Chapter 5

Bis-Ligated Complexes of Chelating N-Heterocyclic Carbene Ligands on Group IV Metals

5.1 Abstract

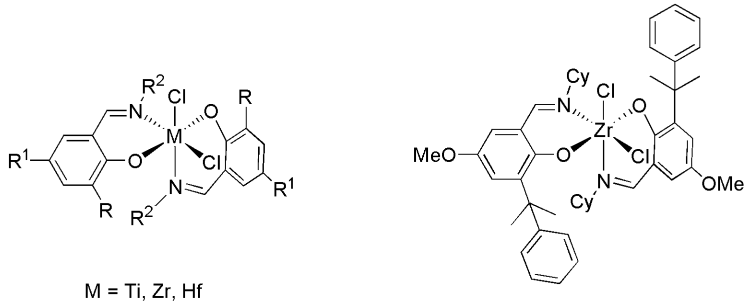
Having had little success with group 10 complexes of our novel chelating NHCs as catalysts, we decided to investigate group 4 complexes. These proved to be excellent catalysts for the polymerization of ethylene and the copolymerization of ethylene with norbornene and 1-octene.

5.2 Introduction

Despite the interesting reactivity observed in the synthesis of Ni complexes of our novel chelating NHCs, their lack of catalytic activity for ethylene polymerization and ethylene/polar monomer copolymerization was disappointing. Indeed, it remained to be seen whether the new NHCs were viable ligands for transition metal catalysts at all. Therefore, we began to look for other examples of sal ligands in transition metal catalysis for which our NHC ligands could be substituted.[1]

In the past decade, there has been extensive research into non-metallocene complexes of group 4 metals as catalysts for ethylene and α-olefin polymerization.[2] One of the most active avenues of research has been in group 4 (Ti, Zr and Hf) bis-ligated complexes of salicylaldimine ligands (Figure 1.1).

Figure 5.1. Group 4 salicylaldimine catalysts for olefin polymerization.



M = Ti, Zr, Hf
R, R^1, R^2 = alkyl, aryl

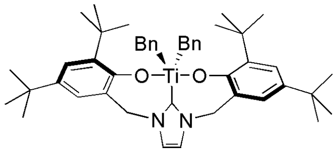
5.1

Upon treatment of these compounds with methaluminoxane (MAO), they become quite active olefin polymerization catalysts. It has been demonstrated that, as in the case of group 10 diimine complexes, steric shielding of the catalyst active site by bulky ligands leads to increased catalytic activity. For instance, polymer production of 7.22 x 10^6 g PE (mmol cat.)$^{-1}$ (hr)$^{-1}$ was obtained with cumyl-substituted Zr catalyst **5.1**.[3] In general, it was observed that bulk at the site ortho to the phenoxide was necessary for high polymerization activity. Specifically, steric shielding of the catalytically active cationic metal center from its corresponding anion allows ethylene to coordinate more easily.[4]

We reasoned that our chelating NHC ligands would be excellent surrogates for sal ligands for group 4 catalysts, as they had been designed with that very role in mind. In addition, we had synthesized one very bulky chelating NHC ligand (adamantyl-substituted **3.24**) which would presumably provide the steric bulk necessary to shield the metal center. It was also possible that there would be a beneficial electronic affect arising from replacement of the imine moieties with NHCs.

Aihara and coworkers have reported ethylene polymerization by a Ti complex of a chelating NHC ligand similar to ours (Figure 5.2).[5] Complex **5.2**, which features a tridentate bis(carbene)-phenoxide ligand, was shown to possess moderate activity (290 g PE (mmol cat.)$^{-1}$ (hr)$^{-1}$) for ethylene polymerization. It seems that the lower activity of **5.2**, compared to bis-ligated sal complexes such as **5.1**, is due to the decreased shielding of the active site due to the more open coordination site afforded by the wider angle of the tridentate ligand.

Figure 5.2. A chelating NHC complex of Ti.

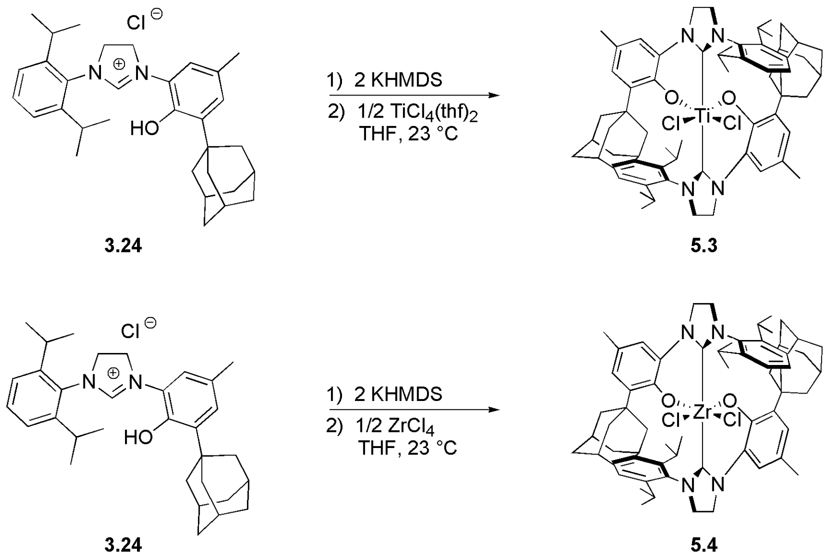


5.2

5.3 Synthesis of Group 4 Catalysts

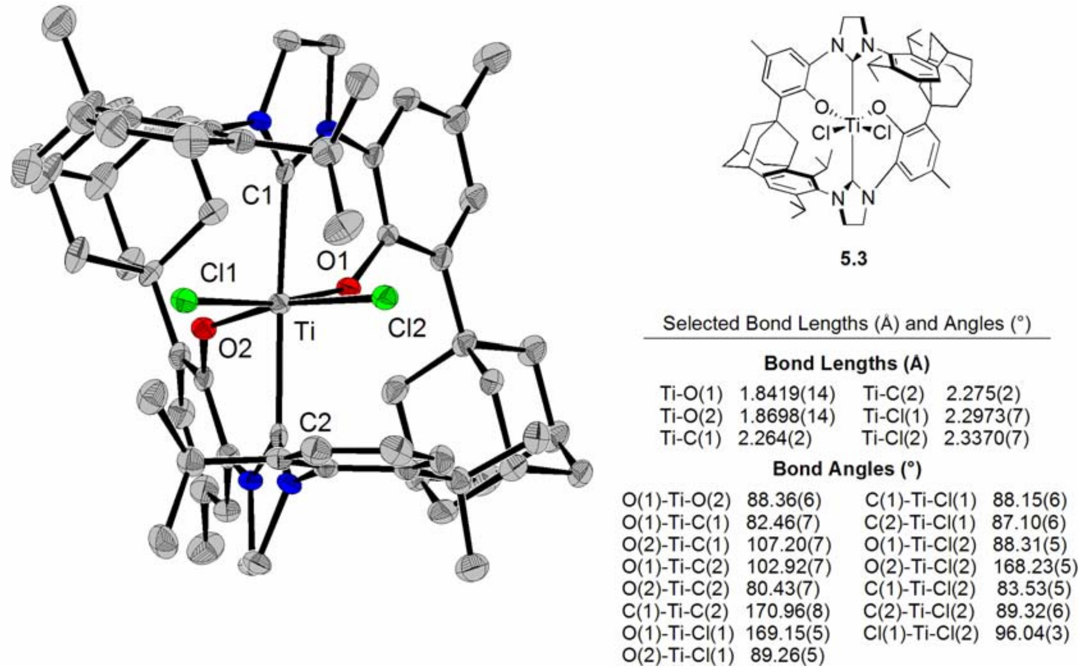
The synthesis of group 4 complexes of the adamantyl-substituted ligand **3.24** proceeded simply via the activation of ligand precursor **3.24** with two equivalents of KHMDS, followed by treatment of the resulting solution with half an equivalent of the corresponding metal starting materials, $TiCl_4(thf)_2$ and $ZrCl_4$ (Scheme 5.1).

Scheme 5.1. The synthesis of group 4 complexes of chelating NHCs.



The Ti complex (**5.3**) proved to be a red-brown solid, while the Zr complex (**5.4**) was light yellow. These colors are typical of the bis-ligated sal complexes of Ti and Zr.[3,4] Crystals of both compounds suitable for X-ray crystallographic analysis were grown, and structures were obtained (Ti: Figure 5.3; Zr: Figure 5.4).

Figure 5.3. Molecular structure of Ti complex **5.3** (hydrogen atoms have been omitted for clarity). Atoms are represented by thermal ellipsoids at 50% probability.



5.3

Selected Bond Lengths (Å) and Angles (°)

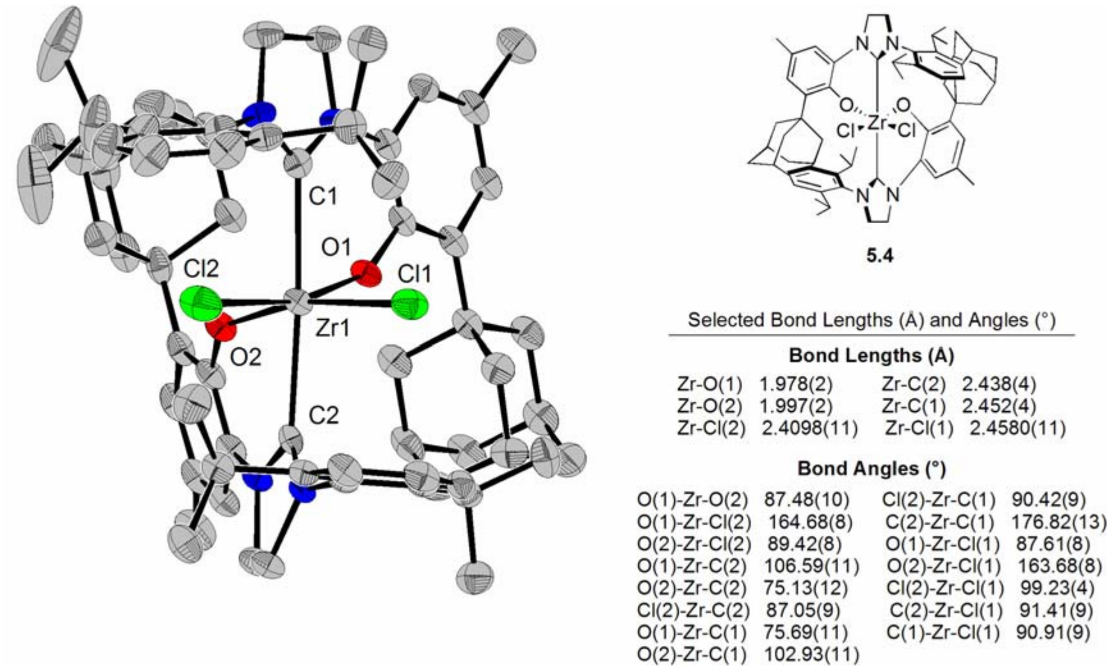
Bond Lengths (Å)

Ti-O(1)	1.8419(14)	Ti-C(2)	2.275(2)
Ti-O(2)	1.8698(14)	Ti-Cl(1)	2.2973(7)
Ti-C(1)	2.264(2)	Ti-Cl(2)	2.3370(7)

Bond Angles (°)

O(1)-Ti-O(2)	88.36(6)	C(1)-Ti-Cl(1)	88.15(6)
O(1)-Ti-C(1)	82.46(7)	C(2)-Ti-Cl(1)	87.10(6)
O(2)-Ti-C(1)	107.20(7)	O(1)-Ti-Cl(2)	88.31(5)
O(1)-Ti-C(2)	102.92(7)	O(2)-Ti-Cl(2)	168.23(5)
O(2)-Ti-C(2)	80.43(7)	C(1)-Ti-Cl(2)	83.53(5)
C(1)-Ti-C(2)	170.96(8)	C(2)-Ti-Cl(2)	89.32(6)
O(1)-Ti-Cl(1)	169.15(5)	Cl(1)-Ti-Cl(2)	96.04(3)
O(2)-Ti-Cl(1)	89.26(5)		

Figure 5.4. Molecular structure of Zr complex **5.4** (hydrogen atoms have been omitted for clarity). Atoms are represented by thermal ellipsoids at 50% probability.



5.4

Selected Bond Lengths (Å) and Angles (°)

Bond Lengths (Å)

Zr-O(1)	1.978(2)	Zr-C(2)	2.438(4)
Zr-O(2)	1.997(2)	Zr-C(1)	2.452(4)
Zr-Cl(2)	2.4098(11)	Zr-Cl(1)	2.4580(11)

Bond Angles (°)

O(1)-Zr-O(2)	87.48(10)	Cl(2)-Zr-C(1)	90.42(9)
O(1)-Zr-Cl(2)	164.68(8)	C(2)-Zr-C(1)	176.82(13)
O(2)-Zr-Cl(2)	89.42(8)	O(1)-Zr-Cl(1)	87.61(8)
O(1)-Zr-C(2)	106.59(11)	O(2)-Zr-Cl(1)	163.68(8)
O(2)-Zr-C(2)	75.13(12)	Cl(2)-Zr-Cl(1)	99.23(4)
Cl(2)-Zr-C(2)	87.05(9)	C(2)-Zr-Cl(1)	91.41(9)
O(1)-Zr-C(1)	75.69(11)	C(1)-Zr-Cl(1)	90.91(9)
O(2)-Zr-C(1)	102.93(11)		

Both complexes are octahedral and not surprisingly, display nearly identical coordination geometry. Interestingly, the coordination stereochemistry of **5.3** and **5.4** is different from that of sal complexes of Ti and Zr (such as **5.1**). In the sal complexes, the phenoxide moieties are typically coordinated axially, while the neutral imine portions of the ligands are equatorial. Calculations suggest that this geometry is favored over the reversed geometry (*i.e.,* phenoxides equatorial, imines axial) by 6.05 kJ/mol.[4] However, in **5.3** and **5.4**, the reverse geometry is observed, with the neutral NHC moieties occupying the axial positions, and the anionic phenoxides the equatorial. It is not clear if this difference in geometry is due to steric or electronic considerations. The strong trans influence of the NHCs may favor their mutually trans arrangement. However, the great size of adamantyl-substituted ligand **3.24** may accommodate only the observed geometry. Were the geometry reversed, it appears likely that the bulky diisopropylphenyl groups would experience significant destabilizing interactions.

5.4 Polymerization Activity

Having synthesized the targeted metal complexes, it remained to be determined whether they were effective catalysts for olefin polymerization. This was carried out by treating the complexes with MAO in toluene and then pressurizing the solution with ethylene. The various conditions used and results obtained are summarized in Table 5.1.

Table 5.1. Conditions and results for olefin polymerization by complexes **5.3** and **5.4**.

	Catalyst	MAO equiv	Ethylene pressure (psi)	Comonomer (equiv)	Comonomer incorporation (%)	Polymer yield (g)	Activity g (mmol cat.)$^{-1}$hr^{-1}
1	**5.3**	1000	400	-	-	1.62	216
2	**5.3**	1500	400	-	-	1.84	245
3	**5.3**	1000	200	1-octene (6360)	15.2	1.12	224
4	**5.3**	1000	400	1-octene (6360)	13.6	1.71	342
5	**5.4**	1000	120	-	-	0.80	131
6	**5.4**	1000	400	-	-	1.35	180
7	**5.4**	1500	400	-	-	1.94	259
8	**5.4**	1000	400	norbornene (1456)	26.7	1.30	130
9	**5.4**	1000	200	norbornene (1746)	65.9	3.31	661
10	**5.4**	1000	400	norbornene (1746)	72.5	3.81	761

Overall, the activities of these catalysts compare favorably with those observed for bis-ligated sal complexes of group 4 metals. For instance, the activity of Ti complex **5.3** averages approximately 230 g PE (mmol. cat.)$^{-1}$ (hr)$^{-1}$ (entries 1-2), which is well within the range of activities demonstrated for Ti catalysts. The activity for Zr catalyst **5.4** averages approximately 190 g PE (mmol. cat.)$^{-1}$ (hr)$^{-1}$ (entries 5-7), which is somewhat low for Zr catalyst activities. It is possible that the extreme bulk of the two diisopropylphenyl substituents flanking the catalyst active site may slow ethylene association at that position. It has been demonstrated that Zr complexes of extremely bulky sal ligands are not active polymerization catalysts.[4] It is also possible that the use of strongly σ-donating NHC moieties decreases catalyst activity, although the origin of this effect is not clear.

Copolymerizations of ethylene with norbornene, 1-octene and styrene were also attempted.[6] In all cases, polymer was formed, but it appears that only norbornene and 1-octene were incorporated. It is interesting to note the very high levels of comonomer incorporation (up to 72.5%), particularly in copolymerization of ethylene with norbornene by Zr catalyst **5.4**. Polymerization of propylene was attempted with both Ti and Zr catalysts.[7] While Zr catalyst **5.4** showed some propylene uptake during reaction, only trace polymer was obtained. No polymer was obtained during an attempted polymerization of propylene by Ti catalyst **5.3**. It is not clear why propylene polymerizations did not work for **5.3** and **5.4**.

5.5 Conclusion

It has been demonstrated that bis-ligated Ti and Zr complexes (**5.3** and **5.4**) of our [C,O]-chelating, adamantyl-substituted ligand **3.24** are effective catalysts for the polymerization of ethylene and the copolymerization of ethylene with 1-octene and norbornene when activated with MAO. It is no small measure of relief that, after the disappointing results of ligating our chelating NHC ligands to Ni, we finally struck upon success with group 4 metals. The results of the experiments described above suggest that, barring the occasional ring-opening reaction, [C,O]-chelating NHCs can be effective ligands for transition metal-based catalysts.

5.6 Acknowledgments

This work was supported by the Rohm and Haas Corporation. Lester McIntosh (Rohm and Haas) assisted with olefin polymerizations and polymer analysis. Jeff Byers (Bercaw group) provided MAO and helpful advice for polymerizations. Larry Henling and Mike Day performed the X-ray crystallographic analysis of compounds **5.3** and **5.4**.

5.7 Experimental Details

Materials and Methods. All reactions involving metal complexes were conducted in oven-dried glassware under a nitrogen atmosphere using standard glovebox techniques. Solvents were prepared by passage through alumina. All commercially obtained reagents were used as received. Organic reagents were purchased from Sigma-Aldrich and metal salts obtained from Strem. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 500 spectrometer (at 500 MHz, 125 MHz and respectively) and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C spectra are reported in terms of chemical shift.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolyl titanium(IV) dichloride (5.3). 1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolium chloride **(3.24)** (262 mg, 0.520 mmol, 1.00 equiv) and potassium hexamethyldisilazide (216 mg, 1.04 mmol, 2.10 equiv) were weighed together in a vial in the glovebox. THF (~5 mL) was added to the mixture of solids to provide a light yellow solution with a light precipitate. This was added to a round-bottomed flask and allowed to stir for 10 min. At this point, a suspension of (thf)$TiCl_4$ (86 mg, 0.260 mmol, 0.50 equiv) in THF (~5 mL) was added. The resulting yellow suspension quickly turned to a dark red solution with a light precipitate. It was allowed to stir at 25 °C for 1 hr, then filtered through Celite. The solvent was then removed under reduced pressure, to afford **5.3** as a dark red/brown solid (115 mg, 0.108 mmol, 42.4% yield). Crystals suitable for X-ray crystallographic analysis were obtained by layering a saturated toluene solution of **5.3** with pentane and storing the layered solution at –40 °C for several days. The ^1H NMR (500 MHz, CD_2Cl_2) spectrum of **5.3** is very complicated, resulting from a large number of inequivalent protons. ^{13}C NMR (125 MHz, CD_2Cl_2): δ 226.8, 159.2, 129.6, 128.4, 125.0, 124.6, 123.8, 120.5, 116.5, 114.5, 112.9, 55.9, 50.9, 42.0, 41.4, 41.2, 41.2, 41.1, 40.6, 37.7, 37.5, 37.4, 37.2, 36.5, 30.0, 29.9, 29.8, 28.8, 29.7, 29.1, 29.0, 28.9, 28.7, 25.9, 25.6, 24.3, 21.6; HRMS: Calc'd. for $C_{64}H_{82}N_4O_2Cl_2Ti$ (M^+): 1056.529. Found 1056.534.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolyl zirconium(IV) dichloride (5.4). 1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolium chloride (**3.24**) (255 mg, 0.500 mmol, 1.00 equiv) and potassium hexamethyldisilazide (210 mg, 1.00 mmol, 2.10 equiv) were weighed together in a vial in the glovebox. THF (~5 mL) was added to the mixture of solids to provide a light yellow solution with a light precipitate. This was added to a round-bottom flask and allowed to stir for 10 min. At this point, a suspension of (thf)$ZrCl_4$ (58 mg, 0.25 mmol, 0.50 equiv) in THF (~5 mL) was added. The resulting yellow suspension quickly turned to a deeper yellow solution with a light precipitate. The mixture was allowed to stir at 25 °C for 1 hr, and was then filtered through Celite. The solvent was then removed under reduced pressure. The resulting light yellow solid was washed with pentane, and then collected by filtration (129 mg, 0.120 mmol, 46.6% yield). Crystals suitable for X-ray crystallographic analysis were obtained by layering a saturated THF solution of **5.4** with pentane and storing the layered solution at –40 °C for several days. The ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **5.3** is very complicated, resulting from a large number of inequivalent protons. ^{13}C NMR (125 MHz, CD_2Cl_2): δ 226.8, 147.7, 147.3, 146.9, 137.5, 132.0, 129.0, 127.3, 124.6, 124.3, 124.0, 123.7, 116.7, 116.5, 50.3, 41.4, 41.0, 37.8, 37.5, 37.4, 34.7, 29.9, 29.9, 29.8, 29.7, 29.1, 29.0, 28.7, 28.6, 27.1, 26.9, 26.3, 24.3, 24.2, 23.6, 22.9, 21.8, 21.6, 14.4; HRMS: Calc'd. for $C_{64}H_{82}N_4O_2Cl_2Zr$ (M^+): 1101.494. Found: 1101.497.

Ethylene polymerization studies – general protocol. All polymerization studies were performed using an Argonaut Endeavor automated parallel multi-reactor synthesizer. A measured amount of a standard solution of catalyst in toluene (such that 5 μmol are used) was added to each reaction vessel. The desired pressure of ethylene was introduced to each vessel, and each vessel was allowed to warm to the desired temperature. At this point, any comonomer that was to be used was added via syringe to each vessel. After this, stirring was begun. The ethylene uptake was monitored remotely. After the prescribed reaction interval, the reaction was terminated by venting the ethylene. The samples were removed from the glovebox and any polymer that formed was precipitated from solution by addition of methanol. Excess MAO was quenched by the addition of 3 M HCl solution. After stirring each sample overnight, any polymer that had precipitated was collected by filtration, and dried in a vacuum oven overnight.

5.8 References

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[1] It should be noted that the ligation of our [C,O]-chelating NHCs to Ru was attempted as well, with a view toward the synthesis of new catalysts for olefin metathesis (Funk, T; Connell, B.; Grubbs, R. H., unpublished results). Unfortunately, no Ru-alkylidene complex of the novel chelating NHCs was ever isolated. It is not clear why.

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[3] Matsukawa, N.; Matsui, S.; Mitani, M.; Saito, J.; Tsuru, K.; Kashiwa, N.; Fujita, T. *J. Mol. Cat. A: Chemical* **2001**, *169,* 99–104.

[4] Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847–6856.

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[6] For an example of ethylene/norbornene copolymerization catalyzed by a Ti complex similar to **5.3** and **5.4**, see: Yoshida, Y.; Saito, J.; Mitani, M; Takagi, Y.; Matsui, S.; Ishii, S.; Nakano, T.; Kashiwa, N.; Fujita, T. *Chem. Commun.* **2002**, 1298–1299. For an example of α-olefin polymerization with Ti(sal)$_2$ catalysts, see: Saito, J.; Mitani, M.; Matsui, S.; Kashigawa, N.; Fujita, T. *Macromol. Rapid Commun.* **2000**, *21*, 1333–1336.

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