Chapter 1

Preparation of *ansa*-Niobocene Olefin Hydride Complexes as Transition State Analogues in Metallocene-Catalyzed Olefin Polymerization

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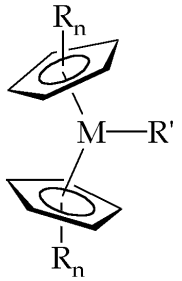
Abstract

To examine the effects of cyclopentadienyl and olefin substitution on preferred stereochemistry, a series of singly [$SiMe_2$]-bridged *ansa*-niobocene olefin hydride complexes has been prepared via reduction and alkylation of the corresponding dichloride complexes. In this manner, [$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)$]$Nb(CH_2{=}CHR')H$ (R = $CHMe_2$, CMe_3; R' = H, C_6H_5), and *rac*- and *meso*-[$Me_2Si(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)$]$Nb(CH_2{=}CH_2)H$ (R = CMe_3) have been prepared and characterized by NMR spectroscopy and in some cases, X-ray diffraction. These compounds serve as stable transition state analogues for the much more kinetically labile group 4 metallocenium cationic intermediates in metallocene-catalyzed olefin polymerization. Characterization of the thermodynamically preferred isomers of niobocene olefin hydride complexes reveals that placement of a single alkyl substituent on the cyclopentadienyl ligand array may have a moderate effect on the stereochemistry of olefin coordination.

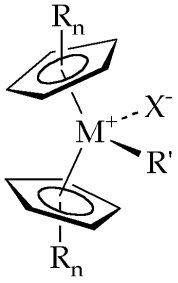
Introduction

Stereospecific olefin polymerization promoted by group 3 and 4 *ansa*-metallocene catalysts represents one of the most enantioselective chemical transformations known.[1] Elucidation of the steric and electronic factors that control this remarkable selectivity may aid in the design of new catalysts and also result in the development of new asymmetric transformations. Considerable effort has been devoted toward understanding the nature of the transition state for the C–C bond forming step with metallocene polymerization catalysts. The electronic requirements for an active catalyst are fairly well accepted: a metallocene alkyl with two vacant orbitals (Chart 1), where one orbital is used to accommodate the incoming olefin while the other allows for α-agostic assistance[2] in the transition state for carbon-carbon bond formation.[3]

Chart 1



M = Sc, Y, lanthanide
R' = hydride or alkyl

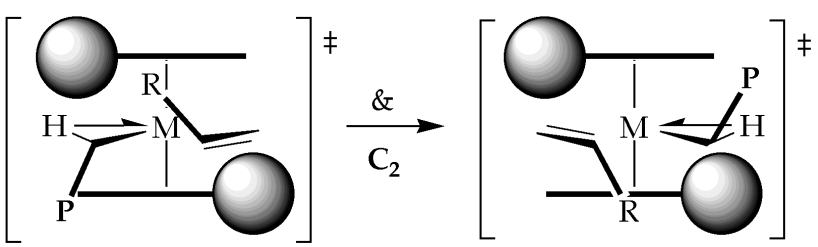


M = Ti, Zr, Hf
R' = hydride or alkyl
X^- = weakly coordinating anion

Understanding the key steric interactions in the olefin insertion transition state has also been the focus of many experimental and theoretical investigations. Calculations by Corradini[4] demonstrate that the enantiofacial approach of the olefin is determined by the orientation of the metal alkyl unit, such that the olefin

substituent is placed in a trans relationship with the β-carbon of the metal polymeryl unit. The polymeryl is believed to orient toward the most open portion of the metallocene framework (Scheme 1; schematic view of C_2-symmetric metallocene looking into the wedge). The first experimental evidence in support of this model was provided by Pino.[5] Hydrooligomerization

Scheme 1

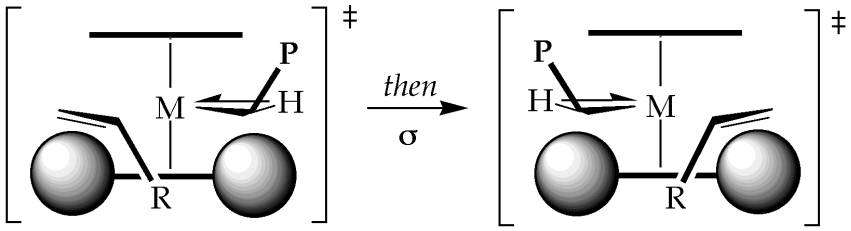


of α-olefins with optically pure [ethylenebis(4,5,6,7-tetrahydroindenyl)]-zirconium dichloride (EBTHIZrCl_2) produced chiral hydrotrimers and hydrotetramers with the predicted absolute configurations.[6] In contrast to polymerizations/oligomerizations, deuteriations of α-olefins such as styrene and pentene produced lower ee's with the opposite enantiofacial selectivity.[7] Similarly, work from our laboratories defined the diastereoselective transition structures for 1-pentene addition to yttrium–hydride and yttrium–pentyl bonds.[8] An optically pure, isotopically chiral 1-pentene was prepared and used to evaluate the stereoselectivity with an optically pure yttrocene. The absolute diastereoselectivities were established: insertion into yttrium–hydride bond proceeds with modest selectivity (34% ee); insertion into yttrium–pentyl bond proceeds via the other diastereomeric transition state with very high levels (> 95% ee) of selectivity. Analogous transition state arguments have been proposed

for the titanocene-catalyzed asymmetric hydrogenation of olefins reported by Buchwald and co-workers.[9]

The stereochemical model developed in the C_2-symmetric isospecific systems has since been extended to include C_s-symmetric syndiospecific catalysts.[10] The favored transition state geometry for syndiospecific catalysts is shown in Scheme 2 (schematic view of a C_s-symmetric metallocene looking into the wedge), where again the dominant stereo-directing interaction is a trans relationship between propylene methyl and the C_α–C_β bond of the polymer chain. Whether on the left or right side of the metallocene wedge, the growing polymer chain extends up and away from the more sterically demanding cyclopentadienyl moiety, thus forcing the propylene methyl group down. In syndiospecific catalysts, this lower cyclopentadienyl ligand contains an open region to accommodate the methyl substituent on the incoming monomer. Essential to the stereospecificity is a regular alternation of propylene approach from one side of the metallocene wedge and then the other.[11]

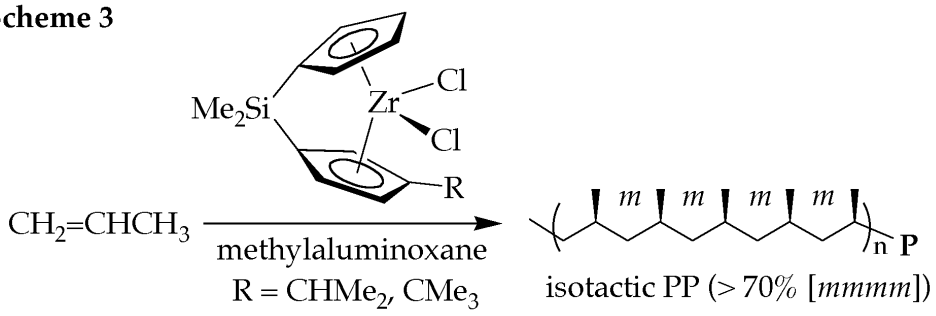
Scheme 2



Although these stereochemical models have been quite successful in explaining the high levels of stereocontrol observed with C_2- and C_s-symmetric catalysts, the stereospecificity of some metallocene catalysts cannot be readily rationalized. For example, the C_1-symmetric, monosubstituted, singly

silylene-bridged zirconocene [$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)$]$ZrCl_2$/MAO (R = CMe_3, $CHMe_2$), originally reported by Miya,[12a] polymerizes propylene with [*mmmm*] contents exceeding 70% (Scheme 3). Obviously, the stereocontrol mechanisms of Schemes 1 and 2 do not apply, and thus one cannot readily explain such high isospecificity.

Scheme 3

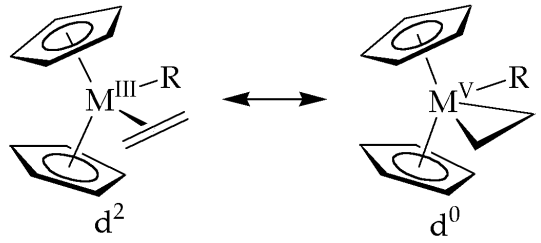


A possible approach to understanding the stereochemistry of olefin insertion would be to model the carbon-hydrogen or carbon-carbon bond-forming transition states of a group 4 metallocene catalyst using the *ground-state analogue*, a (stable) group 5 (M = Nb, Ta) metallocene olefin hydride or olefin alkyl complex. These complexes have been used to investigate the steric and electronic effects for olefin insertion into metal–hydride bonds with *bis*(cyclopentadienyl) and related *ansa*-niobocene and -tantalocene olefin hydride complexes.[13] The niobocene and tantalocene complexes are formally M(III), d^2 metal centers (Scheme 4) that stabilize the olefin–metal bond through a strong π-back-bonding interaction.

Conventional NMR and X-ray diffraction experiments may be used to determine the structure of the metallocenes and thus to establish the direction and magnitude of steric effects (shown for one of the enantiomers of

{[$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R^1)$]M} in Chart 2). There are three stereoisomeric relationships between the olefin hydride complexes: (1) the preference for the

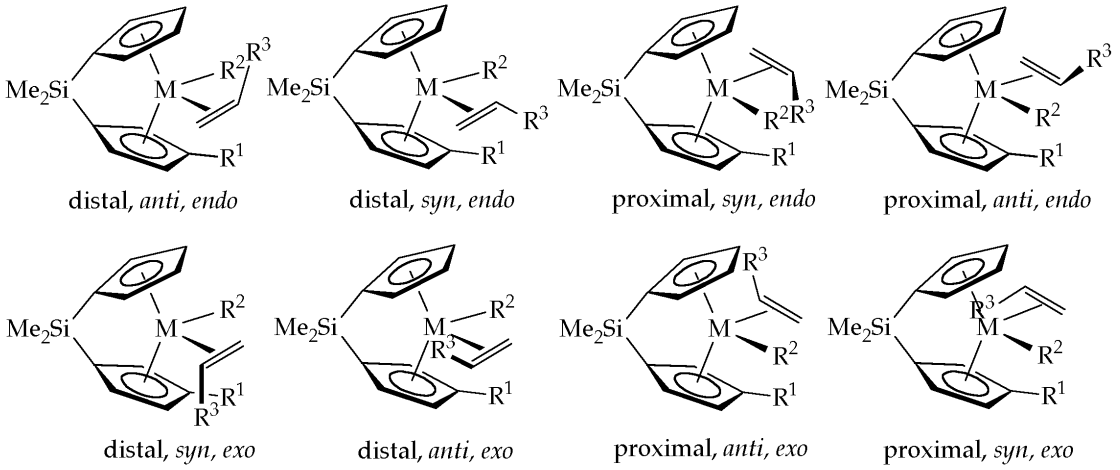
Scheme 4



(M = Nb, Ta; R = H, alkyl)

olefin to be on the side of the metallocene wedge distal or proximal to the cyclopentadienyl substituent R^1, (2) the preference for olefin coordination with its substituent R^3 syn or anti to the substituted cyclopentadienyl ring and (3) the preference for the olefin substituent R^3 to position itself endo or exo relative to the metallocene hydride or metallocene alkyl fragment R^2.

Chart 2



(M = Nb, Ta; R^1, R^3 = alkyl; R^2 = H, alkyl)

Reports of group 5 *ansa*-metallocenes are limited and generally restricted to C_{2v}-symmetric metallocene frameworks,[14,15ab,16,17,18] except for one report of

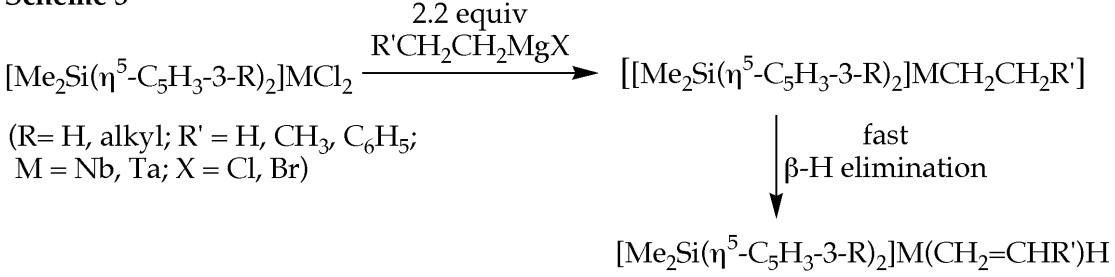
C_1-symmetric *ansa*-niobocene imido complexes.[17c] In this report we describe the synthesis and characterization of a series of low-symmetry, singly [$SiMe_2$]-bridged niobocene olefin hydride complexes. The preferred structures of these complexes have been examined regarding the important stereodirecting interactions between the coordinated olefin and the cyclopentadienyl ligand substituents. These olefin hydride complexes are potential precursors for the preparation of olefin alkyl complexes. Using these structures as transition state analogues, we hope to gain some insight into the basis of stereoselectivity for propylene polymerizations with group 4 metallocene catalysts.

Results and Discussion

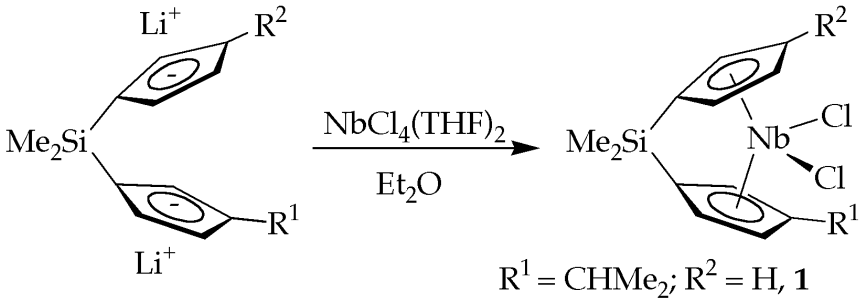
Preparation of Singly [$SiMe_2$]-Bridged Olefin Hydride Complexes.

The synthetic strategy for the preparation of group 5 *ansa*-metallocene olefin hydride complexes is based upon the methodology developed for unlinked metallocene complexes. Essential to the synthesis is a convenient route to the corresponding group 5 metallocene dichloride complex, which in turn may be simultaneously reduced and alkylated via addition of an excess of the appropriate Grignard reagent (Scheme 5).

Scheme 5



Preparation of *ansa*-niobocene dichloride complexes is accomplished by extension of previously reported synthetic protocols. Metalation of singly [$SiMe_2$]-bridged cyclopentadienyl ligands proceeds via addition of the dilithio salt of the ligand to a slurry of $NbCl_4(THF)_2$ in diethyl ether.[17a] In this manner, [$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}CHMe_2)$]$NbCl_2$ (iPrSpNbCl$_2$, **1**); [$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}CMe_3)$]$NbCl_2$ (tBuSpNbCl$_2$, **2**) and [$Me_2Si(\eta^5\text{-}C_5H_3\text{-}3\text{-}CMe_3)_2$]$NbCl_2$ (DpNbCl$_2$, **3**) have been prepared (eq 1). Each

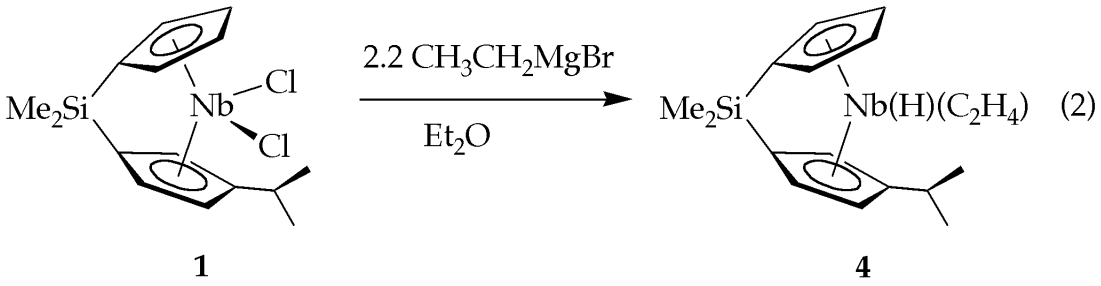


(1)

$R^1 = CHMe_2$; $R^2 = H$, **1**
$R^1 = CMe_3$; $R^2 = H$, **2**
$R^1 = R^2 = CMe_3$, **3** (*meso* and *racemic* isomers)

dichloride complex is first extracted into CH_2Cl_2 to remove LiCl. This purification is satisfactory for **1**, but further purification is necessary for **2** and **3**. Complex **2** is isolated after sublimation at 160 ˚C. Complex **3** is obtained as a mixture of racemic and meso isomers (vide infra), and this mixture is isolated after a second extraction into petroleum ether. Characterization of the paramagnetic Nb(IV) dichloride complexes has been accomplished by ambient-temperature EPR spectroscopy and by elemental analysis. The EPR spectra for **1** - **3** display 10-line patterns indicative of a single electron localized on a Nb(IV) center (^{93}Nb = 100%, S = 9/2).

Addition of 2.2 equiv of CH_3CH_2MgBr to **1** in diethyl ether results in formation of the ethylene hydride complex, iPrSpNb(η^2-CH_2CH_2)H (**4**) (eq 2).



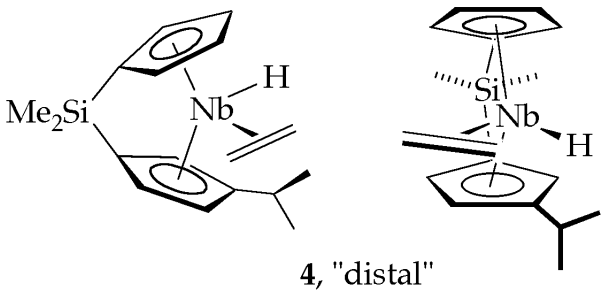
(2)

1 **4**

^{1}H NMR spectroscopy reveals that, of the two possible ethylene hydride isomers, one isomer is formed preferentially in a 95:5 ratio. A diagnostic upfield metal hydride resonance is observed at -2.60 ppm for **4**. The ^{1}H NMR spectrum for **4** at 25 ˚C contains broad resonances for the niobium hydride and for the coordinated ethylene, indicative of rapid and reversible olefin insertion and β-hydrogen elimination.[13]

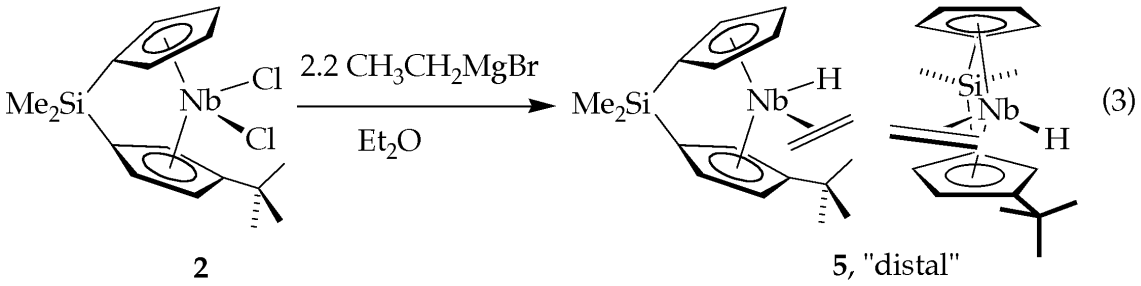
Structural assignment of the predominant ethylene hydride isomer for **4** has been accomplished with NOE difference NMR spectroscopy.[19] Irradiation of the metal hydride affords a strong NOE enhancement in the isopropyl methine, isopropyl methyl groups, and the *endo*-ethylene protons. Likewise, irradiation of the isopropyl methine results in enhancement in the metal hydride resonance. No enhancement in any ethylene peaks is observed. These data, taken together with more subtle cyclopentadienyl and [$SiMe_2$] NOE enhancements, allow the assignment of the major isomer. The ethylene is coordinated in the more open portion of the metallocene wedge, away from the isopropyl substituent (i.e., the distal isomer). The formation of predominantly

one ethylene hydride isomer (95%) demonstrates the moderate stereodirecting ability of a monosubstituted *ansa*-metallocene.



4, "distal"

Addition of CH_3CH_2MgBr to **2** affords the *ansa*-niobocene ethylene hydride complex tBuSpNb(η^2-CH_2CH_2)H (**5**) in modest yield (eq 3). Only one isomer is observed by ^1H NMR spectroscopy. Slow cooling of a petroleum ether



2 **5**, "distal" (3)

solution of **5** affords yellow crystals suitable for X-ray diffraction. The solid-state structure of **5** is shown in Figure 1 and reveals that the ethylene ligand is coordinated in the open portion of the metallocene wedge away from the *tert*-butyl substituent. The niobium hydride was located in a difference map, and the Nb–H bond length was refined to 1.68(2) Å. The C(17)-C(18) bond distance of 1.411(2) Å is consistent with other group 5 olefin adducts, indicative of substantial metallocyclopropane character.[20]

Reaction of complex **3** with CH_3CH_2MgBr results in a mixture of two isomers in a 50:50 ratio. The number of cyclopentadienyl resonances in the ^1H

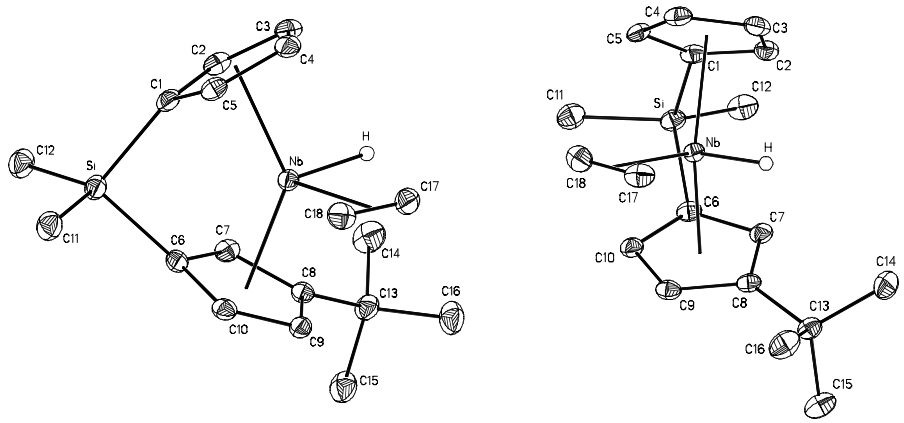
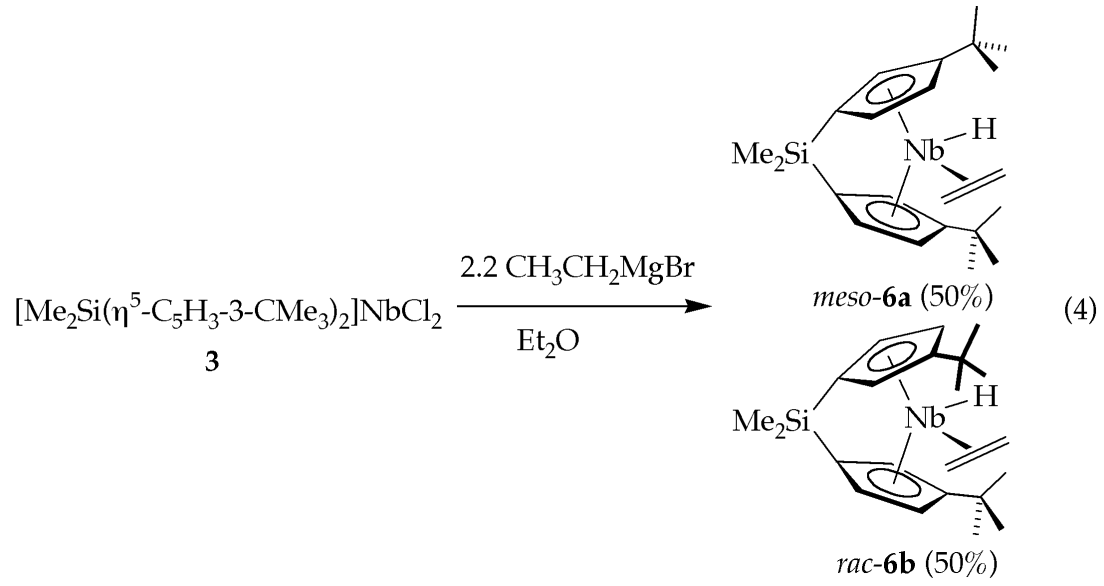


Figure 1. Molecular structure of **5** with 50% probability ellipsoids. Hydrogen atoms (other than hydride shown at arbitrary scale) have been omitted.

NMR indicate that one isomer is of C_s-symmetry, *meso*-DpNb(η^2-CH_2CH_2)H (**6a**); the other isomer, *rac*-DpNb(η^2-CH_2CH_2)H (**6b**), is C_1-symmetric. The isomers **6a** and **6b** can be separated by fractional recrystallization from cold petroleum ether. NOE difference experiments for the *meso* isomer **6a** indicate that the ethylene is coordinated away from the *tert*-butyl substituents (eq 4).

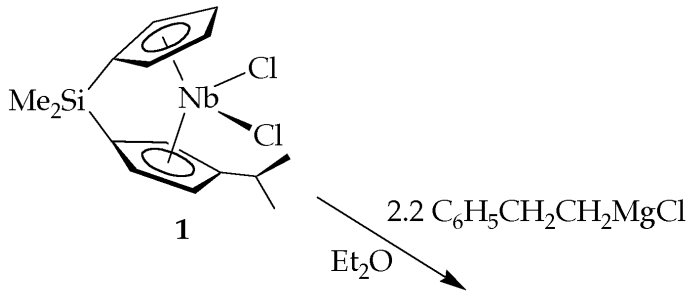
Preparation of *ansa*-niobocene complexes with α-olefins is accomplished via addition of the appropriate Grignard reagent to the dichloride complexes. Addition of 2.2 equiv of $C_6H_5CH_2CH_2MgCl$ to an ethereal solution of **1** affords the styrene hydride complex iPrSpNb(η^2-$CH_2CHC_6H_5$)H (**7**, eq 5). Three isomers are formed in a 53:38:9 ratio for **7** (major:minor:trace isomers).

Analysis of the product mixture by NOE difference ^1H NMR spectroscopy allows assignment of the major and minor styrene hydride complexes.



(4)

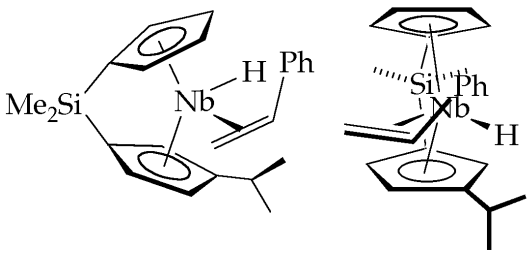
Irradiation of the metal hydride resonance results in strong NOE enhancements in the isopropyl substituent, one olefinic styrene resonance, and the ortho hydrogens of the phenyl ring. Likewise, irradiation of the isopropyl substituent results in no enhancement of the styrene protons. These data indicate that for the major isomer, the styrene is coordinated anti to the isopropyl substituents and in



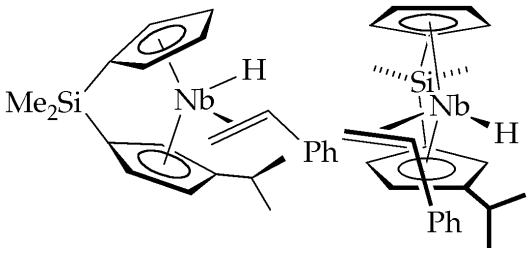
[Me2Si(η5-C5H4)(η5-C5H3-3-CHMe2)]Nb(CH2=CHC6H5)H, **7** (5)

an endo fashion, where the phenyl ring is directed toward the interior of the metallocene wedge. Presumably unfavorable steric interactions between the phenyl ring and the [Me_2Si] linker discourage formation of exo isomers that were

observed with unlinked niobocene and tantalocene styrene hydride complexes.[15ab]



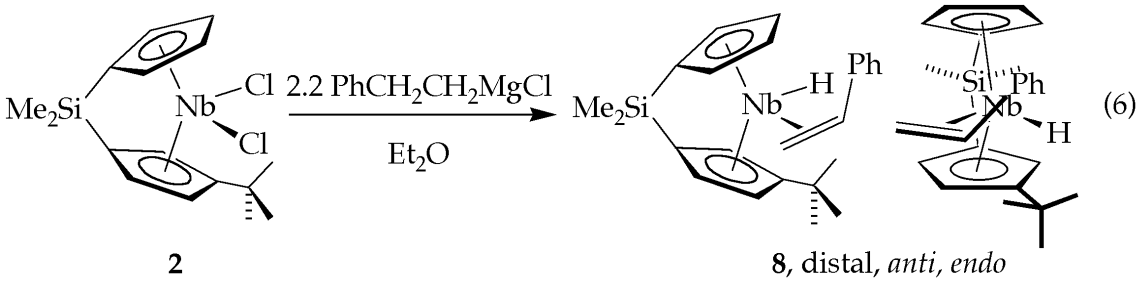
7a: distal, *anti*, *endo* (53%)



7b: distal, *syn*, *endo* (38%)

Differentiation between the enantiofacial preference of styrene hydride isomers has been obtained from more subtle NOE enhancements between the cyclopentadienyl, dimethylsilylene, and styrene hydrogens. For **7** the major styrene hydride isomer is the one for which the phenyl ring is directed away from the isopropyl substituent, whereas in the minor isomer, the phenyl ring is directed toward the isopropyl group, with the diastereoselectivity for olefin coordination for **7** being approximately 15%. A small enantiofacial differentiation was also noted for insertion of 1-pentene into the Y–H bond of a C_2-symmetric yttrocene catalyst and for α-olefin deuteriations.[9,10] Although the enantiofacial preference for olefin coordination is poor, the site selectivity is quite good, where for **7** approximately 90% of the styrene coordination occurs with phenyl away from the isopropyl substituent, i.e., "distally."[21]

Alkylation of **2** with $C_6H_5CH_2CH_2MgCl$ in diethyl ether affords two isomers of tBuSpNb(η^2-CH_2CHPh)H, **8**, in a 90:10 ratio (eq 6). Slow cooling of a petroleum ether solution of **8** provides yellow crystals (major isomer, **8a**) suitable for X-ray diffraction analysis, as shown in Figure 2. The solid-state structure reveals that the preferred isomer has the styrene coordinated in an endo fashion



2 **8**, distal, *anti, endo*

in the open portion of the metallocene wedge with the phenyl group directed anti to the *tert*-butyl substituent. The Nb–H was located in a difference map; the distance was refined to 1.70(2) Å. The phenyl ring exhibits a modest 3.2° twist with respect to the olefinic plane. The C(17)-C(18) bond distance of 1.418(3) Å is similar to that of the complexes described herein and elsewhere.[22] Thus, a *tert*-

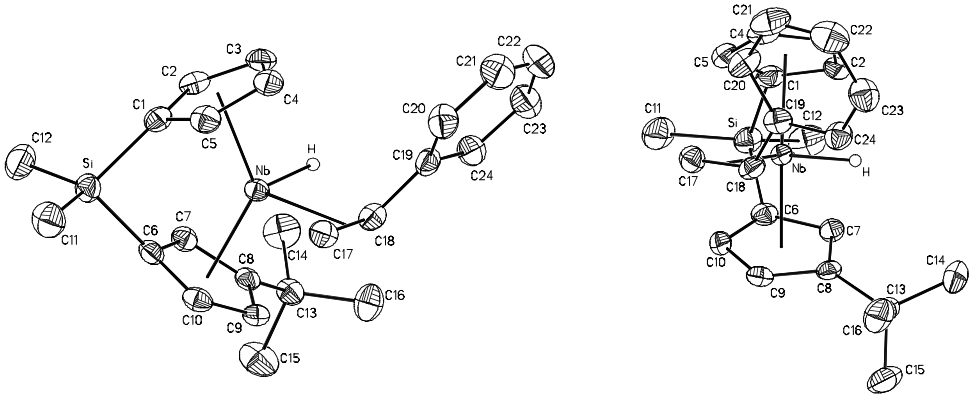


Figure 2. Molecular structure of **8a** with 50% probability ellipsoids. Hydrogen atoms (other than hydride shown at arbitrary scale) have been omitted.

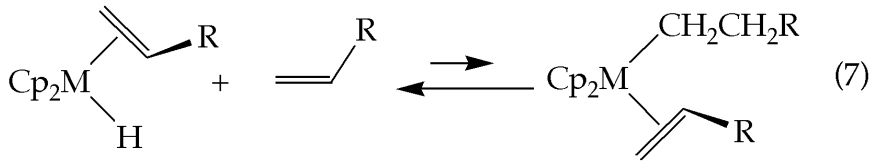
butyl substituent more strongly enforces the enantiofacial preference for olefin coordination than an isopropyl substituent. It is interesting to note that lower isospecificity was observed for propylene polymerizations with iPrSpZrCl$_2$/MAO as compared with tBuSpZrCl$_2$/MAO (ca. 75% vs 85% [*mmmm*], respectively).[12b]

Conclusions

A series of singly [$SiMe_2$]-bridged *ansa*-niobocene olefin hydride complexes have been prepared via reduction and alkylation of the corresponding niobocene dichloride complexes. Their geometries have been determined in solution by NOE difference NMR spectroscopy, and in several cases the solid-state structures have been established by X-ray diffraction. Monosubstitution of the cyclopentadienyl framework with an isopropyl or *tert*-butyl group ([$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)$]Nb(olefin)H; R = $CHMe_2$, CMe_3) directs ethylene coordination such that the olefin is distal from R, ca. 20:1 for isopropyl and >50:1 for *tert*-butyl. The methyl groups of the [$SiMe_2$] linker force α-olefins such as propylene and styrene to coordinate with the olefin substituent directed toward the hydride ligand (endo), unlike the "parent" [$(\eta^5\text{-}C_5H_5)_2M$] olefin hydride complexes, for which approximately equal amounts of endo and exo isomers are obtained for the propylene and styrene hydrides. As for the ethylene hydride complexes, distal coordination of α-olefins is preferred; however, neither isopropyl nor *tert*-butyl substitution of one cyclopentadienyl ligand enforces a strong enantiofacial preference for olefin coordination for the niobium olefin hydrides.

Thus, the placement of a single isopropyl or *tert*-butyl substituent on a cyclopentadienyl ligand of [$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)$]Nb(olefin)H has a modest effect in directing the olefin coordination geometry. It would, of course, be of interest to establish the stereodirecting effects of these substituents on the conformations of the M–R' group for the corresponding

[$Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}R)$]M(olefin)R' complexes, particularly for those metal alkyls that mimic the polymeryl groups during propylene polymerization, e.g., [M-$CH_2CH(CH_3)CH_2CHMe_2$], since it has been established that the



(7)

interactions of the olefin substituents with the polymeryl group are greater than with the ligand substituents (vide supra). Unfortunately, all attempts to induce olefin insertion and olefin coordinative trapping of the resultant alkyls using these *ansa*-olefin hydrides were unsuccessful. Presumably, the equilibrium needed to provide such olefin alkyls (eq 7) lies too far to the left, even for α-olefins.

Experimental

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere as described previously.[23] Argon, dinitrogen, and dihydrogen gases were purified by passage over columns of MnO on vermiculite and activated molecular sieves. Toluene and petroleum ether were distilled from sodium and stored under vacuum over titanocene.[24] Tetrahydrofuran, dimethoxyethane, and ether were distilled from sodium benzophenone ketyl. $NbCl_4(THF)_2$, 3.0 M CH_3CH_2MgBr in diethyl ether, and 1.0

M $PhCH_2CH_2MgCl$ in THF were purchased from Aldrich and used as received. All dilithio salts of ligands were prepared according to standard procedures.[25]

NMR spectra were recorded on a JEOL GX-400 (^1H, 399.78 MHz, ^{13}C, 100.53 MHz) or a Varian Inova 500 (^1H, 500.13 MHz, ^{13}C, 125.77 MHz). All chemical shifts are relative to TMS for ^1H (residual) and ^{13}C (solvent as a secondary standard). Nuclear Overhauser difference experiments were carried out on a Varian Inova 500 MHz spectrometer. Elemental analyses were carried out at the Caltech Analytical Facility by Fenton Harvey or by Midwest Microlab, Indianapolis, IN.

$[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}CHMe_2)]NbCl_2$ (1). In the dry box, 6.23 g (16.4 mmol) $NbCl_4(THF)_2$ and 4.00 g (16.4 mmol) of $Li_2[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}CHMe_2)]$ were combined in a 300 mL round-bottom flask. On the vacuum line, 175 mL Et_2O was added by vacuum transfer. The reaction was stirred overnight. The Et_2O was removed in vacuo leaving a light brown powder. The product was isolated by dissolving the crude mixture in 100 mL of CH_2Cl_2 followed by filtration of the LiCl. The CH_2Cl_2 was removed in vacuo, leaving 5.63 g (87.2%) of a dark brown solid identified as **1**. Anal. Calcd for $Nb_1Si_1C_{15}H_{20}Cl_2$ C, 46.05%, H, 4.90%; Found C, 46.04%; H, 4.97%. EPR (CH_2Cl_2): $g_{iso} = 2.01$; $a_{iso} = 99.0$ G.

$[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}CMe_3)]NbCl_2$ (2). This compound was prepared in a manner analogous to that for **1**, employing 1.00 g (3.91 mmol) of $Li_2[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}CMe_3)]$ and 1.48 g of $NbCl_4(THF)_2$ (3.91 mmol),

to afford 1.20 g (75.9%) of a dark brown solid identified as **2**. The isolated solid was sublimed, leaving 0.276 g (17.5%) of product. Anal. Calcd for $Nb_1Si_1C_{16}H_{22}Cl_2$ C, 47.30%, H, 5.35%; Found C, 46.88%; H, 5.46%. EPR (CH_2Cl_2): g_{iso} = 2.00; a_{iso} = 103.8 G.

[$Me_2Si(\eta^5$-C_5H_3-3-$CMe_3)_2$]$NbCl_2$ (3). This compound was prepared in a manner analogous to that for **1**, employing 3.00 g (9.60 mmol) of $Li_2[Me_2Si(\eta^5$-C_5H_3-3-$CMe_3)_2]$ and 3.64 g of $NbCl_4(THF)_2$ (9.60 mmol), to afford a dark brown solid identified as **3**. The isolated solid was further purified by extraction into petroleum ether. The solvent was removed leaving 1.26 g (28.4%) of product. Anal. Calcd. for $Nb_1Si_1C_{20}H_{30}Cl_2$: C, 52.00; H, 6.54. Found C, 52.42; H, 6.79. EPR (CH_2Cl_2): g_{iso} = 2.00; a_{iso} = 103.8 G.

[$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-C_5H_2-3-$CHMe_2)$]$Nb(\eta^2$-$CH_2CH_2)H$ (4ab). In the drybox, a fine swivel frit assembly was charged with 1.50 g (3.824 mmol) **1**. On the vacuum line, approximately 25 mL of dimethoxyethane was added by vacuum transfer. At -80 ˚C, against an Ar counterflow, 3.00 mL (9.0 mmol) of a 3.0 M CH_3CH_2MgBr solution in Et_2O was added by syringe. The reaction mixture was stirred and slowly warmed to room temperature. After 2 h, a yellow solution and an off-white precipitate form. The reaction mixture was stirred for 16 h after which time the solvent was removed and replaced with 10 mL of petroleum ether. The product was extracted several times with petroleum ether followed by slow cooling to -78 ˚C to afford 0.205 g (15.3%) of an oily yellow solid identified as **4**.

Major isomer (**4a**) (95%) ^{1}H NMR -30 ˚C (toluene-d_8): δ = -2.60 (s, 1H, Nb-*H*); 0.16 (s, 3H, SiMe_2); 0.08 (s, 3H, SiMe_2); 0.85 (m, 2H, CH_2=CH_2, exo); 1.22 (d, 7 Hz, 3H, CHMe_2); 1.26 (d, 7 Hz, 3H, CHMe_2); 1.37 (m, 1H, CH_2=CH_2, endo); 1.48 (m, 1H, CH_2=CH_2, endo); 2.81 (sept, 7 Hz, 1H, C*H*Me_2); 3.18, 3.19, 4.24, 4.28, 5.24, 5.26, 5.80 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ = -6.79 (SiMe_2); -4.19 (SiMe_2); 11.25 (*C*H_2=CH_2, endo); 20.54 (CH_2=CH_2, exo); 23.93 (CHMe_2); 24.52 (CHMe_2); 28.96 (*C*HMe_2); 70.56, 71.97, 82.94, 84.66, 91.71, 93.00, 103.30, 104.65, 106.23, 136.86 (Cp).

Minor isomer (**4b**) (5%) ^{1}H NMR -30 ˚C (toluene-d_8): δ = -2.69 (s, 1H, Nb-*H*); 0.13 (s, 3H, SiMe_2); *not located* (s, 3H, SiMe_2); 0.96 (m, 2H, CH_2=CH_2, exo); 1.57 (m, 2H, CH_2=CH_2, endo); *2 not located* (CHMe_2); 2.67 (m, 1H, C*H*Me_2); 3.43, 5.03 (2H), 5.53, 5.76, *2 not located* (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ = -6.53 (SiMe_2); -4.49 (SiMe_2); 12.88 (*C*H_2=CH_2, endo); 18.27 (CH_2=CH_2, exo); 21.58 (CHMe_2); 25.77 (CHMe_2); 31.72 (*C*HMe_2); 85.01, 85.22, 93.29, 100.13, 102.26, 105.70, *4 not located* (Cp).

[Me_2Si(η^5-C_5H_4)(η^5-C_5H_3-3-CMe_3)]Nb(η^2-CH_2CH_2)H (5). This compound was prepared in a manner similar to that for **4** employing 0.180 g (0.444 mmol) of **2**, 326 μL (0.98 mmol) of a 3.0 M CH_3CH_2MgBr solution in Et_2O, and Et_2O as the solvent. Extraction with petroleum ether followed by slow cooling to -40 ˚C afforded 0.044 g (27%) of a yellow crystalline solid identified as **5**. ^{1}H NMR (benzene-d_6): δ = -2.56 (s, 1H, Nb-*H*); 0.10 (s, 3H, SiMe_2); 0.19 (s, 3H, SiMe_2); 0.91

(m, 2H, CH_2=CH_2, exo); 1.33 (s, 9H, CMe_3); 1.42 (m, 2H, CH_2=CH_2, endo); 3.16, 3.19, 4.19, 4.25, 5.27 (2H), 5.86 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ = -6.94 (SiMe_2); -4.04 (SiMe_2); 11.17 (CH_2=CH_2, endo); 21.51 (CH_2=CH_2, exo); 31.85 (CMe_3); 32.00 (CMe_3); 70.18, 71.62, 81.22, 83.97, 92.09, 93.60, 102.55, 103.58, 105.46, 142.81 (Cp).

[$Me_2Si(\eta^5$-C_5H_3-3-$CMe_3)_2$]Nb(η^2-CH_2CH_2)H (6ab). This compound was prepared in a manner similar to that for **4** employing 0.286 g (0.619 mmol) of **3**, 0.480 mL (1.4 mmol) of a 3.0 M CH_3CH_2MgBr solution in Et_2O, and Et_2O as the solvent. Extraction with petroleum ether followed by slow cooling to -40 ˚C afforded a yellow crystalline solid identified as the *meso* isomer **6a**. Subsequent fractional recrystallization allows separation of *rac* and *meso* isomers (0.030 g *meso* isomer **6a** isolated; 12% of total yield). The *rac* isomer (**6b**) is isolated as an orange oil.

meso Isomer (**6a**) (50%) ^{1}H NMR (500 MHz, toluene-d_8): δ = -2.70 (s, 1H, Nb-*H*); 0.15 (s, 3H, SiMe_2); 0.21 (s, 3H, SiMe_2); 0.87 (m, 2H, CH_2=CH_2, exo); 1.28 (s, 18H, CMe_3); 1.37 (m, 2H, CH_2=CH_2, endo); 3.16, 4.28, 5.26 (m, 2H, Cp). ^{13}C NMR (300 MHz, toluene-d_8): δ = -6.91 (SiMe_2); -3.73 (SiMe_2); 12.57 (CH_2=CH_2, endo); 22.60 (CH_2=CH_2, exo); 26.16 (CMe_3); 32.14 (CMe_3); 69.64, 81.19, 92.99, 102.13, 143.10 (Cp).

rac Isomer (**6b**) (50%) ^{1}H NMR (300 MHz, toluene-d_8): δ = -2.39 (s, 1H, Nb-*H*); 0.18 (s, 3H, SiMe_2); 0.25 (s, 3H, SiMe_2); *not located* (CH_2=CH_2, exo); 0.89 (s, 9H,

C*Me*$_3$); *not located* (C*H*$_2$=CH$_2$, endo); 1.29 (s, 9H, C*Me*$_3$); 3.15, 4.24, 4.27, 5.25, 5.34, 5.89 (m, 1H, Cp). ^{13}C NMR (500 MHz, toluene-*d*$_8$): δ = -6.84 (Si*Me*$_2$); -3.33 (Si*Me*$_2$); 11.10 (*C*H$_2$=CH$_2$, endo); 17.85 (CH$_2$=*C*H$_2$, exo); 30.60, 32.07 (C*Me*$_3$); *not located* (*C*Me$_3$); 69.97, 72.42, 81.38, 85.96, 91.70, 95.65, 102.06, 102.43, 130.65, 142.87 (Cp).

[Me$_2$Si(η^5-C$_5$H$_4$)(η^5-C$_5$H$_3$-3-CHMe$_2$)]Nb(η^2-CH$_2$CHPh)H (7abc). This compound was prepared in a manner similar to that for **4** employing 2.00 g (5.09 mmol) of **1**, 12 mL (12 mmol) of a 1.0 M PhCH$_2$CH$_2$MgCl solution in THF, and Et$_2$O as the solvent. Extraction with petroleum ether followed by removal of the solvent in vacuo afforded 0.325 g (15.0%) of an oily yellow solid identified as **7**.

Major isomer (**7a**) (53%) ^{1}H NMR (benzene-*d*$_6$): δ = -1.96 (s, 1H, Nb-*H*); -0.04 (s, 3H, Si*Me*$_2$); 0.08 (s, 3H, Si*Me*$_2$); 1.07 (dd, 10 Hz, 5 Hz, 1H, C*H*$_2$=CHPh, *trans*); 1.21 (d, 7 Hz, 3H, CH*Me*$_2$); 1.32 (d, 7 Hz, 3H, CH*Me*$_2$); 1.46 (dd, 13 Hz, 5 Hz, 1H, C*H*$_2$=CHPh, *cis*); 2.80 (sept, 7 Hz, 1H, C*H*Me$_2$); 3.50 (m, 1H, CH$_2$=C*H*Ph); 3.58, 3.60, 4.35, 4.38, 4.96, 5.14, 5.49 (m, 1H, Cp). ^{13}C NMR (benzene-*d*$_6$): δ = -6.04 (Si*Me*$_2$); -3.94 (Si*Me*$_2$); 19.96 (*C*H$_2$=CHPh); 24.77 (CH*Me*$_2$); 25.15 (CH*Me*$_2$); 29.67 (*C*HMe$_2$); 39.43 (CH$_2$=*C*HPh); 73.63, 75.06, 85.55, 88.63, 94.21, 96.06, 105.15, 108.73, 113.36, 136.53 (Cp); 122.49 (C$_6$H$_5$, *para*); *not located* (C$_6$H$_5$, *ortho*); 128.20 (C$_6$H$_5$, *meta*); 153.23 (C$_6$H$_5$, *ipso*).

Minor isomer (**7b**) (38%) ^{1}H NMR (benzene-d_6): δ = -2.15 (s, 1H, Nb-*H*); -0.02 (s, 3H, Si*Me*$_2$); 0.09 (s, 3H, Si*Me*$_2$); 0.74 (d, 7 Hz, 3H, CH*Me*$_2$); 1.12 (dd, 10 Hz, 5 Hz, 1H, C*H*$_2$=CHPh, *trans*); 1.23 (d, 7 Hz, 3H, CH*Me*$_2$); 1.36 (dd, 13 Hz, 5 Hz, 1H, C*H*$_2$=CHPh, cis); 1.52 (sept, 7 Hz, 1H, CH*Me*$_2$); 3.50 (m, 1H, CH$_2$=C*H*Ph); 3.42, 3.45, 4.27, 4.30, 5.19, 5.55, 5.95 (m, 1H, Cp). 13C NMR (benzene-d_6): δ = -6.24 (Si*Me*$_2$); -3.67 (Si*Me*$_2$); 20.63 (*C*H$_2$=CHPh); 22.53 (CH*Me*$_2$); 26.43 (CH*Me*$_2$); 26.79 (*C*HMe$_2$); 37.93 (CH$_2$=*C*HPh); 73.83, 75.04, 82.96, 86.81, 95.31, 96.15, 104.16, 110.15, 113.34, 138.34 (Cp); 122.15 (C$_6$H$_5$, *para*); 127.45 (C$_6$H$_5$, *ortho*); not located (C$_6$H$_5$, *meta*); 152.95 (C$_6$H$_5$, *ipso*).

Trace isomer (7c) (9%) 1H NMR (benzene-d6): δ = -2.09 (s, 1H, Nb-*H*); -0.05 (s, 3H, Si*Me*$_2$); 0.06 (s, 3H, Si*Me*$_2$); 0.38 (dd, 10 Hz, 5 Hz, 1H, C*H*$_2$=CHPh, *trans*); 0.94 (d, 7 Hz, 3H, CH*Me*$_2$); *not located* (CH*Me*$_2$); *not located* (C*H*$_2$=CHPh, *cis*); *not located* (*C*HMe$_2$); *not located* (CH$_2$=*C*HPh); 4.15, 4.46, 4.67, 4.76, 4.92, 5.21, 5.32 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ = -5.40 (Si*Me*$_2$); -4.71 (Si*Me*$_2$); 18.77 (*C*H$_2$=CHPh); 23.32 (*C*HMe$_2$); 24.36 (CH*Me*$_2$); 27.03 (CH*Me*$_2$); 39.21 (CH$_2$=*C*HPh); 89.41, 90.51, 92.66, 95.20, 100.53, 105.09, 112.02, 137.66 (Cp); 122.34 (C$_6$H$_5$, *para*); *not located* (C$_6$H$_5$, *ortho*); *not located* (C$_6$H$_5$, *meta*); 154.24 (C$_6$H$_5$, *ipso*).

[Me$_2$Si(η^5-C$_5$H$_4$)(η^5-C$_5$H$_3$-3-CMe$_3$)]Nb(η^2-CH$_2$CHPh)H (8ab). This compound was prepared in a manner similar to that for **4** employing 0.205 g (0.506 mmol) **2**, 1.11 mL (1.1 mmol) of a 1.0 M PhCH$_2$CH$_2$MgCl solution in THF, and Et$_2$O as the solvent. Extraction with petroleum ether followed by cooling to -40 ˚C afforded

0.054 g (24%) of a crystalline yellow solid identified as **8**.

Major isomer (**8a**) (90%) ^{1}H NMR (toluene-d_8): δ = -2.07 (s, 1H, Nb-*H*); -0.01 (s, 3H, SiMe_2); 0.12 (s, 3H, SiMe_2); 0.99 (dd, 10 Hz, 5 Hz, 1H, CH_2=CHPh, *trans*); 1.34 (s, 9H, CMe_3); 1.42 (dd, 13 Hz, 5 Hz, 1H, CH_2=CHPh, *cis*); 3.53 (dd, 13 Hz, 10 Hz, 1H, CH_2=C*H*Ph); 3.25, 3.44, 4.13, 4.18, 5.16, 5.25, 5.49 (m, 1H, Cp). ^{13}C NMR (toluene-d_8): δ = -6.94 (SiMe_2); -4.13 (SiMe_2); 20.96 (*C*H_2=CHPh); 32.13 (*C*Me_3); 32.21 (CMe_3); 37.81 (CH_2=*C*HPh); 73.00, 73.94, 82.70, 86.73, 96.48, 94.62, 104.20, 104.62, 111.90, 143.06 (Cp); 121.97 (C_6H_5, *para*); 127.28 (C_6H_5, *ortho*); 127.53 (C_6H_5, *meta*); 153.23 (C_6H_5, *ipso*).

Minor isomer (**8b**) (10%) ^{1}H NMR (toluene-d_8): δ = -1.98 (s, 1H, Nb-*H*); 0.05 (s, 3H, SiMe_2); 0.15 (s, 3H, SiMe_2); 0.83 (s, 9H, CMe_3); *not located* (1H, CH_2=CHPh, *trans*); *not located* (1H, CH_2=CHPh, *cis*); 3.18 (dd, 13 Hz, 10 Hz, 1H, CH_2=C*H*Ph); 3.07, 3.41, 4.00, 4.07, 5.09, 5.55, 6.13 (m, 1H, Cp). ^{13}C NMR (toluene-d_8): δ = -7.09 (SiMe_2); -3.51 (SiMe_2); *not located* (*C*H_2=CHPh); *not located* (*C*Me_3); 32.83 (CMe_3); 35.29 (CH_2=*C*HPh); 83.45, 85.24, 96.00, 100.23, 103.88, 106.11, 107.25, 121.59; *2 not located* (Cp); *not located* (C_6H_5, *ortho*); *not located* (C_6H_5, *meta*); *not located* (C_6H_5, *para*); *not located* (C_6H_5, *ipso*).

Crystallography: Crystal data, intensity collection, and refinement details are presented in Table 1 for compounds **5** and **8a**.

Data Collection and Processing: Data for compounds **5** and **8a** were collected on a Bruker SMART 1000 area detector running SMART.[26] The diffractometer was equipped with a Crystal Logic CL24 low temperature device and all datasets were collected at low temperature. The diffractometer used graphite-monochromated MoKα radiation with λ = 0.71073 Å.

The crystals were mounted on glass fibers with Paratone-N oil. Data were collected as ω–scans at three to six values (depending on the sample) of φ. For all crystals, the detector was 5 cm (nominal) distant at a θ angle of -28 °. The data were processed with SAINT.[31]

Table 1. X-ray Experimental Data.

Compound	**5**	**8a**
formula	$C_{18}H_{27}NbSi$	$C_{24}H_{31}NbSi$
formula weight	364.40	440.49
crystal system	monoclinic	Triclinic
space group	P $2_1/c$ (# 14)	P $\bar{1}$ (# 2)
a, Å	9.2022(6)	10.3001(11)
b, Å	21.1677(14)	10.5568(11)
c, Å	9.2632(6)	11.2207(12)
α, °	90	74.243(2)
β, °	108.940(1)	84.333(2)
γ, °	90	66.971(2)
volume, Å^3	1706.68(19)	1080.6(2)
Z	4	2

P_{calc}, g/cm^3	1.418	1.354
μ, mm^{-1}	0.76	0.62
F_{000}	760	460
crystal shape	lozenge	Lozenge
crystal color	yellow	Yellow
crystal size, mm	0.10 x 0.26 x 0.26	0.14 x 0.20 x 0.31
T, K	98	98
type of diffractometer	SMART 1000 ccd	SMART 1000 ccd
θ range, $^\circ$	1.9, 28.5	1.9, 28.5
h,k,l limits	-12, 12; -28, 28; -12, 12	-13, 13; -13, 14; -14, 14
data measured	25466	22478
unique data	4105	5072
data, $F_O>4\sigma(F_O)$	3597	4407
parameters / restraints	289/0	359/0
R1[a],wR2[b]; all data	0.028, 0.048	0.037, 0.051
R1[a],wR2[b]; $F_O>4\sigma(F_O)$	0.023, 0.048	0.031, 0.050
GOF[c] on F^2	1.84	1.53
$\Delta\rho$max,min, e·Å^{-3}	0.51, -0.37	0.60, -0.43

All data were collected with graphite monochromated MoKα radiation (λ=0.71073 Å).

[a] $R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma |F_o|$

[b] $wR2 = \{ \Sigma[w(F_o^2-F_c^2)^2] \, / \, \Sigma[w(F_o^2)^2] \}^{1/2}$

[c] $GOF = S = \{ \Sigma[w(F_o^2-F_c^2)^2] \, / \, (n-p) \}^{1/2}$

Structure Analysis and Refinement: SHELXTL v5.1[31] was used to solve, via direct methods or by the Patterson method, and to refine all structures using full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. For **5**, there is one molecule in the asymmetric unit. All hydrogen atoms, including the hydride, were refined isotropically. For **8a**, there is one molecule in the asymmetric unit. All hydrogen atoms, including the hydride, were refined isotropically.[27]

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