Organometallics **2001,** *20,* 71−78

Niobium and Zirconium Complexes Incorporating Asymmetrically Substituted *ansa* Ligands. X-ray Crystal Structures of $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]Nb({=}N^tBu)Cl$ (R = Me, ^{i}Pr) and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H, Me)

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Received August 2, 2000

The asymmetric *ansa*-ligand precursors $(C_5Me_4H)SiMe_2(C_5H_4R)$ (R = H (**1**), Me (**2**), $SiMe_3$ (**3**), ^{i}Pr (**4**)) and their lithium derivatives $[Me_2Si(C_5Me_4)(C_5H_3R)]Li_2$ (R = H (**5**), Me (**6**), $SiMe_3$ (**7**), ^{i}Pr (**8**)) have been prepared. The *ansa*-niobocene imido complexes $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]Nb({=}N^tBu)Cl$ (R = H (**9**), Me (**10**), $SiMe_3$ (**11**), ^{i}Pr (**12**)) were synthesized by the reaction of $Nb({=}N^tBu)Cl_3(py)_2$ with $[Me_2Si(C_5Me_4)(C_5H_3R)]Li_2$ in THF. The *ansa*-zirconocene complexes $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H (**13**), Me (**14**), $SiMe_3$ (**15**), ^{i}Pr (**16**)) were prepared by the reaction of $ZrCl_4$ and the corresponding lithiated *ansa*-derivative. The molecular structures of **10**, **12**, **13**, and **14** were determined by single-crystal X-ray diffraction studies. Preliminary results for the catalytic activity of **13**−**16** in the polymerization of ethylene are reported.

Introduction

The use of *ansa*-cyclopentadienyl ligands has received wide attention in the chemistry of group 4 metals,[1] due mainly to their ability to impart to their complexes a selective degree of catalytic activity.[2] Recent studies have demonstrated that the incorporation of an *ansa* bridge may have a profound influence on the chemistry of the metallocene system.[3]

The initially reportd *ansa* compounds of group 5 metals normally exhibited a σ-bond between the *ansa* ligand and the metal.[4] We recently reported the first *ansa*-niobocene complexes, in which both cyclopentadienyl rings are bound only in an η^5 mode to niobium, $[Me_2Si(C_5H_4)_2]NbCl_2$, $[Me_2Si(C_5H_4)_2]NbCl(RC{\equiv}CR)$ (R = Me, Ph),[5] and since then several complexes of this type have been described, $[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}NR)Cl$ (R = ^{t}Bu, $SiMe_3$),[6] $[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb(\mu\text{-}H_2)BH_2$,[7] $[Me_2C(\eta^5\text{-}C_5H_4)_2]NbH(PMe_3)$,[7] $[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}N\text{-}C_6H_4iPr_2\text{-}2,6)Cl$,[8] and $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Nb({=}N^tBu)Cl$.[9]

Furthermore, the use of substituted *ansa*-cyclopentadienyl ligands in the stereoselective synthesis of group 4 metal complexes and their importance in catalysis is receiving special attention,[10] but there are only a few examples for group 5, $[2,2'(1,1'\text{-biphenyldiyl})(C_5H_2Me_2\text{-}3,4)]VCl_2$,[10] $[Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2]Nb({=}N^tBu)Cl$,[9] $[Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2]NbCl_2$,[9] $[Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2]NbCl(RC{\equiv}CR)$ (R = Me, Ph),[9] $[Me_4C_2(\eta^5\text{-}C_5H_3{}^tBu)_2]Nb(\mu\text{-}H_2)BH_2$,[11] and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]TaH_3$.[3b]

However, the incorporation of *ansa* ligands containing asymmetrically substituted cyclopentadienyl rings in group 5 metallocene complexes has not previously been reported. Some examples of asymmetric *ansa*-zirconocene complexes have been described,[12] and the great majority contain indenyl or fluorenyl systems.[13]

It has been shown that steric effects in the transition metal catalyst greatly affect the polymerization of

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10.1021/om0006662 CCC: $20.00

olefins and that bulky ligands, such as substituted *ansa* ligands, would therefore aid stereospecific olefin coordination and the stereoregularity of the polymers obtained using these metallocene catalysts.[14] In addition, the chiral nature of these ligands would also strongly influence stereoselectivity.[15]

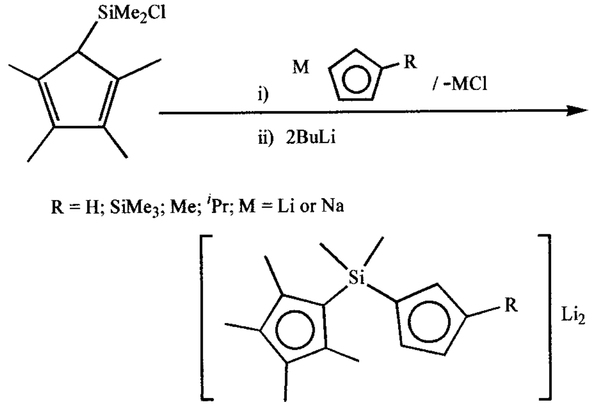
The importance of catalysts based on group 5 precursors is now growing due in part to the less air-sensitive nature of their complexes in comparison with their group 4 analogues.[15]

We report here the synthesis and characterization of novel chiral *ansa*-niobocene and -zirconocene complexes, which incorporate *ansa* ligands with asymmetrically substituted cyclopentadienyl rings. The polymerization of ethylene using the *ansa*-zirconocene complexes as catalysts is described.

Results and Discussion

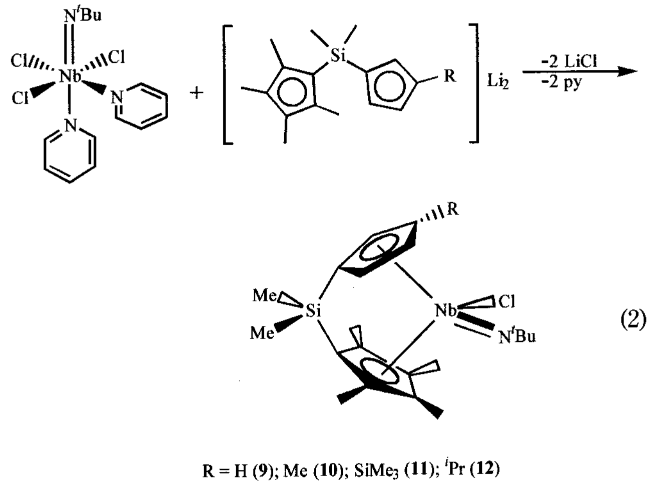
The preparation of the asymmetrically substituted *ansa* ligand precursors $(C_5Me_4H)SiMe_2(C_5H_4R)$ (R = H (**1**), Me (**2**), $SiMe_3$ (**3**), ^{i}Pr (**4**)) was achieved by the reaction of $Me_2Si(C_5Me_4H)Cl$ and the alkali metal derivative of the desired cyclopentadiene (see eq 1). The resulting products' ligands were then lithiated in the normal manner with *n*-butyllithium. The method employed is similar to that previously reported for $(C_5Me_4H)SiMe_2(C_5H_5)$.[16]

The possibility of various isomers was confirmed by ^{1}H NMR spectroscopy. For **1**−**4** one isomer was shown to be predominant (see Experimental Section). In addition **1**−**4** were characterized by electron impact mass spectroscopy.



(1)

The reaction of the dilithium derivatives of the *ansa* ligands $[Me_2Si(C_5Me_4)(C_5H_3R)]Li_2$ (R = H (**5**), Me (**6**), $SiMe_3$ (**7**), ^{i}Pr (**8**)) with $Nb({=}N^tBu)Cl_3(py)_2$[17] gave the *ansa*-niobocene imido complexes $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]Nb({=}N^tBu)Cl$ (R = H (**9**), Me (**10**), $SiMe_3$ (**11**), ^{i}Pr (**12**)) in high yield (see eq 2).



(2)

Complexes **9**−**12** were characterized spectroscopically. The ^{1}H NMR spectrum of **9** shows the lack of symmetry in this chiral complex, with the four methyl groups attached to the cyclopentadienyl ring being inequivalent, as are the methyl groups of the $SiMe_2$ bridge and the four protons of the unsubstituted cyclopentadienyl moiety (see Experimental Section).

In the case of complexes **10**−**12** the monosubstitution of one of the cyclopentadienyl rings of the *ansa* ligands gives rise to the possibility of two different isomers (I and II) (Figure 1) depending on the configuration of the cyclopentadienyl rings in which the substituent R can be orientated toward or away from the imido group. The niobium atom is chiral and thus in both cases I and II should exist as pairs of enantiomers Ia and IIa (Figure 1).

The ^{1}H spectra of **10**−**12** are similar to that observed in **9** and in addition show the existence of only one of these isomers. It is assumed that this isomer is I, i.e., that the substituent R is pointing away from the bulky imido group. The isomer II is probably heavily disfavored due to steric effects, although the influence of electronic effects cannot be ruled out. This phenomenon has previously been observed in the complex $[Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2]Nb({=}N^tBu)Cl$, which was stereoselectively synthesized as the *meso* isomer.[9]

The molecular structures of **10** and **12** were established by X-ray crystal studies. The molecular structures

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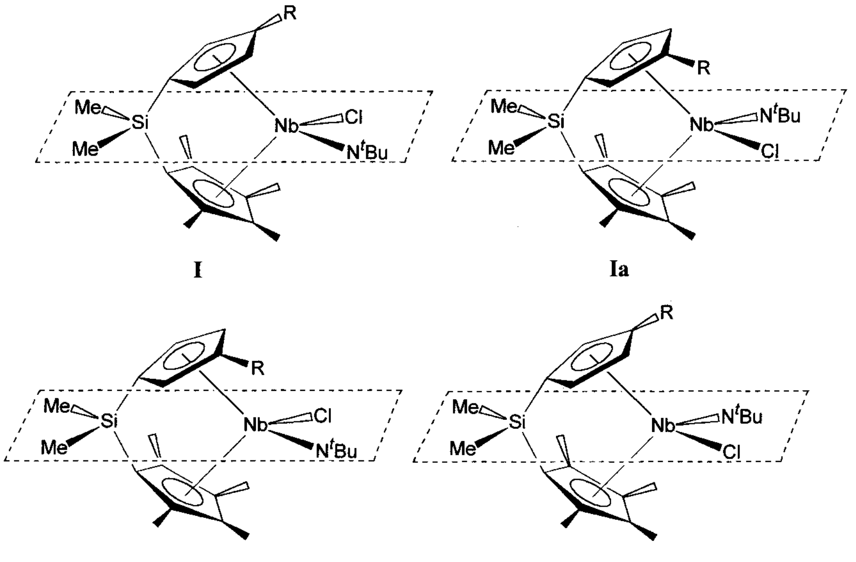


I **Ia**

II **IIa**

Figure 1. Possible isomers for complexes $[\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3R})]\mathrm{Nb}(=\mathrm{N}^t\mathrm{Bu})\mathrm{Cl}$.

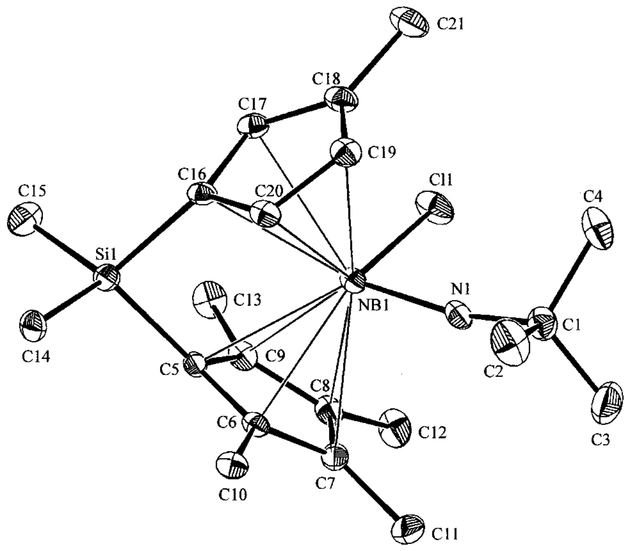


Figure 2. Molecular structure and atom-labeling scheme for (S)-$[\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3Me})]\mathrm{Nb}(=\mathrm{N}^t\mathrm{Bu})\mathrm{Cl}$ (**10**), with thermal ellipsoids at 20% probability.

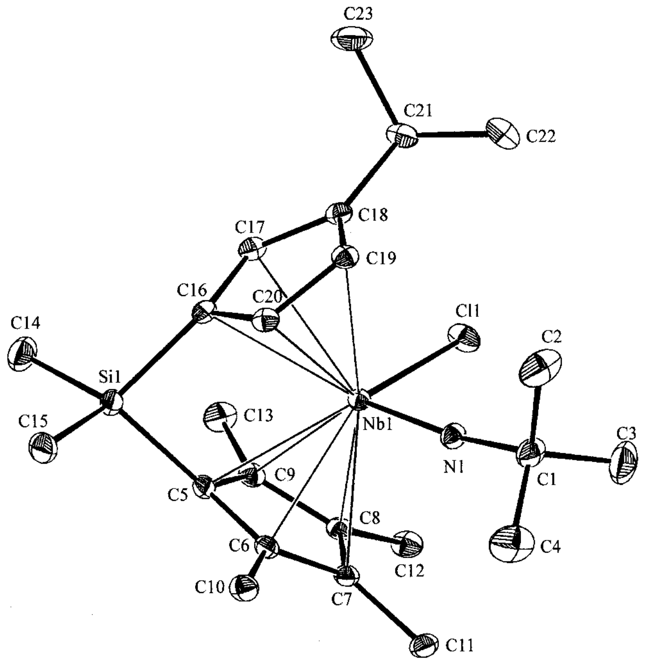


Figure 3. Molecular structure and atom-labeling scheme for $[\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3}i\mathrm{Pr})]\mathrm{Nb}(=\mathrm{N}^t\mathrm{Bu})\mathrm{Cl}$ (**12**), with thermal ellipsoids at 20% probability.

and atomic numbering scheme are shown in Figures 2 and 3, respectively. Selected bond lengths and angles for **10** and **12** are given in Table 1.

The structure of **10** consists of discrete molecules separated by van der Waals distances. Complex **10** is chiral about the niobium atom. There are two molecules per asymmetric unit corresponding to the two enantiomers. The structure of **12** is similar in all aspects to that of **10** except that the two enantiomers are related by the symmetry operation. The niobium atoms in both structures show a geometry that is typical for pseudotetrahedral niobocene(V) imido derivatives. The $\mathrm{Me_2Si(C_5Me_4)(C_5H_3R)}$ *ansa* ligand chelates the niobium center, and both cyclopentadienyl rings are bound to the metal in an η^5 mode adopting the typical bent metallocene conformation. The environment of the niobium atom is completed by a chlorine atom, and the imido group is bonded through the nitrogen atom to the niobium. The structure also reveals that the alkyl group in the monosubstituted $\mathrm{C_5}$ ring is oriented away from the imido group. This adds validity to the assumption that in **11** the monosubstituted ring has its substituent pointing away from the imido group. The cent−Nb−cent angles (122.7° and 122.3° **10**; 122.1° **12**) are similar to those reported for other *ansa*-niobocene complexes containing the $\mathrm{SiMe_2}$-bridged *ansa* ligand (see Table 2).

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 would be linear. In **10** and **12** the angle $\mathrm{Nb{-}N{-}C}_{ipso}$ of 168.0(4)° and 167.5(4)° (**10**) and 172.3(2)° (**12**) deviates from linearity. Deviation from linearity of the $\mathrm{Nb{-}N{-}C}_{ipso}$ angles has been reported for some niobocene imido complexes and is normally in

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 10 and 12[a]

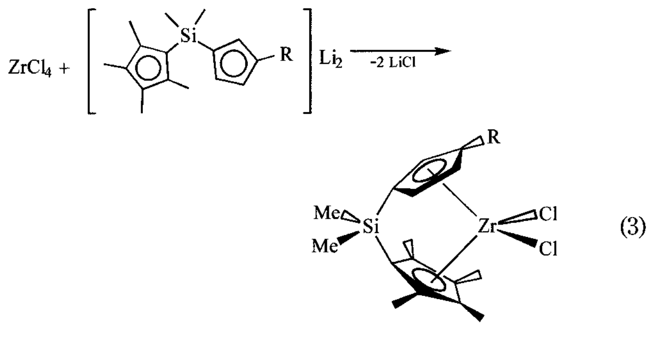
	10 (*S*)	**10** (*R*)	**12**
Nb(1)−Cent(1)	2.249	2.250	2.245
Nb(1)−Cent(2)	2.225	2.227	2.228
av Nb(1)−C(5−9)	2.558	2.556	2.550
av Nb(1)−C(16−20)	2.534	2.531	2.531
Nb(1)−Cl(1)	2.458(1)	2.460(1)	2.4372(6)
Nb(1)−N(1)	1.790(5)	1.782(5)	1.772(2)
N(1)−C(1)	1.457(8)	1.463(8)	1.455(3)
Cent(1)−Nb(1)−Cent(2)	122.7	122.3	122.1
Nb(1)−N(1)−C(1)	168.0(4)	167.5(4)	172.3(2)
Si(1)−C(5)−Cent(1)	161.4	160.3	161.8
Si(1)−C(16)−Cent(2)	162.3	161.8	163.2
C(5)−Si(1)−C(16)	93.7(2)	94.4(2)	93.3(1)
Cl(1)−Nb(1)−Cent(1)	103.3	103.6	103.7
Cl(1)−Nb(1)−Cent(2)	103.7	103.4	103.9
N(1)−Nb(1)−Cent(1)	114.3	114.9	113.4
N(1)−Nb(1)−Cent(2)	111.2	111.5	112.8
Cl(1)−Nb(1)−N(1)	97.0(1)	96.2(1)	96.33(7)

[a] Cent(1) and Cent(2) are the centroids of C(5)−C(9) and C(16)−C(20), respectively.

the range of 12−15° (see Table 2). These complexes in general contain aryl-imido and/or sterically demanding ligands. In the case of $(\eta^5\text{-}C_5H_4SiMe_3)_2Nb({=}NPh)Cl$ extended-Hückel molecular-orbital calculations established that the imido bond angles for a "linear imide" in this class of complexes can vary up to 140° with little effect on the Nb−N bonding.[19] Therefore we propose that in **10** and **12** the nitrogen atom is sp hybridized and that the two limiting descriptions proposed by Bercaw and co-workers for $(\eta^5\text{-}C_5Me_5)_2Ta({=}NPh)(H)$ may explain the true bonding situation.[21]

The Nb−N bond distances of 1.790(5) and 1.782(5) Å (**10**) and 1.772(2) Å (**12**) are in agreement with a triple bond between the niobium and nitrogen atoms, comparable with those thus far observed for complexes of this type (see Table 2). The formal electron count of **10** and **12** is 20 electrons with the excess 2 electrons probably being located in a nonbonding orbital similar to that proposed by Green et al. for $(\eta^5\text{-}C_5H_5)_2Mo({=}N^tBu)$.[22] Similar 20-electron niobocene imido complexes $(\eta^5\text{-}C_5H_4SiMe_3)_2Nb({=}NR)Cl$ have shown a lengthening of the Nb−centroid distances in comparison with their 18- and 17-electron analogues,[20] and for **10** and **12** this observation may also prove to be true.

The *ansa*-zirconocene complexes $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H (**13**),[23] Me (**14**), SiMe$_3$ (**15**), ^{i}Pr (**16**)) were prepared by the reaction of ZrCl$_4$ with $[Me_2Si(C_5Me_4)(C_5H_3R)]Li_2$ (R = H (**5**), Me (**6**), SiMe$_3$ (**7**), ^{i}Pr (**8**)), respectively (see eq 3).



(3)

R = H (**13**); Me (**14**); SiMe$_3$ (**15**); ^{i}Pr (**16**)

13−**16** were characterized by NMR spectroscopy. The ^{1}H spectrum for **13** showed the expected signals for the C_s symmetrical complex. Thus for the cyclopentadienyl ring protons H2 and H5, and H3 and H4, become equivalent and two multiplets corresponding to the AA′BB′ system are observed. Two singlets are observed corresponding to the methyl groups of the tetramethylcyclopentadienyl moiety. The methyl groups of the SiMe$_2$ bridging unit are equivalent and give a unique signal (see Experimental Section).

The symmetry of the molecule changes from C_s to C_1 when a substituent is introduced in the unsubstituted C$_5$ ring, as is the case of the chiral complexes **14**−**16**. The ^{1}H NMR spectra of **14**−**16** gives three multiplets for the protons of the monosubstituted C$_5$ ring, four singlets for the nonequivalent methyl groups of the tetramethyl-substituted C$_5$ ring, and two singlets corresponding to the now inequivalent methyl groups of the SiMe$_2$ bridging unit. Further signals were observed for the corresponding substituent.

The molecular structures of **13** and **14** were established by X-ray crystal studies. The molecular structures and atomic numbering scheme are shown in Figures 4 and 5, respectively. Selected bond lengths and angles for **13** and **14** are given in Table 3. For **14** the two enantiomers were located in the unit cell.

The structures of **13** and **14** show the typical bent metallocene conformation observed in zirconocene dichlorides. The *ansa* ligand chelates the zirconium atom, and both C$_5$ rings are bound to the metal in an η^5 mode. A comparison of **13** and **14** with related zirconocene and *ansa*-zirconocene complexes is given in Table 4 and shows that the molecular structures of all these complexes are essentially the same. The Cent−Zr−Cent angles of **13** and **14** are of values between those of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$ and less than that observed for the non-*ansa* complex $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]ZrCl_2$ (see Table 4).

Our initial studies of the polymerization of ethylene were carried out at under mild conditions (25 °C, 1.5 bar) in the presence of **13**/MAO, **14**/MAO, **15**/MAO, **16**/MAO, and Cp$_2$ZrCl$_2$/MAO in a ratio 1:125. The results of the experiments are given in Table 5. The *ansa* complexes **13**−**16** exhibit activities in the polymerization of ethylene approximately a third of the activity that was observed for the non-*ansa* complex Cp$_2$ZrCl$_2$ under the same conditions.

In conclusion, we describe in this paper the straightforward preparation of new asymmetric *ansa* ligands and their incorporation into niobium imido and zir-

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Table 2. Selected Structural Data for *ansa*-Niobocene and Niobocene Imido Complexes

	Cp-Nb−Cp, deg	Nb−N−C, deg	Nb−N, Å	ref
(*S*) $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]Nb({=}N^tBu)Cl$ (**10**)	122.7	168.0(4)	1.790(5)	this work
(*R*) $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]Nb({=}N^tBu)Cl$ (**10**)	122.3	167.5(4)	1.782(5)	this work
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\mathit{i}Pr)]Nb({=}N^tBu)Cl$ (**12**)	122.1	172.3(2)	1.772(2)	this work
$[Me_2Si(\eta^5\text{-}C_5H_4)_2]Nb({=}N^tBu)Cl$	121.21	178.8(2)	1.756(3)	9
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}NSiMe_3)Cl$	114.2	167.71(7)	1.777(1)	6
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}N^tBu)Cl$	113.3	178.4(3)	1.762(3)	6
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}N^tBu)Br$	113.4	178.3(2)	1.765(2)	6
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}N^tBu)I$	114.2	171.8(2)	1.770(2)	6
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}NAr)Cl^a$	114.4	167.5(1)	1.798(2)	8
$[Me_2C(\eta^5\text{-}C_5H_4)_2]Nb({=}NAr)(NMe_2)[B(C_6H_5)_4]^a$	114.0	166.8(1)	1.803(2)	8
$(\eta^5\text{-}C_5H_5)_2Nb({=}N^tBu)Cl^b$	122.7	173.6(4)	1.789(4)	18
	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)	19
$(\eta^5\text{-}C_5H_4SiMe_3)_2Nb({=}NC_6H_4OMe\text{-}4)Cl$	125.23	163.0(2)	1.787(3)	20

[a] Ar = $C_6H_3{}^iPr_2$-2,6. [b] Two independent molecules exist in the unit cell.

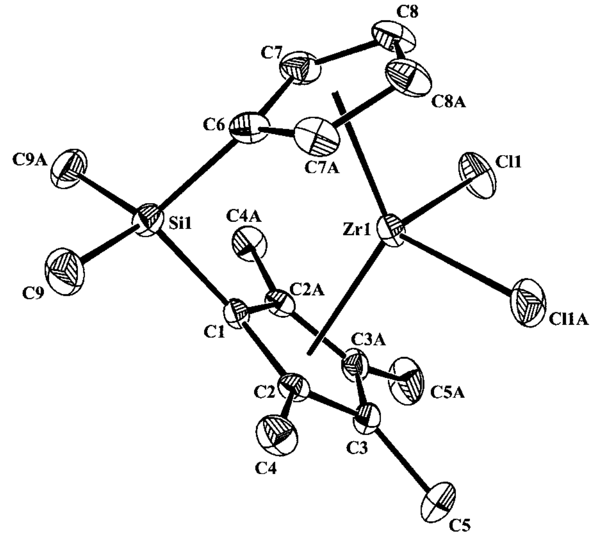

Figure 4. Molecular structure and atom-labeling scheme for $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**13**), with thermal ellipsoids at 20% probability.

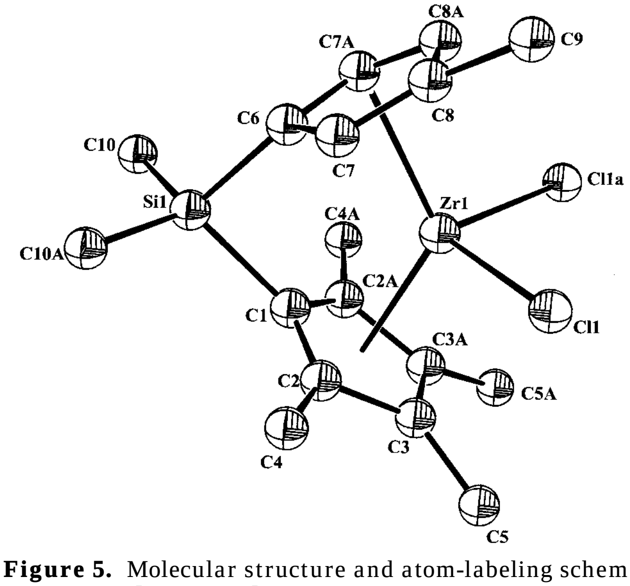

Figure 5. Molecular structure and atom-labeling scheme for $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$ (**14**), with thermal ellipsoids at 20% probability.

conocene systems. The structural characterization of these complexes is also described. The catalytic activity of the zirconocene complexes in the polymerization of ethylene has been tested.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 13 and 14[a]

	13	14
Zr(1)−Cent(1)	2.198	2.184
Zr(1)−Cent(2)	2.202	2.194
av Zr(1)−C(1−3)	2.509	2.49
av Zr(1)−C(6−8)	2.508	2.48
Zr(1)−Cl(1)	2.451(1)	2.414(4)
Cent(1)−Zr(1)−Cent(2)	128.10	126.25
Si(1)−C(1)−Cent(1)	165.22	167.64
Si(1)−C(6)−Cent(2)	161.4	161.53
C(1)−Si(1)−C(6)	95.2(2)	92.4(8)
Cl(1)−Zr(1)−Cent(1)	105.27	106.88
Cl(1)−Zr(1)−Cent(2)	105.76	106.50
Cl(1)−Zr(1)−Cl(1A)	104.60(7)	101.1(2)

[a] Cent(1) and Cent(2) are the centroids of C(1)−C(2A) and C(6)−C(7A), respectively. Symmetry transformations used to generate equivalent atoms A; *x*, −*y*+1/2, *z*.

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.

$Nb({=}N^tBu)Cl_3(py)_2$ was prepared as described earlier.[17] $ZrCl_4$ and $Me_2Si(C_5Me_4H)Cl$ were purchased from Aldrich and used directly. IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. ^1H 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. Mass spectroscopic analyses were performed on a VG Autospec instrument or a Hewlett-Packard 5988A (*m/z* 50−1000) (electron impact).

$(C_5Me_4H)SiMe_2(C_5H_5)$ (1). $ClMe_2Si(C_5Me_4H)$ (2.50 g, 11.64 mmol) in THF (50 mL) was added to a solution of $Li(C_5H_5)$ (0.84 g, 11.64 mmol) in THF (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo, and hexane (150 mL) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a dark orange oil (2.72 g, 95%). ^1H NMR (200 MHz, C_6D_6) (for the predominant isomer): $-\delta$ 0.22 (s, 6H, $Si\mathit{Me}_2$), 1.76 (6H), 1.86 (6H) (s, $C_5\mathit{Me}_4$), 2.80 (1H), 3.47 (1H) (m, $\mathit{H}C_5$), 6.50 (2H), 6.69 (2H) (m, $C_5\mathit{H}_4$). MS electron impact (*m/e* (relative intensity)): 244 (29) (M^+, $(C_5Me_4H)SiMe_2(C_5H_5)^+$), 179 (47) ($M^+$, $-C_5H_5$), 123 (100) (M^+, $-C_5Me_4H$).

$(C_5Me_4H)SiMe_2(C_5H_4Me)$ (2). The preparation of **2** was carried out in an identical manner to **1** using $ClMe_2Si(C_5Me_4H)$ (2.50 g, 11.64 mmol) and $Na(C_5H_4Me)$ (1.19 g, 11.64 mmol). Yield: 2.85 g, 95%. ^1H NMR (200 MHz, C_6D_6) (for the predominant isomer): δ 0.12 (s, 6H, $Si\mathit{Me}_2$), 1.75 (6H), 1.89 (6H) (s, $C_5\mathit{Me}_4$), 1.99 (s, 3H, $C_5H_3\mathit{Me}$), 3.30 (1H), 3.52 (1H) (m,

Table 4. Selected Structural Data of Some Zirconocene Complexes

complex	Zr−Cp[a]	Zr−Cl	Cp−Zr−Cp	Cl−Zr−Cl	$C_{(cp)}$−Si−$C_{(cp)}$	ref
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	2.21(1)	2.441(5)		97.1(2)		24
$(\eta^5\text{-}C_5H_4Me)_2ZrCl_2$	2.206(5)	2.443(1)	128.9(2)	95.10(5)		25
$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)ZrCl_2$	2.209 Cp 2.219 Cp*	2.442	130.01	97.78		26
$[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$	2.197(6)	2.452	125.4(3)	97.98(4)	93.2(2)	27
$[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ZrCl_2$	2.329	2.4334(7)	128.6	92.28	95.7(1)	28
$[EtMeSi(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$	2.219(2) Cp 2.218(2) Cp*	2.4336(8)	126.70(4)	101.17(5)	93.82(14)	12d
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**13**)	2.198(4) Cp* 2.202(3) Cp	2.451(1)	128.10(2)	104.60(7)	95.2(2)	this work
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$ (**14**)	2.184(6) Cp* 2.194(2) Cp	2.414(4)	126.25(6)	101.1(2)	93.1(8)	this work

[a] Cp refers to the C_5H_4 or C_5H_3Me moiety; Cp* refers to the C_5Me_4 moiety.

Table 5. Ethylene Polymerization Results for $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)]ZrCl_2$ (R = H (13), Me (14), $SiMe_3$ (15), ^iPr (16)) and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$[a]

catalyst	activity[b]	M_w (g mol^{-1})	M_w/M_η
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (**13**)	284	22 900	6.80
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]ZrCl_2$ (**14**)	260	26 700	7.01
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3SiMe_3)]ZrCl_2$ (**15**)	200	41 440	8.26
$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^iPr)]ZrCl_2$ (**16**)	257	15 540	4.59
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	669	64 330	11.39

[a] At 25 °C, 1.5 bar monomer pressure,150 mL of toluene, [MAO] = 5×10^{-3} mol L^{-1}, [Zr] = 4×10^{-5} mol L^{-1}, t_{Pol} = 60 min. [b] In kg Pol (mol Zr·h)$^{-1}$.

HC_5), 6.11 (1H), 6.48 (1H), 6.52 (1H) (m, C_5H_3). MS electron impact (*m*/*e* (relative intensity)): 258 (23) (M^+, $(C_5Me_4H)SiMe_2(C_5H_4Me)^+$), 179 (57) ($M^+$, $-C_5H_4Me$), 137 (100) (M^+, $-C_5Me_4H$).

$(C_5Me_4H)SiMe_2(C_5H_4SiMe_3)$ (3). The preparation of **3** was carried out in an identical manner to **1** using $ClMe_2Si(C_5Me_4H)$ (2.50 g, 11.64 mmol) and $Li(C_5H_4SiMe_3)$ (1.68 g, 11.64 mmol). Yield: 3.38 g, 92%. ^1H NMR (200 MHz, C_6D_6) (for the predominant isomer): δ −0.16, (s, 9H, $SiMe_3$), 0.22, (s, 6H, $SiMe_2$), 1.79 (6H), 1.92 (6H) (s, C_5Me_4), 3.05 (1H), 3.28 (1H) (m, HC_5), 6.44 (1H), 6.58 (1H), 6.62 (1H) (m, C_5H_3). MS electron impact (*m*/*e* (relative intensity)): 316 (68) (M^+, $(C_5Me_4H)SiMe_2(C_5H_4SiMe_3)^+$), 196 (80) ($M^+$, $-C_5Me_4H$), 179 (100) (M^+, $-C_5H_4SiMe_3$), 123 (65) (M^+, $-C_5Me_4H$ $-SiMe_3$).

$(C_5Me_4H)SiMe_2(C_5H_4{}^iPr)$ (4). The preparation of **4** was carried out in an identical manner to **1** using $ClMe_2Si(C_5Me_4H)$ (2.50 g, 11.64 mmol) and $Na(C_5H_4{}^iPr)$ (1.51 g, 11.64 mmol). Yield: 3.21 g, 96%. ^1H NMR (200 MHz, C_6D_6) (for the predominant isomer): δ −0.18 (s, 6H, $SiMe_2$), 1.12 (3H), 1.16 (3H) (d, $HCMe_2$) 1.78 (6H), 1.90 (6H) (s, C_5Me_4), 3.30 (m, 1H, $HCMe_2$), 2.75 (1H), 2.88 (1H) (m, HC_5), 6.01 (1H), 6.36 (1H), 6.54 (1H) (m, C_5H_3). MS electron impact (*m*/*e* (relative intensity)): 286 (38) (M^+, $(C_5Me_4H)SiMe_2(C_5H_4{}^iPr)^+$), 271 (28) ($M^+$, −Me), 179 (100) ($M^+$, $-C_5H_4{}^iPr$), 165 (71) (M^+, $-C_5Me_4H$).

$[Me_2Si(C_5Me_4)(C_5H_4)]Li_2$ (5). ^{n}BuLi (1.6 M in hexane) (13.9 mL, 22.26 mmol) was added via syringe to a solution of **1** (2.72 g, 11.13 mmol) in Et_2O at −78 °C. The mixture was allowed to warm to 25 °C and stirred for 15 h. Solvent was removed in vacuo to give a white solid, which was washed with hexane and dried under vacuum to yield a free-flowing white solid of the title complex (2.68 g, 94%). Anal. Calcd for $C_{16}H_{22}Li_2Si$: C, 74.98; H, 8.65. Found: C, 74.50; H, 8.52.

$[Me_2Si(C_5Me_4)(C_5H_3Me)]Li_2$ (6). The preparation of **6** was carried out in an identical manner to **5** using **2** (2.85 g, 11.03 mmol) and ^{n}BuLi (1.6 M in hexane) (13.8 mL, 22.06 mmol). Yield: 2.73 g, 92%. Anal. Calcd for $C_{17}H_{24}Li_2Si$: C, 75.53; H, 8.95. Found: C, 75.26; H, 8.84.

$[Me_2Si(C_5Me_4)(C_5H_3SiMe_3)]Li_2$ (7). The preparation of **7** was carried out in an identical manner to **5** using **3** (3.38 g, 10.67 mmol) and ^{n}BuLi (1.6 M in hexane) (13.3 mL, 21.34 mmol). Yield: 3.25 g, 93%. Anal. Calcd for $C_{19}H_{30}Li_2Si_2$: C, 69.47; H, 9.20. Found: C, 69.12; H, 9.10.

$[Me_2Si(C_5Me_4)(C_5H_3{}^iPr)]Li_2$ (8). The preparation of **8** was carried out in an identical manner to **5** with **4** (3.21 g, 11.20 mmol) and ^{n}BuLi (1.6 M in hexane) (14.4 mL, 22.40 mmol). Yield: 3.23 g, 97%. Anal. Calcd for $C_{19}H_{28}Li_2Si$: C, 76.48; H, 9.46. Found: C, 76.27; H, 9.33.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]Nb(=N^tBu)Cl$ (9). THF (50 mL) was added to a solid mixture of $Nb(=N^tBu)Cl_3(py)_2$ (1.25 g, 2.92 mmol) and $[Me_2Si(C_5Me_4)(C_5H_4)]Li_2$ (**5**) (0.75 g, 2.92 mmol). The resulting brown solution was stirred for 12 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 yellow solid that precipitated from the solution was isolated by filtration (0.89 g, 62%). IR (Nujol): $\nu_{Nb=N}$ 1245 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 0.18 (3H), 0.43 (3H) (s, $SiMe_2$), 1.00 (s, 9H, CMe_3), 1.69 (3H), 1.97 (3H), 2.00 (3H), 2.28 (3H) (s, C_5Me_4) 5.82 (1H), 5.91 (1H), 6.32 (1H), 6.58 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −1.8, −0.5 ($SiMe_2$), 12.0, 13.7, 14.2, 16.5 (C_5Me_4), 31.5 (CMe_3), 69.2 (CMe_3), 100.9, 112.3 (C^{ipso}), 114.2, 115.8, 117.8 (C_5H_4), 122.8, 124.7, 126.9, 129.0, 130.0 (C_5Me_4). Anal. Calcd for $C_{20}H_{31}ClNNbSi$: C, 54.36; H, 7.07; N, 3.17. Found: C, 54.04; H, 6.99; N, 3.20.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)]Nb(=N^tBu)Cl$ (10). The synthesis of **10** was carried out in an identical manner to **9** using $Nb(=N^tBu)Cl_3(py)_2$ (0.96 g, 2.92 mmol) and $[Me_2Si(C_5Me_4)(C_5H_3Me)]Li_2$ (**6**) (0.79 g, 2.96 mmol). Yield: 1.02 g, 72%. IR (Nujol): $\nu_{Nb=N}$ 1275 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 0.18 (3H), 0.46 (3H) (s, $SiMe_2$), 0.98 (s, 9H, CMe_3), 1.72 (3H), 1.90 (3H), 2.07 (3H), 2.32 (3H), 2.34 (3H) (s, C_5Me_4, C_5H_3Me), 5.32 (1H), 5.93 (1H), 6.15 (1H), (m, C_5H_3Me). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −1.6, −0.4 ($SiMe_2$), 12.4, 13.8, 14.0, 15.6, 16.6 (C_5Me_4, C_5H_3Me), 31.6 (CMe_3), 68.9 (CMe_3), 99.9, 112.5 (C^{ipso}), 115.9, 116.0 (C^{ipso}), 116.6 (C_5H_3), 120.7, 126.2, 126.9, 128.3, 128.8 (C_5Me_4). Anal. Calcd for $C_{21}H_{33}ClNNbSi$: C, 55.32; H, 7.29; N, 3.07. Found: C, 55.15; H, 7.21; N, 3.05.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3SiMe_3)]Nb(=N^tBu)Cl$ (11). The synthesis of **11** was carried out in an identical manner to **9** using $Nb(=N^tBu)Cl_3(py)_2$ (1.20 g, 2.80 mmol) and $[Me_2Si(C_5Me_4)(C_5H_3SiMe_3)]Li_2$ (**7**) (0.92 g, 2.80 mmol). Yield: 1.05 g, 73%. IR (Nujol): $\nu_{Nb=N}$ 1260 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 0.28 (3H), 0.49 (3H) (s, $SiMe_2$), 0.47 (s, 9H, $SiMe_3$), 1.04 (s, 9H, CMe_3), 1.68 (3H), 1.78 (3H), 1.97 (3H), 2.25 (3H) (s, C_5Me_4) 5.74 (1H), 6.16 (1H), 6.63 (1H), (m, C_5H_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −2.4, −1.3 ($SiMe_2$), 0.3 ($SiMe_3$), 12.6, 13.5, 13.6, 16.4 (C_5Me_4), 31.9 (CMe_3), 69.8 (CMe_3), 103.6, 115.2, 119.5 (C^{ipso}), 120.3, 121.8 (C^{ipso}) (C_5H_3), 125.6, 128.5, 129.5, 131.0, 131.6 (C_5Me_4). Anal. Calcd for $C_{23}H_{39}ClNNbSi_2$: C, 53.74; H, 7.65; N, 2.72. Found: C, 53.61; H, 7.55; N, 2.80.

$[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3{}^iPr)]Nb(=N^tBu)Cl$ (12). The synthesis of **12** was carried out in an identical manner to **9** using $Nb(=N^tBu)Cl_3(py)_2$ (1.05 g, 2.45 mmol) and $[Me_2Si(C_5Me_4)(C_5H_3{}^iPr)]Li_2$ (**8**) (0.73 g, 2.45 mmol). Yield: 0.72 g, 61%.

Table 6. Crystal Data and Structure Refinement for 10, 12, 13, and 14

	10	**12**	**13**	**14**
formula	$C_{21}H_{33}ClNNbSi$	$C_{23}H_{37}ClNNbSi$	$C_{16}H_{22}ClSiZr$	$C_{17}H_{24}ClSiZr$
fw	455.94	483.99	404.54	417.56
T (K)	200(2)	200(2)	250(2)	250(2)
cryst syst	orthorhombic	monoclinic	orthorhombic	othorhombic
space group	$P2_12_12_1$	$P2_1/c$	$Pnma$	$Pnma$
a (Å)	15.681(1)	12.155(1)	10.1068(7)	10.626(8)
b (Å)	17.003(1)	14.580(1)	13.8030(10)	13.839(3)
c (Å)	17.059(1)	14.857(1)	12.402(3)	12.470(8)
β (deg)		110.52(1)		
V (Å^3)	4548.3(5)	2465.9(3)	1730.1(5)	1833.8(19)
Z	4	4	8	8
D_c (g cm^{-3})	1.332	1.304	1.553	1.512
μ (mm^{-1})	0.703	0.653	1.002	0.948
F(000)	1904	1016	824	852
cryst dimens (mm)	0.5 × 0.4 × 0.4	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.2	0.5 × 0.3 × 0.2
θ range (deg)	2.13 to 27.82	2.02 to 27.96	2.21 to 27.99	2.20 to 27.97
hkl ranges	$-20 \le h \le 20, 0 \le k \le 22, 0 \le l \le 22$	$-16 \le h \le 15, 0 \le k \le 19, 0 \le l \le 19$	$0 \le h \le 13, 0 \le k \le 17, 0 \le l \le 16$	$0 \le h \le 14, 0 \le k \le 18, 0 \le l \le 16$
no. of rflns measd	11 441	6150	2133	2293
no. of indep rflns	10 750	5925	2133	2293
no. of obsd rflns	8170	4768	1308	490
goodness-of-fit on F^2	1.014	1.047	0.974	0.827
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.1010$	$R_1 = 0.0314$, $wR_2 = 0.0696$	$R_1 = 0.0396$, $wR_2 = 0.0752$	$R_1 = 0.0953$, $wR_2 = 0.1551$
largest diff peak (e Å^{-3})	0.509/−0.492	0.439/−0.292	0.485/−0.441	0.652/−0.630

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

IR (Nujol): $\nu_{Nb=N}$ 1240 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.23 (3H), 0.49 (3H) (s, Si*Me*$_2$), 1.03 (s, 9H, C*Me*$_3$), 1.25 (3H), 1.28 (3H) (d, HC*Me*$_2$) ($^3J(^1H-^1H)$ 7.0 Hz), 1.74 (3H), 1.77 (3H), 2.08 (3H), 2.28 (3H) (s, C_5*Me*$_4$), 3.37 (sep, 1H, *H*CMe$_2$), 5.30 (1H), 6.00 (1H), 6.20 (1H), (m, C_5H_3). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −1.3, −0.7 (Si*Me*$_2$), 12.7, 13.5, 13.6, 16.4 (C_5*Me*$_4$), 22.1, 24.3 (HC*Me*$_2$), 28.8 (*H*CMe$_2$), 31.7 (C*Me*$_3$),69.3 (*C*Me$_3$), 99.2, 110.0, 110.6, 113.5 (C^{ipso}), 117.7 (C^{ipso}) (C_5H_3), 121.5, 125.1, 126.1, 129.7, 142.8 (*C*$_5$Me$_4$). Anal. Calcd for $C_{23}H_{37}ClNNbSi$: C, 57.08; H, 7.71; N, 2.89. Found: C, 56.88; H, 7.60; N, 2.93.

[Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]ZrCl$_2$ (13). THF (50 mL) was added to a solid mixture of $ZrCl_4$ (1.05 g, 4.51 mmol) and [Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)]Li$_2$ (**5**) (1.15 g, 4.51 mmol). The resulting pale yellow solution was stirred for 15 h. Solvent was removed in vacuo and toluene added (75 mL) to the resulting solid. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to −30 °C to yield white crystals of the title complex (0.73 g, 40%). ^{1}H NMR (200 MHz, C_6D_6): δ 0.28 (s, 6H, Si*Me*$_2$), 1.62 (6H), 1.94 (6H), (s, C_5*Me*$_4$), 5.29 (2H), 6.84 (2H), (m, C_5*H*$_4$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.8 (Si*Me*$_2$), 12.3, 14.9 (C_5*Me*$_4$), 107.5 (C^{ipso}), 112.2, 126.9, (*C*$_5$H$_4$), 125.2, 129.0, 135.6 (*C*$_5$Me$_4$). Anal. Calcd for $C_{16}H_{22}Cl_2SiZr$: C, 47.50; H, 5.48. Found: C, 47.38; H, 5.43.

[Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Me)]ZrCl$_2$ (14). The synthesis of **14** was carried out in an identical manner to **13** using $ZrCl_4$ (1.00 g, 4.29 mmol) and [Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$Me)]Li$_2$ (**6**) (1.16 g, 4.29 mmol). Yield: 0.69 g, 38%. ^{1}H NMR (200 MHz, C_6D_6): δ 0.28 (3H), 0.31 (3H) (s, Si*Me*$_2$), 1.57 (3H), 1.67 (3H), 1.97 (3H), 1.99 (3H) (s, C_5*Me*$_4$), 2.24 (s, 3H, C_5H_3*Me*), 4.93 (1H), 5.32 (1H), 6.55 (1H) (m, C_5*H*$_3$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.7, −0.6 (Si*Me*$_2$), 12.3, 12.4, 14.8, 15.0, 15.6 (C_5*Me*$_4$, C_5H_3*Me*), 105.7 (C^{ipso}), 113.1, 113.5, 124.5 (C^{ipso}), 127.0 (*C*$_5$H$_3$), 125.3, 128.4, 134.9, 135.5, 137.8 (*C*$_5$Me$_4$). Anal. Calcd for $C_{17}H_{24}Cl_2SiZr$: C, 48.78; H, 5.78. Found: C, 48.59; H, 5.71.

[Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$SiMe$_3$)]ZrCl$_2$ (15). The synthesis of **15** was carried out in an identical manner to **13** using $ZrCl_4$ (1.10 g, 4.72 mmol) and [Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$SiMe$_3$)]Li$_2$ (**7**) (1.55 g, 4.72 mmol). Yield: 1.02 g, 45%. ^{1}H NMR (200 MHz, C_6D_6): δ 0.34 (3H), 0.38 (3H) (s, Si*Me*$_2$), 0.43 (s, 9H, SiMe$_3$), 1.65 (3H), 1.66 (3H), 1.90 (3H), 1.91 (3H) (s, C_5*Me*$_4$), 5.56 (1H), 5.73 (1H), 7.13 (1H) (m, C_5*H*$_3$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −1.0, −0.1 (Si*Me*$_2$), −0.2 (SiMe$_3$), 12.1, 12.4, 14.9, 15.1 (C_5*Me*$_4$), 109.8 (C^{ipso}), 115.8, 118.7, 121.5 (C^{ipso}), 135.7 (*C*$_5$H$_3$), 125.4, 129.3, 135.0, 135.4, 136.4 (*C*$_5$Me$_4$). Anal. Calcd for $C_{19}H_{30}Cl_2Si_2Zr$: C, 47.87; H, 6.34. Found: C, 47.78; H, 6.32.

[Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*i*Pr)]ZrCl$_2$ (16). The synthesis of **16** was carried out in an identical manner to **13** using $ZrCl_4$ (1.05 g, 4.51 mmol) and [Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$*i*Pr)]Li$_2$ (**8**) (1.34 g, 4.51 mmol). Yield: 0.76 g, 38%. ^{1}H NMR (200 MHz, C_6D_6): δ 0.30 (3H), 0.35 (3H) (s, Si*Me*$_2$), 1.09 (3H), 1.32 (3H) (d, HC*Me*$_2$) ($^3J(^1H-^1H)$ 7.0 Hz), 1.62 (3H), 1.68 (3H), 1.96 (3H), 1.99 (3H) (s, C_5*Me*$_4$), 3.33 (sep, 1H, *H*CMe$_2$), 5.16 (1H), 5.36 (1H), 6.76 (1H) (m, C_5*H*$_3$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ −0.8, −0.6 (Si*Me*$_2$), 12.3, 12.4, 14.9, 15.0 (C_5*Me*$_4$), 21.6, 25.0 (HC*Me*$_2$), 29.0 (*H*CMe$_2$), 96.9 (C^{ipso}), 105.5 (C^{ipso}), 111.4, 112.6, 124.5 (*C*$_5$H$_3$), 125.3, 128.0, 135.0, 135.5, 148.2 (*C*$_5$Me$_4$). Anal. Calcd for $C_{19}H_{28}Cl_2SiZr$: C, 51.09; H, 6.32. Found: C, 50.90; H, 6.23.

Polymerization Experiments. The *ansa*-zirconocene catalyst **13**−**16** (6 μmol), MAO (10% in toluene) (750 μmol), and toluene (150 mL) were mixed together in a Schlenk tube. The N_2 pressure inside the Schlenk tube was reduced by applying vacuum. Ethylene pressure of 1.5 bar was then applied to the Schlenk tube and stirring of the mixture commenced. After exactly 1 h, stirring was halted and the ethylene pressure was released. Excess MAO was then destroyed by adding cautiously a mixture of methanol/HCl (90:10). The polymer formed was isolated by filtration, washed with ethanol, and dried under vacuum at 60 °C for 12 h.

X-ray Structure Determinations for [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$R)]Nb(=N^{t}Bu)Cl (R = Me (10), ^{i}Pr (12)) and [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$R)]ZrCl$_2$ (R = H (13), Me (14)). Crystals were mounted at low temperature in inert oil on a glass fiber. Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using an $\omega/2\theta$ scan technique at 200 K (**10** and **12**) and 250 K (**13** and **14**). For **14**, the specimen diffracted weakly. The final unit cell parameters were determined from 25 well-centered reflections and refined by the least-squares method. Data were corrected for Lorentz and polarization effects but not for absorption. The space group was determined from the systematic absences, and this was vindicated by the success of the subsequent solutions and refinements. The structures were solved by direct methods using the SHELXS computer program[29] and refined on F^2 by full-matrix least-squares (SHELXL-97).[30] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 6.

Acknowledgment. We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica, Spain (Grant. No. PB 98-0159-C02-01-02), and for a postdoctoral grant to S.P. under the Programa Nacional de Formación de Personal Investigador. We also thank Dr. M. Laguna for providing mass spectroscopy data.

Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **10**, **12**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0006662

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