Cyclopentadienyl titanium hydroxylaminato complexes as highly active catalysts for the polymerization of propylene†

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Half sandwich complexes of titanium bearing η^1 or η^2 bound nitroxide ligands are highly active catalysts for the polymerisation of propylene to high molecular weight atactic poly(propylene).

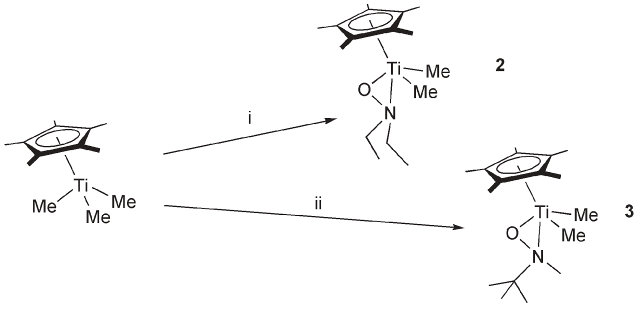
The catalytic polymerization of olefins is the basis of an industry that produces over 100 billion lbs of polyolefins per year. Group 4 complexes based on metals bearing one or two cyclopentadienyl ligands are an important class of the new generation of polymerization catalysts; the mono-cyclopentadienyl titanium complexes [$Me_2Si(Cp')(RN)]TiMe_2$ constitute a prototypical example that is currently in commercial use.[1,2] The substituted cyclopentadienyl ring tethered by a dialkylsilyl bridge to an electron rich σ-, π-donating amido ligand leads to high polymerization activities, and excellent incorporation of higher olefins, thought to be mainly due to the open co-ordination geometry of the ligand. More recently, several unbridged cyclopentadienyl titanium complexes have been reported employing a variety of non-cp ligands such as aryloxides,[3] phosphoraneimides[4] and imidazolineimides.[5] These more sterically hindered complexes also show high activities for ethylene/α-olefin copolymerizations with good incorporation of the olefin, suggesting that steric considerations may not be the only factors contributing to their copolymerization behavior.[6]

Hydroxylamines provide an interesting class of ligands for group 4 metals as the steric and electronic properties of these ligands can be varied widely and the binding of the hydroxylaminato ligand depends sensitively on the nature of the hydroxylamine and the ancillary ligation at the metal.[7–12] We recently reported the synthesis and polymerization behavior of an η^1 bound TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) titanium complex, Cp*Ti(Me)$_2$(TEMPO), **1**, prepared by reduction of Cp*TiCl$_3$, followed by trapping with the TEMPO radical and alkylation. The sterically encumbered monoanionic TEMPO ligand is comparable in size to that of the 2,6-^{i}Pr$_2$C$_6$H$_3$O$^-$ ligand.[11] Complex **1** is an active catalyst precursor for ethylene/1-hexene copolymerization and showed very good incorporation of the α-olefin.[11] Furthermore, cyclopentadienyl zirconium hydroxylamine complexes have been reported in the patent literature and were shown to slowly polymerize ethylene and ethylene/butene at elevated temperatures.[12] As alkoxides and amides are potential 4-electron donors by virture of σ- and π-donation, and hydroxylamines can adopt either η^1 or η^2 coordination geometries, we sought to investigate the role of both η^1 and η^2 bound ligands in the polymerization behavior of this class of compounds.

In this contribution, we report facile synthetic routes to several monocyclopentadienyl hydroxylamine complexes and illustrate how the diversity in co-ordination chemistry of this versatile ligand class affects the polymerization activity. To investigate the influence of coordination geometry on the polymerization behavior, we first targeted the synthesis of Cp*Ti(Me)$_2$(ONEt$_2$), **2**. Addition of diethylhydroxylamine to Cp*TiMe$_3$ in pentane, followed by recrystallization from a cold pentane solution yielded analytically pure yellow crystals in 76% yield. As relatively few hydroxylamines are available due to their tendency to form the nitroxyl radicals, we investigated alternative synthetic routes to these complexes. Tilley and Doxsee's reports that nitroso compounds insert into group 4 metallacycles provided an intriguing synthetic entry.[13,14] Addition of 2-methyl-2-nitrosopropane to Cp*TiMe$_3$ led to the clean insertion into one titanium methyl bond to generate the unsymmetrically substituted Cp*Ti(Me)$_2$(ONMe(^{t}Bu)), **3** (Scheme 1). Initial attempts to insert 2-methyl-2-nitrosopropane into Cp*TiBz$_3$, Cp*Ti(CH$_2$SiMe$_3$)$_3$ or Cp*Ti(NMe$_2$)$_3$ in C$_6$D$_6$ at ambient temperature were unsuccessful, probably as a result of the high steric demands of the Cp* and bulky alkyl ligands.

The ^{1}H NMR of complexes **2** and **3** are indicative of an η^2 coordination geometry for the hydroxylamine ligand in solution at 20 °C, consistent with that observed for CpTi(Cl)$_2$(ONMe$_2$) in the solid-state.[8] Complex **2** displays diastereotopic CH$_2$ resonances for the *N*-ethyl substituents, and complex **3** exhibits diastereotopic Ti–Me resonances at $\delta = 0.1$ and 0.05 ppm. At elevated temperatures, these diastereotopic signals coalesce. Dynamic ^{1}H NMR studies yield activation barriers of $\Delta H^\ddagger = 25$ and 14 kcal mol^{-1} for **2** and **3** respectively, consistent with an η^2–η^1 interconversion.†

Confirmation of the hapticity of the hydroxylamine ligand in **3** was determined by X-ray diffraction.† Crystals of suitable quality



Scheme 1 Synthesis of **2** and **3**. Conditions: (i) HONEt$_2$, pentane; (ii) ^{t}BuNO, pentane.

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† Electronic supplementary information (ESI) available: experimental details, variable temperature NMR data, crystal structure data and polymer tacticity data. See http://www.rsc.org/suppdata/cc/b4/b418778d/
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were grown from a saturated pentane solution at −30 °C.‡ The structure of **3** is shown in Fig. 1 and reveals that the hydroxylamine ligand is bound with an η^2-coordination geometry to the titanium center in the solid state. The Ti–O and Ti–N bond lengths are similar to those observed in the analogous $CpTi(Cl)_2(ONMe_2)$,[8] and the Ti–O bond is longer than that observed for the η^1 bound TEMPO ligand of **1**.[11] In addition, the hydroxylamine ligand is twisted about the plane bisecting the angle of C(11), Ti and C(12) such that the oxygen is skewed to the left, the nitrogen atom lying to the right. This results in the alkyl groups being twisted with the methyl group pushed forward and the *tert*-butyl group being twisted away from possible steric interactions with C(12).

The hydroxylaminato titanium complexes were studied as catalyst precursors for the polymerization of propylene and compared to related monocyclopentadienyl titanium complexes from the literature.[2,3,17] Activation by triphenylcarbenium pentafluorophenylborate $[Ph_3C^+][B(C_6F_5)_4^-]$ in the presence of triisobutylaluminium (TIBA) in propylene/toluene mixtures provides catalysts with high activities and yields atactic polypropylenes with high molecular weight (Table 1). Under these conditions, the productivity of **2** (153 kg poly(propylene)/mmol Ti.h) is comparable in activity to some of the most active group 4 metallocene and half-sandwich catalysts,[15,16] and significantly higher than that obtained from the constrained-geometry catalyst, $[Me_2Si(Me_4Cp)(^tBuN)]TiMe_2$,[2] **4**, the aryloxide, $Cp^*Ti(Me)_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, **5**,[3] and Cp^*TiMe_3, **6** under these conditions.[17] This was unexpected as related η^2-bound hydrazido complexes exhibit low productivities for ethylene polymerization.[18,19] The order of activity **2** > **3** > **1**, may simply reflect the steric demands of the hydroxylamine ligands, but the high activity of **2** may also be a consequence of additional electron density provided by the nitrogen lone pair of the η^2-coordinated hydroxylamine.

Table 1 Propylene polymerization using Cp^*TiMe_2X complexes[a]

Complex	Yield (g)	Prod[b]	M_n (kg mol^{-1})[c]	M_w (kg mol^{-1})[c]	PDI[c]
1	0.5	11.4	1220	2502	2.04
2[d]	1.3	153.2	1350	2520	1.86
3	1.6	38.8	1350	2650	1.96
4	0.1	2.2	1220	2540	2.08
5[e]	0.4	17.9	1520	2820	1.85
6	0.03	0.7	337	1127	3.34

[a] Polymerizations were carried out in 90 mL liquid propylene, 10 mL toluene containing 60 mg TIBA at 20 ± 1 °C for 20 min, $[Ti] = [Ph_3C^+][B(C_6F_5)_4^-] = 1.25\ \mu M$. [b] Catalyst productivity (kg poly(propylene)/mmol Ti.h). [c] Determined by gel permeation chromatography (GPC). [d] $[Ti] = 0.25\ \mu M$. [e] $[Ti] = 0.75\ \mu M$.

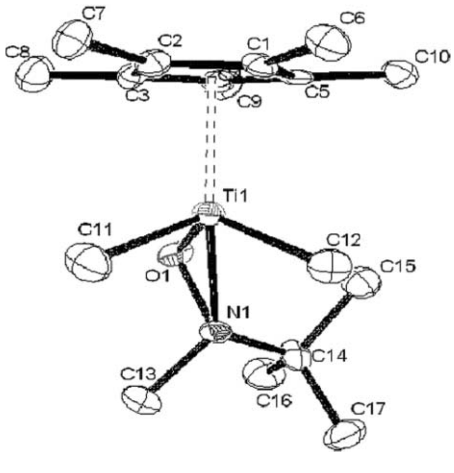

Fig. 1 X-ray crystal structure of **3**. Selected bond lengths (Å) and angles (°): Ti–O 1.895(3); Ti–N 2.178(4); Ti–C(11) 2.114(5); Ti–C(12) 2.142(5); O–Ti–C(11) 104.31(17); O–Ti–C(12) 127.66(17); C(11)–Ti–C(12) 93.8(2); O–Ti–N 40.19(13); O–N–Ti 59.16(19); N–O–Ti 80.7(2); C(11)–Ti–N 95.26(17); C(12)–Ti–N 90.30(17).

All of the monocyclopentadienyl titanium complexes yield high molecular weight atactic polypropylenes.† The polydispersities of polymers produced by **2** and **3** are consistent with single-site behavior $M_w/M_n \approx 2$ (Table 1), and are comparable to those produced by **4**. The higher activities and lower polydispersities of polymers derived from **2** and **3** relative to those derived from **6** imply that the hydroxylamine ligands remain ligated to titanium in the active catalysts. The regioselectivities of complexes **2** and **3** are comparable to that of **4** (≈ 3% regioerrors).

The development of rapid screening methods has recently proved an extraordinarily powerful tool for the discovery of new families of polymerization catalysts.[20–22] Many of these methods rely on the generation of novel coordination compounds *in situ*. For this strategy to be successful, facile, high yielding and rapid synthetic procedures are necessary to generate the requisite coordination compounds. For this reason, the insertion of nitroso compounds to generate hydroxylamine ligands prompted us to investigate the formation of the $Cp^*Ti(Me)_2(ONMe(R))$ catalysts *in situ*. Addition of a variety of nitrosoalkanes RNO (R = ^tBu, Ph, $3,5\text{-}^tBu_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$ and $2,6\text{-}Br_2C_6H_3$) to Cp^*TiMe_3 **6** in C_6D_6 cleanly generated $Cp^*Ti(Me)_2(ONMe(R))$. This reaction enabled us to screen a variety of these complexes for propylene polymerization (Table 2). Injection of a mixture of **6** and the nitrosoalkane, RNO, in toluene into liquid propylene containing TIBA, followed by activation with $[Ph_3C^+][B(C_6F_5)_4^-]$ generated active catalysts for propylene polymerization. The productivity of the *in-situ* generated $Cp^*Ti(Me)_2(ONMe(^tBu))$ was slightly lower than that using a purified sample of **3**, but both routes yielded a polypropylene of comparable molecular weight, polydispersity, and microstructure (Table 1, 2, SI). The higher productivity and narrow polydispersity observed in this run, compared to that of

Table 2 Propylene polymerization screening results using (cyclopentadienyl)$TiMe_2(ONMe(R))$ complexes generated *in situ* by the insertion reaction[a]

RN=O	Prod[b]	M_n (kg mol^{-1})[c]	M_w (kg mol^{-1})[c]	PDI[c]	% m^{4}[d]	% r^{4}[d]
^tBu	27.3	1270	2678	2.11	2.3	18.3
Ph	18.9	1910	3430	1.79	1.6	18.2
$3,5\text{-}^tBu_2C_6H_3$	6.9	1480	3120	2.10	2.1	15.5
$2,4,6\text{-}Me_3C_6H_2$[e]	0.06	990	2180	2.20	2.0	15.1
$2,6\text{-}Br_2C_6H_3$	0.07	90	198	2.21	4.5	14.8

[a] Polymerizations were carried out in 90 mL liquid propylene, 10 mL toluene containing 60 mg TIBA at 20 ± 1 °C for 20 minutes. [b] Catalyst productivity (kg poly(propylene)/mmol Ti.h). [c] Determined by gel permeation chromatography (GPC). [d] Determined by ^{13}C NMR. [e] Nitroso and **6** combined in Schlenk tube in pentane, solvent removed, resultant powder used for polymerization.

Cp^*TiMe_3, **6** provides clear evidence for the *in-situ* generation of **3** under these conditions.

The results of these screening studies reveal that catalysts derived from $Cp^*Ti(Me)_2(ONMe(R))$ where R = ^{t}Bu, Ph, 3,5-^{t}Bu$_2$C$_6$H$_3$, yield the most active propylene polymerization catalysts (Table 2). The catalyst derived from 3,5-^{t}Bu$_2$C$_6$H$_3$NO was less active than that generated from PhNO, and catalysts derived from *ortho*-substituted aryl nitrosoalkanes 2,4,6-Me$_3$C$_6$H$_2$NO and 2,6-Br$_2$C$_6$H$_3$NO were considerably less active, and in the case of 2,6-Br$_2$C$_6$H$_3$NO generated polypropylenes of lower molecular weight. Nevertheless, analysis of the polymers by GPC revealed narrow molecular weight distributions. Analysis by ^{13}C NMR revealed that all of these derivatives yield atactic polypropylenes with only subtle differences in the microstructure for the different hydroxylaminato ligands (Table 2, SI).

The lower activity of catalysts derived from the *ortho*-substituted aryl nitroso compounds may be a consequence of the increased steric demands of these ligands and/or less stable η^2-coordination of these NO ligands to titanium. Examination of the ^{1}H NMR spectrum of the unsymmetrically substituted $Cp^*Ti(Me)_2(ONMe(2,4,6\text{-}Me_3C_6H_2))$ **7** reveals a single broad Ti–Me resonance at $\delta = 0.12$ ppm, consistent with either an η^1-coordination geometry or rapid η^1–η^2 interconversion. Further studies are underway to test the hypothesis that the η^2-coordination of these ligands is an important factor leading to high polymerization activity.

The production of polypropylenes in this manner shows that rapid screening of the *in-situ* generated hydroxylaminato compounds provides a useful synthetic entry into this class of polymerization catalysts, suggesting that the insertion of nitroso complexes will provide a facile means of screening new classes of hydroxylamine complexes for polymerization behavior. The low polydispersities (M_w/M_n = *ca.* 2) and comparable polymer properties to those produced using the well-defined hydroxylaminato complexes, indicate that the desired complexes are being formed and polymerization is occurring without loss of hydroxylaminato ligand. Current efforts are directed toward modifying the cyclopentadienyl ligand and extending the generality of the nitroso insertion chemistry to investigate the potential of this family of catalysts for stereospecific olefin polymerization and olefin copolymerization.

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Notes and references

‡ Crystal Data. $C_{17}H_{33}NOTi$, $M = 315.34$, rhombic, $a = 9.060(2)$, $b = 16.210(3)$, $c = 12.450(2)$ Å, $\beta = 100.767(3)^\circ$, $U = 8876(1)$ Å^3, $T = 143$ K, space group $P2_1/n$, $Z = 4$, μ(0.71073 Å radiation) 0.47 cm^{-1}, 8041 reflections measured, 3002 unique (Rint = 0.1111) which were used in all calculations, Residuals: $R1$; $wR2$ 0.0637; 0.1501. CCDC 260262. See http://www.rsc.org/suppdata/cc/b4/b418778d/ for crystallographic data in .cif or other electronic format. **2**: ^{1}H NMR ($C_6D_5CD_3$, 300 MHz): δ 3.16, 3.00 (ddq, $\mathrm{ONC}\mathit{H}_2\mathrm{CH}_3$, $^3J_{H\text{–}H}$ = 6.8, 7.3 Hz, $^2J_{H\text{–}H}$ = 13.5 Hz, 4H), 1.86 (s, $\mathrm{C_5(C}\mathit{H}_3)_5$, 15H), 1.07 (t, $\mathrm{ONCH_2C}\mathit{H}_3$, $^3J_{H\text{–}H}$ = 7.2 Hz, 6H), 0.05 (s, $\mathrm{TiC}\mathit{H}_3$, 6H). ^{13}C {^{1}H} NMR (C_6D_6, 500 MHz): δ 120.2 ($\mathit{C}_5\mathrm{(CH_3)_5}$), 51.4 ($\mathrm{ON}\mathit{C}\mathrm{H_2CH_3}$), 46.6 ($\mathrm{Ti}\mathit{C}\mathrm{H_3}$), 11.3 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 9.8 ($\mathrm{ONCH_2}\mathit{C}\mathrm{H_3}$). Elemental Analysis for $C_{16}H_{26}ONTi$ (found): C, 63.78 (63.72); H, 10.37 (10.34); N, 4.65 (4.61). **3**: ^{1}H NMR (C_6D_6, 500 MHz): δ 2.88 (s, $\mathrm{ONC}\mathit{H}_3$, 3H), 1.87 (s, $\mathrm{C_5(C}\mathit{H}_3)_5$, 15H), 1.06 (s, $\mathrm{ONC(C}\mathit{H}_3)_3$, 9H), 0.47, −0.03 (s, $\mathrm{TiC}\mathit{H}_3$, 3H). ^{13}C {^{1}H} NMR (C_6D_6, 500 MHz): δ 120.5 ($\mathit{C}_5\mathrm{(CH_3)_5}$), 62.9 ($\mathrm{ONC(}\mathit{C}\mathrm{H_3)_3}$), 52.4, 44.3 ($\mathrm{Ti}\mathit{C}\mathrm{H_3}$), 43.7 ($\mathrm{ON}\mathit{C}\mathrm{H_3}$), 26.4 ($\mathrm{ONC(}\mathit{C}\mathrm{H_3)_3}$), 11.5 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$). Elemental Analysis for $C_{17}H_{28}ONTi$ (found): C, 64.75 (64.56); H, 10.55 (10.58); N, 4.44 (4.49). **7**: ^{1}H NMR (C_6D_6, 500 MHz): δ 6.70 (s, Ar, 2H), 3.01 (s, $\mathrm{ONC}\mathit{H}_3$, 3H), 2.62 (s, Ar-*o*-$\mathrm{C}\mathit{H}_3$, 6H), 2.05 (s, Ar-*p*-$\mathrm{C}\mathit{H}_3$, 3H), 1.83 (s, $\mathrm{C_5(C}\mathit{H}_3)_5$, 15H), 0.12 (br s, $\mathrm{TiC}\mathit{H}_3$, 6H).^{13}C {^{1}H} NMR (C_6D_6, 500 MHz): δ 146.9, 135.1, 132.4, 131.1 (Ar), 120.2 ($\mathit{C}_5\mathrm{(CH_3)_5}$), 50.9 ($\mathrm{ON}\mathit{C}\mathrm{H_3}$), 48.7 ($\mathrm{Ti}\mathit{C}\mathrm{H_3}$), 21.1 (Ar-*o*-$\mathit{C}\mathrm{H_3}$), 20.5 (Ar-*p*-$\mathit{C}\mathrm{H_3}$), 11.4 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$). Elemental Analysis for $C_{22}H_{35}ONTi$ (found): C, 70.02 (69.02); H, 9.35 (9.24); N, 3.71 (3.71).

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