Ethylene-Bridged Tetramethylcyclopentadienylamidine Titanium Complexes: Ligand Synthesis and Olefin Polymerization Properties

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The N-alkyl-2,3,4,5-tetramethylcyclopentadienyl)-ethylamines C₄Me₅H(CH₂)₂NHR (R = i-Pr, t-Bu) were obtained from the reaction of 2,3,4,5-tetramethylcyclopent-2-enone with deprotonated imines LiCH₂CH=NR followed by dehydration and reduction using LiAlH₄. The parent compound with R = H was obtained via a similar procedure using deprotonated acetoacetite and derivatized to the R = Me species. The Ti(IV) complexes [C₄Me₅(C₂H₄NR)]TiCl₂ (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 SiMe₂-bridge that readily homopolymerize propene under similar conditions.

Introduction

Titanium complexes of linked dianionic \( \eta^5 \eta^1 \)-cyclopentadienylamide ancillary ligands are effective catalysts for the (co-)polymerization of olefins when activated with the appropriate cocatalysts. 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 metalloocene catalysts 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 cyclopentadienylligands \([C₂H₄(CH₂)₃NR]\) (n = 2, 3; R = Me, Et, i-Pr, t-Bu) and their Ti, Zr, and V 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 \([C₄Me₅(SiMe₂)₃NR]\) ligands (A). In the complexes studied by us, the cyclopentadienyl group is unsubstituted. It was observed early on that, in the (cyclopentadienyl-SiMe₂-amide)Ti(IV) system, the ligands with the tetramethyl-substituted cyclopentadieny moieties give catalysts that are superior in performance to those with the unsubstituted cyclopentadienyl moiety. 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 tetramethylcyclopentadienylamidine ligands \([C₄Me₅(C₂H₄)₂NR]\) (R = Me, i-Pr, t-Bu) and their titanium dichloride derivatives (B).

The synthesis of the amines \( C₄Me₅H(CH₂)₂NHR \) is nontrivial for several reasons. In principle, tetramethylcyclopentadienide could be used as ligand precursor, but the regioselectivity of the alkylation of tetramethylycyclopentadienide is generally poor (with the geminal substitution products usually dominant). The use of 2,3,4,5-tetramethylcyclopent-2-ene (I) as precursor in

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2 For a recent overview of the research in this area, see: McKnight, A. L.; Waymouth, R. M. Chem. Rev. 1998, 98, 2587.


a synthesis of these ligands (comparable with the synthesis of C₅Me₅H)³⁹ is limited due to the instability of the appropriate 2-heteroatom-functionalized alkylmagnesium or lithium compounds.³⁹ Dialkylamine derivatives C₅Me₅H(CH₂)₂NR₂ are available through double sec-butylenylation of the esters R'O(O)(C(CH₃)₂)NR₂, followed by dehydration and cyclization.³⁵ The dimethylamine derivative C₅Me₅H(CH₂)₂NMe₂ 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, C₅Me₅H(CH₂)₂NH(i-Pr), was described in a patent as being synthesized (with unspecified yield) by reaction of LiC₅Me₅ with ethylbromocacetate followed by transformation to the corresponding 1,2-Bu-acetamide and reduction with LiAlH₄.¹³

We have found a versatile route to various ethylene-bridged tetramethylcyclopentadienylamines using the readily available 2,3,4,5-tetramethylcyclopent-2-ene³⁹ (1) as starting material. It is based on the reaction of the cyclopentenone with deprotonated nitriles or imines followed by reduction with LiAlH₄ and aqueous workup. Here the synthesis by this route of the compounds C₅Me₅H(CH₂)₂NHR (R = H, Me, i-Pr) 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 C₅Me₅H(CH₂)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 C₅Me₅H(CH₂)₂NHR (R = t-Bu, i-Pr) via the reaction of 2,3,4,5-tetramethylcyclopent-2-ene (1) with lithiated acetaldehyde N-alkylamines and subsequent hydrolysis, followed by reduction and dehydration (Scheme 1).

Acetaldehyde N-isopropylamine or acetaldehyde N-tert-butylamine was lithiated in THF at -20 °C with the weakly nucleophilic base LiN(i-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 C₅Me₅H₂C=CHNH=NHR (3a, 3b) could be obtained and spectroscopically characterized via this procedure. Fortunately, direct reduction of the crude alcohohates with LiAlH₄ in diethyl ether followed by aqueous workup and an acid-base separation yielded the desired cyclopentadiene products C₅Me₅H(CH₂)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 ¹³C NMR spectroscopy, and exact mass spectroscopy. The cyclopentadilaminylanes 4a and 4b consist of a mixture of the three endocyclic double-bond isomers C-E as shown.

**Synthesis of C₅Me₅H(CH₂)₂NHR (R = H, Me).** For the synthesis of the methylamino derivative C₅Me₅H(CH₂)₂NHMe a different strategy is required, as the appropriate imine, acetaldehyde N-methylamine, is too unstable under basic conditions to be used as a reagent.¹¹ We therefore employed deprotonated acetoo
nitrile as nucleophile for the reaction with the tetramethylcyclopentene 1. Dehydration and reduction yields the parent amine C₅H₅N(C₂H₅)₂NH₂ (4d), which was subsequently converted to the methylene derivative (4c, Scheme 2).

Lithiated acetonitrile reacted in THF with the cyclopentene 1 to give, after acidic workup and vacuum distillation, the (tetramethylcyclopentadienyl)acetionitrile 3d as a mixture of isomers in an almost quantitative yield (98%). Reduction of this nitrile with LiAlH₄ in diethyl ether, followed by hydrolysis and vacuum distillation, yielded the amine C₅H₅N(CH₂)₂NH₂ (4d, 70%). Formylation of the amine in refluxing ethylformate gave the crude N-formyl species C₅H₅N(CH₂)₂NHCHO (4e). Subsequent reduction of 4e with LiAlH₄ in diethyl ether followed by aqueous workup and vacuum distillation produced the methylene derivative C₅H₅N(CH₂)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, C₅Me₅H=C-CHR’ (R’ = CN, 3d; CH₂NH₂, 4d; CH₂-NHCHO, 4e; CH₂NHMe, 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 [C₅Me₅(CH₂)₃]TiCl₄ (R = t-Bu, i-Pr, Me).** The complex [C₅Me₅(CH₂)₃]Sr-Bu]TiCl₄ (5a) was reportedly isolated from the reaction of the dilithium salt of the tetramethylcyclopentadienylamido ligand 4a with TiCl₄(THF)₂ followed by oxidation of the intermediate Ti(III) species with AgCl to the Ti(IV) product 5a (36% isolated yield). Using the ligand as obtained from our alternative synthesis route and using a slightly modified oxidation procedure (PhCl₄ as oxidizing agent, Scheme 3), we obtained 5a in comparable yield (33%). The corresponding isopropylamide derivative [C₅Me₅(CH₂)₃]Ni-Pr]TiCl₄ (5b) was obtained by the same procedure in 60% isolated yield. The methylene 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%).

The titanium complexes were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. The spectroscopic features of the compounds are in accordance with the expected C₁ symmetry for monomeric species. In comparing the three species, the most prominent feature is that the bridge NCH₃ ¹³C NMR resonance for R = Me (5c, 8 79.5 ppm) is considerably downfield from the corresponding resonances in the compounds with R = i-Pr, t-Bu (δ 8 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 (C₅Me₅)Ti(NMe₂)Cl₃. The observed NMR spectra for 5c as synthesized here corroborate this identification.

**Olefin Homopolymerization with [C₅Me₅(CH₂)₃-NR]TiCl₄/MAO.** The linked tetramethylcyclopentadienylamido titanium dichloride complexes are known to be efficient catalysts for the polymerization of olefins. Most of the available data pertain to the SiMe₃-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 [C₅Me₅(CH₂)₃]N-Bu]TiCl₄ (5a) implied that the catalyst productivity is even higher than for the corresponding SiMe₃-bridged analogue [C₅Me₅(SiMe₃)N-Bu]TiCl₄ (6)/MAO, but with a much reduced incorporation of comonomer compared with the latter catalyst. A brief screening of 5a and 6 in ethene homopolymerization (toluene solvent, MAO cocatalyst, Al/Ti = 500, [Ti] = 6.0 × 10⁻⁵, 1 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, Mₘ = 115 000, [Mₘ]ₙ = 2.5; 6: 4100 kg(PE) mol⁻¹ h⁻¹, Mₘ = 253 000, [Mₘ]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 [C₅Me₅(CH₂)₃]N-Bu]TiCl₄/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, Mₘ = 110 000, [Mₘ]ₙ = 1.9). This is remarkable, as under similar conditions the catalyst with the SiMe₂-bridge [C₅Me₅(SiMe₂)N-Bu]TiCl₄ (6)/MAO (10000 kg(PP) mol⁻¹ h⁻¹, Mₘ = 140 000, [Mₘ]ₙ = 1.8) readily catalyzes the homopolymerization of propene. As was reported previ-

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

**Discussion**

By making use of the nucleophiles LiCH$_2$CH=NR and LiCH$_2$CN, which, due to the CN unsaturation, is not possible in contrast with species such as LiCH$_2$CH$_2$NRR', it is now possible to use the readily available tetramethylcyclopent-2-enone 1 as starting material for ethylene-bridged tetramethylcyclopentadienylamide ancillary ligands. The main drawback of this procedure is the relative lability of the C$_2$C bond in the intermediate alcohols C$_5$Me$_3$H$_2$(OH)CH$_2$C=NRR' (2a,b). This makes it necessary (at least for R = t-Bu) to perform the imine reduction prior to the alkene 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$_5$Me$_3$H$_2$(CH$_2$)$_2$X derivatives (X = NH$_3$, NHR, NRR', OH, OR).

The observation that under the applied conditions the catalyst system [C$_5$Me$_4$(CH$_2$)$_2$NR]TiCl$_3$/MAO is unable to polymerize 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. The fact that the analogous system with the unsubstituted Cp-ligand, [C$_5$H$_4$(CH$_2$)$_2$NR-Bu]TiCl$_3$/MAO, also readily homopolymerizes propene suggests that steric factors may be important here. Still it is remarkable that decreasing the size of R in [C$_5$Me$_4$(CH$_2$)$_2$NR]TiCl$_3$/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$_5$Me$_4$(bridge)NR-Bu]TiCl$_3$ with the SiMe$_2$ and the (CH$_2$)$_2$ bridge, it can be seen that the C$_p$(centroid)-Ti-N bite angles of the two ligand systems are practically identical, 107.7° for Me$_2$Si, 107.9° for (CH$_2$)$_2$, as are the Ti-N distances (1.909 Å for both). 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-(t-Bu) angle is expected for the ethylene bridge; compare, for example, Ti-N-C(t-Bu) for [C$_5$H$_4$(CH$_2$)$_2$NR-Bu]TiCl$_3$ of 124.1° with the 128.1° for [C$_5$H$_4$(Me$_2$Si)-NR-Bu]Ti(NMe$_2$)$_2$. 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$_5$Me$_4$(CH$_2$)$_2$NR]TiCl$_3$ (R = t-Bu, 124.1°, R = i-Pr, 114.2°). An additional electronic difference is that the amide in the ethylene-bridged system is expected to be a somewhat better π-donor.

Considering these relatively subtle differences, it is remarkable that the nature of the bridge in the [C$_5$Me$_4$-(bridge)NR-Bu]TiCl$_3$/MAO catalyst system exerts such a strong influence that a change from the Me$_2$Si 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$_5$Me$_4$(CH$_2$)$_2$NR]TiCl$_3$ (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$_5$Me$_4$-(SiMe$_2$)NR-Bu]TiCl$_3$ system. Changing the bridge from Me$_2$Si 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), LiAIH$_4$ (Merck), PbCl$_2$, disopropylamine, acetonitrile, and ethyl formate (Acros) were used as purchased. The 2,3,4,5-tetramethylcyclopent-2-enone (1), TiCl$_3$(THF)$_2$, and the im-
nes CH,CH=NR (R = t-Pr2, t-Bu+) 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 disopropylamine (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-butylamine (10.0 g, 100 mmol) was slowly added. After 30 min the tetramethylcyclopentenone I (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 LiAlH4 (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, the mixture was cooled to ambient temperature and water (15 mL) was added, followed by the tetramethylcyclopentenone I (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 Na2SO4, and concentrated. The residue was distilled to give 15.8 g (98.0 mmol, 98%) of 4a as a mixture of isomers (bp 56-65 °C, 0.03 mmHg). NMR data of the major isomer (2,3,4,5-tetramethylcyclopentadien-2-yl): H NMR (CDCl3, 25 °C): δ 3.48 (d, J = 7.1 Hz, 1H, CHMe), 2.13 (br q, J = 7 Hz, 1H, CHMe), 1.82 and 1.65 (br s, 3H each, =CMe), 1.26 and 1.05 (d, J = 7 Hz, 3H each, CHMe). 13C NMR (CDCl3, 25 °C): δ 174.35 (c=CH), 155.38 (=CMe=), 128.57 (=CMe=), 116.54 (CMe), 79.32 (=C), 49.20 and 42.47 (CH), 16.17, 11.35, 10.40, and 7.22 (Me). Exact MS calculated for C35H53N: 615.1620, obsd 615.1620.

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 LiAlH4 (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, Na2SO4 (50 g) was added. The salts were filtered off and washed with five portions of ether (100 mL each). The combined filtrates were washed with ether, dried on Na2SO4, and concentrated. This was dissolved in 30 mL of ether and slowly added to a suspension of LiAlH4 (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 washed over Na2SO4 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). H NMR (CDCl3, 25 °C): δ 2.90-2.10 (CH, 2H, i-Pr CH, CHMe), 1.94-1.72 (=CMe), 1.18-0.95 (i-Pr Me, CHMe). 13C NMR (CDCl3, 25 °C): δ 137.5-130.9 (10×s=), 52.4, 49.0 and 47.0 (ring CH), 46.0 (NCH), 45.4, 44.6, and 40.5 (NCH), 25.7, 24.6, and 24.2 (CCH), 20.4 (i-Pr Me), 11.7-8.5 (10×s=). Exact MS calculated for C37H57N: 207.199, obsd 207.198.

**Attempted Dehydration of CMe4Me2(=O)HCH=CH=NR (R = t-Bu, 2a; i-Pr, 2b).** The crude alcohols 2a and 2b (characterized in their 1H 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 I. Stirring an ether solution of the alcohol on P2O5 followed by short-path distillation yielded the imine CMe4Me2HCH=CH=N=t- Bu (3a) in about 15% yield. Use of the base solution still containing 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 CMe4Me2CH=CH=N=i-Pr (3b) in approximately equimolar amounts.

3a: 1H NMR (CDCl3, 25 °C): δ 8.12 (d, J = 9.5 Hz, 1H, CH), 5.92 (d, J = 9.5 Hz, 1H, i-CH2), 2.60 (br q, J = 7.1 Hz, CHMe; the other CHMe 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, CHMe).

(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) for 15 min. Over 1 h the tetramethylcyclopentenone I (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 Na2SO4, 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-tetramethylcyclopentadien-2-yl): H NMR (CDCl3, 25 °C): δ 4.88 (d, J = 7.1 Hz, 1H, CH), 2.61 (br q, J = 7 Hz, 1H, CHMe), 2.13. (br q, J = 7 Hz, 3H, CHMe), 1.82 and 1.65 (br s, 3H each, =CMe), 1.26 and 1.05 (d, J = 7 Hz, 3H each, CHMe). 13C NMR (CDCl3, 25 °C): δ 174.35 (c=CH), 155.38 (=CMe=), 128.57 (=CMe=), 116.54 (CMe), 79.32 (=C), 49.20 and 42.47 (CH), 16.17, 11.35, 10.40, and 7.22 (Me). Exact MS calculated for C25H37N: 361.1200, obsd 361.1200.
and 39.49(CHMe), 34.41(NCH)

Ethylenoxide-Bridged Titanium Complexes

N-Methyl-2-(2,3,4,5-tetramethycyclopentadienyl)-
ethylamine (4c). A solution of crude 4e (13.5 g) in ether (50 mL) was added to a suspension of LiAlH₄ (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 Na₂SO₄ 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: ¹H NMR (CDCl₃, 25 °C): δ 5.07 (d, J = 6.4 Hz, 1H, =CH), 3.20 (m, 2H, NCH₂), 2.35 (s, 3H, NMe), 2.30 and 1.95 (br q, 1H each, CHMe), 1.62 and 1.53 (s, 3H each, =CMe), 0.92 and 0.88 (d, J = 7 Hz, 3H each, CHMe). ¹³C(APT) NMR (CDCl₃, 25 °C): δ 151.77 (C=CH), 141.82 (=CMeC), 127.98 (CMe=CMe), 111.27 (=CHMe), 49.03 (CHMe), 74.49 (NCH), 39.62 (CHMe), 19.17, 16.72, 10.49, and 7.58 (Me). Exact MS calcd for C₂₄H₂₄N₂O: 352.2. Calcd for C₂₄H₂₄N₂O: 352.2. Found: C, 51.85; H, 7.13; N, 4.27; Ti, 14.66.

The R = Me derivative 5e was obtained similarly on a 3 mmol scale, using the cyclopentadienylamine dichloride salt derived from 4e 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 5e. ¹H NMR (CDCl₃, 25 °C): δ 3.89 (t, J = 7.3 Hz, 2H, NCH₃), 3.37 (s, 3H, NMe), 2.67 (t, J = 7.3 Hz, 2H, CCH₃), 1.97 and 1.83 (s, 6H each, Cp Me). ¹³C(APT) NMR (CDCl₃, 25 °C): δ 139.7, 129.4 and 125.7 (Cp C), 79.5 (NCH), 45.7 (NMe), 24.4 (CCH₃), 12.8 and 12.6 (Cp Me). Anal. Found: C, 53.03; H, 6.36; N, 4.69; Ti, 16.01. Calcd for C₂₄H₂₄N₂TiCl₃: C, 53.42; H, 6.47; N, 4.73; Ti, 16.18.

The R = i-Pr 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%). ¹H NMR (CDCl₃, 25 °C): δ 4.04 (t, J = 7.3 Hz, 2H, CCH₃), 2.62 (t, J = 7.3 Hz, 2H, CCH₂), 2.02 and 1.91 (s, 6H each, Cp Me), 1.41 (s, 9H, i-Bu). ¹³C(APT) NMR (CDCl₃, 25 °C): δ 138.1, 129.4 and 128.6 (Cp C), 69.5 (NCH), 63.0 (NC), 29.0 (CMe₂), 25.3 (CCH₃), 13.4 and 12.8 (Cp Me). Anal. Found: C, 53.03; H, 7.36; N, 4.02; Ti, 14.03. Calcd for C₂₄H₂₄N₂TiCl₃: C, 53.28; H, 7.45; N, 4.14; Ti, 14.16.

Olefine 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 μmol 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 polyethylene 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 ¹³C NMR in C₂D₃Cl₄ solution at 100 °C.

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