Synthesis, Structure, and Reactivity of Niobocene Imido Complexes Containing Alkynyl Ligands. X-ray Crystal Structure of [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)]

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The following alkynyl niobocene imido complexes have been prepared: [Nb(=NBu^t)(η^5-C_5H_5)$_2$(C≡CR)] (R = Me (**1**), SiMe$_3$ (**2**), Bu^t (**3**), CH$_2$Ph (**4**)), [Nb(=NC$_6$H$_4$Me-4)(η^5-C_5H_5)$_2$(C≡CR)] (R = SiMe$_3$ (**5**), Bu^t (**6**)), [Nb(=NBu^t)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] (R = SiMe$_3$ (**7**), Bu^t (**8**)), [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] (R = Ph (**9**), Bu^t (**10**)), [Nb(=NC$_6$H$_4$Me-4)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] (R = SiMe$_3$ (**11**), Bu^t (**12**)), [Nb(=NC$_6$H$_4$OMe-4)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CR)] (R = SiMe$_3$ (**13**), Bu^t (**14**)), and [Nb(=NBu^t){Me$_2$Si(η^5-C_5H_4)$_2$}(C≡CR)] (R = SiMe$_3$ (**15**), Bu^t (**16**)). The synthetic path involved the reaction of either BrMg(C≡CR) or Mg(C≡CR)$_2$ with the metallocene imido complex Nb(=NR′)(Cp)$_2$Cl, Cp = η^5-cyclopentadienyl. The molecular structure of **9** has been determined by single-crystal X-ray diffraction studies. Protonation of **2** by CF$_3$COOH and **9** by HBF$_4$ gave the cationic amide species [Nb(NHBu^t)(η^5-C_5H_5)$_2$(C≡CSiMe$_3$)]$^+$ (**17**) and [Nb(NHPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)]$^+$ (**18**), respectively.

Introduction

Half-sandwich complexes are well-known in niobium imido chemistry,[1] but their metallocene counterparts have not been so extensively studied. However in recent years several new complexes of this type have been reported.[2] Furthermore, the chemistry of d-block transition metals with alkynyl ligands has been well-documented.[3] During the past years several families of imido-containing[4] and alkynyl-containing[5] niobocene complexes have been reported by our group. Particularly, a straightforward synthetic method was described for the preparation of alkynyl-containing niobocene complexes, which are rarely encountered in the literature, by the reaction of the corresponding haloniobium(II) complexes with the appropriate alkynylmagnesium compounds, Mg(C≡CR)$_2$. To expand this poorly explored field and to study reactivity, we have prepared new niobocene imido complexes incorporating alkynyl ligands. Our group has previously carried out reactions of protonation with imido[4b] and alkynyl[5] complexes, and it should be interesting to explore the reactivity of compounds that contain both of these groups. This paper will focus on the synthesis and structural characterization of alkynyl-imido niobocene complexes and some aspects of their reactivity.

Results and Discussion

The reaction of the Grignard reagent BrMg(C≡CMe) with [Nb(=NBu^t)(η^5-C_5H_5)$_2$Cl] gave the alkynyl complex [Nb(=NBu^t)(η^5-C_5H_5)$_2$(C≡CMe)] (**1**) as the unique product (eq 1). **1** was spectroscopically characterized. The IR spectrum shows a characteristic band at 2055 cm^{-1} ($\nu_{C≡C}$), which corresponds to the coordinated alkynyl unit, and in addition the ^{13}C NMR spectrum exhibits two characteristic resonances for the alkynyl C$_\alpha$ and C$_\beta$

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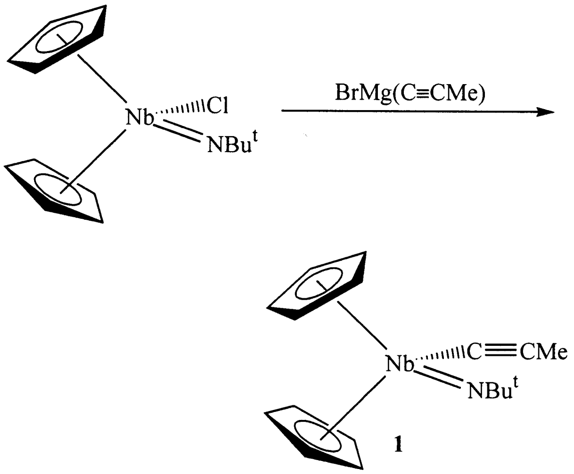
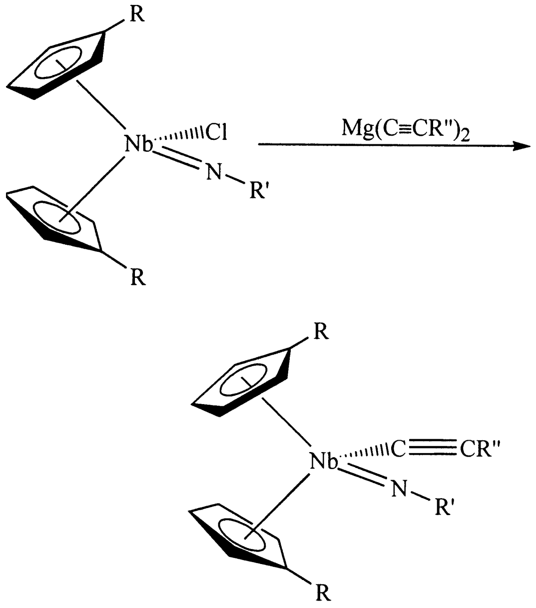
carbons at 128.3 and 111.9 ppm, respectively (see Experimental Section).



(1)

However when this substitution reaction was repeated with other starting niobocene imido chloride complexes, the desired compound was not isolated as the pure product but as a mixture of starting material and its bromo derivative caused by halide exchange. However, good results were obtained when bisalkynyl magnesium derivatives, $Mg(C{\equiv}CR)_2$, were used in this process. In our experience the magnesium bisalkynyl compounds are normally more reactive than their Grignard counterparts, and in the synthesis of the alkynyl derivatives this factor is critical to avoid contamination of the desired product with unreacted starting material.[5] We have observed that when the reactions were carried out in refluxing THF, the process did not always go to completion and a mixture of both starting material and appropriate alkynyl-containing complex was isolated. This is probably due to the partial deactivation of $Mg(C{\equiv}CR)_2$ caused by THF coordination. This problem was overcome by conducting all the reactions in a noncoordinating solvent, such as toluene. In this solvent, the corresponding reactions at 100 °C afford the alkynyl complexes $[Nb({=}NBu^t)(\eta^5\text{-}C_5H_5)_2(C{\equiv}CR)]$ (R = $SiMe_3$ (**2**), Bu^t (**3**), CH_2Ph (**4**)), $[Nb({=}NC_6H_4\text{-}Me\text{-}4)(\eta^5\text{-}C_5H_5)_2(C{\equiv}CR)]$ (R = $SiMe_3$ (**5**), Bu^t (**6**)), $[Nb({=}NBu^t)(\eta^5\text{-}C_5H_4SiMe_3)_2(C{\equiv}CR)]$ (R = $SiMe_3$ (**7**), Bu^t (**8**)), $[Nb({=}NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2(C{\equiv}CR)]$ (R = Ph (**9**), Bu^t (**10**)), $[Nb({=}NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2(C{\equiv}CR)]$ (R = $SiMe_3$ (**11**), Bu^t (**12**)), and $[Nb({=}NC_6H_4OMe\text{-}4)(\eta^5\text{-}C_5H_4\text{-}SiMe_3)_2(C{\equiv}CR)]$ (R = $SiMe_3$ (**13**), Bu^t (**14**)), which were obtained, after appropriate workup, as air-sensitive yellow crystalline solids uncontaminated by starting materials (eq 2) (see Experimental Section).



(2)

R = H; R' = Bu^t; R" = $SiMe_3$ (**2**)
R = H; R' = Bu^t; R" = Bu^t (**3**)
R = H; R' = Bu^t; R" = CH_2Ph (**4**)
R = H; R' = C_6H_4Me-4; R" = $SiMe_3$ (**5**)
R = H; R' = C_6H_4Me-4; R" = Bu^t (**6**)
R = $SiMe_3$; R' = Bu^t; R" = $SiMe_3$ (**7**)
R = $SiMe_3$; R' = Bu^t; R" = Bu^t (**8**)
R = $SiMe_3$; R' = Ph; R" = Ph (**9**)
R = $SiMe_3$; R' = Ph; R" = Bu^t (**10**)
R = $SiMe_3$; R' = C_6H_4Me-4; R" = $SiMe_3$ (**11**)
R = $SiMe_3$; R' = C_6H_4Me-4; R" = Bu^t (**12**)
R = $SiMe_3$; R' = C_6H_4OMe-4; R" = $SiMe_3$ (**13**)
R = $SiMe_3$; R' = C_6H_4OMe-4; R" = Bu^t (**14**)

Compounds **2**−**14** were characterized spectroscopically. IR spectroscopy showed a band, at 2050−2110 cm^{-1}, assigned to the $\nu(C{\equiv}C)$ of the alkynyl ligand and a band between 1230 and 1300 cm^{-1} characteristic of the terminal imido ligand.[1a] Several vibrational spectroscopic studies of group 5 imido complexes have been carried out.[6] The ^1H NMR spectra of the unsubstituted cyclopentadienyl complexes **2**−**6** exhibited the expected singlet for the cyclopentadienyl ligand. In addition for **2** and **3** singlets were observed for the alkynyl substituent $SiMe_3$ or Bu^t, and in the case of **4**, where R = CH_2-Ph, a singlet was observed for the CH_2 protons and various multiplets for the phenyl ring. When the trimethylsilyl-substituted cyclopentadienyl complexes **7**−**14** are considered, their ^1H NMR spectra are similar to those of their unsubstituted analogues. The C_s symmetry of **7**−**14** results in the appearance of four multiplets for the C_5 ring protons. In addition, the ^{13}C NMR spectra of theses complexes show two characteristic resonances for the alkynyl C_α and C_β carbons at ca. 110 and 128 ppm, respectively (see Experimental Section).

ansa-Niobocene imido complexes have only recently been reported.[7] To prepare *ansa*-niobocenes containing simultaneously both imido and alkynyl ligands, we have carried out reactions analogous to those described in the preparation of **2**−**14** (eq 3). Thus the reactions of the appropriate starting materials with the corresponding $Mg(C{\equiv}CR)_2$ reagents gave rise to the isolation of

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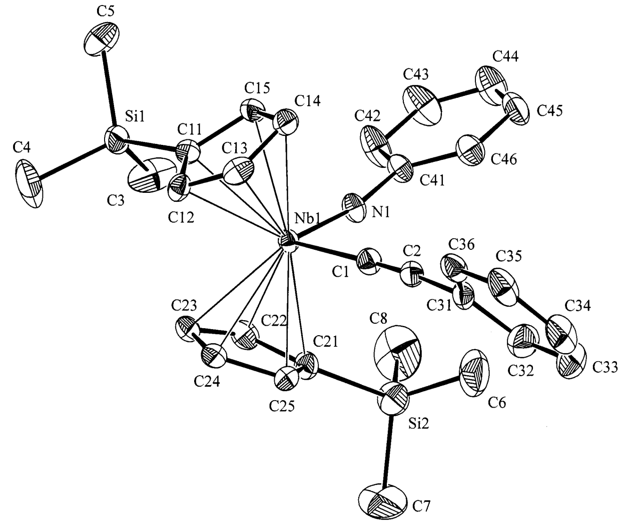
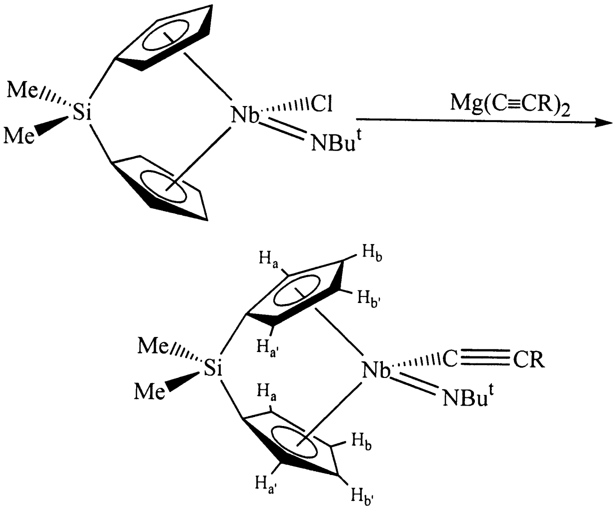


Figure 1. Molecular structure and atom-labeling scheme for [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)] (**9**), with thermal ellipsoids at 20% probability.

complexes [Nb(=NBu^t){Me_2Si(η^5-C_5H_4)$_2$}(C≡CR)] (R = $SiMe_3$ (**15**), Bu^t (**16**)), which were isolated, after appropriate workup, as yellow crystalline solids. Their ^1H NMR spectra reveal the presence of a system similar to that obtained for the previously reported [Nb{Me_2Si(η^5-C_5H_4)$_2$}Cl(RC≡CR)][8] and [Nb(=NBu^t){Me_2Si(η^5-C_5H_4)$_2$}Cl],[7] where the symmetry of the molecule (C_s) in solution is such that there is only one plane of symmetry and the two methyl groups of $SiMe_2$ become inequivalent, as do the cyclopentadienyl protons (Ha, Hb, Ha′, Hb′) (eq 3). In addition, the ^{13}C NMR spectra exhibit the appropriate carbon alkynyl resonances (see Experimental Section).



(3)

R = $SiMe_3$ (**13**), Bu^t (**14**)

The molecular structure of [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)] (**9**) was established by X-ray crystal diffraction studies. The molecular structure and atomic numbering scheme are shown in Figure 1. Selected bond lengths and angles for **9** are give in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)] (9)[a]

Nb(1)−Cent(1)	2.164
Nb(1)−Cent(2)	2.196
av Nb(1)−C(11−15)	2.473
av Nb(1)−C(21−25)	2.497
Nb(1)−C(1)	2.170(7)
Nb(1)−N(1)	1.804(5)
N(1)−C(41)	1.376(8)
C(1)−C(2)	1.20(1)
C(2)−C(31)	1.46(1)
Cent(1)−Nb(1)−Cent(2)	128.2
Nb(1)−N(1)−C(41)	167.9(6)
Nb(1)−C(1)−C(2)	177.9(6)
C(1)−C(2)−C(31)	175.4(8)
C(1)−Nb(1)−Cent(1)	101.1
C(1)−Nb(1)−Cent(2)	102.0
N(1)−Nb(1)−Cent(1)	109.5
N(1)−Nb(1)−Cent(2)	113.2
C(1)−Nb(1)−N(1)	95.9(3)

[a] Cent(1) and Cent(2) are the centroids of C(11)−C(15) and C(21)−C(25), respectively.

Compound **9** presents a typical bent metallocene structure with two additional ligands. Both cyclopentadienyl rings are η^5 bonded to the metal with the Cent−Nb−Cent angle of 128.2°. The alkynyl ligand is σ bonded to the metal as indicated by the C(1)−C(2) distance of 1.20(1) Å, which is typical for a C−C triple bond, and the Nb−C(1)−C(2) angle of 177.9(6)°, whose linear nature confirms that the C(1) and C(2) atoms are sp hybridized. The Nb−N bond distance of 1.804(5) Å is at the upper limit for those observed for niobium imido complexes (1.73−1.80 Å) (see Table 2) and is indicative of a Nb−N triple bond.

The imide ligand is able to act as either a two- or four-electron donor. In the first case the nitrogen atom would be sp^2 hybridized and therefore result in the bending back of the imide substituent. In the second case the nitrogen would be sp hybridized and the metal−nitrogen−substituent angle linear. In **9** the angle Nb−N−C_{ipso} of 167.9(6)° deviates slightly from linear. Such deviations from linear of the Nb−N−C_{ipso} angles have been reported for some niobocene imido complexes and are normally in the range 12−15° (see Table 2). These complexes in general contain aryl-imido and/or sterically demanding ligands. In the case of [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$Cl] extended-Hückel molecular-orbital calculations established that the imido bond angles for "linear imide" in this class of complexes can vary up to 140° with little effect on the Nb−N bonding.[4a] Therefore we propose that in **9** the nitrogen atom is sp hybridized and that the two limiting descriptions, Nb^-≡N^+−R and Nb═N̈−R, proposed by Bercaw and co-workers for (η^5-C_5Me_5)$_2$Ta(=NPh)(H) may explain the true bonding situation.[9]

The formal electron count of **9** is 20 electrons with the excess 2 electrons probably being located in a nonbonding orbital similar to that proposed by Green et al. for [Mo(=NBu^t)(η^5-C_5H_5)$_2$].[10] Similar "20-electron" niobocene imido complexes [Nb(=NR)(η^5-$C_5H_4SiMe_3$)$_2$Cl] have shown a lengthening of the Nb−centroid

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Table 2. Selected Structural Data on Niobocene Imido Complexes

	Cp-Nb−Cp, deg	Nb−N−C, deg	Nb−N, Å	ref
$[Nb(=NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2(C\equiv CPh)]$ (**9**)	128.2	167.9(6)	1.804(5)	this work
$[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl]^a$	122.7	168.0(4)	1.790(5)	13
	122.3	167.5(4)	1.782(5)	
$[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Pr^i)\}Cl]$	122.1	172.34(4)	1.772(2)	13
$[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Cl]$	121.21	178.8(2)	1.756(3)	7a
$[Nb(=NSiMe_3)\{Me_2C(\eta^5\text{-}C_5H_4)_2\}Cl]$	114.2	167.71(7)	1.777(1)	7b
$[Nb(=NBu^t)\{Me_2C(\eta^5\text{-}C_5H_4)_2\}Cl]$	113.3	178.4(3)	1.762(3)	7b
$[Nb(=NBu^t)\{Me_2C(\eta^5\text{-}C_5H_4)_2\}Br]$	113.4	178.3(2)	1.765(2)	7b
$[Nb(=NBu^t)\{Me_2C(\eta^5\text{-}C_5H_4)_2\}I]$	114.2	171.8(2)	1.770(2)	7b
$[Nb(=Ar)\{Me_2C(\eta^5\text{-}C_5H_4)_2\}Cl]^b$	114.4	167.5(1)	1.798(2)	7c
$[Nb(=Ar)\{Me_2C(\eta^5\text{-}C_5H_4)_2\}(NMe_2)][B(C_6H_5)_4]^b$	114.0	166.8(1)	1.803(2)	7c
$[Nb(=NBu^t)(\eta^5\text{-}C_5H_5)_2Cl]^a$	122.7	173.6(4)	1.789(4)	2a
	124.0	179.4(5)	1.737(6)	
$[Nb(=NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$	124.9	165.1(2)	1.792(2)	4a
$[Nb(=NC_6H_4OMe\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$	125.23	163.0(2)	1.787(3)	11

[a] Two independent molecules exist in the unit cell. [b] Ar= $C_6H_3Pr^i_2$-2,6.

Table 3. Comparison of Nb−Cent Distances in Selected Cp′-Containing Niobocene Complexes[a]

compound	average Nb−Cent (Å)	ref
$[Nb(=NC_6H_4OMe\text{-}4)Cp'_2Cl]$	2.189	11
$[\{NbCp'_2Cl\}_2(\mu\text{-}1,3\text{-}N_2C_6H_4)]$	2.188	4b
$[Nb(=O)Cp'_2Me]$	2.181	14
$[Nb(=NPh)Cp'_2(C\equiv CPh)]]$ (**9**)	2.180	this work
$[Nb(=NPh)Cp'_2Cl]$	2.180	4a
$[NbCp'_2Cl(\eta^2\text{-}N,C\text{-}OCNPh)]$	2.121	4b
$[NbCp'_2Cl_2]$	2.079	14, 15
$[\{NbCp'_2Cl\}_2]$	2.07	4a
$[NbCp'_2(C_6F_5)(CO)]$	2.04	14

[a] Cp′ = η^5-$C_5H_4SiMe_3$; Cent = the centroid of the C_5 ring.

distances in comparison with their 18- and 17-electron analogues, and this too is the case in **9** (see Table 3).[11]

The reactivity of the alkynyl imido complexes **1**−**16** with the protic reagents CF_3COOH and HBF_4 has been studied. Protonation of these complexes may occur at the alkynyl and/or the imido moiety as observed previously in complexes containing only one of these ligands.[4a,5] In nearly all cases the final product could not be identified due probably to the evolution of the desired protonated species, although a residual broad signal, which may correspond to its N−H proton, was observed in the ^1H NMR spectrum, indicating that amide-containing species may have initially been formed. However, in the reactions of **2** and **9** with CF_3COOH and HBF_4, respectively, the protonated compounds could be isolated (eqs 4 and 5). It was found that in these imido/alkynyl complexes protonation takes place preferentially at the nitrogen atom of the imido group, leading to the formation of the cationic amide species $[Nb(NHBu^t)(\eta^5\text{-}C_5H_5)_2(C\equiv CSiMe_3)]^+$ (**17**) and $[Nb(NHPh)(\eta^5\text{-}C_5H_4SiMe_3)_2(C\equiv CPh)]^+$ (**18**). The complexes were isolated as red crystalline very air-sensitive solids after appropriate workup (see Experimental Section). Compounds **17**−**18** were characterized by IR and ^1H NMR spectroscopy. Bands at 2090 cm^{-1} for **17** and 2071 cm^{-1} for **18**, assigned to the $\nu(C\equiv C)$ of the alkynyl ligand, were observed in the IR spectra. Broad signals at 8.55 ppm for **17** and 8.22 ppm for **18**, due to the proton bonded to the nitrogen atom, were also observed in the ^1H NMR spectra. In addition in **17** the signal due to the Bu^t group (1.45 ppm) is shifted downfield with respect to the signal observed in the parent complex (1.01 ppm), thus reflecting the change from imide to amide of the nitrogen-containing ligand. Unfortunately, the instability of these complexes in solution precludes the ^{13}C NMR from being recorded. The normally greater Bronsted basicity of the imido ligand relative to the alkynyl ligand may explain the selective nature of the protonation reaction of these alkynyl-imido niobocene complexes.

In conclusion we have observed a different reactivity when either $BrMg(C\equiv CR)$ or $Mg(C\equiv CR)_2$ is employed in the preparation of alkynyl niobocene imido complexes. We report the first alkynyl-containing *ansa*-niobocene complexes. Finally protonation processes of two complexes have been studied and indicate that the reaction takes place preferentially at the imido group, giving rise to the corresponding amido complexes.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use.

$[Nb(=NBu^t)(\eta^5\text{-}C_5H_5)_2Cl]$,[2b] $[Nb(=NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_5)_2Cl]$,[11] $[Nb(=NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$,[4a] $[Nb(=NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$,[11] $[Nb(=NC_6H_4OMe\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$,[11] and $[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Cl]$[7a] were prepared as described earlier. The synthesis of the alkynylmagnesium compounds $Mg(C\equiv CR)_2$ was performed by following a previously reported method.[12] $BrMg(C\equiv CMe)$, HBF_4, and CF_3COOH were purchased from Aldrich and used directly. IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. ^1H and ^{13}C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer.

$[Nb(=NBu^t)(\eta^5\text{-}C_5H_5)_2(C\equiv CMe)]$ (1). A 0.5 M solution of $BrMg(C\equiv CMe)$ in THF (2.12 mL, 1.06 mmol) was added to a stirring solution of $[Nb(=NBu^t)(\eta^5\text{-}C_5H_5)_2Cl]$ (0.35 g, 1.06 mmol) in THF (25 mL) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and the remaining yellow oil extracted in hexane. A yellow crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.24 g, 69%). IR (Nujol mull): $\nu_{Nb=N}$ 1295 cm^{-1}; $\nu_{C\equiv C}$ 2055 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 0.96 (s, 9H, $C(CH_3)_3$), 2.06 (s, 3H, *Me*), 5.78 (s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 7.1 (*Me*), 29.7 ($C(CH_3)_3$), 70.7 ($C(CH_3)_3$), 108.4 (C_5H_5), 111.9

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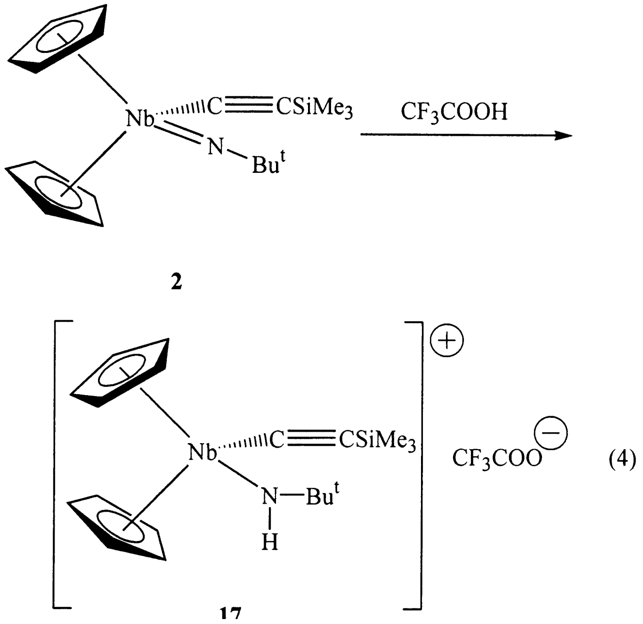

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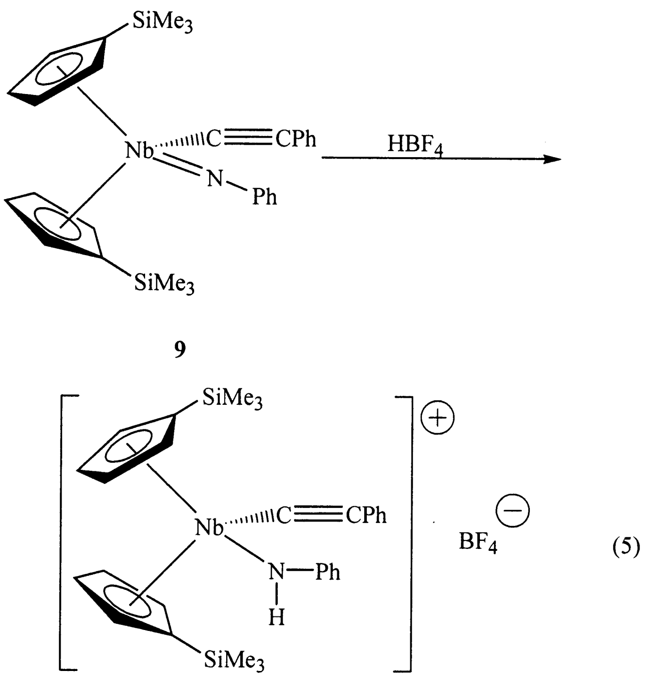
(4)



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(5)

(*C*≡CNb), 128.3 (C≡*C*Nb). Anal. Calcd for $C_{17}H_{22}NNb$: C, 61.27; H, 6.65; N, 4.20. Found: C, 61.03; H, 6.58; N, 4.11.

$[Nb({=}NBu^t)(\eta^5\text{-}C_5H_5)_2(C{\equiv}CSiMe_3)]$ (2). Toluene (50 mL) was added to a mixture of $Mg(C{\equiv}CSiMe_3)_2$ (0.12 g, 0.55 mmol) and $[Nb({=}NBu^t)(\eta^5\text{-}C_5H_5)_2Cl]$ (0.36 g, 1.09 mmol). The mixture was stirred at 100 °C for 7 h. Solvent was removed in vacuo and the remaining yellow oil extracted in hexane (50 mL). A yellow crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.27 g, 63%). IR (Nujol mull): $\nu_{Nb=N}$ 1250 cm^{-1}; $\nu_{C\equiv C}$ 2100 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.36 (s, 9H, SiMe$_3$), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 5.71 (s, 10H, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 1.3 (Si*Me*$_3$), 30.4 (C(*C*H$_3$)$_3$), 70.1 (*C*(CH$_3$)$_3$), 108.5 (*C*$_5$H$_5$), 107.6 (*C*≡CNb), 128.3 (C≡*C*Nb). Anal. Calcd for $C_{19}H_{28}NNbSi$: C, 58.30; H, 7.21; N, 3.58. Found: C, 58.22; H, 7.11; N, 3.65.

$[Nb({=}NBu^t)(\eta^5\text{-}C_5H_5)_2(C{\equiv}CBu^t)]$ (3). The synthesis of **3** was carried out in a manner identical to that of **2**. $Mg(C{\equiv}CBu^t)_2$ (0.09 g, 0.48 mmol) and $[Nb({=}NBu^t)(\eta^5\text{-}C_5H_5)_2Cl]$ (0.30 g, 0.91 mmol) were used. Yield: 0.24 g, 69%. IR (Nujol mull): $\nu_{Nb=N}$ 1235 cm^{-1}; $\nu_{C\equiv C}$ 2075 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.97 (s, 9H, NC(C*H*$_3$)$_3$), 1.42 (s, 9H, CC(C*H*$_3$)$_3$), 5.74 (s, 10H, C$_5$*H*$_5$). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 28.8 (C*C*(CH$_3$)$_3$), 30.5, 32.5 (C(*C*H$_3$)$_3$), 70.5 (N*C*(CH$_3$)$_3$), 108.6 (*C*$_5$H$_5$), 107.8 (*C*≡CNb), 128.4 (C≡*C*Nb). Anal. Calcd for $C_{20}H_{28}NNb$: C, 64.00; H, 7.52; N, 3.73. Found: C, 63.78; H, 7.40; N, 3.78.

$[Nb({=}NBu^t)(\eta^5\text{-}C_5H_5)_2(C{\equiv}CCH_2Ph)]$ (4). The synthesis of **4** was carried out in a manner identical to that of **2**. $Mg(C{\equiv}CCH_2Ph)_2$ (0.14 g, 0.55 mmol) and $[Nb({=}NBu^t)(\eta^5\text{-}C_5H_5)_2Cl]$ (0.35 g, 1.06 mmol) were used. Yield: 0.28 g, 65%. IR (Nujol mull): $\nu_{Nb=N}$ 1250 cm^{-1}; $\nu_{C\equiv C}$ 2090 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.96 (s, 9H, C(C*H*$_3$)$_3$), 3.86 (s, 2H, C*H*$_2$Ph), 5.76 (s, 10H, C$_5$*H*$_5$), 7.07−7.26, 7.56 (m, 5H, *Ph*). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 28.7 (*C*H$_2$Ph), 30.7 (C(*C*H$_3$)$_3$), 71.2 (*C*(CH$_3$)$_3$), 108.6 (*C*$_5$H$_5$), 108.7 (*C*≡CNb), 128.4 (C≡*C*Nb), 126.3, 132 3, 140.3 (*Ph*) (C$_{ipso}$ not observed). Anal. Calcd for $C_{23}H_{26}NNb$: C, 67.48; H, 6.40; N, 3.42. Found: C, 67.19; H, 6.27; N, 3.35.

$[Nb({=}NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_5)_2(C{\equiv}CSiMe_3)]$ (5). The synthesis of **5** was carried out in a manner identical to that of **2**. $Mg(C{\equiv}CSiMe_3)_2$ (0.12 g, 0.55 mmol) and $[Nb({=}NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_5)_2Cl]$ (0.40 g, 1.10 mmol) were used. Yield: 0.29 g, 62%. IR (Nujol mull): $\nu_{Nb=N}$ 1280 cm^{-1}; $\nu_{C\equiv C}$ 2070 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.39 (s, 9H, SiMe$_3$), 2.12 (s, 3H, NC$_6$H$_4$C*H*$_3$), 5.67 (s, 10H, C$_5$*H*$_5$), 6.53 (2H), 6.94 (2H) (d, NC$_6$*H*$_4$CH$_3$) (J 8.5 Hz). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 1.3 (Si*Me*$_3$), 20.9 (NC$_6$H$_4$*C*H$_3$), 108.6 (*C*$_5$H$_5$), 111.0 (*C*≡CNb), 127.0 (C≡*C*Nb), 117.9, 128.3, 129.0 (C$_{ipso}$) 130.4 (C$_{ipso}$) (N*C*$_6$H$_4$CH$_3$). Anal. Calcd for $C_{22}H_{26}NNbSi$: C, 62.11; H, 6.16; N, 3.29. Found: C, 61.88; H, 6.03; N, 3.28.

$[Nb({=}NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_5)_2(C{\equiv}CBu^t)]$ (6). The synthesis of **6** was carried out in a manner identical to that of **2**. $Mg(C{\equiv}CBu^t)_2$ (0.09 g, 0.48 mmol) and $[Nb({=}NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_5)_2Cl]$ (0.34 g, 0.93 mmol) were used. Yield: 0.23 g, 61%. IR (Nujol mull): $\nu_{Nb=N}$ 1295 cm^{-1}; $\nu_{C\equiv C}$ 2055 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 1.43 (s, 9H, C(C*H*$_3$)$_3$), 2.13 (s, 3H, NC$_6$H$_4$C*H*$_3$), 5.71 (s, 10H, C$_5$*H*$_5$), 6.55 (2H), 6.92 (2H) (d, NC$_6$*H*$_4$-CH$_3$) (J 8.5 Hz). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 23.0 (NC$_6$H$_4$*C*H$_3$), 29.4 (*C*(CH$_3$)$_3$), 32.4 (C(*C*H$_3$)$_3$), 108.6 (*C*$_5$H$_5$), 112.0 (*C*≡CNb), 128.8 (C≡*C*Nb), 118.1, 129.1, 133.4 (C$_{ipso}$) 146.1 (C$_{ipso}$) (N*C*$_6$H$_4$CH$_3$). Anal. Calcd for $C_{23}H_{26}NNb$: C, 67.48; H, 6.40; N, 3.42. Found: C, 67.41; H, 6.36; N, 3.44.

$[Nb({=}NBu^t)(\eta^5\text{-}C_5H_4SiMe_3)_2(C{\equiv}CSiMe_3)]$ (7). The synthesis of **7** was carried out in a manner identical to that of **2**. $Mg(C{\equiv}CSiMe_3)_2$ (0.11 g, 0.49 mmol) and $[Nb({=}NBu^t)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.46 g, 0.97 mmol) were used. Yield: 0.38 g, 73%. IR (Nujol mull): $\nu_{Nb=N}$ 1240 cm^{-1}; $\nu_{C\equiv}$ 2085 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.33 (s, 18H, C$_5$H$_4$Si*Me*$_3$), 0.36 (m, 9H, C≡CSi*Me*$_3$), 1.00 (s, 9H, C(C*H*$_3$)$_3$), 5.68 (2H), 5.91 (2H), 5.99 (2H), 6.29 (2H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 0.5 (C$_5$H$_4$Si*Me*$_3$), 1.1 (C≡CSi*Me*$_3$), 30.4 (C(*C*H$_3$)$_3$), 70.8 (*C*(CH$_3$)$_3$), 107.3, 111.6, 113.7 (C$_{ipso}$), 119.3, 119.8 (*C*$_5$H$_4$), 108.6 (*C*≡CNb), 131.1 (C≡*C*Nb). Anal. Calcd for $C_{25}H_{44}NNbSi_3$: C, 56.04; H, 8.28; N, 2.61. Found: C, 55.83; H, 8.19; N, 2.60.

$[Nb({=}NBu^t)(\eta^5\text{-}C_5H_4SiMe_3)_2(C{\equiv}CBu^t)]$ (8). The synthesis of **8** was carried out in a manner identical to that of **2**. $Mg(C{\equiv}CBu^t)_2$ (0.09 g, 0.49 mmol) and $[Nb({=}NBu^t)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.46 g, 0.97 mmol) were used. Yield: 0.38 g, 76%. IR (Nujol mull): $\nu_{Nb=N}$ 1250 cm^{-1}; $\nu_{C\equiv C}$ 2100 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.34 (s, 18H, C$_5$H$_4$Si*Me*$_3$), 1.02 (s, 9H, NC(C*H*$_3$)$_3$), 1.41 (s, 9H, CC(C*H*$_3$)$_3$), 5.80 (2H), 5.97 (2H), 6.01 (2H), 6.29 (2H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 0.5 (C$_5$H$_4$Si*Me*$_3$), 30.5, 32.2 (C(*C*H$_3$)$_3$), 39.8 (C*C*(CH$_3$)$_3$), 68.1 (N*C*(CH$_3$)$_3$), 106.9, 111.8, 112.5 (C$_{ipso}$), 120.0, 120.1 (*C*$_5$H$_4$), 106.9 (*C*≡CNb), 127.0 (C≡*C*Nb). Anal. Calcd for $C_{26}H_{44}NNbSi_2$: C, 60.09; H, 8.53; N, 2.70. Found: C, 59.89; H, 8.46; N, 2.72.

$[Nb({=}NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2(C{\equiv}CPh)]$ (9). The synthesis of **9** was carried out in a manner identical to that of **2**. $Mg(C{\equiv}CPh)_2$ (0.12 g, 0.52 mmol) and $[Nb({=}NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.50 g, 1.01 mmol) were used. Yield: 0.49 g, 86%. IR (Nujol mull): $\nu_{Nb=N}$ 1265 cm^{-1}; $\nu_{C\equiv C}$ 2100 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.26 (s, 18H, $C_5H_4SiMe_3$), 5.69 (2H), 5.86 (2H), 6.17 (2H), 6.23 (2H) (m, C_5H_4), 6.63 (2H), 6.69 (2H), 7.12 (1H) (m, NPh), 7.03 (1H), 7.19 (2H), 7.68 (2H) (m, $C\equiv CPh$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.3 ($C_5H_4SiMe_3$), 109.7, 110.7, 115.5, 115.8 (C_{ipso}), 118.0 (C_5H_4), 120.9, 126.5, 128.5, 160.0 (C_{ipso}) (NPh), 126.9, 128.6, 131.1, 132.7 (C_{ipso}) ($C\equiv CPh$), 107.4 ($C\equiv CNb$), 129.2 ($C\equiv CNb$), Anal. Calcd for $C_{30}H_{36}NNbSi_2$: C, 64.38; H, 6.48; N, 2.50. Found: C, 64.68; H, 6.52; N, 2.40.

$[Nb(=NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2(C\equiv CBu^t)]$ (10). The synthesis of **10** was carried out in a manner identical to that of **2**. $Mg(C\equiv CBu^t)_2$ (0.09 g, 0.48 mmol) and $[Nb(=NPh)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.46 g, 0.93 mmol) were used. Yield: 0.44 g, 88%. IR (Nujol mull): $\nu_{Nb=N}$ 1280 cm^{-1}; $\nu_{C\equiv C}$ 2080 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.27 (s, 18H, $C_5H_4SiMe_3$), 1.45 (s, 9H, $C(CH_3)_3$), 5.67 (2H), 5.81 (2H), 6.17 (2H), 6.28 (2H) (m, C_5H_4), 6.61 (2H), 6.69 (2H), 7.13 (1H) (m, NPh). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.4 ($C_5H_4SiMe_3$), 29.7 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 110.0, 110.3, 115.5 (C_{ipso}), 118.1, 121.5 (C_5H_4), 120.7, 127.0, 128.5, 160.0 (C_{ipso}) (NPh), 114.9 ($C\equiv CNb$), 134.7 ($C\equiv CNb$), Anal. Calcd for $C_{28}H_{40}NNbSi_2$: C, 62.31; H, 7.47; N, 2.60. Found: C, 62.09; H, 7.38; N, 2.56.

$[Nb(=NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2(C\equiv CSiMe_3)]$ (11). The synthesis of **11** was carried out in a manner identical to that of **2**. $Mg(C\equiv CSiMe_3)_2$ (0.11 g, 0.50 mmol) and $[Nb(=NC_6H_4\text{-}Me\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.50 g, 0.98 mmol) were used. Yield: 0.43 g, 77%. IR (Nujol mull): $\nu_{Nb=N}$ 1280 cm^{-1}; $\nu_{C\equiv C}$ 2090 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.25 (s, 18H, $C_5H_4SiMe_3$), 0.39 (s, 9H, $C\equiv CSiMe_3$), 2.08 (s, 3H, $NC_6H_4CH_3$), 5.65 (2H), 5.77 (2H), 6.12 (2H), 6.21 (2H) (m, C_5H_4), 6.52 (2H), 6.89 (2H) (d, $NC_6H_4CH_3$) (J 8.3 Hz). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.4 ($C_5H_4SiMe_3$), 1.1 ($C\equiv CSiMe_3$), 20.9 ($NC_6H_4CH_3$), 109.8, 110.9, 115.2, 117.5 (C_{ipso}), 118.1 (C_5H_4), 108.4 ($C\equiv CNb$), 128.3 ($C\equiv CNb$), 121.1, 129.0, 130.2 (C_{ipso}) 157.9 (C_{ipso}) ($NC_6H_4CH_3$). Anal. Calcd for $C_{28}H_{42}NNbSi_3$: C, 59.02; H, 7.43; N, 2.46. Found: C, 58.79; H, 7.30; N, 2.50.

$[Nb(=NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2(C\equiv CBu^t)]$ (12). The synthesis of **12** was carried out in a manner identical to that of **2**. $Mg(C\equiv CBu^t)_2$ (0.09 g, 0.48 mmol) and $[Nb(=NC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.46 g, 0.91 mmol) were used. Yield: 0.36 g, 72%. IR (Nujol mull): $\nu_{Nb=N}$ 1290 cm^{-1}; $\nu_{C\equiv C}$ 2100 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.25 (s, 18H, $SiMe_3$), 1.43 (s, 9H, $C(CH_3)_3$), 2.10 (s, 3H, $NC_6H_4CH_3$), 5.68 (2H), 5.80 (2H), 6.16 (2H), 6.28 (2H) (m, C_5H_4), 6.55 (2H), 6.91 (2H) (d, $NC_6H_4CH_3$) (J 8.1 Hz). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.2 ($SiMe_3$), 20.8 ($NC_6H_4CH_3$), 32.1 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 110.6, 114.0 (C_{ipso}), 115.4, 118.2, 118.4 (C_5H_4), 108.3 ($C\equiv CNb$), 127.0 ($C\equiv CNb$), 121.4, 128.8, 129.8 (C_{ipso}) 157.9 (C_{ipso}) ($NC_6H_4CH_3$). Anal. Calcd for $C_{29}H_{42}NNbSi_2$: C, 62.90; H, 7.64; N, 2.53. Found: C, 62.74; H, 7.55; N, 2.46.

$[Nb(=NC_6H_4OMe\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2(C\equiv CSiMe_3)]$ (13). The synthesis of **13** was carried out in a manner identical to that of **2**. $Mg(C\equiv CSiMe_3)_2$ (0.10 g, 0.46 mmol) and $[Nb(=NC_6H_4OMe\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.46 g, 0.88 mmol) were used. Yield: 0.35 g, 69%. IR (Nujol mull): $\nu_{Nb=N}$ 1275 cm^{-1}; $\nu_{C\equiv C}$ 2110 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.26 (s, 18H, $SiMe_3$), 0.39 (s, 9H, $SiMe_3$), 3.23 (s, 3H, $NC_6H_4OCH_3$), 5.71 (2H), 5.77 (2H), 6.11 (2H), 6.21 (2H) (m, C_5H_4), 6.54 (2H), 6.69 (2H) (d, $NC_6H_4OCH_3$) (J 9.0 Hz). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.4 ($C_5H_4SiMe_3$), 1.1 ($C\equiv CSiMe_3$), 54.8 (OCH_3), 109.7, 111.3, 113.7, 113.8 (C_{ipso}), 115.4 (C_5H_4), 108.4 ($C\equiv CNb$), 129.2 ($C\equiv CNb$), 119.5, 120.8, 154.3 (C_{ipso}) 155.0 (C_{ipso}) ($NC_6H_4OCH_3$). Anal. Calcd for $C_{28}H_{42}NNbOSi_3$: C, 57.41; H, 7.23; N, 2.39. Found: C, 57.16; H, 7.13; N, 2.41.

$[Nb(=NC_6H_4OMe\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2(C\equiv CBu^t)]$ (14). The synthesis of **14** was carried out in a manner identical to that of **2**. $Mg(C\equiv CBu^t)_2$ (0.09 g, 0.48 mmol) and $[Nb(=NC_6H_4OMe\text{-}4)(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ (0.50 g, 0.95 mmol) were used. Yield: 0.37 g, 69%. IR (Nujol mull): $\nu_{Nb=N}$ 1285 cm^{-1}; $\nu_{C\equiv C}$ 2080 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.26 (s, 18H, $SiMe_3$), 1.44 (s, 9H, $C(CH_3)_3$), 3.25 (s, 3H, $NC_6H_4OCH_3$), 5.74 (2H), 5.81 (2H), 6.16 (2H), 6.27 (2H) (m, C_5H_4), 6.56 (2H), 6.71 (2H) (d, $NC_6H_4OCH_3$) (J 9.0 Hz). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.5 ($SiMe_3$), 54.9 ($NC_6H_4OCH_3$), 32.2 ($C(CH_3)_3$), 34.1 ($C(CH_3)_3$), 110.0, 111.2, 113.8, 114.0 (C_{ipso}), 115.7 (C_5H_4), 108.5 ($C\equiv CNb$), 127.8 ($C\equiv CNb$), 119.8, 121.3, 128.3 (C_{ipso}) 154.9 (C_{ipso}) ($NC_6H_4OCH_3$). Anal. Calcd for $C_{29}H_{42}NNbOSi_2$: C, 61.14; H, 7.43; N, 2.46. Found: C, 60.88; H, 7.38; N, 2.45.

Table 4. Crystal Data and Structure Refinement for 9

formula	$C_{30}H_{36}NNbSi_2$
fw	559.69
T (K)	293(2)
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.415(1)
b (Å)	10.858(1)
c (Å)	13.604(1)
α (deg)	101.90(1)
β (deg)	97.95(1)
γ (deg)	94.85(1)
V (Å^3)	1480.7(2)
Z	2
D_c (g cm^{-3})	1.255
μ (mm^{-1})	0.505
F(000)	584
cryst dimens (mm)	0.2 × 0.3 × 0.3
θ range (deg)	2.19 to 28.00
hkl ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $0 \le l \le 17$
no. of rflns measd	7433
no. of indep rflns	7137
no. of obsd rflns	3635
goodness-of-fit on F^2	1.022
final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0642$, $wR_2 = 0.1510$
largest diff peak and hole (e Å^{-3})	0.612/−0.672

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

$[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}(C\equiv CSiMe_3)]$ (15). The synthesis of **15** was carried out in a manner identical to that of **2**. $Mg(C\equiv CSiMe_3)_2$ (0.11 g, 0.50 mmol) and $[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Cl]$ (0.38 g, 0.98 mmol) were used. Yield: 0.32 g, 73%. IR (Nujol mull): $\nu_{Nb=N}$ 1235 cm^{-1}; $\nu_{C\equiv C}$ 2050 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ −0.05 (3H), 0.22 (3H) (s, $SiMe_2$), 0.39 (s, 9H, $SiMe_3$), 0.96 (s, 9H, $C(CH_3)_3$), 5.91 (2H), 5.95 (2H), 6.36 (2H), 6.63 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −6.7, −5.4 ($SiMe_2$), 1.4 ($SiMe_3$), 30.6 ($C(CH_3)_3$), 68.0 ($C(CH_3)_3$), 101.5, 113.4, 114.4, 114.5, 125.6 (C_{ipso}) (C_5H_4), 107.1 ($C\equiv CNb$), 128.4 ($C\equiv CNb$). Anal. Calcd for $C_{21}H_{32}NNbSi_2$: C, 56.36; H, 7.21; N, 3.13. Found: C, 56.17; H, 7.12; N, 3.15.

$[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}(C\equiv CBu^t)]$ (16). The synthesis of **16** was carried out in a manner identical to that of **2**. $Mg(C\equiv CBu^t)_2$ (0.10 g, 0.54 mmol) and $[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Cl]$ (0.40 g, 1.04 mmol) were used. Yield: 0.30 g, 67%. IR (Nujol mull): $\nu_{Nb=N}$ 1255 cm^{-1}; $\nu_{C\equiv C}$ 2080 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.01 (3H), 0.28 (3H) (s, $SiMe_2$), 0.98 (s, 9H, $NC(CH_3)_3$), 1.45 (s, 9H, $CC(CH_3)_3$), 5.91 (2H), 6.00 (2H), 6.40 (2H), 6.62 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −6.5, −5.3 ($SiMe_2$), 29.1 ($CC(CH_3)_3$), 30.7, 32.5 ($C(CH_3)_3$), 72.6 ($NC(CH_3)_3$), 101.0, 114.0, 114.3, 114.5, 116.2 (C_{ipso}) (C_5H_4), 125.5 ($C\equiv CNb$), 128.9 ($C\equiv CNb$). Anal. Calcd for $C_{22}H_{32}NNbSi$: C, 61.24; H, 7.47; N, 3.25. Found: C, 61.00; H, 7.36; N, 3.22.

$[Nb(NHBu^t)(\eta^5\text{-}C_5H_5)_2(C\equiv CSiMe_3)][CF_3COO]$ (17). CF_3COOH (0.08 g, 0.69 mmol) was added to a solution of **2** (0.27 g, 0.69 mmol) in Et_2O (50 mL) at 0 °C. A red precipitate was formed, which was isolated by filtration and washed with Et_2O. Drying under vacuum gave a red crystalline solid (0.30 g, yield 86%). IR (Nujol mull): $\nu_{C\equiv C}$ 2090 cm^{-1}; ν_{N-H} 3100 cm^{-1}. ^{1}H NMR (200 MHz, d_6-acetone): δ 0.18 (s, 9H, $SiMe_3$), 1.46 (s, 9H, $C(CH_3)_3$), 6.32 (s, 10H, C_5H_5), 8.55 (br, 1H, NH). Anal. Calcd for $C_{21}H_{29}F_3NNbO_2Si$: C, 49.90; H, 5.78; N, 2.77. Found: C, 49.62; H, 5.64; N, 2.69.

[Nb(NHPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)][BF$_4$] (18). HBF_4 (10% in Et_2O) (0.09 mL, 0.50 mmol) was added to a solution of **7** (0.27 g, 0.50 mmol) in Et_2O (50 mL) at 0 °C. A red precipitate was formed, which was isolated by filtration and washed with Et_2O. Drying under vacuum gave a red crystalline solid (0.27 g, yield 87%). IR (Nujol mull): $\nu_{C\equiv C}$ 2070 cm^{-1}; ν_{N-H} 3115 cm^{-1}. ^1H NMR (200 MHz, CD_3CN): δ 0.29 (s, 18H, C_5H_4-Si*Me*$_3$), 6.90 (2H), 6.92 (2H), 6.97 (2H), 7.03 (2H) (m, C_5*H*$_4$), 7.20 (2H), 7.26 (2H), 7.39 (1H) (m, NH*Ph*), 7.45−7.56 (m, 5H, C≡C*Ph*), 8.22 (br, 1H, N*H*). Anal. Calcd for $C_{30}H_{37}BF_4NNbSi_2$: C, 55.65; H, 5.76; N, 2.16. Found: C, 55.41; H, 5.60; N, 2.11.

X-ray Crystal Structure Determination for [Nb(=NPh)(η^5-$C_5H_4SiMe_3$)$_2$(C≡CPh)] (9). Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using an $\omega/2\theta$ scan technique. The final unit cell parameters were determined from 25 well-centered reflections and refined by least-squares methods. Data were corrected for Lorentz and polarization effects but not for absorption. The space group was determined from the systematic absences, and this was vindicated by the success of the subsequent solutions and refinements. The structures were solved by direct methods using the SHELXS computer program[16] and refined on F^2 by full-matrix least-squares (SHELXL-97).[17] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 4.

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Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complex **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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