

## Borohydride, hydride, halide, and carbonyl derivatives of bis(pentamethylcyclopentadienyl)niobium

Robert A. Bell, Steven A. Cohen, Nancy M. Doherty, Richard S. Threlkel, and John E. Bercaw

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100995-46-8; W(CO)<sub>5</sub>(DEH), 101009-61-4; Cr(CO)<sub>5</sub>(DEH), 100995-47-9; W(CO)<sub>5</sub>(MIPH) (isomer 1), 100995-48-0; W(CO)<sub>5</sub>(MIPH) (isomer 2), 100995-58-2; Cr(CO)<sub>5</sub>(MIPH) (isomer 1), 100995-49-1; Cr(CO)<sub>5</sub>(MIPH) (isomer 2), 100995-59-3; W(CO)<sub>5</sub>(EIPH), 100995-50-4; W(CO)<sub>5</sub>(*trans*-MED) (isomer 1), 100995-51-5; W(CO)<sub>5</sub>(*trans*-MED) (isomer 2), 100995-57-1; W(CO)<sub>5</sub>(*cis*-MED), 101141-35-9; W(CO)<sub>5</sub>(*trans*-DED), 100995-52-6; Cr(CO)<sub>5</sub>(*trans*-DED), 100995-53-7; W(CO)<sub>5</sub>(*trans*-MIPD) (isomer

1), 100995-54-8; W(CO)<sub>5</sub>(*trans*-MIPD) (isomer 2), 100995-60-6; W(CO)<sub>5</sub>(*cis*-MIPD), 101053-60-5; Cr(CO)<sub>5</sub>(*trans*-MIPD), 100995-55-9; W(CO)<sub>5</sub>(*trans*-EIPD), 100995-56-0; W(CO)<sub>5</sub>(*trans*-EIPD), 100995-61-7; W(CO)<sub>5</sub>(*cis*-EIPD), 101053-61-6; Cr(CO)<sub>5</sub>(*cis*-MIPD), 101053-62-7; W(CO)<sub>5</sub>(*cis*-DED), 101053-63-8; Cr(CO)<sub>5</sub>(*cis*-DED), 101053-64-9; W(CO)<sub>5</sub>(H<sub>2</sub>C=NNHCH<sub>2</sub>CH<sub>3</sub>), 100995-64-0; W(CO)<sub>5</sub>THF, 15038-41-2; Cr(CO)<sub>5</sub>THF, 36477-75-5; MnO<sub>2</sub>, 1313-13-9.

## Borohydride, Hydride, Halide, and Carbonyl Derivatives of Bis(pentamethylcyclopentadienyl)niobium<sup>†</sup>

Robert A. Bell, Steven A. Cohen, Nancy M. Doherty, Richard S. Threlkel, and John E. Bercaw\*

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

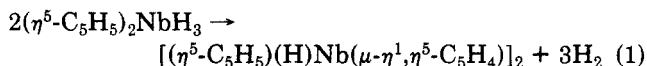
Received August 2, 1985

A synthetic entry to the chemistry of permethylcyclopentadiene compounds is provided via the borohydride derivative ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>NbBH<sub>4</sub>, obtained in 30–50% yield from NbCl<sub>5</sub>, LiC<sub>5</sub>Me<sub>5</sub>, and NaBH<sub>4</sub> in 1,2-dimethoxyethane. Bridge ⇌ terminal hydride exchange occurs with an exceptionally large barrier ( $\Delta G^\ddagger = 16.4 \pm 0.4 \text{ kcal}\cdot\text{mol}^{-1}$  at  $388 \pm 8 \text{ K}$ ). A reinvestigation of the same process for Cp<sub>2</sub>NbBH<sub>4</sub> reveals, contrary to an earlier report, a comparable barrier ( $\Delta G^\ddagger = 14.6 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1}$  at  $346 \pm 3 \text{ K}$ ). Treatment of Cp\*<sub>2</sub>NbBH<sub>4</sub> with pyridine under 1 atm H<sub>2</sub> affords Cp\*<sub>2</sub>NbH<sub>3</sub>. When heated with ethylene or carbon monoxide, Cp\*<sub>2</sub>NbH<sub>3</sub> yields Cp\*<sub>2</sub>NbH(C<sub>2</sub>H<sub>4</sub>) or Cp\*<sub>2</sub>NbH(CO), respectively. Reaction of Cp\*<sub>2</sub>NbH(CO) with HCl affords Cp\*<sub>2</sub>NbCl(CO), which is cleanly converted to Cp\*<sub>2</sub>Nb(CH<sub>3</sub>)(CO) with methylolithium. Paramagnetic Cp\*<sub>2</sub>NbCl<sub>2</sub> is obtained via treatment of Cp\*<sub>2</sub>NbBH<sub>4</sub> with 3 M hydrochloric acid.

### Introduction

Alkyl, hydride, olefin, and carbonyl derivatives of niobocene are among the most extensively investigated organometallic compounds of niobium.<sup>1-7</sup> Following Tebbe and Parshall's report of its synthesis in 1971,<sup>1a</sup> Cp<sub>2</sub>NbH<sub>3</sub> (Cp =  $\eta^5\text{-C}_5\text{H}_5$ ) has been shown to effect hydrogen-deuterium exchange between H<sub>2</sub> and C<sub>6</sub>D<sub>6</sub>,<sup>1a,c</sup> to catalyze hydrogenation of ethylene,<sup>1a</sup> and to promote carbon monoxide hydrogenation to methane,<sup>7</sup> albeit in rather low yield. Cp<sub>2</sub>NbH<sub>3</sub> also serves as a convenient synthetic precursor to a number of derivatives which possess important metal-ligand bonding types (e.g., the first isolable *cis* hydride-olefin complex,<sup>1a,3</sup> some early examples of alkylidenes,<sup>4e</sup> Lewis acid adducts of Nb-H<sup>1b</sup>) or which cleanly undergo some fundamental organometallic transformations (e.g., olefin insertion and  $\beta$ -H elimination<sup>3</sup> and reversible  $\alpha$ -H elimination and alkyl migration for zirconoxy carbene derivatives<sup>6</sup>). Cp<sub>2</sub>NbH<sub>3</sub> has also been used in the preparation of some heterobimetallic dimers.<sup>7,8</sup>

A favored decomposition pathway for niobocene derivatives involves activation of a cyclopentadienyl C-H bond, as for example, in the generation of "dimeric niobocene"<sup>9</sup> from Cp<sub>2</sub>NbH<sub>3</sub> (eq 1), a mode of reactivity reminiscent of



titanocene, zirconocene, and their hydrides.<sup>10</sup> In view of the greater stabilities exhibited by permethyltitanocene and permethylzirconocene, permethylniobocene derivatives are expected to be thermally more robust. Moreover, due to the increased steric demands of pentamethylcyclopentadienyl ligands, reactions which generate dimeric or

polymeric species should be discouraged and a strong steric preference for a single isomeric form of a derivative (e.g., for *endo*-Cp\*<sub>2</sub>NbH(CH<sub>2</sub>=CHR))<sup>11</sup> should be obtained.

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<sup>†</sup>Contribution No. 7259.

Table I. NMR<sup>a</sup> and IR Data<sup>b</sup>

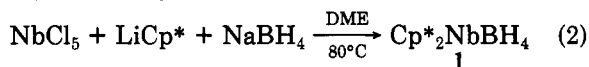
compd	IR, cm <sup>-1</sup>	chem shift, $\delta$	assignt
Cp* <sub>2</sub> NbBH <sub>4</sub> (1)	2452, 2428, 1728, 1620, 1171	1.67 (s) -18.2 (b) 5.2 (b)	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> NbH <sub>2</sub> BH <sub>2</sub> NbH <sub>2</sub> BH <sub>2</sub>
Cp* <sub>2</sub> NbH <sub>3</sub> (2)	1747, 1695	1.81 (s) -2.31 (b d, <sup>2</sup> J <sub>HH</sub> = 4 Hz) -1.23 (b t)	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> NbH <sub>2</sub> H NbH <sub>2</sub> H
Cp* <sub>2</sub> NbH(CO) (4)	1865, 1700	1.80 (s) -5.6 (b s) 11.6 (q, <sup>1</sup> J <sub>CH</sub> = 126 Hz) 100.4 (s)	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> NbH C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>
Cp* <sub>2</sub> NbCl(CO) (5)	1885	279.3 (b s) 1.64 (s)	Nb(CO) C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>
Cp* <sub>2</sub> Nb(CH <sub>3</sub> )(CO) (6)	1853	1.53 (s) -0.93 (s)	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> NbCH <sub>3</sub>

<sup>a</sup> <sup>1</sup>H (90-MHz) and <sup>13</sup>C (22.5-MHz) NMR spectra measured in benzene-d<sub>6</sub> at ambient temperature. <sup>b</sup> IR spectra obtained as Nujol mulls.

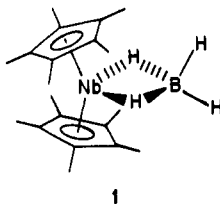
We report herein a convenient synthesis of Cp\*<sub>2</sub>NbBH<sub>4</sub>, a key starting material for the preparation of hydride, halide, olefin, and carbonyl derivatives of permethyl-niobocene.

### Results and Discussion

A convenient entry into the chemistry of permethyl-niobocene compounds is through bis(pentamethylcyclopentadienyl)niobium(III) borohydride, Cp\*<sub>2</sub>NbBH<sub>4</sub> (1). Compound 1 is obtained in 30–50% yield from reaction of very pure NbCl<sub>5</sub> with excess LiCp\* and NaBH<sub>4</sub> in dimethoxyethane (eq 2). Green, air-sensitive 1 exhibits an



infrared spectrum characteristic of bidentate coordination of the borohydride ligand:<sup>12</sup>  $\nu(\text{BH}_2^t) = 2452, 2428 \text{ cm}^{-1}$ ;  $\nu(\text{BH}_2^b) = 1728, 1620 \text{ cm}^{-1}$ ;  $\delta(\text{BH}_2) = 1171 \text{ cm}^{-1}$ .



Its <sup>1</sup>H NMR spectrum consists of a sharp singlet at  $\delta$  1.67 and two very broad resonances at  $\delta$  5.2 and -18.2 in the intensity ratio 30:2:2, respectively. Transition-metal borohydrides commonly undergo rapid intramolecular exchange of terminal and bridging hydrogens, which has been slowed or stopped on the NMR time scale for very few compounds, and in these cases very low activation energies ( $\leq 11 \text{ kcal}\cdot\text{mol}^{-1}$ ) have been found.<sup>12,13</sup>



Variable-temperature (183–400 K) NMR spectra (toluene-d<sub>6</sub>) were recorded to confirm the finding that the room-temperature spectrum was indeed for *static* 1. At low temperatures ( $\leq 250 \text{ K}$ ) the spin-lattice relaxation time ( $T_1$ ) is decreased sufficiently to effectively decouple the boron nuclei from the protons.<sup>14</sup> At 283 K <sup>1</sup>H line shapes

are dominated by spin-spin coupling to <sup>11</sup>B ( $I = 3/2$ , 80.22% natural abundance), with the narrower, upfield resonance (tentatively assigned to the bridging pair of hydrogens<sup>15</sup>) more weakly coupled (<sup>1</sup>J<sub>11B-1H</sub>  $\approx 50 \text{ Hz}$ ) than the downfield resonance (tentatively assigned to the terminal pair of hydrogens,<sup>15</sup> <sup>1</sup>J<sub>11B-1H</sub>  $\approx 130 \text{ Hz}$ <sup>16,17</sup>). Above 307 K the resonances broaden and shift toward each other as bridge  $\rightleftharpoons$  terminal exchange commences.<sup>18</sup> Coalescence is observed at  $388 \pm 8 \text{ K}$  ( $\Delta G^\ddagger = 16.4 \pm 0.4 \text{ kcal}\cdot\text{mol}^{-1}$ ).<sup>19</sup> Some sharpening of the averaged resonance at ca.  $\delta -7$  is observed at 403 K.

The <sup>1</sup>H NMR spectrum for Cp<sub>2</sub>NbBH<sub>4</sub> has been previously reported as a sharp singlet at  $\delta$  5.07 and a broad singlet at  $\delta$  -16.2, which was assigned to ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) and four averaged hydrogens of the (BH<sub>4</sub>) ligand, respectively.<sup>12b</sup> On the basis of these data, the activation energy for bridge  $\rightleftharpoons$  terminal exchange is calculated to be  $< 5.6 \text{ kcal}\cdot\text{mol}^{-1}$ . A difference of this magnitude for Cp\*<sub>2</sub>NbBH<sub>4</sub> and Cp<sub>2</sub>NbBH<sub>4</sub> is not readily explained. Since the upfield resonance reported for Cp<sub>2</sub>NbBH<sub>4</sub> is at a position close to that we find for the bridging hydrogens of Cp\*<sub>2</sub>NbBH<sub>4</sub> and the cyclopentadienyl hydrogens of Cp<sub>2</sub>NbBH<sub>4</sub> resonate in close proximity to the terminal hydrogens of Cp\*<sub>2</sub>NbBH<sub>4</sub>, we considered it likely that the earlier assignments for Cp<sub>2</sub>NbBH<sub>4</sub> were in error, probably because the signal for the cyclopentadienyl hydrogens partially obscure that for the terminal hydrogens of the borohydride ligand. Accordingly, we reexamined variable-temperature <sup>1</sup>H NMR spectra for Cp<sub>2</sub>NbBH<sub>4</sub>. Indeed, the behavior of Cp<sub>2</sub>NbBH<sub>4</sub> is found to be very similar to that for Cp\*<sub>2</sub>NbBH<sub>4</sub>. At 202 K the pair of terminal hydrogens appear at  $\delta$  5.7 and the pair of bridging hydrogens at  $\delta$  -16.5. Coalescence is observed at  $346 \pm 3 \text{ K}$  ( $\Delta G^\ddagger = 14.6 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1}$ ), and at 393 K a single broad peak centered at ca.  $\delta$  -5.4 is observed. Moreover, the 13.6-MHz <sup>2</sup>H NMR spectrum (34 °C, C<sub>6</sub>H<sub>6</sub>) for Cp<sub>2</sub>NbBD<sub>4</sub> reveals two broad peaks at  $\delta$  5.7 and -16.5. Thus we conclude that both Cp\*<sub>2</sub>NbBH<sub>4</sub> and Cp<sub>2</sub>NbBH<sub>4</sub> have relatively large barriers for bridge  $\rightleftharpoons$  terminal hydrogen exchange, probably via a Nb( $\eta^1$ -BH<sub>4</sub>) intermediate.

As with borohydride derivatives of zirconocene,<sup>20</sup> treatment of Cp\*<sub>2</sub>NbBH<sub>4</sub> with amines effects extraction

(15) Assignments of H<sub>1</sub> and H<sub>2</sub> are by analogy to ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NbH<sub>2</sub>Al(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. See ref 1b.

(16) The doublet observed for the resonance for H<sub>1</sub> is due to the special condition  $J(^{11}\text{B}-\text{H}_1) \approx 1/T_1$ .<sup>14c</sup>

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(18) The resonance due to pentamethylcyclopentadienyl hydrogens remains sharp throughout the experiment, and all spectral change observed for the borohydride hydrogens are reversible.

(19)  $\Delta\nu = 2090 \pm 30 \text{ Hz}$ ;  $T = 388 \pm 8 \text{ K}$ .

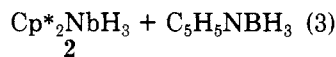
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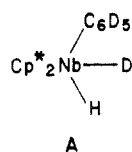
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of a borane equivalent. Under an atmosphere of H<sub>2</sub> the initially formed [Cp\*<sub>2</sub>NbH] is efficiently converted to Cp\*<sub>2</sub>NbH<sub>3</sub> (2) (eq 3). Recrystallization from octane under

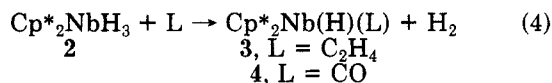


an atmosphere of H<sub>2</sub> affords white crystalline 2, free of all highly colored impurities. Like Cp<sub>2</sub>NbH<sub>3</sub>,<sup>21</sup> 2 exhibits a broad AX<sub>2</sub> pattern for the three hydride hydrogens (Table I) and also a sharp resonance at δ 1.81 attributable to the pentamethylcyclopentadienyl hydrogens. Preparation of 2-d<sub>2</sub> may be accomplished by treating 1 with pyridine under D<sub>2</sub>. H/D exchange between Cp\*<sub>2</sub>NbH<sub>3</sub> (or Cp\*<sub>2</sub>NbHD<sub>2</sub>) and D<sub>2</sub> at 25 °C is very slow. At 40 °C deuterium incorporation into the hydride positions is substantial after 3 days, whereas extensive H/D exchange into the ring methyl groups is noted only on heating at 80 °C for 2 days.

Although 2 is indefinitely stable in solution at 25 °C, samples in C<sub>6</sub>D<sub>6</sub> sealed under vacuum become yellow on heating at 75 °C concomitant with the appearance of a new singlet in the NMR spectrum at δ 1.61, which maximizes after 45 min to approximately 15% of the intensity of the Cp\* resonance of 2. On standing for 6–10 weeks at 25 °C the yellow color and the singlet at δ 1.61 disappear and reappear on resumed heating. We have been unable to isolate this new species so that its identity remains obscure; however, we have made the following relevant observations: (1) its formation is suppressed by the addition of 1 atm of H<sub>2</sub>; (2) no H/D exchange between C<sub>6</sub>D<sub>6</sub> and the (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) or NbH<sub>3</sub> hydrogens is observed after several days at 80 °C; (3) attempts to generate higher concentrations of the yellow species by repeated thermolysis of solutions of 2 followed by removal of the liberated H<sub>2</sub> with a Toepler pump led instead to very deep green solutions which contain at least two paramagnetic niobium complexes (EPR). Thus, the available evidence suggests structures such as Cp\*<sub>2</sub>Nb(H)(η<sup>2</sup>-C<sub>6</sub>D<sub>6</sub>), fluxional (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>, η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>)NbH<sub>2</sub>, Cp\*<sub>2</sub>NbH, or nonfluxional A. Unfortunately, our data do not allow a distinction between these various possibilities.

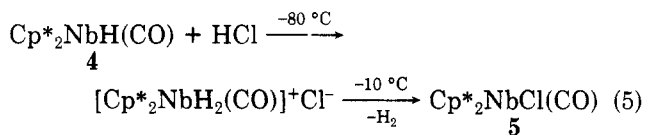


When heated in the presence of ethylene in toluene or benzene at 85 °C, 2 affords yellow-green Cp\*<sub>2</sub>Nb(H)(C<sub>2</sub>H<sub>4</sub>) (3)<sup>11b</sup> in quantitative yield (NMR). Like Cp<sub>2</sub>Nb(H)(C<sub>2</sub>H<sub>4</sub>) 3 reacts cleanly with H<sub>2</sub> liberating ethane on formation of the trihydride complex. When heated under an atmosphere of carbon monoxide, 2 cleanly yields Cp\*<sub>2</sub>Nb(H)(CO) (4) (eq 4). The increased electron density at the



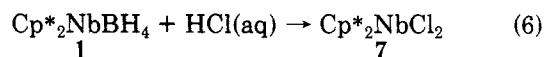
niobium center induced by the pentamethylcyclopentadienyl ligands of 4 is evidenced by its lower carbonyl stretching frequency (1865 cm<sup>-1</sup> vis-à-vis Cp<sub>2</sub>Nb(H)(CO)

(ν(CO) = 1900 cm<sup>-1</sup>)).<sup>1a</sup> Treatment of Cp\*<sub>2</sub>NbH(CO) with HCl in toluene affords Cp\*<sub>2</sub>NbCl(CO) (5) and H<sub>2</sub> via an intermediate presumed to be [Cp\*<sub>2</sub>NbH<sub>2</sub>(CO)]<sup>+</sup>Cl<sup>-</sup>, analogous to the reactivity for Cp<sub>2</sub>NbH(CO) reported previously by Otto and Brintzinger<sup>4f</sup> (eq 5). Treatment



of 5 with methyllithium cleanly yields Cp\*<sub>2</sub>Nb(CH<sub>3</sub>)(CO) (6). Like Cp<sub>2</sub>Nb(CH<sub>3</sub>)(CO),<sup>22</sup> 6 could not be induced to undergo methyl migration, even under ~3 atm of CO at 120 °C for several days. This lack of reactivity contrasts with the ethyl and phenethyl carbonyl derivatives Cp\*<sub>2</sub>Nb(CH<sub>2</sub>CH<sub>2</sub>R)(CO) (R = H, Ph) which cleanly afford the acyl carbonyl complexes at 80 °C (2 atm of CO).<sup>23</sup>

The paramagnetic compound Cp\*<sub>2</sub>NbCl<sub>2</sub> (7) can be prepared in good yield by the reaction of 1 with deoxycyanogenated 3 M hydrochloric acid (eq 6). Brown microcrystalline 7 exhibits a ten-line EPR spectrum (<sup>93</sup>Nb, I = 9/2) centered at g = 2.01 and a magnetic moment at 25 °C of 1.91 μ<sub>B</sub>.



## Conclusions

The synthesis of Cp\*<sub>2</sub>NbBH<sub>4</sub> from NbCl<sub>5</sub>, LiCp\*, and NaBH<sub>4</sub> provides an entry to permethylniobocene chemistry. This borohydride is of some interest in its own right, since the barrier for bridge ⇌ terminal hydride exchange (16.4 ± 0.4 kcal·mol<sup>-1</sup>) is by far the largest yet reported, probably reflecting the instability of the coordinatively unsaturated Cp\*<sub>2</sub>Nb(η<sup>1</sup>-BH<sub>4</sub>) intermediate (although we have not ruled out the possibility that the fluxional process is mediated by an alternative such as [Cp\*(η<sup>3</sup>-Cp\*)Nb(η<sup>3</sup>-BH<sub>4</sub>)]). Indeed, the large Nb-L bond strengths for Cp\*<sub>2</sub>NbH(L) (L = CO, olefin) derivatives, as evidenced by their large thermal stabilities, as well as the relatively slow rates of olefin insertion into the Nb-H bond for Cp\*<sub>2</sub>Nb(H)(olefin) complexes<sup>23</sup> appear to point more generally to a very high energy for 16-electron, d<sup>2</sup> derivatives of the type [Cp\*<sub>2</sub>NbX] vis-à-vis the closed-shell, 18-electron compounds. The very slow fluxional behavior of Cp\*<sub>2</sub>NbBH<sub>4</sub> prompted a reinvestigation of the parent Cp<sub>2</sub>NbBH<sub>4</sub> compound, and a comparable barrier of 14.6 ± 0.2 kcal·mol<sup>-1</sup> is found. This value is more readily accommodated than the very low value (<5.6 kcal·mol<sup>-1</sup>) previously reported by Marks et al.,<sup>12</sup> considering that for Cp<sub>2</sub>NbBH<sub>4</sub> ΔG<sup>‡</sup> = 7.6 ± 0.3 kcal·mol<sup>-1</sup> at -87 ± 7 °C.<sup>12b</sup>

Extraction of BH<sub>3</sub> from Cp\*<sub>2</sub>NbBH<sub>4</sub> with pyridine generates the reactive fragment [Cp\*<sub>2</sub>NbH], which is cleanly trapped by H<sub>2</sub> to afford Cp\*<sub>2</sub>NbH<sub>3</sub>, a useful precursor to adducts of the type Cp\*<sub>2</sub>NbH(L) (L = CO, olefin). Alternatively, Cp\*<sub>2</sub>NbBH<sub>4</sub> may be converted with hydrochloric acid to Cp\*<sub>2</sub>NbCl<sub>2</sub>, an equally useful precursor to permethylniobocene compounds.<sup>23,24</sup>

## Experimental Section

Synthesis and manipulation of compounds were carried out by using high vacuum/inert-atmosphere techniques. Argon, dinitrogen, dihydrogen, and dideuterium (Matheson, 98.7% D<sub>2</sub>)

(21) A recent report (Curtis, M. D.; Bell, L. G.; Butter, W. M. *Organometallics* 1985, 4, 701–707) has noted an unusual temperature and field dependence of the <sup>1</sup>H NMR spectrum of the hydride region for Cp<sub>2</sub>NbH<sub>3</sub>. We have not investigated such features for 2, but the 90-MHz spectra of Cp<sub>2</sub>NbH<sub>3</sub> and 2 at ambient temperature are qualitatively very similar.

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were purified by passage over MnO on vermiculite, followed by 4-Å molecular sieves. Toluene, benzene, petroleum ether (35–60 °C), and octane were dried over LiAlH<sub>4</sub> and then vacuum transferred from titanocene. Pyridine was dried and vacuum transferred from CaH<sub>2</sub>. Dimethoxyethane (DME) was distilled from sodium benzophenone ketyl. Methylene chloride was distilled in vacuo from molecular sieves. Ethylene was collected at –196 °C, freeze–pump–thaw degassed, and vacuum transferred at –78 °C. Carbon monoxide (MCB) was used without purification. Cp<sub>2</sub>NbBH<sub>4</sub> and Cp<sub>2</sub>NbBD<sub>4</sub> were prepared by literature methods,<sup>25</sup> the latter using NaBD<sub>4</sub> (Stohler, 99% D). Lithium pentamethylcyclopentadienide was prepared by literature methods.<sup>26</sup> Niobium pentachloride was initially sublimed at 110 °C (10<sup>–4</sup> torr) to remove most of the NbOCl<sub>3</sub>, followed by one or more sublimations at <100 °C (10<sup>–4</sup> torr). NbCl<sub>5</sub> free of oxochlorides is essential for the successful preparation of Cp<sub>2</sub>NbBH<sub>4</sub>.

Infrared spectra were recorded as Nujol mulls on a Beckman 4240 spectrophotometer. Nuclear magnetic resonance spectra were recorded on Varian EM-390 and JEOL FX90Q spectrometers. EPR spectra were measured on an X-band Varian E-line Century Series spectrometer. Magnetic susceptibilities were determined by using a Cahn/Ventron susceptibility balance. Benzene-*d*<sub>6</sub> (Aldrich, 99.5% D) and toluene-*d*<sub>8</sub> (Stohler, 99.5% D) were dried over molecular sieves and vacuum transferred from titanocene.

**Procedures.** Cp<sub>2</sub>NbBH<sub>4</sub> (1). A dimethoxyethane slurry (250 mL) of LiCp\* (31.4 g, 0.22 mol) and NaBH<sub>4</sub> (22.7 g, 0.67 mol) was cooled to –80 °C. Under an argon counterflow NbCl<sub>5</sub> (27.0 g, 0.10 mol) was slowly added over a 30-min period with efficient stirring. The resulting brown mixture was allowed to warm to 25 °C and then heated at reflux for 3 days. Volatiles were removed in vacuo, and the purple solid was sublimed at 120 °C (10<sup>–3</sup> torr). The green sublimate was washed with petroleum ether in a frit assembly and then subjected to a second sublimation: yield 12.1 g (32%); mp 239–241 °C slight dec. Anal. Calcd for C<sub>20</sub>H<sub>34</sub>Nb: C, 63.52; H, 9.06; B, 2.86; Nb, 24.56; *m/e*, 378.181. Found: C, 63.36; H, 8.96; B, 2.92; Nb, 25.04; *m/e* 378.178. IR: 2716 (w), 2452 (s), 2428 (s), 2312 (m), 1728 (w), 1620 (m), 1516 (m), 1483 (s), 1417 (m), 1390 (w), 1171 (s), 1028 (s), 864 (s), 798 (w), 420 (m) cm<sup>–1</sup>.

Cp<sub>2</sub>NbH<sub>3</sub> (2). Pyridine (15 mL) was added to a toluene solution (10 mL) of 1 (5.61 g, 14.8 mmol) at –196 °C. One atmosphere of H<sub>2</sub> was added as the solution was allowed to warm to room temperature and was stirred for 8 h. The red solution was filtered and cooled to produce a light pink solid. The solid was washed with cold petroleum ether and dried under vacuum

to yield 4.3 g (13.2 mmol) of pink 5 (89%). Repeated recrystallizations from octane and petroleum ether under 1 atm of H<sub>2</sub> gave the white, air-sensitive product in 78% yield. Anal. Calcd for C<sub>20</sub>H<sub>33</sub>Nb: C, 65.56; H, 9.08; Nb, 23.36. Found: C, 64.92; H, 9.29; Nb, 25.07. IR: 1752, 1697, 1027, 773 cm<sup>–1</sup>.

Cp<sub>2</sub>NbH(CO) (4). A toluene solution (25 mL) of 2 (1.2 g) was heated to 95 °C under an atmosphere of CO for 16 h. The volatiles were removed in vacuo, and the residue was recrystallized from cold octane; yield 1.1 g (90%). Anal. Calcd for C<sub>21</sub>H<sub>31</sub>NbO: C, 64.28; H, 7.96; Nb, 23.68. Found: C, 64.13; H, 8.06; Nb, 23.90. IR: 2730 (w), 1865 (s), 1700 (m), 1031 (s), 480 (m) cm<sup>–1</sup>.

Cp<sub>2</sub>NbCl(CO) (5). A 300-mg sample of Cp<sub>2</sub>NbH(CO) was dissolved in 30 mL of toluene. Two equivalents of HCl were condensed into the flask at –196 °C. The mixture was warmed to –80 °C, whereupon the red solution became yellow. Toepler pumping indicated no H<sub>2</sub> evolution. On warming to –10 °C gas evolution commenced and was complete after 30 min. Toepler pumping to dryness indicated 1 equiv of H<sub>2</sub> was evolved. The green residue was washed with petroleum ether and found to be pure 5 (<sup>1</sup>H NMR). Anal. Calcd C, 59.09; H, 7.08; Cl, 8.31. Found: C, 59.14; H, 7.30; Cl, 8.43.

Cp<sub>2</sub>Nb(CH<sub>3</sub>)(CO) (6). A 210-mg sample of Cp<sub>2</sub>NbCl(CO) was dissolved in 30 mL of diethyl ether. Four-tenths milliliter of 1.6 M methyl lithium in diethyl ether was syringed into the solution at 25 °C. Diethyl ether was removed in vacuo, and the green residue was extracted with toluene. Removal of toluene in vacuo, suspension in 20 mL of cold petroleum ether, and filtration of green crystals of 6 afforded 190 mg (90% yield).

Cp<sub>2</sub>NbCl<sub>2</sub> (7). A 5.3-g sample of Cp<sub>2</sub>NbBH<sub>4</sub> dissolved in 100 mL of benzene was treated with 15 mL of deoxygenated 3 M HCl at 0 °C. Vigorous evolution accompanied a change in color from green to brown with a yellow precipitate. After 20 min all volatiles were removed in vacuo. The brown residue was transferred to a Soxhlet thimble and extracted with benzene. Concentration of the extract afforded a brown microcrystalline product which was dissolved in 120 mL of CH<sub>2</sub>Cl<sub>2</sub>, added to 500 mg of degassed grade III alumina, and filtered. Recrystallization of the residue obtained from removal of CH<sub>2</sub>Cl<sub>2</sub> in vacuo from the filtrate yielded 4.1 g (67%) of Cp<sub>2</sub>NbCl<sub>2</sub>. Anal. Calcd: C, 55.31; H, 6.96; Nb, 21.39; Cl, 16.33. Found: C, 55.41; H, 7.03; Nb, 21.52; Cl, 16.29. EPR (benzene): ten-line spectrum at *g* = 2.01. Magnetic susceptibility measurement by the Faraday method indicated a magnetic moment of 1.91 μ<sub>B</sub>.

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