New *ansa*-Niobocene Complexes. X-ray Crystal Structure of [Me₂Si(η^5-C₅H₄)₂]Nb(=NᵗBu)Cl. Stereoselective Synthesis of *meso*-[Me₂Si(η^5-C₅H₃SiMe₃)₂]Nb(=NᵗBu)Cl

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The *ansa*-niobocene complex [Me₂Si(η^5-C₅H₄)₂]Nb(=NᵗBu)Cl (**1**) has been prepared and its structure determined by single-crystal X-ray diffraction. The alkyl complexes [Me₂Si-(η^5-C₅H₄)₂]Nb(=NᵗBu)(R) (R = Me (**2**), Et (**3**), CH₂Ph (**4**), CH₂CH=CH₂ (**5**)) were prepared by the reaction of **1** and the corresponding Grignard reagent. Using the trimethylsilyl-substituted *ansa* ligand Me₂Si(C₅H₃SiMe₃)₂, [Me₂Si(η^5-C₅H₃SiMe₃)₂]Nb(=NᵗBu)Cl (**6**) was prepared and isolated uniquely as the *meso*-isomer. Nevertheless the synthesis of [Me₂Si-(η^5-C₅H₃SiMe₃)₂]NbCl₂ (**7**) yielded a mixture of *meso*- and *rac*-isomers. Reduction of **7** in the presence of ligand (RC≡CR) (R = Me, Ph) gave [Me₂Si(η^5-C₅H₃SiMe₃)₂]NbCl(RC≡CR) (R = Me (**8**), Ph (**9**)). Both complexes were initially isolated as mixtures of *meso*- and *rac*-isomers and in the case of **9** could be separated due to their differing solubilities in hexane.

Introduction

The use of *ansa*-cyclopentadienyl ligands has received wide attention in the chemistry of group 4 metals,[1] due mainly to its ability to impart on its complexes a high and selective degree of catalytic activity.[2]

For group 5 metals few such compounds are known and normally exhibit a σ-bond between the *ansa* ligand and the metal.[3] We recently reported the first *ansa*-niobocene complexes in which the cyclopentadienyl rings are bound only in an η^5 mode to niobium.[4] Since this first account, some *ansa*-niobocene complexes of this type have been described, [Me₂C(η^5-C₅H₄)₂]Nb(=NR)-Cl (R = ᵗBu, SiMe₃),[5] [Me₂C(η^5-C₅H₄)₂]Nb(μ-H₂)BH₂,[6] [Me₂C(η^5-C₅H₄)₂]NbH(PMe₃),[6] and [Me₂C(η^5-C₅H₄)₂]Nb-(=NC₆H₄Me₂-2,5)Cl.[7]

Furthermore the use of substituted *ansa* ligands in the stereoselective synthesis of group 4 metal complexes and their importance in catalysis is receiving special attention,[8] although only one example for group 5, an *ansa*-vanadocene complex, has been reported.[8] It has been shown that steric effects in the transition metal catalyst greatly affect the polymerization of olefins, and bulky ligands, such as substituted *ansa* ligands, would therefore aid stereospecific olefin coordination and polymerization.[9] In addition the chiral nature of these ligands would also strongly influence stereoselectivity.[9]

The importance of catalysts based on group 5 precursors is now growing due in part to the less air-sensitive nature of their complexes in comparison with their group 4 analogues.[10]

Our recent results in the chemistry of *ansa*-niobocene complexes encouraged us to explore the preparation of this class of complexes for group 5 elements using the trimethylsilyl-substituted *ansa* ligand Me₂Si(C₅H₃-SiMe₃)₂. We report here our results on the synthesis and structural details of new *ansa*-niobocene complexes [Me₂Si(η^5-C₅H₄)₂]Nb(=NᵗBu)X, as an extension of the work previously communicated,[4] as well as the isolation and characterization of the first substituted *ansa*-niobocene complexes, [Me₂Si(η^5-C₅H₃SiMe₃)₂]Nb(X)(Y).

Results and Discussion

We have previously described[4] the synthesis of the *ansa*-niobocene dichloride complexes [Me₂Si(η^5-C₅H₄)₂]-

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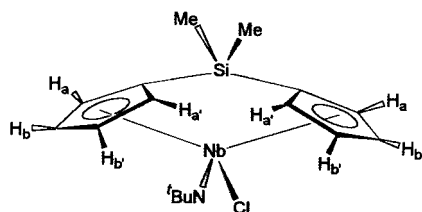
Figure 1. Proposed structure for $[Me_2Si(\eta^5-C_5H_4)_2]Nb(=N^tBu)Cl$ (**1**).
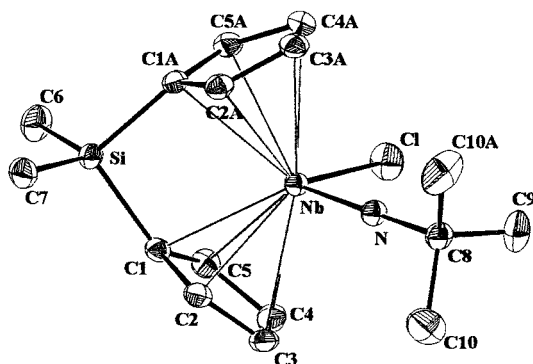
Figure 2. Molecular structure and atom-labeling scheme for $[Me_2Si(\eta^5-C_5H_4)_2]Nb(=N^tBu)Cl$ (**1**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 with ESDs in Parentheses[a]

Nb−Cp(1)	2.110(2)
Nb−Cl	2.448(1)
Nb−N	1.756(3)
Nb−C(8)	1.449(4)
Cp(1)−Nb−Cp(1A)	121.21
Nb−N−C(8)	178.8(2)
Si−C(1)−Cp(1)	160.2(2)
C(1)−Nb−C(1A)	94.17(6)
Cl−Nb−Cp(1)	104.27
N−Nb−Cp(1)	113.61
Cl−Nb−N	95.15(9)

[a] Symmetry element A is $x, -y + \frac{1}{2}, z$. Cp(1) is the centroid of the cyclopentadienyl ring C(1)−C(5).

$NbCl_2$ by the reaction of $NbCl_4(THF)_2$ and $[Me_2Si(\eta^5-C_5H_4)_2]Tl_2$, and from this some alkyne-containing *ansa*-niobocene compounds $[Me_2Si(\eta^5-C_5H_4)_2]NbCl(RC\equiv CR)$ were also isolated. Now, we have considered an alternative method to prepare *ansa*-niobocene complexes using $Nb(=N^tBu)Cl_3(py)_2$[11] as starting material. The preparation of $[Me_2Si(\eta^5-C_5H_4)_2]Nb(=N^tBu)Cl$ (**1**) was achieved by the reaction of $Nb(=N^tBu)Cl_3(py)_2$ and $[Me_2Si(\eta^5-C_5H_4)_2]Li_2$[12] in THF. Complex **1** was isolated as a yellow solid after appropriate workup, and X-ray quality crystals were obtained by the slow recrystallization of **1** in toluene. It was spectroscopically characterized. The ^1H NMR spectrum reveals the presence of a system similar to that obtained for the previously reported $[Me_2Si(\eta^5-C_5H_4)_2]NbCl(MeC\equiv CMe)$,[4] where the symmetry of the molecule (C_s) in solution is such that there is only one plane of symmetry and the two methyl groups of $SiMe_2$ become inequivalent, as do the cyclopentadienyl protons (H_a, H_b, $H_{a'}$, and $H_{b'}$), thus giving two singlets for the former and four multiplets for the latter (Figure 1) (see Experimental Section).

The molecular structure of **1** was established by X-ray crystal studies. The molecular structure and atomic numbering scheme are shown in Figure 2. Selected bond lengths and angles are given in Table 1.

The structure shows the $Me_2Si(C_5H_4)_2$ *ansa* ligand chelating the niobium center, where both cyclopentadienyl rings are bound to the metal in an η^5 mode. The cent(1)−Nb−cent(2) angle of 121.21° is somewhat smaller than that observed for the only other identical *ansa* system group 5 compound reported, namely, $[Me_2Si(\eta^5-C_5H_3SiMe_3)_2]NbCl(MeC\equiv CMe)$,[4] which exhibits a cent(1)−Nb−cent(2) angle of 130.0°. For similar niobium complexes containing the CMe_2-bridged *ansa* ligand

the cent(1)−Nb−cent(2) angle is 6−7° smaller ($[Me_2C(\eta^5-C_5H_4)_2]Nb(=N^tBu)Cl$ 113.3°)[5] and thus clearly illustrates the fundamental difference between the two types of *ansa* ligands (see Table 2). The cent(1)−Nb−cent(2) angles of the non-*ansa*-niobocene complexes $(\eta^5-C_5H_5)_2Nb(=N^tBu)Cl$ (124.0°)[11] and $(\eta^5-C_5H_4SiMe_3)_2Nb(=NC_6H_5)Cl$ (124.9°)[14] are of values similar to that of **1**.

The imide ligand is able to act as either a two- or four-electron donor. In the first case the nitrogen atom would be sp^2 hybridized and therefore result in the bending back of the imide substituent. In the second case the nitrogen would be sp hybridized and the metal−nitrogen−substituent angle linear. In **1** this angle Nb−N−C(8) of 178.8(2)° reveals the latter case to prevail. This phenomenon is also seen in the other *ansa*-imido and non-*ansa*-niobocene complexes reported, although steric effects cause some degree of bending back (see Table 2). The formal electron count is 20 electrons. The Nb−N bond distance of 1.756(3) Å is in agreement with a triple bond between the niobium and nitrogen atoms and is similar to those observed for other complexes of this type (see Table 2).

Alkylation reactions on complex **1** were also considered. The alkylation of **1** by the appropriate alkylmagnesium chloride gave the corresponding alkyl products $[Me_2Si(\eta^5-C_5H_4)_2]Nb(=N^tBu)(R)$, R = Me (**2**); Et (**3**); CH_2Ph (**4**); $CH_2CH=CH_2$ (**5**), which were isolated after appropriate workup, as air-sensitive yellow crystalline solids in modest yields (see Experimental Section). The different complexes were characterized spectroscopically. In the ^1H NMR spectrum of **3**, as illustrated in Figure 3, the ethyl group displays an A_3BC pattern, indicating the presence of an unusually weak agostic interaction between an α-hydrogen atom of the ethyl group and the metal center (J_{AB} = 8.0 Hz, J_{AC} = 7.5 Hz, J_{BC} = 14.0 Hz). This proposal should be considered cautiously, because in the ^{13}C NMR spectrum we have not been able to distinguish the two $^1J(^{13}C-^1H)$ constants corresponding to the CH_2 group. Two ethyl complexes of niobium have been reported in which a similar agostic interaction between the methylene group of ethyl and the metal has been observed.[15]

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Table 2. Selected Structural Data on *ansa*- and Non-*ansa*-niobocene Imido Complexes

	Cp–Nb–Cp (deg)	Nb–N–C (deg)	Nb–N (Å)	ref
$[Me_2Si(\eta^5\text{-}C_5H_4)_2]Nb(=N^tBu)Cl$	121.21	178.8(2)	1.756(3)	this work
$[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl(MeC\equiv CMe)$	130.0			4
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(=NSiMe_3)Cl$	114.2	167.71(7)	1.777(1)	5
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(=N^tBu)Cl$	113.3	178.4(3)	1.762(3)	5
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(=N^tBu)Br$	113.4	178.3(2)	1.765(2)	5
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(=N^tBu^)I$	114.2	171.8(2)	1.770(2)	5
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(\mu\text{-}H_2)BH_2$	125.0			6
$[Me_2C(\eta^5\text{-}C_5H_4)_2]NbH(PMe_3)$	126.1			6
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(=NAr)Cl^a$	not reported	167.5(1)	1.798(2)	7
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(=NAr)N(Me)_2[B(C_6H_5)_4]^a$	not reported	166.8(1)	1.803(2)	7
$(\eta^5\text{-}C_5H_5)_2Nb(=N^tBu)Cl^b$	122.7	173.6(4)	1.789(4)	13
	124.0	179.4(5)	1.737(6)	
$(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(=NC_6H_5)Cl$	124.9	165.1(2)	1.792(2)	14

a Ar = $C_6H_4Me_2$-2,5. *b* Two independent molecules exist in the unit cell.
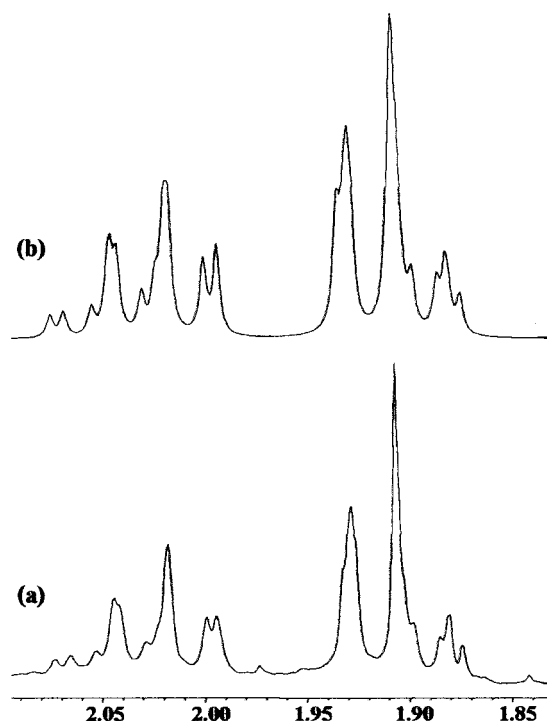
Figure 3. ^1H NMR spectra of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Nb(=N^tBu)$-(Et) in the ethyl region: (a) experimental; (b) simulated.

Figure 4. Different isomers for complexes $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Nb(X)(Y)$.

In the ^1H NMR spectrum of compound **4** the CH_2 protons of the benzyl group are equivalent, indicating free rotation of the niobium–carbon bond in solution. This is also observed in **5**, which furthermore shows an AB system for the terminal olefinic protons of the η^1-allyl group (see Experimental Section).

The complete absence of niobium complexes containing substituted *ansa* ligands and the stereoselective catalytic properties of their group 4 analogues has led us to investigate these compounds. To prepare substituted *ansa*-niobocenes, we have considered the use of the trimethylsilyl-substituted *ansa* ligand $Me_2Si(C_5H_3\text{-}SiMe_3)_2$, and different families of substituted *ansa*-niobocene complexes of the stoichiometry $[Me_2Si(\eta^5\text{-}C_5H_3\text{-}SiMe_3)_2]Nb(X)(Y)$ have been prepared. The preparation of substituted *ansa* ligand complexes of niobium can lead to a variety of isomers depending on the configuration of the cyclopentadienyl rings. The carbon atoms linked to the $SiMe_3$ substituent become chiral in the niobocene complexes due to the fact that they are also linked to niobium and two distinct carbon atoms in the

C_5 ring. This effect gives rise to the stereoisomer *meso*-(*R,S*) (I) and the enantiomers *rac*-(*R,R*) (III) and (*S,S*) (IV) (Figure 4). In addition, if groups X and Y are different, there exists another *meso* form (II) in which the $SiMe_3$ substituents are pointing either toward or away from X. By varying X or Y and therefore their steric or electronic properties, the stereoselective synthesis of only one of these isomers should be possible.

^1H NMR spectroscopy will show clearly the existence of the *meso*- and *rac*-isomers. The *meso*-complex contains a plane of symmetry (C_s), and thus the two cyclopentadienyl rings of the *ansa* ligand will be equivalent. They are however inequivalent in the *rac*-complex due to the lack of symmetry (C_1).

First, using the identical synthetic method employed in the preparation of **1**, complex $[Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2]$-$Nb(=N^tBu)Cl$ (**6**) was prepared by the reaction of Nb-$(=N^tBu)Cl_3(py)_2$ and $[Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2]Li_2$ in a 1:1 molar ratio. It was prepared in a stereoselective synthesis uniquely as the *meso*-isomer as was revealed by ^1H NMR spectroscopy. The *meso*-isomer contains a plane of symmetry, which makes the cyclopentadienyl rings of the *ansa* ligand equivalent, and hence only three signals for the ring protons are observed in its ^1H NMR spectrum, which in addition gave the expected signals for the ^tBu and the $SiMe_3$ groups and two for $SiMe_2$ (see Experimental Section). In the case of **6**, the *rac*-isomer is probably disfavored due to steric effects, and for this
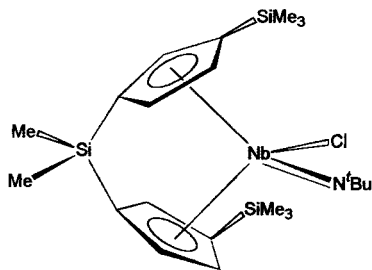
Figure 5. Proposed structure for *meso*-[Me$_2$Si(η^5-C$_5$H$_3$-SiMe$_3$)$_2$]Nb(=N^{t}Bu)Cl (**6**).

same reason the SiMe$_3$ groups should be pointing away from the bulky imido group (Figure 5), although the influence of electronic effects cannot be ruled out.

Complex [Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl$_2$ (**7**) was prepared by a similar method employed in the synthesis of [Me$_2$Si(η^5-C$_5$H$_4$)$_2$]NbCl$_2$,[4] using the lithium reagent [Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]Li$_2$ instead of the corresponding thallium derivative. The compound isolated should be a mixture of *rac*- and *meso*-isomers, although only one set of 10 signals was observed in its ESR spectrum. This is most certainly due to the small difference between the *rac*- and *meso*-isomers, which the resolution of the spectrometer was unable to differentiate. The values of g_{iso} (1.9847) and $\langle a 93_{Nb} \rangle$ (104.36 G) are analogous to other niobocene(IV) complexes, with the unpaired electron mainly located at the metal center.[16]

We have considered the reduction processes of **7** in the presence of the appropriate alkyne ligands. The reduction of **7** with Na/Hg in a 1:1 molar ratio in the presence of the alkyne RC≡CR, R = Me, Ph, yields the alkyne-containing complexes [Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]-NbCl(RC≡CR), R = Me (**8**); Ph (**9**), in a behavior similar to that previously described for complex [Me$_2$Si(η^5-C$_5$-H$_4$)$_2$]NbCl$_2$.[4] **9** was initially isolated from toluene extraction of the reaction as an approximately 1:1 mixture of its *rac*- and *meso*-isomers, which supports the proposal that **7** is also a mixture of its *rac*- and *meso*-isomers. These isomers were separated on cooling a hexane solution. The green *meso*-isomer was highly soluble and the yellow *rac*-isomer only partially soluble in this medium. However, for **8** no notable difference in solubility of the *rac*- and *meso*-isomers was observed, and thus separation was not possible. **8** was isolated as a green solid corresponding to an approximately 1:1 mixture of its *rac*- and *meso*-isomers. The ^{1}H spectra of the *rac*-isomer of **8** and **9** show the expected signals for a complex that does not contain a plane of symmetry; that is, the cyclopentadienyl rings of the *ansa* ligand are inequivalent and give rise to six signals. In the *meso*-isomer there is a plane of symmetry, which makes the cyclopentadienyl rings of the *ansa* ligand equivalent, and hence three signals are observed in its ^{1}H NMR spectrum (see Experimental Section).

According to Figure 4, when X ≠ Y, two isomers are possible for the *meso*-confirmation. However, in both **8** and **9** only one *meso*-complex is observed. It is reasonable to assume that due to steric effects, this isomer would have the SiMe$_3$ substituents of the cyclopentadienyl ring pointing away from the voluminous acetylene group.

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Concluding Remarks

In conclusion we report the synthesis and characterization of new halo and alkyl *ansa*-niobocene complexes, as well as the preparation of the first substituted *ansa*-niobocene complexes, with the substituted *ansa* ligand Me$_2$Si(C$_5$H$_3$SiMe$_3$)$_2$, [Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]Nb(X)(Y).

Experimental Section

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

The complexes [Me$_2$Si(η^5-C$_5$H$_4$)$_2$]Li$_2$,[12] NbCl$_4$(THF)$_2$,[17] and Nb(=N^{t}Bu)Cl$_3$(py)$_2$[11] were prepared as described earlier. THF or Et$_2$O solutions of ClMgR (R = Me, Et, CH$_2$Ph, and CH$_2$-CH=CH$_2$) were purchased from Aldrich and used directly. Me$_2$Si(C$_5$H$_4$SiMe$_3$)$_2$[18] was prepared by the published method and converted into its lithium salt by reaction with a slight excess of *n*-butyllithium in hexane. ESR spectra were taken at the X-band with a Bruker ESP 300 spectrometer. IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. ^{1}H and ^{13}C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer.

[Me$_2$Si(η^5-C$_5$H$_4$)$_2$]Nb(=N^{t}Bu)Cl (1). THF (50 mL) was added to a solid mixture of Nb(=N^{t}Bu)Cl$_3$(py)$_2$ (1.56 g, 3.64 mmol) and [Me$_2$Si(η^5-C$_5$H$_4$)$_2$]Li$_2$ (0.73 g, 3.65 mmol). The resulting yellow solution was stirred under reflux for 8 h. Solvent was removed in vacuo and hexane added (75 mL) to the resulting solid. The mixture was filtered and the filtrate concentrated (ca. 10 mL) and cooled to −30 °C. The resulting yellow solid that precipitated from the solution was isolated by filtration (1.02 g, 72%). IR (Nujol): $\nu_{Nb=C}$ 1245 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.03 (3H), 0.23 (3H) (s, Si*Me*$_2$), 0.97 (s, 9H, C*Me*$_3$), 5.94 (2H), 6.05 (2H), 6.31 (2H), 6.51 (2H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −6.78, −5.09 (Si*Me*$_2$), 30.22 (C*Me*$_3$), 72.34 (*C*Me$_3$), 100.49, 117.07, 117.99, 119.73, 130.37 (C^1) (C$_5$*H*$_4$)$_2$. Anal. Calcd for C$_{16}$H$_{23}$ClNNbSi: C, 49.81; H, 6.01; N, 3.63. Found: C, 49.58; H, 5.91; N, 3.60.

[Me$_2$Si(η^5-C$_5$H$_4$)$_2$]Nb(=N^{t}Bu)(Me) (2). A 3 M solution of ClMgMe in THF (0.32 mL, 0.94 mmol) was added to a stirring solution of **1** (0.30 g, 0.78 mmol) in THF (25 cm^3) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and the remaining green oil extracted in hexane. A yellow crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.12 g, 42%). IR (Nujol): $\nu_{Nb=C}$ 1260 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.10 (3H), 0.32 (3H) (s, Si*Me*$_2$), 0.96 (s, 9H, C*Me*$_3$), 1.08 (s, 3H, *Me*), 5.55 (2H), 5.86 (2H), 5.94 (2H), 6.40 (2H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −6.25, −5.15, (Si*Me*$_2$), 4.41 (*Me*), 30.91 (C*Me*$_3$), 66.55 (*C*Me$_3$), 100.11, 113.39, 113.97, 114.35, 123.77 (C^1) (C$_5$*H*$_4$). Anal. Calcd for C$_{17}$H$_{26}$NNbSi: C, 55.88; H, 7.17; N, 3.83. Found: C, 56.12; H, 7.24; N, 3.81.

Me$_2$Si(η^5-C$_5$H$_4$)$_2$]Nb(=N^{t}Bu)(Et) (3). A 2 M solution of ClMgEt in Et$_2$O (0.50 mL, 1.00 mmol) was added to a stirring solution of **1** (0.32 g, 0.83 mmol) in THF (25 mL) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and the remaining green oil extracted in hexane. A yellow crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.16 g, 52%). IR (Nujol): $\nu_{Nb=C}$ 1245 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.13 (3H), 0.34 (3H) (s, Si*Me*$_2$),

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0.97 (s, 9H, CMe_3), 1.91 (m, 3H CH$_2$CH_3), 2.02 (m, 2H, CH_2-CH$_3$), 5.36 (2H), 5.80 (2H), 6.06 (2H), 6.34 (2H) (m, C$_5H_4$). ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −5.71, −5.51 (SiMe_2), 20.20 (CH$_2$$CH_3$), 22.39 ($CH_2CH_3$), 31.33 ($CMe_3$), 70.80 ($CMe_3$), 101.44, 111.68, 111.89, 116.89, 120.98 (C^1) (C$_5$H$_4$). Anal. Calcd for C$_{18}$H$_{28}$NNbSi: C, 56.98; H, 7.44; N, 3.69. Found: C, 56.74; H, 7.31; N, 3.63.

Me$_2$Si(η^5-C$_5$H$_4$)$_2$]Nb(=N^{t}Bu)(CH$_2$Ph) (4). A 1 M solution of ClMgCH$_2$Ph in Et$_2$O (0.96 mL, 0.96 mmol) was added to a stirring solution of **1** (0.30 g, 0.78 mmol) in THF (25 mL) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and the remaining green oil extracted in hexane. A dark yellow crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.15 g, 44%). IR (Nujol): $ν_{Nb=C}$ 1241 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ −0.05 (3H), 0.26 (3H) (s, SiMe_2), 0.96 (s, 9H, CMe_3), 3.34 (s, 2H, CH_2Ph), 5.49 (2H), 5.66 (2H), 5.98 (2H), 6.32 (2H) (m, C$_5H_4$), 6.80−7.45 (m, 5H, CH$_2$$Ph$). ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −6.64, −4.76 (SiMe_2), 32.43 (CH$_2$Ph), 31.87 (CMe_3), 71.39 (CMe$_3$), 101.55, 101.67, 108.55, 116.57 (C^1), 117.64 (C$_5$H$_4$), 125.06, 130.45, 147.12 (C^1) (CH$_2$$Ph$). Anal. Calcd for C$_{23}H_{30}$NNbSi: C, 62.57; H, 6.85; N, 3.17. Found: C, 62.80; H, 6.94; N, 3.15.

[Me$_2$Si(η^5-C$_5$H$_4$)$_2$]Nb(=N^{t}Bu)(CH$_2$CH=CH$_2$) (5). A 2 M solution of ClMgCH$_2$CH=CH$_2$ in THF (0.56 mL, 1.12 mmol) was added to a stirring solution of **1** (0.36 g, 0.93 mmol) in THF (25 mL) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and the remaining green oil extracted in hexane. A yellow crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.16 g, 43%). IR (Nujol): $ν_{Nb=C}$ 1258 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.09 (3H), 0.30 (3H) (s, SiMe_2), 0.93 (s, 9H, CMe_3), 2.82 (d, 2H, CH_2−CH=CH$_2$) ^2J(^{1}H−^{1}H) 8.5 Hz, 4.85 (*cis*), 5.04 (*trans*) (dd, 2H, CH$_2$−CH=CH_2) $^2J_{gem}$(^{1}H−^{1}H) 2.6 Hz, $^2J_{cis}$(^{1}H−^{1}H) 9.9 Hz, $^2J_{trans}$(^{1}H−^{1}H) 16.8 Hz, 5.41 (2H), 5.86 (2H), 5.91 (2H), 6.33 (2H), (m, C$_5H_4$), 6.61 (m, 1H, CH$_2$−CH=CH$_2$). ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −6.12, −5.40 (SiMe_2), 31.02 (CMe_3), 37.30 (CH$_2$−CH=CH$_2$), 68.40 (CMe$_3$), 101.24, 113.21, 113.57, 117.30, 123.13 (C^1) (C$_5$H$_4$), 103.78 (CH$_2$−CH=CH$_2$), 150.40 (CH$_2$−CH=CH$_2$). Anal. Calcd for C$_{19}$H$_{28}$NNbSi: C, 58.30; H, 7.21; N, 3.58. Found: C, 58.01; H, 7.09; N, 3.49.

meso-[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]Nb(=N^{t}Bu)Cl (6). THF (50 mL) was added to a solid mixture of Nb(=N^{t}Bu)Cl$_3$(py)$_2$ (0.55 g, 1.28 mmol) and [Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]Li$_2$ (0.44 g, 1.28 mmol). The resulting yellow solution was stirred under reflux for 8 h. Solvent was removed in vacuo and hexane added (75 mL) to the resulting solid. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to −30 °C. The resulting orange solid that precipitated from the solution was isolated by filtration (0.47 g, 69%). IR (Nujol): $ν_{Nb=C}$ 1234 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.08 (3H), 0.35 (3H) (s, SiMe_2), 0.45 (s, 18H, SiMe_3), 0.99 (s, 9H, CMe_3), 6.23 (4H), 6.58 (2H), (m, C$_5H_3$SiMe$_3$). ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −7.12, −4.05 (SiMe_2), 0.48 (SiMe_3), 30.81 (CMe_3), 69.76 (CMe$_3$), 102.15, 122.56, 125.52, 125.66 (C$_{ipso}$), 134.55 (C$_{ipso}$) (C$_5$H$_3$SiMe$_3$). Anal. Calcd for C$_{22}$H$_{39}$ClNNbSi$_3$: C, 49.84; H, 7.41; N, 2.64. Found: C, 49.68; H, 7.37; N, 2.64.

[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl$_2$ (7). THF (200 mL) was added to a mixture of NbCl$_4$(THF)$_2$ (8.65 g, 22.83 mmol) and [Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]Li$_2$ (7.87 g, 22.83 mmol). The reaction mixture was stirred at room temperature for 16 h, after which solvent was removed in vacuo. The resulting solid was extracted several times in toluene (4 × 150 mL), solvent was removed under reduced pressure, and the resulting brown solid was dried under vacuum (9.55 g, 84%). IR (Nujol): $ν_{Si−Me}$ 1302 cm^{-1}, $ν_{C−C(Cp)}$ 1200, 1043, 834 cm^{-1}, $ν_{Nb−Cl}$ 270 cm^{-1}. Anal. Calcd for C$_{18}$H$_{30}$Cl$_2$NbSi$_3$: C, 43.72; H, 6.11. Found C, 43.56; H, 6.02.

[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl(MeC≡CMe) (8). **7** (0.95 g, 1.92 mmol) was added to sodium amalgam (0.044 g, 1.92 mmol

of Na). To the mixture was added THF (100 mL). To this stirred solution was added via microsyringe MeC≡CMe (0.151 mL, 1.92 mmol), and the reaction mixture was allowed to stir at room temperature for 3 h. The solvent was removed under reduced pressure and toluene (50 mL) was added. The suspension was filtered and solvent removed in vacuo from the filtrate, yielding a green solid (0.68 g, 69%). A displacement reagent ((S)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol) was added to a sample of **8** in the NMR tube, and the ^{1}H NMR resonances of the *rac*-isomer were doubled. A ^{1}H ^{13}C correlation experiment (HETCOR) carried out on these isomers has allowed us to assign the resonances corresponding to the different types of carbon atoms. IR (Nujol): $ν_{C≡C}$ 1700 cm^{-1}. *rac*-[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl(MeC≡CMe), **8a**, ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.05 (3H), 0.22 (3H) (s, SiMe_2), 0.18 (9H), 0.40 (9H) (s, SiMe_3), 2.27 (3H), 2.39 (3H) (s, MeC≡CMe), 4.63 (1H), 5.10 (1H), 5.14 (1H), 5.35 (1H), 5.50 (1H), 6.53 (1H) (m, C$_5H_3$SiMe$_3$). *meso*-[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl(MeC≡CMe), **8b**, ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.15 (3H), 0.17 (3H) (s, SiMe_2), 0.31 (s, 18H, SiMe_3), 2.27 (3H), 2.39 (3H) (s, MeC≡CMe), 4.98 (2H), 5.27 (2H), 5.64 (2H) (m, C$_5H_3$SiMe$_3$). **8a** ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −8.34, −7.52 (SiMe_2), 4.05, 10.56 (SiMe_3), 11.83, 18.86 (≡CMe), 96.36, 96.54, 97.51, 97.74, 98.40, 99.32, 116.88, 118.00, 125.80, 126.12 (C$_5$H$_3$SiMe$_3$), 126.71, 149.98 (≡CMe). **8b** ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −4.34, −3.52 (SiMe_2), 7.85, (SiMe_3), 11.83, 18.86 (≡CMe), 96.48, 97.67, 98.96, 117.45, 125.72 (C$_5$H$_3$SiMe$_3$), 126.71, 149.98 (≡CMe). Anal. Calcd for C$_{22}$H$_{36}$ClNbSi$_3$: C, 51.49; H, 7.07. Found: C, 51.30; H, 6.97.

[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl(PhC≡CPh) (9). **7** (1.05 g, 2.12 mmol) was added to sodium amalgam (0.049 g, 2.12 mmol of Na). To the mixture was added THF (100 mL). To this stirred solution was added PhC≡CPh (0.38 g, 2.12 mmol) and the reaction mixture was allowed to stir at room temperature for 3 h. The solvent was removed under reduced pressure, and toluene (50 mL) was added. The suspension was filtered and solvent removed in vacuo from the filtrate, yielding a green solid (0.98 g, 72.6%). The mixture of isomers was separated by adding hexane to the green solid. The resultant yellow precipitate of *rac*-[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl(PhC≡CPh), **9a**, was isolated by filtration and dried under vacuum (0.45 g). Solvent was removed from the green filtrate under reduced pressure to give a green solid of *meso*-[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]-NbCl(PhC≡CPh), **9b** (0.53 g). IR (Nujol): $ν_{C≡C}$ 1750 cm^{-1}. *rac*-[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl(PhC≡CPh), **9a**, ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.19 (3H), 0.22 (3H) (s, SiMe_2), −0.17 (9H), 0.19 (9H) (s, SiMe_3), 5.15 (1H), 5.37 (1H), 5.48 (1H), 5.93 (1H), 6.21 (1H), 6.67 (1H) (m, C$_5H_3$SiMe$_3$), 7.08−7.32, 7.66, 7.83 (m, 10H, PhC≡CPh). *meso*-[Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$]NbCl(PhC≡CPh), **9b**, ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.22 (3H), 0.24 (3H) (s, SiMe_2), 0.14 (s, 18H, SiMe_3) 5.60 (2H), 5.74 (2H), 6.18 (2H) (m, C$_5H_3$-SiMe$_3$). **9a** ^{13}C{^{1}H} NMR (300 MHz, acetone-d_6): δ −6.34, −4.52 (SiMe_2), 3.34, 10.88 (SiMe_3), 96.36, 96.54, 97.51, 97.74, 98.40, 99.32, 116.88, 118.00, 125.80, 126.12 (C$_5$H$_3$SiMe$_3$), 141.59, 159.68 (≡CPh), 126.24, 127.56, 127.74, 128.06, 128.20, 128.35, 128.94, 131.82, 139.20, 140.08 (≡$C$$Ph$). **9b** ^{13}C{^{1}H} NMR (300 MHz, acetone-d_6): δ −4.34, −3.52 (SiMe_2), 7.85, (SiMe_3), 96.48, 97.67, 98.96, 117.45, 125.72 (C$_5$H$_3$SiMe$_3$), 141.59, 159.68 (≡CPh), 126.24, 127.56, 127.74, 128.06, 128.20, 128.35, 128.94, 131.82, 139.20, 140.08 (≡$C$$Ph$). Anal. Calcd for C$_{32}H_{40}$ClNbSi$_3$: C, 60.31; H, 6.33. Found: C, 60.68; H, 6.45.

X-ray Structure Determination for [Me$_2$Si(η^5-C$_5$H$_4$)$_2$]-Nb(=NBu^t)Cl (1). A crystal of **1** was sealed in a Lindemann capillary under dry nitrogen and used for data collection. Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with graphite-monochromated Mo Kα radiation ($λ$ = 0.710 73 Å) using an $ω/2θ$ scan technique to a maximum value of 56°. The final unit cell was determined from 25 well-centered high-angle reflections that were widely scattered in reciprocal space. Data were corrected for Lorentz and polarization effects, and absorption correction was carried

Table 3.   Crystal Data and Structure Refinement for 1

empirical formula	$C_{16}H_{23}ClNNbSi$
fw	385.80
temp	293(2) K
wavelength	0.710 70 Å
cryst syst, space group	monoclinic, $P2_1/m$
unit cell dimens	$a = 6.942(2)$ Å, $\alpha = 90°$
	$b = 10.5000(10)$ Å,
	$\beta = 98.33(2)°$
	$c = 12.370(2)$ Å, $\gamma = 90°$
volume	892.1(3) Å^3
Z, calcd density	4, 1.436 g/cm^3
abs coeff	8.82 cm^{-1}
transmission range	0.721−1.000
$F(000)$	396
cryst size	$0.5 \times 0.4 \times 0.4$ mm
θ range for data collection	2.56−27.98°
index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 13$,
	$-16 \leq l \leq 16$
no. of reflns collected/unique	2265/2265 [R(int) = 0.0000]
completeness to 2θ	27.98, 99.8%
refinement method	full-matrix least-squares on F^2
no. of data/restraints/parameters	2265/0/103
goodness-of-fit on F^2	0.708
final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0252$, $wR_2 = 0.0712$
R indices (all data)	$R_1 = 0.0309$, $wR_2 = 0.0844$
largest diff peak and hole	0.526 and -0.459 e Å^{-3}

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

out on the basis of a ψ scan.[19] Analysis of systematic absences in the data was consistent with monoclinic space group $P2_1$ and $P2_1/m$, and the choice of the latter alternative was vindicated by the success of the subsequent solution and refinement. The asymmetric unit comprises one independent half-molecule of **1**. The structure was solved by the direct methods,[20] and refinement was carried out by full-matrix least-squares (SHELXL-97).[21] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculation positions but nonrefined. Weights were optimized in the final cycles. Atomic scattering factors were taken from ref 22. Crystallographic data are given in Table 3. Other detailed data are supplied in the Supporting Information.

Supporting Information Available: Tables of complete crystal data (Table SI), non-hydrogen atom coordinates (Table SII), complete bond distances and angles (Table SIII), anisotropic displacement parameters (Table SIV), hydrogen atom coordinates (Table SV), weighted least-squares planes (Table SVI), intermolecular contacts less than 3.50 Å (Table SVII), possible hydrogen bonds (Table SVIII), and ORTEP and crystal packing drawings (29 pages). Ordering information is given on any current masthead page. A list of structure factors is available on request from the authors.

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