

# Cp<sub>2</sub>NbH<sub>2</sub>SbPh<sub>2</sub>: Synthesis and Structure of the First Antimony-Substituted Niobocene

Georgii I. Nikonov,<sup>\*,†</sup> Lyudmila G. Kuzmina,<sup>‡,§</sup> and Judith A. K. Howard<sup>‡</sup>

Chemistry Department, Moscow State University, Vorob'evy Gory, 119899 Moscow, Russia, and University of Durham, South Road, Durham DH1 3LE, U.K.

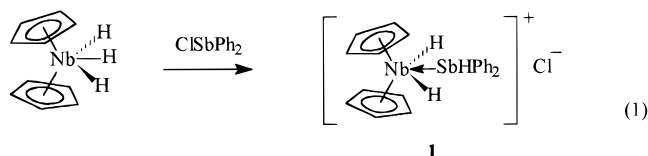
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**Summary:** The first antimony-substituted niobocene, Cp<sub>2</sub>NbH<sub>2</sub>SbPh<sub>2</sub> (**2**), was prepared by the reaction of ClSbPh<sub>2</sub> of Cp<sub>2</sub>NbH<sub>3</sub> in the presence of amine. The molecular structure of **2** is reported.

Antimony-substituted transition metal complexes are much less studied than the corresponding phosphorus and arsenic derivatives.<sup>1–5</sup> Their chemistry is mainly presented by the cluster compounds,<sup>1</sup> whereas terminal antimony ligands are very rare.<sup>2–5</sup> Moreover, only few complexes with the terminal M–SbR<sub>2</sub> (R = alkyl, aryl) groups are known,<sup>3</sup> and none of them have been structurally characterized.<sup>4</sup> To the best of our knowledge, only one hydridostibide compound, the iridium complex Ir(CO)ClH(PET<sub>3</sub>)<sub>2</sub>(SbH<sub>2</sub>), has been reported.<sup>5</sup> This compound was prepared by oxidative addition of SbH<sub>3</sub> and is unstable at room temperature. The lack of stable stibines HSbR<sub>2</sub><sup>6,7</sup> prevents the synthesis of other hydridostibide compounds H–M–SbR<sub>2</sub> by oxidative addition of the H–Sb bond, and thus alternative routes are required. We have shown recently that the insertion<sup>8–10</sup> of halides of group 15 organyls XER<sub>2</sub> (E = P, As, Bi; X = Cl, Br) into the M–H bond of Cp<sub>2</sub>MH<sub>3</sub>

(M = Nb, Ta) presents a convenient route to the phosphorus,<sup>8</sup> arsenic,<sup>9</sup> and bismuth<sup>10</sup> substituted complexes. Here, we report the application of this approach to the synthesis of the first antimony-substituted group 5 metallocene Cp<sub>2</sub>NbH<sub>2</sub>SbPh<sub>2</sub> (**2**) and its X-ray structure determination.

Addition of ClSbPh<sub>2</sub> to an ether solution of Cp<sub>2</sub>NbH<sub>3</sub> results in the expected precipitation of an orange material, eq 1. The NMR spectra revealed formation



of an ionic complex [Cp<sub>2</sub>NbH<sub>2</sub>(HSbPh<sub>2</sub>)]Cl (**1**) together with a mixture of some other hydride derivatives, the structures of which are at present unknown. This result is in contrast to the high selectivity of the formation of [Cp<sub>2</sub>MH<sub>2</sub>(HPR<sub>2</sub>)]Cl (M = Nb, Ta) and [Cp<sub>2</sub>NbH<sub>2</sub>(HASR<sub>2</sub>)]-Br by the analogous insertion of halophosphines and arsines into the M–H bond. The lack of selectivity in reaction 1 can be attributed either to impurities in the starting ClSbPh<sub>2</sub><sup>11</sup> or to the inherent instability of **1**. Indeed, complex **1** decomposes when kept in the mother liquor. The decomposition is especially noticeable when THF is added. However, in the form of a dry solid, complex **1** can be kept under inert atmosphere for some days. To summarize our study on the complexes of the type [Cp<sub>2</sub>NbH<sub>2</sub>(HER<sub>2</sub>)]Hal (E = P,<sup>8</sup> As,<sup>9</sup> Sb, Bi<sup>10</sup>) the order of stability can be written as follows: [Cp<sub>2</sub>NbH<sub>2</sub>(HPR<sub>2</sub>)]Cl > [Cp<sub>2</sub>NbH<sub>2</sub>(HASR<sub>2</sub>)]Br > [Cp<sub>2</sub>NbH<sub>2</sub>(HSbR<sub>2</sub>)]Cl > [Cp<sub>2</sub>NbH<sub>2</sub>(HBiR<sub>2</sub>)]Cl. Evidently, this order of stability correlates with the decrease of basicity of the related hydrides HER<sub>2</sub>.

The structure of **1** was established by the <sup>1</sup>H NMR spectrum and in comparison with the corresponding data for [Cp<sub>2</sub>NbH<sub>2</sub>(HPR<sub>2</sub>)]Cl<sup>8a</sup> and [Cp<sub>2</sub>NbH<sub>2</sub>(HASR<sub>2</sub>)]-Br.<sup>9</sup> The Cp ligands give rise to a singlet at 5.54 ppm (integrated as 10), while the hydride resonance was found at –2.45 ppm (integrated as 2). The phenyl protons give rise to multiplets at 8.17 and 7.24 ppm. The Sb–H signal was not observed, apparently due to

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(11) Compound ClSbPh<sub>2</sub> was obtained in the form of a viscous oil by the reaction of SbPh<sub>3</sub> with SbCl<sub>3</sub>. This procedure was reported<sup>12</sup> to give ClSbPh<sub>2</sub> in near quantitative yield, but isolation of this product in the undoubtedly pure crystalline form is complicated because of its low melting point. Thus, in this study ClSbPh<sub>2</sub> was used as prepared. Since there is no way to check the purity of this material, we cannot exclude that it contains some impurities (SbCl<sub>3</sub>, Cl<sub>2</sub>SbPh, and SbPh<sub>3</sub>) amenable to the reaction with Cp<sub>2</sub>NbH<sub>3</sub>.

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<sup>†</sup> Moscow University.

<sup>‡</sup> University of Durham.

<sup>§</sup> Permanent address: Institute of General and Inorganic Chemistry, RAS, Leninsky prosp. 31, 117907 Moscow, Russia.

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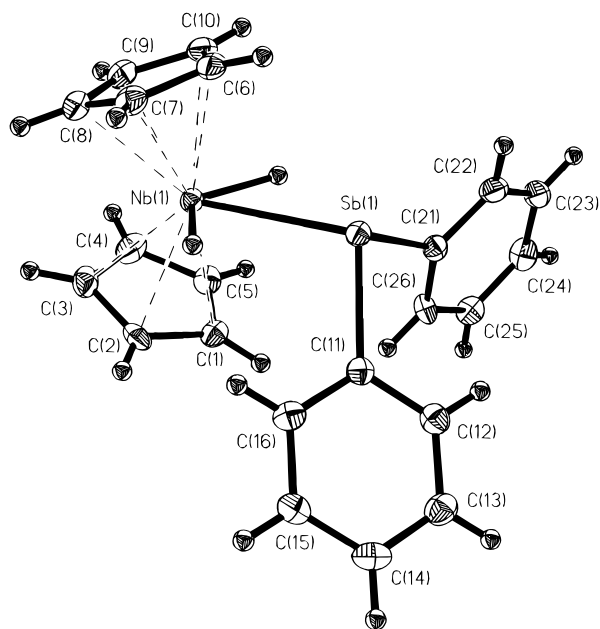
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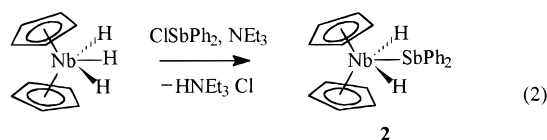
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**Figure 1.** Molecular structure of **2**.

the fast proton for deuterium exchange with the solvent.<sup>8a</sup> However, the presence of the Sb–H bond was confirmed by the band at 1856 cm<sup>-1</sup> in the IR spectrum.

The precipitate obtained in reaction 1 was treated with aqueous NaOH to give a mixture of hydride compounds, the predominant component being Cp<sub>2</sub>NbH<sub>2</sub>SbPh<sub>2</sub> (**2**). Complex **2** was also made by the reaction of ClSbPh<sub>2</sub> with Cp<sub>2</sub>NbH<sub>3</sub> in the presence of NEt<sub>3</sub> (eq 2). Compound **2** was isolated in the crystalline



form from an ether solution and studied by means of spectroscopic methods and X-ray diffraction analysis. The <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>) spectrum of **2** reveals the Cp proton signal at 4.56 ppm and the resonance due to the Nb–H protons at –3.18 ppm. The presence of the Nb–H bond is also supported by the band at 1739 cm<sup>-1</sup> in the IR spectrum. Complex **2** is a yellow air-sensitive compound, quite stable at room temperature under inert atmosphere both as a solid and in solution. This thermal stability of **2** is analogous to that of Cp<sub>2</sub>NbH<sub>2</sub>AsEt<sub>2</sub><sup>9</sup> and is in contrast to the instability of Cp<sub>2</sub>NbH<sub>2</sub>BiPh<sub>2</sub>.<sup>10</sup> Complex **2** is even stable when heated at 50 °C for 1 h, however, it decomposes in reflux THF after 16 h to give a mixture of unidentified products. In contrast, the previously reported hydridostibide complex Ir(CO)ClH(PEt<sub>3</sub>)<sub>2</sub>(SbH<sub>2</sub>) decomposes at room temperature.<sup>5</sup>

Complex **2** is the first example of a compound having neighboring M–H and M–SbR<sub>2</sub> groups. Also, no stibide complexes L<sub>n</sub>M–SbR<sub>2</sub> (R = alkyl, aryl) have been studied structurally yet,<sup>4</sup> which prompted the X-ray diffraction analysis of **2**. The molecular structure of **2** is shown in Figure 1, and the selected bond distances and bond angles are given in Table 1. The crystal

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**Table 1.** Selected Bond Lengths (Å) and Angles (deg)

Nb(1)–Sb(1)	2.8929(4)	Nb(1)–H(1)	1.635
Nb(1)–H(2)	1.692	Nb(1)–C(1)	2.400(4)
Nb(1)–C(3)	2.378(4)	Nb(1)–C(2)	2.399(4)
Nb(1)–C(5)	2.404(4)	Nb(1)–C(4)	2.372(4)
Nb(1)–C(7)	2.408(4)	Nb(1)–C(6)	2.398(4)
Nb(1)–C(10)	2.422(4)	Nb(1)–C(8)	2.396(4)
Sb(1)–C(11)	2.175(4)	Nb(1)–C(9)	2.403(4)
Sb(1)–C(21)	2.187(4)		
H(1)–Nb(1)–H(2)	122.6	C(11)–Sb(1)–C(21)	94.32(14)
C(11)–Sb(1)–Nb(1)	106.05(10)	C(21)–Sb(1)–Nb(1)	105.95(10)

structures of some related complexes Cp<sub>2</sub>TaH<sub>2</sub>SiPhMe<sub>2</sub>,<sup>13</sup> Cp<sub>2</sub>TaH<sub>2</sub>PPh<sub>2</sub>,<sup>8b</sup> and Cp<sub>2</sub>NbH<sub>2</sub>AsEt<sub>2</sub><sup>9</sup> were reported earlier. Complex **2** is a typical trisubstituted d<sup>0</sup> niobocene with a central position of the stibido group and the Nb–Sb distance of 2.8929(4) Å. This bond length is 0.067 Å less than the calculated distance of 2.96 Å (obtained by combining the niobocene radius of 1.55 Å<sup>14</sup> with the Sb covalent radius of 1.41 Å<sup>15</sup>). It is also noteworthy that the Sb–C(11) and Sb–C(21) bond lengths of 2.175(4) and 2.187(4) Å are longer than the calculated value of 2.08 Å obtained by combining the Sb covalent radius of 1.41 Å with the sp<sup>2</sup> carbon radius of 0.67 Å.<sup>15</sup> These observations can be attributed to the higher Sb s orbital character in the Nb–Sb bond and hence higher Sb p orbital contribution into the Sb–Ph bonds. Earlier Bulychev et al. showed that the M–Sn bonds (M = Mo, W, Ta) were shortened due to the high contribution of the Sn s orbital.<sup>16</sup> The geometry around antimony can be described as pyramidal with the stereoactive lone pair of the Sb directed toward one of the Cp rings, thus minimizing repulsion from the Nb–H bonds. Two hydrides were also located and refined isotropically to the distances 1.635 and 1.692 Å, close to that found for Cp<sub>2</sub>NbH<sub>3</sub> (average 1.69(4) Å, X-ray diffraction study).<sup>17</sup> The true Nb–H bond length is probably about 0.1 Å longer and is close to the average Ta–H bond length of 1.773 Å found in Cp<sub>2</sub>TaH<sub>3</sub><sup>17</sup> (neutron diffraction study). The H(1)–Nb–H(2) angle of 122.6° in **2** is close to that in Cp<sub>2</sub>NbH<sub>3</sub> (126(3)°) but is greater than the H–Nb–H angle in Cp<sub>2</sub>NbH<sub>2</sub>AsEt<sub>2</sub><sup>9</sup> (112.1°), which in turn is larger than the corresponding angle in Cp<sub>2</sub>TaH<sub>2</sub>PPh<sub>2</sub><sup>8b</sup> (102.0°). The decrease of the H–M–H angle in complexes of the type Cp<sub>2</sub>MH<sub>2</sub>ER<sub>2</sub> (E = P, As) may be due to a weak bonding interaction of the M–H bonds with the p<sub>E</sub>–c\* antibonding orbital of the ER<sub>2</sub> moiety that is mainly located on atom E. This orbital is collinear with the C(11)–C(21) vector (C(11), C(21)–carbons connected with atom E) and thus almost exactly lays in the bisecting plane of the Cp<sub>2</sub>M moiety in all three structures studied. This weak secondary interaction should decrease with the increase of the M–E bond length, i.e., in the order P > As > Sb.

In summary, we have prepared the first antimony-substituted group 5 metallocene complex Cp<sub>2</sub>NbH<sub>2</sub>SbPh<sub>2</sub>. This compound has a unique combination of neighboring M–H and M–SbR<sub>2</sub> groups and is the first

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**Table 2. Crystal Data and Structure Refinement for 2**

empirical formula	C <sub>22</sub> H <sub>22</sub> NbSb
fw	501.06
color, habit	light-yellow, prism
cryst size	0.04 × 0.06 × 0.18
cryst syst	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
unit cell dimens	
<i>a</i> , Å	9.1912(2)
<i>b</i> , Å	16.3299(3)
<i>c</i> , Å	12.5275(3)
β, deg	99.412(1)
volume, Å <sup>3</sup>	1854.96(7)
<i>Z</i>	4
density (calcd), g/cm <sup>3</sup>	1.794
abs coeff, mm <sup>-1</sup>	2.074
<i>F</i> (000)	984
diffractometer	Siemens Smart
temperature, K	150.0(2)
radiation, (λ Å)	Mo Kα (0.710 73)
scan mode	ω
scan step (in ω), deg	0.3
time per step, s	30
θ range for data collection, deg	2.07–29.00
index ranges	–12 ≤ <i>h</i> ≤ 11, –20 ≤ <i>k</i> ≤ 22, –17 ≤ <i>l</i> ≤ 17
no. of reflns collected	14 502
no. of independent reflns	4885 [ <i>R</i> (int) = 0.0579]
abs corr	empirical
max transmission	0.497 10
min transmission	0.405 31
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
data/restraints/params	4481/0/226
goodness-of-fit on <i>F</i> <sup>2</sup>	1.072
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0379, <i>wR</i> 2 = 0.0626
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0645, <i>wR</i> 2 = 0.0761
ext coeff	0.00056(11)

complex with the M–SbR<sub>2</sub> group that was studied by X-ray diffraction analysis.

### Experimental Section

All manipulations were carried out using conventional Schlenck techniques. Solvents were dried over sodium or sodium benzophenone ketyl. NMR spectra were recorded on a Varian VXR-400 spectrometer (<sup>1</sup>H, 400 MHz; <sup>13</sup>C, 100.4 MHz). IR spectra were obtained in Nujol with a FTIR Perkin-Elmer 1600 series spectrometer. SbCl<sub>3</sub> and SbPh<sub>3</sub> were purchased from Aldrich. ClSbPh<sub>2</sub> was prepared according to the literature method.<sup>12</sup> Cp<sub>2</sub>NbH<sub>3</sub> was prepared by the modified procedure as reported earlier.<sup>8a</sup>

**Reaction of Cp<sub>2</sub>NbH<sub>3</sub> with ClSbPh<sub>2</sub> To Give [Cp<sub>2</sub>NbH<sub>2</sub>(SbHPh<sub>2</sub>)]Cl (1).** A solution of 1.03 g (4.56 mmol) of Cp<sub>2</sub>NbH<sub>3</sub> in 70 mL of ether was added to 1.70 g (5.46 mmol) of ClSbPh<sub>2</sub> in 10 mL of ether. An orange precipitate was formed immediately. In 3 min, the solution was filtered and the residue was washed by 10 mL of ether. Yield: 1.55 g (mixture of 1

and two more cyclopentadienylhydride compounds). [Cp<sub>2</sub>NbH<sub>2</sub>(HSbPh<sub>2</sub>)]Cl. IR (Nujol): ν<sub>Sb–H</sub> 1856, ν<sub>Nb–H</sub> 1637 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 8.17 (d, *J*<sub>H–H</sub> = 6.0 Hz, 4, Ph), 7.24 (m, 6, Ph), 5.54 (s, 10, Cp), –2.45 (s, 2, Nb–H).

**Preparation of Cp<sub>2</sub>NbH<sub>2</sub>SbPh<sub>2</sub> (2).** An ether solution of ClSbPh<sub>2</sub> (40 mL), prepared *in situ*<sup>12</sup> from 0.174 g (0.764 mmol) of SbCl<sub>3</sub> and 0.540 g (1.528 mmol) of SbPh<sub>3</sub>, was added to a mixture of 0.540 g (2.292 mmol) of Cp<sub>2</sub>NbH<sub>3</sub> and 1 mL of NET<sub>3</sub> in 30 mL of ether. An orange precipitate is formed immediately. The mixture was stirred for 30 min. The solution was filtered, and the residue was washed by 15 mL of ether. Yellow crystals were formed from an ether solution after some hours at room temperature. Yield: 0.117 g (0.238 mmol, 10%).

IR (Nujol): ν<sub>Nb–H</sub> = 1739 cm<sup>-1</sup>. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): 7.98 (dd, *J*<sub>H–H</sub> = 7.8, *J*<sub>H–H</sub> = 1.5 Hz, 4, Ph), 7.23 (dt, *J*<sub>H–H</sub> = 8.1, *J*<sub>H–H</sub> = 1.2 Hz, 4, Ph), 4.56 (s, 10, Cp), –3.18 (s, 2, Nb–H). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): 137.49, 126.17, 129.20, 89.57 (Cp). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>NbSb: C, 52.81; H, 4.43. Found: C, 52.59; H, 4.40.

**Crystal Structure Determination of 2.** The yellow crystals of **2** were grown from an ether solution. The crystals were covered by polyperfluor oil and mounted directly to the Siemens three-circle diffractometer with CCD area detector (SMART system) at –120 °C. The crystallographic data are given in Table 2. The structure amplitudes for 4885 independent reflections were obtained after the Lorentz and polarization corrections. An empirical absorption correction based on measurements of equivalent reflections was applied. The structure was solved by heavy-atom methods<sup>18</sup> and refined by full-matrix least-squares procedures,<sup>19</sup> using (*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup> as the refined function. All hydrogen atoms were found from the difference map. In the final cycles of refinement, all the non-hydrogen atoms were refined with anisotropic temperature parameters. The hydride ligands were refined isotropically, other hydrogen atoms were refined using the riding scheme with *B*<sub>iso</sub> = 1.2*B*<sub>eq</sub> of the corresponding C atoms. The largest residuals in the final difference Fourier map were about 0.8 Å<sup>3</sup>, and the location and magnitude of the residual electron density was of no chemical significance.

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**Supporting Information Available:** Tables of non-hydrogen atom positional parameters, bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom positional and isotropic displacement parameters for **2** (4 pages). Ordering information is given on any current masthead page.

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