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Synthesis of neutral nickel catalysts for ethylene polymerization – the influence of ligand size on catalyst stability†

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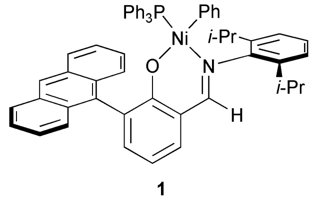
A facile synthesis of nickel salicylaldimine complexes with labile dissociating ligands is described. In addition to producing highly active ethylene polymerization catalysts, important insights into the effect of ligand size on catalyst stability and information on the mechanism of polymerization are provided.

The incorporation of directly functionalized olefinic monomers, such as acrylates, into a linear polyethylene backbone has long been a target of academic and industrial research.[1] Several approaches to this problem have met with varying success, including the use of protected monomers,[2] post-functionalization of the polymer,[3] and the direct incorporation of functionalized monomers using late transition-metal catalysts.[4] To date, however, there exists no effective means of directly incorporating functionality into a linear polyethylene chain by an industrially feasible process. In approaching this problem, we were inspired by examples of neutral group 10 transition metal complexes that serve as effective catalysts for the oligomerization and polymerization of ethylene, and tolerate functionality.[5] Additionally, it has been shown, by Brookhart and others, that the presence of a bulky ligand set leads to high-molecular weight polymer – the bulk serving to decrease the rate of chain transfer by preventing coordination of incoming ethylene at the axial site of the active catalytic species.[4a]

We have reported a class of neutral nickel-based complexes with bulky salicylaldimine (sal) ligands (of which **1** is an example)[6] that serve as single-component catalysts for the homopolymerization of ethylene and the co-polymerization of ethylene and non-vinyl functionalized monomers such as esters, alcohols, anhydrides and amides.[7] These were synthesized by treatment of the sodium salt of the ligand with $NiClPh(PPh_3)_2$. Although this synthetic approach provided for moderately active catalysis, the presence of a relatively strongly coordinating phosphine ligand slowed down the rates of dissociation and propagation.

Herein, we describe the synthesis of 'phosphine free' nickel (sal) complexes with highly labile dissociating ligands. Treatment of free phenolic ligand with (tmeda)$NiMe_2$ (tmeda = *N*, *N*, *N*′, *N*′-tetramethylethylenediamine) in acetonitrile proved a general and useful method for ligation of salicylaldimine ligands to the metal (Scheme 1).[8] Attempts to form complexes **5–7** with ligands **2–4** using this 'phosphine free' synthesis led not only to more active ethylene polymerization catalysts, but also provided insight on the important role played by ligand size in catalytic activity and on mechanistic behavior.



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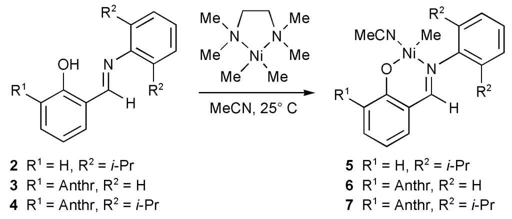
Reacting (tmeda)$NiMe_2$ with ligand **2** in deuterated acetonitrile initially provided the expected square planar complex **5**, which could be observed by ^{1}H-NMR. However, after one hour, crystals of bis-ligated **8** began to form (Fig. 1). X-Ray crystallographic analysis revealed that the two bulky diisopropylphenyl groups are *trans* to each other.‡ Complex **5** could not be isolated. Structure **8** appears to be a thermodynamic sink for nickel(sal) compounds. Bis-ligation of chelating ligands has been noted in a similar system,[9] and as is the case with **8**, the bis-ligated complex was not an active catalyst for ethylene polymerization. Thus, bis-ligation has an important implication in catalyst stability and lifetime.

Interestingly, when ligand **3** was used in the 'phosphine free' synthesis, complex **9** was obtained (Fig. 1). Although it was not



Scheme 1

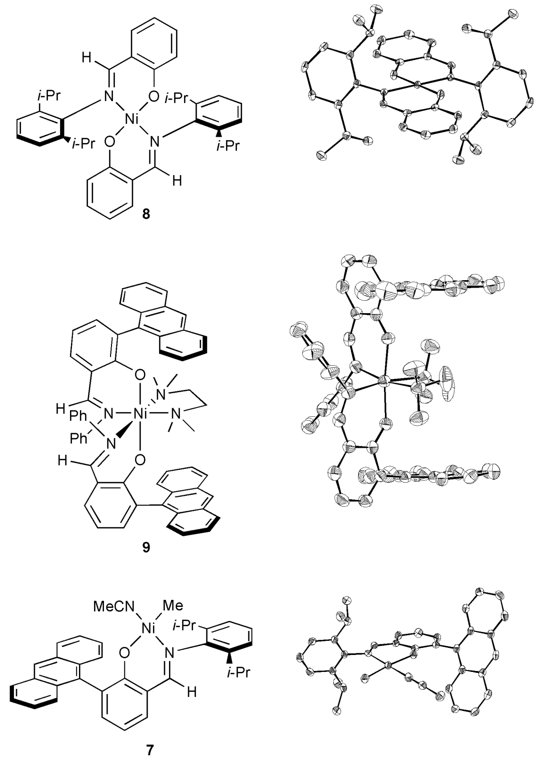


Fig. 1 Displacement ellipsoid representations of complexes **7**, **8** and **9**.

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† Electronic supplementary information (ESI) available: experimental protocol for (tmeda)$Ni(Me)_2$ and compounds **3,4,7,8,9** and **10** and ^{1}H-NMR magnetization transfer data for compound **7**. See http://www.rsc.org/suppdata/cc/b3/b306701g/

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observed, mono-ligated **6** presumably is formed first, but then reacts further to give **9**. In this complex, the tmeda ligand remains bound to give an octahedral coordination complex in which the bulky anthracenyl groups are oriented *trans* to each other. This structure illustrates the importance of balancing the ligand bulk evenly around the metal center. Similar to **8**, complex **9** was not active for ethylene polymerization. Based on the behaviour of ligands **2** and **3**, it was reasoned that combining the two bulky groups in one ligand might lead to mono-ligation, and complexes capable of ethylene polymerization.

The use of bulky ligand **4** in the 'phosphine free' synthesis provided crystals of the desired mono-ligated complex **7**. The presence of both bulky groups on **4** hinders the coordination of two chelating ligands on the same metal center. As expected, **7** is a highly active catalyst for ethylene polymerization, producing up to 6×10^3 kg PE mol^{-1} h^{-1} (10 °C, 250 psig of ethylene).[7] This activity is attributed to the lability of the acetonitrile ligand, as demonstrated by its ready displacement by more coordinating ligands such as phosphines.

Initially, bulky ligands were targeted to provide high molecular weight polymer. When comparing the products of the 'phosphine free' synthesis from ligands **2** and **3** with that from **4**, it is realized that steric bulk also plays a role in slowing deactivation of polymerization catalysts by preventing bis-ligation. If a strongly coordinating dissociating ligand (a phosphine for example) is used, ligands such as **2** and **3** provide viable (though less active) polymerization catalysts. If, however, a weaker dissociating ligand is used, there exists a higher concentration of coordinatively unsaturated nickel species which will bind another ligand, if the size allows it. Only when the ligand is sufficiently bulky do compounds featuring highly labile ligands remain mono-ligated, as is necessary for catalysis.

While the bis-ligated analogue of **4** was not formed *via* the 'phosphine-free' synthesis, it could be synthesized by treatment of the sodium salt of **4** with $NiBr_2(PPh_3)_2$ (Fig. 2). The high strain experienced in fitting two very large ligands around a single metal center is exhibited by a significant distortion from square planar geometry (31.2°). In addition, while compounds **8** and **9** are air- and moisture-stable, **10** rapidly decomposes when exposed to air. The instability of **10** illustrates that mono-ligation is preferred when the ligand is sufficiently bulky.

The presence of acetonitrile in complex **7** provided insight into the mechanism of ethylene polymerization previously unavailable in phosphine-containing systems by revealing the nature of the catalyst's resting state. The ^{1}H-NMR spectrum of **7**, with Ni–Me resonances at -0.98 and -1.45 ppm (CD_2Cl_2), showed that, in solution, the catalyst exists as *cis* and *trans* isomers with the *trans* isomer (as determined by ^{1}H-NOE between the Ni–Me and ligand isopropyl groups) being dominant (3 : 1), with a difference in ground state energy of 0.65 kcal mol^{-1} at 298 K. Proton magnetization transfer revealed that the methyl group isomerizes within the NMR time scale with an estimated barrier to migration of 17 kcal mol^{-1}.[10] An isomerization/insertion pathway has been observed for the insertion of alkyl groups into CO using palladium catalysts with unsymmetrical ligands.[11] Such a propagation cycle has also been predicted computationally for phosphine-based nickel(sal) complexes[12] where isomerization occurs upon olefin complexation, followed by insertion of ethylene to generate the energetically favored *trans* isomer. Given the observed epimerization behavior of **7**, it is possible that this mechanism holds true for it also.

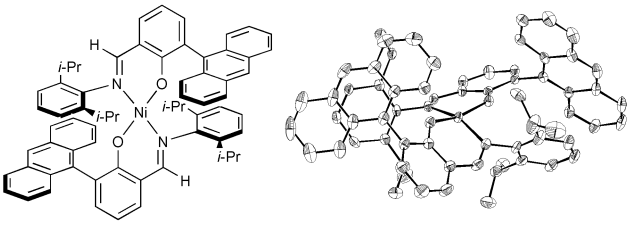

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Fig. 2 Displacement ellipsoid representation of complex **10**.

This synthetic approach to neutral nickel salicylaldimine complexes has led to more active ethylene polymerization catalysts, and has provided mechanistic insight. It is clear that a ligand framework must be sufficiently bulky to allow for a catalytically active mono-ligated complex, as is the case with **7**. In addition, based on the isomerization behavior of complex **7**, the use of acetonitrile as a ligand may allow the complex to reach an energetically favored state between insertions, allowing for faster catalysis.

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Notes and references

‡ *Crystallographic data for* **7**: $C_{36}H_{36}N_2NiO$, M = 571.38, Orthorhombic, space group *Pbca* (#61), $a = 18.0982(13)$, $b = 14.400(1)$, $c = 22.3830(16)$ Å, $V = 5833.3(7)$ Å^3, $Z = 8$, $T = 98$ K, $\mu = 0.70$ mm^{-1}, 4213 independent reflections, $R_{int} = 0.061$, $R1 = 0.029$, $wR2 = 0.052$ [$F_0 > 4\sigma(F_0)$]. CCDC 212728. **8**: $C_{38}H_{44}N_2NiO_2$, M = 619.46, Triclinic, space group $P\bar{1}$ (#2), $a = 8.0050(5)$, $b = 10.1054(6)$, $c = 11.0123(7)$ Å, $\alpha = 113.519(1)°$, $\beta = 97.426(1)°$, $\gamma = 97.673(1)°$, $V = 793.01(8)$ Å^3, $Z = 1$, $T = 93$ K, $\mu = 0.65$ mm^{-1}, 3382 independent reflections, $R_{int} = 0.035$, $R1 = 0.029$, $wR2 = 0.071$ [$F_0 > 4\sigma(F_0)$]. CCDC 162674. **9**: $C_{60}H_{52}N_4NiO_2$, M = 919.77, Orthorhombic, space group *Pbca* (#61), $a = 17.8013(6)$, $b = 19.2789(6)$, $c = 27.0247(9)$ Å, $V = 9274.6(5)$ Å^3, $Z = 8$, $T = 98$ K, $\mu = 0.47$ mm^{-1}, 11208 independent reflections, $R_{int} = 0.078$, $R1 = 0.044$, $wR2 = 0.057$ [$F_0 > 4\sigma(F_0)$]. CCDC 161495. **10**·2(CH_3CN): $C_{70}H_{66}N_4NiO_2$, M = 1053.98, Monoclinic, space group $P2_1/c$ (#14), $a = 10.8701(8)$, $b = 28.890(2)$, $c = 18.3122(14)$ Å, $\beta = 97.839(1)°$, $V = 5697.0(7)$ Å^3, $Z = 4$, $T = 93$ K, $\mu = 0.39$ mm^{-1}, 13770 independent reflections, $R_{int} = 0.097$, $R1 = 0.050$, $wR2 = 0.078$ [$F_0 > 4\sigma(F_0)$]. CCDC 212729. See http://www.rsc.org/suppdata/cc/b3/b306701g/ for crystallographic data in .cif or other electronic format.

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