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Ethylene-Bridged Tetramethylcyclopentadienylamide Titanium Complexes: Ligand Synthesis and Olefin Polymerization Properties[†]

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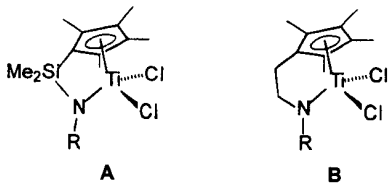
The *N*-alkyl-2-(2,3,4,5-tetramethylcyclopentadienyl)ethylamines $C_5Me_4H(CH_2)_2NHR$ (R = *i*-Pr, *t*-Bu) were obtained from the reaction of 2,3,4,5-tetramethylcyclopent-2-enone with deprotonated imines $LiCH_2CH{=}NR$ followed by dehydration and reduction using $LiAlH_4$. The parent compound with R = H was obtained via a similar procedure using deprotonated acetonitrile and derivatized to the R = Me species. The Ti(IV) complexes $[C_5Me_4(CH_2)_2NR]TiCl_2$ (R = *t*-Bu, *i*-Pr, Me) were prepared and tested for catalytic propene homopolymerization using methylaluminoxane (MAO) cocatalyst. Surprisingly, the catalysts with R = *i*-Pr, *t*-Bu were found to be inactive, and only for R = Me was catalytic formation of atactic polypropene observed. This is in marked contrast with the analogous systems with ligands with a $SiMe_2$-bridge that readily homopolymerize propene under similar conditions.

Introduction

Titanium complexes of linked dianionic h^5,h^1-cyclopentadienylamide ancillary ligands are effective catalysts for the (co-)polymerization of olefins when activated with the appropriate cocatalysts.[1,2] In addition to their useful catalytic properties, the increased electron deficiency and reduced steric encumbrance of these complexes relative to the well-known group 4 metallocene catalysts[3] make these systems of particular interest for fundamental studies on the effect of the ligand system, activator, and electronic state of the metal on catalyst performance. With this in mind, a range of di- and trimethylene-bridged cyclopentadienyl ligands $[C_5H_4(CH_2)_nNR]^{2-}$ (n = 2, 3; R = Me, Et, *i*-Pr, *t*-Bu) and their Ti,[4] Zr,[5] and V[6] derivatives were synthesized and studied by our group. In ethene and propene polymerization experiments with the Ti-catalysts based on these ligands with n = 2,[7] we observed a dependence of polymer molecular weight on the size of the amide substituent R (increasing M_w with decreasing size of R) that is opposite that observed for the "archetypal" catalysts with the $[C_5Me_4(SiMe_2)NR]^{2-}$ ligands (**A**).[1,2] In the complexes studied by us, the cyclopentadienyl group is unsubstituted. It was observed early on that, in the (cyclopentadienyl-$SiMe_2$-amide)Ti(IV) system, the ligands with the tetramethyl-substituted cyclopentadienyl moiety give catalysts that are superior in performance to those with the unsubstituted cyclopentadienyl moiety.[1c,2] To separate the effects of the nature of the bridge and the substitution pattern of the cyclopentadienyl ligand, we set out to prepare the ethylene-bridged tetramethylcyclopentadienylamide ligands $[C_5Me_4(CH_2)_2NR]^{2-}$ (R = Me, *i*-Pr, *t*-Bu) and their titanium dichloride derivatives (**B**).



The synthesis of the amines $C_5Me_4H(CH_2)_2NHR$ is nontrivial for several reasons. In principle, tetramethylcyclopentadienide could be used as ligand precursor, but the regioselectivity of the alkylation of tetramethylcyclopentadienide is generally poor (with the geminal substitution products usually dominant).[8] The use of 2,3,4,5-tetramethylcyclopent-2-enone (**1**) as precursor in

[†] Netherlands Institute for Catalysis Research (NIOK) publication no. RUG-00-4-2.

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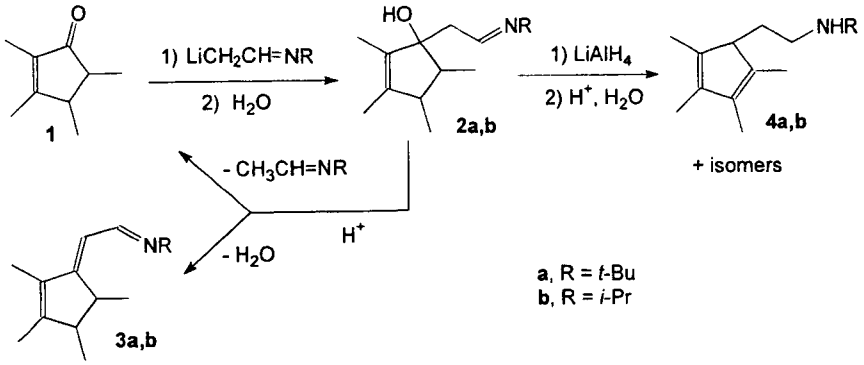
Scheme 1



a synthesis of these ligands (comparable with the synthesis of C_5Me_5H)[9] is limited due to the instability of the appropriate 2-heteroatom-functionalized alkylmagnesium or lithium compounds.[10] Dialkylamine derivatives $C_5Me_4H(CH_2)_2NR_2$ are available through double *sec*-butenylation of the esters $R'O(O)C(CH_2)_2NR_2$, followed by dehydration and cyclization.[8a] The dimethylamine derivative $C_5Me_4H(CH_2)_2NMe_2$ prepared in this way was recently used as precursor for the 4,5,6,7-tetramethylspiro[2,4]cyclohepta-4,6-diene.[11] Various carbon-, phosphorus-, or arsenic-centered nucleophiles are known to give ring-opening of such spiro compounds, but this was not observed for amides.[12] One of the targeted ligands, $C_5Me_4H(CH_2)_2NH(t\text{-Bu})$, was described in a patent as being synthesized (with unspecified yield) by reaction of LiC_5Me_4 with ethylbromoacetate followed by transformation to the corresponding *t*-Bu-acetamide and reduction with $LiAlH_4$.[1c]

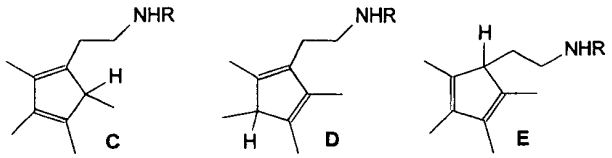
We have found a versatile route to various ethylene-bridged tetramethylcyclopentadienylamines using the readily available 2,3,4,5-tetramethylcyclopent-2-enone[9] (**1**) as starting material. It is based on the reaction of the cyclopentenone with deprotonated nitriles or imines followed by reduction with $LiAlH_4$ and aqueous workup. Here the synthesis by this route of the compounds $C_5Me_4H(CH_2)_2NHR$ (R = H, Me, *i*-Pr, *t*-Bu) is described, together with the preparation of their cyclopentadienylalkylamide titanium dichloride derivatives. Catalytic ethene and propene homopolymerization tests using the titanium dichloride complexes activated with methyl aluminoxane (MAO) cocatalyst show a strong influence of the ancillary ligand on catalyst performance.

Results

Synthesis of $C_5Me_4H(CH_2)_2NHR$ (R = *t*-Bu, *i*-Pr). The basic reaction sequence and some of the intermediates involved are illustrated by the synthesis of the isopropyl- and *tert*-butyl-amine derivatives $C_5Me_4H(CH_2)_2NHR$ (R = *t*-Bu, *i*-Pr) via the reaction of 2,3,4,5-tetramethylcyclopent-2-enone (**1**) with lithiated acetaldehyde *N*-alkylimines and subsequent hydrolysis, followed by reduction and dehydration (Scheme 1).

Acetaldehyde *N*-isopropylimine or acetaldehyde *N*-tert-butylimine was lithiated in THF at -20 °C with the weakly nucleophilic base $LiN(i\text{-Pr})_2$ (generated in situ from *n*-BuLi and diisopropylamine) and reacted with the cyclopentenone **1**. Subsequent hydrolysis of the reaction mixture yielded the crude alcohols **2a** (R = *t*-Bu) and **2b** (R = *i*-Pr). These intermediates are not very stable and decompose upon distillation, re-forming the starting materials. Attempts to perform acid-catalyzed dehydration of the alcohols also resulted mainly in reformation of the cyclopentenone, although small amounts of the imines $C_4Me_4H_2C{=}CHCH{=}NR$ (**3a**, **3b**) could be obtained and spectroscopically characterized via this procedure. Fortunately, direct reduction of the crude alcoholates with $LiAlH_4$ in diethyl ether followed by aqueous workup and an acid-base separation yielded the desired cyclopentadiene products $C_5Me_4H(CH_2)_2NHR$ (R = *t*-Bu, **4a**; R = *i*-Pr, **4b**). The isolated yields, after vacuum distillation, are rather modest (based on the starting cyclopentenone): 39% for **4b** and 21% for **4a**. Especially for R = *t*-Bu concomitant formation of a substantial amount of tetramethylcyclopentadiene is observed, again probably due to the reversibility of the C,C bond formation and subsequent reduction of the cyclopentenone evolved.

The various products were characterized by combinations of IR, ^1H and ^{13}C NMR spectroscopy, and exact mass spectroscopy. The cyclopentadienylamines **4a** and **4b** consist of a mixture of the three endocyclic double-bond isomers **C**-**E** as shown.



Synthesis of $C_5Me_4H(CH_2)_2NHR$ (R = H, Me). For the synthesis of the methylamino derivative $C_5Me_4H(CH_2)_2NHMe$ a different strategy is required, as the appropriate imine, acetaldehyde *N*-methylimine, is too unstable under basic conditions to be used as a reagent.[13] We therefore employed deprotonated aceto-

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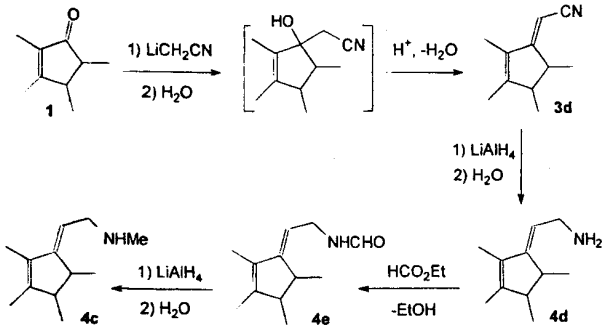
Scheme 2



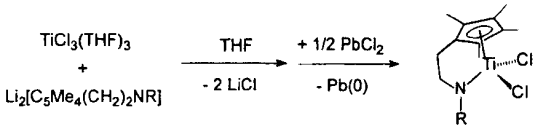
nitrile as nucleophile for the reaction with the tetramethylcyclopentenone **1**. Dehydration and reduction yields the parent amine $C_5Me_4H(CH_2)_2NH_2$ (**4d**), which was subsequently converted to the methylamine derivative (**4c**, Scheme 2).

Lithiated acetonitrile reacted in THF with the cyclopentenone **1** to give, after acidic workup and vacuum distillation, the (tetramethylcyclopentadienyl)acetonitrile **3d** as a mixture of isomers in an almost quantitative yield (98%). Reduction of this nitrile with $LiAlH_4$ in diethyl ether, followed by hydrolysis and vacuum distillation, yielded the amine $C_5Me_4H(CH_2)_2NH_2$ (**4d**, 70%). Formylation of the amine in refluxing ethylformate gave the crude N-formyl species $C_5Me_4H(CH_2)_2NHCHO$ (**4e**). Subsequent reduction of **4e** with $LiAlH_4$ in diethyl ether followed by aqueous workup and vacuum distillation produced the methylamine derivative $C_5Me_4H(CH_2)_2$-NHMe (**4c**) in a yield of 91 %. The overall isolated yield of **4c** based on the cyclopentenone **1** was 62%.

From the NMR spectra of the products it was seen that, in contrast with the compounds with R = *i*-Pr and *t*-Bu, the dominant isomer of the four species described here is the isomer with one exocyclic double bond, C_4-$Me_4H_2C{=}CHR'$ (R' = CN, **3d**; CH_2NH_2, **4d**; CH_2-NHCHO, **4e**; CH_2NHMe, **4c**), as shown in Scheme 2. This is probably caused by the stability of the conjugated system for R' = CN. In the subsequent derivatizations, employing basic or neutral conditions, this exocyclic double bond is retained. Acid-base treatment of **4c** followed by Kugelrohr distillation yielded exclusively the corresponding mixture of endocyclic double-bond isomers, showing that under acidic conditions these systems will isomerize.

Synthesis of $[C_5Me_4(CH_2)_2NR]TiCl_2$ (R = *t*-Bu, *i*-Pr, Me). The complex $[C_5Me_4(CH_2)_2N$*t*-Bu$]TiCl_2$ (**5a**) was reportedly isolated from the reaction of the dilithium salt of the tetramethylcyclopentadienylamide ligand **4a** with $TiCl_3(THF)_3$ followed by oxidation of the intermediate Ti(III) species with AgCl to the Ti(IV) product **5a** (36% isolated yield).[1c] Using the ligand as obtained from our alternative synthesis route and using a slightly modified oxidation procedure ($PbCl_2$ as oxidizing agent,[14] Scheme 3), we obtained **5a** in comparable yield (33%). The corresponding isopropyl amide derivative $[C_5Me_4(CH_2)_2N$*i*-Pr$]TiCl_2$ (**5b**) was obtained by the same procedure in 60% isolated yield. The methylamide derivative **5c** was obtained in 39% yield when using the ligand **4c**, which was previously isomerized to the mixture of isomers with exclusively endocyclic double bonds (see above). The use of portions of **4c** that consist predominantly of the isomers with an exocyclic double bond resulted in significantly lower yields of **5c** (10-20%).

Scheme 3



R = *t*-Bu, **5a**; R = *i*-Pr, **5b**; R = Me, **5c**

The titanium complexes were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The spectroscopic features of the compounds are in accordance with the expected C_s symmetry for monomeric species. In comparing the three species, the most prominent feature is that the bridge NCH_2 ^{13}C NMR resonance for R = Me (**5c**, *d* 79.5 ppm) is considerably downfield from the corresponding resonances in the compounds with R = *i*-Pr, *t*-Bu (*d* 67.7 and 69.4 ppm for **5b** and **5a**, respectively). The complex **5c** (in impure form with unspecified yield) was recently suggested by Mena et al. to be one of the products in the thermolysis of $(C_5Me_5)Ti(NMe_2)Cl_2$.[15] The observed NMR spectra for **5c** as synthesized here corroborate this identification.

Olefin Homopolymerization with $[C_5Me_4(CH_2)_2$-NR]$TiCl_2$/MAO. The linked tetramethylcyclopentadienylamide titanium dichloride complexes are known to be efficient catalysts for the polymerization of olefins. Most of the available data pertain to the $SiMe_2$-bridged ligand system, and very little information is available on the performance of the comparable ethylene-bridged catalysts. One reported ethene/1-octene copolymerization experiment using $[C_5Me_4(CH_2)_2N$*t*-Bu$]TiCl_2$ (**5a**)/MAO suggested that the catalyst productivity is even higher than for the corresponding $SiMe_2$-bridged analogue $[C_5Me_4(SiMe_2)N$*t*-Bu$]TiCl_2$ (**6**)/MAO, but with a much reduced incorporation of comonomer compared with the latter catalyst.[1c,16] A brief screening of **5a** and **6** in ethene homopolymerization (toluene solvent, MAO cocatalyst, Al/Ti = 500, [Ti] = 6.0×10^{-5}, 2 bar ethene, 50 °C, 30 min run time) corroborated the greater efficiency of the ethylene-bridged catalyst (**5a**: 8400 kg(PE) mol^{-1} h^{-1}, M_w = 115 000, M_w/M_n = 2.5; **6**: 4100 kg(PE) mol^{-1} h^{-1}, M_w = 253 000, M_w/M_n = 2.8).

Surprisingly, in the homopolymerization of propene (toluene solvent, Al/Ti = 500, [Ti] = 6.0×10^{-5}, 2 bar propene, 50 °C, 30 min run time) the $[C_5Me_4(CH_2)_2NR]$-$TiCl_2$/MAO catalysts with R = *t*-Bu and R = *i*-Pr (**5a**,**b**) proved to be completely inactive, and only the catalyst with R = Me (**5c**) showed activity in the production of atactic polypropene (2400 kg(PP) mol^{-1} h^{-1}, M_w = 110 000, M_w/M_n = 1.9). This is remarkable, as under similar conditions the catalyst with the $SiMe_2$-bridge $[C_5Me_4(SiMe_2)N$*t*-Bu$]TiCl_2$ (**6**)/MAO (10000 kg(PP) mol^{-1} h^{-1}, M_w = 140 000, M_w/M_n = 1.8) readily catalyzes the homopolymerization of propene. As was reported previ-

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ously,[17] the polypropene formed by **6**/MAO is syndiotactically enriched (in our sample the ratio of *mm*:*rr* triads is 14:37) and contains about 2% regioerrors, as seen by ^{13}C NMR. In contrast, the polypropene produced by the **5c**/MAO catalyst is nearly fully atactic (ratio of *mm*:*rr* triads is 22:28) and noticeably more regioregular (<0.5% regioerrors).

Discussion

By making use of the nucleophiles $LiCH_2CH{=}NR$ and $LiCH_2CN$, which, due to the CN unsaturation, are stable in contrast with species such as $LiCH_2CH_2NRR'$, it is now possible to use the readily available tetramethylcyclopentenone **1** as starting material for ethylene-bridged tetramethylcylopentadienylamide ancillary ligands. The main drawback of this procedure is the relative lability of the C-CH_2 bond in the intermediate alcohols $C_5Me_4H_2(OH)CH_2C{=}NR$ (**2a**,**b**). This makes it necessary (at least for R = *t*-Bu) to perform the imine reduction prior to the alcohol dehydration. The latter takes place readily during the acid-base separation of the product mixture, but is still accompanied to some extent by the C,C cleavage retro reaction. Fortunately the desired product is easily separated from the reformed cyclopentenone. The retro reaction appears to be no problem in the nitrile derivative, which under acidic conditions is readily dehydrated to give the conjugated nitrile **3c** in nearly quantitative yield. In addition to imines and acetonitrile we have also applied this method using esters and amides. From our preliminary findings it appears that the route has sufficient scope for the synthesis of a wide range of $C_5Me_4H(CH_2)_2X$ derivatives (X = NH_2, NHR, NRR', OH, OR).

The observation that under the applied conditions the catalyst system $[C_5Me_4(CH_2)_2NR]TiCl_2$/MAO is unable to effect the catalytic homopolymerization of propene for R = *t*-Bu, *i*-Pr is of interest. It puts into perspective the observation by Stevens et al. that for R = *t*-Bu the catalyst system is highly active in ethene/1-octene copolymerization, but that the amount of incorporated comonomer appears to be very small.[1c,16] The fact that the analogous system with the unsubstituted Cp-ligand, $[C_5H_4(CH_2)_2Nt\text{-}Bu]TiCl_2$/MAO, also readily homopolymerizes propene[7] suggests that steric factors may be important here. Still it is remarkable that decreasing the size of R in $[C_5Me_4(CH_2)_2NR]TiCl_2$/MAO from *t*-Bu to *i*-Pr is insufficient to restore at least some of the propene homopolymerization activity; this is only observed for R = Me. Comparing the structures of $[C_5Me_4(\text{bridge})Nt\text{-}Bu]TiCl_2$ with the $SiMe_2$ and the $(CH_2)_2$ bridge, it can be seen that the Cp(centroid)-Ti-N bite angles of the two ligand systems are practically identical, 107.7° for Me_2Si, 107.9° for $(CH_2)_2$, as are the Ti-N distances (1.909 Å for both).[16] One possible difference may be found in the distribution of the angles around the planar amide nitrogen for the two bridges. A smaller Ti-N-C(*t*-Bu) angle is expected for the ethylene bridge; compare, for example, Ti-N-C(*t*-Bu) for $[C_5H_4(CH_2)_2Nt\text{-}Bu]TiCl_2$[7b] of 124.1° with the 128.1° for $[C_5H_4(Me_2Si)Nt\text{-}Bu]Ti(NMe_2)_2$.[18] This would bring the substituent on the amide functionality closer to the active site in the case of the catalyst with the ethylene-bridged ligand. Reducing the size of the amide substituent from *t*-Bu to *i*-Pr should reduce the steric hindrance around the metal center, but this also leads to a further significant reduction of the Ti-N-C(R) angle, as seen by comparing the structures of $[C_5H_4(CH_2)_2NR]TiCl_2$ (R = *t*-Bu,[7b] 124.1°, R = *i*-Pr,[4] 114.2°). An additional electronic difference is that the amide in the ethylene-bridged system is expected to be a somewhat better *p*-donor.

Considering these relatively subtle differences, it is remarkable that the nature of the bridge in the $[C_5Me_4(\text{bridge})Nt\text{-}Bu]TiCl_2$/MAO catalyst system exerts such a strong influence that a change from the Me_2Si to the ethylene bridge effectively shuts down activity toward propene, while even enhancing it for ethene. At present we are unable to attribute the observed effects to any one specific feature of the catalyst system.

Concluding Remarks

The reaction of the 2,3,4,5-tetramethylcyclopent-2-enone with deprotonated imines or acetonitrile, followed by dehydration and reduction, provides a relatively straightforward and versatile synthesis route to ethylene-bridged tetramethylcyclopentadienylamide ligands. The route appears to be suitable for the preparation of other heteroatom-substituted derivatives as well, and we are presently investigating the scope of this method. The synthesis of the cyclopentadienylamide titanium complexes $[C_5Me_4(CH_2)_2NR]TiCl_2$ (R = *t*-Bu, *i*-Pr, Me) allowed us to make a first comparison of the propene polymerization characteristics (using MAO cocatalyst) of these catalysts with that of the well-known $[C_5Me_4(SiMe_2)Nt\text{-}Bu]TiCl_2$ system. Changing the bridge from Me_2Si to $(CH_2)_2$ resulted in a drastic change in the propene polymerization activity, effectively shutting down the catalysis for R = *t*-Bu and R = *i*-Pr. It is at present difficult to attribute this effect to anyone of the (relatively subtle) changes in complex geometry that accompanies the change of the bridge. We are presently trying to elucidate the origins of the observed effect.

Experimental Section

The experiments described were performed under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques, except for the aqueous workup procedures for the organic compounds, which were performed under aerobic conditions. Solvents were distilled from Na/K alloy (diethyl ether, pentane, hexane, THF) or sodium (toluene) under nitrogen atmosphere before use. For the polymerization experiments, the solvent (toluene, Aldrich anhydrous, 99.5%) was passed over alumina (Fluka), supported Cu scavenger (BASF R3-11), and molecular sieves (4 Å) before use. Ethene and propene (AGA, polymer grade) were passed over columns of supported Cu scavenger (BASF R3-11) and molecular sieves (4 Å) before being passed to the reactor. Deuterated benzene (Aldrich) was dried on Na/K alloy and vacuum transferred before use. The reagents *n*-BuLi (2.5 M in hexane, Aldrich), $LiAlH_4$ (Merck), $PbCl_2$, diisopropylamine, acetonitrile, and ethyl formate (Acros) were used as purchased. The 2,3,4,5-tetramethylcyclopent-2-enone (**1**),[9] $TiCl_3(THF)_3$,[19] and the imi-

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nes $CH_3CH{=}NR$ (R = *i*-Pr,[20] *t*-Bu[21]) were prepared according to literature procedures. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrometer. NMR spectra were run on Varian Gemini 200, VXR-300, and Unity 500 spectrometers. Exact mass spectrometry was performed on a JEOL JMS 600 instrument. GPC was performed at 135 °C on 1,2,4-trichlorobenzene solutions of the polymers with a Polymer Laboratories PL-GPC210 instrument. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

***N*-*tert*-Butyl-2-(2,3,4,5-tetramethylcyclopentadienyl)-ethylamine (4a).** To a solution of diisopropylamine (14 mL, 100 mmol) in 125 mL of THF, cooled to -20 °C, was added 40 mL of a 2.5 M solution of *n*-BuLi in hexane. The stirred mixture was cooled to -80 °C, and acetaldehyde *N*-*tert*-butylimine (10.0 g, 100 mmol) was slowly added. After 30 min the tetramethylcyclopentenone **1** (13.8 g, 100 mmol) was added, and the mixture was stirred for another 30 min at -70 °C. Over 1 h the temperature was allowed to rise to -40 °C, and then $LiAlH_4$ (4.7 g, 125 mmol) was added to the stirred mixture and the temperature was gradually raised to 40 °C. After 2 h the mixture was cooled to ambient temperature and water (15 mL) was carefully added. After the gray suspension changed color to yellow, the mixture was dried with Na_2SO_4 (25 g) and then filtered. The solids were washed with four portions of ether (50 mL each). The filtrates were combined and concentrated. The concentrate (19 g) was dissolved in 50 mL of ether. To the stirred solution 100 mL of 2 N HCl was gradually added, keeping the temperature below 25 °C. The aqueous phase was first washed with ether, and then a solution of 10 g of NaOH in water (50 mL) was added followed by extraction with ether. The combined ether fractions were dried on Na_2SO_4, concentrated, and distilled to give 4.66 g (21.0 mmol, 21%) of **4a** as a mixture of isomers (bp 65-70 °C, 0.03 mmHg). ^{1}H NMR ($CDCl_3$, 25 °C): *d* 2.70-1.85 (CH_2, C*H*Me), 1.80-1.68 (=C*Me*), 1.10-0.93 (*t*-Bu Me, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 25 °C): *d* 137.4-131.0 (=C-), 52.7, 49.1 and 47.0 (ring CH), 47.7 (NCMe_3), 40.5, 39.8, and 35.8 (NCH_2), 26.4 (*t*-Bu Me), 25.4 and 25.0 (CCH_2), 11.7-8.5 (8× Me).

***N*-Isopropyl-2-(2,3,4,5-tetramethylcyclopentadienyl)-ethylamine (4b).** To a solution of diisopropylamine (10.5 mL, 75 mmol) in 100 mL of THF, cooled to -20 °C, was added 30 mL of a 2.5 M solution of *n*-BuLi in hexane (75 mmol). After 15 min acetaldehyde *N*-isopropylimine (6.38 g, 75 mmol) was added, followed by the tetramethylcyclopentenone **1** (10.35 g, 75 mmol). Over 1.5 h the mixture was allowed to warm to 10 °C. The mixture was washed with water (2 × 10 mL), dried over Na_2SO_4, and concentrated to give 15 g of the crude alcohol **2b**. This was dissolved in 30 mL of ether and slowly added to a suspension of $LiAlH_4$ (3 g, 80 mmol) in 100 mL of ether. After stirring for 4 h at ambient temperature, water (8 mL) was slowly added. After standing overnight the white suspension was dried over Na_2SO_4 and filtered. The filtrate was worked up as described above for the preparation of **4a**. Distillation yielded 6.02 g (29.0 mmol, 39%) of **4b** as a mixture of three isomers (bp 63-65 °C, 0.03 mmHg). ^{1}H NMR ($CDCl_3$, 25 °C): *d* 2.90-2.10 (CH_2, *i*-Pr CH, C*H*Me), 1.94-1.72 (=C*Me*), 1.18-0.95 (*i*-Pr Me, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 25 °C): *d* 137.5-130.9 (10× =*C*-), 52.4, 49.0 and 47.0 (ring CH), 46.0 (NCH), 45.4, 44.6, and 40.5 (NCH_2), 25.7, 24.6, and 24.2 (CCH_2), 20.4 (*i*-Pr Me), 11.7-8.5 (10× Me). Exact MS calcd for $C_{14}H_{25}N$: 207.199, obsd 207.198.

Attempted Dehydration of $C_5Me_4H_2(OH)CH_2CH{=}NR$ (R = *t*-Bu, 2a; *i*-Pr, 2b). The crude alcohols **2a** and **2b** (characterized in their ^{1}H NMR spectra by a triplet at 7.73 ppm, *J* = 4.2 Hz, for the imine proton), obtained as described above in the synthesis of **4b**, were subjected to attempts to effect acid-catalyzed dehydration. For R = *t*-Bu, aqueous HCl/aqueous NaOH acid-base treatment of an ether solution of the alcohol led to recovery of cyclopentenone **1**. Stirring an ether solution of the alcohol on P_2O_5 followed by short-path distillation yielded the imine $C_5Me_4H_2CHCH{=}N$-*t*-Bu (**3a**) in about 15% yield based on **1** used initially, still contaminated with about 10% of **1**. For R = *i*-Pr the acid-base procedure resulted, after evaporation of the ether solvent, in a product mixture that contained **1** and the imine $C_5Me_4H_2CHCH{=}N$-*i*-Pr (**3b**) in approximately equimolar amounts.

3a: ^{1}H NMR ($CDCl_3$, 25 °C): *d* 8.12 (d, *J* = 9.5 Hz, 1H, CH=N), 5.92 (d, *J* = 9.5 Hz, 1H, C=CH), 2.60 (br q, *J* = 7.1 Hz, C*H*Me; the other C*H*Me resonance is obscured), 1.73 and 1.63 (s, 3H each, Me), 1.18 (s, 9H, *t*-Bu), 1.08 and 0.98 (d, *J* = 7.1 Hz, 3H each, CH*Me*).

(2,3,4,5-Tetramethylcyclopentadienyl)acetonitrile (3d). To a solution of acetonitrile (6.0 mL, 110 mmol) in THF (125 mL) cooled to -80 °C was added 44.0 mL of a 2.5 M solution of *n*-BuLi in hexane (110 mmol). After 15 min tetramethylcyclopentenone **1** (15 mL, 13.8 g, 100 mmol) was added at -80 °C over a period of 45 min. Over 3 h the temperature was allowed to rise to 0 °C. Water (25 mL) was added, and the organic layer was washed with two portions of water (10 mL). Then 2 N HCl (10 mL) was added, the mixture was shaken, and after 16 h the layers were separated. The organic phase was washed with brine, dried on Na_2SO_4, and concentrated. The residue was distilled to give 15.8 g (98.0 mmol, 98%) of **3d** as a mixture of isomers (bp 73-85 °C, 0.2 mmHg). IR (neat): 2207 cm^{-1} (CN). NMR data of the major isomer (2,3,4,5-tetramethylcyanomethylenecyclopent-2-ene): ^{1}H NMR ($CDCl_3$, 25 °C): *d* 4.88 (d, $^4J_{HH}$ = 1.7 Hz, 1H, =CH), 2.61 (br q, *J* = 7 Hz, 1H, C*H*Me), 2.13 (br q, *J* = 7 Hz, 1H, C*H*Me), 1.82 and 1.65 (br s, 3H each, =C*Me*), 1.26 and 1.05 (d, *J* = 7 Hz, 3H each, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 25 °C): *d* 174.35 (*C*=CH), 155.38 (=*C*MeC=), 128.57 (*C*Me=CMe), 116.54 (*C*N), 79.32 (=*C*H), 49.20 and 42.47 (CH), 16.17, 11.35, 10.40, and 7.22 (Me). Exact MS calcd for $C_{11}H_{15}N$: 161.120, obsd 161.120.

2-(2,3,4,5-Tetramethylcyclopentadienyl)ethylamine (4d). A solution of **3d** (15.68 g, 97 mmol) in ether (50 mL) was slowly added to a suspension of $LiAlH_4$ (6 g, 0.15 mol) in 200 mL of ether. The mixture was refluxed for 3 h, after which water (15 mL) was slowly added. After 19 h, Na_2SO_4 (50 g) was added. The salts were filtered off and washed with five portions of ether (100 mL each). The combined filtrates were concentrated, and the residue was distilled to give 11.19 g (68.5 mmol, 70%) of **4d** as a mixture of isomers (bp 56-65 °C, 0.03 mmHg). NMR data of the major isomer (with exocyclic double bond): ^{1}H NMR ($CDCl_3$, 25 °C): *d* 5.15 (t, *J* = 7.0 Hz, 1H, =CH), 3.38 (d, *J* = 7.0 Hz, 2H, NCH_2), 2.30 (br q, *J* = 7 Hz, 1H, C*H*Me), 2.04 (br m, 1H, C*H*Me), 1.66 and 1.58 (br s, 3H each, =CMe), 1.02 and 0.97 (d, *J* = 7.0 Hz, 3H each, CH*Me*), N*H* not observed. ^{13}C(APT) NMR ($CDCl_3$, 25 °C): *d* 150.58 (*C*=CH), 141.87 (=*C*MeC=), 127.85 (*C*Me=CMe), 114.31 (=CH), 48.72 (*C*HMe), 37.94 (NCH_2), 39.47 (*C*HMe), 19.30, 16.69, 10.49, and 7.56 (Me).

***N*-Formyl-2-(2,3,4,5-tetramethylcyclopentadienyl)-ethylamine (4e).** A mixture of **4d** (11.8 g, 68 mmol) and ethyl formate (40 mL) was refluxed for 6 h. Excess formate and evolved ethanol were distilled off (70 °C bath temperature, 20 mmHg) to give 13.3 g of crude **4e** as a red oil. This was used without further purification for the synthesis of the methylamine derivative **4c**. IR (neat): 3293 (NH), 1665 (amide I), 1532 (amide II) cm^{-1}. NMR data of the major isomer: ^{1}H NMR ($CDCl_3$, 25 °C): *d* 8.12 (s, 1H, C(O)H), 5.8 (br, 1H, NH), 4.99 (t, *J* = 7.0 Hz, 1H, =CH), 3.95 (m, 2H, NCH_2), 2.31 and 1.98 (br q, *J* = 7 Hz, 1H each, C*H*Me), 1.64 and 1.53 (br s, 3H each, =CMe), 0.95 and 0.90 (d, *J* = 7 Hz, 3H each, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 25 °C): *d* 161.97 (N*C*(O)H), 154.20 (*C*=CH), 143.81 (=*C*MeC=), 127.61 (*C*Me=CMe), 107.16 (=CH), 48.80

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and 39.49(*C*HMe), 34.41(NCH_2), 19.18, 16.69, 10.60, and 7.58 (Me). Exact MS calcd for $C_{12}H_{19}NO$: 193.147, obsd 193.148.

***N*-Methyl-2-(2,3,4,5-tetramethylcyclopentadienyl)-ethylamine (4c).** A solution of crude **4e** (13.3 g) in ether (50 mL) was slowly added to a suspension of $LiAlH_4$ (4.7 g, 123 mmol) in 200 mL of ether. The mixture was refluxed for 4 h, then water (10 mL) was slowly added. After 19 h, 30 g of Na_2SO_4 was added, and the salts were filtered off and washed with five portions of ether (100 mL each). The filtrates were concentrated, and the residue was distilled to give 11.1 g (62.3 mmol, 91% based on the amount of **4d** used in the above preparation of **4e**) of the methylamine derivative **4c** as a mixture of isomers, the major isomer having an exocyclic double bond (bp 46-50 °C, 0.03 mmHg). IR (neat): 3295 (NH), 1645, 1532 (C=C) cm^{-1}. NMR data of the major isomer: ^{1}H NMR ($CDCl_3$, 25 °C): *d* 5.07 (d, *J* = 6.4 Hz, 1H, =CH), 3.20 (m, 2H, NCH_2), 2.35 (s, 3H, NMe), 2.30 and 1.95 (br q, 1H each, C*H*Me), 1.62 and 1.53 (s, 3H each, =CMe), 0.92 and 0.88 (d, *J* = 7 Hz, 3H each, CH*Me*). ^{13}C(APT) NMR ($CDCl_3$, 25 °C): *d* 151.77 (*C*=CH), 141.82 (=*C*MeC=), 127.98 (*C*Me=CMe), 111.27 (=CH), 49.03 (*C*HMe), 47.49 (NCH_2), 39.62 (*C*HMe), 33.62 (NCH_3), 19.17, 16.72, 10.49, and 7.58 (Me). Exact MS calcd for $C_{12}H_{21}N$: 179.167, obsd 179.167.

A portion of 5 g of the product as obtained above was isomerized by warming at 50 °C in 10% aqueous HCl followed by addition of base, extraction into diethyl ether, and Kugelrohr distillation (130 °C, 0.5 mmHg) to give 4 g (80% yield) of a mixture of isomers of **4c** with exclusively endocyclic double bonds. ^{1}H NMR ($CDCl_3$, 25 °C): *d* 2.70-2.40 and 2.25-2.0 (CH_2, C*H*Me), 2.30-2.20 (N*Me*), 1.85-1.60 (=C*Me*), 1.0-0.95 (CH*Me*).

$[C_5Me_4(CH_2)_2NR]TiCl_2$ (R = *t*-Bu, 5a; *i*-Pr, 5b; Me, 5c). For the preparations of these compounds, the dilithium salts of the cyclopentadienylamide ligands were prepared by reaction of $C_5Me_4H(CH_2)_2NHR$ with 2 equiv of *n*-BuLi (hexane solution) in diethyl ether solvent at ambient temperature as described for the R = *t*-Bu derivative in ref 1c. The precipitates formed after stirring for 4 days were filtered off and rinsed repeatedly with pentane. These were dried in vacuo and used as such without further characterization (NMR spectra in THF-d_8 were poorly resolved).

For the R = *i*-Pr derivative, a mixture of $TiCl_3(THF)_3$ (2.75 g, 7.4 mmol) and the corresponding dilithium salt (1.52 g, 6.9 mmol) was dissolved in 25 mL of THF and stirred at ambient temperature for 1 h. To this dark green solution was added 2.3 g (8.3 mmol) of $PbCl_2$. The resulting orange-brown suspension was stirred for one more hour, after which the solvent was pumped off. The residue was subsequently extracted with 25 mL of pentane. Concentration and cooling of the extract to -25 °C yielded 1.44 g (4.44 mmol, 60%) of analytically pure **5b** as an orange microcrystalline solid. ^{1}H NMR (C_6D_6, 25 °C): *d* 5.53 (sp, *J* = 6.2 Hz, 1H, *i*-Pr CH), 3.94 (t, *J* = 7.3 Hz, 2H, NCH_2), 2.68 (t, *J* = 7.3 Hz, 2H, CCH_2), 2.01 and 1.84 (s, 6H each, Cp Me), 0.91 (d, *J* = 6.2 Hz, 6H, *i*-Pr Me). ^{13}C(APT) NMR (C_6D_6, 25 °C): *d* 139.6, 128.7, and 125.8 (Cp C), 67.7 (NCH_2), 52.1 (NCH), 24.6(C*C*H2), 17.9(*i*Pr Me), 12.8 and 12.6 (Cp Me). Anal. Found: C, 51.85; H, 7.13; N, 4.27; Ti, 14.66. Calcd for $C_{14}H_{23}NTiCl_2$: C, 51.88; H, 7.15; N, 4.32; Ti, 14.78.

The R = Me derivative **5c** was prepared similarly on a 3 mmol scale, using the cyclopentadienylamide dilithium salt derived from **4c** that was previously isomerized to a mixture of isomers with exclusively endocyclic double bonds (see above). The product mixture was extracted with pentane after which the solvent was removed in vacuo. Recrystallization from 10 mL of toluene at -60 °C yielded 0.36 g (1.21 mmol, 39%) of orange crystalline **5c**. ^{1}H NMR (C_6D_6, 25 °C): *d* 3.89 (t, *J* = 7.3 Hz, 2H, NCH_2), 3.37 (s, 3H, NMe), 2.67 (t, *J* = 7.3 Hz, 2H, CCH_2), 1.97 and 1.83 (s, 6H each, Cp Me). ^{13}C(APT) NMR (C_6D_6, 25 °C): *d* 139.7, 129.4 and 125.7 (Cp C), 79.5 (NCH_2), 45.7 (NMe), 24.4 (CCH_2), 12.8 and 12.6 (Cp Me). Anal. Found: C, 49.03; H, 6.36; N, 4.69; Ti, 16.01. Calcd for $C_{12}H_{19}NTiCl_2$: C, 48.68; H, 6.47; N, 4.73; Ti, 16.18.

The R = *t*-Bu derivative **5a** was prepared on 5.9 mmol scale according to the procedure described for R = *i*-Pr. Yield: 0.65 g (1.92 mmol, 33%). ^{1}H NMR (C_6D_6, 25 °C): *d* 4.04 (t, *J* = 7.3 Hz, 2H, NCH_2), 2.62 (t, *J* = 7.3 Hz, 2H, CCH_2), 2.02 and 1.91 (s, 6H each, Cp Me), 1.41 (s, 9H, *t*-Bu). ^{13}C(APT) NMR (C_6D_6, 25 °C): *d* 138.1, 129.4 and 128.6 (Cp C), 69.5 (NCH_2), 63.0 (N*C*), 29.0 (CMe_3), 25.3 (CCH_2), 13.4 and 12.8 (Cp Me). Anal. Found: C, 53.03; H,7.36; N, 4.02; Ti, 14.03. Calcd for $C_{15}H_{25}NTiCl_2$: C, 53.28; H, 7.45; N, 4.14; Ti, 14.16.

Olefin Homopolymerization. Polymerization experiments were carried out in a thermostated (electrical heating, water cooling) 1 L stainless steel autoclave (Medimex), equipped with solvent and catalyst injection systems. The autoclave was predried by heating in vacuo at 120 °C for 1 h. After cooling to the desired reaction temperature toluene (200 mL) was injected, followed by 5 mL of a 1.5 M MAO/toluene solution. Propene or ethene (2 bar) was admitted, and the mixture was allowed to equilibrate for 15 min. Polymerization was initiated by injection of a solution of 12-15 *m*mol of the appropriate titanium dichloride complex in 10 mL of toluene. The total amount of toluene in the reactor (including portions used to rinse the injector) was 250 mL. During the run the monomer pressure was kept constant within 0.1 bar. After 30 min the reaction was stopped by the addition of 10 mL of methanol. After venting, the reactor was opened to ambient atmosphere. For the ethene polymerizations, the reaction mixture was poured into acidified methanol and stirred for several hours. The polyethene was then collected on a frit, rinsed repeatedly with methanol, and dried in vacuo at 70 °C. For the atactic polypropene, the solvent was removed from the mixture in vacuo, the residue was dissolved in dichloromethane, and the solution was filtered. The solvent was removed on a rotary evaporator and the resulting polymer dried overnight in vacuo at 70 °C. The polypropenes were characterized by ^{13}C NMR in $C_2D_2Cl_4$ solution at 100 °C.

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