New Niobocene Alkyne Complexes: Synthesis and Characterization of Neutral and Cationic Niobium Complexes with Functionalized Alkynes. X-ray Crystal Structure of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(Cl)(η^2(*C*,*C*)-$R^1C\equiv CR^2$)] (R^1 = $C\equiv CPh$, R^2 = Ph (2b); R^1 = $CH_2CH{=}C(CH_3)_2$, R^2 = Ph (3b))

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The diyne-containing niobocene complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C*,*C*)-$R^1C\equiv CR^2$) (R^1 = $C\equiv CSiMe_3$, R^2 = $SiMe_3$ (**2a**); R^1 = $C\equiv CPh$, R^2 = Ph (**2b**); R^1 = $CH_2CH_2C\equiv CH$, R^2 = H (**2c**)) were prepared by the reaction of Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl (**1**) with the diyne reagents, $R-C\equiv C-C\equiv C-R$ (R = $SiMe_3$ or Ph) and 1,5-hexadiyne. The enyne-containing niobocene complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C*,*C*)-$R^1C\equiv CR^2$) (R^1 = $CH_2CH{=}CH_2$, R^2 = Ph (**3a**); R^1 = $CH_2CH{=}C(CH_3)_2$, R^2 = Ph (**3b**); R^1 = $CH_2C(CH_3){=}CH_2$, R^2 = Ph (**3c**); R^1 = $C(CH_3){=}CH_2$, R^2 = H (**3d**)) were also prepared in the same way, namely by the reaction of **1** with the appropriate enyne reagents. The paramagnetic niobocene complex Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-$R^1C\equiv CR^2$) (R^1 = $C\equiv CSiMe_3$, R^2 = $SiMe_3$ (**4a**)) was also synthesized from **2a** and subsequently oxidized in the presence of different neutral ligands to give the stable cationic d^2 derivatives [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-$R^1C\equiv CR^2$)(L)][BPh_4] (L = CH_3CN (**5a**); L = ^tBuNC (**5a′**)). Some diyne- and enyne-containing chloroniobocenes were alkylated by reacting with the appropriate dialkylmagnesium reagent to give the corresponding alkyl−alkyne compounds Nb(η^5-$C_5H_4SiMe_3$)$_2$(R^3)(η^2(*C*,*C*)-$R^1C\equiv CR^2$) (R^1 = $C\equiv CSiMe_3$, R^2 = $SiMe_3$, R^3 = Me (**6a**); R^1 = $CH_2CH{=}CH_2$, R^2 = Ph, R^3 = CH_2Ph (**7a**); R^1 = $CH_2CH{=}C(Me)_2$, R^2 = Ph, R^3 = Me (**7b**)). Furthermore, complex **2b** undergoes clean reaction with $Co_2(CO)_8$ to give the complex Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C*,*C*)-$R^1C\equiv CR^2$) (R^1 = CCPh(Co(CO)$_3$)$_2$, R^2 = Ph (**8b**)) through the coordination of both Co(CO)$_3$ moieties to the uncoordinated triple bond. Finally, the enyne-containing niobocene complexes **3a** and **3b** can be hydrogenated at the C=C bond using Pd/C as catalyst to give the alkyne complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C*,*C*)-$R^1C\equiv CR^2$) (R^1 = $CH_2CH_2CH_3$, R^2 = Ph (**9a**); R^1 = $CH_2CH_2CH(CH_3)_2$, R^2 = Ph (**9b**)). The structures of **2b** and **3b** were determined by single-crystal diffractometry.

Introduction

The chemistry of d-block transition metals with alkyne ligands has been well-documented.[1] However, while η^2-alkyne compounds of group 6 metals are extensively known, the range of alkyne complexes of group 5 metals is much less developed and, in the majority of the complexes described, cyclopentadienyl or aryloxide ligands are also present.[2] Certain niobium or tantalum complexes enable the polymerization and cyclization of alkynes,[3] and hence it is important to prepare and study the reactivity of new alkyne-containing complexes of these metals in order to better under-

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stand the mechanisms involved in such processes, especially as alkyne complexes of low oxidation state are likely to be intermediates. In the past few years several families of alkyne-containing bis((trimethylsilyl)cyclopentadienyl)niobium complexes have been reported by our group[4] and we are now interested in the preparation of new species with alkynes which possess, in addition to the coordinated triple bond, additional functional groups such as diynes and enynes. Diynes are versatile building blocks in organometallic synthesis,[5] and they have attracted attention in oligomerization reactions forming unsaturated macrocycles[6] or organosilicon polymers,[7] compounds which are of interest in material science or in the formation of new types of carbon networks.[8] In addition, group 4 metallocene-mediated cycloaddition reactions of diynes and enynes have been widely and extensively researched and have become powerful methods for the construction of cyclic compounds.[9]

Several examples of the interaction of disubstituted butadiynes with group 4 metallocenes "MCp_2" (Cp = cyclopentadienyl) have been described. They can react to form mononuclear complexes which exhibit a structure of type I (Figure 1).[10]Additionally, the formation of binuclear complexes of types II and III (Figure 1), both with and without cleavage of the internal C−C bond, has been observed. In fact, for different disubstituted butadiynes $R^1C{\equiv}CC{\equiv}CR^2$ ($R^1 = R^2 = Ph$, ^tBu; $R^1 = SiMe_3$, $R^2 = Ph$, ^tBu) the C_4 unit remains intact for M = Ti, giving binuclear complexes with tetradehydro-*trans*,*trans*-butadiene moieties (μ-(1−3-η):(2−4-η)-*trans*,*trans*-butadiene or "zigzag butadiyne") between the Ti centers (type III).[11] In contrast, cleavage of the diyne appears to be favored for M = Zr, giving rise to σ,π-alkynyl bridge systems (type II).[12] Recently, as a continuation of our studies on the use of unsaturated molecules in the synthesis of organometallic niobium compounds, Lewis-base-containing niobocene alkyne cationic complexes were prepared.[4f] These results encouraged us to explore the reactivity of the 16-electron species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ toward functionalized alkynes. We report here our results on the isolation of new alkyne−niobocene complexes with diyne and enyne ligands, as well as several aspects of their reactivity.

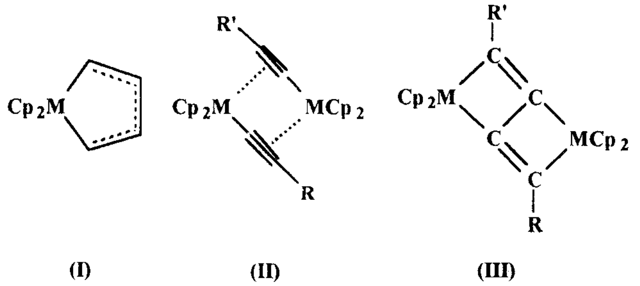

Figure 1.

Results and Discussion

We have previously reported[4] the preparation of alkyne−niobocene complexes, as well as extensive studies on their reactivity. Pursuing these results, we have now studied the behavior of the 16-electron species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**) toward functionalized alkynes, with the principal aim of extending the knowledge of this class of complexes. Thus, **1** reacts with diynes to give, in a straightforward manner, the corresponding alkyne−niobocene complexes **2a**−**c** (eq 1). The different

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl + R^1C{\equiv}CR^2 \longrightarrow Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}R^1C{\equiv}CR^2) \qquad (1)$$

2a, $R^1{=}C{\equiv}CSiMe_3$, $R^2{=}SiMe_3$
2b, $R^1{=}C{\equiv}CPh$, $R^2{=}Ph$
2c, $R^1{=}CH_2CH_2C{\equiv}CH$, $R^2{=}H$

compounds were isolated, after appropriate workup (see Experimental Section), as air-sensitive solids. In the complexes, only one of the alkyne bonds coordinates to the metal center, giving well-defined mononuclear species; no bridging alkyne was observed. This behavior contrasts with that previously described for group 4 metallocenes,[11,12] since for these complexes the reaction with disubstituted 1,3-butadiynes gives rise to complexes of the types described in Figure 1 (see above). In some cases, the central C−C single bond was cleaved and dimeric complexes containing bridged σ,π-acetylide groups were formed. In other cases, binuclear complexes

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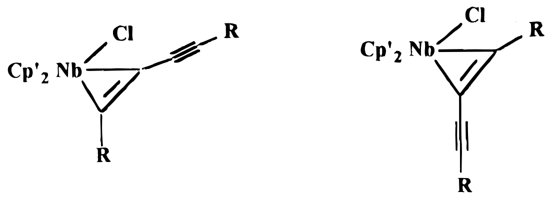

endo *exo*

Figure 2. *endo* and *exo* isomers for diyne complexes **2a** and **2b**.

with tetradehydro-*trans*,*trans*-butadiene moieties (μ-(1−3-η):(2−4-η)-*trans*,*trans*-butadiene) were isolated. The size of the metal centers and the electronic influences of the substituents were proposed as the factors influencing the different behaviors. In our reaction the cleavage of the central C−C single bond has never been observed, and a similar behavior has also been observed by Rehder and co-workers[13] in the reaction of NbI(CO)$_3$(PR$_3$)$_3$ with several diynes, where the coordination of only one acetylenic bond, to give mononuclear species, was also observed.

However, in the reaction of **1** with 1,5-hexadiyne, further reaction of the initially formed complex **2c** to give a binuclear species, [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl]$_2$(η^2(*C*,*C*)-(μ-HC≡CCH$_2$CH$_2$C≡CH)) (**2d**), takes place. In this species the diyne acts as a bridge between the niobium centers of two Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl units. Steric arguments, based on the longer length of the carbon chain in the diyne, may be used to justify the greater stability of the binuclear against the mononuclear compound.

Complex **2a** was isolated as a pure isomer from the reaction between Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl and Me$_3$SiC≡CC≡CSiMe$_3$ and purified by recrystallization from CH$_3$CN at −30 °C to give a yellow, microcrystalline solid, indefinitely stable under an argon atmosphere. However, recrystallization from pentane at −50 °C gives rise to a different isomer. This new isomer was found to rearrange in pentane or acetonitrile solutions, at room temperature, to give the former. The isomer initially obtained is considered to be thermodynamically more stable than that crystallized from pentane solution, at low temperature. The formation of this new isomer is deemed to result from a crystallization effect. On the basis of the stability of these compounds, we tentatively propose that the initially isolated species corresponds to the *endo* isomer, with the triple carbon−carbon bond in the inside position with respect to the chloro atom (see Figure 2). The second one, therefore, corresponds to the *exo* isomer, with the SiMe$_3$ group in the inside position with respect to the chloro atom, an arrangement sterically more hindered. We have previously reported several examples of this class of isomers in neutral haloketene and haloketenimine, and cationic ketenimine and alkyne complexes of niobocene,[4,14] in which the proportion of isomers was governed by steric factors, but this is the first time that the separation of both *endo* and *exo* isomers has proved possible. For complex **2b**, only the thermodynamically favored *endo* isomer was observed, whereas a mixture of both isomers was isolated in the synthesis of the nonconjugated diyne-containing complex Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl(η^2(*C*,*C*)-HC≡CCH$_2$CH$_2$C≡CH) (**2c**).

We have also studied the *exo* → *endo* isomerization process for **2a**, and to establish an intra- or intermolecular mechanism, some chemical experiments were carried out. Thus, to a solution of the *exo* isomer of **2a** (monitored by ^{1}H NMR spectroscopy in C$_6$D$_6$) was added 1,4-diphenylbutadiyne in a 1:1 molar ratio, at room temperature. After a few hours, the *endo* isomer of **2a** was quantitatively formed but none of the complex **2b** was observed. Previously, competitive kinetic studies using Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl (**1**) along with 1:1 mixtures of both diynes were carried out, from which it was concluded that the reaction rates of **1** toward 1,4-bis(trimethylsilyl)butadiyne and 1,4-diphenylbutadiyne are practically identical. Furthermore, when an equimolar mixture of **2b** and 1,4-bis(trimethylsilyl)butadiyne was dissolved in C$_6$D$_6$ and monitored by ^{1}H NMR spectroscopy over several hours, no changes were observed, showing that **2b** is stable against possible ligand exchange. These results allow us to discard a dissociative process and thus indicate that an intramolecular rearrangement takes place in the *endo*/*exo* isomerization.

The rate of conversion of the *exo* to the *endo* isomer of **2a**, monitored by the loss of its cyclopentadienyl ring proton resonances in the ^{1}H NMR (C$_6$D$_6$) spectra over a 25 °C temperature range, indicates that the reaction is first-order in the *exo* isomer. The rate constant varies from 0.5×10^{-4} s^{-1} at 293 K to 7.0×10^{-4} s^{-1} at 318 K. Above this temperature decomposition of **2a** was observed. A linear Eyring plot (5 points, $R^2 = 0.989$) of the kinetic data yielded the activation parameters for the isomerization process: $\Delta H^{\ddagger} = 76 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -66 \pm 10$ J K^{-1} mol^{-1}. Despite the apparent uncertainty affecting the thermodynamic functions, particularly $\Delta S^{\ddagger}$, due to the narrow temperature range within which the rearrangement occurs, these data provide some useful mechanistic information. In particular, the negative entropy confirms a nondissociative mechanism while the first-order law is also consistent with an intramolecular process. However, we do not have conclusive data to establish which of the reaction pathways, (i) slippage of the diyne or (ii) rotation of the diyne, operates (see Figure 3).

Following the study on the coordination of functionalized alkynes, we have also examined the behavior of the niobocene complex **1** with some enyne compounds. **1** reacted with 1 equiv of the corresponding enyne to give the enyne-containing niobocene complexes **3a**−**d** (eq 2), which were isolated, after appropriate workup (see Experimental Section), as air-sensitive solids. A mononuclear species, with the carbon−carbon triple bond coordinated to the niobium center and the carbon−carbon double bond uncoordinated, was obtained in all cases. In addition, the *endo* isomer, with the uncoordinated double bond in the inside position (see below for the X-ray crystal structure determination of **3b**), was the only isomer obtained for complexes **3a**−**d**. Therefore,

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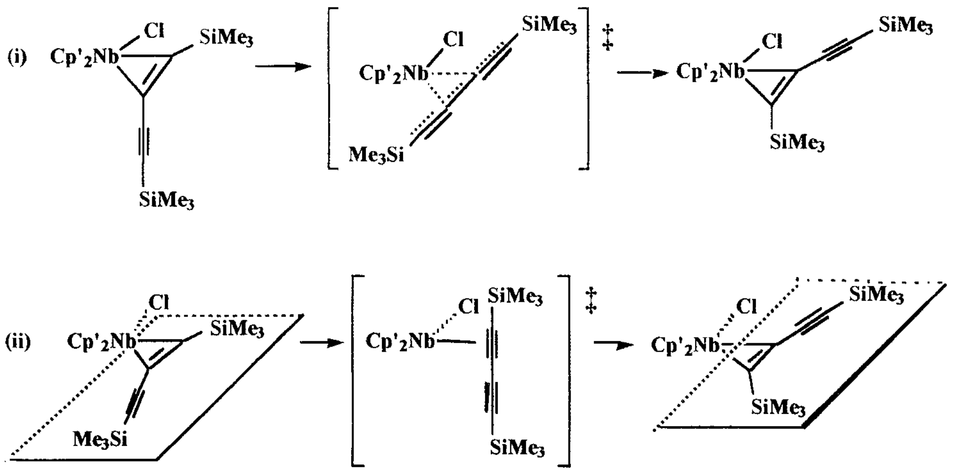

Figure 3. Proposed reaction pathways for the *endo*–*exo* isomerization in butadiyne niobocene complexes.

a selective coordination of the triple bond on the niobium center was observed.[15]

$$\underset{\mathbf{1}}{\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2Cl} + R^1C{\equiv}CR^2 \longrightarrow \mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}R^1C{\equiv}CR^2) \qquad (2)$$

$\mathbf{3a}$, $R^1{=}CH_2CH{=}CH_2$, $R^2{=}Ph$

$\mathbf{3b}$, $R^1{=}CH_2CH{=}C(CH_3)_2$, $R^2{=}Ph$

$\mathbf{3c}$, $R^1{=}CH_2C(CH_3){=}CH_2$, $R^2{=}Ph$

$\mathbf{3d}$, $R^1{=}C(CH_3){=}CH_2$, $R^2{=}H$

The paramagnetic niobium(IV) diyne complex $\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}R^1C{\equiv}CR^2)$ ($R^1 = C{\equiv}CSiMe_3$, $R^2 = SiMe_3$ (**4a**)) was easily prepared by a one-electron reduction of **2a** using Na/Hg as reducing agent and isolated, after appropriate workup (see Experimental Section), as an air-sensitive red oil. Similar reactions with **2b** gave rise to mixtures of products from which the isolation of the corresponding paramagnetic Nb(IV) species was not possible. However, the reduction (Na/Hg) of **2b** followed by treatment with $BrCH_2CH{=}CH_2$, in pentane solution, led to a mixture of products from which the bromo derivative $\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2Br(\eta^2(C,C)\text{-}PhC{\equiv}CC{\equiv}CPh)$ (**2e**) was identified, indicating that the formation of the niobium(IV) species occurs in the reduction process. We recently showed that related Nb(IV) alkyne complexes undergo reactions with alkyl halides to give mixtures of alkyl–alkyne and halo–alkyne compounds, but in this case only the niobium halo–alkyne complex was observed.[4f]

Furthermore, **4a** was reacted with 1 equiv of $[FeCp_2][BPh_4]$ ($Cp = \eta^5\text{-}C_5H_5$), in the presence of the appropriate Lewis base, to give the corresponding cationic d^2 niobocene–alkyne complexes $[\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(L)][BPh_4]$, ($L = CH_3CN$ (**5a**); $L = {}^tBuNC$ (**5a′**)), which were isolated as pure air-stable solids. The synthesis of both the paramagnetic complex **4a** and the cationic compounds **5** do not depend on which of *endo* or *exo* isomer of **2a** is employed as starting material in these reactions.

In addition, alkyl–alkyne–niobocene complexes were prepared from **2a**, **3a**, and **3b** by reaction with the appropriate dialkylmagnesium reagents, namely $Mg(CH_3)_2$ and $Mg(CH_2Ph)_2(THF)_2$. Thus, treatment of **2a** with $Mg(CH_3)_2$ gave rise to the corresponding alkyl–alkyne complex $\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(R^3)(\eta^2(C,C)\text{-}R^1C{\equiv}CR^2)$ ($R^1 = C{\equiv}CSiMe_3$, $R^2 = SiMe_3$, $R^3 = Me$ (**6a**)). The alkylation of some enyne-containing complexes was also achieved, and the corresponding alkyl derivatives $\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(R^3)(\eta^2(C,C)\text{-}R^1C{\equiv}CR^2)$ ($R^1 = CH_2CH{=}CH_2$, $R^2 = Ph$, $R^3 = CH_2Ph$ (**7a**); $R^1 = CH_2CH{=}C(Me)_2$, $R^2 = Ph$, $R^3 = Me$ (**7b**)) were isolated, after appropriate workup (see Experimental Section), by the reaction of **3a** and **3b** with $Mg(CH_2Ph)_2(THF)_2$ and $Mg(CH_3)_2$, respectively. However, the alkylation of diyne– and enyne–niobocene complexes does not always lead to the expected alkyl complexes, and instead, a mixture of intractable products is sometimes observed (for instance, this occurs in the reaction of **3a** with $Mg(CH_3)_2$ and in the reactions of both **2a** and **3b** with $Mg(CH_2Ph)_2(THF)_2$). Some niobocene alkyl–alkyne complexes have previously been synthesized.[2f,4f]

The structural characterization of functionalized alkyne-containing complexes was carried out by spectroscopic and X-ray diffraction studies. The IR spectra of the different complexes show a characteristic band at 1785–1690 cm^{-1} ($\nu_{C{\equiv}C}$) which corresponds to the coordinated alkyne unit and, in addition, one or two bands at 2133–2069 cm^{-1} corresponding to $\nu_{C{\equiv}C}$ of the uncoordinated alkyne and one band at 1660–1605 cm^{-1} corresponding to $\nu_{C{=}C}$ of the uncoordinated alkene, in the diyne- or enyne-containing complexes, respectively. In the cationic complexes **5a** and **5a′**, two additional bands (2300–2135 cm^{-1}) corresponding to $\nu_{C{\equiv}N}$[15] for nitrile or isonitrile groups are also observed.

The paramagnetic niobium(IV) complex **4a** was spectroscopically characterized by its ESR spectrum. It exhibits the characteristic 10 well-defined bands due to splitting with the ^{93}Nb nucleus ($I = {}^9/_2$, 100% abundance) centered on $g_{iso} = 2.0106$. The value of the hyperfine splitting constant ($a_{iso} = 14.4$ G) is indicative of extensive delocalization of unpaired spin density onto the acetylenic ligand and agrees with the data previously reported for other niobocene complexes with unsaturated ligands.[14a,c,17] The study of the electrochemical behavior of **4a** was undertaken in tetrahydro-

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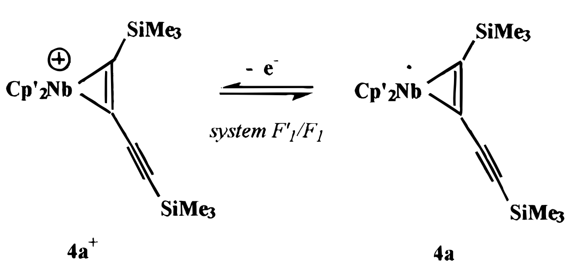
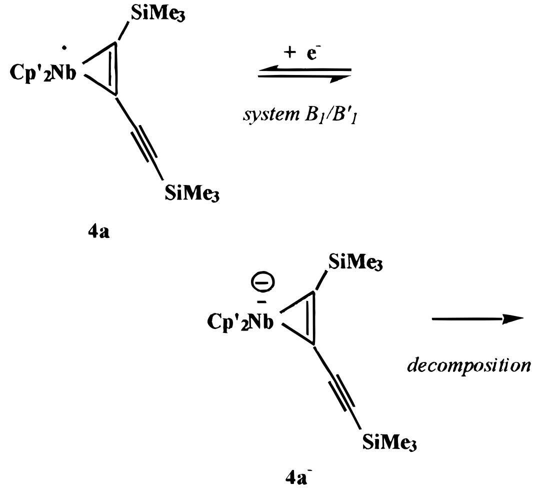
[15] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

furan, containing 0.2 M NBu_4PF_6 as supporting electrolyte, at scan rates varying between 0.02 and 10 V s^{-1}. Figure 4 shows the cyclic voltammogram recorded at $v = 0.2$ V s^{-1} on a vitreous carbon electrode between +0.2 and −2 V/ECS. The main features consist of a one-electron-oxidation process (labeled F'_1/F_1; $E_{1/2} = -0.15$ V/ECS) and a one-electron-reduction process (labeled B_1/B'_1; $E_{1/2} = -1.68$ V/ECS). Oxidation is found to be electrochemically reversible ($\Delta E_p = 80$ mV, taking into account the ohmic drop) and may be described by eq 3′,



(3)



(3″)

yielding the 16-electron species **4a**$^+$, which probably adds a THF molecule to obtain the more stable 18-electron configuration. In the presence of a suitable ligand (CH_3CN or ^tBuNC) the corresponding adducts, **5a** and **5a′**, can be isolated from chemical oxidation of **4a** (see above).

The electroreduction process seems to be more complicated. It affords initially the corresponding anionic derivative **4a**$^-$ (eq 3″), which is oxidized at the potential of peak B'_1. The latter seems to be unstable, since the size of B'_1 relative to B_1 decreases as the scan rate becomes lower as a broad peak emerges at −1.2 V, but we do not have precise information about the chemical evolution of **4a**$^-$.

The ^1H and ^{13}C NMR spectra for complexes **2**, **3**, **5**, **6**, and **7** show the characteristic resonances for the diyne and enyne ligands (see Experimental Section). In complexes **5a** and **5a′**, the signals of the coordinated nitrile and isonitrile in the ^1H NMR spectrum, measured in CD_3CN solution, are slightly shifted with respect to those of the free ligands. The ^1H and ^{13}C NMR spectra of the alkyl−alkyne complexes **6a** and **7a**,**b** show the characteristic resonances of an alkyl group bound to a niobium atom. The ^{13}C NMR spectra of both neutral and cationic alkyne complexes exhibit two resonances between ca. 140 and 165 ppm assigned to the two, nonequivalent η^2-alkyne carbon atoms (see Experimental Section and Tables1 and 2). In the diyne-containing complexes two additional resonances around 100 ppm, which correspond to the nonequivalent uncoordinated alkyne carbon atoms, are also observed. The coordination shifts $\Delta\delta = \delta_{\text{coord diyne}} - \delta_{\text{free diyne}}$ amount to ca. 12 ppm (internal carbon atom) and ca. 20−25 ppm (external carbon atom), indicating that a typical carbon−carbon triple bond character remains in this uncoordinated bond after the coordination of the diyne (see Table 1). Similarly, the ^{13}C NMR spectra of the enyne-containing complexes show two additional resonances between 140 and 110 ppm for the olefinic carbon atoms (see Table 2), which are weakly influenced by the coordination of the corresponding enyne through the carbon−carbon triple bond. The coordination shifts $\Delta\delta = \delta_{\text{coord enyne}} - \delta_{\text{free enyne}}$ amount to ca. 0 ppm for both olefinic carbon atoms in the case of the nonconjugated enyne-containing complexes, and the $\Delta\delta$ values are slightly higher for **3d**, which possesses a conjugated double bond.

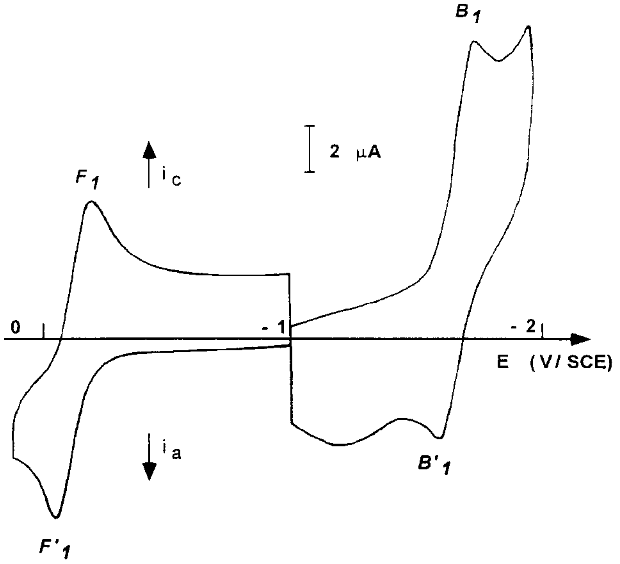


Figure 4. Cyclic voltammogram of **4a** in THF/0.2 M NBu_4PF_6 on a carbon-disk electrode (sweep rate, 200 mV s^{-1}; initial potential, −1 V).

The proposed structures for complexes **2** and **3** were unequivocally confirmed by the X-ray crystal structures for **2b** and **3b**. Views of both complexes, which adopt the typical bent-metallocene structure, are shown in Figures 5 and 6, respectively, together with the atom-numbering schemes. Selected bond distances and angles are given in Table 3. The critical feature in both structures is the alkyne unit (diyne and enyne, respectively) which adopts an *endo* conformation with respect to the chloride ligand. The values of the angles Nb(1)−C(5)−C(15) and Nb(1)−C(6)−C(7) (Figure 5) and Nb(1)−C(2)−C(3) and Nb(1)−C(1)−C(11) (Figure 6) are clear evidence of almost sp^2 hybridization at those acetylenic

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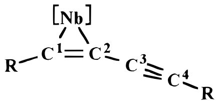
(16) (a) Antiñolo, A.; Fajardo, M.; Gil-Sanz, R.; López-Mardomingo, C.; Otero, A.; Atmani, A.; Kubicki, M. M.; El Krami, S.; Mugnier, Y.; Mourad, Y. *Organometallics* **1994**, *13*, 1200. (b) Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406. (c) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610.

(17) (a) Chollet, H.; Lucas, D.; Mugnier, Y.; Antiñolo, A.; Otero, A.; Fajardo, M. *J. Organomet. Chem.* **1992**, *441*, 45. (b) Antiñolo, A.; Fajardo, M.; de Jesús, E.; Otero, A.; Mugnier, Y. *J. Organomet. Chem.* **1994**, *470*, 127.

Table 1. Selected ^{13}C NMR Spectral Data for Neutral and Cationic Diyne−Niobocene Complexes 2a,b,d and 5a,a′



	δ C^1			δ C^2			δ C^3			δ C^4		
	coord alkyne	free alkyne	$\Delta\delta(C^1)$	coord alkyne	free alkyne	$\Delta\delta(C^2)$	coord alkyne	free alkyne	$\Delta\delta(C^3)$	coord alkyne	free alkyne	$\Delta\delta(C^2)$
2a-endo[a]	155.95	86.06	69.89	148.83	89.49	59.34	101.94	89.49	12.45	105.76	86.06	19.70
2a-exo[b]	164.71	86.06	78.65	144.54	89.49	55.05	100.48	89.49	10.99	103.63	86.06	17.57
2b[a]	163.63	83.00	80.63	136.72	75.70	61.02	89.35	75.70	13.65	109.54	83.00	26.54
2e[a]	159.72	83.00	76.72	136.23	75.70	60.53	90.01	75.70	14.31	111.60	83.00	28.60
5a[c]	148.13	86.06	62.07	141.79	89.49	52.30	102.58	89.49	13.09	108.60	86.06	22.54
5a'[c]	140.42	86.06	54.36	121.63	89.49	32.14	102.23	89.49	12.74	109.56	86.06	23.50

[a] Solvent C_6D_6. [b] Solvent $CD_3C_6D_5$; temperature −40 °C. [c] Solvent CD_3CN.

Table 2. Selected ^{13}C NMR Spectral Data for the Enyne−Niobocene Complexes 3a−d and 7a,b

$PhC{\equiv}CCH_2CR{=}CR^1R^2$

	$Ph\boldsymbol{C}{\equiv}C-$			$PhC{\equiv}\boldsymbol{C}-$			$-\boldsymbol{C}H_2-$			$-\boldsymbol{C}R{=}CR^1R^2$			$-CR{=}\boldsymbol{C}R^1R^2$		
	coord enyne	free enyne[b]	$\Delta\delta$	coord enyne	free enyne[b]	$\Delta\delta$	coord enyne	free enyne[b]	$\Delta\delta$	coord enyne	free enyne[b]	$\Delta\delta$	coord enyne	free enyne[b]	$\Delta\delta$
3a[a]	147.81	86.52	61.29	140.26	82.85	57.41	33.65	23.61	10.04	136.35	132.38	3.97	115.50	116.09	-0.59
3b[a]	146.89	88.90	57.99	142.32	80.03	62.29	28.31	29.46	-1.15	122.27	124.03	−1.76	137.76	133.82	3.94
3c[a]	147.11	87.08	60.03	144.45	82.80	61.65	36.84	28.15	8.69	140.18	140.52	−0.34	112.42	111.77	0.60
7a[a]	146.71	86.52	60.19	139.74	82.85	56.89	32.45	23.61	8.84	135.85	132.38	3.47	114.50	116.09	-1.59
7b[a]	147.78	88.90	58.88	144.96	80.03	64.93	27.70	29.46	−1.76	123.19	124.03	-0.84	139.44	133.82	5.66

$HC{\equiv}CC(Me){=}CH_2$[b]

	$H\boldsymbol{C}{\equiv}C-$			$HC{\equiv}\boldsymbol{C}-$			$-\boldsymbol{C}(Me){=}CH_2$			$-C(Me){=}\boldsymbol{C}H_2$		
3d[b]	133.12	76.03	57.09	158.78	84.84	73.94	140.95	125.92	15.03	119.60	123.23	−3.63

[a] Solvent C_6D_6. [b] Solvent $CDCl_3$.

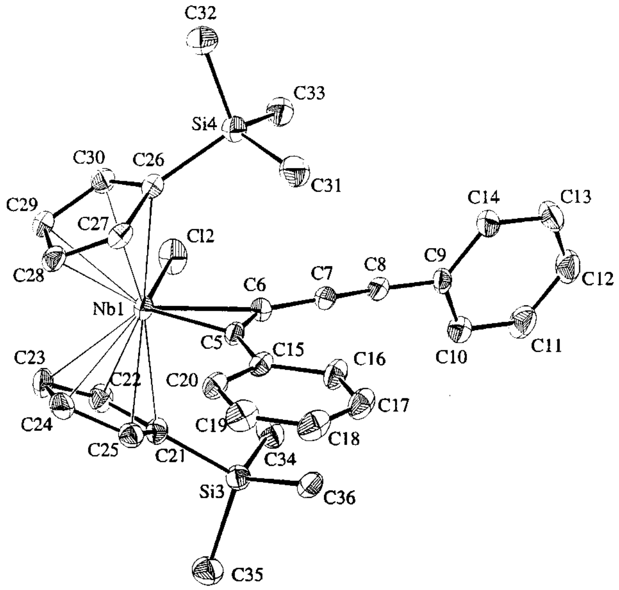


Figure 5. ORTEP drawing of complex **2b**.

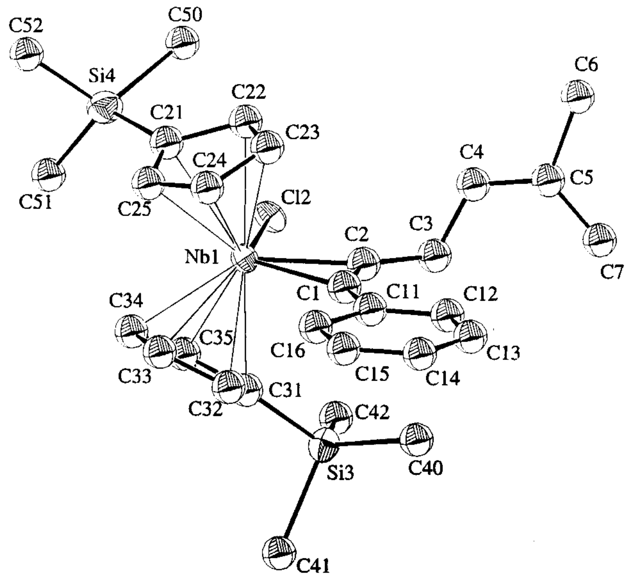


Figure 6. ORTEP drawing of complex **3b**.

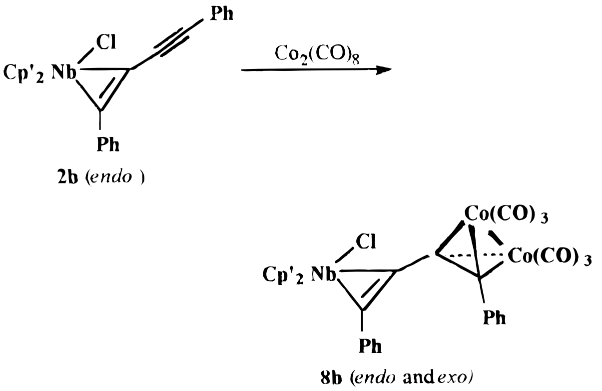
carbon atoms. Further proof of this hybridization is provided by the bond distances C(5)−C(6) (1.282(7) Å) and C(1)−C(2) (1.22(2) Å), which are slightly shorter than a typical carbon−carbon double bond. ^{13}C NMR spectroscopic data (see above) support these results, indicating that the coordinated alkyne in **2b** and **3b** behaves as a two-electron ligand.[18] The bond distance of the uncoordinated alkyne in **2b** (C(7)−C(8) = 1.200(6) Å) does not deviate from that of the free alkyne.[19] In

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2b and 3b.

	Compound **2b**		
Nb(1)−C(5)	2.155(4)	C(5)−Nb(1)−C(6)	34.4(2)
Nb(1)−C(6)	2.177(5)	C(6)−C(5)−C(15)	137.9(4)
Nb(1)−Cl(2)	2.513(5)	Nb(1)−C(5)−C(15)	148.2(3)
C(5)−C(6)	1.282(6)	C(5)−C(6)−C(7)	144.1(5)
C(5)−C(15)	1.468(6)	Nb(1)−C(6)−C(7)	143.8(4)
C(6)−C(7)	1.402(6)	C(8)−C(7)−C(6)	176.8(5)
C(7)−C(8)	1.200(6)	C(7)−C(8)−C(9)	177.5(5)
C(8)−C(9)	1.434(6)		
	Compound **3b**		
Nb(1)−C(2)	2.136(14)	C(2)−Nb(1)−C(1)	32.7(5)
Nb(1)−C(1)	2.197(13)	C(2)−C(1)−C(11)	144(1)
Nb(1)−Cl(2)	2.660(3)	Nb(1)−C(1)−C(11)	144(1)
C(1)−C(2)	1.22(2)	C(1)−C(2)−C(3)	142(2)
C(1)−C(11)	1.43(2)	Nb(1)−C(2)−C(3)	141(1)
C(2)−C(3)	1.51(2)	C(4)−C(3)−C(2)	116(2)
C(3)−C(4)	1.43(2)	C(5)−C(4)−C(3)	127(2)
C(4)−C(5)	1.31(2)	C(4)−C(5)−C(7)	126(2)
C(5)−C(6)	1.53(3)	C(4)−C(5)−C(6)	116(2)
C(5)−C(7)	1.46(3)	C(7)−C(5)−C(6)	118(2)

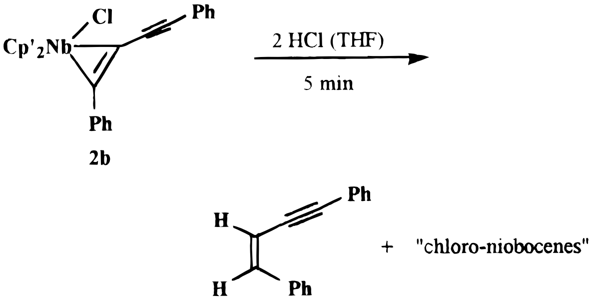
the structure of **2b**, the four atoms Nb(1), C(5), C(6), and Cl(2) are essentially coplanar and the phenyl group is also coplanar with the Nb(1), C(5), and C(6) atoms. Similarly, in the structure of **3b** the phenyl group is practically coplanar with the Nb(1), C(1), and C(2) atoms, while the plane which contains the olefinic moiety deviateds 107° from the Nb(1)−C(1)−C(2) plane.

Finally, several aspects of the reactivity of complexes **2** and **3** were considered. First, we studied the reactivity of the uncoordinated alkyne bond in **2b**. This complex did not react with $Zr(\eta^5\text{-}C_5H_5)_2(H)(Cl)$ or $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)$ (**1**). However, a successful reaction with $Co_2(CO)_8$ was found. In fact, complex **2b** reacts cleanly with $Co_2(CO)_8$ to give, after appropriate workup, the niobocene complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}R^1C{\equiv}CR^2)$ ($R^1 = CCPh(Co(CO)_3)_2$, $R^2 = Ph$ (**8b**) (eq 4)). The complex **8b** was isolated as a mixture of both *endo* and *exo* isomers, where the carbon−carbon triple bond is coordinated to both $Co(CO)_3$ moieties. The reagent $Co_2(CO)_8$ has been extensively employed as a protecting group for alkynes.[20] The IR spectrum of complex **8b** exhibits three characteristic ν(CO) bands at ca. 2000 cm^{-1}, in accordance with the data described previously for analogous complexes.[21] The signals in the ^{13}C NMR spectrum for the alkyne carbon atoms coordinated to the two metal centers, four signals for each isomer, fall in the range 166−136 ppm, and in addition, we observe two resonances at ca. 200 ppm which correspond to the carbonyl groups (see Experimental Section).



(4)

The treatment of **2b** with a THF solution of HCl, in a slight excess of the 1:2 molar ratio, gave rise to the selective formation of (*Z*)-1,4-diphenyl-1-buten-3-yne along with a mixture of Nb(V)-containing chloro−niobocene complexes, from which $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ was identified in a small amount (eq 5). In this reaction, the coordinated triple bond of **2b** behaves as a 1,2-dianion which undergoes a double selective protonation. A similar behavior was previously described for niobium complexes containing nonfunctionalized alkynes[17a] and imines[22] as ligands. The organic product was identified by comparison of its spectroscopic data with those of a genuine sample.[23]



(5)

In addition, catalytic hydrogenations of the uncoordinated carbon−carbon double bond in complexes **3a** and **3b** were carried out. Thus, the C═C bonds were selectively reduced with H_2 (1.2 atm) in the presence of Pd/C(5%) as catalyst, giving rise to the corresponding alkyne complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}R^1C{\equiv}CR^2)$ ($R^1 = CH_2CH_2CH_3$, $R^2 = Ph$ (**9a**); $R^1 = CH_2CH_2CH(CH_3)_2$ $R^2 = Ph$ (**9b**)). The complexes were spectroscopically characterized, the IR spectra showing a band at ca. 1700 cm^{-1} ($\nu_{C\equiv C}$) characteristic of the coordinated alkyne unit and the ^1H NMR spectra showing a pattern of signals characteristic of the saturated R^1 alkyl groups.

Furthermore, the alkyne ligand can be cleanly separated from the niobium moiety by irradiation of $CHCl_3$ or CH_2Cl_2 solutions of the halo−alkyne−niobocene complexes. These reactions were first essayed with several nonfunctionalized alkyne-containing complexes and then with the diyne and enyne compounds, and from these experiments, the reaction conditions were determined. For instance, **9a** and **9b** were separately irradiated for 1 h at room temperature in $CDCl_3$ (monitored by ^1H NMR spectroscopy) and the ^1H NMR spectra of the reaction mixtures showed the presence of the corresponding enyne ligand with none of the starting complexes. In these experiments, the complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ crystallized as green needles from the solution and was separated by filtration. The remaining solution, which contains the free alkyne and

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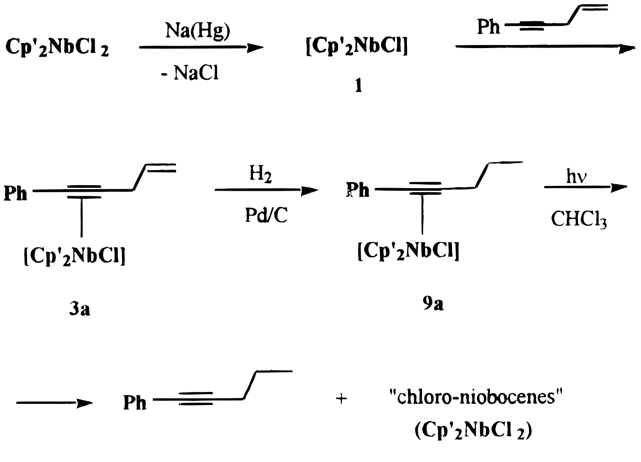
Scheme 1



a residue of nonidentified chloro−niobocenes, was distilled under vacuum and the alkyne ligand isolated, after removal of the solvent. Despite the low number of examples studied, these reactions show that the complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**) can probably be considered as a protective group for the carbon−carbon triple bond in the catalytic hydrogenation of enynes. The reaction sequence followed for a nonconjugated enyne complex is depicted in Scheme 1. Complex **1** is easily obtained from the one-electron reduction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ and then coordinated to the enyne to give the corresponding complex **3a**. The uncoordinated C=C bond is hydrogenated, giving rise to the alkyne complex **9a**, and finally, the ligand containing the unaffected triple bond is separated from the organometallic fragment.

Concluding Remarks

We have considered the behavior of the 16-electron species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**) toward functionalized alkynes, such as diynes and enynes. The reaction is highly regioselective and has allowed the synthesis of new families of mononuclear η^2-C≡C niobocene complexes where uncoordinated alkyne and olefin units, respectively, are also present.

Reduction, oxidation, and alkylation reactions of these complexes were carried out to give new families of neutral or cationic diyne- and enyne-containing niobocene complexes. This study has revealed that the behavior of the diyne or enyne compounds is similar to that found for the nonfunctionalized alkyne-containing niobocene derivatives.

Finally, several aspects of the reactivity of the uncoordinated unit in these complexes were studied. Particularly, the treatment of the enyne complexes with H_2 produced the exclusive reduction of the noncoordinated carbon−carbon double bond of the enyne ligands. We believe that the results reported offer a significant advance in the chemistry of the functionalized alkyne toward organometallic complexes, and work in this field is ongoing.

Experimental Section

General Considerations. The complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**)[24] and the enynes $PhC{\equiv}CCH_2CH{=}CH_2$, $PhC{\equiv}CCH_2CH{=}C(CH_3)_2$, and $PhC{\equiv}CCH(CH_3)CH{=}CH_2$[25] were prepared by published methods. The synthesis of the alkylmagnesium compounds MgR_2 has also been previously reported.[26]

All reactions were carried out under an inert atmosphere (argon) using standard Schlenk techniques. Solvents were freshly distilled from appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin-Elmer 240B microanalyzer. NMR spectra were recorded on Varian Unity FT-300 and FT-500 PLUS instruments. IR spectra were recorded as Nujol mulls between CsI windows or with the sample pressed into a KBr disk (in the region 4000−200 cm^{-1}) on a Perkin-Elmer PE 833 IR spectrometer. Mass spectral analyses were performed on a VG Autospec instrument using FAB techniques and NBA as matrix for cationic compounds, while for most of the neutral compounds they were recorded on a Hewlett-Packard 5988A, *m*/*z* 50−1000, using chemical ionization techniques.

Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode (SCE) separated from the analyzed solution by a sintered-glass disk; the auxiliary electrode was a platinum wire. For all voltammetric measurements the working electrode was a carbon-disk electrode initially polished with alumina. Supporting electrolytes were purchased from Fluka (purissimum p.a. for electrochemical grade), the salts being dried and deoxygenated under vacuum immediately before use.

Synthesis. $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)$ (2a). To a suspension of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**; 909 mg, 2.26 mmol) in hexane (20 mL) was added $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (449 mg, 2.31 mmol). The mixture was stirred for 7 h, giving a brown solution, which was then evaporated to dryness to give a brown oily solid (1.11 g, 1.86 mmol, 82%).The compound prepared in this way was sufficiently pure for subsequent use, but it could also be recrystallized from cold acetonitrile (−40 °C), precipitating a yellow powder which was subsequently isolated by filtration and dried in vacuo. The spectroscopic data confirmed that both the oil and the yellow solid were each a pure isomer of one of the two possible *endo*−*exo* isomers. The second isomer was isolated in a pure form by slow recrystallization of the first one from a saturated pentane solution at −50 °C. The complexes obtained were assigned to the *endo* and *exo* isomers of **2a,** respectively. *endo* isomer: IR (pure product): 2069, 2118 (free C≡C), 1715 (coord C≡C) cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 0.26 (s, 18H, $C_5H_4Si\mathit{Me}_3$), 0.28, 0.56 (s, 9H, $\mathit{Me}_3SiC{\equiv}CC{\equiv}CSi\mathit{Me}_3$), 5.34−5.44 (2H), 5.52−5.64 (4H), 5.78−5.86 (2H) (m, $C_5\mathit{H}_4SiMe_3$); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 0.37 ($C_5H_4Si\mathit{Me}_3$), 1.20 ($\mathit{Me}_3SiC{\equiv}CC{\equiv}CSi\mathit{Me}_3$), 101.94 ($Me_3SiC{\equiv}\mathit{C}C{\equiv}CSiMe_3$, $C{\equiv}C_{free}$), 105.76 ($Me_3Si\mathit{C}{\equiv}CC{\equiv}CSiMe_3$, $C{\equiv}C_{free}$), 104.47, 107.80, 115.88, 118.77, 120.30 ($\mathit{C}_5H_4SiMe_3$), 148.83 ($Me_3SiC{\equiv}C\mathit{C}{\equiv}CSiMe_3$, $C{\equiv}C_{coord}$), 155.95 ($Me_3Si\mathit{C}{\equiv}CC{\equiv}CSiMe_3$, $C{\equiv}C_{coord}$); CI-MS *m*/*e* (relative intensity) 597 (5) ($[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(Cl)]^+ + 1$), 561 (12) ($M^+ - Cl$), 546 (14) ($M^+ - Cl - Me$), 402 (68) ($M^+ - Me_3SiC{\equiv}CC{\equiv}CSiMe_3$), 367 (4) ($M^+ - Cl - Me_3SiC{\equiv}CC{\equiv}CSiMe_3$). Anal. Calcd for $C_{26}H_{44}ClNbSi_4$: C, 52.30; H, 7.47. Found: C, 51.81; H, 7.45. *exo* isomer: IR (Nujol mull) 2098, 2133 (free C≡C), 1691 (coord C≡C) cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 0.25, 0.34 (s, 9H, $\mathit{Me}_3SiC{\equiv}CC{\equiv}CSi\mathit{Me}_3$), 0.34 (s, 18H, $C_5H_4Si\mathit{Me}_3$), 4.90−4.95 (2H), 5.20−5.25 (2H), 5.45−5.50 (2H), 5.80−5.85 (2H) (m, $C_5\mathit{H}_4SiMe_3$);$^{13}C\{^1H\}$ NMR (75 MHz, $CD_3C_6D_5$, −40 °C): δ 0.46 ($C_5H_4Si\mathit{Me}_3$), 0.57, 0.71 ($\mathit{Me}_3SiC{\equiv}CC{\equiv}CSiMe_3$), 100.48 ($Me_3SiC{\equiv}\mathit{C}C{\equiv}CSiMe_3$, $C{\equiv}C_{free}$), 103.63 ($Me_3Si\mathit{C}{\equiv}CC{\equiv}CSiMe_3$, $C{\equiv}C_{free}$), 107.62, 108.60, 115.64, 122.36, 122.75 ($\mathit{C}_5H_4SiMe_3$),

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144.54 ($Me_3SiC{\equiv}\mathit{C}C{\equiv}CSi(CH_3)_3$, $C{\equiv}C_{coord}$), 164.71 ($Me_3Si\mathit{C}{\equiv}CC{\equiv}CSiMe_3$, $C{\equiv}C_{coord}$). Anal. Calcd for $C_{26}H_{44}ClNbSi_4$: C, 52.30; H, 7.47. Found: C, 51.95; H, 7.38.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}PhC{\equiv}CC{\equiv}CPh)$ (2b). To a suspension of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**; 960 mg, 2.38 mmol) in hexane (25 mL) was added $PhC{\equiv}CC{\equiv}CPh$ (482 mg, 2.38 mmol). The resulting suspension was stirred for 7 h at room temperature to give a yellow solid. After filtration, the solid was washed twice with cold hexane, dried under vacuum, and identified as a pure isomer of **2b** (1.18 g, 1.95 mmol, 82.5%). The yellow powder was recrystallized from a mixture of dichloromethane and hexane, giving yellow monocrystals of **2b**. The X-ray diffraction studies confirmed the *endo* configuration of this complex. IR (KBr): 2158 (free $C{\equiv}C$), 1729 (coord $C{\equiv}C$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 0.26 (s, 18H, $Si\mathit{Me}_3$), 5.12−5.16 (2H), 5.23−5.27 (2H), 5.81−5.85 (2H), 6.09−6.13 (2H) (m, $C_5\mathit{H}_4SiMe_3$), 6.92−6.98 (1H), 7.01−7.08 (2H), 7.12−7.18 (1H), 7.30−7.37 (2H), 7.71−7.78 (4H) (m, H phenyl groups). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ −0.11 ($Si\mathit{Me}_3$), 89.35 ($PhC{\equiv}\mathit{C}C{\equiv}CPh$, $C{\equiv}C_{free}$), 109.54 ($Ph\mathit{C}{\equiv}CC{\equiv}CPh$, $C{\equiv}C_{free}$), 101.55, 104.29, 113.74, 116.22, 127.32 ($\mathit{C}_5H_4SiMe_3$), 124.38, 128.68, 130.19, 132.18 (C phenyl group *endo*), 125.81, 128.56, 129.00, 132.32 (C phenyl group *exo*), 136.72 ($PhC{\equiv}\mathit{C}C{\equiv}CPh$, $C{\equiv}C_{coord}$), 163.63 ($Ph\mathit{C}{\equiv}CC{\equiv}CPh$, $C{\equiv}C_{coord}$). Anal. Calcd for $C_{32}H_{36}ClNbSi_2$: C, 63.54; H, 5.95. Found: C, 63.45; H, 5.90.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}HC{\equiv}CCH_2CH_2C{\equiv}CH)$ (2c). To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**; 700 mg, 1.74 mmol) in hexane (100 mL) was added $HC{\equiv}CCH_2CH_2C{\equiv}CH$ (138 mg, 1.76 mmol). The mixture was stirred for 6 h at room temperature, and the formation of a yellow precipitate was observed. The solid was separated by filtration, and the resulting solution was evaporated to dryness to yield an oily solid which was identified as an equimolar mixture of the *endo* and *exo* isomers of **2c** (170 mg, 0.35 mmol, 20%). The yellow solid isolated above was recrystallized from toluene to yield yellow needles identified as the binuclear complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]_2(\eta^2(C,C)\text{-}(\mu\text{-}HC{\equiv}CCH_2CH_2C{\equiv}CH))$ (**2d**; 530 mg, 0.6 mmol, 69%). The mononuclear complex **2c** rearranged in solution, at room temperature, to give the binuclear derivative **2d**, which is highly insoluble in the usual solvents. **2c**: IR (pure oily product) 3310 (stretch $H{-}C{\equiv}$), 2115 (free $C{\equiv}C$), 1731 (coord $C{\equiv}C$) cm^{-1}; ^1H NMR (300 MHz, C_6D_6; 1:1 mixture of *endo*−*exo* isomers) δ 0.16, 0.23 (s, 18H, $Si\mathit{Me}_3$), 1.78, 1.82 (t, ^4J = 2.56 Hz, 1H, $\mathit{H}C{\equiv}CCH_2CH_2C{\equiv}CH$, $C{\equiv}C_{free}$), 2.37 (td, ^3J = 7.65, ^4J = 2.56 Hz, 2H), 2.48 (td, ^3J = 6.90, ^4J = 2.56 Hz, 2H) ($HC{\equiv}C\mathit{CH}_2CH_2C{\equiv}CH$, methylene groups next to $C{\equiv}C_{free}$), 2.59 (t, ^3J = 7.65 Hz, 2H), 3.19 (t, ^3J = 6.90 Hz, 2H) ($HC{\equiv}C\mathit{CH}_2CH_2C{\equiv}CH$, methylene groups next to $C{\equiv}C_{coord}$), 4.82−4.87 (2H), 5.05−5.10 (2H), 5.12−5.17 (2H), 5.37−5.42 (2H), 5.40−5.45 (2H), 5.45−5.53 (4H), 5.85−5.90 (2H) (m, $C_5\mathit{H}_4SiMe_3$), 7.10, 8.14 (s, 1H, $\mathit{H}C{\equiv}CCH_2CH_2C{\equiv}CH$, $C{\equiv}C_{coord}$). **2d**: IR (KBr) 1731 (coord $C{\equiv}C$) cm^{-1}; FAB MS *m/e* (relative intensity) 882 (4) ($\{[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]_2(\eta^2(C,C)\text{-}\mu\text{-}HC{\equiv}CCH_2CH_2C{\equiv}CH)\}^+$), 847 (2) ($M^+ - Cl$), 481 (9) ($[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}HC{\equiv}CCH_2CH_2C{\equiv}CH)]^+$), 402.1 (100) ($[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]^+$). Anal. Calcd for $C_{38}H_{58}Cl_2Nb_2Si_2$: C, 51.60; H, 6.56. Found: C, 51.45; H, 6.84.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}PhC{\equiv}CCH_2CH{=}CH_2)$ (3a). To a suspension of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ (**1**; 590 mg, 1.48 mmol) in hexane (20 mL) was added $PhC{\equiv}CCH_2CH{=}CH_2$ (230 mg, 1.62 mmol, 20% excess). The mixture was stirred at room temperature for 6 h, and a yellow precipitate was formed. The solid thus obtained was washed twice with cold pentane and dried in vacuo (328 mg, 0.60 mmol, 41%). IR (KBr): 1784 (coord $C{\equiv}C$), 1631 (free $C{=}C$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 0.22 (s, 18 H, $Si\mathit{Me}_3$), 4.17 (m, ^3J = 6.95 Hz, 2H, $PhC{\equiv}C\mathit{CH}_2CH{=}CH_2$), 5.04 (ddt, ^3J = 9.88, ^2J = 1.83, ^4J = 1.83 Hz, 1H, $PhC{\equiv}CCH_2CH{=}C\mathit{H}_2$), 5.25 (ddt, ^3J = 16.88, ^2J = 1.83, ^4J = 1.83 Hz, 1H, $PhC{\equiv}CCH_2CH{=}C\mathit{H}_2$), 5.08−5.14 (2H), 5.39−5.45 (2H), 5.71−5.77 (2H), 5.88−5.94 (2H) (m, $C_5\mathit{H}_4SiMe_3$), 6.07−6.22 (m, 1H, $PhC{\equiv}CCH_2C\mathit{H}{=}CH_2$), 7.12−7.18 (m, 1H, $p\text{-}C_6\mathit{H}_5$), 7.30−7.37 (m, 2H, $m\text{-}C_6\mathit{H}_5$), 7.43−7.48 (m, 2H, $o\text{-}C_6\mathit{H}_5$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 0.16 ($Si\mathit{Me}_3$), 33.65 ($PhC{\equiv}C\mathit{C}H_2CH{=}CH_2$), 101.07, 108.43, 111.00, 118.80, 119.57 ($\mathit{C}_5H_4SiMe_3$), 115.50 ($PhC{\equiv}CCH_2CH{=}\mathit{C}H_2$), 127.51, 128.78, 130.43, 131.71, (*C* phenyl group), 136.35 ($PhC{\equiv}CCH_2\mathit{C}H{=}CH_2$), 140.26 ($PhC{\equiv}\mathit{C}CH_2CH{=}CH_2$), 147.81 ($Ph\mathit{C}{\equiv}CCH_2CH{=}CH_2$). Anal. Calcd for $C_{27}H_{36}ClNbSi_2$: C, 59.50; H, 6.61. Found: C, 59.40; H, 6.48.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}PhC{\equiv}CCH_2CH{=}C(CH_3)_2)$ (3b). This complex was obtained in 45% yield by following the same procedure as described for **3a**. IR (KBr): 1785 (coord $C{\equiv}C$), 1642 (free $C{=}C$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 0.23 (s, 18 H, $Si\mathit{Me}_3$), 1.68, 1.83 (s, 3H, $PhC{\equiv}CCH_2CH{=}C(C\mathit{H}_3)_2$), 4.19 (d, ^3J = 7.32 Hz, 2H, $PhC{\equiv}CC\mathit{H}_2CH{=}C(CH_3)_2$), 5.54−5.59 (m, 1H, $PhC{\equiv}CCH_2C\mathit{H}{=}C(CH_3)_2$), 5.05−5.11 (2H), 5.39−5.45 (2H), 5.72−5.78 (2H), 5.92−5.98 (2H) (m, $C_5\mathit{H}_4SiMe_3$), 7.18−7.22 (m, 1H, $p\text{-}C_6\mathit{H}_5$), 7.32−7.37 (m, 2H, $m\text{-}C_6\mathit{H}_5$), 7.45−7.51 (m, 2H, $o\text{-}C_6\mathit{H}_5$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 0.16 ($Si\mathit{Me}_3$), 18.35, 25.85 ($PhC{\equiv}CCH_2CH{=}C(\mathit{C}H_3)_2$), 28.31 ($PhC{\equiv}C\mathit{C}H_2CH{=}C(CH_3)_2$), 101.15, 108.28, 111.03, 119.06, 119.48 ($\mathit{C}_5H_4SiMe_3$), 122.27 ($PhC{\equiv}CCH_2\mathit{C}H{=}C(CH_3)_2$), 127.37, 128.77, 130.33, 131.96 (*C* phenyl group), 137.76 ($PhC{\equiv}CCH_2CH{=}\mathit{C}(CH_3)_2$), 142.32 ($PhC\infty\mathit{C}CH_2CH{=}C(CH_3)_2$), 146.89 ($Ph\mathit{C}{\equiv}CCH_2CH{=}C(CH_3)_2$). Anal. Calcd for $C_{29}H_{40}ClNbSi_2$: C, 60.78; H, 6.98. Found: C, 60.94; H, 6.80.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}PhC{\equiv}CCH_2C(CH_3){=}CH_2)$ (3c). This complex was obtained in 40% yield by following the same procedure as described for **3a**. IR (KBr): 1782 (coord $C{\equiv}C$), 1650 (free $C{=}C$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 0.23 (s, 18H, $Si\mathit{Me}_3$), 1.72 (s, 3H, $PhC{\equiv}CCH_2C(C\mathit{H}_3){=}CH_2$), 4.17 (s, 2H, $PhC{\equiv}CC\mathit{H}_2C(CH_3){=}CH_2$), 4.90−4.94 (1H), 5.05−5.09 (1H) (m, $PhC{\equiv}CCH_2C(CH_3){=}C\mathit{H}_2$), 5.12−5.18 (2H), 5.40−5.46 (2H), 5.67−5.73 (2H), 5.84−5.90 (2H) (m, $C_5\mathit{H}_4SiMe_3$), 7.10−7.14 (m, 1H $p\text{-}C_6\mathit{H}_5$), 7.30−7.36 (m, 2H $m\text{-}C_6\mathit{H}_5$), 7.47−7.53 (m, 2H $o\text{-}C_6\mathit{H}_5$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 0.18 ($Si\mathit{Me}_3$), 23.52 ($PhC{\equiv}CCH_2C(\mathit{C}H_3){=}CH_2$), 36.84 ($PhC{\equiv}C\mathit{C}H_2C(CH_3){=}CH_2$), 100.92, 108.31, 112.10, 118.03, 119.26 ($\mathit{C}_5H_4SiMe_3$), 112.42 ($PhC{\equiv}CCH_2C(CH_3){=}\mathit{C}H_2$), 128.30, 128.70, 130.67, 137.36 (*C* phenyl group), 140.18 ($PhC{\equiv}CCH_2\mathit{C}(CH_3){=}CH_2$), 144.45 ($PhC{\equiv}\mathit{C}CH_2C(CH_3){=}CH_2$), 147.11 ($Ph\mathit{C}{\equiv}CCH_2C(CH_3){=}CH_2$). Anal. Calcd for $C_{28}H_{38}ClNbSi_2$: C, 60.14; H, 6.80. Found: C, 60.03; H, 6.75.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}PhC{\equiv}CC(CH_3){=}CH_2)$ (3d). This complex was obtained in 74% yield by following the same procedure as described for **3a**. IR (KBr): 1694 (coord $C{\equiv}C$), 1605 (free $C{=}C$) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 18H, $Si\mathit{Me}_3$), 2.12 (s, 3H, $HC{\equiv}CC(C\mathit{H}_3){=}CH_2$), 4.92 (1H), 5.43 (1H) (m, $HC{\equiv}CC(CH_3){=}C\mathit{H}_2$), 5.50−5.60 (2H), 5.60−5.70 (2H), 5.95−6.05 (2H), 6.05−6.15 (2H) (m, $C_5\mathit{H}_4SiMe_3$), 7.47 (s, 1H, $\mathit{H}C{\equiv}CC(CH_3){=}CH_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ −0.52 ($Si\mathit{Me}_3$), 25.09 ($HC{\equiv}CC(\mathit{C}H_3){=}CH_2$), 100.90, 103.58, 111.72, 115.02, 125.86 ($\mathit{C}_5H_4SiMe_3$), 119.60 ($HC{\equiv}CC(CH_3){=}\mathit{C}H_2$), 133.12 ($H\mathit{C}{\equiv}CC(CH_3){=}CH_2$), 140.95 ($HC{\equiv}C\mathit{C}(CH_3){=}CH_2$), 158.78 ($HC{\equiv}\mathit{C}C(CH_3){=}CH_2$). Anal. Calcd for $C_{21}H_{32}ClNbSi_2$: C, 53.8; H, 6.83. Found: C, 53.76; H, 6.94.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)$ (4a). $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)$ (**2a**; 900 mg, 1.50 mmol) was reduced with 1.74 mequiv of Na/Hg in THF. The mixture was vigorously stirred for 1 h, and then the THF was removed in vacuo. The residue was extracted with 100 mL of hexane at room temperature and the solvent subsequently removed to give a red oil (710 mg, 1.26 mmol, 84%). **4a** was characterized by IR, mass, and ESR spectroscopy (see Results and Discussion). IR (pure product): 2114 cm^{-1} (free $C{\equiv}C$), 1720 cm^{-1}(coord $C{\equiv}C$). CI MS: *m/e* (relative intensity) 562 (44) ($M^+ + 1$), 561 (28) (M^+, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)]^+$), 546 (47) ($M^+ - Me$), 473 (51) ($M^+ - Me - SiMe_3$), 367 (36) ($M^+ - Me_3SiC{\equiv}CC{\equiv}CSiMe_3$).

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(^tBuNC)][BPh_4]$ (5a). The paramagnetic complex **4a** (220 mg, 0.39 mmol) was oxidized with 1 equiv of $[FeCp_2][BPh_4]$ (200 mg, 0.39 mmol), in the presence of an excess of *tert*-butyl isocyanide (0.51 mmol), in THF at −25 °C. The reaction mixture was then stirred for 1 h while being warmed from −25 °C to room temperature. After this time, the mixture was evaporated to dryness and the residue washed with cold diethyl ether to yield a brown solid identified as **5a** (138 mg, 0.246 mmol, 63%). IR (KBr): 2174 ($C\equiv N$), 2115, 2135 (free $C\equiv C$), 1719 (coord $C\equiv C$) cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ 0.26, 0.28 (s, 9H, $Me_3SiC\equiv CC\equiv CSiMe_3$, nonequivalent *endo−exo* methyl groups), 0.29 (s, 18H, $C_5H_4SiMe_3$), 1.71 (s, 9H, ^tBu), 5.43−5.49 (2H), 5.53−5.59 (2H), 5.61−5.66 (2H), 5.87−5.93 (2H) (m, $C_5H_4SiMe_3$), 6.78−6.88 (m, 4H, *p*-C_6H_5), 6.94−7.04 (m, 8H, *m*-C_6H_5), 7.22−7.32 (m, 8H, *o*-C_6H_5) (phenyl groups of $[BPh_4]^-$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ −0.01 ($C_5H_4SiMe_3$), 0.18, 0.26 ($Me_3SiC\equiv CC\equiv CSiMe_3$, nonequivalent *endo−exo* methyl groups), 30.27 ($CNC(CH_3)_3$), 62.63 ($CNC(CH_3)_3$), 102.23 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{free}$), 109.56 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{free}$), 103.71, 107.65, 111.34, 117.19, 117.63 ($C_5H_4SiMe_3$), 121.63 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{coord}$), 122.77, 126.58, 136.83 (C phenyl groups of $[BPh_4]^-$), 140.42 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{coord}$), 164.56 (c, $J_{^{11}B-^{13}C} = 49.45$ Hz, C_{ipso} of $[BPh_4]^-$), 207.34 (^tBuNC). Anal. Calcd for $C_{55}H_{73}BNNbSi_4$: C, 68.55; H, 7.57; N, 1.45. Found: C, 68.07; H, 7.46; N, 1.46.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC\equiv CC\equiv CSiMe_3)(CH_3CN)][BPh_4]$ (5a′). A solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3Si\equiv CC\equiv CSiMe_3)$ (**4a**; 710 mg, 1.26 mmol) in 10 mL of CH_3CN was treated with 1 equiv of $[FeCp_2][BPh_4]$ (640 mg, 1.26 mmol) at −50 °C for 30 min. The mixture was evaporated to dryness, and an olive green powder was then precipitated by addition of cold hexane to the residue (660 mg, 718 mmol, 57%). IR (Nujol): 2300, 2279 ($CH_3C\equiv N$), 2119, 2067 (free $C\equiv C$), 1709 (coord $C\equiv C$) cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ 0.24, 0.26 (s, 9H, $Me_3SiC\equiv CC\equiv CSiMe_3$, nonequivalent *endo−exo* methyl groups), 0.28 (s, 18H, $C_5H_4SiMe_3$), 2.49 (s, 3H, CH_3CN), 5.60−5.65 (2H), 5.82−5.90 (4H), 6.01−6.06 (2H) (m, $C_5H_4SiMe_3$), 6.81−6.88 (m, 4H, *p*-C_6H_5), 6.95−7.04 (m, 8H, *m*-C_6H_5), 7.24−7.33 (m, 8H, *o*-C_6H_5) (phenyl groups of $[BPh_4]^-$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ −0.09 ($C_5H_4Si(CH_3)_3$), 0.07, 0.95 ($(CH_3)_3SiC\equiv C\ C\equiv CSi(CH_3)_3$, nonequivalent *endo−exo* groups), 6.17 (CH_3CN), 102.58 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{free}$), 108.60 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{free}$), 106.35, 114.36, 117.62, 118.54, 120.43 ($C_5H_4SiMe_3$), 122.64, 126.50, 136.64 (C phenyl groups of $[BPh_4]^-$), 126.46 (CH_3CN), 141.79 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{coord}$), 148.13 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{coord}$); 164.35 (c, $J_{^{11}B-^{13}C} = 49.5$ Hz, C_{ipso} of $[BPh_4]^-$). Anal. Calcd for $C_{52}H_{67}BNNbSi_4$: C, 62.76; H, 7.27; N, 1.52. Found: C, 62.90; H, 7.14; N, 1.64.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Me)(\eta^2(C,C)\text{-}Me_3SiC\equiv CC\equiv CSiMe_3)$ (6a). To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}Me_3SiC\equiv CC\equiv CSiMe_3)$ (**2a**; 100 mg, 0.17 mmol) in diethyl ether was added 1.3 mL (0.37 mmol) of a 0.29 M solution of $MgMe_2$ in Et_2O. The mixture was stirred for 24 h at room temperature, and then the solvent was removed in vacuo. The alkyl derivative **6a** was extracted with cold pentane and subsequently isolated by removal of the solvent, as a green oil (60 mg, 0.11 mmol, 63%). The ^1H NMR spectrum showed a mixture of *endo* and *exo* isomers of **6a**. IR (pure product): 2122, 2070 (free $C\equiv C$), 1700 (coord $C\equiv C$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, major isomer): δ 0.26 (s, 18H, $C_5H_4Si(CH_3)_3$), 0.34, 0.45 (s, 9H, $(CH_3)_3SiC\equiv CC\equiv CSi(CH_3)_3$), 0.99 (s, 3H, Nb−*Me*), 4.88−4.93 (2H), 5.22−5.27 (4H), 5.32−5.36 (2H) (m, $C_5H_4SiMe_3$). ^1H NMR (300 MHz, C_6D_6, minor isomer): δ 0.19 (s, 18H, $C_5H_4Si(CH_3)_3$), 0.37, 0.39 (s, 9H, $(CH_3)_3SiC\equiv CC\equiv CSi(CH_3)_3$), 1.02 (s, 3H, Nb−*Me*), 4.99−5.03 (2H), 5.06−5.12 (4H), 5.36−5.40 (2H) ($C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, both isomers): δ 0.24, 0.33, 0.46, 0.82, 0.94, 1.23 (methyl groups of $SiMe_3$), 3.03 (Nb−CH_3), 99.06, 103.87, 104.20, 105.56, 108.60, 109.06, 112.82, 114.21, 114.55, 115.45 ($C_5H_4SiMe_3$), 103.48, 104.00, 104.45, 106.68 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{free}$), 150.60, 156.89, 160.97, 168.67 ($Me_3SiC\equiv CC\equiv CSiMe_3$, $C\equiv C_{coord}$). CI MS: *m/e* (relative intensity) 576 (10) ($[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}Me_3SiC\equiv CC\equiv CSiMe_3)(CH_3)]^+$), 561 (100) ($M^+ - Me$), 382 (71) ($M^+ - L$), 367 (1) ($M^+ - Me - L$) ($L = Me_3SiC\equiv CC\equiv CSiMe_3$). Anal. Calcd for $C_{27}H_{44}NbSi_4$: C, 56.54; H, 7.68. Found: C, 56.95; H, 7.93.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CH_2Ph)(\eta^2(C,C)\text{-}PhC\equiv CCH_2CH{=}CH_2)$ (7a). To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}PhC\equiv CCH_2CH{=}CH_2)$ (**3a**; 200 mg, 0.37 mmol) in 1,4-dioxane was added $Mg(CH_2Ph)_2(THF)_2$ (140 mg, 0.40 mmol), and the resulting solution was stirred for 2 h at 75 °C. The solvent was then removed in vacuo, and the alkyl derivative was isolated as a brown oil (155 mg, 0.26 mmol, 70%). IR (pure product): 1780 (coord $C\equiv C$), 1630 (free $C{=}C$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ −0.07 (s, 18 H, $SiMe_3$), 3.24 (s, 2H, Nb−CH_2Ph), 3.80 (m, $^3J = 6.59$ Hz, 2H, $PhC\equiv CCH_2CH{=}CH_2$), 5.05 (ddt, $^3J = 9.88$, $^2J = 1.83$, $^4J = 1.83$ Hz, 1H, $PhC\equiv CCH_2CH{=}CH_2$), 5.19 (ddt, $^3J = 16.88$, $^2J = 1.83$, $^4J = 1.83$ Hz, 1H, $PhC\equiv CCH_2CH{=}CH_2$), 5.93−6.04 (m, 1H, $PhC\equiv CCH_2CH{=}CH_2$), 5.00−5.06 (2H), 5.28−5.34 (2H), 5.68−5.74 (2H), 5.87−5.93 (2H) (m, $C_5H_4SiMe_3$), 7.06−7.66 (m, 10H phenyl groups). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 0.10 ($SiMe_3$), 23.56 ($PhCH_2$−Nb), 32.45 ($PhC\equiv CCH_2CH{=}CH_2$), 100.09, 109.45, 111.20, 119.02, 120.17 ($C_5H_4SiMe_3$), 114.50 ($PhC\equiv CCH_2CH{=}CH_2$), 122.08, 127.51, 128.09, 128.55, 128.78, 130.43, 131.71, 159.52 (*C* phenyl groups), 135.85 ($PhC\equiv CCH_2CH{=}CH_2$), 139.74 ($PhC\equiv CCH_2CH{=}CH_2$), 146.71 ($PhC\equiv CCH_2CH{=}CH_2$). Anal. Calcd for $C_{34}H_{43}NbSi_2$: C, 68.00; H, 7.17. Found: C, 68.35; H, 6.97.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Me)(\eta^2(C,C)\text{-}PhC\equiv CCH_2CH{=}CMe_2)$ (7b). The synthesis of compound **7b** is the same as that described for **6a**. Thus, a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}PhC\equiv CCH_2CH{=}C(Me)_2)$ (100 mg, 0.17 mmol) in diethyl ether was treated with 1.76 mL (0.52 mmol) of a 0.29 M solution of $MgMe_2$ in Et_2O. The mixture was stirred for 24 h at room temperature, and the solvent was then removed in vacuo to give **7b** as a green oil after extraction of the residues with pentane (69.5 mg, 0.12 mmol, 72%). IR (KBr): 1780 (coord $C\equiv C$), 1640 (free $C{=}C$) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 0.06 (s, 18 H, $SiMe_3$), 0.92 (s, 3H, Nb−*Me*), 1.63, 1.74 (s, 3H, $PhC\equiv CCH_2CH{=}C(CH_3)_2$), 3.87 (d, $^3J = 7.32$ Hz, 2H, $PhC\equiv CCH_2CH{=}C(CH_3)_2$), 5.02−5.08 (2H), 5.24−5.30 (2H), 5.32−5.38 (2H), 5.43−5.49 (2H) (m, $C_5H_4SiMe_3$), 7.35−7.43 (3H), 7.65−7.72 (2H) (m, H phenyl groups). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 0.00 ($SiMe_3$), 1.36 (Nb−CH_3), 18.91, 25.84 ($PhC\equiv CCH_2CH{=}C(CH_3)_2$), 27.70 ($PhC\equiv CCH_2CH{=}C(CH_3)_2$), 99.19, 104.53, 107.00, 112.56, 113.30 ($C_5H_4SiMe_3$), 123.19 ($PhC\equiv CCH_2CH{=}C(CH_3)_2$), 126.75, 128.75, 130.54, 130.85 (C phenyl groups), 139.44 ($PhC\equiv CCH_2CH{=}C(CH_3)_2$), 144.96 ($PhC\equiv CCH_2CH{=}C(CH_3)_2$), 147.78 ($(PhC\equiv CCH_2CH{=}C(CH_3)_2$). Anal. Calcd for $C_{29}H_{43}NbSi_2$: C, 64.44; H, 7.96. Found: C, 64.37; H, 7.95.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}R^1C\equiv CR^2)$ (R^1 = CCPh-(Co(CO)$_3$), R^2 = Ph (8b)). To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,C)\text{-}R^1C\equiv CR^2)$ ($R^1 = C\equiv CPh$, R^2 = Ph (**2b**); 140 mg, 0.23 mmol) in hexane was added $Co_2(CO)_8$ (80 mg, 0.23 mmo), and the mixture was stirred for 5 h at room temperature. The solvent was then removed, giving an oily residue which was extracted with cold pentane to give a green solution containing a 1:2 mixture of the *endo* and *exo* isomers of complex **8b** (152 mg, 0.17 mmol, 73%). IR (pure product): 2082, 2048, 2013 (CO), 1747 ($C\equiv C$ coordinated to Nb) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): major isomer, δ 0.17 (s, 18 H, $SiMe_3$), 5.73−5.78 (2H), 5.86−5.91 (2H), 5.91−5.96 (2H), 5.96−6.00 (2H) (m, $C_5H_4SiMe_3$), 7.11−7.65 (m, 10 H phenyl group); minor isomer, δ 0.14 (s, 18 H, $SiMe_3$), 5.43−5.48 (2H), 5.65−5.70 (2H), 5.81−5.86 (2H), 6.09−6.14 (2H) (m, $C_5H_4SiMe_3$), 7.11−7.65 (m, 10 H phenyl group). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): both isomers, δ 0.10, 0.30 ($SiMe_3$), 102.48, 104.28, 106.57, 110.37, 116.37, 119.04, 119.26, 120.19, 125.29, 126.43 ($C_5H_4SiMe_3$), 126.86, 126.93, 128.58, 128.85, 129.15, 129.23, 130.30, 130.67 (C phenyl groups, both isomers), 136.58, 138.22 ($PhC\equiv CC\equiv CPh$ coordinated to Nb), 140.08, 144.32, 152.04, 152.53 ($PhC\equiv CC\equiv$

Table 4. Crystallographic Data and Structure Refinement Details for 2b and 3b

	2b	**3b**
empirical formula	$C_{32}H_{36}ClNbSi_2$	$C_{29}H_{40}ClNbSi_2$
fw	605.15	573.15
temp, K	293(2)	293(2)
wavelength, Å	0.710 70	0.710 70
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$
unit cell dimens		
a, Å	15.05(3)	12.585(4)
b, Å	22.095(3)	15.054(2)
c, Å	19.760(10)	15.855(2)
β, deg	110.27(9)	
V, Å^3	6164(13)	3003.8(11)
Z	4	4
density (calcd), g/cm^3	1.304	1.267
abs coeff. cm^{-1}	5.73	5.84
F(000)	2512	1200
cryst size, mm	0.5 × 0.3 × 0.2	0.5 × 0.4 × 0.4
θ range for data collecn, deg	2.09−26.00	2.07−27.97
index ranges	$0 \leq h \leq 18$, $0 \leq k \leq 27$, $-22 \leq l \leq 22$	$0 \leq h \leq 16$, $0 \leq k \leq 19$, $0 \leq l \leq 20$
no. of rflns collected	12 099	4021
no. of data/restraints/params	12 099/0/649	4021/0/177
goodness of fit on F^2	1.084	0.876
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0380, wR2 = 0.0955	R1 = 0.0747, wR2 = 0.1680
R indices (all data)[a]	R1 = 0.0888, wR2 = 0.1316	R1 = 0.1719, wR2 = 0.2458
largest diff peak and hole, e/Å^3	0.527 and −0.603	0.840 and −0.482

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$.

CPh coordinated to Co), 164.63, 166.58 (Ph*C*$\equiv$CC$\equiv$CPh, Nb coordinated), 200.22, 201.00 (*C*O groups). FAB MS: *m/e* (relative intensity) 750 (12) ([{Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl}{Co_2-(CO)$_6$}(μ-η^2:μ-η^2-PhC$\equiv$CC$\equiv$CPh)]$^+$ − 5(CO)), 722 (18) (M$^+$ − 6(CO)), 569 (2) (M$^+$ − 6(CO) − 2(Co) − Cl), 402.1 (100) ([Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl]$^+$). Anal. Calcd for $C_{35}H_{36}O_3CoNbSi_2$: C, 58.99; H, 6.74. Found: C, 58.35; H, 6.87.

Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C,C*)-PhC$\equiv$$CCH_2CH_2CH_3$) (9a). To a solution of Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C,C*)-PhC$\equiv$$CCH_2CH$=$CH_2$) (**3a**; 100 mg, 0.18 mmol) in toluene was added 5% Pd/C catalyst (1.95 mg, 0.017 mmol), and the reaction mixture was placed under an H_2 atmosphere (1.2 atm). After the mixture was stirred for 1 h, the solvent was removed in vacuo and the residue extracted with ether. The solvent was then evaporated to dryness to give complex **9a** as a yellowish green powder (70 mg, 0.13 mmol, 71%). IR (KBr): 1773 (coord C$\equiv$C) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 0.23 (s, 18H, Si*Me*$_3$), 1.01 (t, ^3J = 7.32 Hz, 3H, PhC$\equiv$$CCH_2CH_2C$*H*$_3$), 1.63−1.76 (m, 2H, PhC$\equiv$$CCH_2C$*H*$_2$$CH_3$), 3.42 (t, ^3J = 7.69 Hz, 2H, PhC$\equiv$CC*H*$_2$$CH_2CH_3$), 5.04−5.11 (2H), 5.40−5.48 (2H), 5.72−5.80 (2H), 5.85−5.93 (2H) (m, C_5*H*$_4$$SiMe_3$), 7.10−7.20 (m, 1H, *p*-C_6*H*$_5$), 7.29−7.38 (m, 2H, *m*-C_6*H*$_5$), 7.41−7.50 (m, 2H, *o*-C_6*H*$_5$).^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 0.21 (Si*Me*$_3$), 15.00 (PhC$\equiv$$CCH_2CH_2$*C*$H_3$), 22.06 (PhC$\equiv$$CCH_2$*C*$H_2CH_3$), 31.29 (PhC$\equiv$C*C*$H_2CH_2CH_3$), 100.71, 109.01, 111.03, 118.53, 119.67 (*C*$_5$$H_4SiMe_3$), 127.68, 128.34, 130.04, 131.03 (C phenyl groups), 143.00 (PhC$\equiv$*C*$CH_2CH_2CH_3$), 147.11 (Ph*C*$\equiv$$CCH_2CH_2CH_3$). Anal. Calcd for $C_{27}H_{38}ClNbSi_2$: C, 59.30; H, 6.95. Found: C, 58.95; H, 6.93.

Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C,C*)-PhC$\equiv$$CCH_2CH_2CH$-($CH_3$)$_2$) (9b). The synthetic procedure is analogous to that described for **9a**. Thus, to a solution of Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl-(η^2(*C,C*)-PhC$\equiv$$CCH_2CH$=C($CH_3$)$_2$) (**3b**; 100 mg, 0.17 mmol) in toluene was added 5% Pd/C catalyst (0.19 mg, 0.02 mmol), and the reaction mixture was stirred for 1 h under an H_2 atmosphere (1.2 atm). Then, the solvent was removed in vacuo and the residue extracted with ether to yield **9b** as a yellow solid (75 mg, 0.13 mmol, 76%). IR (KBr): 1778 (coord C$\equiv$C) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 0.24 (s, 18H, Si*Me*$_3$), 1.03 (d, ^3J = 6.22 Hz, 6H, PhC$\equiv$$CCH_2CH_2CH$(C*H*$_3$)$_2$), 1.58−1.67 (m, 3H, unresolved signals of PhC$\equiv$$CCH_2C$*H*$_2$C*H*($CH_3$)$_2$), 3.50 (t, ^3J = 7.32 Hz, 2H, PhC$\equiv$CC*H*$_2$$CH_2CH$($CH_3$)$_2$), 5.05−5.11 (2H), 5.41−5.46 (2H), 5.72−5.77 (2H), 5.89−5.94 (2H) (m, C_5*H*$_4$$SiMe_3$), 7.31−7.39 (3H), 7.44−7.50 (2H) (m, H phenyl groups). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 0.21 (Si*Me*$_3$), 21.90 (PhC$\equiv$$CCH_2CH$(*C*$H_3$)$_2$), 29.15 (PhC$\equiv$$CCH_2$*C*H($CH_3$)$_2$), 37.29 (PhC$\equiv$C*C*$H_2$-CH($CH_3$)$_2$), 101.71, 109.52, 111.50, 118.45, 119.67 (*C*$_5$$H_4SiMe_3$), 127.74, 128.35, 130.24, 131.89 (C phenyl groups), 140.87 (PhC$\equiv$*C*CH_2CH(CH_3)$_2$), 148.31 (Ph*C*$\equiv$$CCH_2CH$($CH_3$)$_2$). Anal. Calcd for $C_{29}H_{42}ClNbSi_2$: C, 60.59; H, 7.30. Found: C, 60.53; H, 7.25.

Photochemical Reactions of Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2-(*C,C*)-$R^1C$$\equiv$$CR^2$) Complexes. Photochemical reactions were carried out in Pyrex vessels containing a solution of an alkyne, diyne or enyne complex in CH_2Cl_2, $CHCl_3$, or $CDCl_3$. The samples were irradiated for approximately 50−70 min using a mercury lamp (Philips Belgium, HPK, 125 W). A typical procedure is as follows. A solution of 50 mg (0.09 mmol) of Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(*C,C*)-PhC$\equiv$$CCH_2CH_2CH_3$) (**9a**) in 1 mL of $CDCl_3$ was irradiated for 60 min. The solution was then studied by ^{1}H NMR spectroscopy, which showed the presence of 1-phenyl-1-pentyne. The paramagnetic niobium(IV) complex Nb(η^5-$C_5H_4SiMe_3$)$_2$$Cl_2$ crystallized from the solution as a green solid (24 mg, 60%). The solution was filtered, and the filtrate was distilled under vacuum to give a mixture of 1-phenyl-1-pentyne and $CDCl_3$, which were collected in a liquid-nitrogen-cooled trap.

X-ray Structural Determination of 2b and 3b. Crystal, data collection, and refinement parameters are collected in Table 4. Suitable crystals were selected and mounted on fine glass fibers with epoxy cement. The unit cell parameters were each determined from the angular settings of a least-squares fit of 25 strong high-angle reflections. The asymmetric unit for **2b** contained two independent but chemically equivalent molecules, but these exhibited similar structural parameters. Reflections were collected at 25 °C on a NONIUS-MACH3 diffractometer equipped with graphite-monochromated radiation (λ = 0.710 73 cm^{-1}). Each sample showed no significant intensity decay over the duration of the data collection. For **3b**, the specimen diffracted weakly and broadly.

Data were corrected in the usual fashion for Lorentz and polarization effects and empirical absorption correction for **2b** was based on a Ψ scan[27] (range of transmission factors 0.548−1.00). The space group was determined from the systematic absences in the diffraction data. The structures were solved

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by direct methods (SIR92),[28] and refinements on F^2 were carried out by full-matrix least-squares analysis (SHELXL-93).[29] For **2b**, anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated positions but not refined. For **3b** the final least-squares refinement was carried out using anisotropic thermal parameters on the Nb, Cl, and Si atoms and isotropic parameters on the remaining atoms. For the disordered carbon atoms in the $SiMe_3$ ligands, occupancies were refined initially and then fixed. While poor-quality data left the structure determination too inaccurate to merit detailed comparative discussion of bond lengths, the overall coordination polyhedron has been unambiguously determined.

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Supporting Information Available: For **2b** and **3b**, all crystallographic data (Tables SI and SI′), final atomic coordinates for the non-hydrogen atoms (Tables SII and SII′), all bond distances and angles (Tables SIII and SIII′), anisotropic thermal parameters (Tables SIV and SIV′), and final atomic coordinates for the hydrogen atoms (Tables SV and SV′). This material is available free of charge via the Internet at http://pubs.acs.org.

OM980786Y

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