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Alkyl Alkyne Mono((trimethylsilyl)cyclopentadienyl) Niobium Complexes. Synthesis and Chemical Behavior in Insertion Processes. X-ray Crystal Structures of [NbCp′(CH_2SiMe_3)$_2$($Me_3SiCCSiMe_3$)] and [NbCp′(NAr){η^4-CH($SiMe_3$)C($SiMe_3$)C(CH_2SiMe_3)=CH($SiMe_3$)}], (Cp′ = η^5-$C_5H_4SiMe_3$, Ar = 2,6-$Me_2C_6H_3$). DFT Studies of the Model Complexes [Nb(η^5-C_5H_5)R_2(HCCH)] (R = Cl, Me)

Agustín Galindo,[†] Manuel Gómez,*[,‡] Pilar Gómez-Sal,[‡] Avelino Martín,[‡]
Diego del Río,[†] and Fernando Sánchez[‡]

Departamento de Química Inorgánica, Universidad de Alcalá de Henares,
Campus Universitario, E-28871 Alcalá de Henares, Spain, and Departamento de
Química Inorgánica, Universidad de Sevilla, Aptdo. 553, E-41071 Sevilla, Spain

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The dichloro niobium complex [NbCp′Cl_2(R′CCR′)] (Cp′ = η^5-$C_5H_4SiMe_3$; R′ = $SiMe_3$; **1**) can be obtained by reduction of NbCp′Cl_4 with excess of aluminum in the presence of 1 equiv of bis(trimethylsilyl)acetylene. The dialkyl derivatives [NbCp′R_2(R′CCR′)] (Cp′ = η^5-$C_5H_4SiMe_3$; R′ = $SiMe_3$; R = Me (**2**), CH_2SiMe_3 (**3**), CH_2CMe_3 (**4**), $CH_2C_6H_5$ (**5**)) were obtained by treating **1** with the stoichiometric amounts of the appropriate alkylating reagents. Reactions of the dialkyl alkyne complexes [NbCp′R_2(R′CCR′)] (**2**−**5**) with 1 equiv of 2,6-$Me_2C_6H_3NC$ in C_6D_6 resulted in migration of only one of the two alkyl groups to give the alkyl alkyne η^2-iminoacyl complexes [NbCp′R{η^2-C(R)=NAr}(R′CCR′)] (Cp′ = η^5-$C_5H_4SiMe_3$; R′ = $SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; R = Me (**6**), CH_2SiMe_3 (**7**), CH_2CMe_3 (**8**)). However, when hexane solutions of the dialkylated complexes **2** and **3** were treated with 1 equiv of isocyanide at 40−50 °C (**2**) and 80 °C (**3**), respectively, the imido niobacyclopent-3-ene [NbCp′(NAr)-{η^4-CH($SiMe_3$)C($SiMe_3$)=C(Me)CH_2}] (**9**) and the imido niobacyclopropane(vinyl) [NbCp′-(NAr){η^4-CH($SiMe_3$)C($SiMe_3$)C(CH_2SiMe_3)=CH($SiMe_3$)}] (**10**) (Cp′ = η^5-$C_5H_4SiMe_3$; Ar = 2,6-$Me_2C_6H_3$) can be isolated, probably via azaniobacyclopropane intermediates. In the case of the dialkylated complex **4** the reaction with 1 equiv of isocyanide at room temperature gives initially the alkyne neopentyl η^2-iminoacyl complex **8**, which is slowly transformed into the imido niobacyclohept-2-ene [NbCp′(NAr){η^2-$CH_2CMe_2CH_2CH$(CH_2CMe_3)C($SiMe_3$)=C($SiMe_3$)}] (Cp′ = η^5-$C_5H_4SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; **11**), but the intermediate species were not observed. All the new compounds have been characterized by IR spectrophotometry, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and elemental analyses. The molecular structures of the complexes **3** and **10** have been determined by X-ray diffraction analyses. DFT calculations have been carried out on the model complexes [Nb(η^5-C_5H_5)R_2(HCCH)] (R = Cl, Me). The theoretical studies rationalize the disposition of the alkyne ligand in complex **3**.

Introduction

Early transition metal complex[1] promoted coupling of unsaturated organic substrates constitutes a powerful strategy for C−C bond formation in organic synthesis[2] and catalytic polymerization.[3] In particular, niobium and tantalum alkyne complexes have provided convenient routes to carbonylic derivatives[4] and nitrile[5] coupling reactions via metallacyclic intermediates.[6] Therefore, if the organic substrate is a nitrile, the resulting products can be vicinal diamines[5a] and polyfunctionalized aromatic compounds,[5b] via the initial formation of a metallacyclic imine, which may subsequently rearrange[7] or dimerize.[8] Furthermore, it has been reported that in the reaction between alkyne tantalum(III) derivatives and nitriles, the azatantalacyclopentene complexes formed may participate in an intermolecular tautomerization process to enamines.[5c] Alkyne niobium and tantalum(III) complexes are known as very efficient catalysts for the oligomerization and polimerization of internal alkynes.[3] The catalytic process can be explained by alkylidene[9] and alkenyl[10] pathways.

In the literature, a great deal of alkyne niobium and tantalum complexes containing halo,[11] aryloxide,[5c] cyclopentadienyl,[12] and hydridotris(pyrazolyl)borate[13] type groups can be found, the number of alkyl mono(cyclopentadienyl) derivatives being scarce. In this paper, we

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* To whom correspondence should be addressed. Fax: 34-91-885 46 83. E-mail: manuel.gomez@uah.es.

[†] Universidad de Sevilla.

[‡] Universidad de Alcalá de Henares.

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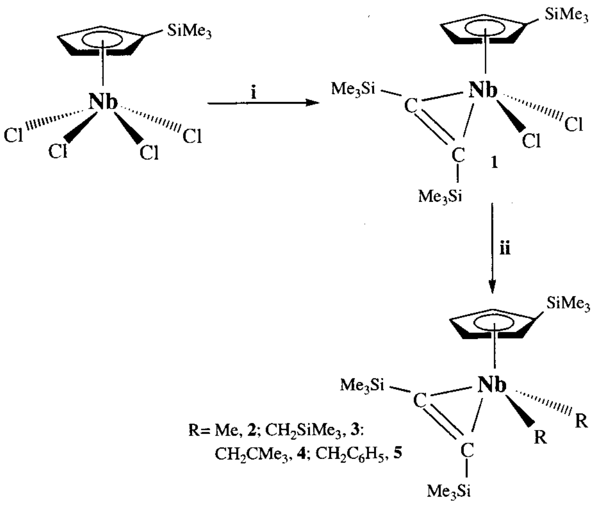
report new alkyl alkyne (trimethylsilyl)cyclopentadienyl niobium complexes and the insertion and intramolecular rearrangement processes observed in the reactions with 2,6-$Me_2C_6H_3NC$. All compounds were fully characterized, and in addition, some of the complexes were studied by X-ray diffraction methods. In particular, the molecular structure of the complex $[NbCp'(CH_2SiMe_3)_2(Me_3SiCCSiMe_3)]$ ($Cp' = \eta^5$-$C_5H_4SiMe_3$; **3**), shows an almost perpendicular conformation of the alkyne ligand with respect to the Cp′ plane. The relative orientation of an alkyne ligand with respect to $[MCpL_2]$[14] ($Cp = \eta^5$-C_5H_5) or $[MTpL_2]$[13e,f] (Tp = hydridotris(pyrazolyl)borate) type fragments has been analyzed in several papers for different combinations of electronic configurations, metals, and L ligands.[15] We report herein a DFT study of the model complexes $[Nb(\eta^5$-$C_5H_5)R_2(HCCH)]$ (R = Cl, Me) that serves to rationalize the disposition of the alkyne ligand and other structural parameters on these types of compounds.

Scheme 1[a]



[a] Reagents and conditions: (i) Al excess, $HgCl_2$, $C_2(SiMe_3)_2$, THF, 12 h, room temperature; (ii) 2 equiv of MgClR (R = Me (**2**), CH_2SiMe_3 (**3**), $CH_2C_6H_5$ (**5**)) or $LiCH_2CMe_3$ (**4**), hexane, 12 h, −78 °C to room temperature.

Results and Discussion

Synthesis of Dichloro and Dialkyl Alkyne Derivatives. $[NbCp'Cl_2(Me_3SiCCSiMe_3)]$ ($Cp' = \eta^5$-$C_5H_4SiMe_3$; **1**) was synthesized in high yield by reaction of $NbCp'Cl_4$ with an excess of aluminum powder and mercury(II) chloride in the presence of 1 equiv of $C_2(SiMe_3)_2$ (see Scheme 1). When *n*-hexane solutions of **1** were treated with stoichiometric amounts of the alkylating reagents MgClR (R = Me, CH_2SiMe_3, CH_2Ph) or $LiCH_2CMe_3$ under rigorously anhydrous conditions at room temperature, suspensions were obtained from which the dialkyl alkyne complexes $[NbCp'R_2(Me_3SiCCSiMe_3)]$ ($Cp' = \eta^5$-$C_5H_4SiMe_3$; R = Me (**2**), CH_2SiMe_3 (**3**), CH_2Ph (**4**), CH_2CMe_3 (**5**)) could be isolated in good yields. Complexes **1**−**5** were found to be air- and moisture-sensitive and soluble in hexane, THF, and aromatic solvents.

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The spectroscopic properties of the complexes **1**−**5** are basically similar to those reported for metallacyclopropene derivatives,[12a,16] in which the alkyne ligand acts as a 4e donor. The IR spectra of all the complexes show the characteristic absorptions for the (trimethylsilyl)cyclopentadienyl ($\bar{\nu}$(C−H) at ca. 837 cm^{-1})[17] ring and for the trimethylsilyl substituent ($\bar{\nu}_{\delta s}$(CH$_3$) at ca. 1246 cm^{-1}).[17,18] Furthermore, the absorption band observed at ca. 1582 cm^{-1} and assigned to the stretching vibration $\bar{\nu}$(C=C) is consistent with the hybridization change of the carbon atoms in the alkyne ligand,[16,19] while the corresponding Nb−C band[17,20] in the dialkyl derivatives is located at ca. 480 cm^{-1}. The NMR spectroscopic data are in agreement with the structures proposed in Scheme 1. The ^{1}H NMR spectrum of complex **2** shows a singlet for the trimethylsilyl substituents of the alkyne ligand; however, complexes **3**−**5** show a broad signal for the same groups in the ^{1}H NMR spectrum. This fact is consistent with the free rotation of the alkyne ligand in complex **2** and the slow rotation of the alkyne ligand in complexes **3**−**5** due to the bulkier alkyl substituent. Moreover, when a CDCl$_3$ solution of compound **3** is cooled from 303 to 223 K, the alkyne trimethylsilyl substituents signal broadens and, at 223 K, splits into two signals. The kinetic parameters of this process (log A = 14.2 ± 0.33; E_a = 14.6 ± 0.4 kcal mol^{-1}; $\Delta H^{\ddagger}$ = 14.0 ± 0.4 kcal mol^{-1}; $\Delta S^{\ddagger}$ = 4.7 ± 1.4 eu; $\Delta G^{\ddagger}$(298 K) = 12.6 kcal mol^{-1}) calculated on the basis of the DNMR data[21a,b] show that this transformation is an intramolecular pseudorotation process similar to those reported for other mono(cyclopentadienyl) complexes with a four-legged piano-stool structure.[21c] The ^{13}C{^{1}H} NMR spectra show only one signal for the trimethylsilyl substituents of the alkyne ligand, which is broad in the case of complex **4**. The alkyl groups directly bonded to the niobium atom are also equivalent, but in the complexes **3**−**5** the diasterotopic α-CH$_2$ protons of such groups appear as an AB spin system. The ^{13}C{^{1}H} NMR spectra show broad signals for all carbon atoms directly bonded to the metal center due to the quadrupole moment interaction[21d] with the ^{93}Nb nucleus. Chemical shifts of the acetylenic carbon atoms, at ca. δ 244, are in agreement with a four-electron-donor alkyne ligand.[22] The ^{1}H NMR spectra of complexes **1**−**5** show an AA′BB′ spin system for the proton atoms of the (trimethylsilyl)cyclopentadienyl ring, whereas the ^{13}C{^{1}H} NMR spectra show three carbon resonances for the same group, in accordance with C_s symmetry.

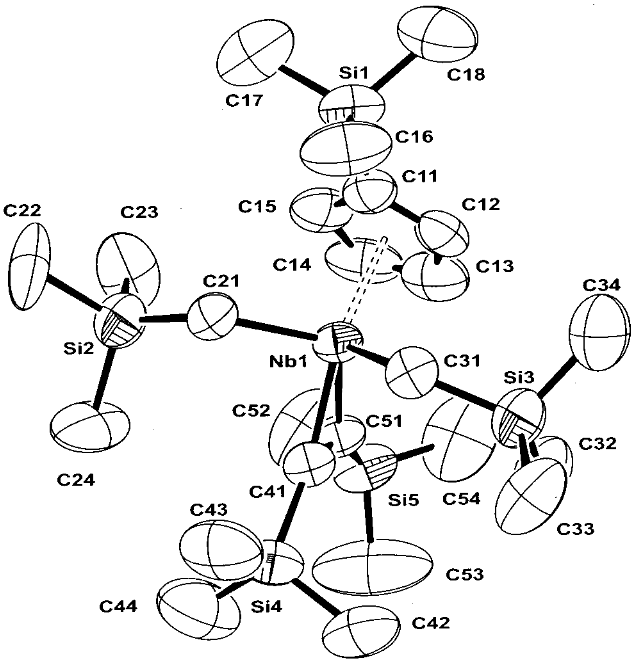

Figure 1. ORTEP drawing of compound **3**. Thermal ellipsoids are shown at the 50% level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Nb(1)−C(41)	2.087(6)	Nb(1)−C(51)	2.092(5)
Nb(1)−C(21)	2.193(6)	Nb(1)−C(31)	2.198(5)
Si(2)−C(21)	1.834(6)	Si(3)−C(31)	1.841(6)
Si(4)−C(41)	1.856(6)	Si(5)−C(51)	1.888(5)
C(41)−C(51)	1.323(7)		
C(41)−Nb(1)−C(51)	36.9(2)	C(41)−Nb(1)−C(21)	90.5(2)
C(51)−Nb(1)−C(21)	111.2(2)	C(41)−Nb(1)−C(31)	89.2(2)
C(51)−Nb(1)−C(31)	110.7(2)	C(21)−Nb(1)−C(31)	106.6(2)
Si(2)−C(21)−Nb(1)	129.8(3)	Si(3)−C(31)−Nb(1)	129.0(3)
C(51)−C(41)−Si(4)	139.7(5)	C(51)−C(41)−Nb(1)	71.7(4)
Si(4)−C(41)−Nb(1)	148.4(3)	C(41)−C(51)−Si(5)	140.7(5)
C(41)−C(51)−Nb(1)	71.3(3)	Si(5)−C(51)−Nb(1)	147.9(3)

The molecular structure of compound **3** is shown in Figure 1. Selected bond distances and angles are presented in Table 1. The complex **3** can be described as a monomer with a typical three-legged piano-stool environment for the niobium atom if we assume that the centroid of the alkyne ligand is occupying a single coordination site. The most relevant aspects of the structure are the perpendicular disposition of the alkyne ligand with respect to the Cp′ ring and the plane formed by the alkyl substituents at the niobium center; the angles formed by the Si4−C41−C51−Si5 plane with both are 86.8(2) and 86.1(2)°, respectively. Furthermore, the Si2 and Si3 atoms of the (trimethylsilyl)methyl groups are close to equidistant to the silicon atoms of the trimethylsilyl substituents of the Cp′ ring and the alkyne ligand, Si1, Si4, and Si5. The average of the distances Nb−C(alkyne) is 2.090 (6) Å, and the C41−C51 distance is 1.323(7) Å; both values are just inside the range expected for a four-electron-donor alkyne ligand[7f,12b,16,22,23] in which the C−C bond order is less

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Table 2. Calculated Bond Distances (Å) and Angles (deg) for $NbCpCl_2(HCCH)$ Model Complex and, for Comparison, Selected Experimental Data for $Nb(\eta^5\text{-}C_5H_4Me)Cl_2(4\text{-}Me\text{-}C_6H_4CCC_6H_4\text{-}4\text{-}Me)$

	$NbCpCl_2(HCCH)$				
	parallel conformn		perpendicular conformn		
structural data	BP86	B3LYP	BP86	B3LYP	exptl
Nb−C(1)	2.497	2.511	2.581	2.584	2.447
Nb−C(2)	2.474	2.485	2.457	2.462	2.417
Nb−C(3)	2.441	2.443	2.421	2.430	2.380
Nb−C(4)	2.439	2.442	2.458	2.462	2.377
Nb−C(5)	2.472	2.485	2.581	2.584	2.428
Nb−C(6)	2.099	2.092	2.077	2.069	2.063(5)
Nb−C(7)	2.099	2.092	2.086	2.081	2.079(5)
Nb−Cl(1)	2.383	2.390	2.385	2.392	2.353(2)
Nb−Cl(2)	2.382	2.390	2.385	2.392	2.365(2)
C(6)−C(7)	1.328	1.314	1.334	1.321	1.307(7)
Cl(1)−Nb−Cl(2)	102.0	101.7	112.0	112.2	99.4(1)
Cl(1)−Nb−C(6)	89.1	89.3	109.5	109.5	88.6(1)
Cl(1)−Nb−C(7)	118.4	118.4	89.6	89.8	119.3(2)
Cl(2)−Nb−C(6)	118.3	118.4	109.5	109.5	119.3(2)
Cl(2)−Nb−C(7)	89.1	89.3	89.6	89.8	92.5(2)
C(6)−Nb−C(7)	36.9	36.6	37.4	37.1	36.8(2)
H−C(6)−C(7)	140.5	141.4	139.4	140.2	142.3[a]
H−C(7)−C(6)	140.5	141.4	138.5	139.5	144.4[a]

[a] C−C−C bond angle.

Table 3. Calculated Bond Distances (Å) and Angles (deg) for $NbCpMe_2(HCCH)$ Model Complex and, for Comparison, Selected Experimental Data for 3

	$NbCpMe_2(HCCH)$				
	parallel conformn		perpendicular conformn		
structural data	BP86	B3LYP	BP86	B3LYP	exptl
Nb−C(1)	2.574	2.597	2.573	2.582	2.544(6)
Nb−C(2)	2.534	2.554	2.526	2.539	2.490(7)
Nb−C(3)	2.462	2.474	2.446	2.462	2.403(8)
Nb−C(4)	2.461	2.474	2.446	2.462	2.400(6)
Nb−C(5)	2.532	2.553	2.526	2.539	2.461(6)
Nb−C(6)	2.092	2.084	2.074	2.068	2.092(5)
Nb−C(7)	2.092	2.084	2.103	2.098	2.087(6)
Nb−C(8)	2.198	2.201	2.208	2.209	2.193(6)
Nb−C(9)	2.198	2.201	2.208	2.209	2.198(5)
C(6)−C(7)	1.342	1.331	1.341	1.329	1.323(7)
C(8)−Nb−C(9)	101.0	97.8	111.2	110.7	106.6(2)
C(8)−Nb−C(6)	87.2	87.9	109.3	109.3	111.2(2)
C(8)−Nb−C(7)	116.5	116.4	89.1	89.1	90.5(2)
C(9)−Nb−C(6)	116.7	116.4	109.3	109.3	110.7(2)
C(9)−Nb−C(7)	87.4	87.9	89.1	89.1	89.2(2)
C(6)−Nb−C(7)	37.4	37.3	37.5	37.2	36.9(2)
H−C(6)−C(7)	136.3	136.6	137.7	138.0	140.7(5)[a]
H−C(7)−C(6)	136.4	136.6	134.3	135.1	139.7(5)[a]

[a] Si−C−C bond angle.

than 3. Furthermore, the C51−C41−Si4 (139.7(5)°) and C41−C51−Si5 (140.7(5)°) bond angles show a considerable distortion from those of the free ligand, as has been reported for similar tantalum derivatives.[12b,16] In accord with such distortion, the metal−alkyne moiety may be viewed as a metallacyclopropene with the niobium atom in a formal +5 oxidation state.[24] The C21−Nb−C31 (106.6(2)°) bond angle is larger than the Cl1−Nb−Cl2 (99.4°) bond angle found in the dichloride complex $[Nb(\eta^5\text{-}C_5H_4Me)Cl_2(ArCCAr)]$ ($Ar = 4\text{-}MeC_6H_4$),[12b] in which the alkyne ligand adopts a parallel disposition to the $\eta^5\text{-}C_5H_4Me$ ring.

DFT Calculations on $[Nb(\eta^5\text{-}C_5H_5)R_2(HCCH)]$ (R = Cl, Me) Model Complexes. A theoretical analysis was carried out within the density functional theory (DFT) on $[Nb(\eta^5\text{-}C_5H_5)R_2(HCCH)]$ (R = Cl, Me) model complexes. Our aim was the study of the preferential disposition of the alkyne ligand in these type of complexes, and we have considered the parallel and the perpendicular conformations (always with respect to the Cp plane) of the HCCH ligand in these two models. Selected calculated parameters and, for comparison, experimental data from X-ray crystallography have been collected in Tables 2 and 3. The use of BP86 or B3LYP functionals does not produce significant changes in the structural parameters or in the energetics of the system. The final optimized geometries are shown in Figures 2 and 3, and their coordinates are collected as Supporting Information (Tables S6−S17).

In general, we can observe a quite satisfactory agreement between the calculated and experimental values of geometrical parameters. The former corresponds to the *parallel* conformation in $[NbCpCl_2(HCCH)]$ and the *perpendicular* disposition in $[NbCpMe_2(HCCH)]$ model complexes, while for the latter we have selected the compounds $[NbCp'Cl_2(ArCCAr)]$ ($Cp' = \eta^5\text{-}C_5H_4Me$; $Ar = 4\text{-}MeC_6H_4$)[12b] and **3**, respectively. Bond distances concerning the niobium−cyclopentadienyl moiety are slightly overestimated (maximum deviation 0.07 Å), probably due to the consideration of the Cp model instead of the actual cyclopentadienyl groups. A similar overestimation of the Nb−Cp bond distances has been recently observed.[25] The other bond distances agree within ca. 0.03 Å. On the other hand, there is good agreement found with respect to the bond angles. The largest deviation appears to be about 5°. The calculated Cl−Nb−Cl and Me−Nb−Me bond angles change substantially with the orientation of the alkyne ligand. Thus, for example, in the chloro complex the Cl−Nb−Cl angle goes from ca. 102° (parallel; experimental data 99.4(1)°) to ca. 112° (perpendicular), while for the methyl derivative the corresponding Me−Nb−Me bond angle changes from ca. 99° (parallel) to ca. 111° (perpendicular; experimental data 106.6(2)°). A second comparison can be made with a Ta complex,[26] $[TaCp^*Me_2(\eta^2\text{-}C_6H_4)]$, which possesses a benzyne perpendicular to the Cp plane. The bond distances around the Ta center, the C−C alkyne length (1.364(5) Å), and the main angles (for example, Me−Ta−Me at 107.7(3)°) compares well, despite the different metal, with the computed analogous values for the perpendicular conformation in the $[NbCpMe_2(HCCH)]$ model.

With regard to the energetics of the system (see Table 4), the perpendicular conformation is always found to be more stable than the parallel one. The energy difference between the two conformations is computed to be around 1.5 kcal mol^{-1} when chlorides are the coligands, while for the methyl derivative the stabilization of the perpendicular isomers increases up to ca. 7.5 kcal mol^{-1}. We located the transition state connecting

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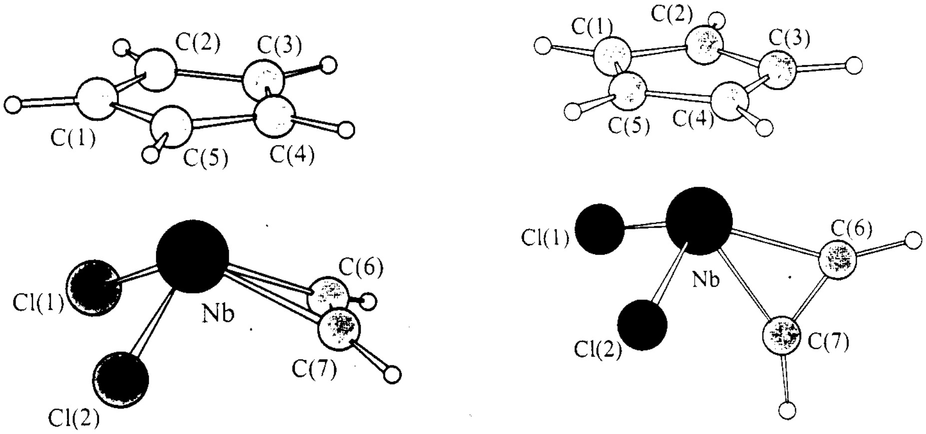


Figure 2. Optimized structures of the [NbCpCl$_2$(HCCH)] model complex (parallel and perpendicular conformations).

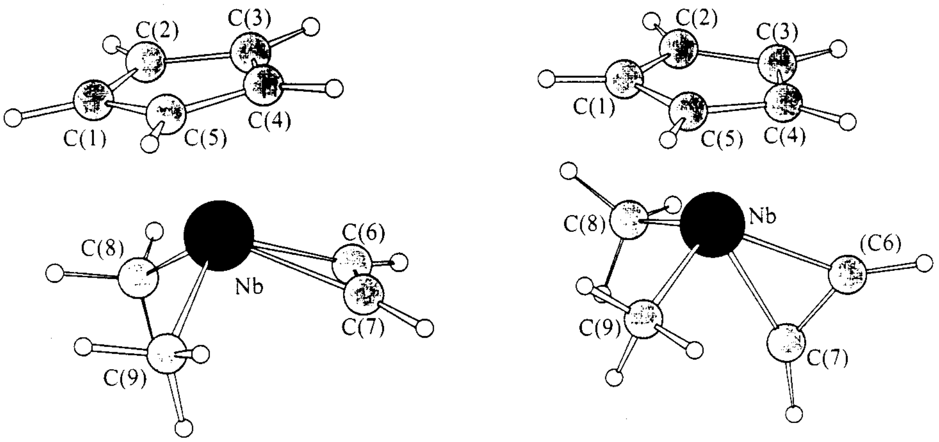


Figure 3. Optimized structures of the [NbCpMe$_2$(HCCH)] model complex (parallel and perpendicular conformations).

Table 4. Relative Energies (kcal/mol) of [Nb(η^5-C$_5$H$_5$)R$_2$(HCCH)] (R = Cl, Me) Model Complexes

	parallel conformn		perpendicular conformn		barrier of rotation	
model complex	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP
NbCpCl$_2$(HCCH)	1.1	1.4	0	0	3.5	3.5
NbCpMe$_2$(HCCH)	8.1	7.5	0	0	8.3	7.9

the parallel and perpendicular conformations of the alkyne ligand for the two models. The computed values for the barrier of rotation (Table 4) are around 3.5 kcal mol^{-1} when chlorines are the coligands and around 8 kcal mol^{-1} for the methyl derivative.

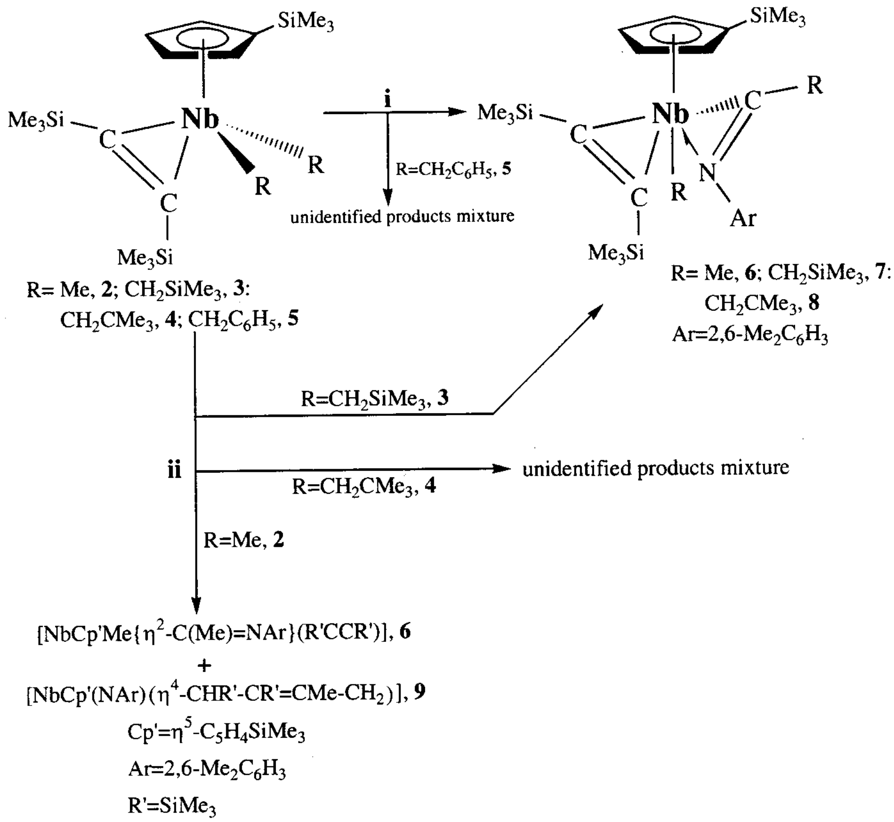
Previous EHMO calculations have been reported for the [NbCpCl$_2$(HCCH)] model[12b] and also for the [NbTpCl$_2$(HCCH)] model.[13e] The barrier to rotation of the alkyne ligand was calculated to be ca. 6 kcal mol^{-1} when the Cp is present, the parallel conformation being the most stable. In contrast, for the Tp model, although the alkyne lies in the molecular plane which bisects the N−Nb−N angle ("perpendicular conformation"), there is only a small energy difference between the two possible orientations for the ligand. Our data (computed barrier of 3.5 kcal mol^{-1}) agrees with such analyses, and it seems that for dichloride compounds of model formulation [NbCpCl$_2$(HCCH)] the importance of the electronic and steric properties of the substituents in the actual alkyne can govern the preferential adoption of one conformation.

On the other hand, the theoretical data for dialkyl compounds of model formulation [NbCpR$_2$(HCCH)] are in agreement with a preferential disposition of the alkyne ligand lying perpendicular to the Cp plane, such as that observed in the structure of **3**. This conformation is characterized by a R−Nb−R angle higher than that observed for the parallel conformation, to maximize the overlap with the $\pi_\perp$ (b$_1$) and $\pi_{||}$* (b$_2$) MO orbitals of the alkyne ligand.[24a] The rather low computed barrier of rotation (8 kcal mol^{-1}) compares well with the data obtained by DNMR spectroscopy for **3** (with bulkier substituents).

Reactions with 2,6-Me$_2$C$_6$H$_3$NC. When 1 equiv of the isocyanide 2,6-Me$_2$C$_6$H$_3$NC was added to benzene-d_6 solutions of the dialkyl alkyne complexes **2**−**4** under a rigorously dry inert gas in a sealed NMR tube, reddish solutions corresponding to alkyl alkyne η^2-iminoacyl [NbCp′R{η^2-C(R)=NAr}(Me$_3$SiCCSiMe$_3$)] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$; R = Me (**6**), CH$_2$SiMe$_3$ (**7**), CH$_2$CMe$_3$ (**8**)) complexes as the unique reaction products were obtained (see Scheme 2). Complexes **6**−**8** were characterized by NMR spectroscopy. The insertion process is instantaneous. After the coordination of the isocyanide, the migration of one alkyl group to the electrophilic isocyanide carbon atom takes place, giving an η^2-iminoacyl complex.

When the same reactions were carried out in a Schlenk tube using hexane as solvent, only the complex **7** could be isolated as a crystalline red solid. The

Scheme 2[a]



[a] Reagents and conditions: (i) 1 equiv of ArNC, NMR tube, benzene-d_6, room temperature; (ii) 1 equiv of ArNC, Schlenk tube, hexane, room temperature.

complexes **6** and **8** are unstable at room temperature, and while **6** is partially transformed into the imido niobacyclopent-3-ene complex **9**, the η^2-iminoacyl derivative **8** decomposes to an unidentified products mixture.

The imido niobacyclopent-3-ene complex [NbCp′(NAr){η^4-CH(SiMe$_3$)C(SiMe$_3$)=C(Me)CH$_2$}] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$; **9**) can be prepared by treatment of the alkyne dimethyl derivative **2** with 1 equiv of isocyanide in hexane at 40−50 °C over 12 h. On the other hand, if the alkyne (trimethylsilyl)methyl η^2-iminoacyl complex **7** is heated to 80 °C in hexane over 12 h, the imido niobacyclopropane(vinyl) derivative [NbCp′(NAr){η^4-CH(SiMe$_3$)C(SiMe$_3$)C(CH$_2$SiMe$_3$)=CH(SiMe$_3$)}] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$; **10**) can be isolated as a crystalline red solid, whose structure was determined by X-ray diffraction methods (see Scheme 3). Identical results can be obtained by thermal treatment of the 1:1 mixture of **3** and 2,6-Me$_2$C$_6$H$_3$NC. In contrast to this behavior, the reaction between the alkyne bis(neopentyl) complex **4** and isocyanide leads, in the first step, to an alkyne neopentyl η^2-iminoacyl complex but this species is gradually transformed into the imido niobacyclohept-2-ene complex [NbCp′(NAr){η^2-CH$_2$CMe$_2$CH$_2$CH(CH$_2$CMe$_3$)C(SiMe$_3$)=C(SiMe$_3$)}] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$; **11**), whose structure may be proposed on the basis of the NMR spectroscopic data.

When the formation processes of the complexes **9**−**11** are followed by ^{1}H NMR spectroscopy, only in the case of complex **9** can the intermediate alkyne azaniobacyclopropane derivative **9i**[27] be detected. This transformation can be rationalized in terms of migration of the second metal-bonded methyl group to the iminoacyl carbon center to give the intermediate **9i** (see Scheme 4). Similar azametallacyclopropane species have been proposed and isolated in the reactions of dichloro dimethyl pentamethylcyclopentadienyl niobium[28] and tantalum[29] complexes with isocyanides and their structures confirmed by X-ray diffraction methods. Rearrangement of the intermediate **9i** leads probably to an imido niobacyclobutene species, and then the migration of a hydrogen atom takes place and a last rearrangement gives the imido niobacyclopent-3-ene complex **9**.

The formation of complexes **10** and **11** can be explained via imido niobacyclobutene intermediates, and when R″ = SiMe$_3$, the migration of the hydrogen atom and subsequent rearrangement leads to **10**, which is a niobacyclopropane complex with a vinyl substituent η^2-coordinated to the metal center. However, a different pathway may be proposed by formation of an azaniobacyclopentatriene species[12i,30] as a result of the intramolecular coupling between both alkyne and iminoacyl ligands. When R″ = CMe$_3$, the C−H activation of a methyl group of the *tert*-butyl fragment and a last rearrangement leads to the imido niobacyclohept-2-ene complex **11**. This behavior is probably due to the steric

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(27) **9i**: ^{1}H NMR (δ, ppm; in benzene-d_6) 6.40 (m, 1H), 6.12 (m, 1H), 5.79 (m, 1H), 5.35 (m, 1H, H_4C$_5$SiMe$_3$), 2.36 (s, 6H, Nb−CMe_2−N(2,6-Me$_2$C$_6$H$_3$)), 2.32 (s, 3H), 1.81 (s, 3H, Nb−CMe$_2$N(2,6-Me_2C$_6$H$_3$)), 0.46 (s, 9H), 0.30 (s, 9H, Me_3SiCCSiMe_3), 0.25 (s, 9H, Me_3SiC$_5$H$_4$).

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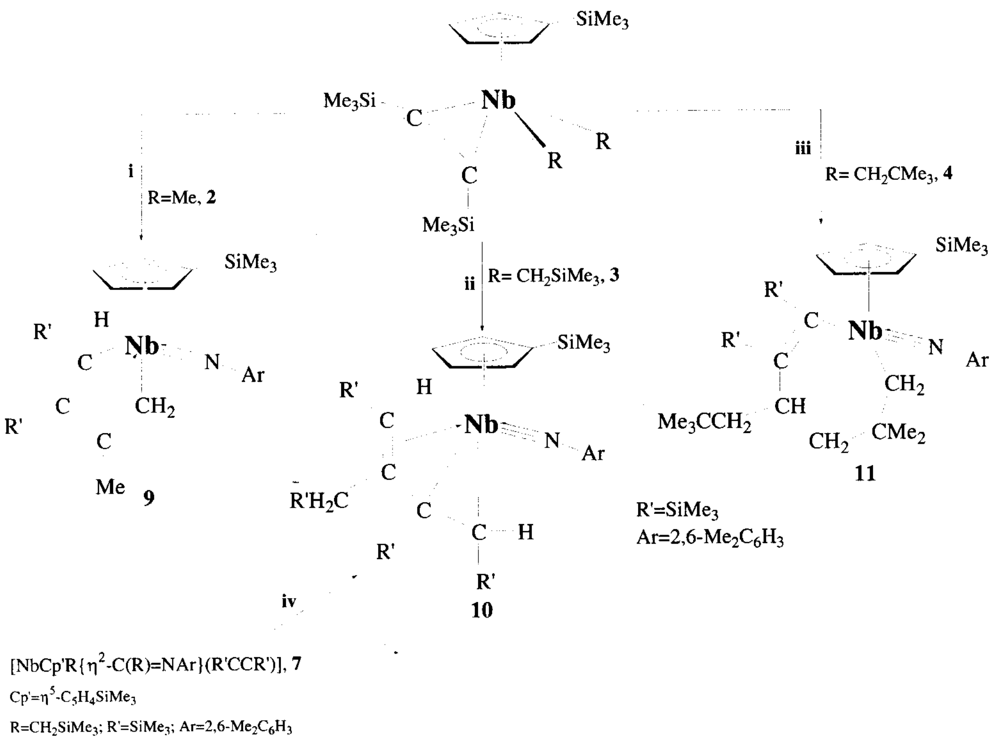
(29) Galakhov, M. V.; Gómez, M.; Jimenez, G.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1995**, *14*, 1901.

Scheme 3[a]



[a] Reagents and conditions: (i) 1 equiv of ArNC, hexane, 12 h, 40−50 °C; (ii) 1 equiv of ArNC, hexane, 12 h, 80 °C; (iii) 1 equiv of ArNC, benzene-d_6, 6 days, room temperature; (iv) hexane, 12 h, 80 °C.

and electronic differences between $-SiMe_3$ and $-CMe_3$ groups. Therefore, the decreased steric hindrance of the *tert*-butyl group permits a closer approach to the metal and the activation of a C−H bond gives the complex **11**.

All of the complexes **6**−**11** were found to be soluble in most organic solvents, including alkanes. They are extremely air- and moisture-sensitive, and rigorously dried solvents and handling under dry inert gases were found to be imperative for sucessful preparations.

The alkyl alkyne η^2-iminoacyl complex **7** shows the $\bar{\nu}(C{=}C)$[16,19] and $\bar{\nu}(C{=}N)$[28,31,32] IR absorptions at 1573 and 1585 cm^{-1}, while the presence of the imido ligand in the complexes **9** and **10** is confirmed by the absorption bands located at 1297 and 1286 cm^{-1}, respectively, corresponding to the $\bar{\nu}(Nb{=}N)$[17,32] stretching vibration.

The ^1H and $^{13}C\{^1H\}$ NMR data (see the Experimental Section) of the complexes **6**−**11** are in agreement with the proposed structures for the alkyl alkyne η^2-iminoacyl (**6**−**8**), imido niobacyclopent-3-ene (**9**), imido niobacyclopropane(vinyl) (**10**), and imido niobacyclohept-2-ene (**11**) complexes. The pseudooctahedral complexes **6**−**8** show in their ^1H NMR spectra two inequivalent methyl groups for the 2,6-$Me_2C_6H_3$ moiety, which is consistent with the slow rotation of the aryl group around the N−C_i(aryl) bond. Furthermore, the ^1H and $^{13}C\{^1H\}$ NMR spectra of such complexes show an ABCD spin system and five carbon resonances, respectively, for the (trimethylsilyl)cyclopentadienyl ring due to the chiral character of the metal center.

The complex **9** exhibits a NMR behavior which is consistent with a diene ligand in an s-cis conformation similar to that observed in other group 5 metal−diene derivatives.[33] The three resonances assigned to the proton and carbon atoms of the three trimethylsilyl groups show that these groups are bonded to three different carbon atoms. The proton and carbon atoms of the cyclopentadienyl ring are inequivalent, but while in its $^{13}C\{^1H\}$ NMR spectrum there are five carbon resonances, in the ^1H NMR spectrum we only detected three signals in a 1:2:1 relation, due probably to the overlapping between the resonances of the proton atoms located in the 3- and 4-positions of the ring, whose carbon atoms resonate at very close chemical shifts (δ). The inequivalent *o*-methyl (phenyl) groups of the imido moiety show two signals in the characteristic region for

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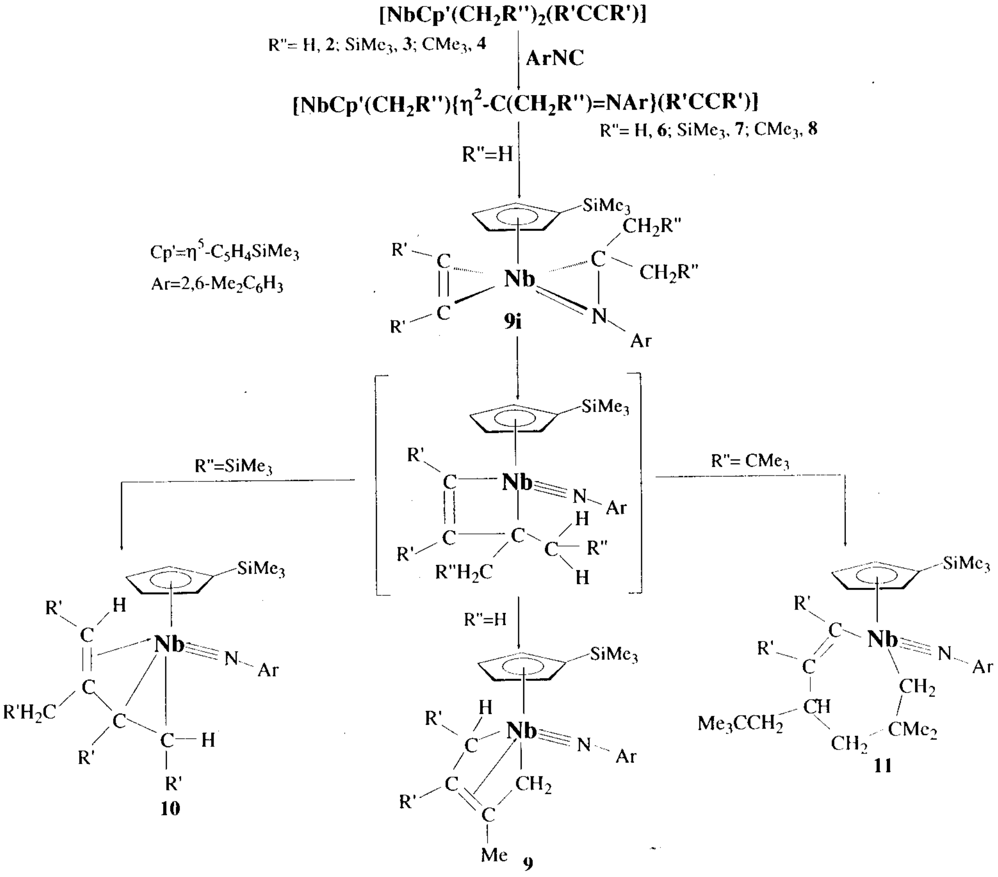
Scheme 4



such ligands.[17,32g] Although the assignment of the resonances at δ 2.33 (Me) and δ 0.20 (SiMe$_3$) to the substituents of the central carbon atoms $-C(Me)=C(SiMe_3)-$ in the niobacyclopent-3-ene fragment is unequivocal, in the $^{13}C\{^1H\}$ NMR spectrum the carbon atoms C$_3$ and C$_4$ present very close chemical shifts and therefore we have tentatively assigned to such carbon atoms the signals at δ 123.5 and 122.05, respectively. The relative shielding of these olefinic carbons (they usually appear at δ >130) can be ascribed to the π-electronic density transfer to an electronically deficient niobium(V) center. The proton resonance located at δ 3.40 corresponds to the Nb$-$C*H*(SiMe$_3$) fragment, while the diasterotopic methylene protons of the Nb$-$C*H*$_2$C(Me)= moiety appear as an AB system. In the $^{13}C\{^1H\}$ NMR spectra broad resonances are observed for both carbon atoms, as is usual for sp^3 carbon atoms directly bonded to the niobium. In accord with these data, we propose an s-cis conformation for the diene ligand in a η^4-niobacyclopent-3-ene bond system.

The unusual conformation of the diene ligand in the complex **10** was deduced after a detailed and combined analysis of the NMR spectroscopic and X-ray diffraction data, which strongly suggests that the diene ligand is bonded in a η^2-niobacyclopropane fashion with a vinyl substituent η^2-coordinated to the metal center. The complex **10** exhibits the ^{1}H NMR signals of two different C*H*(SiMe$_3$) groups (δ 3.10, 1.80), the resonance located at low field being assigned to the group bonded to the vinyl fragment. The relative shielding of this proton can be rationalized by the coordination of the carbon atom to the metal center. In the $^{13}C\{^1H\}$ NMR spectrum the signal at δ 88.4 ($^1J_{C-H}$ = 118.8 Hz) is assigned to the vinylic carbon C$_4$, while the resonance at δ 76 ($^1J_{C-H}$ = 114.9 Hz) corresponds to C$_1$ of the niobacyclopropane moiety. The signal located at δ 121.1 can be assigned to the C$_3$ atom of the vinyl fragment, but that corresponding to the C$_2$ atom of the niobacyclopropane system cannot be observed, probably because of its low intensity and broad signal. The rest of the resonances for the five SiMe$_3$ substituents and for the C$_5$H$_4$SiMe$_3$ ring are as expected for the proposed structure.

The molecular structure and atom-labeling scheme of **10** are shown in Figure 4, while relevant geometrical parameters are summarized in Table 5. Compound **10** can be described as a 18e monomer species with a niobium atom coordinated to a (trimethylsilyl)cyclopentadienyl ligand and to an imido group and forms a niobacyclopropane system with a η^2-vinyl susbstituent. In relation to the imido disposition, the Nb1$-$N1 bond distance (1.806(3) Å) and the Nb1$-$N1$-$C21 angle (166.1(3)°) are similar to those found in other imido niobium and tantalum derivatives.[34] However, the 2,6-Me$_2$C$_6$H$_3$ moiety is slightly folded toward the Cp′ ring.

Frequently, in the diene mono(cyclopentadienyl) niobium and tantalum compounds,[33a,d,35] the diene ligand

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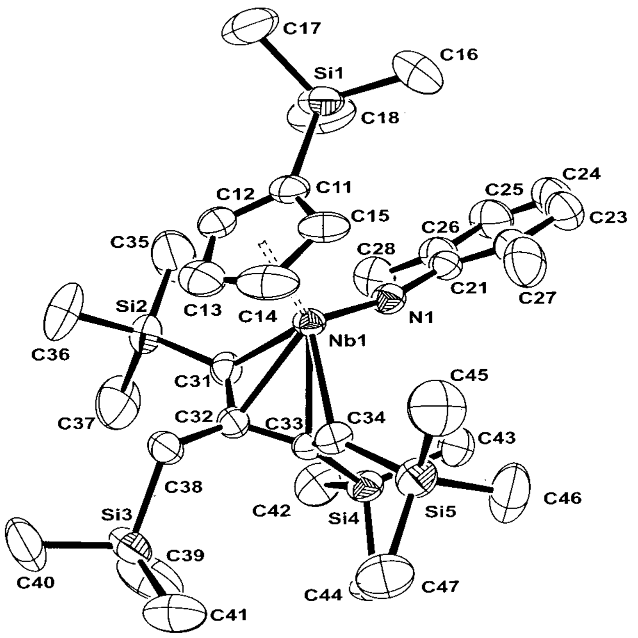

Figure 4. ORTEP drawing of compound **10**. Thermal ellipsoids are shown at the 50% level.

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 10

Nb(1)−N(1)	1.806(3)	Nb(1)−C(33)	2.267(4)
Nb(1)−C(34)	2.329(4)	Nb(1)−C(32)	2.379(4)
Nb(1)−C(31)	2.426(4)	Si(2)−C(31)	1.876(4)
Si(3)−C(38)	1.897(4)	Si(4)−C(33)	1.905(4)
Si(5)−C(34)	1.866(4)	N(1)−C(21)	1.385(5)
C(31)−C(32)	1.406(6)	C(32)−C(33)	1.456(5)
C(32)−C(38)	1.528(5)	C(33)−C(34)	1.460(6)
N(1)−Nb(1)−C(33)	99.1(1)	N(1)−Nb(1)−C(34)	107.7(1)
C(33)−Nb(1)−C(34)	37.0(1)	N(1)−Nb(1)−C(32)	119.3(1)
C(33)−Nb(1)−C(32)	36.4(1)	C(34)−Nb(1)−C(32)	63.9(1)
N(1)−Nb(1)−C(31)	102.2(1)	C(33)−Nb(1)−C(31)	62.8(1)
C(34)−Nb(1)−C(31)	96.6(1)	C(32)−Nb(1)−C(31)	34.0(1)
C(21)−N(1)−Nb(1)	166.1(3)	N(1)−C(21)−C(26)	118.9(4)
N(1)−C(21)−C(22)	120.8(4)	C(26)−C(21)−C(22)	120.4(4)
C(32)−C(31)−Si(2)	131.3(3)	C(32)−C(31)−Nb(1)	71.2(2)
Si(2)−C(31)−Nb(1)	135.1(2)	C(31)−C(32)−C(33)	117.8(3)
C(31)−C(32)−C(38)	120.7(3)	C(33)−C(32)−C(38)	120.7(3)
C(31)−C(32)−Nb(1)	74.8(2)	C(33)−C(32)−Nb(1)	67.6(2)
C(38)−C(32)−Nb(1)	119.5(3)	C(34)−C(33)−C(32)	117.3(3)
C(34)−C(33)−Si(4)	124.1(3)	C(32)−C(33)−Si(4)	118.6(3)
C(34)−C(33)−Nb(1)	73.8(2)	C(32)−C(33)−Nb(1)	76.0(2)
Si(4)−C(33)−Nb(1)	121.8(2)	C(33)−C(34)−Si(5)	135.9(3)
C(33)−C(34)−Nb(1)	69.2(2)	Si(5)−C(34)−Nb(1)	134.2(2)
C(32)−C(38)−Si(3)	117.0(3)		

forms a metallacyclopent-3-ene system with a preferred supino conformation, although there are examples with a prono conformation. Furthermore, the diene ligand can adopt an s-trans conformation, as has been observed in bis(cyclopentadienyl) zirconium,[36] mono(cyclopentadienyl) molybdenum,[37] and cationic bis(cyclopentadienyl) tantalum[38] complexes. In our case, the crystallographic data determined for the C−C ligand and Nb−C(ligand) distances do not permit us to propose the same bonding system between the niobium center and such ligands (see Figure 4). Thus, C31−C32, C32−C33, and C33−C34 bond distances of 1.406(6), 1.456(5), and 1.460(6) Å, respectively, show that the first corresponds to the vinyl group and is shorter than the other two. The Nb−C33 (2.267(4) Å) and Nb−C34 (2.329(4) Å) bond distances correspond to the carbon atoms of the niobacylopropane fragment and are shorter than the Nb−C31 (2.426(4) Å) and Nb−C32 (2.379(4) Å) bond distances. The torsion angle formed by the carbon atoms of the ligand C31−C32−C33−C34 is 120.62(1)°, while in the case of a normal diene ligand this angle would be 0°. Moreover, the carbon atom C31 is located 1.07 Å away from the plane formed by C32, C33, and C34. In summary, we propose this bonding system to be constituted of a "diene" C31−C32−C33−C34 fragment linked to the metal through the C33−C34 atoms, forming a niobacyclopropane ring and the donor vinyl substituent C31═C32.

The complex **11** shows in its ^{1}H NMR spectrum the expected four signals for the methyl protons of the trimethylsilyl and *tert*-butyl fragments and simultaneously presents inequivalency for the proton atoms of the $C_5H_4SiMe_3$ ring and the methyl groups of the 2,6-$Me_2C_6H_3$ moiety in the imido ligand. The proton atoms of the methylene group directly bonded to niobium show an AB spin system, while the corresponding $-CH_2$-$CHCH_2-$ fragment exhibits an ABCDE spin system, which permits us to make the assignment. In the ^{13}C-{^{1}H} NMR spectrum all expected resonances are present, in agreement with the proposed structure.

Conclusions

The direct alkylation of [NbCp′Cl_2($Me_3SiCCSiMe_3$)] (Cp′ = η^5-$C_5H_4SiMe_3$; **1**) with the appropriate amount of alkylating reagent leads to the formation of the dialkyl alkyne complexes [NbCp′R_2($Me_3SiCCSiMe_3$)] (Cp′ = η^5-$C_5H_4SiMe_3$; R = Me (**2**), CH_2SiMe_3 (**3**), CH_2CMe_3 (**4**), $CH_2C_6H_5$ (**5**)), whose structural studies reveal consistency with the expected three-legged piano-stool environment. Theoretical studies on the [Nb(η^5-C_5H_5)R_2(HCCH)] (R = Cl, Me) model complexes rationalize the disposition of the alkyne ligand in these complexes. Reaction of dialkyl alkyne derivatives **2**−**4** with 1 equiv of 2,6-$Me_2C_6H_3$NC occurs through the initial formation of the alkyl alkyne η^2-iminoacyl compounds [NbCp′R{η^2-C(R)═NAr}($Me_3SiCCSiMe_3$)] (Cp′ = η^5-$C_5H_4SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; R = Me (**6**), CH_2SiMe_3 (**7**), CH_2CMe_3 (**8**)) but leads to different coupling products, depending on R. When hexane solutions of **2** and **3** were treated with 1 equiv of isocyanide at 40−50 °C (**2**) and 80 °C (**3**), respectively, the imido niobacyclopent-3-ene [NbCp′(NAr){η^4-CH($SiMe_3$)C($SiMe_3$)═C(Me)CH_2}] (Cp′ = η^5-$C_5H_4SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; **9**) and imido niobacyclopropane(vinyl) [NbCp′(NAr){η^4-CH($SiMe_3$)C($SiMe_3$)C(CH_2SiMe_3)═CH($SiMe_3$)}] (Cp′ = η^5-$C_5H_4SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; **10**) complexes are obtained, probably via azaniobacyclopropane intermediates. If R = CH_2CMe_3, after the initial formation of the non-stable η^2-iminoacyl complex **8**, its spontaneous conversion takes place to give the imido niobacylohept-2-ene [NbCp′(NAr){η^2-CH_2-$CMe_2CH_2CH(CH_2CMe_3)C(SiMe_3)$═C($SiMe_3$)}] (Cp′ = η^5-$C_5H_4SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; **11**) complex, but the intermediate species could not be observed when the

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reaction was followed by ^{1}H NMR spectroscopy. The NMR spectroscopic data of the coupling products confirmed for the diene ligand an s-cis conformation in the complex **9**, while in the complex **10** such a ligand presents an unusual coordination mode and forms with the metal center a niobacyclopropane system with an η^2-vinyl substituent.

Experimental Section

All operations were carried out under a dry argon atmosphere using standard Schlenk-tube and cannula techniques or in a conventional argon-filled glovebox. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use: benzene-d_6 and hexane (Na/K alloy) and tetrahydrofuran (sodium−benzophenone). $NbCp'Cl_4$[39] and $LiCH_2CMe_3$[40] were prepared as described previously. Reagent grade $Me_3SiC{\equiv}CSiMe_3$ (Aldrich), MgClR (R = Me, 3 M in OEt_2; R = CH_2SiMe_3, 1 M in OEt_2; R = $CH_2C_6H_5$, 2 M in THF; Aldrich), 2,6-$Me_2C_6H_3NC$ (Fluka), and Al and $HgCl_2$ (Panreac) were purchased from commercial sources and were used without further purification.

Infrared spectra were recorded on Perkin-Elmer 883 and Spectrum 2000 spectrophotometers (4000−200 cm^{-1}) with samples as Nujol mulls between CsI plates or in polyethylene pellets. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian Unity 300 and Varian Unity 500 Plus spectrometers; chemical shifts were referenced to the ^{13}C (δ 128) and residual ^{1}H (δ 7.15) resonances of the benzene-d_6 solvent. C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer.

Synthesis of [Nb(η^5-$C_5H_4SiMe_3$)Cl_2($Me_3SiCCSiMe_3$)] (1). Tetrahydrofuran (100 mL) was added to a weighed mixture of [Nb(η^5-$C_5H_4SiMe_3$)Cl_4] (2.00 g, 5.38 mmol), aluminum powder (0.50 g, 18.52 mmol), and mercury(II) chloride (0.10 g, 0.37 mmol) at room temperature. The mixture was stirred and $Me_3SiC{\equiv}CSiMe_3$ (1.22 mL, 5.38 mmol) added under rigorously anhydrous conditions. After 12 h, the resulting suspension was decanted and filtered and the solvent was removed under reduced pressure. The residue was extracted with hexane (2 × 25 mL), and after filtration, the purple solution was concentrated to 15 mL and cooled to −40 °C to afford **1** as purple crystals. Yield: 1.95 g (77%). IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1638 (m), 1249 (vs), 1168 (m), 1040 (w), 888 (m), 839 (vs), 630 (w), 341 (m). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.03 (m, 2H), 5.71 (m, 2H, $H_4C_5SiMe_3$), 0.28 (s, 9H, $Me_3SiC_5H_4$), 0.23 (s, 18H, $Me_3SiCCSiMe_3$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-d_6): 231.72 ($Me_3SiCCSiMe_3$), 122.11 (C_i, $C_5H_4SiMe_3$), 121.91 ($C_{2,5}$), 111.91 ($C_{3,4}$, $C_5H_4SiMe_3$), 0.35 ($Me_3SiCCSiMe_3$), −0.52 ($Me_3SiC_5H_4$). Anal. Calcd for $C_{16}H_{31}Cl_2Si_3Nb$: C, 40.76; H, 6.63. Found: C, 40.80; H, 6.49.

Synthesis of [NbCp′R_2(R′CCR′)] (Cp′ = η^5-$C_5H_4SiMe_3$; R′ = $SiMe_3$; R = Me (2), CH_2SiMe_3 (3), CH_2CMe_3 (4), $CH_2C_6H_5$ (5)). A solution of **1** (1.00 g, 2.12 mmol) in hexane (30 mL) was treated with MgClR (4.24 mmol; R = Me, 1.42 mL of a 3 M solution in diethyl ether; R = CH_2SiMe_3, 4.20 mL of a 1 M solution in diethyl ether; R = $CH_2C_6H_5$, 2.12 mL of a 2 M solution in tetrahydrofuran) or $LiCH_2CMe_3$ (0.33 g, 4.24 mmol) at −78 °C, and the mixture was warmed slowly to room temperature and then stirred for a further 12 h. The resulting suspension was decanted and filtered and the filtrate concentrated to 10 mL; when the temperature was lowered overnight to −40 °C, **2**−**5** were deposited as brown-orange microcrystalline solids.

The data for **2** are as follows. Yield: 0.55 g (60%). IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1581 (m), 1247 (vs), 1177 (m), 1046 (m), 919 (w), 835 (vs), 692 (w), 632 (w), 480 (w). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.17 (m, 2H), 5.74 (m, 2H, $H_4C_5SiMe_3$), 0.55 (s, 6H, Nb−Me_2), 0.36 (s, 18H, $Me_3SiCCSiMe_3$), 0.21 (s, 9H, $Me_3SiC_5H_4$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-d_6): 249.49 ($Me_3SiCCSiMe_3$), 116.6 ($C_{2,5}$), 114.6 (C_i), 103.02 ($C_{3,4}$, $C_5H_4SiMe_3$), 40.4 (br, Nb−Me_2), 0.94 ($Me_3SiCCSiMe_3$), 0.36 ($Me_3SiC_5H_4$). Anal. Calcd for $C_{18}H_{37}Si_3Nb$: C, 50.20; H, 8.66. Found: C, 50.26; H, 8.54.

The data for **3** are as follows. Yield: 0.85 g (70%). IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1570 (s), 1244 (vs), 1177 (m), 1046 (m), 908 (m), 839 (vs), 682 (w), 626 (w). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.65 (m, 2H), 5.74 (m, 2H, $H_4C_5SiMe_3$), 1.61, 1.13 (AB, 4H, $^2J_{H-H}$ = 9 Hz, Nb−(CH_2SiMe_3)$_2$), 0.39 (br, 18H, $Me_3SiCCSiMe_3$), 0.34 (s, 9H, $Me_3SiC_5H_4$), −0.08 (s, 18H, Nb−(CH_2SiMe_3)$_2$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-d_6): 250 ($Me_3SiCCSiMe_3$), 118.92 ($C_{2,5}$), 117.08 (C_i), 100.11 ($C_{3,4}$, $C_5H_4SiMe_3$), 56.28 (br, Nb−($\mathbf{C}H_2SiMe_3$)$_2$), 3.42 (Nb−(CH_2SiMe_3)$_2$), 1.45 ($Me_3SiCCSiMe_3$), 0.57 ($Me_3SiC_5H_4$). Anal. Calcd for $C_{24}H_{53}Si_5Nb$: C, 50.13; H, 9.29. Found: C, 49.96; H, 9.37.

The data for **4** are as follows. Yield: 0.63 g (55%). IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1566 (m), 1246 (vs), 1176 (m), 1044 (m), 909 (m), 834 (vs), 676 (w), 630 (w), 485 (m). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.85 (m, 2H), 5.68 (m, 2H, $H_4C_5SiMe_3$), 2.58, 0.92 (AB, 4H, $^2J_{H-H}$ = 9 Hz, Nb−(CH_2CMe_3)$_2$), 0.87 (s, 18H, Nb−(CH_2CMe_3)$_2$), 0.41 (br, 18H, $Me_3SiCCSiMe_3$), 0.36 (s, 9H, $Me_3SiC_5H_4$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-d_6): 249.8 ($Me_3SiCCSiMe_3$), 119.55 ($C_{2,5}$), 116.11 (C_i), 98.6 ($C_{3,4}$, $C_5H_4SiMe_3$), 82.40 (br, Nb−(CH_2CMe_3)$_2$), 36.07 (Nb−(CH_2CMe_3)$_2$), 35.7 (br, Nb−(CH_2CMe_3)$_2$), 1.91 (br, $Me_3SiCCSiMe_3$), 0.66 ($Me_3SiC_5H_4$). Anal. Calcd for $C_{26}H_{53}Si_3Nb$: C, 57.53; H, 9.84. Found: C, 57.24; H, 9.77.

The data for **5** are as follows. Yield: 0.49 g (40%). IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1556 (m), 1246 (vs), 1177 (m), 1096 (w), 1042 (m), 903 (s), 834 (vs), 689 (m), 624 (w), 479 (w). ^{1}H NMR (δ, ppm; in benzene-d_6): 7.03 (t, 4H), 6.90 (m, 6H, Nb−($CH_2C_6H_5$)$_2$), 5.66 (m, 2H), 5.17 (m, 2H, $H_4C_5SiMe_3$), 2.40, 2.14 (AB, 4H, $^2J_{H-H}$ = 9 Hz, Nb−($CH_2C_6H_5$)$_2$), 0.38 (br, 18H, $Me_3SiCCSiMe_3$), 0.004 (s, 9H, $Me_3SiC_5H_4$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-d_6): 240.43 ($Me_3SiCCSiMe_3$), 143.56, 130.29, 124.38 (C_o, C_p, C_m, Nb−($CH_2C_6H_5$)$_2$), 114.09 ($C_{2,5}$), 113.03 (C_i), 109.7 ($C_{3,4}$, $C_5H_4SiMe_3$), 58.41 (br, Nb−($CH_2C_6H_5$)$_2$), 1.94 ($Me_3SiCCSiMe_3$), 0.77 ($Me_3SiC_5H_4$). Anal. Calcd for $C_{30}H_{45}Si_3Nb$: C, 61.82; H, 7.78. Found: C, 61.61; H, 7.66.

Synthesis of [NbCp′R{η^2-C(R)=NAr}(R′CCR′)] (Cp′ = η^5-$C_5H_4SiMe_3$; R′ = $SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; R = Me (6), CH_2SiMe_3 (7), CH_2CMe_3 (8)). Compounds 6 and 8. To a solution of **2** or **4** (0.15 g; R = Me, 0.35 mmol; R = CH_2CMe_3, 0.26 mmol) in benzene-d_6 (0.7 mL) was added 2,6-$Me_2C_6H_3NC$ (R = Me, 0.046 g, 0.35 mmol; R = CH_2CMe_3, 0.034 g, 0.26 mmol) in a valved NMR tube under rigorously anhydrous conditions. The reaction was monitored by ^{1}H NMR spectroscopy until no further changes were observed. The final spectrum was indicative of complete transformation of the starting material and confirmed the formation of **6** and **8** in quantitative yield.

The data for **6** are as follows. ^{1}H NMR (δ, ppm; in benzene-d_6): 6.86 (m, 2H), 6.72 (m, 1H, Nb−C(Me)=N(2,6-$Me_2C_6H_3$)), 5.66 (m, 1H), 5.62 (m, 1H), 5.52 (m, 1H), 5.38 (m, 1H, $C_5H_4SiMe_3$), 2.37 (s, 3H, Nb−C(Me)=NAr), 1.70 (s, 3H), 1.14 (s, 3H, Nb−C(Me)=N(2,6-$Me_2C_6H_3$)), 0.84 (s, 3H, Nb−Me), 0.40 (s, 18H, $Me_3SiCCSiMe_3$), 0.13 (s, 9H, $C_5H_4SiMe_3$).

The data for **8** are as follows. ^{1}H NMR (δ, ppm; in benzene-d_6): 6.87 (m, 2H), 6.77 (m, 1H, Nb−C(CH_2CMe_3)=N(2,6-$Me_2C_6H_3$)), 6.57 (m, 1H), 6.15 (m, 1H), 5.99 (m, 2H, $C_5H_4SiMe_3$), 2.79, 2.70 (AB, 2H, $^2J_{H-H}$ = 14.4 Hz, Nb−C(CH_2CMe_3)=NAr), 2.44, 2.10 (AB, 2H, $^2J_{H-H}$ = 13.2 Hz, Nb−CH_2CMe_3), 1.85 (s, 3H), 1.45 (s, 3H, Nb−C(CH_2CMe_3)=N(2,6-$Me_2C_6H_3$)), 1.06 (s, 9H, Nb−C(CH_2CMe_3)=NAr), 0.99 (s, 9H, Nb−CH_2CMe_3), 0.49 (s, 18H, $Me_3SiCCSiMe_3$), 0.07 (s, 9H, $C_5H_4SiMe_3$).

Compound 7. Under rigorously anhydrous conditions, hexane (30 mL) was added to a mixture of the complex **3** (0.70

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g, 1.22 mmol) and 2,6-Me$_2$C$_6$H$_3$NC (0.16 g, 1.22 mmol). After this mixture was stirred for 3 h at room temperature, the resulting solution was filtered and the filtrate was concentrated to a volume of ca. 10 mL. Cooling at −40 °C overnight led to the deposition of a red microcrystalline solid identified as **7**.

The data for **7** are as follows. IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1585 (w), 1561 (m), 1244 (s), 1178 (m), 1095 (w), 1041 (m), 904 (m), 837 (vs), 666 (w), 625 (w), 478 (w). ^{1}H NMR (δ, ppm; in benzene-*d*$_6$): 6.84 (m, 2H), 6.74 (m, 1H, Nb−C(CH$_2$SiMe$_3$)=N(2,6-Me$_2$C$_6$*H*$_3$)), 6.17 (m, 1H), 5.84 (m, 1H), 5.79 (m, 2H, C$_5$*H*$_4$SiMe$_3$), 3.06, 2.90 (AB, 2H, $^{2}J_{\mathrm{H-H}} = 11.5$ Hz, Nb−C(C*H*$_2$SiMe$_3$)=NAr), 1.90 (s, 3H), 1.54 (s, 3H, Nb− C(CH$_2$SiMe$_3$)=N(2,6-*Me*$_2$C$_6$H$_3$)), 1.04, 0.88 (AB, 2H, $^{2}J_{\mathrm{H-H}} = 12.5$ Hz, Nb−C*H*$_2$SiMe$_3$), 0.49 (s, 18H, *Me*$_3$SiCCSi*Me*$_3$), 0.13 (s, 9H, C$_5$H$_4$Si*Me*$_3$), 0.04 (s, 9H, Nb−C(CH$_2$Si*Me*$_3$)=NAr), −0.20 (s, 9H, Nb−CH$_2$Si*Me*$_3$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-*d*$_6$): 247.32 (Me$_3$Si*CC*SiMe$_3$), 220.53 (Nb−*C*(CH$_2$SiMe$_3$)=NAr), 144.84 (C$_\mathrm{i}$, Nb−C(CH$_2$SiMe$_3$)=N(2,6-Me$_2$*C*$_6$H$_3$)), 131.2, 130, 126.2 (C$_\mathrm{o}$, C$_\mathrm{p}$, C$_\mathrm{m}$, Nb−C(CH$_2$SiMe$_3$)=N(2,6-Me$_2$*C*$_6$H$_3$)), 109.58 (C$_\mathrm{i}$, *C*$_5$H$_4$SiMe$_3$), 112.11, 106.34, 105.35, 104.97 (*C*$_5$H$_4$SiMe$_3$), not observed (Nb−*C*H$_2$SiMe$_3$), 33.74 (Nb−C(*C*H$_2$SiMe$_3$)=NAr), 19.37, 19.16 (Nb−C(CH$_2$SiMe$_3$)=N(2,6-*Me*$_2$C$_6$H$_3$)), 4.16 (*Me*$_3$SiCCSi*Me*$_3$), 2.67 (C$_5$H$_4$Si*Me*$_3$), 0.54 (Nb−C(CH$_2$Si*Me*$_3$)=NAr), 0.46 (Nb−CH$_2$Si*Me*$_3$). Anal. Calcd for C$_{33}$H$_{62}$NSi$_5$Nb: C, 56.13; H, 8.85; N, 1.98. Found: C, 56.07; H, 9.08; N, 1.84.

Synthesis of [NbCp′(NAr){η^4-CH$_2$C(Me)=C(SiMe$_3$)CH(SiMe$_3$)}] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$; 9). 2,6-Me$_2$C$_6$H$_3$NC (0.21 g, 1.63 mmol) was added to a solution of **2** (0.70 g, 1.63 mmol) in hexane (30 mL) and the reaction mixture heated for 12 h at 40−50 °C. The brown solution was filtered, concentrated to ca. 10 mL, and cooled to −40 °C to give **9** as brown crystals. Yield: 0.64 g (70%). IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1586 (m), 1297 (m), 1245 (vs), 1178 (s), 1093(s), 1045 (s), 903 (s), 833 (vs), 629 (w), 483 (w). ^{1}H NMR (δ, ppm; in benzene-*d*$_6$): 6.93 (m, 2H), 6.67 (m, 1H, Nb=N(2,6-Me$_2$C$_6$*H*$_3$)), 6.19 (m, 1H), 6.06 (m, 2H), 5.14 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 3.70, −0.33 (AB, 2H, $^{2}J_{\mathrm{H-H}} = 8$ Hz, Nb−C*H*$_2$−), 3.40 (s, 1H, Nb−C*H*(SiMe$_3$)−), 2.33 (s, 3H, Nb−CH$_2$C(*Me*)=C(SiMe$_3$)−), 2.13 (s, 3H), 2.06 (s, 3H, Nb=N(2,6-*Me*$_2$C$_6$H$_3$)), 0.21 (s, 9H), 0.20 (s, 9H), 0.01 (s, 9H, Nb−CH(Si*Me*$_3$)−, Nb−CH(SiMe$_3$)C(Si*Me*$_3$)=C(Me)−, C$_5$H$_4$Si*Me*$_3$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-*d*$_6$): 139.10 (C$_\mathrm{i}$, Nb=N(2,6-Me$_2$*C*$_6$H$_3$)), 127.98, 127.38, 126.90 (C$_\mathrm{o}$, C$_\mathrm{p}$, C$_\mathrm{m}$, Nb=N(2,6-Me$_2$*C*$_6$H$_3$)), 123.5 (Nb− CH$_2$*C*(Me)=C(SiMe$_3$)−), 122.05 (Nb−CH$_2$C(Me)=*C*(SiMe$_3$)−), 111 (C$_\mathrm{i}$, *C*$_5$H$_4$SiMe$_3$), 112.45, 110.72, 106.3, 106.06 (*C*$_5$H$_4$SiMe$_3$), 64.5 (br, Nb−*C*H$_2$C(Me)=C(SiMe$_3$)−), 63.75 (br, Nb-*C*H(SiMe$_3$)C(SiMe$_3$)=), 28.15 (Nb−CH$_2$C(*Me*)=C(SiMe$_3$)−), 19.93, 18.95 (Nb=N(2,6-*Me*$_2$C$_6$H$_3$)), 3.28, 2.03, 0.62 (Nb−CH(Si*Me*$_3$)−, Nb−CH(SiMe$_3$)C(Si*Me*$_3$)=C(Me)−, C$_5$H$_4$Si*Me*$_3$). Anal. Calcd for C$_{27}$H$_{46}$NSi$_3$Nb: C, 57.72; H, 8.25; N, 2.49. Found: C, 57.80; H, 8.20; N, 2.20.

Synthesis of [NbCp′(NAr){η^4-CH(SiMe$_3$)C(SiMe$_3$)C(CH$_2$SiMe$_3$)=CH(SiMe$_3$)}] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$; 10). A hexane (30 mL) solution of **7** (0.70 g, 0.99 mmol) was heated at 80 °C for 12 h in a sealed tube. After the tube was opened, the solution was filtered, concentrated to ca. 10 mL, and cooled to −40 °C to give **10** as red crystals, which were filtered out and dried under vacuum. Yield: 0.56 g (80%). IR (Nujol mull; $\bar{\nu}$, cm^{-1}): 1586 (w), 1286 (m), 1245 (vs), 1169 (w), 1093 (w), 1047 (w), 906 (m), 832 (vs), 694 (w), 636 (w). ^{1}H NMR (δ, ppm; in benzene-*d*$_6$): 6.92 (m, 1H), 6.82 (m, 1H), 6.68 (m, 1H, Nb=N(2,6-Me$_2$C$_6$*H*$_3$)), 6.70 (m, 1H), 6.06 (m, 1H), 5.85 (m, 1H), 4.55 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 3.10 (s, 1H, *H*(SiMe$_3$)C=C(CH$_2$SiMe$_3$)−), 2.52 (s, 3H), 2.25 (s, 3H, Nb=N(2,6-*Me*$_2$C$_6$H$_3$)), 1.8 (s, 1H, Nb−C*H*(SiMe$_3$)C(SiMe$_3$)−), 1.55, 0.95 (AB, 2H, $^{2}J_{\mathrm{H-H}} = 13$ Hz, −C(C*H*$_2$SiMe$_3$)=CH(SiMe$_3$)), 0.54 (s, 9H), 0.43 (s, 9H), 0.18 (s, 9H), 0.15 (s, 9H), 0.08 (s, 9H, Nb−CH(Si*Me*$_3$)C(Si*Me*$_3$)−, −C(CH$_2$Si*Me*$_3$)=CH(Si*Me*$_3$), C$_5$H$_4$Si*Me*$_3$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-*d*$_6$): 147.82 (C$_\mathrm{i}$, Nb=N(2,6-Me$_2$*C*$_6$H$_3$)), 131.6, 127.7, 122.23 (C$_\mathrm{o}$, C$_\mathrm{p}$, C$_\mathrm{m}$, Nb=N(2,6-Me$_2$*C*$_6$H$_3$)), 121.11 (−*C*(CH$_2$SiMe$_3$)=CH(SiMe$_3$)), 117 (C$_\mathrm{i}$, *C*$_5$H$_4$SiMe$_3$), 110.88, 107.44, 107.25, 104.70 (*C*$_5$H$_4$SiMe$_3$), not observed (Nb−CH(SiMe$_3$)*C*(SiMe$_3$)−), 88.4 ($^{1}J_{\mathrm{C-H}} = 118.8$ Hz, *C*H(SiMe$_3$)=C(CH$_2$SiMe$_3$)−), 76 ($^{1}J_{\mathrm{C-H}} = 114.9$ Hz, Nb−*C*H(SiMe$_3$)C(SiMe$_3$)−), 30.8 (−C(*C*H$_2$SiMe$_3$)=CH(SiMe$_3$)), 21.03, 20.14 (Nb=N(2,6-*Me*$_2$C$_6$H$_3$)), 4.83, 3.83, 2.57, 0.09, 0.00 (Nb−CH(Si*Me*$_3$)C(Si*Me*$_3$)−, −C(CH$_2$Si*Me*$_3$)=CH(Si*Me*$_3$), C$_5$H$_4$Si*Me*$_3$). Anal. Calcd for C$_{33}$H$_{62}$NSi$_5$Nb: C, 56.13; H, 8.85; N, 1.98. Found: C, 56.18; H, 8.89; N, 1.79.

Table 6. Crystal Data and Structure Refinement Details for 3 and 10

	3	**10**
chem formula	$C_{24}H_{53}NbSi_5$	$C_{33}H_{62}NNbSi_5$
fw	575.02	706.20
T (K)	293(2)	293(2)
λ (Mo Kα), Å	0.71073	0.71073
space group	$P2_1/c$	$P\bar{1}$
a, Å	9.785(3)	10.243(5)
b, Å	18.734(4)	10.381(4)
c, Å	19.007(6)	20.174(8)
α, deg		89.38(2)
β, deg	93.94(2)	89.48(2)
γ, deg		70.63(2)
V, Å^3	3476.0(17)	2023.6(15)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.099	1.159
μ, mm^{-1}	0.528	0.466
θ range, deg	3.01−25.09	3.03−24.98
index ranges	$0 \le h \le 11$, $0 \le k \le 22$, $-22 \le l \le 22$	$0 \le h \le 12$, $-11 \le k \le 12$, $-23 \le l \le 23$
no. of data collected	6500	7502
no. of unique data	6119 (*R*(int) = 0.0390)	7070 (*R*(int) = 0.0194)
no. of params refined	298	361
goodness of fit on F^2	0.979	0.878
final *R* indices ($I > 2\sigma(I)$)^a	R1 = 0.0550, wR2 = 0.1295	R1 = 0.0536, wR2 = 0.1508
R indices (all data)	R1 = 0.1460, wR2 = 0.1641	R1 = 0.0639, wR2 = 0.1701
largest diff peak and hole, e Å^{-3}	0.491 and −0.464	1.390 and −1.214

[a] $\mathrm{R1} = \sum||F_\mathrm{o}| - |F_\mathrm{c}||/\sum|F_\mathrm{o}|$; $\mathrm{wR2} = \{[\sum w(F_\mathrm{o}^2 - F_c^2)^2]/[\sum w(F_\mathrm{o}^2)^2]\}^{1/2}$.

Synthesis of [NbCp′(NAr){η^2-C(SiMe$_3$)=C(SiMe$_3$)CH(CH$_2$CMe$_3$)CH$_2$CMe$_2$CH$_2$}] (Cp′ = η^5-C$_5$H$_4$SiMe$_3$; Ar = 2,6-Me$_2$C$_6$H$_3$; 11). A benzene-*d*$_6$ (0.7 mL) solution of the complex **8** was prepared as we have described above and heated at room temperature for several days in a sealed NMR tube. The transformation was monitored by NMR spectroscopy until no further change was observed. After 6 days, the formation of **11** was confirmed by its ^{1}H and ^{13}C{^{1}H} NMR spectra and the data are as follows. ^{1}H NMR (δ, ppm; in benzene-*d*$_6$): 6.93 (m, 2H), 6.84 (m, 1H, Nb=N(2,6-Me$_2$C$_6$*H*$_3$)), 6.00 (m, 1H), 5.73 (m, 1H), 5.31 (m, 1H), 5.21 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 3.46 (m, H_e), 2.77, 2.38 (AB, 2H, $^{2}J_{\mathrm{H-H}} = 13$ Hz, Nb−C*H*$_2$−), 2.36 (s, 6H, Nb=N(2,6-*Me*$_2$C$_6$H$_3$)), 1.95 (dd, H_d, $^{2}J_{\mathrm{c-d}} = 14.6$ Hz), 1.65 (dd, H_c, $^{3}J_{\mathrm{c-e}} = 1.6$ Hz), 1.40 (s, 3H), 0.96 (s, 3H, −CH$_2$C*Me*$_2$CH$_2$−), 1.16 (dd, H_b), 0.95 (dd, H_a), 0.69 (s, 9H, −C(SiMe$_3$)CH(CH$_2$C*Me*$_3$)CH$_2$−), 0.43 (s, 9H), 0.24 (s, 9H), 0.13 (s, 9H, Nb−C(Si*Me*$_3$)−, −C(SiMe$_3$)=C(Si*Me*$_3$), C$_5$H$_4$Si*Me*$_3$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-*d*$_6$): 215.3 (Nb−(Me$_3$Si)*C*=C(SiMe$_3$)−), 149.70 (Nb−(Me$_3$Si)C=*C*(SiMe$_3$)−), 135.96 (C$_\mathrm{i}$, Nb=N(2,6-Me$_2$*C*$_6$H$_3$)), 135.54, 128.73, 125.05 (C$_\mathrm{o}$, C$_\mathrm{p}$, C$_\mathrm{m}$, Nb=N(2,6-Me$_2$*C*$_6$H$_3$)), 119.54 (C$_\mathrm{i}$, *C*$_5$H$_4$SiMe$_3$), 113.94, 113.45, 111.39, 109.66 (*C*$_5$H$_4$SiMe$_3$), 61.03 (−*C*H$_\mathrm{e}$(CH$_2$CMe$_3$)), 53.57 (Nb−*C*H$_2$−), 52.74 (−CH(*C*H$_\mathrm{a,b}$CMe$_3$)), 47.01 (−*C*H$_\mathrm{c,d}$−), 36.66, 33.64 (Nb−CH$_2$C*Me*$_2$CH$_2$−), 30.43 (−C(SiMe$_3$)CH(CH$_2$C*Me*$_3$)CH$_2$−), 23.44, 22.9 (Nb=N(2,6-*Me*$_2$C$_6$H$_3$)), 2.79, 1.88, 0.47 (Nb−C(Si*Me*$_3$)−, −C(SiMe$_3$)=C(Si*Me*$_3$), C$_5$H$_4$Si*Me*$_3$). After recrystallization in hexane the complex **11** was always isolated as an impure microcrystalline reddish solid; therefore, satisfactory elemental analyses could not be obtained.

Crystal Structure Determination of Compounds 3 and 10. Crystallographic and experimental details of the crystal structure determinations are given in Table 6. Suitable crystals of complexes **3** and **10** were mounted on an Enraf-Nonius Cad 4 automatic four-circle diffractometer with bisecting geometry, equipped with a graphite-oriented monochromator and Mo Kα radiation (λ = 0.710 73 Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made.

The structures were solved, using the WINGX package,[41] by direct methods (SHELXS-97) and refined by least squares against F^2 (SHELXL-97).[42] In **3**, disorder appeared for the carbon atoms of the methyl groups linked to Si2 and were refined in two positions with 50% of occupancy. All non-hydrogen atoms were anisotropically refined. The deepest hole, −0.46, is located 1.06 Å from Nb1 and the highest peak, 0.49, at 1.07 Å from C12. The hydrogen atoms were positioned geometrically and refined by using a riding model, except those of the disordered methyl groups. In **10**, all non-hydrogen atoms were anisotropically refined. The deepest holee, −1.21, is located 0.95 Å from Nb1 and the highest peak, 1.39, at 1.02 Å from Nb1. The hydrogen atoms were positioned geometrically and refined by using a riding model.

Computational Details. The electronic structure and geometries of the [Nb(η^5-C_5H_5)R_2(HCCH)] (R = Cl, Me) model complexes were computed within the density functional theory at the BP86[43] and B3LYP[44] level using the LANL2DZ[45] basis set. A set of d polarization functions was added on C and Cl atoms. Geometries were optimized under no symmetry constraint. Parallel and perpendicular conformations of the alkyne ligand, with respect to the Cp group, were considered. The optimized geometries were characterized as energy minima or first-order saddle points (transition structures) by diagonalization of the analytically computed Hessian (vibrational frequency calculations). The calculations were performed using the Gaussian-98 package.[46]

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Note Added in Proof. Due to the consideration of *d* polarization functions (C and Cl atoms) in the calculations at the B3LYP level in our work, there are small differences in the structural parameters and energies with respect to those reported by E. Le Grognec, R. Poli, P. Richard in *J. Chem. Soc., Dalton Trans.* **2000**, 1499 for the model complex $NbCpCl_2$(HCCH).

Supporting Information Available: Tables of experimental details of the X-ray studies, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **3** and **10** (Tables S1−S5 for **3** and S18−S22 for **10**) and tables of atomic coordinates for optimized structures of [$NbCpCl_2$(HCCH)] and [NbCp$(Me)_2$(HCCH)] model complexes (Tables S6−S17). This material is available free of charge via the Internet at http://pubs.acs.org.

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