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Niobocene Alkyne Complexes: Synthesis and Characterization of Neutral and Cationic d^2 Metal Alkyne Derivatives. X-ray Crystal Structure of [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}HC{\equiv}CPh)(CH_2Ph)$]

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The paramagnetic niobocene alkyne complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')$ (**2**) have been synthesized from $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')(Cl)$ (**1**) and subsequently oxidized in the presence of different ligands to give stable cationic d^2 derivatives, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')(L)][BPh_4]$ ($L = CH_3CN$, $R = R' = Ph$ (**3a**); $L = CH_3CN$, $R = R' = CO_2Me$ (**3b**); $L = CH_3CN$, $R = R' = Me$ (**3c**); $L = CH_3CN$, $R = Me$, $R' = CO_2Me$ (**3d**); $L = tBuCN$, $R = R' = Ph$ (**4a**); $L = tBuCN$, $R = R' = CO_2Me$ (**4b**); $L = tBuCN$, $R = R' = Me$ (**4c**); $L = tBuCN$, $R = Me$, $R' = CO_2Me$ (**4d**); $L = tBuNC$, $R = R' = Ph$ (**5a**); $L = tBuNC$, $R = R' = CO_2Me$ (**5b**); $L = tBuNC$, $R = R' = Me$ (**5c**); $L = THF$, $R = R' = Me$ (**6c**); $L = THF$, $R = Me$, $R' = CO_2Me$ (**6d**); $L = Py$, $R = R' = Ph$ (**7a**); $L = Py$, $R = R' = Me$ (**7c**)). Oxidation of the complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC{\equiv}CCO_2Me)$ (**2d**) under different experimental conditions gave rise to the divinylidene binuclear d^2 niobocene complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Nb{=}C{=}C(CH_3)(CH_3)C{=}C{=}Nb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$ (**8a**). A mechanism involving the intermediacy of a σ-acetylide species is proposed for the formation of this compound. Thus, the divinylidene complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Nb{=}C{=}C(Ph)(Ph)C{=}C{=}Nb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$ (**8c**) was easily synthesized by oxidation of the corresponding Nb(III) alkynyl derivative $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)(C{\equiv}CPh)$ (**13**), obtained from $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Cl$ and $Mg(C{\equiv}CPh)_2$. Furthermore, the paramagnetic Nb(IV) complexes (**2**) undergo clean reactions with alkyl halides to give a mixture of both alkyl−alkyne and halo−alkyne compounds. The former complexes, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')(R'')$ ($R = R' = Ph$, $R'' = Me$ (**9a**); $R = R' = R'' = Me$ (**9c**); $R = H$, $R' = Ph$, $R'' = Me$ (**9e**); $R = R' = Me$, $R'' = Et$ (**10c**); $R = R' = Me$, $R'' = CH_2Ph$ (**11c**); $R = H$, $R' = Ph$, $R'' = CH_2Ph$ (**11e**); $R = H$, $R' = Ph$, $R'' = CH_2CH{=}CH_2$ (**12e**)), were also prepared by an alternative procedure in which the corresponding chloro derivatives **1** were reacted with the appropriate dialkylmagnesium reagents. The structure of **11e** was determined by single-crystal diffractometry.

Introduction

The chemistry of d-block transition metals with alkyne ligands has been well documented.[1] For early transition metals extensive studies have been reported on alkyne complexes of group 6 metals, but in contrast the study of analogous group 5 metal complexes has been much less thorough, and in the majority of the complexes described, cyclopentadienyl or aryloxide ligands are also present.[2] Certain niobium or tantalum complexes polymerize and cyclize alkynes,[3] and hence, it is important to prepare and study the reactivity of new alkyne complexes of these metals in order to better understand the mechanisms involved in such processes.

In the last few years several families of alkyne-containing halobis((trimethylsilyl)cyclopentadienyl)niobium complexes have been reported by our group,[4] and of late, alkyne-containing *ansa*-niobocenes were also synthesized.[5] Recently, as a continuation of our studies on the use of unsaturated molecules in the synthesis of niobium organometallics, Lewis-base-containing niob-

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(1) (a) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33. (b) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(2) This list is meant to be representative and not exhaustive: (a) Labinger, J. A.; Schwartz, J.; Townsend, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4009. (b) Labinger, J. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 1596. (c) Green, M. L. H.; Jousseaume, B. *J. Organomet. Chem.* **1980**, *193*, 339. (d) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (e) Herberich, G. E.; Mayer, H. *Organometallics* **1990**, *9*, 2655. (f) Yasuda, H.; Yamamoto, H.; Arai, T.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1991**, *10*, 4058. (g) Biasotto, F.; Etienne, M.; Dahan, F. *Organometallics* **1995**, *14*, 1870. (h) Etienne, M. *Organometallics* **1994**, *13*, 410. (i) Etienne, M.; Biasotto, F.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1661. (j) Lorente, P.; Etienne, M.; Donnadieu, B. *An. Quim. Int. Ed.* **1996**, *92*, 88.

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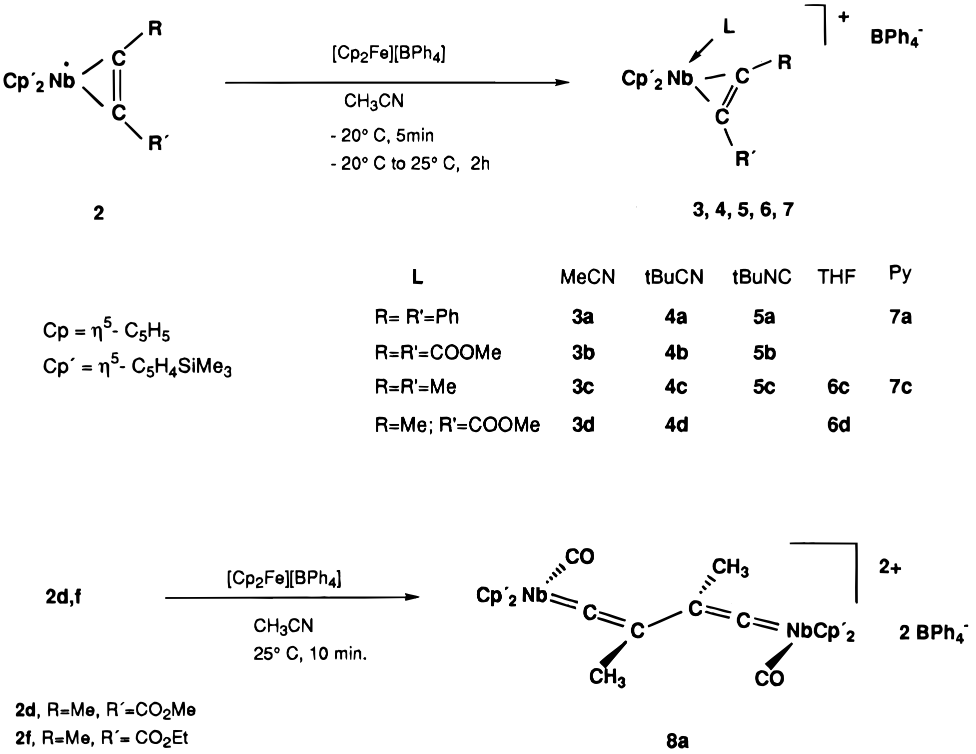
Scheme 1



2

3, 4, 5, 6, 7

$Cp = \eta^5$- C_5H_5
$Cp' = \eta^5$- $C_5H_4SiMe_3$

L	MeCN	tBuCN	tBuNC	THF	Py
R= R'=Ph	**3a**	**4a**	**5a**		**7a**
R=R'=COOMe	**3b**	**4b**	**5b**		
R=R'=Me	**3c**	**4c**	**5c**	**6c**	**7c**
R=Me; R'=COOMe	**3d**	**4d**		**6d**	

2d,f

2d, R=Me, R'=CO_2Me
2f, R=Me, R'= CO_2Et

8a

ocene ketenimine cationic complexes were prepared[6] by a one-electron oxidation of the Nb(IV) ketenimine complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*N*)-ArN=C=CRR′) with ferrocenium salts with the aim of further studying insertion processes between heterocumulenes and the Lewis-base molecule.[7] The results encouraged us to explore the reactivity of the analogous Nb(IV) alkyne complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-RC≡CR′), which had been previously prepared[4c] by reduction of the corresponding Nb(V) complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-(*C*,*C*)-RC≡CR′)(Cl) with ferrocenium salts in the presence of appropriate basic molecules. The method was successful and allowed the synthesis of a number of cationic complexes, which were isolated in good yields as nitrile or isonitrile adducts, [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-(*C*,*C*)-RC≡CR′)(L)]$^+$.

However, a surprising behavior was found in the reaction of Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-MeC≡CCO_2Me) with the ferrocenium salt, in that, under appropriate experimental conditions, a divinylidene binuclear complex which resulted from an oxidatively induced C−C coupling was obtained. This class of complexes, as well as higher-cumulene-containing transition complexes, model reactive intermediates arising from surface carbides in heterogeneous catalytic processes such as CO reduction and alkyne conversion reactions[8] and are known to participate in several fine organic syntheses.[9] This paper will focus on the synthesis and structural details of alkyne-containing cationic niobocene complexes, the preparation of divinylidene binuclear species through C−C coupling processes, and the isolation and characterization of niobocene alkyl−alkyne complexes. Part of this work was previously reported.[10]

Results and Discussion

The starting niobium(IV) complexes Nb(η^5-C_5H_4-$SiMe_3$)$_2$(η^2(*C*,*C*)-RC≡CR′) (**2**) were prepared by reduction of the corresponding niobium(V) species Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-RC≡CR′)(Cl) (**1**) with 1 equiv of Na(Hg).[4c] Complexes **2** reacted with 1 equiv of [$FeCp_2$]-[BPh_4] (Cp = η^5-C_5H_5) in the presence of an appropriate Lewis base to give the cationic d^2 niobocene alkyne complexes **3**−**7** (Scheme 1). Complexes **3**−**5** were isolated in high yield (50−97%) as pure air-stable crystalline solids after recrystallization from acetonitrile/diethyl ether. The oxidation of **2a** and **2b** in THF at low temperature (−30 °C) did not lead to the corresponding THF-containing cationic complexes **6a** and **6b** but resulted in a mixture of intractable products. However, the same reaction for **2c** and **2d** yielded the

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(3) (a) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473. (b) Cotton, F. A.; Hall, K. J. *Macromolecules* **1985**, *18*, 2109. (c) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (d) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.

(4) (a) Antiñolo, A.; Gómez-Sal, P.; Martínez de Ilarduya, J. M.; Otero, A.; Royo, P.; Martínez-Carrera, S.; García-Blanco, S. *J. Chem. Soc., Dalton Trans.* **1987**, 975. (b) Antiñolo, A.; Fajardo, M.; Jalón, F. A.; López-Mardomingo, C.; Otero, A.; Sanz-Bernabé, C. *J. Organomet. Chem.* **1989**, *369*, 187. (c) Antiñolo, A.; Fajardo, M.; Gil-Sanz, R.; López-Mardomingo, C.; Otero, A.; Lucas, D.; Chollet, H.; Mugnier, Y. *J. Organomet. Chem.* **1994**, *481*, 27.

(5) Antiñolo, A.; Martínez-Ripoll, M.; Mugnier, Y.; Otero, A.; Prashar, S.; Rodríguez, A. M. *Organometallics* **1996**, *15*, 3241.

(6) 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.

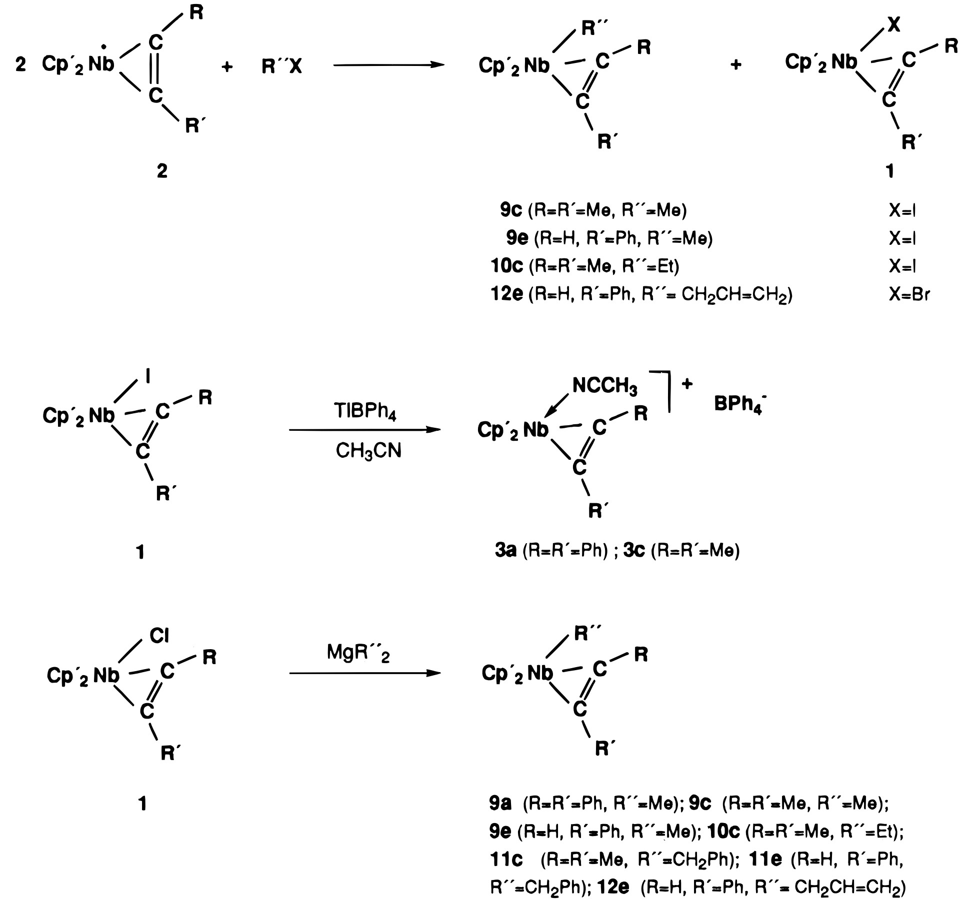
(7) For a selected reference, see: Aumann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456.

(8) (a) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. (b) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (c) Somorjai, G. A. *Chem. Soc. Rev.* **1984**, *13* (3), 321. (d) Erley, W.; McBreen, P. H.; Ibach, H. *J. Catal.* **1983**, *84*, 229. (e) McCandlish, L. E. *J. Catal.* **1983**, *83*. 362. (f) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: Orlando, FL, 1984; p 211.

(9) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490. (c) Beckhaus, R.; Sang, J.; Oster, J.; Wagner, T. *J. Organomet. Chem.* **1994**, *484*, 179.

(10) Antiñolo, A.; Otero, A.; Fajardo, M.; García-Yebra, C.; Gil-Sanz, R.; López-Mardomingo, C.; Martín, A.; Gómez-Sal, P. *Organometallics* **1994**, *13*, 4679.

Scheme 2



corresponding cationic complexes **6c** and **6d**, which were isolated as brown powdery solids after appropriate workup (see Experimental Section) and were stored under argon at low temperature. Following a similar procedure, complexes **7a** and **7c** were generated from **2a** and **2c** and isolated as air-sensitive solids when the oxidation was carried out in pyridine at low temperature.

Furthermore, an interesting reaction was observed when some Nb(IV) paramagnetic complexes **2** were treated with organic halides. Indeed, these compounds reacted with the corresponding R″X to give rise to mixtures of niobocene alkyl−alkyne and halo-alkyne species and no other byproduct (Scheme 2). Analogous behavior was recently found in the reaction of the tantalum 17-electron metal-centered radical Ta(CO)$_2$dppe (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with alkyl halides.[11] The reactions of aliphatic and aromatic halides with low-valent transition-metal complexes are of synthetic interest, since they are useful in the formation of new carbon−metal bonds,[12] and in this context we previously described[13] the behavior of Nb(III) complexes Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$X with several alkyl and aryl halides. The formation of the alkyl−alkyne and the halo−alkyne derivatives probably takes place through the interaction of the unpaired electron of the Nb(IV) paramagnetic species **2** with the appropriate radical, R″$^\bullet$ or X$^\bullet$, resulting in the homolytic cleavage of the carbon−halogen bond, although other alternative pathways cannot be definitively excluded. The halo−alkyne and alkyl−alkyne niobocenes appear in a ratio of approximately 1:1, and this proportion does not depend on the ratio of the reactants. The mixture of products can be easily resolved, since they show different solubilities in cold hexane or pentane (see Experimental Section). Indeed, the procedure has allowed us to isolate new niobium iodo alkyne derivatives, which have proven to be useful starting materials in the synthesis of other niobocene compounds. Thus, complexes Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2(*C*,*C*)-RC≡CR′)(I) (R = R′ = Ph, Me) react with 1 equiv of TlBPh$_4$ in acetonitrile to give the corresponding cationic alkyne complexes (**3a** and **3c**) through an iodide abstraction process (Scheme 2). The same procedure, however, for the analogous 1-alkyne complexes, for example Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2(*C*,*C*)-HC≡CPh)(I), gave mixtures of intractable products.

The niobocene alkyl−alkyne complexes could alternatively be prepared in better yields by substitution of the halogen of complexes **1** with the appropriate alkylating reagents. Thus, using Grignard reagents, R″MgI, mixtures of both the alkyl and the iodide derivatives were obtained in ratios which depended on the experimental conditions (reaction time and temperature). Furthermore, when dialkylmagnesium compounds were employed, the corresponding alkyl complexes were obtained exclusively and were isolated as air-sensitive solids from pentane in good yields (50−89%) (Scheme 2). Some niobocene alkyl−alkyne complexes were pre-

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[11] Koeslag, M. A.; Baird, M. C.; Lovelace, S.; Geiger, W. E. *Organometallics* **1996**, *15*, 3289.

[12] (a) Kochi, K. J. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (b) Lappert, M. F.; Lednor, W. E. Free Radicals in Organometallic Chemistry. *Adv. Organomet. Chem.* **1976**, *14*, 345.

[13] Antiñolo, A.; Fajardo, M.; Otero, A.; Puerta, M. C.; Mugnier, Y. *J. Organomet. Chem.* **1990**, *382*, 389.

viously synthesized[2f] by reacting hydridoniobium−olefin complexes with alkynes. In the reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC{\equiv}CMe)(Cl)$ with $MgEt_2$, the corresponding alkyl derivative **10c** was the only compound isolated. However, when complex **1** contained $PhC{\equiv}CPh$ or $PhC{\equiv}CH$ as the alkyne ligand, evolution of the alkyl complex to the hydrido−olefin derivative $(Nb(\eta^5C_5H_4\text{-}SiMe_3)_2(\eta^2(C,C)\text{-}H_2C{=}CH_2)(H)$ was observed along with the elimination of the alkyne. β-Elimination from the ethyl group is obviously favored, a behavior which is surprising given that alkynes normally exhibit higher π-donating and -accepting properties than olefins.

The new families of alkyne-containing niobocene complexes were characterized by spectroscopic methods. The IR spectra of these complexes show a characteristic band at 1670−1880 cm^{-1} ($\nu_{C\equiv C}$) which corresponds to the coordinated alkyne unit and, in addition, one or two bands (2150−2320 cm^{-1}) corresponding to $\nu_{C\equiv N}$[6,14] for nitrile- or isonitrile-containing cationic complexes. In these complexes the ^1H NMR signals of the coordinated nitrile or isonitrile, measured in CD_3CN solutions, are slightly shifted with respect to those of the free ligands, and in ^{13}C the signal corresponding to the carbon atom directly attached to the heteroatom was not observed in most cases. For complexes **6** and **7** it was necessary to record the NMR spectra at −40 °C, as a rapid exchange of CD_3CN/L (L = THF, Py) was observed at higher temperatures. However, at low temperature the spectra of **6** and **7** exhibited resonances characteristic of coordinated THF or pyridine (see Experimental Section). The ^1H and ^{13}C NMR spectra of the neutral alkyl−alkyne complexes **9**−**12** show the characteristic resonances for an alkyl group bound to a niobium atom. On the basis of the NMR data for complex **12e** the presence of a σ-allyl ligand is proposed (see Experimental Section). The ^{13}C NMR spectra of both neutral and cationic alkyne complexes exhibit two resonances around 140 ppm which are assigned to the two nonequivalent η^2-alkyne carbon atoms (see Experimental Section). In addition, the ^1H NMR data for complexes with symmetrical alkynes indicate that the halves of these ligands are nonequivalent; for example, in the case of **3c**, two signals at 1.97 and 2.34 ppm are observed for the methyl groups. The endo methyl group of this compound was identified by NOE experiments. Irradiation of the acetonitrile methyl signal (1.10 ppm, $CDCl_3$) resulted in an enhancement of the signal due to the 2-butyne endo methyl group. There was no observable enhancement of the signal at 2.34 ppm. The proposed structure for the cationic complexes was unequivocally confirmed by the X-ray crystal structure of $[Nb(\eta^5C_5H_4\text{-}SiMe_3)_2(\eta^2(C,C)\text{-}(MeC{\equiv}CCO_2Me)(CH_3CN)][BPh_4]$ (**3d**) which has been previously published.[10] The structure showed that the alkyne unit adopts an endo configuration with respect to the nitrile ligand (the methoxycarbonyl group is in a cis disposition with respect to the acetonitrile ligand). The angles and the bond distance of the alkyne carbon atoms shows them to be almost sp^2-hybridized, the distance being slightly shorter than in a typical carbon−carbon double bond.[2e,f,4a] Both crystallographic and ^{13}C NMR data (vide supra) indicate that the alkyne ligand in the cationic niobocene complexes behaves as a two-electron ligand.[15]

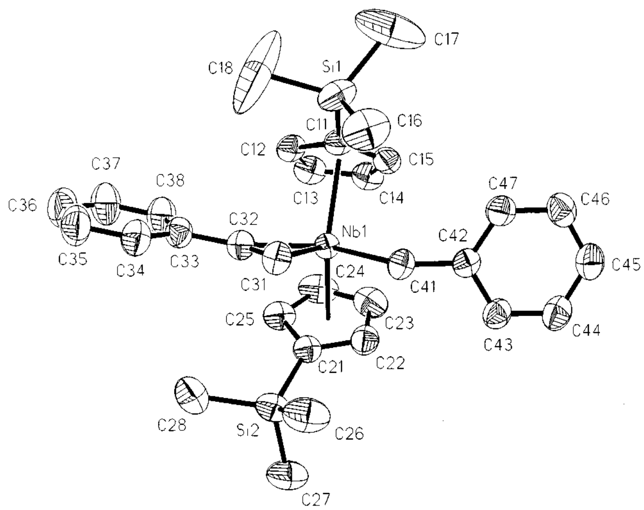

Figure 1. ORTEP drawing of compound **11e** with the atomic labeling scheme. Thermal ellipsoids correspond to 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 11e

Nb(1)−C(31)	2.150(3)	C(21)−C(25)	1.428(5)
Nb(1)−C(32)	2.171(3)	C(22)−C(23)	1.398(6)
Nb(1)−C(41)	2.372(3)	C(23)−C(24)	1.400(6)
C(11)−C(12)	1.421(4)	C(24)−C(25)	1.396(6)
C(11)−C(15)	1.433(5)	C(31)−C(32)	1.268(5)
C(12)−C(13)	1.398(5)	C(32)−C(33)	1.472(5)
C(13)−C(14)	1.401(5)	C(41)−C(42)	1.500(4)
C(14)−C(15)	1.395(5)	Nb(1)−Cp(1)[a]	2.143
C(21)−C(22)	1.405(5)	Nb(1)−Cp(2)[a]	2.148

C(31)−Nb(1)−C(32)	34.12(13)	Cp(1)−Nb(1)−C(31)	114.3
C(31)−Nb(1)−C(41)	76.12(12)	Cp(1)−Nb(1)−C(32)	103.0
C(32)−Nb(1)−C(41)	110.19(12)	Cp(1)−Nb(1)−C(41)	104.5
C(32)−C(31)−Nb(1)	73.9(2)	Cp(1)−Nb(1)−Cp(2)	129.1
C(31)−C(32)−C(33)	141.5(3)	Cp(2)−Nb(1)−C(31)	113.1
C(31)−C(32)−Nb(1)	72.0(2)	Cp(2)−Nb(1)−C(32)	105.2
C(33)−C(32)−Nb(1)	146.3(3)	Cp(2)−Nb(1)−C(41)	104.0
C(42)−C(41)−Nb(1)	126.7(2)		

[a] Cp(1) and Cp(2) are the centroids of the Cp rings.

In the case of the neutral alkyl−alkyne complexes the molecular structure of **11e** was established by X-ray crystal studies. The ORTEP drawing of **11e** is given in Figure 1, and selected bond lengths and angles are presented in Table 1. The structure is typical of bent metallocenes and is closely related to those reported earlier for niobocene alkyne complexes.[2e,f,4a] The alkyne unit adopts an exo conformation with respect to the benzyl group, and this is the only isomer formed in the synthesis of this compound. The exo geometry for some of the other nonsymmetrical alkyl−alkyne complexes was assigned by NOE studies (**9e** and **12e**, see Experimental Section). Structural data for **3d**[10] and **11e** indicate that the endo and exo isomers, respectively, seem to be thermodynamically favored over the exo and endo alternatives. We have previously described[16] several neutral haloketene, haloketenimine, and cationic ketenimine complexes of niobocene where the exo isomer, with the bulkier substituent in the outside position, is always favored over the endo isomer. The angles in the alkyne system are similar to the corre-

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(14) (a) Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406. (b) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610.

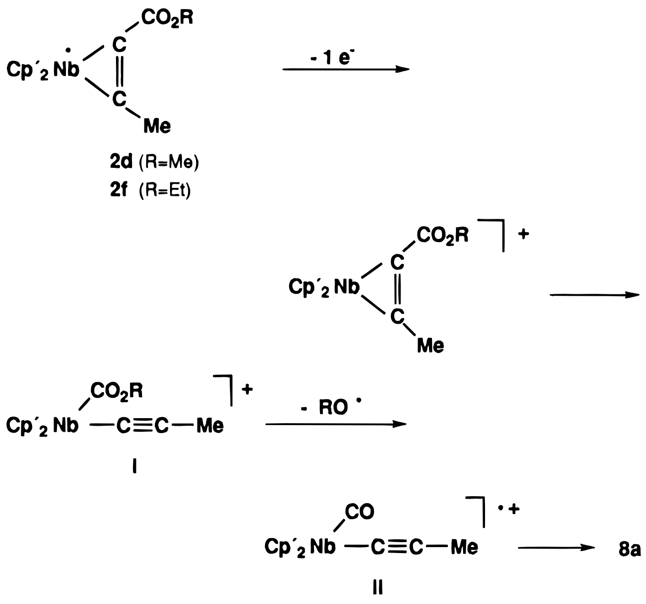
(15) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.

sponding angles in **3d**, and the distance C(31)−C(32) = 1.268(5) Å indicates a almost sp^2 hybridization of the alkyne carbon atoms. All these data together with the ^{13}C NMR data (vide supra) indicate again that the alkyne ligands in the neutral alkyl complexes behave as two-electron ligands. In Figure 1 the Nb, C(31), C(32), and C(41) atoms form a plane with a maximum distance from the plane of 0.03 Å for carbon C(31) and −0.03 Å for C(32). No agostic interaction of the Nb with the CH_2 moiety of the benzyl group was observed either by crystallographic analysis or by NMR studies,[2f] with both hydrogen atoms being equivalent. In accordance with the results described, our alkyne complexes of niobocene may be considered as d^2 alkyne complexes or as d^0 niobacyclopropene compounds, are isoelectronic with a wide range of neutral group 4 complexes, $M(\eta^5\text{-}C_5H_4SiMe_3)_2(\text{alkyne})(\text{Lewis base})$,[17] and are closely related to the base-free group 4 complexes $M(\eta^5\text{-}C_5H_4SiMe_3)_2(\text{alkyne})$.[18]

When $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC{\equiv}CCO_2Me)$ (**2d**) was reacted with 1 equiv of $[FeCp_2][BPh_4]$ in CH_3CN, tBuCN, or THF at room temperature the divinylidene d^2 complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Nb{=}C{=}C(Me)(Me)\text{-}C{=}C{=}Nb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$ (**8a**) was isolated (Scheme 1) as a yellow precipitate in good yield (60−70%). Both concentration and temperature have been established as determining factors in the chemoselectivity of the reaction of **2d** with the ferrocenium salt. No conversion of **3d** to **8a** was observed even on refluxing in THF. The same reaction for **2d** using hexane as solvent in the presence of an excess of tBuNC gave the divinylidene complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2(tBuNC)\text{-}Nb{=}C{=}C(Me)(Me)C{=}C{=}Nb(tBuNC)(\eta^5\text{-}C_5H_4SiMe_3)_2]\text{-}[BPh_4]_2$ (**8b**). Since **8b** was alternatively obtained by reacting **8a** with tBuNC, we can conclude that the formation of **8b** takes place *via* substitution of CO by tBuNC.

Studies to obtain an insight into the mechanism of the binuclear niobocene divinylidene moiety formation have been carried out. Remarkably, the nature of the products resulting from the reaction of **2d** with the ferrocenium salt depends dramatically on the choice of both temperature and concentration of reactants. Thus, to isolate **8a** or **8b**, temperatures and concentrations higher than those required for the formation of mononuclear compounds **3d**, **4d**, and **6d** are needed. Liberation of CO does not take place during the formation of the dimeric product, since the corresponding labeled complex was not isolated when the reaction was carried out under a ^{13}CO atmosphere. Furthermore, when the oxidation was carried out in the presence of $BF_3{\cdot}Et_2O$ with THF as solvent, the only product formed was **8a** and none of the $CO{\cdot}BF_3$ adduct was observed. These results suggest that the only source of CO ligand in **8a** is from the methoxycarbonyl group of **2d** *via* an intramolecular process. The reaction was monitored by ^{1}H NMR (20 °C, in THF-d_8 solution), but no resonance attributable to a methoxy group or methanol was found, although a signal at 9.13 ppm was observed which disappeared within a few minutes and may tentatively be assigned to the methylene group of formaldehyde,[19] one of the possible products formed from “$MeO^•$”. Unfortunately, GC experiments to identify organic products derived from the $MeO^•$ evolution were unsuccessful. In view of this difficulty, the ethoxy derivative $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC{\equiv}CCO_2Et)$ (**2f**) was synthesized and then oxidized (in THF-d_8 solution) to give **8a**. In the ^{1}H NMR spectrum of the reaction mixture, ethanol and acetaldehyde, products probably formed from the ethoxy radical disproportionation, were easily identified.

Scheme 3. Proposed Mechanism for the Formation of Complex 8a



Taking into consideration the well-known conversion of terminal alkynes to metal vinylidenes *via* alkynyl intermediates,[20] we then explored the possible participation of an alkynyl radical cation intermediate, $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)NbC{\equiv}CMe]^{•+}$ (**II**), in the formation of **8a** by ligand−ligand coupling (Scheme 3). The formation of divinylidene ligands bridging two metal atoms has been described to occur both by ligand−ligand coupling of an unstable radical alkynyl species and by oxidatively induced coupling of vinylidene species.[21] In order to prove the intermediacy of a radical alkynyl complex in the formation of the divinylidene moiety, the

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(16) (a) Antiñolo, A.; Fajardo, M.; López-Mardomingo, C.; Otero, A.; Mugnier, Y.; Mourad, Y.; Sanz-Aparicio, J.; Fonseca, I.; Florencio, F. *Organometallics* **1990**, *9*, 2919. (b) Antiñolo, A.; Fajardo, M.; López-Mardomingo, C.; Gil-Sanz, R.; Martín-Villa, P.; Otero, A.; Kubicki, M. M.; Mugnier, Y.; El Krami, S.; Mourad, Y. *Organometallics* **1993**, *12*, 381. (c) Antiñolo, A.; Otero, A.; Fajardo, M.; López-Mardomingo, C.; Lucas, D.; Mugnier, Y.; Lanfranchi, M.; Pellinghelli, M. A. *J. Organomet. Chem.* **1992**, *435*, 55.

(17) Leading references: (a) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1799. (b) Demerseman, B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1981**, 665. (c) Demerseman, B.; Mahé, R.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1394. (d) Alt, H. G.; Herrmann, G. S.; Rausch, M. D.; Mallin, D. T. *J. Organomet. Chem.* **1988**, *356*, C53. (e) Alt, H. G.; Herrmann, G. S. *J. Organomet. Chem.* **1990**, *390*, 159. (f) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **1993**, *105*, 1228.

(18) See, for example: (a) Vaughan, G. A.; Sofield, C. D.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491. (b) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994.

(19) (a) Shapiro, B. L.; Kopchik, R. M.; Ebersole, S. J. *J. Chem. Phys.* **1963**, *39*, 3154. (b) Bercovici, T.; King, J.; Berker, R. S. *J. Chem. Phys.* **1972**, *56*, 3956. (c) Page, M.; Lin, M. C.; He, Y.; Choudhury, T. K. *J. Phys. Chem.* **1989**, *93*, 4404. (d) Choudhury, T. K.; He, Y.; Sanders, W. A.; Lin, M. C. *J. Phys. Chem.* **1990**, *94*, 2394.

(20) Leading references: (a) García Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406 and references therein. (b) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474. (c) Schneider, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 700.

alkynyl complex Nb(η^5-$C_5H_4SiMe_3$)$_2$(CO)(C≡CPh) (**13**) was synthesized by reacting the complex Nb(η^5-$C_5H_4SiMe_3$)$_2$(CO)(Cl) with Mg(C≡CPh)$_2$. The reaction of **13** with 1 equiv of the ferrocenium salt was subsequently carried out, and the expected divinylidene complex [(η^5-$C_5H_4SiMe_3$)$_2$(CO)Nb═C═C(Ph)(Ph)C═C═Nb(CO)(η^5-$C_5H_4SiMe_3$)$_2$][BPh$_4$]$_2$ (**8c**) was isolated as a stable yellow solid which was fully characterized. This result confirms that in fact the formation of the divinylidene moiety takes place through carbon−carbon coupling of alkynyl radical cations. We assumed in our proposal that the first step of the mechanism would be the one-electron oxidation of **2d**, followed by an intramolecular rearrangement of the η^2-alkyne to the σ-alkynyl species (**I**),[22] which would lead to the proposed alkynyl radical cation (**II**).

Complexes **8** constitute unusual d^2 niobocene species which contain both a π-acid ligand (carbonyl or *tert*-butyl isocyanide), and a C$_4$ chain ligand, 2,3-(dimethyl or diphenyl)-1,3-butadiene-1,4-diylidene. The complexes have been spectroscopically characterized. The IR spectra of **8a** and **8c** exhibit a band at 2081 and 2075 cm^{-1}, respectively, which corresponds to ν(CO) of the carbonyl ligand. The position of the band may be ascribed to a slight back-donation from the Nb═C═C bonding orbital to the in-plane CO π^* orbital, in a manner similar to that previously described[6,23] for the cationic d^2 carbonyl complexes [Nb(η^5-C_5R_5)$_2$(CO)$_2$]$^+$. For **8b** the band at 2179 cm^{-1} must be assigned to ν(C≡N) of the isocyanide ligand. NMR spectra of complexes **8a** and **8c** indicate the presence of only one isomer, unlike the case for **8b**, where a mixture of two isomers is observed. The molecular structure of **8a** was previously reported,[10] and it was indicated that the CO ligands were located in a trans disposition with respect to the C$_4$ chain−divinylidene ligand, so as to avoid adverse steric interactions (see Scheme 1). This structural arrangement is also proposed for **8c** and one of the isomers of **8b**, while an alternative cis disposition might be tentatively considered for the other isomer of **8b** (Figure 2). The formation of a mixture of isomers for **8b** can be envisaged to be the result of the alternative coordination of the tBuNC ligand to one side or the other of the Nb═C═C chain in the substitution process of the CO ligand noted above. The ^{13}C NMR signal for the carbonyl ligand in **8a** and **8c** and for the carbon attached to the metal of the isocyanide in **8b** is observed neither in solution nor in the solid state. This could be attributed to the quadrupolar moment of the ^{93}Nb nucleus (spin $I = {}^9/_2$, natural abundance 100%), which could cause such broadening of the signal so as to make it undetectable at room temperature.[24] The vinylidene α- and β-carbons exhibited resonances at ca. 377 and 144 ppm, respectively, in the ^{13}C NMR spectra, which are entirely consistent with the presence of a vinylidene complex.[25] Related mononuclear vinylidene tantalocene and niobocene complexes have been described,[26] and some divinylidene complexes of late transition metals have also been reported.[21,27]

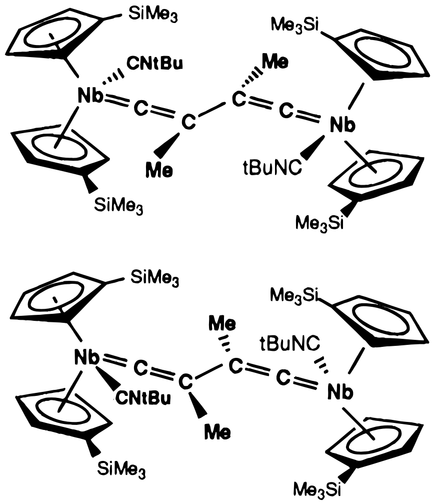

Figure 2. Structural arrangements proposed for complex **8b**.

Concluding Remarks

This study has revealed that the paramagnetic niobocene alkyne complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-RC≡CR′) (**2**) react easily with 1 equiv of ferrocenium salt in the presence of an appropriate Lewis base, nitrile, isonitrile, or THF, giving rise to the cationic d^2 alkyne complexes [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-RC≡CR′)(L)][BPh$_4$] (**3**−**7**). However, oxidation of **2d** under alternative experimental conditions opens the way to the divinylidene binuclear d^2 niobocene species [(η^5-$C_5H_4SiMe_3$)$_2$(CO)Nb═C═C(CH$_3$)(CH$_3$)C═C═Nb(CO)(η^5-$C_5H_4SiMe_3$)$_2$][BPh$_4$]$_2$ (**8a**), through an intramolecular process which involves the alkynyl cation intermediate [(η^5-$C_5H_4SiMe_3$)$_2$(CO) NbC≡CMe]$^{\bullet+}$.

The paramagnetic Nb(IV) complexes **2** are also useful starting materials for the preparation of mixtures of both alkyl−alkyne and halo−alkyne complexes by reaction with different alkyl halides. The former complexes could, however, be aternatively synthesized from the appropriate chloro species **1** in their reactions with dialkylmagnesium reagents. We believe that the results reported offer a significant advance in the chemistry of alkyne- and vinylidene-containing niobocene complexes, and work in this field is ongoing.

Experimental Section

General Considerations. Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-RC≡CR′)(Cl)[4a,b] (**1**), Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-RC≡CR′)[4c] (**2**), [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C*,*C*)-MeC≡CCOOMe)(CH$_3$CN)][BPh$_4$][10] (**3d**), and the divinylidene complex [(η^5-$C_5H_4SiMe_3$)$_2$(CO)Nb═C═C(CH$_3$)(CH$_3$)C═C═Nb(CO)(η^5-$C_5H_4SiMe_3$)$_2$][BPh$_4$]$_2$[10] (**8a**) were prepared by published methods. The

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(21) (a) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. (b) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129. (c) Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910.

(22) Not only terminal alkynes but also internal alkynes can undergo intramolecular rearrangement.[20c]

(23) Eckart, E. H. O.; Brintzinger, H. H. *J. Organomet. Chem.* **1978**, *148*, 29.

(24) See: (a) Green, M. L. H.; Hughes, A. K.; McGowan, P. C.; Mountford, P.; Scott, P.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1591. (b) Green, M. L. H.; O'Hare, D.; Watkin, J. G. *J. Chem. Soc., Chem. Commun.* **1989**, 698.

(25) Birdwhistell, K. R.; Nieter Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789 and references therein.

(26) (a) Van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347. (b) Gibson, V. C.; Parkin, G.; Bercaw, J. E. *Organometallics* **1991**, *10*, 220. (c) Fermin, M. C.; Bruno, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 7511.

(27) Rappert, T.; Nürnberg, O.; Werner H. *Organometallics* **1993**, *12*, 1359.

syntheses of the alkylmagnesium compounds MgR_2 have also been previously reported.[28]

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 or CCl_4 mulls between CsI plates (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 neutral compounds they were recorded on a Hewlett-Packard 5988A (*m*/*z* 50−1000), using chemical ionization techniques.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)(CH_3CN)][BPh_4]$ (3a). Method A. To an equimolar mixture of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)$ (**2a**; 360 mg, 0.66 mmol) and $[FeCp_2][BPh_4]$ (330 mg, 0.66 mmol) was added 30 mL of CH_3CN at −20 °C via vacuum transfer. The solution was stirred at this temperature for 5 min and then warmed to room temperature for 2 h. The solvent was removed in vacuo, and the resulting oily brown solid was washed with diethyl ether to remove the $FeCp_2$. The crude white solid was recrystallized from a mixture of acetonitrile and diethyl ether to yield **3a** as white needles (410 mg, 0.45 mmol, 69%).

Method B. To a mixture of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)(I)$ (50 mg, 0.074 mmol) and thallium tetraphenylborate (40 mg, 0.082 mmol) was added 10 mL of acetonitrile. The mixture was stirred at room temperature for 24 h and filtered to separate a yellow precipitate of TlI. The orange solution thus obtained was evaporated to dryness, and an orange solid was isolated and identified as **3a** (85%).

IR (Nujol mull): 2280, 2310 ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, CD_3CN): δ 0.09 (s, 18 H, $SiMe_3$), 2.31 (s, 3H, CH_3CN coordinated), 5.90 (2H), 5.96 (2 H), 6.30 (2 H), 6.35 (2 H), (m, $C_5H_4SiMe_3$), 6.84 (m, 4H, *p*-C_6H_5), 6.99 (m, 8H, *m*-C_6H_5), 7.28 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-), 7.30−7.56 (m, 10H, phenyl groups of diphenylacetylene). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ −1.54 ppm ($SiMe_3$), 4.92 (CH_3CN coordinated), 103.31, 112.02, 115.80, 125.12, 126.65 ($C_5H_4SiMe_3$), 125.23, 125.30, 128.35, 128.48, 128.55, 128.78, 129.49, 135.44 (C phenyl groups of acetylene ligand), 121.44, 125.27, 135.46 (C phenyl groups of BPh_4^-), 126.08, (CH_3CN coordinated), 140.47, 144.86 ($PhC\equiv CPh$), 163.51 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz). Anal. Calcd for $C_{56}H_{59}BNNbSi_2$: C, 74.28; H, 6.52; N, 1.54. Found: C, 74.30; H, 6.48; N, 1.49.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeOOCC\equiv CCOOMe)(CH_3CN)][BPh_4]$ (3b). This complex was isolated in a way similar to that for **3a** (method A) and recrystallized from a mixture of acetonitrile and diethyl ether to yield white needles in 40% yield.

IR (Nujol mull): 2308, 2281 cm^{-1} ($\nu_{C\equiv N}$); 1784 cm^{-1} ($\nu_{C\equiv C}$); 1700 cm^{-1} ($\nu_{C=O}$); 1208 cm^{-1} (ν_{C-O}). ^1H NMR (300 MHz, CD_3CN): δ 0.20 (s, 18H, $SiMe_3$), 2.48 (s, 3H, CH_3CN), 3.78 (s, 3H, $\equiv CCO_2CH_3$), 3.87 (s, 3H, $\equiv CCO_2CH_3$), 5.99 (2H), 6.03 (2H), 6.27 (2H), 6.36 (2H), (m, $C_5H_4SiMe_3$), 6.88 (m, 4H, *p*-C_6H_5), 7.03 (m, 8H, *m*-C_6H_5), 7.28−7.36 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ −0.54 ($SiMe_3$), 5.94 (CH_3CN coordinated), 53.00, 53.41 ($\equiv CCO_2CH_3$), 106.59, 113.05, 119.31, 122.01, 126.57 ($C_5H_4SiMe_3$), 122.79, 126.62, 136.82 (C phenyl groups of BPh_4^-), 141.00, 151.46 ($\equiv CCO_2CH_3$), 164.86 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz), 168.92, 172.15 ($\equiv CCO_2CH_3$). Anal. Calcd for $C_{48}H_{55}BNO_4NbSi_2$: C, 66.30; H, 6.32; N, 1.61. Found: C, 66.25; H, 6.31; N, 1.58. FAB MS (*m*/*e* (relative intensity)): 550 (36) (M^+, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2[\eta^2(C,C)\text{-}CH_3O_2C\equiv CO_2CH_3)(CH_3CN)]^+$); 509 (100) ($M^+ - CH_3CN$); 494 (10) ($M^+ - CH_3CN - CH_3$), 405 (5) ($[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CH_3CN)]^+$).

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC\equiv CMe)(CH_3CN)][BPh_4]$ (3c). Method A. This compound was prepared by oxidation of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC\equiv CMe)$ (**2c**) as described for **3a** (method A) and recrystallized from a mixture of acetonitrile and diethyl ether as pale yellow needles in 97% yield.

Method B. $Tl[BPh_4]$ (80 mg, 0.16 mmol) was added to a solution of 90 mg of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeC\equiv CMe)(I)$ in 10 mL of acetonitrile, and this mixture was stirred at room temperature for 48 h. A yellow precipitate of TlI was formed. After filtration, the solvent was removed from the light brown solution to give **3c** as a pale brown solid in 80% yield.

IR (Nujol mull): 2274, 2305 cm^{-1} ($\nu_{C\equiv N}$); 1842 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, CD_3CN): δ 0.14 (s, 18H, $SiMe_3$), 2.13, 2.43 (q, *J* = 1.2 Hz, 3H, $\equiv CCH_3$), 2.54 (s, 3H, CH_3CN), 5.62−5.68 (4H), 5.80 (2H), 6.04 (2H), (m, $C_5H_4SiMe_3$), 6.84 (m, 4H, *p*-C_6H_5), 6.99 (m, 8H, *m*-C_6H_5), 7.22−7.32 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). ^1H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 18H, $SiMe_3$), 1.10 (s, 3H, CH_3CN coordinated), 1.97 (s, 3H, CH_3 endo), 2.34 (s, 3H, CH_3 exo), 5.26−5.31 (4H), 5.36−5.41 (2H), 5.46−5.51 (2H), (m, $C_5H_4SiMe_3$), 6.48−6.95 (m, 4H, *p*-C_6H_5), 7.00−7.15 (m, 8H, *m*-C_6H_5), 7.45−7.55 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ −0.30 ($SiMe_3$), 5.73 (CH_3CN coordinated), 12.71, 19.73 ($CH_3C\equiv CCH_3$), 102.83, 107.97, 113.12, 115.33, 118.03 ($C_5H_4SiMe_3$), 122.74, 126.55, 136.70 (C phenyl groups of BPh_4^-), 138.67, 141.75 ($MeC\equiv CMe$), 164.76 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.6 Hz). Anal. Calcd for $C_{46}H_{55}BNNbSi_2$: C, 70.68; H, 7.09; N, 1.79. Found: C, 70.72; H, 7.03; N, 1.82.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)(tBuCN)][BPh_4]$ (4a). To an equimolar mixture of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)$ (**2a**; 260 mg, 0.48 mmol) and $[FeCp_2][BPh_4]$ (240 mg, 0.48 mmol) was added 15 mL of acetonitrile at 0 °C. The solution was stirred for 45 min at room temperature, then the solvent was removed in vacuo and the resulting residue was washed with Et_2O and recrystallized from a mixture of tBuCN and CH_3CN to give yellow needles (360 mg, 0.38 mmol, 80%).

IR (Nujol mull): 2256 cm^{-1} ($\nu_{C\equiv N}$); 1790 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, CD_3CN): δ 0.15 (s, 18 H, $SiMe_3$), 1.33 (s, 9H, tBuCN coordinated), 5.88−5.94 (2H), 5.94−6.00 (2 H), 6.26−6.32 (2 H), 6.34−6.40 (2 H), (m, $C_5H_4SiMe_3$), 6.80−6.90 (m, 4H, *p*-C_6H_5), 6.94−7.06 (m, 8H, *m*-C_6H_5), 7.29 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-), 7.32−7.60 (m, 10H, phenyl groups of acetylene). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ 0.06 ($SiMe_3$), 27.40 ($(CH_3)_3CCN$, coordinated), 31.94, (Me_3CCN coordinated), 104.02, 109.30, 112.93, 118.34, 118.95 ($C_5H_4SiMe_3$), 127.50, (^tBuCN, coordinated), 127.79, 129.29, 129.78, 130.05, 130.77, 135.95, 138.30 (C of phenyl groups of $PhC\equiv CPh$), 122.69, 126.53, 136.68 (C of phenyl groups of BPh_4^-), 146.75, 147.79 ($PhC\equiv CPh$), 164.82 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz). Anal. Calcd for $C_{59}H_{65}BNNbSi_2$: C, 74.80; H, 6.86; N, 1.48. Found: C, 74.65; H, 6.77; N, 1.60.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeOOCC\equiv CCOOMe)(tBuCN)][BPh_4]$ (4b). This complex was obtained in 60% yield by following the same procedure as described for **4a**, after recrystallization from a mixture of tBuCN and Et_2O.

IR (Nujol mull): 2275 cm^{-1} ($\nu_{C\equiv N}$); 1781 cm^{-1} ($\nu_{C\equiv C}$); 1693 cm^{-1} ($\nu_{C=O}$); 1214 cm^{-1} (ν_{C-O}). ^1H NMR (300 MHz, CD_3CN): δ 0.21 (s, 18H, $SiMe_3$), 1.54 (s, 9H, tBuCN coordinated), 3.77, 3.86 (s, 3H, $-CO_2CH_3$), 5.97 (2H), 6.09 (2H), 6.31 (2H), 6.34 (2H), (m, $C_5H_4SiMe_3$), 6.85 (4H, *p*-C_6H_5), 7.00 (8H, *m*-C_6H_5), 7.24−7.32 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ 0.52 ($SiMe_3$), 27.50 ($(CH_3)_3CCN$), 31.90 ($(CH_3)_3CCN$), 52.93, 53.40 ($-CO_2CH_3$), 105.92, 112.43, 113.20, 119.00, 124.54 ($C_5H_4SiMe_3$), 122.72, 126.54, 136.69 (phenyl groups of BPh_4^-), 129.13, (tBuCN), 147.18, 150.95 ($MeO_2CC\equiv CCO_2CH_3$), 164.74 (C-ipso of BPh_4^-; q, $J_{^{13}C-^{11}B}$ = 49.7 Hz), 169.22, 172.08 ($-CO_2CH_3$). Anal. Calcd for $C_{51}H_{61}BNNbO_4Si_2$: C, 67.17; H, 6.74; N, 1.54. Found: C, 66.89; H, 6.71; N, 1.55.

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(28) (a) Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262. (b) Eisch, J. J.; Sanchez, R. *J. Organomet. Chem.* **1985**, *296*, C-27.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-MeC$\equiv$CMe)(tBuCN)]-[BPh$_4$] (4c). The procedure described before for **4a** was again followed to obtain **4c** in 59% yield as a light brown solid after recrystallization from tBuCN and Et_2O.

IR (Nujol mull): 2261 ($\nu_{C\equiv N}$); 1835 ($\nu_{C\equiv C}$) cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN): δ 0.15 (s, 18H, $SiMe_3$), 1.56 (s, 9H, tBuCN coordinated), 2.15 (q, J = 1.2 Hz, 3H, $\equiv CCH_3$), 2.45 (q, J = 1.2 Hz, 3H, $\equiv CCH_3$), 5.59−5.63 (2H), 5.68−5.72 (2H), 5.82−5.86 (2H), 6.00−6.04 (2H) (m, $C_5H_4SiMe_3$), 6.78−6.86 (m, 4H, *p*-C_6H_5), 6.94−7.02 (m, 8H, *m*-C_6H_5), 7.22−7.29 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ −0.16 ($SiMe_3$), 12.83, 20.07 ($CH_3C\equiv CCH_3$), 27.84 (($CH_3)_3$CCN coordinated), 32.04 (($CH_3)_3$CCN coordinated), 102.22, 108.31, 112.71, 115.43, 119.90 ($C_5H_4SiMe_3$), 122.71, 126.55, 136.70 (phenyl groups of BPh_4^-), 138.98, 148.26 ($CH_3C\equiv CCH_3$), 164.76 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.6 Hz). Anal. Calcd for $C_{49}H_{61}BNNbSi_2$: C, 71.43; H, 7.46; N, 1.70. Found: C, 69.95; H, 7.31; N, 1.71.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-MeOOCC$\equiv$CMe)(tBuCN)]-[BPh$_4$] (4d). This compound was obtained as a mixture of the endo and exo isomers (6:1) in 65% total yield. The experimental procedure was the same as described for **4a−c**. The major isomer could easily be separated by crystallization from a mixture of tBuCN and Et_2O.

IR (Nujol mull): 2270 cm^{-1} ($\nu_{C\equiv N}$); 1779 cm^{-1} ($\nu_{C\equiv C}$); 1699 cm^{-1} ($\nu_{C=O}$); 1220 cm^{-1} (ν_{C-O}). ^{1}H NMR (*major isomer*, 300 MHz, CD_3CN): δ 0.17 (s, 18 H, $SiMe_3$), 1.54 (s, 9H, tBuCN coordinated), 2.70 (s, 3H, $\equiv CCH_3$), 3.72 (s, 3H, $\equiv CCO_2CH_3$), 5.74−5.80 (2H), 5.91−5.96 (2H), 5.96−6.02 (2H), 6.19−6.24 (2H) (m, $C_5H_4SiMe_3$), 6.82−6.90 (m, 4H, *p*-C_6H_5), 6.96−7.06 (m, 8H, *m*-C_6H_5), 7.24−7.34 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (*major isomer*, 300 MHz, CD_3CN): δ −0.54 (Si($CH_3)_3$), 21.94 ($\equiv CCH_3$), 27.62 (($CH_3)_3$CCN coordinated), 31.80 (($CH_3)_3$CCN coordinated), 52.29 ($\equiv CCOOCH_3$), 103.60, 111.96, 112.39, 116.62, 122.20 ($C_5H_4SiMe_3$), 122.71, 126.55, 136.70 (phenyl groups of BPh_4^-), 147.04 ($CH_3C\equiv CCO_2CH_3$), 164.71 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz), 166.83 ($CH_3C\equiv CCO_2CH_3$), 170.70 (CO_2CH_3). ^{13}C NMR data for the minor isomer are not provided because of the low intensity of the signals in the spectrum of the isomer mixture. Anal. Calcd for $C_{50}H_{61}BNNbO_2Si_2$: C, 69.13; H, 7.08; N, 1.61. Found: C, 68.95; H, 7.20; N, 1.47.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-PhC$\equiv$CPh)(tBuNC)]-[BPh$_4$] (5a). Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-PhC$\equiv$CPh) (240 mg, 0.44 mmol) dissolved in hexane was slowly added to [FeCp$_2$][BPh$_4$] (220 mg, 0.44 mmol) and 66 μL of ^{t}BuNC (20% excess, 48 mg, 53 mmol). The mixture was stirred at room temperature for 36 h and evaporated to dryness. The residue was washed with diethyl ether and recrystallized from a mixture of diethyl ether and acetonitrile to yield **5a** as white needles in 71% yield.

IR (Nujol mull): 2180 cm^{-1} ($\nu_{N\equiv C}$); 1791 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (300 MHz, CD_3CN): δ 0.14 (s, 18 H, $SiMe_3$), 1.44 (s, 9H, tBuNC coordinated), 5.75 (2H), 5.88 (2 H), 6.15 (2 H), 6.20 (2 H) (m, $C_5H_4SiMe_3$), 6.78−6.90 (m, 4H, *p*-C_6H_5), 6.92−7.60 (m, 8H, *m*-C_6H_5), 7.22−7.32 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-), 7.30−7.66 (m, 10H, phenyl groups of PhC$\equiv$CPh). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ −0.08 ($SiMe_3$), 29.66 (($CH_3)_3$CNC coordinated), 62.03 (($CH_3)_3$CNC coordinated), 101.98, 108.80, 110.98, 112.00, 112.44 ($C_5H_4SiMe_3$) 127.98, 129.03, 129.68, 129.75, 129.95, 130.68, 135.87 (phenyl groups of PhC$\equiv$CPh), 121.68, 126.55, 136.68 (phenyl groups of BPh_4^-), 139.10, 139.61, (Ph*C*$\equiv$*C*Ph), 164.73 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz). Anal. Calcd for $C_{59}H_{65}BNNbSi_2$: C, 74.80; H, 6.86; N, 1.48. Found: C, 74.40; H, 6.88; N, 1.35.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-MeO$_2$CC$\equiv$CCO$_2$Me)(tBuNC)]-[BPh$_4$] (5b). This compound was obtained by following the same procedure as described for **5a** in 56% yield.

IR (Nujol mull): 2195 cm^{-1} ($\nu_{N\equiv C}$); 1786 cm^{-1} ($\nu_{C\equiv C}$); 1705 cm^{-1} ($\nu_{C=O}$); 1213 cm^{-1} (ν_{C-O}). ^{1}H NMR (300 MHz, CD_3CN): δ 0.21 (s, 18H, $SiMe_3$), 1.70 (s, 9H, tBuNC coordinated), 3.78, 3.88 (s, 3H, $\equiv CCO_2CH_3$), 5.62−5.70 (2H), 6.06−6.10 (2H), 6.10−6.15 (2H), 6.20−6.26 (2H), (m, $C_5H_4SiMe_3$), 6.81−6.90 (m, 4H, *p*-C_6H_5), 6.96−7.05 (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 (300 MHz, CD_3CN): δ −0.50 ($SiMe_3$), 29.86 (($CH_3)_3$CNC coordinated), 53.14, 53.46 ($\equiv CCO_2CH_3$), 62.37 (($CH_3)_3$CNC coordinated), 103.41, 110.06, 112.08, 113.12, 118.22 ($C_5H_4SiMe_3$), 122.71, 126.55, 136.7 (phenyl groups of BPh_4^-), 143.88 (MeO$_2$C*C*$\equiv$*C*CO$_2$CH$_3$; only one acetylene carbon is observed), 164.74 (C-ipso of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz), 169.51, 172.25, ($\equiv CCO_2CH_3$). Anal. Calcd for $C_{51}H_{61}BNNbO_4Si_2$: C, 67.17; H, 6.74; N, 1.54. Found: C, 66.63; H, 6.59; N, 1.59.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-MeC$\equiv$CMe)(tBuNC)]-[BPh$_4$] (5c). To an equimolar mixture of Nb(η^5-$C_5H_4SiMe_3$)$_2$-(η^2(*C,C*)-MeC$\equiv$CMe) (**2c**; 200 mg, 0.46 mmol) and [FeCp$_2$][BP$_4$] (230 mg, 0.46 mmol) was added THF at −20 °C followewd by 70 μL of tBuNC (30% excess, 50 mg, 0.6 mmol). The solution was stirred and slowly warmed to room temperature for 30 min. The solvent was then removed in vacuo, and the resulting oily solid was washed with diethyl ether to give **5c** as a pale brown powder in 50% yield.

IR (Nujol mull): 2168 cm^{-1} ($\nu_{C\equiv N}$); 1879 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (300 MHz, CD_3CN): δ 0.20 (s, 18H, $SiMe_3$), 1.73 (s, 9H, tBuNC coordinated), 2.32, 2.51 (q, J = 1.2 Hz, 3H, $\equiv CCH_3$), 5.38−5.40 (2H), 5.63−5.66 (2H), 5.66−5.70 (2H), 5.86−5.88 (2H) (m, $C_5H_4SiMe_3$), 6.83−6.90 (m, 4H, *p*-C_6H_5), 6.99−7.01 (m, 8H, *m*-C_6H_5), 7.26 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ −0.28 ($SiMe_3$), 15.16, 19.66 ($\equiv CCH_3$), 30.29 (($CH_3)_3$CNC coordinated), 61.62 (($CH_3)_3$CNC coordinated), 99.74, 107.85, 109.16, 109.94, 113.63 ($C_5H_4SiMe_3$), 122.71, 126.53, 136.70 (phenyl groups of BPh_4^-), 164.23 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.6 Hz). The acetylenic carbons are not observed. Anal. Calcd for $C_{49}H_{61}BNNbSi_2$: C, 71.43; H, 7.43; N, 1.70. Found: C, 70.90; H, 7.32; N, 1.84.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-$CH_3C\equiv CCH_3$)(THF)]-[BPh$_4$] (6c). To an equimolar mixture of Nb(η^5-$C_5H_4SiMe_3$)$_2$-(η^2(*C,C*)-$CH_3C\equiv CCH_3$) (**2c**; 230 mg, 0.54 mmol) and [FeCp$_2$]-[BPh$_4$] (170 mg, 0.54 mmol) was added 20 mL of THF at −30 °C. The solution was stirred at this temperature for 10 min and then warmed to room temperature for 30 min. The solvent was removed in vacuo, and the brown oily solid obtained was washed with diethyl ether at 0 °C to precipitate a light brown solid (228 mg, 0.28 mmol, 53%). This product easily decomposes through loss of coordinated THF, unless stored below 5 °C.

IR (Nujol mull): 1830 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (300 MHz, CD_3CN): δ 0.16 (s, 18 H, $SiMe_3$), 1.72−1.82 (m, 4H, β-C_4H_8O), 1.55, 1.57 (s, 3H, $\equiv CCH_3$), 3.55−3.67 (m, 4H, α-C_4H_8O), 5.83 (2H), 5.89 (2H), 6.23 (2H), 6.46 (2H) (m, $C_5H_4SiMe_3$), 6.95−7.05 (m, 4H, *p*-C_6H_5), 7.15−7.25 (m, 8H, *m*-C_6H_5), 7.25−7.32 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN, −40 °C): δ −1.08 ($SiMe_3$), 16.01, 24.71 ($CH_3C\equiv CCH_3$), 25.83 (C_β of THF), 67.83, (C_α of THF), 111.35, 112.14, 114.80, 121.05, 122.40 ($C_5H_4SiMe_3$), 125.75, 127.57, 133.38 (phenyl groups of BPh_4^-), 151.38 ($CH_3C\equiv CCH_3$, only one acetylenic carbon was observed), 164.19 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz). Anal. Calcd for $C_{48}H_{60}BNbOSi_2B$: C, 70.92; H, 7.44. Found: C, 70.45; H, 7.20.

[Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-$CH_3C\equiv CCO_2CH_3$)(THF)]-[BPh$_4$] (6d). This reaction has to be carried out at low temperature (−30 °C) to avoid the formation of the divinylidene complex **8a**, as has been described earlier.[10] Thus, to a mixture of Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2(*C,C*)-$CH_3C\equiv CCO_2CH_3$) (220 mg, 0.47 mmol) and [FeCp$_2$][BPh$_4$] (240 mg, 0.47 mmol) was added THF at −30 °C. The solution was stirred at this temperature for 5 min and then slowly warmed to 25 °C. Then, the solvent was removed and the remaining product was washed with a cold mixture of THF and hexane and isolated as a pale brown powdery solid. Both endo and exo isomers (6:1) were obtained (280 mg, 0.32 mmol, 70%).

IR (Nujol mull): 1730 cm^{-1} ($\nu_{C\equiv C}$); 1678 cm^{-1} ($\nu_{C=O}$); 1210 cm^{-1} (ν_{C-O}). ^{1}H NMR (300 MHz, THF-d_8): δ 0.15 (s, 18 H, $SiMe_3$), 1.77 (m, 4H, H_β of THF coordinated), 2.59 (s, 3H,

$\equiv CCH_3$), 3.62 (m, 4H, H_α of THF coordinated), 3.66 (s, 3H, $\equiv CCO_2CH_3$), 5.62−5.70 (2H), 5.92−6.04 (4H), 6.06−6.14 (2H) (m, $C_5H_4SiMe_3$), 6.70−6.82 (m, 4H, *p*-C_6H_5), 6.82−7.00 (m, 8H, *m*-C_6H_5), 7.22−7.44 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-). $^{13}C\{^1H\}$ NMR (300 MHz, THF-d_8, −40 °C): δ −0.80 ($SiMe_3$), 23.50 ($CH_3C\equiv CCO_2CH_3$), 26.20 (C_β of THF), 52.00 ($CH_3CO_2\equiv CCH_3$), 68.10 (C_α of THF), 103.99, 110.76, 111.20, 114.72, 120.96 ($C_5H_4SiMe_3$), 121.88, 127.83, 137.16 (phenyl groups of BPh_4^-), 137.48 ($CH_3C\equiv CCO_2CH_3$), 181.59 ($CH_3C\equiv CCO_2CH_3$), 165.14 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.45 Hz), 173.94 (CO_2CH_3). NMR data for the minor isomer are not given because of the low intensity of the signals in the spectra of the isomer mixture. Anal. Calcd for $C_{49}H_{60}BNbO_3Si_2B$: C, 68.72; H, 7.00. Found: C, 68.62; H, 7.10.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)(Py)][BPh_4]$ (7a). To $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)$ (**2a**; 230 mg, 0.42 mmol) was added 210 mg of $[FeCp_2][BPh_4]$ (0.42 mmol) and then 10 mL of pyridine at −30 °C. The solution was stirred at this temperature for 15 min and then was slowly warmed to room temperature and stirred for 12 h. After this time, the solvent was removed in vacuo and the remaining product washed with diethyl ether to give a precipitate which was recrystallized from a mixture of pyridine and hexane to yield **7a** as a yellow solid (200 mg, 0.231 mmol, 55%).

IR (CCl_4 mull): 1739 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, CD_3CN, −40 °C): δ −0.03 (s, 18H, $SiMe_3$), 5.90−5.98 (2H), 6.10−6.22 (6 H) (m, $C_5H_4SiMe_3$), 6.76−6.86 (m, 4H, *p*-C_6H_5), 6.92−7.04 (m, 8H, *m*-C_6H_5), 7.20−7.30 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-), 7.04−7.10 (2H), 7.26−7.36 (5H), 7.38−7.44 (1H), 7.50−7.58 (2H) (m, phenyl groups of $PhC\equiv CPh$), 7.44−7.50 (2H), 7.86−7.94 (1H), 8.50−8.60 (2H), (m, C_5H_5N coordinated). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN, −40 °C): δ 0.94 ($SiMe_3$), 104.73, 109.77, 117.78, 118.77, 121.10 ($C_5H_4SiMe_3$), 126.10, 129.11, 129.30, 129.69, 129.94, 130.61, 134.67, 136.56 (phenyl groups of $pHC\equiv CPh$), 127.43, 140.34, 158.31 (C_5H_5N coordinated), 122.46, 126.40, 136.13 (phenyl groups of BPh_4^-), 138.08, 153.14 ($PhC\equiv CPh$), 164.82 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz). Anal. Calcd for $C_{59}H_{61}BNNbSi_2$: C, 75.10; H, 6.50; N, 1.48. Found: C, 74.95; H, 6.43; N, 1.47.

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}CH_3C\equiv CCH_3)(Py)][BPh_4]$ (7c). This complex was isolated as a deep blue solid, in good yield (61%), in a way similar to that described earlier for **7a**.

IR (CCl_4 mull): 1835 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, CD_3CN, −40 °C): δ −0.08 (s, 18 H, $SiMe_3$), 2.25, 2.42 (s, 3H, $CH_3C\equiv$), 5.60−5.70 (2H), 5.70−5.80 (2H), 5.80−5.90 (2H), 6.25−6.35 (2H) (m, $C_5H_4SiMe_3$), 6.75−6.90 (m, 4H, *p*-C_6H_5), 6.90−7.05 (m, 8H, *m*-C_6H_5), 7.17−7.30 (m, 8H, *o*-C_6H_5) (phenyl groups of BPh_4^-), 7.55−7.65 (2H), 8.00−8.10 (1H), 8.95−9.05 (2H), (C_5H_5N coordinated). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN, −40 °C): δ −1.52 ($SiMe_3$), 15.48, 20.81 ($CH_3C\equiv$), 101.84, 107.20, 113.87, 114.97 ($C_5H_4SiMe_3$, one of the signals is not observed), 122.26, 126.19, 135.58 (phenyl groups of BPh_4^-), 127.47, 140.46, 158.38 (C_5H_5N coordinated), 134.72, 150.70 ($CH_3C\equiv CCH_3$), 164.05 (C_{ipso} of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.7 Hz). Anal. Calcd for $C_{49}H_{57}BNNbSi_2$: C, 71.78; H, 6.95; N, 1.70. Found: C, 71.98; H, 6.73; N, 1.99.

$[(\eta^5\text{-}C_5H_4SiMe_3)_2(tBuNC)NbCC(CH_3)(CH_3)CCNb(tBuNC)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$ (8b). Method A. To an equimolar mixture of **2d**, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}MeO_2CC\equiv CMe)$ (120 mg, 0.26 mmol), and $[FeCp_2][BPh_4]$ (130 mg, 0.26 mmol) was added 25 mL of hexane at −10 °C. tBuNC was then added in 30% excess (38 μL, 28 mg, 0.33 mmol), and the solution was warmed to room temperature and stirred for a further 12 h. The mixture was then filtered and the solid washed with a mixture of THF and hexane to isolate a green-yellow solid. This solid was dissolved in hot acetonitrile, and after the mixture was cooled to room temperature, diethyl ether was added to precipitate a mixture of two isomers as yellow needles (120 mg, 0.07 mmol, 60%).

Method B. To a solution of the divinylidene complex **8a** (100 mg, 0.07 mmol) in THF was added an excess of tBuNC, and the mixture was stirred for 48 h. The solvent was removed in vacuo, and after the residue was washed with diethyl ether, a yellow product was precipitated, which was identified as a mixture of the two isomers of the divinylidene **8b**.

IR (Nujol mull): 2179 cm^{-1} ($\nu_{C\equiv N}$). ^1H NMR (300 MHz, CD_3CN): isomer I, δ 0.26 (s, 36H, $SiMe_3$), 1.53 (s, 18 H, tBuNC coordinated), 1.63 (s, 6H, $-CH_3$), 5.80−5.85 (4H), 5.85−5.90 (4H), 5.93−5.99 (4H), 5.99−6.03 (4H), (m, $C_5H_4SiMe_3$); isomer II, δ 0.27 (s, 36H, $SiMe_3$), 1.56 (s, 18 H, tBuNC coordinated), 1.62 (s, 6H, $-CH_3$), 5.71−5.75 (4H), 5.92−5.99 (12H), (m, $C_5H_4SiMe_3$); phenyl groups of BPh_4^- for both isomers, δ 6.80−6.88 (m, 8H, *p*-C_6H_5), 6.95−7.40 (m, 16H, *m*-C_6H_5), 7.22−7.32 (m, 16H, *o*-C_6H_5). It has not proved possible to measure the $^{13}C\{^1H\}$ NMR spectrum because of the low solubility of the product. Anal. Calcd for $C_{96}H_{116}B_2N_2Nb_2Si_4$: C, 71.26; H, 7.23; N, 1.73. Found: C, 71.00; H, 7.12; N, 1.82. FAB MS (*m/e* (relative intensity)) 978 (6) (M^{2+}); 922 (17) (M^{2+} − $(CH_3)_3C$); 895 (28) (M^{2+} − tBuNC), 838 (9) (M^{2+} − 2 tBuNC); 489 (35) ($[M^{2+}/2]$); 406 (18) ($[M^{2+}/2]$ − tBuNC).

$[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)NbCC(Ph)(Ph)CCNb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$ (8c). To a mixture of the alkynyl complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)(C\equiv CPh)$ (**13**; 100 mg, 0.2 mmol) and $[FeCp_2][BPh_4]$ (100 mg, 0.2 mmol) was added 20 mL of THF at room temperature. A rapid color change from green to black was observed, and the resulting solution was stirred at this temperature for 15 min. It was then stirred for a further 45 min at room temperature, the color changing again to yellow-brown. The solvent was evaporated in vacuo and the residue washed with diethyl ether. A yellow precipitate was obtained and identified as the divinylidene $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)Nb{=}C{=}C(Ph)(Ph)C{=}C{=}Nb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]_2$ (**8c**; 60 mg, 0.12 mmol, 36%).

IR (Nujol mull): 2075 cm^{-1} (ν_{CO}). ^1H NMR (300 MHz, CD_3CN): δ 0.155 (s, 36H, $SiMe_3$), 5.80−5.87 (4H), 5.87−5.94 (4H), 6.02−6.09 (4H), 6.12−6.20 (4H) (m, $C_5H_4SiMe_3$), 6.80−6.90 (m, 8H, *p*-C_6H_5), 6.94−7.06 (m, 16H, *m*-C_6H_5), 7.22−7.34 (m, 16H, *o*-C_6H_5), (phenyl groups of BPh_4^-), 7.38−7.58 (m, 10H, $C_6H_5C{=}C{=}Nb$). $^{13}C\{^1H\}$ NMR (300 MHz, CD_3CN): δ −0.45 ($SiMe_3$), 102.71, 106.36, 106.70, 110.32, 112.26 ($C_5H_4SiMe_3$), 122.73, 126.54, 136.72 (phenyl groups of BPh_4^-), 126.61 (C-4), 129.04 (C-3), 130.65 (C-2), 135.60 (C-1), ($C_6H_5C{=}CNb$), 144.13 ($Nb{=}C{=}C$), 164.76 (C_{ipso} of phenyl groups of BPh_4^-, q, $J_{^{13}C-^{11}B}$ = 49.45 Hz), 376.66 ($Nb{=}C{=}C$). Anal. Calcd for $C_{98}H_{102}B_2Nb_2O_2Si_4$: C, 72.17; H, 6.25. Found: C, 72.23; H, 6.33. FAB MS (*m/e* (relative intensity)): 1311 (2) ($[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)NbCC(Ph)(Ph)CCNb(CO)(\eta^5\text{-}C_5H_4SiMe_3)_2][BPh_4]^+$ ($M[BPh_4])^+$)), 964 (12) ($[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)NbCC(Ph)(Ph)CCNb(\eta^5\text{-}C_5H_4SiMe_3)_2]^{2+}$ (M^{2+} − CO)), 936 (7) (M^{2+} − 2CO), 468 (29) ($[M^{2+}/2]$ − CO), 366 (100) ($[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb]^+$ − 1).

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)(CH_3)$ (9a). A 7.4 mL (2.2 mmol) amount of a diethyl ether solution of $MgMe_2$ (0.1624 M) was evaporated to dryness, and a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)(Cl)$ (**1a**; 350 mg, 0.6 mmol) in 1,4-dioxane was then added. This reaction mixture was then stirred at 90 °C for 2 h, the solvent was removed in vacuo, and hexane added. After filtration, to remove the insoluble magnesium salts, a brown-green solution was obtained and evaporated to dryness. The residue was identified as the alkylated complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)(CH_3)$ and recrystallized from pentane as yellow needles (210 mg, 0.37 mmol, 62%).

IR (Nujol mull): 1735 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ 0.07 (s, 18 H, $SiMe_3$), 0.92 (s, 3H, $CH_3{-}Nb$), 5.07−5.11 (2H), 5.27−5.32 (2 H), 5.35−5.38 (2 H), 5.41−5.46 (2 H) (m, $C_5H_4SiMe_3$), 7.00−7.20 (2H), 7.20−7.40 (6H), 7.64−7.76 (2H) (m, pheny groups of $PhC\equiv CPh$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.13 ($SiMe_3$), 2.24 ($CH_3{-}Nb$), 100.10, 105.95, 107.75, 112.58, 114.06 ($C_5H_4SiMe_3$), 125.06, 127.25, 127.34, 129.75, 131.91 (phenyl groups of diphenylacetylene), 139.00, 142.98 (C-ipso of the groups C_6H_5), 144.22, 155.00 ($PhC\equiv CPh$). Anal. Calcd for $C_{31}H_{39}NbSi_2$: C, 66.44; H, 6.96. Found: C, 66.47; H, 7.00. MS (*m/e* (relative intensity)): 561 (34) (M^+ + 1); 560

(10) (M^+, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CPh)Me]^+$); 545 (41) ($M^+ - Me$); 382 (100) ($M^+ - PhC\equiv CPh$); 367 (27) ($M^+ - PhC\equiv CPh - CH_3$).

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}CH_3C\equiv CCH_3)(CH_3)$ (9c). To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}(CH_3C\equiv CCH_3)(Cl)$ (**1c**; 250 mg, 0.54 mmol) in diethyl ether was added 5 mL of $MgMe_2$ (0.67 mmol from a 0.135 M solution in Et_2O) at 0 °C. The reaction mixture was stirred at this temperature for 7 h and slowly warmed to room temperature. The solvent was removed in vacuo, hexane was added, and after filtration, the solution was once again evaporated to dryness. The methylated product **9c** was isolated as a green oil (160 mg, 0.345 mmol, 64%).

IR (Nujol mull): 1786 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ 0.10 (s, 18H, $SiMe_3$), 0.88 (s, 3H, CH_3−Nb), 2.22, 2.40 (s, 3H, $CH_3C\equiv CCH_3$), 4.80−4.90 (2H), 5.04−5.12 (2H), 5.14−5.18 (2H), 5.18−5.26 (2H), (m, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.13 ($SiMe_3$), 1.83 (CH_3Nb), 11.30, 20.60 ($CH_3C\equiv CCH_3$), 99.59, 105.61, 105.88, 109.13, 116.15 ($C_5H_4SiMe_3$), 131.59, 149.88 ($CH_3C\equiv CCH_3$).

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}HC\equiv CPh)(CH_3)$ (9e). The methyl complex **9e** was obtained in 65% yield by following the same procedure as described for **9a** and recrystallized from hexane to give yellow needles.

IR (Nujol mull): 1685 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ −0.05 (s, 18 H, $SiMe_3$), 1.08 (s, 3H, CH_3−Nb), 4.80−4.90 (2H), 5.15−5.25 (2 H), 5.40−5.55 (4 H) (m, $C_5H_4SiMe_3$), 7.25−7.40 (3H), 7.55−7.65 (2H) (m, phenyl group of $HC\equiv CPh$), 7.63 (s, 1H, $HC\equiv$). The exo geometry was assigned by NOE experiments. Irradiation of the methyl signal at δ 1.08 resulted in an enhancement of the acetylenic proton signal at 7.63 ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.36 ($SiMe_3$), 1.39 (CH_3−Nb), 98.33, 101.12, 107.87, 109.16, 119.45 ($C_5H_4SiMe_3$), 127.15 (C-4 of Ph), 128.61 (C-3 and C-5 of Ph), 131.205 (C-2 and C-6 of Ph), 137.42 (C-ipso of Ph), 137.28 ($\equiv CH$), 160.90 ($\equiv CPh$). Anal. Calcd for $C_{25}H_{35}NbSi_2$: C, 61.99; H, 7.23. Found: C, 62.01; H, 7.25.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}CH_3C\equiv CCH_3)(CH_2CH_3)$ (10c). To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}CH_3C\equiv CCH_3)(Cl)$ (**1c**; 200 mg, 0.43 mmol) in diethyl ether was added 5.73 mL (0.86 mmol) of a 0.15 M solution of $MgEt_2$ in Et_2O. The mixture was stirred at 0 °C for 6 h, and the solvent was then removed in vacuo at the same temperature. The product was obtained as an oily green solid by extraction with cold hexane and subsequent evaporation (95 mg, 0.215 mmol, 50%). This compound decomposes in solution to the hydrido−olefin complex at temperatures greater than 0 °C.

IR (Nujol mull): 1788 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ 0.07 (s, 18 H, $SiMe_3$), 1.77−1.89 (m, 3H, CH_3CH_2−Nb), 1.89−2.00 (m, 2H, CH_3CH_2−Nb), 2.18, 2.44 (s, 3H, $CH_3C\equiv$), 4.66−4.73 (2H), 5.20−5.28 (2 H), 5.36−5.46 (4 H), (m, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.19 ($SiMe_3$), 10.90, 21.54 ($CH_3C\equiv$), 12.53 (CH_3CH_2−Nb), 22.00 (CH_3CH_2−Nb), 98.13, 103.52, 104.01, 118.65, 112.07 ($C_5H_4SiMe_3$), 131.00, 150.48 ($MeC\equiv CMe$).

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}CH_3C\equiv CCH_3)(CH_2Ph)$ (11c). To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}CH_3C\equiv CCH_3)(Cl)$ (280 mg, 0.60 mmol) in diethyl ether at 0 °C was added 230 mg (0.66 mmol) of $Mg(PhCH_2)_2(THF)_2$. The reaction mixture was stirred for 12 h while it was warmed to room temperature. The solvent was removed in vacuo, and hexane was added. After filtration, the solution was evaporated to dryness and a brown-yellow solid isolated, which was identified as $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}CH_3C\equiv CCH_3)(CH_2Ph)$ (220 mg, 0.42 mmol, 71%).

IR (Nujol mull): 1790 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ 0.06 (s, 18 H, $SiMe_3$), 2.17, 2.41 (s, 3H, $CH_3C\equiv$), 3.24 (m, 2H, $PhCH_2$−Nb), 4.62−4.70 (2H), 5.20−5.30 (4 H), 5.55−5.65 (2 H) (m, $C_5H_4SiMe_3$), 7.05−7.15 (m, 1H, *p*-C_6H_5 of $PhCH_2$−Nb), 7.30−7.40 (m, 2H, *m*-C_6H_5 of $PhCH_2$−Nb), 7.45−7.55 (m, 2H, *o*-C_6H_5 of $PhCH_2$−Nb). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.07 ($SiMe_3$), 10.47, 21.84 ($CH_3C\equiv CCH_3$), 24.12 ($PhCH_2$Nb), 99.08, 104.45, 106.32, 108.50, 119.99 ($C_5H_4SiMe_3$), 122.02 (C-4), 128.00 (C-2 and -6), 128.51 (C-3 and -5), 159.52 (C-1) (phenyl group of $PhCH_2$−), 129.46, 150.66 ($CH_3C\equiv CCH_3$). Anal. Calcd for $C_{27}H_{39}NbSi_2$: C, 63.29; H, 7.61. Found: C, 63.31; H, 7.68.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}(PhC\equiv CH)(CH_2Ph)$ (11e). A solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CH)(Cl)$ (**1e**; 400 mg, 0.79 mmol) in 1,4-dioxane was added to $Mg(CH_2Ph)_2(THF)_2$ (300 mg, 0.79 mmol) and the reaction mixture was stirred at 90−95 °C for 2 h. After removal of solvent in vacuo, hexane was added to extract the benzylated product. This solution was then evaporated to dryness and the residue recrystallized from hot hexane (60 °C) to give yellow crystals (390 mg, 0.69 mmol, 89%).

IR (Nujol mull): 1687 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ −0.06 (s, 18 H, $SiMe_3$), 3.43 (s, 2H, $PhCH_2$−Nb), 4.75−4.90 (2H), 5.00−5.15 (2H), 5.70−5.85 (4H), (m, $C_5H_4SiMe_3$), 7.00−7.15 (m, 1H, *p*-C_6H_5 of $PhCH_2$−Nb), 7.25−7.45 (5H), 7.50−7.65 (4H) (phenyl groups of $PhCH_2$−Nb and $PhC\equiv$), 7.68 (s, 1H, $HC\equiv$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.50 ($SiMe_3$), 23.58 (CH_2Ph), 98.69, 102.11, 107.70, 112.07, 119.57 ($C_5H_4SiMe_3$), 127.37 (C-4), 128.58 (C-3 and -5), 131.23 (C-2 and -6), 137.40 (C-ipso) (phenyl group of $PhC\equiv CH$), 122.22 (C-4), 128.19 (C-2 and -6), 128.48 (C-3 and -5), 157.72 (C-1) (carbons of the phenyl group of $PhCH_2$−), 135.74 ($\equiv CH$), 160.05 ($\equiv CPh$). Anal. Calcd for $C_{31}H_{39}NbSi_2$: C, 66.44; H, 6.96. Found: C, 66.26; H, 6.99.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CH)(CH_2CH{=}CH_2)$ (12e). $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC\equiv CH)(Cl)$ (**1e**; 300 mg, 0.59 mmol) was dissolved in 1,4-dioxane and the solution added to the residue from 2.2 mL of $Mg(CH_2CH{=}CH_2)_2$ (0.2974 M in THF), which had previously been evaporated to dryness. This mixture was stirred at −75 °C for 2 h, and the the solvent was removed in vacuo. The residue was extracted with hexane and the solvent again removed to yield a green-yellow product (260 mg, 0.51 mmol, 87%).

IR (Nujol mull): 1682 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ −0.08 (s, 18 H, $SiMe_3$), 2.95 (d, 2H, *J* = 8.5 Hz, $CH_2{=}CHCH_2$−Nb), 4.79−4.85 (2H), 520−5.26 (2H), 5.62−5.70 (4H) (m, $C_5H_4SiMe_3$), 4.98 (ddt, *J* = 12.2, 3.0, 1.5 Hz, 1H, $H_{terminal\ vinyl}$), 5.15 (ddt, *J* = 16.5, 3.0, 1.5 Hz, 1H, $H_{terminal\ vinyl}$), 6.70 (ddt, *J* = 16.5, 12.2, 3.0 Hz, 1H, $H_{internal\ vinyl}$), 7.16−7.18 (m, 1H, *p*-C_6H_5), 7.31−7.36 (m, 2H, *m*-C_6H_5), 7.54−7.59 (m, 2H, *o*-C_6H_5), 7.48 (s, 1H, $HC\equiv$). The exo geometry was assighned by NOE experiments. Irradiation of the methylene signal at 2.95 ppm resulted in an enhancement of the acetylenic proton signal at 7.48 ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −1.21 ($SiMe_3$), 23.21 ($CH_2{=}CHCH_2$−Nb), 96.52, 100.65, 105.46, 111.07, 122.07 ($C_5H_4SiMe_3$), 103.61 ($CH_2{=}CHCH_2$−Nb), 127.85 (C-3 and -5), 130.66 (C-2 and -6), 136.57 (C-ipso) (phenyl group of $PhC\equiv CH$), 134.48 ($\equiv CH$), 151.72 ($CH_2{=}CHCH_2$−Nb), 158.74 ($\equiv CPh$). Anal. Calcd for $C_{26}H_{37}NbSi_2$: C, 62.66; H, 7.42. Found: C, 62.43; H, 7.36.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)(C\equiv CPh)$ (13). To a mixture of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)(Cl)$ (180 mg, 0.41 mmol) and $Mg(C\equiv CPh)_2$ (140 mg, 0.62 mmol) was added toluene, and the suspension was stirred at room temperature for 7 h. The solvent was subsequently removed in vacuo and the residue extracted with hexane. The green solution thus obtained was evaporated to dryness to give an oily product, which was idetified as the alkynyl complex **13** (169 mg, 0.34 mmol, 83%).

IR: 1920 cm^{-1} (ν_{CO}); 2076 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (300 MHz, C_6D_6): δ 0.19 (s, 18 H, $SiMe_3$), 4.70−4.80 (2H), 4.77−4.86 (2H), 4.90−5.00 (2H), 5.20−5.30 (2H) (m, $C_5H_4SiMe_3$), 6.88−7.00 (m, 1H, *p*-C_6H_5 of $PhC\equiv C$), 7.04−7.12 (m, 2H, *m*-C_6H_5 of $PhC\equiv C$), 7.50−7.60 (m, 2H, *o*-C_6H_5 of $PhC\equiv C$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.18 ($SiMe_3$), 92.26, 94.13, 98.59, 99.34, 101.34, ($C_5H_4SiMe_3$), 122.07 (C-1), 123.53 (C-4), 124.62 (C-3 and -5), 130.82 (C-2 and -6) (phenyl group of $PhC\equiv C$), 129.60 ($PhC\equiv C$), 256.00 (*C*O). C_α of $PhC\equiv C$−Nb is not observed. MS (*m*/*e* (relative intensity)): 496 (7) (M^+, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)(C{\equiv}CPh]^+$); 468 (100) ($M^+ - CO$); 367 (67) ($M^+ - (CO) - (C{\equiv}CPh)$).

Reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}RC{\equiv}CR')$ Complexes with Alkyl Halides. Typical procedure: To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)$-**PhC≡**CH) (**2e**; 200 mg, 0.43 mmol) in hexane was added MeI in excess (50 μL, 120 mg, 0.85 mmol) (1:4). After the reaction mixture was stirred for 3 h at room temperature, the solvent was removed in vacuo, giving a brown residue (210 mg) which was observed to be a mixture of both iodo and alkyl complexes in the proportion 1:1. $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC{\equiv}CH)(I)$ (**1e**) was easily separated from the mixture by precipitating from pentane (80 mg, 0.13 mmol), while **9e** stayed in solution. After pentane was removed, a brown residue of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2(C,C)\text{-}PhC{\equiv}CH)(Me)$ was obtained (90 mg, 0.16 mmol). Experiments with different **2e**:MeI proportions (1:1, 1:2, 1:3, and 1:4) gave similar ratios of the methyl and iodo derivatives. No conversion of **9e** to **1e** was observed after treatment of **9e** with MeI.

Crystal Structure Determination of 11e. A suitably sized yellow crystal of **11e** was obtained by recrystallization. The crystal was mounted in an Enraf-Nonius Cad-4 four-circle automatic diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7073$ Å). Crystallographic and experimental details are summarized in Table 2. 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 structure was solved by direct methods (SHELXS-90)[29] and refined by least squares against F_2 (SHELXL-93).[30] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model with thermal parameters fixed at $U = 0.08$ Å^2. Full-matrix least-squares refinment on F^2 for all data and 302 parameters converged to wR2 = 0.1406 and conventional R1 = 0.0418. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.537P)^2 + 0.9605P]$, where $P = (F_o^2 + 2F_c^2)/3$ and σ was obtained from counting statistics. Calculations were carried out on an ALPHA AXP (Digital) workstation.

Table 2. Crystal Data and Structure Refinement Details for 11e

empirical formula	$C_{31}H_{39}NbSi_2$
fw	560.71
wavelength	0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 7.796(3)$ Å
	$b = 10.898(3)$ Å
	$c = 18.703(5)$ Å
	$\alpha = 78.28(2)°$
	$\beta = 84.18(3)°$
	$\gamma = 69.50(3)°$
V	1456.6(8) Å^3
Z	2
density (calcd)	1.278 g/cm^3
abs coeff	0.512 mm^{-1}
$F(000)$	588
cryst size	0.35 × 0.32 × 0.28 mm
θ range for data collection	2.03−26.97°
index ranges	$-9 < h < 0$, $-13 < k < +13$, $-23 < l < +23$
no. of reflns collected	6971
no. of indep reflns	6300 ($R_{int} = 0.0163$)
no. of obsd reflns ($F > 4\sigma(F)$)	5307
no. of data/restraints/params	6295/0/302
goodness of fit on F^2	1.218
final R indices[a] ($F > 4\sigma(F)$)	R1 = 0.0418, wR2 = 0.1092
R indices (all data)	R1 = 0.0647, wR2 = 0.1406
weighing scheme	calc $w = 1/[\sigma^2(F_o^2)+(0.0537P)^2 + 0.9605P]$, where $P = (F_o^2 + 2F_c^2)/3$
largest diff peak and hole	1.007 and −0.901 e/Å^3

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

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Supporting Information Available: X-ray crystal structure data for **11e**, including tables of crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, all bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

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(29) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(30) Sheldrick, G. M. SHELXL 93; University of Gottingen, Gottingen, Germany, 1993.