroids of the Cp' rings are 2.084 and 2.073 Å, and



Table 2. Bond Lengths (Å) and Angles (deg) for  $5^{a}$ 

bond length	ns (Å)	bond angles (deg)		
Nb(1)-H(1)	1.66(4)	Ct(1)-Nb(1)-Ct(2)	135.17	
Nb(1)-Ct(1)	2.084	C(7)-Nb(1)-C(8)	35.7(1)	
Nb(1)-Ct(2)	2.073	C(8) - C(7) - C(1)	124.4(3)	
Nb(1)-C(7)	2.315(3)	C(8) - C(7) - Nb(1)	73.69(16)	
Nb(1)-C(8)	2.356(3)	C(1)-C(7)-Nb(1)	122.5(2)	
C(1) - C(7)	1.481(4)	C(7) - C(8) - C(9)	122.7(3)	
C(7) - C(8)	1.433(4)	C(7) - C(8) - Nb(1)	70.6(2)	
C(8) - C(9)	1.483(4)	C(9)-C(8)-Nb(1)	122.7(2)	
<sup>a</sup> Ct(1) and Ct(2) are the centroids of C(15)-C(19) and C(23)-				
C(27), respectivel	y.			

the angle Ct(1)-Nb(1)-Ct(2) is 135.37° [Ct(1) and Ct(2)] are the centroids of the two cyclopentadienyl rings]. The Cp ligands are nearly staggered, with the two SiMe<sub>3</sub> groups arranged trans to each other. The hydride was located in the structure in the final  $\Delta F$  map. The Nb–H distance is 1.66 (4) Å, and it is comparable to values found in a series of scarce niobium complexes that contain terminal hydride ligands.<sup>21,23</sup> The niobium atom is also bound to the C(7) and C(8) carbon atoms of the dihapto-coordinated alkene. The olefinic carboncarbon bond length [1.433(4) Å] is larger than that of a free olefin, and this may be indicative of substantial back-donation from the metal to the olefin, which would introduce some metallacyclopropane-Nb(V) character into the formally Nb(III) olefin complex. The chirality found in complex 5 is due to the configuration of the coordinated C(7) and C(8) atoms, and both the (S,S) and (R,R) enantiomers are present in the unit cell. The coordination around the metal atom can be described as an irregular flattened tetrahedron with the centroids Ct(1), Ct(2), and M(1) [M(1) is at the midpoint of the olefinic C(7)=C(8) bond] and the hydride at the vertices of the polyhedron. The Nb(1)M(1)H(1) plane is perpendicular to the Nb(1)Ct(1)Ct(2) plane (90.42°). The four atoms Nb(1), C(7), C(8), and H(1) are practically coplanar, and the Nb(1)– H(1) bond is parallel to the C(7)=C(8) bond. In fact, the angles subtended by the two weighted least-squares lines

Figure 2.

Nb(1)H(1) and C(7)C(8) are 0.56°. The Nb(1)C(7)C(8) plane bisects the two Cp' rings [the angles between the weighted least-squares plane Nb(1)C(7)C(8) and the C(15)…C(19) Cp' ring and the C(23)…C(27) Cp' ring are 23.29° and 23.46°, respectively].

#### CONCLUDING REMARKS

In this paper we have described the preparation of a stable hydride stibine niobocene derivative,  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H) (Sb(C_6H_5)_3)$ ] (1), by thermolytic loss of H<sub>2</sub> from the trihydride derivative  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)_3]$  (2) followed by the coordination of a triphenylstibine ligand. Low-temperature protonation with a slight excess of CF<sub>3</sub>CO<sub>2</sub>H leads to the  $\eta^2$ -dihydrogen cationic complex  $[Nb(\eta^5-C_5H_4SiMe_3)_2(\eta^2-H_2) (Sb(C_6H_5)_3)^{\dagger}$  (3), whose  $\eta^2$ -(H<sub>2</sub>) and monodeuterated  $\eta^2$ -(HD) isotopomers show temperature-dependent NMR spectroscopic properties. The free energy of activation for the dihydrogen internal rotation was estimated to be 10.8 kcal/mol. Interestingly, it was observed that complex 3 promotes a rapid H/D interchange. Additionally, a new hydride olefin niobocene complex,  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(trans-\eta^2-C_7C_7)]$ CHPh)] (5), has been prepared, and the molecular structure was determined by X-ray diffraction. This complex represents a rare example of this type of niobocene complex bearing a sterically demanding olefin ligand.

## **EXPERIMENTAL SECTION**

**General Procedures.** All reactions were carried out using standard Schlenk techniques. Oxygen and water were excluded through the use of vacuum lines supplied with purified  $N_2$ . Hexane was distilled from sodium/potassium alloy. THF was distilled from sodium benzophe-

#### Table 3. Crystal Data and Structure Refinement for 5

empirical formula	C <sub>30</sub> H <sub>39</sub> NbSi <sub>2</sub>		
fw	548.70		
temperature	150(2) K		
wavelength	0.71073 Å		
cryst syst	monoclinic		
space group	$P2_{1}/c$		
unit cell dimens	a = 12.6788(9) Å	$\alpha = 90^{\circ}$	
	b = 10.9654(8) Å	$\beta = 94.087(4)^{\circ}$	
	c = 19.9135(15) Å	$\gamma = 90^{\circ}$	
volume	2761.5(3) Å <sup>3</sup>		
Ζ	4		
density (calcd)	1.320 Mg/m <sup>3</sup>		
abs coeff	$0.539 \text{ mm}^{-1}$		
F(000)	1152		
cryst size	$0.23 \times 0.19 \times 0.10 \text{ mm}^3$		
theta range for data collection	1.61° to 28.38°		
index ranges	$\begin{array}{l} -16 \leq h \leq 16,  -14 \leq k \leq 14, \\ -26 \leq l \leq 26 \end{array}$		
reflns collected	33 336		
indep reflns	6872 [R(int) = 0.0803]		
completeness to theta = $28.38^{\circ}$	99.3%		
abs corr	semiempirical from equivalents		
max. and min. transmn	0.9481 and 0.8861		
refinement method	full-matrix least-squares on $F^2$		
data/restraints/params	6872/0/308		
goodness-of-fit on $F^2$	1.090		
final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0451, wR2 = 0.1079		
R indices (all data)	R1 = 0.0715, wR2 = 0.1276		
largest diff peak and hole	0.715 and −0.899 e·Å <sup>-3</sup>		

none. All solvents were deoxygenated prior to use. Deuterated solvents were dried over 4 Å molecular sieves and degassed prior to use. Nb( $\eta^{5}$ C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)<sub>3</sub> (2) was prepared as described in the literature.<sup>24</sup> *cis*-Stilbene, *trans*-stilbene, and triphenylstibine were used as supplied by Aldrich. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Varian Innova 500 MHz spectrometer at room temperature unless stated otherwise. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts ( $\delta$  values) are given in ppm relative to the solvent signal (<sup>1</sup>H, <sup>13</sup>C) or standard resonances. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as Nujol/polyethylene mulls. Microanalyses were carried out on a Perkin-Elmer 2400 microanalyzer.

**Preparation of Nb**( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(SbPh<sub>3</sub>) (1). SbPh<sub>3</sub> (0.190 g, 0.540 mmol) was added to a tan-colored solution of Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)<sub>3</sub> (2) (0.200 g, 0.540 mmol) in THF (40 mL). The mixture was stirred at 343 K for 2 h. The resulting red solution was filtered and evaporated to dryness. Complex 1 was isolated as a red, oily material after maintaining it under vacuum for a lengthy period of time (yield: 95%).

1: Yield 95%. IR (Nujol/polyethylene, cm<sup>-1</sup>): 1696 (Nb–H). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ (ppm) –8.08 (s, 1 H, Nb–H), 0.19 (s, 18 H, SiMe<sub>3</sub>), 3.89, 4.18, 4.74, 5.04 (m, 2 H each a complex signal, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 7.01–7.71 C<sub>6</sub>H<sub>5</sub>. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ (ppm) 0.7 (SiMe<sub>3</sub>), 82.0, 84.6, 87.4, 88.8 (C2–5, exact assignment not possible, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 89\_2 (C1, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 130.0–140.0 (SbPh<sub>3</sub>).

Protonation of Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(SbPh<sub>3</sub>) (1) (Mixture of 3 and 3- $d_1$  Isotopomers). Either CF<sub>3</sub>COOH or CF<sub>3</sub>COOD was added to an acetone- $d_6$  solution of Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)(SbPh<sub>3</sub>) (1) in a 5 mm NMR tube at 183 K, to give either the dihydrogen complex [Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)(SbPh<sub>3</sub>)]CF<sub>3</sub>CO<sub>2</sub> (3) or its isotopomer- $d_1$  [Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>( $\eta^2$ -HD)(SbPh<sub>3</sub>)]CF<sub>3</sub>CO<sub>2</sub> (3- $d_1$ ). 3- $d_1$ : <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) –5.00 (t, 1:1:1,  $J_{HD}$  = 20.7 Hz, 1 H, Nb-HD), 0.07 (s, 18 H, SiMe<sub>3</sub>), 4.38, 5.38, 5.93, 6.27 (m, 2 H each a complex signal, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 7.59–7.72 (m, 15 H, SbPh<sub>3</sub>).

3: <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  (ppm) -4.74 (s, br, 2 H, Nb- $H_2$ ), 0.07 (s, 18 H, SiMe<sub>3</sub>), 4.38, 5.38, 5.93, 6.27 (m, 8 H,  $C_5H_4$ ), 7.59–7.72 (m, 15 H, SbPh<sub>3</sub>).

**Preparation of**  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)_2(SbPh_3)]^+CF_3COO^-$  (4). To a solution of Nb( $\eta^5-C_5H_4SiMe_3)_2(H)(SbPh_3)$  (1) (0.300 g, 0.360 mmol) in toluene (30 mL) at 183 K was added a small excess of CF<sub>3</sub>COOH (0.33 mL, 0.432 mmol) by syringe. The solution was allowed to reach room temperature and was stirred for 2 h. A red precipitate formed. When sedimentation was complete, the solution was filtered and the residue was washed twice with Et<sub>2</sub>O (10 mL) and dried under vacuum. The resulting solution was evaporated to dryness. Complex 4 was obtained as red solid (yield: 80%).

4: IR ( $\nu$ , Nujol/polyethylene):  $\nu$  (cm<sup>-1</sup>), 1673 (Nb–H). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) –2.22 (s, 2 H, Nb–H), 0.06 (s, 18 H, SiMe<sub>3</sub>), 5.23, 6.20 (m, 4 H, each a complex signal, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 7.46, 7.61, 7.75 (SbPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) –0.2 (SiMe<sub>3</sub>), 96.2, 98.1, 105.3 (C2–5, exact assignment not possible, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 116.1 (q, <sup>2</sup>J<sub>CF</sub> = 14.24 Hz, CF<sub>3</sub>COO<sup>-</sup>), 131.8, 135.9, 136.6 (SbPh<sub>3</sub>), 139.0 (C<sub>1</sub>, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 158.6 (q, <sup>1</sup>J<sub>CF</sub> = 32.1 Hz, CF<sub>3</sub>COO<sup>-</sup>). Anal. Calcd for C<sub>36</sub>H<sub>43</sub>F<sub>3</sub>NbO<sub>2</sub>SbSi<sub>2</sub>: C, S1.75; H, 5.19. Found: C, 51.48; H, 5.07.

**Preparation of**  $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(trans-\eta^2-C,C-PhCH=$ CHPh)] (5). Method 1. Nb $(\eta^5-C_5H_4SiMe_3)_2(H)(SbPh_3)$  (1) (0.300 g, 0.360 mmol) was dissolved in THF (40 mL) to form a red solution. To this solution was added *cis*- or *trans*-stilbene, Ph-CH=CH-Ph (0.064 mL, 0.360 mmol). The mixture was stirred at 343 K for 2 h. The resulting red-brown solution was filtered and evaporated to dryness. The red-brown, oily residue was extracted with hexane (20 mL). The resulting solution was filtered and evaporated to dryness. After washing the solid with hexane (10 mL) and recrystallization from diethyl ether, **5** was isolated as a yellowish microcrystalline solid (yield: 80%).

Method 2. Nb( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(H)<sub>3</sub> (2) (0.253 g, 0.680 mmol) was dissolved in THF (40 mL) to form a tan solution. To this solution was added *cis-* or *trans-*stilbene, Ph–CH=CH–Ph (0.12 mL, 0.680 mmol). The mixture was stirred at 343 K for 2 h. The resulting light brown solution was filtered and evaporated to dryness. The light

brown, oily residue was extracted with hexane (20 mL). The resulting solution was filtered and evaporated to dryness. After washing the solid with hexane (10 mL) and recrystallization from diethyl ether, **5** was isolated as a yellowish microcrystalline solid (yield: 85%).

**5:** IR ( $\nu$ , Nujol/polyethylene):  $\nu$  (cm<sup>-1</sup>), 1721 (Nb–H), 1589 (C=C). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) –2.23 (s, 1 H, Nb–H), 0.15, 0.35 (s, 9 H, SiMe<sub>3</sub>), 3.42, 3.79 (dd, 2 H, AB system, J<sub>HbHa</sub> = 13.73 Hz, C<sub>5</sub>H<sub>6</sub>–CH=CH–C<sub>5</sub>H<sub>6</sub>), 3.69, 3.71, 3.86, 4.05, 4.38, 4.63, 4.75, 5.03 (m, 1 H, each a complex signal, C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 6.87–7.48 (m, 10 H, C<sub>5</sub>H<sub>6</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 0.4 (SiMe<sub>3</sub>), 34.3, 34.6 (C=C–H), 90.8, 97.1, 97.2, 98.7, 99.8, 101.0, 102.7, 102.8, 102.9, 106 (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), 122.4, 122.8, 126.9, 128.0, 152.6, 153.6 (C<sub>6</sub>H<sub>5</sub>). Anal. Calcd for C<sub>30</sub>H<sub>39</sub>NbSi<sub>2</sub>: C, 65.67; H, 7.16. Found: C, 65.50; H, 7.11.

**X-ray Structure Determination for 5.** Data were collected on a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite-monochromated Mo K $\alpha$  radiation source ( $\lambda = 0.71073$  Å). The crystal data and data collection, structural solution, and refinement parameters are summarized in Table 3. Data were integrated using SAINT,<sup>25</sup> and an absorption correction was performed with the program SADABS.<sup>26</sup> The structure was solved by direct methods using SHELXTL<sup>27</sup> and refined by full-matrix least-squares methods based on  $F^2$ . All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and are included in the refinement at calculated positions.

# ASSOCIATED CONTENT

#### **Supporting Information**

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#### Notes

The authors declare no competing financial interest.

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