

# Intramolecular Dehydrogenation of Alkyl Groups at Niobium Aryloxy Centers: Bonding and Reactivity of the Ensuing Niobacyclopropane Ring

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The niobium dichloride  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_3\text{Cl}_2]$  ( $\text{OC}_6\text{H}_3\text{Pr}^{i-2,6} = 2,6\text{-diisopropylphenoxide}$ ) undergoes reduction (2 Na per Nb) in tetrahydrofuran (thf) solvent to produce the dark green complex  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^{i-\eta^2}\text{-CMe}=\text{CH}_2)(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_2(\text{thf})]$  (**1**). The solid-state structure of **1** shows the  $\alpha$ -methylvinyl group to be strongly  $\eta^2$ -bound to the niobium metal center. The dehydrogenation of the *ortho*-isopropyl group of an aryloxy group to generate **1** is argued to proceed via CH bond activation within a  $d^2$ -Nb(III) aryloxy followed by  $\beta$ -hydrogen abstraction/elimination of  $\text{H}_2$ . The thf ligand in **1** can be substituted by pyridine (py) and  $\text{Bu}^t\text{NC}$  to yield the adducts  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^{i-\eta^2}\text{-CMe}=\text{CH}_2)(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_2(\text{L})_2]$  ( $\text{L} = \text{py}$ , **2**;  $\text{L} = \text{Bu}^t\text{NC}$ , **3**). The solid-state structure of **3** shows both isocyanide ligands to be terminally bound with no interaction with the  $\eta^2$ -olefin fragment. The spectroscopic properties of these three adducts give insight into the degree of  $\pi$ -back-bonding between the metal and the chelated olefin fragment. The metallacyclopropane ring in **1** will undergo ring expansion (coupling of the olefin) with a variety of unsaturated substrates. The addition of  $\text{Ph}_2\text{C}=\text{O}$  leads to a 2-oxaniobacyclopentane ring in **4** while  $\text{PhC}\equiv\text{CPh}$  produces a niobacyclopent-3-ene derivative,  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^{i-\text{CMeCH}_2\text{CPh}=\text{CPh})(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_2]$  (**5**), which was structurally characterized. In the case of addition of  $\text{PhC}\equiv\text{CH}$  to **1** the initial, kinetic product **6a**, possibly containing a 2-phenylniobacyclopent-2-ene ring, is thermally isomerized to the 3-phenylniobacyclopent-2-ene compound **6b**. With the protic reagents  $\text{HOC}_6\text{H}_3\text{Pr}^{i-2,6}$  and  $\text{PhNH}_2$  the compounds  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^{i-\text{CMe}_2})(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_3]$  (**8**) and  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^{i-\text{CMe}_2})(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_2(\text{NPh})]$  (**9**) are produced. The solid-state structure of **8** confirmed the presence of the cyclometalated aryloxy formed via protonation of the methylene group in **1**.

## Introduction

The early transition metal chemistry supported by sterically demanding aryloxy ligation continues to grow.<sup>1</sup> One continuing complexity in the development of the organometallic chemistry of these ligands is the sometimes facile intramolecular activation (cyclometalation) of the CH bonds attached to the aryloxy ligand.<sup>1,2</sup> We wish to report here on the facile dehydrogenation of the *ortho*-substituent of a 2,6-diisopropylphenoxide, a group that has typically been considered as less susceptible to intramolecular CH bond activation. Despite their somewhat exotic nature, the resulting species do allow valuable insight into the bonding and reactivity of olefin ligands coordinated to this transition metal center. Some aspects of this work have been communicated previously.<sup>3</sup>

## Results and Discussion

**Synthesis and Spectroscopic Properties.** The niobium and tantalum chloride compounds  $[\text{M}(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_2\text{Cl}_3]_2$  and  $[\text{M}(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_3\text{Cl}_2]$  ( $\text{M} = \text{Nb}, \text{Ta}$ ;  $\text{OC}_6\text{H}_3\text{Pr}^{i-2,6} = 2,6\text{-diisopropylphenoxide}$ )<sup>4</sup> are useful starting materials for studying the organometallic chemistry of these metals. With neutral donor ligands such as pyridine,<sup>5</sup> quinoline,<sup>5</sup>  $\text{PMe}_2\text{Ph}$ ,<sup>4</sup> tetrahydrofuran,<sup>6</sup> and diethyl ether<sup>7</sup> adducts of the type *cis-mer*- $[\text{M}(\text{OAr})_2\text{Cl}_3(\text{L})]$  and *trans-mer*- $[\text{M}(\text{OAr})_3\text{Cl}_2(\text{L})]$  are formed and the structures of a number of these adducts have been obtained and analyzed. The trichloride compounds undergo facile reduction leading to a series of  $d^1$ -derivatives, *all-trans*- $[\text{M}(\text{OC}_6\text{H}_3\text{Pr}^{i-2,6})_2\text{Cl}_2(\text{L})_2]$ .<sup>5c,8</sup>

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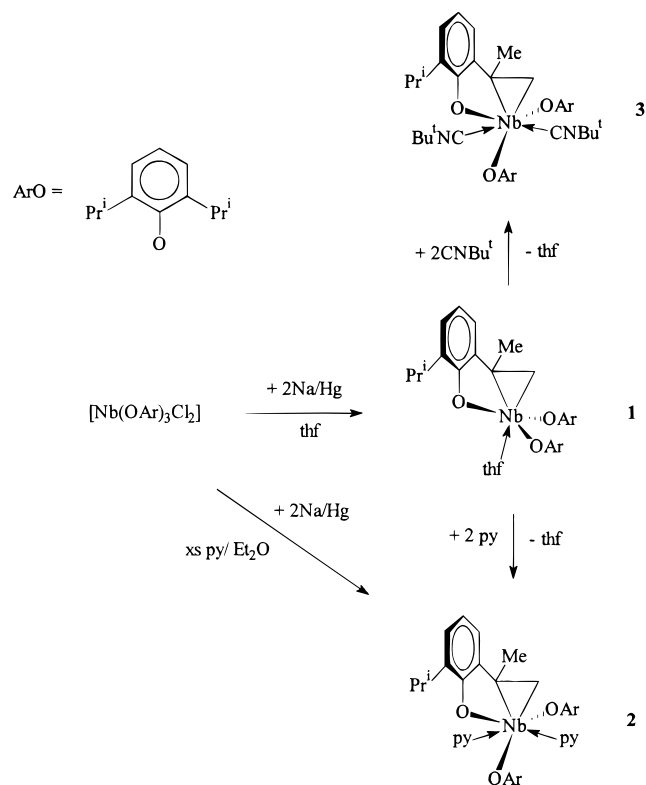
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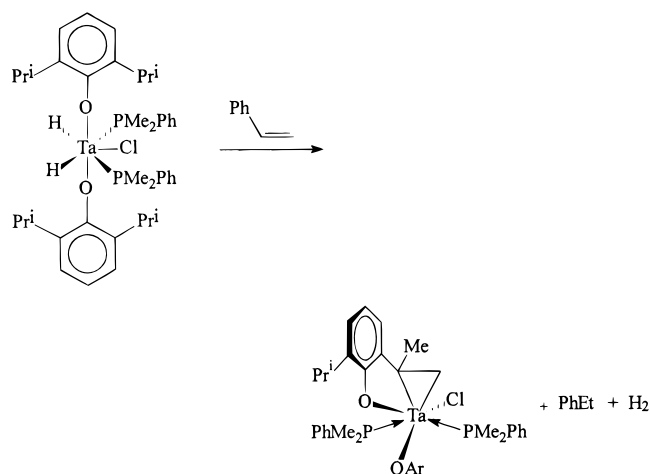
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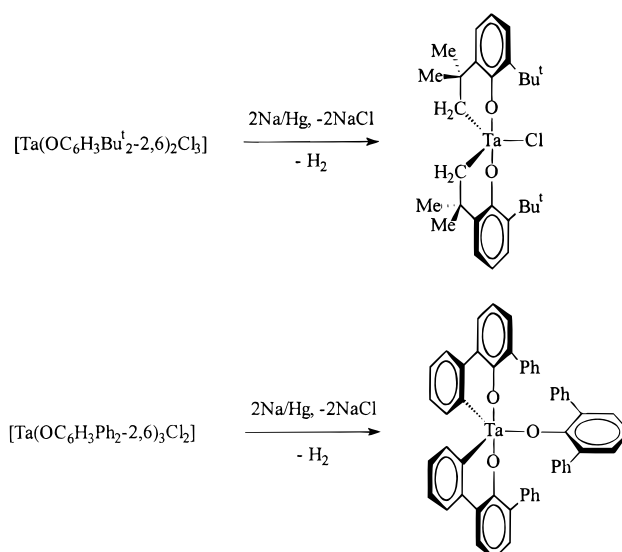
Scheme 1



Scheme 2



Scheme 3



In the case of tantalum more forcing conditions have been shown by Wigley et al. to give access to derivatives such as [ $\eta^2$ -(*N,C*-quin) $\{Ta(OC_6H_3Pr^{i-2,6})_3\}$ ] and [ $\eta^2$ -(*N,C*)-6-methylquinoline] $\{Ta(OC_6H_3Pr^{i-2,6})_2Cl(O-Et_2)\}$ .<sup>5</sup> We have observed that the niobium dichloride  $[Nb(OC_6H_3Pr^{i-2,6})_3Cl_2]$  is reduced in tetrahydrofuran solvent by sodium amalgam (2 Na per Nb) to produce intense green solutions of the complex  $[Nb(OC_6H_3Pr^{i-2,6})_2(\eta^2-CMe=CH_2)(OC_6H_3Pr^{i-2,6})_2(thf)]$  (**1**) (Scheme 1). Compound **1** can be isolated in good yield by simple filtration followed by vacuum removal of thf and addition of hexane solvent. It was noted, however, that the yields of **1** were reduced if the reduction was carried out for periods exceeding 12 h prior to workup. Following isolation, the reactivity of **1** was examined in hydrocarbon solvents, typically benzene. The addition of pyridine or *tert*-butyl isocyanide to solutions of **1** rapidly produced deep red and orange solutions of the bis-ligand complexes  $[Nb(OC_6H_3Pr^{i-2,6})_2(\eta^2-CMe=CH_2)(OC_6H_3Pr^{i-2,6})_2(L)_2]$  (**2**, L = py; **3**, L = CNBu<sup>t</sup>) along with free thf (Scheme 1). It was found possible to generate **2** by direct reduction of  $[Nb(OC_6H_3Pr^{i-2,6})_3Cl_2]$  in the presence of pyridine in diethyl ether solvent. Another example of the dehydrogenation of a 2,6-diisopropylphenoxide ligand involves the reaction of styrene with a tantalum dihydride substrate yielding  $[Ta(OC_6H_3Pr^{i-2,6})_2(\eta^2-CMe=CH_2)(OC_6H_3Pr^{i-2,6})_2(Cl)(PMe_2Ph)_2]$  (Scheme 2).<sup>9</sup>

Previous work has shown that reduction of the chloro-aryloxides  $[Ta(OC_6H_3Bu^{t-2,6})_2Cl_3]$  and  $[M(OC_6H_3Ph-2,6)_3Cl_2]$  (M = Nb, Ta) with 2 equiv of sodium leads to bis-cyclometalated derivatives (Scheme 3).<sup>10</sup> These reactions are believed to proceed via Nb(III) and Ta(III) intermediates which undergo intramolecular

addition of an aryloxy CH bond followed by a second cyclometallation ( $\sigma$ -bond metathesis) leading to elimination of H<sub>2</sub>. This proposal has support in the work of Wolczanski et al. showing the conversion of the tantalum siloxide  $[Ta(OSiBu^t)_3]$  into the compound  $[Ta(OSiBu^t)_2CMe_2CH_2](H)(OSiBu^t)_2$ .<sup>11</sup> There are, however, two possible pathways for the dehydrogenation of the diisopropylphenoxide ligand leading to compounds such as **1**. Both pathways proceed via intermediate monohydride compounds which undergo  $\beta$ -hydrogen elimination (Scheme 4). The uncertainty lies in whether the initial cyclometallation occurs via activation of the methyl or methine CH bonds leading to six- and five-membered metallacycles, respectively. The formation of the six-membered metallacycle is favored statistically, although protonation of **1** leads to compounds containing the five-membered ring (*vide infra*). The literature contains many examples of structurally characterized 4-,<sup>12</sup> 5-,<sup>13</sup> and 6-membered<sup>10,14</sup> metallacycles derived from aryloxy ligation.

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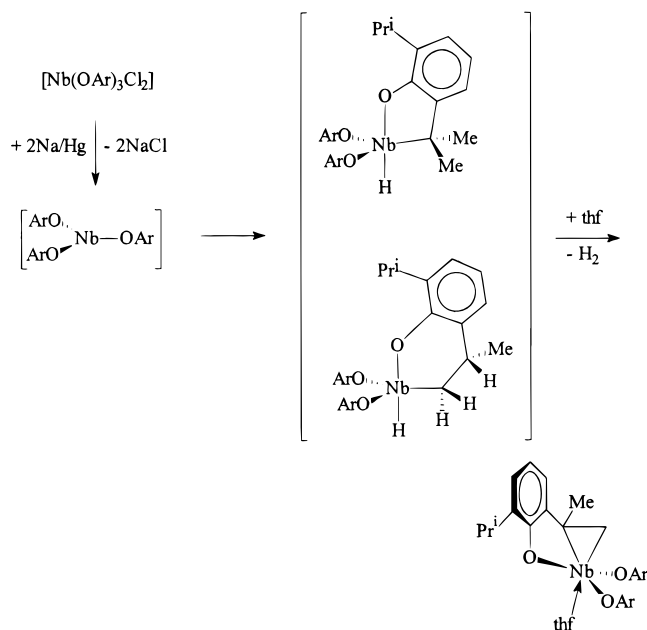
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Scheme 4



The solution spectroscopic properties of compounds **1–3** are of interest. Due to the lack of any symmetry elements in these molecules the aliphatic regions of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are complex. The presence of diastereotopic  $\text{CHMe}_2$  groups from the aryloxy ligands leads to six overlapping methyl doublets (ratio 2:2:2:2:1:1) in the  $^1\text{H}$  NMR spectrum along with three methine septets in the ratio of 2:2:1. The metal bound  $\alpha$ -methylvinyl group appears as a singlet ( $\text{CMe}=\text{CH}_2$ ) and a well-resolved pair of doublets ( $\text{CMe}=\text{CH}_2$ ) in the  $^1\text{H}$  NMR while the  $\text{CMe}=\text{CH}_2$  carbons appear as a broad singlet and triplet in the proton-coupled  $^{13}\text{C}$  NMR spectra. As with nearly all organometallic derivatives of niobium, the quadrupolar broadening of Nb–C resonances necessitates much longer acquisition times in order to detect these signals. Of particular interest are the values of the coupling constants  $^2J(^1\text{H}-^1\text{H})$  and  $^1J(^{13}\text{C}-^1\text{H})$  for the methylene group  $\text{CMe}=\text{CH}_2$ . These data are collected in Table 1.

It can be seen that on moving from **1** to **3** the coupling between the methylene protons drops while the coupling between these protons and the carbon atom increases. We argue that these parameters correlate with the strength of the bonding between the chelated vinyl group and the niobium metal center. In compound **1** there is significant  $\pi$ -back-bonding from the metal center (metallacyclopentane in the Dewar–Chatt–Duncanson model) resulting in a large  $^2J(^1\text{H}-^1\text{H})$  coupling constant approaching that typical of diastereotopic  $\text{sp}^3$ -methylene protons (12–15 Hz) and a reduced  $^1J(^{13}\text{C}-^1\text{H})$  coupling constant compared to that found in free olefins (Table 1). Replacement of the thf (a straightforward  $\sigma$ -donor) by two pyridine ligands (potential  $\pi$ -acceptors)<sup>15</sup> can be seen to decrease the degree of  $\pi$ -back-bonding between the niobium metal center and

the vinyl group as judged by these two parameters. This effect becomes dramatically apparent in complex **3** (Table 3) which contains two strongly  $\pi$ -accepting isocyanide ligands which can compete with the chelated  $\pi$ -vinyl group for the electron density on the metal center. The structural changes associated with this bonding argument are discussed in a separate section later in this paper.

In common with many related early transition metal olefin complexes the niobacyclopentane ring in **1** undergoes ring expansion (coupling) with a variety of unsaturated substrates. Addition of benzophenone to benzene solutions of **1** led to the rapid (as judged by the color change) formation of a bright orange solution of the 2-oxaniobacyclopentane complex  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i-\text{CMeCH}_2\text{CPh}_2\text{O})(\text{OAr})_2]$  (**4**) along with free thf (Scheme 5). Besides the complex signals due to the aryloxy ligands, the  $^1\text{H}$  NMR spectrum of **4** shows an AB pattern (14 Hz coupling) for the methylene protons within the five-membered metallacycle ring. In the  $^{13}\text{C}$  NMR spectrum of **4** a signal at  $\delta$  96.8 ppm can be assigned to the Nb– $\text{CMeCH}_2$  carbon resonance while a peak at  $\delta$  99.6 ppm is due to the Nb– $\text{OCPh}_2$  carbon. This latter assignment was confirmed by synthesis of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i-\text{CMeCH}_2-^{13}\text{CPh}_2\text{O})(\text{OAr})_2]$  (**\*4**) utilizing labeled  $\text{Ph}_2^{13}\text{C}=\text{O}$  as substrate. Interestingly only one of the diastereotopic methylene protons was found to be coupled (5 Hz) with the labeled carbon atom.<sup>16</sup>

Upon addition of  $\text{PhC}\equiv\text{CPh}$  to dark green benzene solutions of **1**, formation of orange solutions of the niobacyclopent-2-ene compound **5** occurs over minutes (Scheme 6). The metal-mediated coupling of olefins and alkynes at transition metal centers has excellent precedence and has its greatest synthetic utility in the enyne cyclization reaction.<sup>17</sup> The spectroscopic characteristics of **5** are entirely consistent with its formulation and observed solid-state molecular structure (*vide infra*). In the  $^{13}\text{C}$  NMR spectrum the Nb– $\text{CMe}$  and Nb– $\text{CPh}=\text{CPh}$  carbon atoms are found to resonate at  $\delta$  96.4 and 200.5 ppm, respectively. Two doublets at  $\delta$  3.91 and 4.15 ppm in the  $^1\text{H}$  NMR spectrum can be assigned to the  $\text{CMeCH}_2\text{CPh}=\text{CPh}$  protons within the metallacycle ring.

The reaction of **1** with  $\text{PhC}\equiv\text{CH}$  in hydrocarbon solvents proved to be more complicated (Scheme 6). Monitoring the reaction in  $\text{C}_6\text{D}_6$  solvent by  $^1\text{H}$  NMR showed the initial rapid formation of a new organometallic product **6a** along with free thf. The  $^1\text{H}$  NMR spectrum of **6a** showed a pattern for the aryloxy ligands very similar to that observed for **5**, and the  $\text{CMeCH}_2$  methyl group can be seen as a sharp singlet at  $\delta$  1.88 ppm. A broad singlet at  $\delta$  3.36 ppm appears to be due to the  $\text{CMeCH}_2$  protons. Slowly over hours at room temperature and over minutes at 100 °C, **6a** is converted completely into a new compound **6b** whose NMR spectra are entirely consistent with its formulation as the 3-phenylniobacyclopent-2-ene compound  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i-2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i-\text{CMeCH}_2\text{CPh}=\text{CH})]$ . A particularly significant peak in the  $^1\text{H}$  NMR spectrum is a sharp singlet at  $\delta$  9.18 ppm assigned to the  $\alpha$ -CH proton of the metallacycle ring. One possible formulation for intermediate **6a** is as a 2-phenylniobacyclopent-2-ene compound  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i-2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i-\text{CMeCH}_2-$

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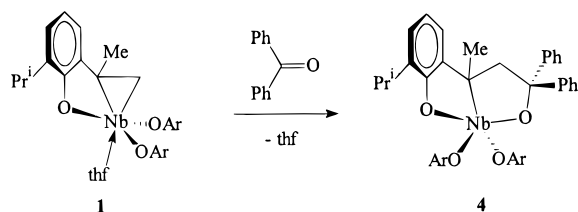
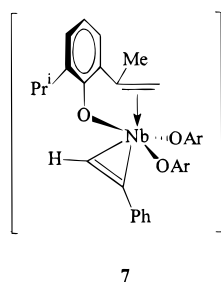
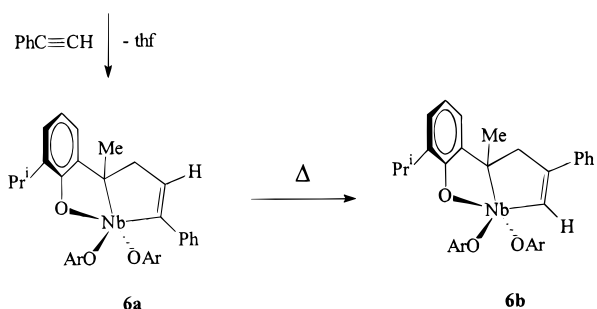
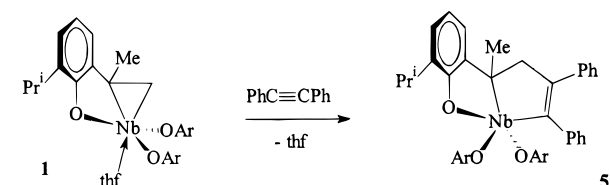
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**Table 1. Coupling Constants Obtained for the CMe=CH<sub>2</sub> Group in 1–3**

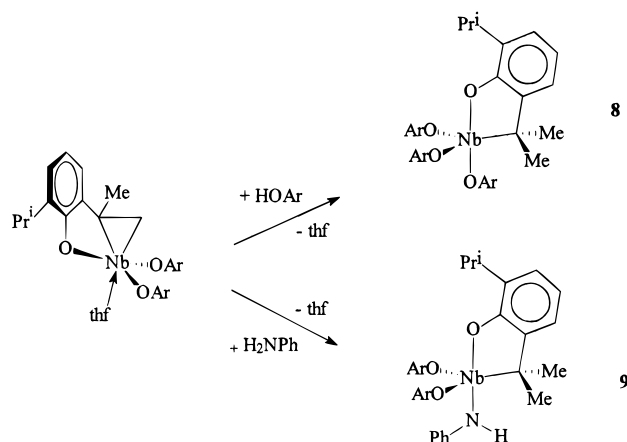
compd	<sup>2</sup> J( <sup>1</sup> H– <sup>1</sup> H)/Hz	<sup>1</sup> J( <sup>13</sup> C– <sup>1</sup> H)/Hz
[Nb(OC <sub>6</sub> H <sub>3</sub> Pr <sup>i</sup> -η <sup>2</sup> -CMe=CH <sub>2</sub> )(OAr) <sub>2</sub> (thf)] ( <b>1</b> )	9.8	140.8
[Nb(OC <sub>6</sub> H <sub>3</sub> Pr <sup>i</sup> -η <sup>2</sup> -CMe=CH <sub>2</sub> )(OAr) <sub>2</sub> (py) <sub>2</sub> ] ( <b>2</b> )	5.5	146.8
[Nb(OC <sub>6</sub> H <sub>3</sub> Pr <sup>i</sup> -η <sup>2</sup> -CMe=CH <sub>2</sub> )(OAr) <sub>2</sub> (CNBu <sup>o</sup> ) <sub>2</sub> ] ( <b>3</b> )	4.2	153.4
HOC <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> CH=CH <sub>2</sub> -2	1.4	156.0

**Scheme 5****Scheme 6**

CH=CPh)]. The broad resonance at  $\delta$  3.36 ppm would then have to be assigned to isochronous CMeCH<sub>2</sub>-CH=CPh protons. The isomerization of metallacycles formed by coupling of alkynes or olefins has precedence.<sup>18</sup> Assuming the formulation of **6a** is correct, then it would represent the kinetic product of the coupling of PhC≡CH with the olefinic group in **1**, and the subsequent isomerization to the thermodynamic isomer **6b** would presumably require fragmentation back into an alkyne complex. Another possible formulation of **6a** is in fact as an alkyne adduct intermediate **7** in which the vinyl substituent on the aryloxy ligand is uncoupled. Stable alkyne adducts of tantalum aryloxides have been isolated and studied by Wigley et al.<sup>19</sup> Due to its thermal instability we have been unable to obtain good-quality <sup>13</sup>C NMR spectra on **6b** (*vide supra*), hindering our attempts to identify the exact chemical nature of this intermediate.

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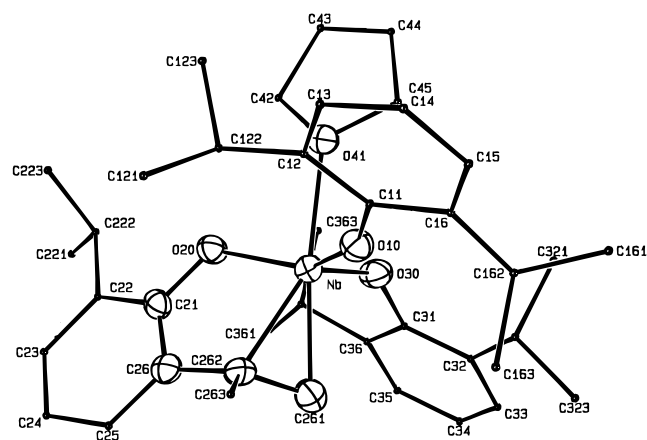
**Scheme 7**

Upon addition of 2,6-diisopropylphenol or aniline to solutions of **1** the initial green color faded over several hours to produce dark orange solutions of the corresponding aryloxy and phenylamido derivatives **8** and **9** (Scheme 7). Both of these molecules contain a five-membered metallacycle formed by protonation of the η<sup>2</sup>-CMe=CH<sub>2</sub> methylene carbon atom of the metallacyclopropane ring within **1**. In the <sup>13</sup>C NMR spectrum the remaining Nb–CMe<sub>2</sub> carbon resonates at  $\delta$  90.2 and 92.4 ppm for **8** and **9**, respectively.

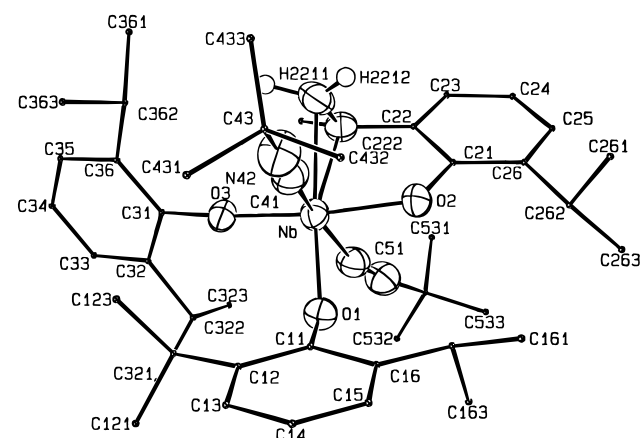
**Solid-State Structures.** The molecular structures of niobacyclopropane compounds **1** and **3**, niobacyclopropane-2-ene compound **5**, and the cyclometalation derivative **8** are shown in Figures 1–4, and selected structural parameters are listed in Tables 2–5. The geometry about the metal center in **1** is best described as trigonal bipyramidal with the η<sup>2</sup>-vinyl group and the thf occupying axial sites. The three aryloxy oxygen atoms form the equatorial plane. In pseudo-octahedral **3** the two isocyanide ligands are mutually trans and the three aryloxy oxygen atoms are meridional. The molecular geometry of **5**, containing two five-membered metallacycles, is a highly distorted trigonal bipyramid with the axial groups bound through O(10) and C(125) being bent toward equatorial C(122) to which they are chelated. A much more regular trigonal-bipyramidal geometry is present for **8**, with the metalation carbon occupying an equatorial site. All four compounds contain one aryloxy which is part of a five-membered metallacycle ring. The angle at oxygen in these systems lies in the narrow range of 120–123°. This compares with much larger M–O–Ar angles typically found for terminal aryloxides.<sup>20</sup> The Nb–O distances and Nb–O–Ar angles for the aryloxy ligands are presented graphically in Figure 5. The most remarkable structural parameter is the unusually long distance found for the ligand bound through O(1) in the isocyanide complex **3**. This ligand is situated directly *trans* to the η<sup>2</sup>-vinyl group as well as *cis* to both isocyanide ligands.

The structural parameters for the η<sup>2</sup>-vinyl groups in **1** and **3** are consistent with the conclusions drawn from

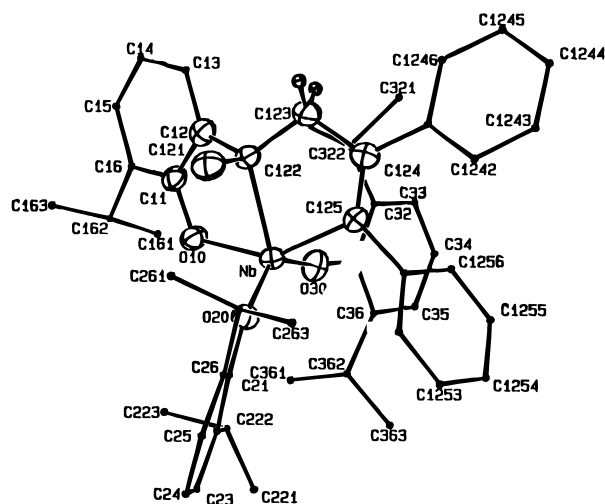
(20) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963.



**Figure 1.** Molecular structure of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{thf})]$  (**1**).

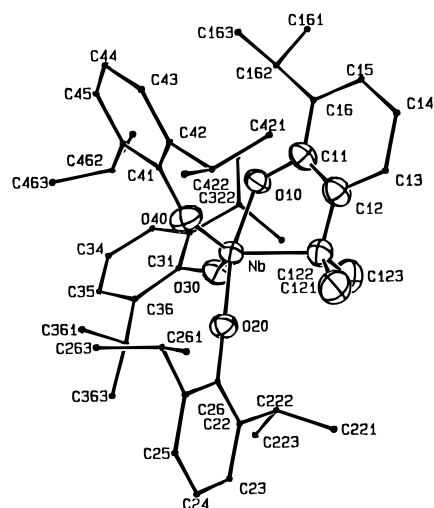


**Figure 2.** Molecular structure of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{CNBu}^t)_2]$  (**3**).



**Figure 3.** Molecular structure of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMeCH}_2\text{-CPh=CPh})(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2]$  (**5**).

the spectroscopic properties. The Nb–C distances within the niobacyclopropane ring within **1** are 2.167(3) and 2.208(2) Å. These compare favorably with the distance of 2.216(3) Å found for the Nb–C(alkyl) bond in **8**. In contrast the distances in **3** are longer at 2.260(9) and 2.230(8) Å, implying significantly reduced  $\pi$ -backbonding. Less striking are the C–C distances of 1.453(4) and 1.42(1) Å in **1** and **3**, respectively. These are shorter than the distance of 1.477 Å found in  $[\text{Cp}^*\text{Ta}(\eta^2\text{-C}_2\text{H}_4)(=\text{CHCMe}_3)(\text{PMe}_3)]^{21}$  but longer than the value of 1.407 Å reported for  $[\text{CpNb}(\eta^2\text{-C}_2\text{H}_4)(\text{C}_2\text{H}_5)]^{22}$



**Figure 4.** Molecular structure of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMe}_2)(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_3]$  (**8**).

**Table 2. Selected Bond Distances (Å) and Angles (deg) for  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{thf})]$  (**1**)**

Nb–O(10)	1.875(2)	Nb–O(41)	2.293(2)
Nb–O(20)	1.949(2)	Nb–C(261)	2.167(3)
Nb–O(30)	1.967(2)	Nb–C(262)	2.208(2)
C(261)–C(262)	1.453(4)		
O(10)–Nb–O(20)	136.40(7)	O(30)–Nb–O(41)	81.24(7)
O(10)–Nb–O(30)	116.40(7)	O(30)–Nb–C(261)	87.22(9)
O(10)–Nb–O(41)	84.18(7)	O(30)–Nb–C(262)	123.04(8)
O(10)–Nb–C(261)	101.1(1)	O(41)–Nb–C(261)	168.47(9)
O(10)–Nb–C(262)	95.50(8)	O(41)–Nb–C(262)	151.68(8)
O(20)–Nb–O(30)	101.84(7)	C(261)–Nb–C(262)	38.8(1)
O(20)–Nb–O(41)	81.62(6)	Nb–O(10)–C(11)	157.6(2)
O(20)–Nb–C(262)	79.25(8)	Nb–O(30)–C(31)	137.7(2)

**Table 3. Selected Bond Distances (Å) and Angles (deg) for  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{CNBu}^t)_2]$  (**3**)**

Nb–O(1)	2.057(5)	Nb–C(51)	2.260(9)
Nb–O(2)	1.973(5)	Nb–C(221)	2.249(8)
Nb–O(3)	1.900(4)	Nb–C(222)	2.341(7)
Nb–C(41)	2.230(8)	C(221)–C(222)	1.42(1)
C(41)–N(42)	1.157(9)	C(51)–N(52)	1.150(9)
O(1)–Nb–O(2)	90.9(2)	O(3)–Nb–C(221)	90.2(3)
O(1)–Nb–O(3)	99.5(2)	O(3)–Nb–C(222)	92.5(2)
O(1)–Nb–C(41)	83.4(2)	C(41)–Nb–C(51)	167.4(3)
O(1)–Nb–C(51)	87.3(2)	C(41)–Nb–C(221)	77.4(3)
O(1)–Nb–C(221)	159.3(3)	C(41)–Nb–C(222)	112.8(3)
O(1)–Nb–C(222)	158.9(2)	C(51)–Nb–C(221)	74.4(3)
O(2)–Nb–O(3)	167.9(2)	C(51)–Nb–C(222)	35.9(3)
O(2)–Nb–C(41)	91.7(2)	Nb–O(1)–C(11)	136.5(4)
O(2)–Nb–C(51)	79.9(2)	Nb–O(2)–C(21)	122.9(4)
O(2)–Nb–C(221)	82.1(3)	Nb–O(3)–C(31)	171.6(4)
O(2)–Nb–C(222)	75.8(2)	Nb–C(41)–N(42)	177.4(7)
O(3)–Nb–C(41)	95.7(2)	Nb–C(51)–N(52)	165.8(7)
O(3)–Nb–C(51)	94.2(2)		

The Nb–C(isocyanide) distances of 2.230(8) and 2.260(9) Å in compound **3** are among the longest so far reported for RNC adducts of either Nb or Ta.<sup>23</sup> They are comparable to the distances of 2.25–2.32 Å found to the terminal isocyanides in the di- and trinuclear compounds  $[\text{Nb}_3\text{Cl}_8(\text{CNBu}^t)_5]$ ,<sup>23a,b</sup>  $[\text{Nb}_2\text{Cl}_6(\text{CNBu}^t)_6]$ , and  $[\text{Ta}_2\text{Cl}_6(\text{CNPr}^i)_6]$ .<sup>23c</sup> All of these bond distances are dramatically longer than the distances of 2.017(7) and 2.022(7) Å found to the two isocyanide ligands in  $[\text{Ta}(\text{CNMe})_2(\text{Cl})(\text{dmpe})_2]$ .<sup>23i</sup>

(21) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

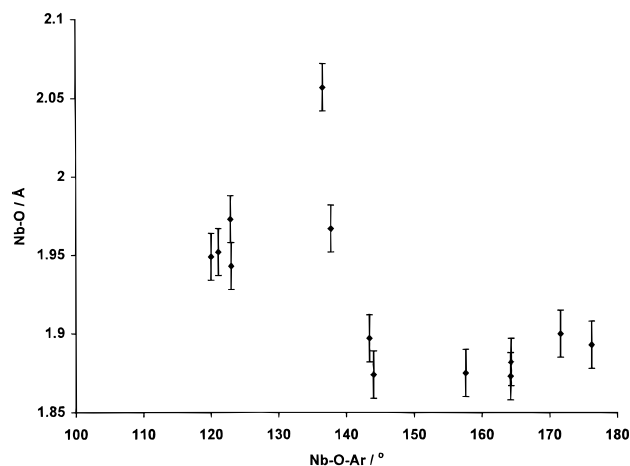
(22) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

**Table 4. Selected Bond Distances (Å) and Angles (deg) for [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-CMeCH<sub>2</sub>CPh=CPh)(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>2</sub>] (5)**

Nb–O(10)	1.943(4)	Nb–C(125)	2.125(6)
Nb–O(20)	1.873(4)	C(122)–C(123)	1.532(8)
Nb–O(30)	1.882(4)	C(123)–C(124)	1.501(9)
Nb–C(122)	2.261(6)	C(124)–C(125)	1.349(8)
O(10)–Nb–O(20)	102.0(2)	O(30)–Nb–C(125)	91.2(2)
O(10)–Nb–O(30)	93.0(2)	C(122)–Nb–C(125)	72.3(2)
O(10)–Nb–C(122)	75.1(2)	Nb–O(10)–C(11)	123.0(4)
O(10)–Nb–C(125)	145.2(2)	Nb–O(20)–C(21)	164.2(4)
O(20)–Nb–O(30)	135.1(2)	Nb–O(30)–C(31)	164.3(4)
O(20)–Nb–C(122)	107.7(2)	Nb–C(122)–C(123)	114.0(4)
O(20)–Nb–C(125)	99.1(2)	Nb–C(122)–C(12)	106.1(4)
O(30)–Nb–C(122)	117.1(2)	Nb–C(125)–C(124)	125.1(5)

**Table 5. Selected Bond Distances (Å) and Angles (deg) for [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-CMe<sub>2</sub>)(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>3</sub>] (8)**

Nb–O(10)	1.952(2)	Nb–O(40)	1.874(2)
Nb–O(20)	1.893(2)	Nb–C(122)	2.216(3)
Nb–O(30)	1.897(2)		
O(10)–Nb–O(20)	166.03(9)	O(30)–Nb–C(122)	117.1(1)
O(10)–Nb–O(30)	91.37(9)	O(40)–Nb–C(122)	111.3(1)
O(10)–Nb–O(40)	89.90(9)	Nb–O(10)–C(11)	121.1(2)
O(10)–Nb–C(122)	76.3(1)	Nb–O(20)–C(21)	176.2(20)
O(20)–Nb–O(30)	94.77(9)	Nb–O(30)–C(31)	143.4(2)
O(20)–Nb–O(40)	95.59(9)	Nb–O(40)–C(41)	144.1(2)
O(20)–Nb–C(122)	89.7(1)	Nb–C(122)–C(12)	106.1(2)
O(30)–Nb–O(40)	130.4(1)		

**Figure 5.** Plot showing Nb–O distances and Nb–O–Ar angles for the aryloxy ligands in molecules **1**, **3**, **5**, and **8**.

## Conclusions

The chemistry outlined in this paper demonstrates that the 2,6-diisopropylphenoxide ligand can undergo the sometimes facile dehydrogenation of a substituent isopropyl group at niobium metal centers. The resulting ligand gives some insight into the bonding and reactivity of olefin ligands attached to niobium. The pathway for dehydrogenation is believed to proceed via cyclometallation of the 2,6-diisopropylphenoxide ligand although it is unclear whether initial attack occurs on a methine

or methyl CH bond. The isolation of stable five-membered metallacycles by protonation of the chelated  $\eta^2$ -CMe=CH<sub>2</sub> methylene carbon supports but does not prove that metallation of the methine CH bond occurs first.

## Experimental Section

All operations were carried out under a dry N<sub>2</sub> atmosphere or *in vacuo* in a Vacuum Atmospheres Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents and tetrahydrofuran (thf) were dried by distillation from sodium/benzophenone and stored under dry N<sub>2</sub>. NbCl<sub>5</sub> was used as supplied by the Alfa Chemical Co. The chemicals HOC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6, PhC≡CPh, HC≡CPh, and Ph<sub>2</sub>C=O were purchased from Aldrich Chemical Co. and were used without further purification. Pyridine and aniline were supplied by Aldrich Chemical Co. and were dried over KOH pellets prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Associates Gemini 200 spectrometer using the protio impurities of commercial benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub> as internal standards. The infrared spectra were obtained by using a Perkin-Elmer 1800 Fourier transform infrared spectrometer. Mass spectra were recorded on a Finnigan 4000 spectrometer using perfluorobutylamine for calibration. Microanalysis data were obtained in-house at Purdue.

**Preparation of [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>- $\eta^2$ -CMe=CH<sub>2</sub>)(thf)] (1).** To a sodium amalgam (0.42 g Na/10 mL of Hg) solution was added [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>3</sub>Cl<sub>2</sub>] (5.0 g, 7.2 mmol) in tetrahydrofuran (100 mL). The mixture was stirred vigorously for 10 h at room temperature resulting in the formation of a dark green suspension. The clear deep green solution was separated from the mercury pool and filtered, and the filtrate was dried under vacuum. The crude product was then dissolved in a minimum quantity of hexane and the solution allowed to stand, whereupon deep-green crystals of product slowly formed. Additional product was obtained by slow evaporation of the supernatant. Yield = 3.72 g (74%). Anal. Calcd for NbC<sub>40</sub>H<sub>57</sub>O<sub>4</sub>: C, 69.15; H, 8.27. Found: C, 68.90; H, 8.78. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C):  $\delta$  1.2–1.5 (doublets, CHMe<sub>2</sub>), 2.15 (s, CMeCH<sub>2</sub>), 2.48 (d) and 2.81 (d, 9.8 Hz, AB pattern, CMeCH<sub>2</sub>), 3.2–3.5 (br multiplets, CHMe<sub>2</sub>), 1.08 (m) and 4.15 (m, CH<sub>2</sub> on thf), 6.8–7.2 (m, aromatics). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C):  $\delta$  90.1 (CMeCH<sub>2</sub>, <sup>1</sup>J(<sup>13</sup>C–<sup>1</sup>H) = 140.8 Hz), 95.9 (CMeCH<sub>2</sub>), 28.7, 27.0, and 24.8 (CHMe<sub>2</sub>), 23.9, 23.7, and 21.7 (CHMe<sub>2</sub>), 28.5 (CMeCH<sub>2</sub>), 162.7, and 161.7 and 158.0 (Nb–O–C), 144.4, 138.6, 137.3, and 134.2 (*ortho*-C's at central phenoxy rings).

**Preparation of [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>- $\eta^2$ -CMe=CH<sub>2</sub>)(py)<sub>2</sub>] (2).** To a sodium amalgam (0.17 g Na/5 mL of Hg) was added [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>3</sub>Cl<sub>2</sub>] (2.0 g, 2.88 mmol) and pyridine (py) (1.0 mL, 12.4 mmol) dissolved in diethyl ether (30 mL). The mixture was stirred vigorously overnight at room temperature resulting in the formation of a brownish red suspension. The clear red solution was filtered from the mixture and dried under vacuum. The crude product was dissolved in a minimum quantity of hexane and the solution allowed to stand, whereupon large red crystals slowly formed. Yield = 1.27 g (57%). Anal. Calcd for NbC<sub>46</sub>H<sub>59</sub>N<sub>2</sub>O<sub>3</sub>: C, 70.75; H, 7.62; N, 3.59. Found: C, 70.83; H, 7.57; N, 3.49. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, –20 °C):  $\delta$  0.9–1.3 (overlapping doublets, CHMe<sub>2</sub>), 2.26 (s, CMeCH<sub>2</sub>), 2.62 (d) and 3.23 (d, 5.5 Hz, AB pattern, CMeCH<sub>2</sub>), 3.04, 3.40, and 3.82 (septets, CHMe<sub>2</sub>), 6.4–7.4 (m, aromatics), 8.88 (d) and 9.67 (d, *ortho*-H's on pyridines). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C):  $\delta$  87.0 (CMeCH<sub>2</sub>, <sup>1</sup>J(<sup>13</sup>C–<sup>1</sup>H) = 146.8 Hz), 88.1 (CMeCH<sub>2</sub>), 20.0–30.0 (CHMe<sub>2</sub>), 118.0–141.0 (aromatics), 150.1 and 151.9 (*ortho*-carbons of py's), 159.5, 158.1, and 155.7 (Nb–O–C).

**Preparation of [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>- $\eta^2$ -CMe=CH<sub>2</sub>)(CNBu<sup>t</sup>)<sub>2</sub>] (3).** To a solution of [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>- $\eta^2$ -CMe=CH<sub>2</sub>)(thf)] (**1**) (0.2 g, 0.29 mmol) in hexane (5 mL) was added Bu<sup>t</sup>NC (0.1 mL, large excess) by syringe. Slow cooling of the resulting dark mixture yielded

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the product as greenish-orange chunks.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  0.87 (br,  $\text{CNCMe}_3$ ), 1.1–1.5 (overlapping doublets,  $\text{CHMe}_2$ ), 3.41, 3.59, 3.94 (septets,  $\text{CHMe}_2$ ), 2.34 (s,  $\text{CMeCH}_2$ ), 2.31 (d), 3.42 (d, 4.2 Hz, AB pattern,  $\text{CMeCH}_2$ ), 6.6–7.4 (m, aromatics).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  68.2 ( $\text{CMeCH}_2$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 153.4$  Hz), 81.9 ( $\text{CMeCH}_2$ ), 23.5, 23.7, 23.8, 24.5, 24.9, 25.0, 25.4, 26.0, 26.4, 29.7, 30.0 ( $\text{CHMe}_2$  and  $\text{CMe}_3$ ), 166.3, 158.2, 155.6, 153.7, 138.3, 137.1, 133.0 (Nb– $\text{CNCMe}_3$ , Nb–O–C, *ortho*-C's at central phenoxy rings). IR (Nujol mull): 2194 (sh), 2172  $\text{cm}^{-1}$ .

**Preparation of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMe-CH}_2\text{CPh}_2\text{O})]$  (4).** To a solution of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{thf})]$  (**1**) (0.4 g, 0.58 mmol) in hexane (10 mL) was added  $\text{Ph}_2\text{C=O}$  (0.11 g, 0.63 mmol). The mixture was stirred for 2 h to afford a yellow solution. The yellow crystalline product was obtained upon slow evaporation of the hexane solution. Additional crystals were obtained by concentration of the supernatant. Yield = 0.33 g (71%). Anal. Calcd. for  $\text{NbC}_{49}\text{H}_{59}\text{O}_4$ : C, 73.12; H, 7.39. Found: C, 72.86; H, 7.35.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  0.7–1.4 (overlapping doublets,  $\text{CHMe}_2$ ), 1.85 (s,  $\text{CMeCH}_2\text{CPh}_2\text{O}$ ), 2.8–3.1 and 4.05 (septets,  $\text{CHMe}_2$ ), 3.85 (d) and 4.52 (d, 14 Hz, AB pattern,  $\text{CMeCH}_2\text{CPh}_2\text{O}$ ), 6.7–7.3 (m, aromatics), 7.49 (d) and 7.78 (d, *ortho*-H's on  $\text{CMeCH}_2\text{CPh}_2\text{O}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  60.5 ( $\text{CMeCH}_2\text{CPh}_2\text{O}$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 127.2$  Hz), 96.8 ( $\text{CMeCH}_2\text{-CPh}_2\text{O}$ ), 99.6 ( $\text{CMeCH}_2\text{CPh}_2\text{O}$ ), 162.6, 160.6, and 158.4 (Nb–O–C), 148.7 and 148.6 (*ipso*-C's on  $\text{NbOCPh}_2$ ), 151.0, 138.4, 137.0, and 134.0 (*ortho*-C's at central phenoxy rings), 121.0–132.0 (aromatics), 22.0–30.0 (diastereotopic  $\text{CHMe}_2$ ). The compound  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMeCH}_2^{13}\text{CPh}_2\text{O})]$  was obtained by addition of  $\text{Ph}_2^{13}\text{C=O}$  to a  $\text{C}_6\text{D}_6$  solution of **1**. The compound was only characterized in the reaction mixture by NMR spectroscopy. Selected  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  3.84 (dd, 14 Hz, 5 Hz) and 4.53 (d, 14 Hz,  $\text{CMeCH}_2^{13}\text{CPh}_2\text{O}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  99.6 ( $\text{CMeCH}_2^{13}\text{CPh}_2\text{O}$ ).

**Preparation of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMe-CH}_2\text{CPh=CPh})]$  (5).** To a solution of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{thf})]$  (**1**) (0.42 g, 0.61 mmol) in hexane (10 mL) was added diphenylacetylene (0.12 g, 0.67 mmol). The initial green solution rapidly changed its color to orange and was stirred for 1 h. The bright orange crystalline product was obtained after slow cooling of the concentrated hexane solution. Yield = 0.37 g (76%). Anal. Calcd for  $\text{NbC}_{50}\text{H}_{59}\text{O}_3$ : C, 74.98; H, 7.42. Found: C, 75.06; H, 7.56.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  0.75–1.45 (doublets,  $\text{CHMe}_2$ ), 2.13 (s,  $\text{CMeCH}_2$ ), 2.91, 3.35, and 3.75 (septets,  $\text{CHMe}_2$ ), 3.91 (d) and 4.15 (d, AB pattern  $\text{CMeCH}_2$ ), 6.7–7.3 (m, aromatics).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  59.2 ( $\text{CMeCH}_2$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 125.1$  Hz), 96.4 (Nb– $\text{CMeCH}_2$ ), 160.8 ( $\text{CMeCH}_2\text{CPh=CPh}$ ), 200.5 (Nb–O), 163.9, 161.4, and 158.9 (Nb–O–C), 150.6 and 139.7 (*ipso*-C's on  $\text{CMeCH}_2\text{CPh=CPh}$ ), 143.4, 139.7, 138.3, and 133.4 (*ortho*-C's at central phenoxy rings), 22.0–30.0 (diastereotopic  $\text{CHMe}_2$ ), 122.0–130.0 (aromatics).

**Spectroscopic Characterization of 6a.** To a solution of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{thf})]$  (**1**) (0.05 g) in  $\text{C}_6\text{D}_6$  (1.0 mL) was added phenylacetylene ( $\text{HC}\equiv\text{CPh}$ ) (0.01 g). The initial deep green solution rapidly changed its color to orange, and the initially formed organometallic product was characterized in solution.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  0.8–1.4 (doublets,  $\text{CHMe}_2$ ), 1.88 (s,  $\text{CMeCH}_2\text{-CH=CPh}$ ), 2.96, 3.28, and 3.78 (septets,  $\text{CHMe}_2$ ), 3.36 (br,  $\text{CMeCH}_2\text{CH=CPh}$ ), 6.7–7.2 (m, aromatics), 7.37 (d, *ortho*-H's on  $\text{CMeCH}_2\text{CH=CPh}$ ).

**Preparation of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMe-CH}_2\text{CPh=CH})]$  (6b).** To a solution of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{thf})]$  (**1**) (0.35 g, 0.5 mmol) in hexane (10 mL) was added phenylacetylene (0.06 g, 0.59

mmol). The mixture changed color from green to orange in several seconds and was stirred for 24 h. The orange crystalline product was isolated upon slow cooling of the concentrated hexane solution. Additional crystalline product was obtained by slow evaporation of the supernatant. Yield = 0.27 g (74%). Anal. Calcd for  $\text{NbC}_{44}\text{H}_{55}\text{O}_3$ : C, 72.91; H, 7.65. Found: C, 72.93; H, 7.58.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  0.9–1.4 (doublets,  $\text{CHMe}_2$ ), 1.90 (s,  $\text{CMeCH}_2\text{CPh=CH}$ ), 3.17, 3.40, and 3.94 (septets,  $\text{CHMe}_2$ ), 3.89 (d) and 4.18 (d, AB pattern,  $\text{CMeCH}_2\text{-CPh=CH}$ ), 6.8–7.2 (m, aromatics), 7.5 (d, *ortho*-H's on  $\text{CMeCH}_2\text{-CPh=CH}$ ), 9.18 (s,  $\text{CMeCH}_2\text{CPh=CH}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  55.4 ( $\text{CMeCH}_2\text{CPh=CH}$ ), 95.8 (Nb– $\text{CMeCH}_2$ ), 168.1 ( $\text{CMeCH}_2\text{CPh=CH}$ ), 185.0 (Nb–O), 168.0 (NbCHCPhCH<sub>2</sub>-CMe), 163.6, 160.8, and 159.1 (Nb–O–C), 149.9 (*ipso*-C's on  $\text{CMeCH}_2\text{CPh=CH}$ ), 138.8, 137.9, 137.7 and 133.7 (*ortho*-C's at central phenoxy rings), 123.0–130.0 (aromatics), 21.0–30.0 (diastereotopic  $\text{CHMe}_2$ ).

**Preparation of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_3(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMe}_2)]$  (8).** To a solution of  $[\text{Nb}(\text{OAr-}2,6\text{Pr}^i)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{thf})]$  (**1**) (3 g, 4.3 mmol) in benzene (25 mL) was added  $\text{HOC}_6\text{H}_3\text{Pr}^i\text{-}2,6$  (0.8 g, 4.5 mmol). The mixture was stirred for 2 h to afford an orange solution. The crystalline product was isolated from the supernatant after slow evaporation of the solvent. Yield = 2.35 g (68%). Anal. Calcd for  $\text{NbC}_{48}\text{H}_{67}\text{O}_4$ : C, 71.98; H, 8.43. Found: C, 70.99; H, 9.10.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  0.93 (d) and 1.12 (d,  $\text{CHMe}_2$ ), 2.51 (s, Nb– $\text{CMe}_2$ ), 2.88 and 3.65 (septets,  $\text{CHMe}_2$ ), 6.6–7.1 (m, aromatics).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  90.2 (Nb– $\text{CMe}_2$ ), 159.2 and 151.8 (Nb–O–C), 138.9 (*ortho*-C's at nonmetalated central phenoxy rings), 134.7 and 138.5 (*ortho*-C's at metalated central phenoxy ring), 122.0–126.0 (aromatics), 22.0–29.0 ( $\text{CHMe}_2$  and Nb– $\text{CMe}_2$ ). Mass spectrometric analysis: +CI, 70 eV (source temp = 250 °C; probe temp = 140 °C) gave the highest mass peak at *m/e* 801 identified as  $[\text{M} + \text{H}]^+$ , the base peak at *m/e* 623 identified as  $[\text{Nb}(\text{OAr-}2,6\text{Pr}^i)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)]$ . –CI, 70 eV (source temp = 250 °C, probe temp = 120 °C) gave the highest mass peak and base peak both at *m/e* 800 identified as  $[\text{M}]^-$ .

**Preparation of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-CMe}_2)\text{-NHPPh}]$  (9).** To a solution of  $[\text{Nb}(\text{OAr-}2,6\text{Pr}^i)_2(\text{OC}_6\text{H}_3\text{Pr}^i\text{-}\eta^2\text{-CMe=CH}_2)(\text{thf})]$  (**1**) (0.5 g, 0.72 mmol) in hexane (10 mL) was added aniline (0.1 g, 1.08 mmol). The mixture was stirred for 4 h to afford an orange solution. The orange crystalline product was obtained after slow evaporation of the hexane solution. Concentration of the supernatant gave additional crystals. Yield = 0.34 g (66%). Anal. Calcd for  $\text{NbC}_{42}\text{H}_{56}\text{NO}_3$ : C, 70.47; H, 7.89; N, 1.96. Found: C, 70.21; H, 8.23; N, 2.04.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  0.9–1.2 (doublets,  $\text{CHMe}_2$ ), 1.91 (s,  $\text{CMe}_2$ ), 3.27 and 3.53 (septets,  $\text{CHMe}_2$ ), 6.6–7.1 (m, aromatics), 8.49 (br s, *NHPPh*).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  92.4 (Nb– $\text{CMe}_2$ ), 152.3, 157.9 and 150.1 (Nb–O–C), 161.8 (*ipso*-C at *NHPPh*), 118.0–140.0 (aromatics), 22.0–28.0 (diastereotopic  $\text{CHMe}_2$ ). Infrared (Nujol mull):  $\nu(\text{N-H}) = 3288$   $\text{cm}^{-1}$ .

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**Supporting Information Available:** Text describing X-ray procedures and tables of experimental details associated with data collection and crystal structure refinement, final atomic coordinates, thermal parameters, and complete bond distances and angles for complexes **1**, **3**, **5**, and **8** (84 pages). Ordering information is given on any current masthead page.

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