phosphines in asymmetric transformations catalyzed by both early- and late-transition-metal complexes.

Acknowledgment. We thank L. Lardear for expert technical assistance in the structure determinations and J. Lazar for obtaining HRMS spectra. We are also grateful to Drs. T. V. RajanBabu, W. A. Nugent, T. Fukunaga (Du Pont CRD), and D. F. Taber (University of Delaware) for invaluable advice and helpful discussions.

Supplementary Material Available: Experimental details, including preparations and spectral and analytical data, for compounds **1**–**7**, X-ray diffraction data for **6**, including tables of atomic coordinates, thermal parameters, bond distances, and bond angles, and a perspective ORTEP diagram of **6** (Figure 1S) with full atom labels (14 pages). Ordering information is given on any current masthead page.

Articles

Niobocene Chemistry: Acetylene Hydrido, Acetylene Alkenyl, and Carbenoid Butadienyl Complexes

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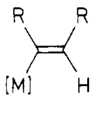
The acetylene hydrido complexes $Cp_2NbH(C_2R_2)$ (**2a**, R = Ph, known; **2b**, R = $SiMe_3$; **2c**, R = Et) were prepared from Cp_2NbH_3/RC≡CR by thermal substitution, and **2d** (R = Me) was obtained from **2b**/MeC≡CMe by a photochemical ligand displacement reaction. The complexes **2** insert acetylenes (as e.g. MeC≡CMe, PhC≡CH, $HC{\equiv}CCO_2Me$) by a nonmigratory insertion process. Stable insertion products $Cp_2Nb(Me_3SiC{\equiv}CSiMe_3)(CR^2{=}CHR^3)$ (**4g**, R^2 = CO_2Me, R^3 = H; **4h**, R^2 = COMe, R^3 = H; **4i**, R^2, R^3 = CO_2Me, *E* isomer) were obtained from **2b**. The *E* configuration of the alkenyl group in **4i** was established from ^{13}C NMR data and by X-ray work: space group $P2_12_12_1$ (No. 19), $a = 1405.3$ (2) pm, $b = 2012.0$ (3) pm, $c = 965.6$ (2) pm, $Z = 4$; $R = 0.034$, $R_w = 0.036$. With less sterically crowded acetylene hydrido compounds **2**, insertion is followed by rearrangement to give the novel carbenoid complexes $Cp_2Nb(CR^1CR^1CR^2CHR^3)$ (**3**). The crystal structure of **3d** (R^1 = Et, R^2, R^3 = CO_2Me) was determined: space group $P2_1/n$ (No. 14), $a = 1649.3$ (1) pm, $b = 840.4$ (1) pm, $c = 1594.1$ (2) pm, $\beta = 116.52$ (1)°, $Z = 4$; $R = 0.023$, $R_w = 0.024$. The bonding in complexes **3** is intermediate between a 1,4-η^2-2-buten-1-yl-4-ylidene and a 1,3,4-η^3-1,3-butadienyl situation.

Introduction

The insertion of acetylenes into metal–hydrogen bonds represents one of the fundamental processes of organometallic chemistry[1] and continues to attract considerable interest,[2-6] especially in terms of the stereochemistry of the resulting alkenyl products and in terms of reaction mechanisms. A priori, cis insertion results in formation of (*E*)-alkenyl products A, while the isomeric *Z* products B are expected from trans insertion reactions. In practice the stereochemistry of the primary insertion step may be obscured by subsequent isomerization steps.



A

B

Broadly, two types of insertion reactions can be discerned, migratory and the nonmigratory insertions. Migratory acetylene insertions resemble the better known migratory olefin insertions[7] and thus should be cis stereospecific. They require a vacant site at the metal center or a substitution-labile ligand to be replaced with the incoming acetylene. In contrast, hydrides that are coordinatively saturated and substitution inert, as e.g. Cp_2ReH, cannot undergo migratory insertion. Such hydrides do, however, insert *activated* acetylenes (HC≡CX or XC≡CX with X = CN, COMe, CO_2Me, CF_3), producing alkenyl complexes of varying stereochemistry. These reactions may be called nonmigratory insertions.

In previous work we have shown that the reactions of the bent metallocene hydrides Cp_2ReH, Cp_2MoH_2, and Cp_2WH_2 with disubstituted activated acetylenes are stereospecific trans insertions *in all cases*.[2] However, the closely related hydride $Cp_2NbH(CO)$ undergoes nonmigratory insertion with dimethyl acetylenedicarboxylate to give, under kinetic control, a mixture of (*Z*)- and (*E*)-alkenyl isomers.[5] In this paper we turn to the corresponding

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niobocene acetylene hydrides and describe nonmigratory insertion reactions with acetylenes. Here we find stereospecific cis insertions. Most of the primary insertion products undergo coupling of their vinyl and acetylene ligands to produce novel η^3-1,3-butadienyl complexes. This result may have some bearing on the mechanism of catalytic acetylene polymerization.[8]

Results

(Acetylene)bis(cyclopentadienyl)hydridoniobium Complexes. Niobocene trihydride, Cp_2NbH_3 (**1**), has long been known to react with simple alkynes (e.g. 2-butyne, 2-hexyne) to form the alkyne hydrido complexes $Cp_2NbH(RC{\equiv}CR')$ (**2**).[9,10] The assertion of the original communication that the alkyne complexes **2** cannot insert a second molecule of the alkyne[9] is incorrect in the case of 2-butyne; here the complex $Cp_2Nb(C_4HMe_4)$ (**3a**, see below) is readily formed as a surprising example of a double insertion.[11] Very few acetylene hydrido complexes of niobocene have been isolated to date. The tolan complex $Cp_2NbH(PhC{\equiv}CPh)$ (**2a**) was first obtained as a yellow solid from the reaction of carbene complexes $Cp_2(RCH_2)Nb{=}CHOZrHCp^*{}_2$ with C_2Ph_2;[12] it may be made quite conveniently from **1** and C_2Ph_2.[12] The bis(trimethylsilyl) analogue $(C_5H_4SiMe_3)_2NbH(PhC{\equiv}CPh)$ is also known.[13] The hexafluoro-2-butyne complex $Cp_2NbH(F_3CC{\equiv}CCF_3)$ was isolated as a minor product from the complex reaction mixture that resulted from the reaction of **1** with $CF_3C{\equiv}CCF_3$.[14] We have obtained the bis(trimethylsilyl)acetylene complex **2b** and the 3-hexyne derivative **2c** using the known thermal reaction of **1** with

$$\underset{\mathbf{1}}{Cp_2NbH_3} + RC{\equiv}CR \rightarrow \underset{\mathbf{2a\text{-}d}}{Cp_2NbH(RC{\equiv}CR)}$$

2a, R = Ph; **2b**, R = $SiMe_3$; **2c**, R = Et; **2d**, R = Me

1 equiv of the appropriate acetylene in toluene at 80 °C. Monitoring by ^1H NMR spectroscopy indicates clean quantitative reactions; workup by sublimation was accompanied by considerable losses.

Table I. Non-Hydrogen Atom Coordinates for 3d

atom	x	y	z	B_{eq}[a]
Nb	0.38552 (1)	0.02186 (2)	0.16685 (1)	2.018 (5)
C(51)	0.2919 (1)	−0.0625 (3)	0.2411 (1)	3.78 (7)
C(52)	0.2611 (1)	−0.1555 (3)	0.1592 (1)	3.49 (7)
C(53)	0.3313 (1)	−0.2545 (2)	0.1663 (1)	3.66 (7)
C(54)	0.4046 (1)	−0.2302 (3)	0.2559 (1)	3.58 (7)
C(55)	0.3802 (1)	−0.1129 (3)	0.3014 (1)	3.91 (8)
C(61)	0.3214 (1)	0.2816 (2)	0.1221 (1)	3.41 (6)
C(62)	0.2504 (1)	0.1735 (3)	0.0793 (1)	3.64 (7)
C(63)	0.2660 (1)	0.0844 (3)	0.0135 (1)	3.65 (7)
C(64)	0.3466 (1)	0.1387 (2)	0.0143 (1)	3.36 (6)
C(65)	0.3814 (1)	0.2612 (2)	0.0812 (1)	3.40 (7)
C(1)	0.4995 (1)	0.1450 (2)	0.2618 (1)	2.34 (5)
C(11)	0.5197 (1)	0.3131 (2)	0.3008 (1)	3.31 (6)
C(12)	0.4890 (2)	0.3478 (3)	0.3756 (2)	5.0 (1)
C(2)	0.56731 (9)	0.0250 (2)	0.2996 (1)	2.30 (5)
C(21)	0.6440 (1)	0.0296 (3)	0.3986 (1)	3.10 (6)
C(22)	0.6174 (1)	−0.0333 (3)	0.4724 (1)	4.25 (9)
C(3)	0.56054 (9)	−0.0997 (2)	0.2396 (1)	2.20 (4)
C(31)	0.6197 (1)	−0.2434 (2)	0.2766 (1)	2.82 (5)
C(32)	0.7237 (1)	−0.4107 (3)	0.2564 (2)	5.0 (1)
O(31)	0.6259 (1)	−0.3248 (2)	0.3414 (1)	4.08 (6)
O(32)	0.66967 (8)	−0.2669 (2)	0.23071 (9)	3.68 (5)
C(4)	0.49905 (9)	−0.0891 (2)	0.13905 (9)	2.30 (5)
C(41)	0.4751 (1)	−0.2341 (2)	0.0840 (1)	2.41 (5)
C(42)	0.4012 (2)	−0.3337 (3)	−0.0714 (1)	4.35 (8)
O(41)	0.48186 (8)	−0.3692 (2)	0.11278 (8)	3.26 (5)
O(42)	0.44029 (9)	−0.2012 (2)	−0.00943 (8)	3.43 (5)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents; in 10^4 pm^2.

As mentioned above, this thermal reaction cannot be used for the preparation of the 2-butyne complex **2d**. Several alternatives were tested. The system Cp_2NbCl_2/2 $LiMeC{=}CHMe$[15] produces pure **2d** in small yields (2%, not optimized). Thermal reaction of C_2Me_2 with the combination Cp_2NbBH_4/NEt_3[16] and irradiation of $Cp_2NbH(CO)/C_2Me_2$ at −30 °C[17] give **2d**, but with an admixture either of the starting complex or, when higher amounts of 2-butyne are used, of the ring compound **3a**. However, the necessary selectivity and purity could be achieved when the bis(trimethylsilyl)acetylene complex **2b** was irradiated in the presence of slightly less than 1 equiv of C_2Me_2; small-scale preparations afforded a 43% yield of pure **2d**.

$$\mathbf{2b} + MeC{\equiv}CMe \xrightarrow{h\nu} \mathbf{2d} + Me_3SiC{\equiv}CSiMe_3$$

(1,3-Butadienyl)bis(cyclopentadienyl)niobium Complexes. The outcome of the reaction between the trihydride **1** and 2-butyne depends on the ratio of the reactants. At a 1/1 ratio ($1/C_2Me_2$) the products are unconsumed trihydride **1**, $Cp_2NbH(MeC{\equiv}CMe)$ (**2d**), and the butadienyl complex **3a**, even at room temperature. With an excess of 2-butyne **3a** is the sole complex product. Independently prepared **2d** readily inserts 2-butyne to give **3a** and thus is a true intermediate.[11] If two different acetylenes are used, the scope of this double insertion can be broadened and, in addition, information about the course of the reaction can be deduced from the product structure. The reactions of the diphenylacetylene complex **2a** with 2-butyne (4 h, 80 °C), dimethyl acetylenedicarboxylate (DMAC; 2 h, 60 °C), methyl propiolate (2 h, 60 °C), and phenylacetylene (3 h, 80 °C) and of the 3-hexyne complex **2c** with DMAC (2 h, 20 °C) yield the ring compounds **3b**–**f**.

$$\underset{\mathbf{2}}{Cp_2NbH(R^1C{\equiv}CR^1)} + R^2C{\equiv}CR^3 \rightarrow \underset{\mathbf{3a\text{-}f}}{Cp_2Nb(CR^1CR^1CR^2CHR^3)}$$

3a, R^1, R^2, R^3 = Me; **3b**, R^1 = Ph, R^2, R^3 = Me;
3c, R^1 = Ph, R^2, R^3 = CO_2Me;
3d, R^1 = Et, R^2, R^3 = CO_2Me;
3e, R^1 = Ph, R^2 = CO_2Me, R^3 = H;
3f, R^1 = Ph, R^2 = H, R^3 = Ph

In our earlier work the structure of **3a** was determined by single-crystal X-ray diffraction.[11] The molecule consists

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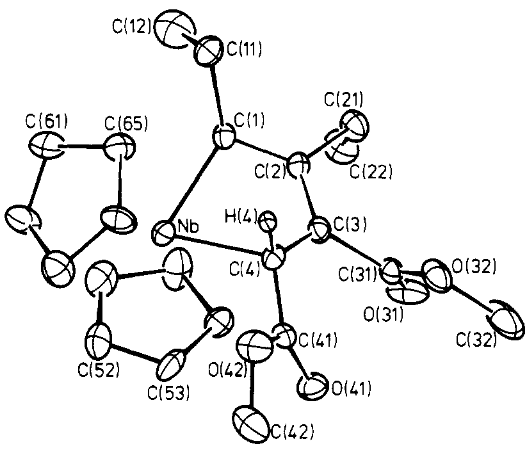
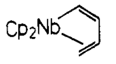
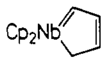


Figure 1. Molecular structure of Cp$_2$Nb[C(Et)C(Et)C(CO$_2$Me)CH(CO$_2$Me)] (**3d**) (ORTEP plot at the 30% probability level).

of a bent niobocene fragment and a butadienyl chain acting as a 3e ligand. The bonding situation has been discussed in terms of two limiting formulas, the formula C with a 1,3,4-η^3-1,3-butadienyl ligand and the formula D with a 1,4-η^2-2-buten-4-yl-1-ylidene ligand.[11,18]



C



D

We now have also determined the structure of **3d** (Tables I and II and Figure 1). In **3d** the two acetylene molecules that build up the butadienyl chain are different. Thus, it can be seen from the structure that the hydride atom of the acetylene hydrido complex is transferred to the acetylene that is being inserted. In the product **3d** this hydrogen atom then assumes the 4-anti[19] position.

For the other compounds the substitution patterns are deduced from their NMR spectra. All compounds **3** show one signal at high field ranging from −0.65 to 0.94 ppm. This signal is assigned to $H_{4\text{-anti}}$. It appears as a quartet for **3a,b** as part of the same doublet–quartet combination that stems from the C(4)HMe part of the butadienyl chain.

The ^{13}C NMR spectra show two characteristic signals for the butadienyl moiety, a broad singlet ranging from 210 (for **3e**) to 244 ppm (for **3c**) for the carbenoid carbon atom C(1) and a somewhat broadened multiplet for C(4) in the range from 47 to 66 ppm; the signals for C(2) and C(3) (for **3a** at 120.7 and 134.2 ppm[11]) usually cannot be discerned from other signals in the same spectral region. For **3e** C(4) appears as a doublet of doublets (^1J = 148, 154 Hz) and hence belongs to a niobium-bonded methylene group. In all other cases coupling of C(4) with $H_{4\text{-anti}}$ gives rise to a doublet. The last two observations establish the structures of **3e,f**, where on the basis of the ^{1}H NMR data alone some ambiguity would be left. We conclude that in the cases of **3e,f** the incorporation of the second acetylene ($HC\equiv CCO_2Me$ and $HC\equiv CPh$, respectively) occurs with opposite regiochemistry.

Table II. Selected Bond Distances, Bond Angles, and Torsional Angles for 3d

(a) Bond Distances (pm)

Nb–C(1)	208.7 (2)	Nb–C(3)	278.0 (2)
Nb–C(2)	279.3 (2)	Nb–C(4)	230.5 (2)
C(1)–C(2)	142.5 (3)	C(3)–C(4)	146.7 (2)
C(2)–C(3)	138.9 (2)	C(4)–H(4)	92.6
C(1)–C(11)	151.9 (3)	C(2)–C(21)	151.9 (2)
C(11)–C(12)	151.8 (3)	C(21)–C(22)	152.3 (3)
C(3)–C(31)	149.8 (3)	C(4)–C(41)	145.0 (2)
C(31)–O(31)	120.5 (3)	C(41)–O(41)	121.1 (2)
C(31)–O(32)	133.9 (2)	C(41)–O(42)	136.4 (2)
C(32)–O(32)	144.7 (2)	C(42)–O(42)	143.6 (3)

	Cp ring C(51)...C(55)	Cp ring C(61)...C(65)
Nb–C (min)	243.3 (2)	239.2 (2)
Nb–C (max)	249.6 (2)	242.9 (2)
Nb–C (av)	247.4	241.1
C–C (min)	138.5 (4)	139.6 (3)
C–C (max)	141.5 (3)	141.8 (3)
C–C (av)	140.0	140.5

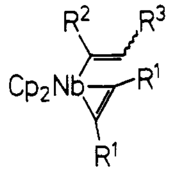
(b) Bond Angles (deg)

Nb–C(1)–C(11)	136.0 (1)	C(1)–C(2)–C(3)	115.9 (2)
Nb–C(1)–C(2)	103.8 (1)	C(1)–C(2)–C(21)	123.6 (2)
C(11)–C(1)–C(2)	119.9 (2)	C(21)–C(2)–C(3)	120.5 (2)
C(1)–C(11)–C(12)	114.3 (2)	C(2)–C(21)–C(22)	113.6 (2)
C(2)–C(3)–C(4)	120.7 (2)	C(3)–C(4)–C(41)	118.6 (2)
C(2)–C(3)–C(31)	119.9 (2)	Nb–C(4)–C(3)	92.2 (1)
C(31)–C(3)–C(4)	119.3 (2)	Nb–C(4)–H(4)	93.9 (1)
C(3)–C(31)–O(31)	125.9 (2)	C(3)–C(4)–H(4)	116.4 (2)
C(3)–C(31)–O(32)	110.8 (2)	C(41)–C(4)–H(4)	114.9 (2)
O(31)–C(31)–O(32)	123.2 (2)	C(4)–C(41)–O(41)	127.2 (2)
C(31)–O(32)–C(32)	114.8 (2)	C(4)–C(41)–O(42)	111.0 (2)
C(1)–Nb–C(4)	78.1 (1)	C(41)–O(42)–C(42)	115.7 (2)

(c) Torsional Angles (deg)

C(4)–Nb–C(1)–C(2)	41.9
Nb–C(1)–C(2)–C(3)	−31.2
C(2)–C(3)–C(4)–Nb	42.4
C(1)–Nb–C(4)–C(3)	−43.2
C(1)–C(2)–C(3)–C(4)	−12.2

(Acetylene)(alkenyl)bis(cyclopentadienyl)niobium Complexes. In the case of the reaction of the diphenylacetylene complex **2a** with DMAC and methyl propiolate intermediate alkenyl complexes **4c** (>−30 °C) and **4e** (20 °C) are observed, which subsequently rearrange to give butadienyl compounds **3c,e**. In contrast, the bis(trimethylsilyl)acetylene complex **2b** reacts with activated acetylenes to afford isolable alkenyl complexes **4g–i**. No formation of metallacycles **3** can be seen up to the temperature of decomposition.



4c: R^1 = Ph, R^2, R^3 = CO$_2$Me
e: R^1 = Ph, R^2 = CO$_2$Me, R^3 = H
g: R^1 = SiMe$_3$, R^2 = CO$_2$Me, R^3 = H
h: R^1 = SiMe$_3$, R^2 = COMe, R^3 = H
i: R^1 = SiMe$_3$, R^2, R^3 = CO$_2$Me

The structure of **4i** was proved directly by means of an X-ray structure determination (Tables III and IV and Figure 2).

All alkenyl complexes **4** show a single resonance for the protons and carbon atoms of both cyclopentadienyl rings; this observation indicates effective mirror symmetry in solution. For **4i** the vicinal coupling constant $^3J(^{13}C-^1H)$ = 15 Hz between the carboxylic α-carbon and the proton of the alkenyl group is in accord with the *E* configuration.[2a] In the case of the intermediate **4c**, where the vicinal coupling constant could not be measured, the configuration of the alkenyl group can be derived from the coupling constant $^1J(^{13}C-^1H)$ (168 Hz) at the β-carbon atom of the

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[18] Note that the numbering of the butadienyl C is retained in the butenylylidene D.

[19] The term anti is used in accord with common practice for butadiene complexes; that is, 4-anti is oriented toward the metal and is roughly opposite to the substituent at C(3) of the butadienyl chain.

Table III. Non-Hydrogen Atom Coordinates for 4i

atom	x	y	z	B_{eq}[a]
Nb	0.44532 (4)	0.81396 (3)	0.85515 (6)	3.29 (1)
C(1)	0.5986 (4)	0.8536 (3)	0.8588 (8)	3.7 (2)
C(11)	0.6473 (5)	0.8593 (3)	0.9962 (8)	4.2 (2)
O(11)	0.6729 (3)	0.8123 (3)	1.0637 (5)	5.3 (2)
O(12)	0.6554 (3)	0.9220 (2)	1.0386 (6)	5.1 (2)
C(12)	0.7054 (6)	0.9307 (4)	1.166 (1)	7.8 (4)
C(2)	0.6547 (5)	0.8605 (3)	0.7465 (7)	4.0 (2)
C(21)	0.7578 (5)	0.8722 (4)	0.7532 (8)	4.6 (3)
O(22)	0.7924 (3)	0.8782 (3)	0.6236 (6)	6.3 (2)
O(21)	0.8085 (3)	0.8739 (3)	0.8519 (7)	5.8 (2)
C(22)	0.8933 (5)	0.8885 (5)	0.615 (1)	6.8 (4)
C(111)	0.3595 (5)	0.8581 (4)	0.6835 (7)	4.3 (3)
C(112)	0.4350 (5)	0.8935 (3)	0.6921 (6)	4.0 (2)
Si(1)	0.2432 (2)	0.8510 (1)	0.5953 (2)	5.67 (9)
Si(2)	0.4786 (2)	0.9747 (1)	0.6304 (3)	8.9 (5)
C(1a)	0.1811 (6)	0.7729 (4)	0.630 (1)	9.7 (5)
C(1b)	0.1646 (6)	0.9170 (5)	0.657 (1)	12.2 (7)
C(1c)	0.2623 (8)	0.8585 (6)	0.4068 (9)	5.14 (8)
C(2a)	0.3770 (6)	1.0227 (4)	0.568 (1)	8.5 (5)
C(2b)	0.5335 (6)	1.0203 (4)	0.7761 (8)	6.1 (3)
C(2c)	0.5568 (8)	0.9664 (5)	0.4801 (9)	8.6 (4)
C(51)	0.4347 (5)	0.8920 (4)	1.0488 (7)	5.1 (3)
C(52)	0.3505 (5)	0.8984 (4)	0.9817 (8)	5.2 (3)
C(53)	0.3035 (5)	0.8402 (4)	0.9864 (8)	5.1 (3)
C(54)	0.3578 (5)	0.7963 (4)	1.0640 (7)	4.9 (3)
C(55)	0.4403 (5)	0.8260 (3)	1.1032 (7)	4.8 (2)
C(61)	0.5528 (6)	0.7201 (3)	0.8274 (9)	5.2 (3)
C(62)	0.5152 (5)	0.7352 (4)	0.6993 (8)	5.4 (3)
C(63)	0.4182 (6)	0.7221 (3)	0.701 (1)	6.2 (4)
C(64)	0.3964 (6)	0.6996 (3)	0.829 (1)	6.1 (3)
C(65)	0.4796 (6)	0.6975 (3)	0.9076 (9)	5.8 (3)

[a] See footnote *a* of Table I.

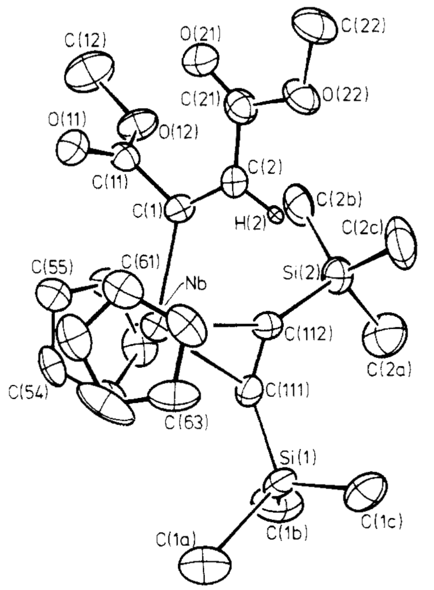

Figure 2. Molecular structure of $Cp_2Nb(Me_3SiC{\equiv}CSiMe_3)[\eta^1\text{-}(E)\text{-}C(CO_2Me){=}CH(CO_2Me)]$ (**4i**) (ORTEP plot at the 30% probability level).

Table IV. Selected Bond Distances and Bond Angles for 4i

(a) Bond Distances (pm)

Nb-C(1)	229.7 (5)	Nb-C(111)	223.5 (6)
Nb-C(112)	225.0 (6)	C(1)-C(2)	134.7 (8)
C(1)-C(11)	149.7 (10)	C(11)-O(11)	120.4 (8)
C(11)-O(12)	133.0 (8)	C(12)-O(12)	143.2 (9)
C(2)-C(21)	147.0 (9)	C(21)-O(21)	119.1 (8)
C(21)-O(22)	134.7 (8)	C(22)-O(22)	143.5 (7)
C(111)-C(112)	128.1 (9)	C(2)-H(2)	98.6 (7)
Si(1)-C(111)	184.8 (7)	Si(2)-C(112)	184.4 (7)
Si(1)-C(1a)	182.9 (8)	Si(2)-C(2a)	182.5 (8)
Si(1)-C(1b)	182.7 (9)	Si(2)-C(2b)	184.8 (7)
Si(1)-C(1c)	184.6 (8)	Si(2)-C(2c)	182.8 (9)

	Cp ring C(51)...C(55)	Cp ring C(61)...C(65)
Nb-C (min)	238.8 (6)	239.5 (7)
Nb-C (max)	248.2 (6)	244.5 (7)
Nb-C (av)	242.9	241.8
C-C (min)	134.5 (10)	135.0 (13)
C-C (max)	143.1 (9)	139.4 (12)
C-C (av)	137.5	137.5

(b) Bond Angles (deg)

C(1)-Nb-C(111)	112.3 (2)	Nb-C(1)-C(11)	118.0 (4)
Nb-C(1)-C(2)	124.9 (5)	C(11)-C(1)-C(2)	116.0 (5)
C(1)-C(11)-O(11)	123.8 (7)	C(1)-C(11)-O(12)	112.6 (6)
O(11)-C(12)-O(12)	123.6 (7)	C(11)-O(12)-C(12)	115.0 (6)
C(1)-C(2)-C(21)	123.9 (6)	C(1)-C(2)-H(2)	119.2 (6)
C(21)-C(2)-H(2)	116.7 (6)	C(2)-C(21)-O(21)	129.0 (7)
C(2)-C(21)-O(22)	109.3 (6)	O(21)-C(21)-O(22)	121.7 (6)
C(21)-O(22)-C(22)	115.1 (7)		
C(112)-C(111)-Si(1)	143.7 (6)	C(111)-C(112)-Si(2)	138.3 (6)
C(111)-Si(1)-C(1a)	113.8 (4)	C(112)-Si(2)-C(2a)	108.4 (4)
C(111)-Si(1)-C(1b)	109.1 (4)	C(112)-Si(2)-C(2b)	109.4 (3)
C(111)-Si(1)-C(1c)	108.6 (4)	C(112)-Si(2)-C(2c)	112.0 (4)
C(1a)-Si(1)-C(1b)	105.9 (4)	C(2a)-Si(2)-C(2b)	108.4 (4)
C(1a)-Si(1)-C(1c)	108.8 (5)	C(2a)-Si(2)-C(2c)	104.9 (5)
C(1b)-Si(1)-C(1c)	110.6 (6)	C(2b)-Si(2)-C(2c)	113.5 (4)

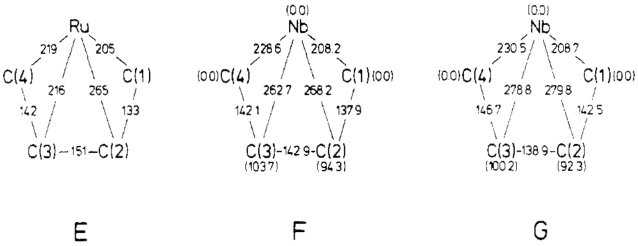

Figure 3. The MC_4 fragment: M–C and C–C distances (pm) for $CpRu(PPh_3)[1,3,4\text{-}\eta^3\text{-}C_4H(CF_3)_4]$ (E), **3a** (F), and **3d** (G). Numbers in parentheses are distances (pm) from the plane C(1),Nb,C(4).

alkenyl group. It has been noted[2a] that the values for fumaric ester derivatives (*Z* configuration: 146–156 Hz,[2a] 155 Hz for $Cp_2Nb(CO)[\eta^1\text{-}(Z)\text{-}C(CO_2Me){=}CHCO_2Me]$[5]) are smaller than those for the corresponding maleic ester derivatives (*E* configuration: 166–167 Hz,[2a] 164 Hz for $Cp_2Nb(CO)[\eta^1\text{-}(E)\text{-}C(CO_2Me){=}CHCO_2Me]$,[5] and 165 Hz for **4i**). Thus, the alkenyl group of **4c** also possesses the *E* configuration.

Crystal Structure of 3d. The molecule of **3d** shows a typical bent-sandwich structure with a bending angle[20] of 128.2°. The (butadienyl)niobium ring is folded along the line C(1)C(4), thus bringing carbon atom C(3) close to the ring C(51)...C(55). This cyclopentadienyl ring is less tightly bonded than the other, with average Nb–C distances of 247.4 and 241.1 pm, respectively. A search for nonbonding contacts gave the C(3)–H(54) distance of 255.3 pm as the most important nonbonding interaction. Most likely, this interaction causes a steric labilization of the ring C(51)...C(55).

Important interatomic distances within the (butadienyl)niobium moiety are summarized in Figure 3 for **3a** (F) and **3d** (G), together with data for the long-known η^3-butadienyl complex $CpRu(PPh_3)[1,3,4\text{-}\eta^3\text{-}C_4H(CF_3)_4]$[21] (E). The Nb–C(4) distance in **3d** (230.5 (2) pm) compares well with the Nb–C bond lengths in $Cp_2Nb(C_2H_4)Et$[22] (Nb–Et

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[20] The bending angle of a bent sandwich is the angle between the perpendiculars of the two cyclopentadienyl best planes.

[21] (a) Blackmore, T.; Bruce, M. I.; Stone, F. G. A.; Davis, R. E.; Garza, A. *J. Chem. Soc. D* **1971**, 852. (b) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106.

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

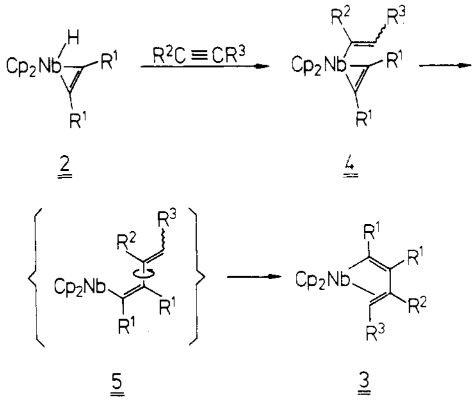
231.6 (8) pm; Nb–C_2H_4, 227.7 (9) (endo), 232.0 (9) pm (exo)) and thus is a typical single bond. The Nb–C(1) bond length (208.7 (2) pm) indicates considerable Nb–C π interactions. Thus, the structural data confirm the carbenoid character of C(1), which had been deduced above from the ^{13}C NMR data of the complexes **3**. The ruthenium complex E shows the pattern of an η^1-vinyl (C(1) and C(2)) and an η^2-olefin (C(3) and C(4)) bonded to the metal, and the connecting σ bond C(2)–C(3) (151 pm) indicates little π interaction across this bond. In contrast, the niobium complexes **3a** and **3d** show a lengthening of the C(1)–C(2) bond, a shortening of the C(2)–C(3) bond, and very long metal–carbon separations for C(2) and C(3) which are unlikely to represent any appreciable bonding interaction.

Bent metallocenes possess three valence orbitals for bonding with ligands in the pseudoequatorial plane; for a d^2 system two of these ($2a_1$ and b_2 in C_{2v} symmetry) are suitable for σ bonding and one ($1a_1$) for π back-bonding.[23] In complexes **3**, two σ bonds anchor C(1) and the double bond C(3)–C(4) to the metal (cf. formula C); the ideal in-plane orientation of the double bond as in $Cp_2Nb(C_2H_4)Et$[22] would require a planar (butadienyl)niobium ring. π bonding, however, requires folding of the (butadienyl)niobium ring and bonding overlap will be most important at C(1) and C(4), where the diene LUMO has large coefficients (cf. formula D). At the C(1) terminus, the ideal orientation of the alkylidene plane C(11),C(1),C(2) would be perpendicular to the pseudoequatorial plane as in $Cp_2Ta(CHR)(CH_2R)$[24] (R = H, Ph) to allow for maximum overlap. However, the butadienyl chain enforces a large deviation from the ideal orientation, and the C(11),C(1),C(2) plane spans an angle of 40.9° with the plane C(1),Nb,C(4). The transfer of electron density from the electron-rich metal center into the butadienyl LUMO, as implied in π bonding, is very pronounced. This is evidenced by the pattern of C–C bond lengths of the butadienyl chain. Finally, details of the available NMR data (reduced coupling constants $^3J(^{13}C(4)-^1H)$ of e.g. 142 Hz for **3f**, increased geminal coupling $^2J(H_{4\text{-syn}}-H_{4\text{-anti}}$ = 6.1 Hz for **3e**) show enhanced sp^3 character at C(4),[25,26b] and the bonding in the C(3)–C(4) region seems to be similar to that of butadiene complexes of early d metals.[25-29]

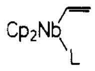
A comparison of **3d** and **3a** reveals more subtle details. The presence of two electron-withdrawing ester groups in **3d** increases the transfer of electron density onto the butadienyl ligand. As a consequence, the C(1)–C(2) bond is more elongated, the C(2)–C(3) bond is more shortened, and the metal–carbon separation for C(2) is longer in **3d** as compared to that in **3a**. Thus, for **3a** formula C has more weight than for **3d**.

Crystal Structure of 4i. The structure of **4i** was determined with the double aim to confirm the *E* configuration of the vinyl group and to document the effects of steric crowding in the pseudoequatorial region of the molecule. The sandwich moiety of **4i** shows a bending angle of 128.4° with the two cyclopentadienyl rings in a staggered conformation. The acetylene and the alkenyl units are in the pseduoequatorial plane, in agreement with the general description of the bonding in bent metallocene derivatives.[23]

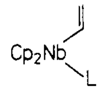
Scheme I



The alkenyl group assumes the parallel conformation H. This conformation is enforced by the proximity of the bulky acetylene and avoids close contact between the central trimethylsilyl group and the α ester group of **4i**. The less crowded analogue $Cp_2Nb(CO)[\eta^1$-(*E*)-$C(CO_2Me){=}CHCO_2Me]$ shows the more common perpendicular conformation I.[5]



H



I

The acetylene shows Nb–C distances of 223.5 (6) and 225.0 (6) pm and a C–C bond length of 128.1 (9) pm. The corresponding distances are 218 (1), 219 (1), and 129 (1) pm in $Cp_2Nb(O_2CCMe_3)(C_2Ph_2)$,[30] 217.1 (8), 218.5 (9), and 127 (1) pm in $(C_5H_4SiMe_3)_2NbCl(PhC{\equiv}CPh)$,[31] and 218.7 (1), 221.4 (1), and 128.1 (1) pm in $CpNb(PMe_3)(C_4H_6)(PhC_2Me)$.[32] The comparatively long Nb–C bond lengths for **4i** indicate that the bis(trimethylsilyl)acetylene ligand is labilized by steric congestion.

Discussion

The results described in this paper suggest a general pattern for the formation of the novel butadienyl complexes **3** (Scheme I). The primary niobocene acetylene hydrido complexes **2** insert the second acetylene by a nonmigratory process to give acetylene alkenyl complexes **4**. The same type of nonmigratory insertion reaction is known e.g. for $Cp_2NbH(CO)$[5,33] and the closely related bent metallocene hydrides Cp_2MoH_2,[1,2a,34] Cp_2WH_2,[1,2a,34] and Cp_2ReH.[1,25] Several papers have discussed possible mechanisms[1,4,6b,33,34] for nonmigratory insertions, and some of this discussion has been restated recently.[3] In contrast, carbon monoxide undergoes migratory insertion.[9] The

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[23] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[24] (a) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578. (b) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

[25] General review: Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

[26] CpTa(diene)$_2$: (a) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *Organometallics* **1988**, *7*, 2266. (b) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

[27] ZrCp$_2$(diene): (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388. (b) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. (c) Erker, G.; Krüger, C.; Müler, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

[28] CpNb(diene)$_2$: Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.

[29] CpMo(NO)(diene): Christensen, N. J.; Hunter, A. D.; Legzdins, P. *Organometallics* **1989**, *8*, 930.

[30] Pasynskii, A. A.; Skripkin, Yu. V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu, T. *J. Organomet. Chem.* **1979**, *165*, 39.

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insertion step is followed by C–C coupling in **4** to give the 16e intermediate **5**, and addition of the butadienyl tail to the niobium center finally produces the ring complexes **3**.

Three situations can be discerned. C–C coupling can be too fast to allow the observation of the intermediate **4**, which then remains entirely hypothetical. This is the case, for instance, for **4b** and **4f**. The presence of electron-withdrawing substituents stabilizes the intermediate **4**. Especially, intermediate **4c** is sufficiently stable to allow for detailed characterization by NMR spectroscopy. In the case of the bis(trimethylsilyl)acetylene complexes **4g–i** the C–C coupling step is blocked, probably by steric hindrance, and these acetylene alkenyl complexes can be readily isolated.

The *E* configuration of **4i** is remarkable. In earlier work we had established that Cp_2MoH_2, Cp_2WH_2, and Cp_2ReH undergo stereospecific trans insertion of DMAC to give kinetic products of *Z* configuration.[2] In the case of the sterically more crowded $Cp_2NbH(CO)$ cis and trans insertions were found to occur in parallel.[5] The even more crowded $Cp_2NbH(Me_3SiC{\equiv}CSiMe_3)$ (**2b**) gives the *E* isomer **4i** exclusively. thus, the reaction of DMAC with **2b** appears to be the limiting case of a stereospecific cis insertion.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Hexane was distilled from Na/K alloy; benzene, toluene, and ether were distilled from sodium benzophenone ketyl. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed by Analytische Laboratorien, D-5270 Gummersbach 1, Elbach, FRG.

NMR spectra were recorded on a Bruker WH 270 PFT spectrometer (^{13}C, 67.88 MHz) and a Bruker WP 80 PFT spectrometer (^1H, 80 MHz). Electron-impact (70 eV) mass spectra were run on a Varian MAT CH5-DF spectrometer. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer and calibrated against the 1601-cm^{-1} band of polystyrene.

Materials. Cp_2NbCl_2,[35] Cp_2NbH_3 (**1**),[36] and $Cp_2NbH(C_2Ph_2)$ (**2a**)[12] were prepared as described in the literature. Other reagents were available commercially. All complexes prepared in this work are air-sensitive.

Preparation of 2b. Cp_2NbH_3 (1.42 g, 6.28 mmol) and $Me_3SiC{\equiv}CSiMe_3$ (1.09 g, 6.40 mmol) in toluene (20 mL) were heated at 80 °C until the evolution of gas had ceased. Removal of all volatiles gave a tan powder of spectroscopically pure **2b** (^1H NMR). Sublimation affords a lemon yellow powder (60–70%): dec pt 93–94 °C; MS *m/z* (I_{rel}, %) 394 (26, M^+), 320 (43, $M^+ - SiMe_3$), 225 (24, $Cp_2NbH_2^+$), 224 (100, Cp_2NbH^+), 223 (78, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 4.63 (s, 2 Cp), 0.38 and 0.32 (s, $SiMe_3$), –1.85 (s, br, NbH); ^{13}C NMR (C_6D_6) δ 160.0 and 149.3 (br, C≡), 94.0 (dqn,[37] $^1J_{CH} = 175$, $^{2,3}J_{CH} = 6._5$ Hz, 2 Cp), 1.4 and 0.2 (q, $^1J_{CH} = 119$ Hz, $SiMe_3$); IR (Nujol, cm^{-1}) 1754 m, 1725 m, 1242 s, 875 s. Anal. Calcd for $C_{18}H_{29}NbSi_2$: C, 54.80; H, 7.41. Found: C, 54.47; H, 7.25.

Preparation of 2c. Cp_2NbH_3 (1.41 g, 6.24 mmol) and 3-hexyne (1.44 g, 17.5 mmol) in toluene (10 mL) were treated as for **2b** to give an oily dark red residue. Two sublimations afforded **2c** as gray fibers (31%): mp 31–33 °C; MS *m/z* (I_{rel}, %) 306 (36, M^+), 226 (29, $Cp_2NbH_3^+$), 225 (100, $Cp_2NbH_2^+$), 224 (65, Cp_2NbH^+); ^1H NMR (C_6D_6) δ 4.79 (d, $^3J = 0.3$ Hz, 2 Cp), 2.88 and 2.77 (qm, $^3J = 7._5$ Hz, CH_2), 1.32 and 1.29 (t, $^3J = 7.3$ Hz, Me), –0.70 (m, br, NbH); ^{13}C NMR (C_6D_6) δ 143.6 and 130.7 (s, br, C≡), 94.6 (dqn, $^1J_{CH} = 175$, $^{2,3}J_{CH} = 6._5$ Hz, 2 Cp), 29.5 (tq, $^1J_{CH} = 126$, $^2J_{CH} = 4$ Hz, CH_2), 28.9 (tqn, $^1J_{CH} = 126$, $^{2,3}J_{CH} = 4$ Hz, CH_2), 15.4 and 14.8 (qt, $^1J_{CH} = 126$, $^2J_{CH} = 4$ Hz, Me). Anal. Calcd for $C_{16}H_{21}Nb$: C, 62.75; H, 6.91. Found: C, 62.63; H, 6.82.

Preparation of 2d. A solution of $Cp_2NbH(Me_3SiC{\equiv}CSiMe_3)$ (500 mg, 1.26 mmol) and 2-butyne (76 mg, 1.41 mmol) in toluene (10 mL) was irradiated for 3 h at 10–13 °C. After removal of all volatiles the residue was sublimed (bath temperature 65 °C/10^{-6} bar) to give **2d** as off-white fibers (43%): mp 109 °C; MS *m/z* (I_{rel}, %) 278 (40, M^+), 225 (23, $Cp_2NbH_2^+$), 224 (100, Cp_2NbH^+), 223 (85, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 4.78 (d, $^3J = 0.3$ Hz, 2 Cp), 2.60 and 2.43 (q, $^5J = 1.0$ Hz, Me), –0.62 (m, br, NbH). Anal. Calcd for $C_{14}H_{17}Nb$: C, 60.44; H, 6.16. Found: C, 60.16; H, 6.24.

Preparation of 3b. $Cp_2NbH(PhC{\equiv}CPh)$ (1.17 g, 2.01 mmol) and 2-butyne (1.0 mL, 12.8 mmol) in toluene (20 mL) were heated at 80 °C for 4 h. After removal of all volatiles the residue was extracted with 20 mL of hexane. Filtration and slow cooling to –70 °C gave **3b** as coppery platelets (51%): mp 143 °C; MS *m/z* (I_{rel}, %) 456 (59, M^+), 224 (100, Cp_2NbH^+), 223 (93, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 6.80–7.16 (m, 2 Ph), 4.87 and 4.65 (m, Cp), 2.09 (d, $^3J = 5.9$ Hz, 4-Me), 1.94 (s, 3-Me), –0.45 (q, $^3J = 5.9$ Hz, $H_{4\text{-anti}}$); ^{13}C NMR (C_6D_6) δ 224 (br, C(1)), 151.6, 143.3, 141.4, and 120.3 (s, 2 C_i, C(2), C(3)), 98.2 dqn ($^1J_{CH} = 186$, $^{2,3}J_{CH} = 6$ Hz, Cp), 95.4 dqn ($^1J_{CH} = 175$, $^{2,3}J_{CH} = 6$ Hz, Cp), 63.7 (d, $^1J_{CH} = 137$ Hz, C(4)), 21.9 and 19.7 (q, $^1J_{CH} = 125$ Hz, Me). Anal. Calcd for $C_{28}H_{27}Nb$: C, 73.68; H, 5.96. Found: C, 73.37; H, 5.97.

Preparation of 3c. DMAC (116 mg, 0.82 mmol) was added to $Cp_2NbH(PhC{\equiv}CPh)$ (320 mg, 0.80 mmol) in toluene (10 mL) at room temperature. The solution was stirred at 60 °C for 2 h. Then the volatiles were removed and the residue was dissolved in toluene (20 mL). Filtration and two crystallizations from toluene/hexane gave **3c** as red-brown microcrystals (62%): mp 177–178 °C; MS *m/z* (I_{rel}, %) 544 (20, M^+), 255 (20, $Cp_2NbH(OMe)^+$), 254 (100, Cp_2NbOMe^+), 224 (62, Cp_2NbH^+), 223 (26, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 6.78–7.29, 6.46–6.63 (m, 2 Ph), 5.26 and 5.01 (s, Cp), 3.55 and 3.53 (s, OMe), 0.78 (s, $H_{4\text{-anti}}$); ^{13}C NMR (C_6D_6) δ 244.2 (s, br, C(1)), 175.9 and 166.9 (m, $^3J_{CH} = 4$ Hz, CO), 151.9 (t, $^3J_{CH} = 7$ Hz), 149.0 (m), 140.4 (t, $^3J_{CH} = 7$ Hz), 130.3 (dt, $^1J_{CH} = 163$, $^3J_{CH} = 5$ Hz), 127.9, 126.9, 126.8, signal hidden under C_6D_6, 124.6 (dt, $^1J_{CH} = 166$, $^3J_{CH} = 7$ Hz), 121.9 (s, C(2) or C(3)), 101.4 (dqn, $^1J_{CH} = 178$, $^{2,3}J_{CH} = 6$ Hz, Cp), 100.3 (dqn, $^1J_{CH} = 176$, $^{2,3}J_{CH} = 6$ Hz, Cp), 51.7 (q, $^1J_{CH} = 148$ Hz, OMe), 50.4 (q, $^1J_{CH} = 145$ Hz, OMe), 47.1 (d, $^1J_{CH} = 148$ Hz, C(4)). Anal. Calcd for $C_{30}H_{27}NbO_4$: C, 66.18; H, 5.00. Found: C, 65.90; H, 5.10.

Preparation of 3d. Cp_2NbH_3 (582 mg, 2.57 mmol) and 3-hexyne (216 mg, 2.63 mmol) in toluene (20 mL) were heated until the evolution of gas had ceased. Then the reaction mixture was layered with DMAC (370 mg, 2.60 mmol) in hexane (10 mL) at room temperature. After 24 h more hexane (10 mL) was added, and cooling to –20 °C gave **3d** as dark red, almost black crystals (67%): mp 142–145 °C, MS *m/z* (I_{rel}, %) 448 (16, M^+), 255 (13, $Cp_2NbOCH_4^+$), 254 (100, Cp_2NbOMe^+), 224 (60, Cp_2NbH^+), 223 (24, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 5.09 and 4.98 (s, Cp), 3.74 and 3.51 (s, OMe), 3.03–1.63 (m, 2 CH_2), 1.25 and 0.90 (t, $^3J = 7.5$ Hz, Me), 0.38 (s, br, $H_{4\text{-anti}}$). Anal. Calcd for $C_{22}H_{27}NbO_4$: C, 58.93; H, 6.07. Found: C, 58.87; H, 5.99.

Preparation of 3e. Methyl propiolate (230 mg, 2.74 mmol) was added to $Cp_2NbH(PhC{\equiv}CPh)$ (1.10 g, 2.73 mmol) in toluene (20 mL) to give a blood red solution. After it was stirred at room temperature for 60 min and then at 60 °C for 2 h, the reaction mixture was filtered. All volatiles were thoroughly (!) removed in vacuo overnight. The dark brown, powdery residue was extracted with ether (50 mL), and the extract was filtered. Cooling to –70 °C gave, after 4 days, **3e** as red platelets. While **3e** was dried in vacuo, the color changed to a red-violet (yield 53%): dec pt 95 °C; MS *m/z* (I_{rel}, %) 486 (58, M^+), 255 (55, $Cp_2NbOCH_4^+$), 254 (100, Cp_2NbOMe^+), 248 (36, $Cp_2NbC_2H_3^+$), 247 (64, $Cp_2NbC_2H_2^+$), 225 (36, $Cp_2NbH_2^+$), 224 (78, Cp_2NbH^+), 223 (70, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 6.82–7.50 (m, 2 Ph), 4.91 and 4.86 (s, Cp), 4.20 (d, $^2J = 6.1$ Hz, $H_{4\text{-syn}}$, 3.36 (s, O*Me*), 0.40 (d, $^2J = 6.1$ Hz, $H_{4\text{-anti}}$); ^{13}C NMR (CD_3COCD_3) δ 210.0 (br, C(1)), 169.7 (br, CO), 150.9 (br), 141.4, 131–124 (solvent and several signals, not resolved), 102.4 and 98.4 (dqn, $^1J_{CH} = 177$, $^{2,3}J_{CH} = 6$ Hz, Cp), 51.3 (q, $^1J_{CH} = 146$ Hz, OMe), 47.5 (dd, $^1J_{CH} = 148$, 154 Hz, CH_2). Anal. Calcd for $C_{28}H_{25}NbO_2$: C, 69.14; H, 5.18. Found: C, 68.95; H, 5.27.

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Table V. Crystallographic Data, Data Collection Parameters, and Refinement Parameters

	3d	**4i**
formula	$C_{22}H_{27}O_4Nb$	$C_{24}H_{35}Si_2O_4Nb$
fw	448.36	536.62
space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)
a, pm	1649.3 (1)	1405.3 (2)
b, pm	840.4 (1)	2012.0 (3)
c, pm	1594.1 (2)	965.6 (2)
β, deg	116.52 (1)	
V, nm^3	1.977 (1)	2.730 (1)
Z	4	4
density (calc), g cm^{-3}	1.506	1.305
cryst size, mm^3	0.30 × 0.60 × 0.78	0.50 × 0.28 × 0.18
μ(Mo Kα), cm^{-1} [a]	6.05	5.31
radiation (λ, pm)	Mo Kα (71.073)	Mo Kα (71.073)
monochromator	graphite	graphite
temp	ambient	ambient
scan mode (θ range, deg)	ω–2θ (1–30)	ω–2θ (1–30)
no. of unique rflns obsd [b]	5082	3328
N_o, no. of unique rflns [c]	4854	2184
N_p, no. of params refined	271	281
goodness of fit [d]	0.78	1.38
R [e]	0.023	0.034
R_w [f]	0.024	0.036
w^{-1}	1	1
decay of control rflns, % [g]	1.9	13.9
residual electron density, 10^{-6} e pm^{-3}	0.35	0.37

[a] An empirical absorption correction was applied with use of the routine DIFABS of the SDP program. [b] $I > \sigma(I)$. [c] $I > 3\sigma(I)$. [d] $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$. [e] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [f] $R_w = [\sum w(|F_o| - |F_e|)^2/\sum w|F_o|^2]^{1/2}$. [g] Corrected by means of the routine CHORT of the SDP program.

Preparation of 3f. $Cp_2NbH(PhC\equiv CPh)$ (2.04 g, 5.08 mmol) and phenylacetylene (520 mg, 5.09 mmol) in toluene (20 mL) were heated at 80 °C for 3 h. All volatiles were pumped off, and the last traces were removed in vacuo at 40 °C. The residue was treated with ether (50 mL), giving **3f** as a brown-red powder (55%), which contains variable amounts of interstitial ether (^1H NMR). Recrystallization from decalin gives red plates that contain $^1/_2$ equiv of decalin: dec pt 209 °C; MS m/z (I_{rel}, %) 504 (62, M^+), 326 (52, $M^+ - C_2Ph_2$), 324 (96, $M^+ - C_2H_2Ph_2$), 282 (76, $Ph_3C_4H_3^+$), 224 (100, Cp_2NbH^+), 223 (95, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 7.46–6.80 (m, 3 Ph), 5.63 (d, ^3J = 9.3 Hz, H_3), 4.98 and 4.64 (s, Cp), 0.94 (d, ^3J = 9.3 Hz, $H_{4\text{-anti}}$); ^{13}C NMR (CD_3COCD_3/THF (1/1)) δ 222 (br, C(1)), 151.9 (t, $^3J_{CH}$ = 6 Hz, C_i), 149.7 (br), 141.3 (br), 136.0 (br), 132–122 (solvent and several signals, not resolved), 101.1 (dqn, ^1J = 177, $^{2,3}J$ = 6 Hz, Cp), 97.0 (dqn, ^1J = 175, $^{2,3}J$ = 6 Hz, Cp), signal of C(4) hidden by solvent signal; ^{13}C NMR (C_6D_6) δ 65.5 (d, ^1J = 142 Hz, C(4)). Anal. Calcd for $C_{32}H_{27}Nb\cdot{}^1/_2C_{10}H_{18}$: C, 77.47; H, 6.33. Found: C, 77.19; H, 6.17.

Intermediate 4c. An NMR tube was charged with **2a** and C_6D_6. One equivalent of DMAC was then added at −10 °C. The resulting reaction mixture contained **4c** and **2a** in a 9/1 ratio. **4c**: ^1H NMR (C_6D_6) δ 6.05 (s, $=$CH), 5.24 (s, 2 Cp), 3.86 and 3.31 (s, OMe), Ph signals hidden by solvent signal; ^{13}C NMR (C_6D_6/CD_3COCD_3 (1/3)) δ 187.4 (br, Nb—C$=$), 180.8 and 167.7 (m, CO), 163.0 and 151.3 (br, C$\equiv$), 132.3 (d, $^1J_{CH}$ = 168 Hz, $=$CH), Ph signals hidden by solvent signal, 104.2 (dqn, $^1J_{CH}$ = 183, $^{2,3}J_{CH}$ = 5.$_5$ Hz, 2 Cp), 50.8 and 50.4 (q, $^1J_{CH}$ = 146 Hz, OMe).

Preparation of 4g. Methyl propiolate (302 mg, 3.60 mmol) was added to $Cp_2NbH(Me_3SiC\equiv CSiMe_3)$ (1.40 g, 3.55 mmol) in ether (30 mL) at room temperature to give a red-brown solution. **4g** is precipitated by dropwise addition of hexane (50 mL) as brown-red microcrystals (63%): dec at 86–88 °C; MS m/z (I_{rel}, %) 478 (0.4, M^+), 477 (0.5, $M^+ - H$), 308 (17, $M^+ - C_2(SiMe_3)_2$), 255 (13, $Cp_2NbH(OMe)^+$), 254 (100, Cp_2NbOMe^+), 225 (5, $Cp_2NbH_2^+$), 224 (40, Cp_2NbH^+), 223 (32, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 6.61 and 5.97 (d, ^2J = 3.8 Hz, $=CH_2$), 5.00 (s, 2 Cp), 3.61 (s, O*Me*), 0.40 and 0.23 (s, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 182.0 (m, CO), 168.3 and 158.4 (br, C$\equiv$), 167.2 (m, br, NbC$=$), 132.1 (dd, ^1J = 151, 158 Hz, $=CH_2$), 102.7 (dqn, ^1J = 176, $^{2,3}J$ = 6.$_5$ Hz, 2 Cp), 50.1 (q, ^1J = 145 Hz, OMe), 2.8 and 1.6 (q, ^1J = 119 Hz, $SiMe_3$); IR (KBr, cm^{-1}) 1730 m (sh), 1700 m, 1678 vs, 1633 m (sh), 1565 w. Anal. Calcd for $C_{22}H_{33}NbO_2Si_2$: C, 55.21; H, 6.95. Found: C, 54.94; H, 6.81.

Preparation of 4h. Butynone (315 mg, 4.62 mmol) was added dropwise to an in situ prepared solution of $Cp_2NbH(Me_3SiC\equiv CSiMe_3)$ (1.82 g, 4.62 mmol) in toluene (20 mL) at room temperature. Then the volume of the red solution was reduced to 5 mL. Dropwise addition of hexane (40 mL) and cooling to −20 °C gave **4h** as brown-red to black crystals (42%): mp 87–88 °C; MS m/z (I_{rel}, %) 462 (56, M^+), 393 (24, $M^+ - CH_3COC{=}CH_2$) 390 (18, $M^+ + 1 - SiMe_3$), 389 (16, $M^+ - SiMe_3$), 372 (26, ?), 320 (49, 393 − $SiMe_3$), 312 (74, ?), 292 (24, $M^+ - C_2(SiMe_3)_2$), 240 (35, Cp_2NbOH^+), 225 (29, $Cp_2NbH_2^+$), 224 (82, Cp_2NbH^+), 223 (100, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 6.36 and 5.99 (d, ^2J = 3.2 Hz, $=CH_2$), 4.95 (s, 2 Cp), 2.36 (s, OMe), 0.34 and 0.23 (s, $SiMe_3$); IR (KBr, cm^{-1}) 1729 (sh), 1694 s, 1646 vs, 1610 (sh), 1562 w. Anal. Calcd for $C_{22}H_{33}NbOSi_2$: C, 57.13; H, 7.19. Found: C, 56.96; H, 7.24.

Preparation of 4i. DMAC (992 mg, 6.98 mmol) was added dropwise to an in situ prepared solution of $Cp_2NbH(Me_3SiC\equiv CSiMe_3)$ (2.75 g, 6.98 mmol) in toluene (25 mL) at room temperature. Light was excluded during workup. The brown-red solution was filtered through sand and slowly cooled to −20 °C to give **4i** as orange crystals. Concentrating the mother liquor, cooling to −20 °C, and recrystallizing from toluene afforded a second crop (total yield 60%): dec pt 119–120 °C; MS m/z (I_{rel}, %) 536 (4, M^+), 366 (66, $M^+ - C_2(SiMe_3)_2$), 254 (100, Cp_2NbOMe^+), 239 (28, Cp_2NbO^+), 224 (96, Cp_2NbH^+), 223 (65, $NbCp_2^+$); ^1H NMR (C_6D_6) δ 6.68 (s, $=$CH), 4.96 (s, 2 Cp), 3.87 and 3.51 (s, OMe), 0.44 and 0.19 (s, $SiMe_3$); ^{13}C NMR (CD_3COCD_3) δ 195.1 (m, NbC$=$), 181.4 (dq, ^3J = 16, ^3J = 4 Hz, CO), 166.5 and 153.9 (br, C$\equiv$), 162.4 (qn, $^{2,3}J$ = 4 Hz, CO), 130.0 (d, ^1J = 165 Hz, $=$CH), 103.9 (dm, ^1J = 178, $^{2,3}J$ = 6.$_5$ Hz, Cp), 50.7 and 50.6 (q, ^1J = 146 Hz, OMe), 2.8 and 1.8 (q, ^1J = 119 Hz, $SiMe_3$); IR (KBr, cm^{-1}) 1697 vs, 1683 s, 1655 m (sh), 1645 m (sh), 1570 m, 1549 s, 1505 w (sh), 1462 m, 1445 m. Anal. Calcd for $C_{24}H_{35}NbO_2Si_2$: C, 53.72; H, 6.57. Found: C, 53.57; H, 6.40.

Crystal Structure Analyses of 3d and 4i (Table V). Crystals of suitable size were mounted in a glass capillary under dinitrogen. Intensity data were collected on a CAD4 four-circle diffractometer (Enraf-Nonius, Delft, The Netherlands). Some decay (total for **3d** 1.9%, total for **4i** 13.9%) was observed; a decay correction was carried out by using the program CHORT of the SDP program system.[38] Both structures were solved and refined by means of standard heavy-atom methods, alternating least-squares refinements, and difference Fourier calculations. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions (d(C–H) = 95 pm, B_{eq} = 5.0 × 10^4 pm^2); isotropic temperature factors were refined for all hydrogen atoms of **3d** and for the alkenyl hydrogen H(2) of **4i**. All calculations were performed on a VAX 11/730 computer using the SDP program system.[38]

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Registry No. 1, 11105-67-2; **2a**, 77299-70-8; **2b**, 128752-91-0; **2c**, 128752-92-1; **2d**, 55534-72-0; **3a**, 109168-56-1; **3b**, 128752-93-2; **3c**, 128752-94-3; **3d**, 128752-95-4; **3e**, 128752-96-5; **3f**, 128752-97-6; **4c**, 128753-01-5; **4g**, 128752-98-7; **4h**, 128752-99-8; **4i**, 128753-00-4; DMAC, 762-42-5; $Me_3SiC\equiv CSiMe_3$, 14630-40-1; 3-hexyne, 928-49-4; 2-butyne, 503-17-3; methyl propionate, 554-12-1; phenylacetylene, 536-74-3; butynone, 1423-60-5.

Supplementary Material Available: Additional information on the crystal structure analyses and tables of positional parameters, thermal parameters, and bond lengths for **3d** and **4i** (11 pages); tables of observed and calculated structure factors for **3d** and **4i** (36 pages). Ordering information is given on any current masthead page.

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