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Neutral Nickel(II)-Based Catalysts for Ethylene Polymerization

Chunming Wang,[†] Stefan Friedrich,[†] Todd R. Younkin,[†] Robert T. Li,[†]
Robert H. Grubbs,*[,†] Donald A. Bansleben,[‡] and Michael W. Day[§]

The Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, Sealed Air Corporation, Cryovac Division, 7500 Grace Drive, Columbia, Maryland 21044, and Beckman Institute, X-Ray Crystallography Laboratory, California Institute of Technology, Pasadena, California 91125

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Summary: Neutral salicylaldiminato Ni(II) complexes have been synthesized, and their structure has been confirmed by an X-ray analysis of complex ***4e****. These compounds are active catalysts for the polymerization of ethylene under mild conditions in the presence of a phosphine scavenger such as Ni(COD)$_2$ or B(C$_6$F$_5$)$_3$.*

In recent years there has been increasing interest in the development of late transition metal based complexes as catalysts for the polymerization of α-olefins and functionalized olefins under moderate conditions.[1b,c,7] Most notable are Brookhart's cationic Ni(II)- and Pd(II)-based catalysts of the type [ArN=C(R)C(R)=NAr]M−CH$_3{}^+$, in which the metal center is efficiently shielded from associative displacement by bulky substituents on the diimine ligands.[1,2] These systems serve as promising alternatives to both traditional Ziegler−Natta[3] and metallocene catalysts[4] for the polymerization of α-olefins to high molecular weight polymers and demonstrate the ability to produce copolymers of ethylene with various functionalized vinyl monomers (M = Pd).[1b,c]

Traditionally, however, late-metal catalysts were only found to produce dimers or low-molecular-weight oligomers due to chain termination *via* β-hydride elimination.[5] For example, the Shell higher olefin process (SHOP) is based in part on the neutral catalyst [Ph$_2$PC(R)=C(R)O]Ni(Ph)L, which was developed to oligomerize ethylene to higher α-olefins.[6] The SHOP catalyst was shown to polymerize ethylene to high molecular weight polymer under extreme conditions[7a] and also under milder conditions in the presence of a phosphine scavenger such as Ni(COD)$_2$.[7b,c] Recently, Cavell demonstrated that neutral Ni(II) systems based on a pyridinecarboxylate ligand can be mildly active in both the polymerization of ethylene and the copolymerization of ethylene and CO without the use of cocatalysts.[8] In this contribution, we report the synthesis of neutral Ni(II) salicylaldiminato complexes and their application as highly active catalysts for the polymerization of ethylene to high molecular weight polymers under moderate conditions.

Organometallic complexes containing Schiff bases have been investigated with a vast array of metals.[9] They are attractive ligands because of their ease of preparation and simple modification of both steric and/or electronic effects. Klein reported the synthesis of Ni(II) salicylaldiminato complexes with alkyl and aryl substituents on the ketimine fragment Ni(Me)(PMe$_3$)-{η^2-1-[C(H)=*N*R]-2-*O*-C$_6$H$_4$} (R = Me, *i*-Pr, *t*-Bu, Ph).[10] We believed that the introduction of bulkier substituents on the ketimine nitrogen and the phenolic ring might block the axial faces of the metal center, retarding the rate of associative displacement, as seen by Brookhart

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* To whom correspondence should be addressed. Fax: (626) 564-9297. E-mail: rhg@cco.caltech.edu.

[†] Arnold and Mabel Beckman Laboratory of Chemical Synthesis, California Institute of Technology.

[‡] Sealed Air Corporation.

[§] X-Ray Crystallography Laboratory, California Institute of Technology.

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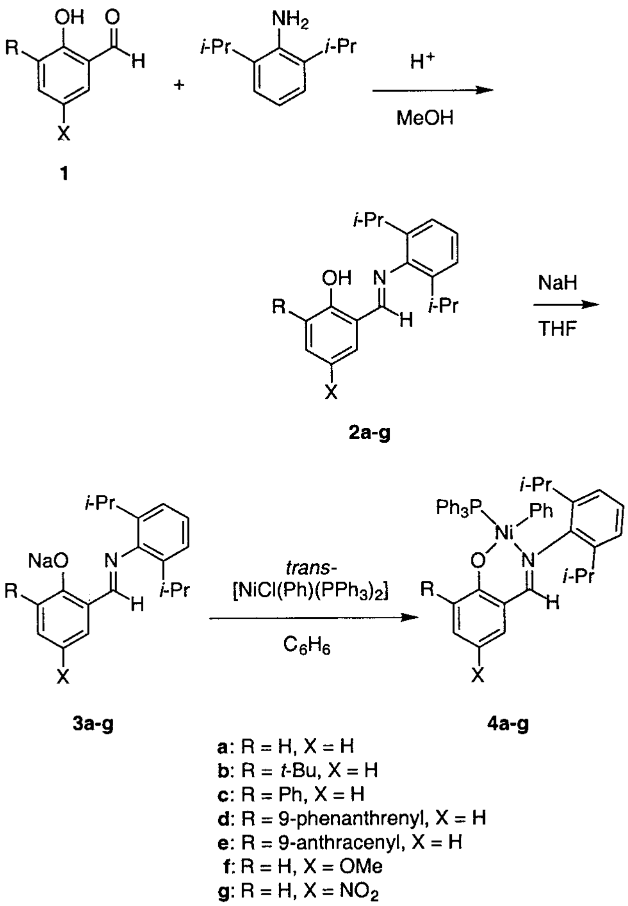
Scheme 1



et al.[1,2] Additionally, bulky groups might decrease the rate of catalyst deactivation, which has been shown to occur by ligand disproportionation and dimerization in the analogous SHOP system.[11] Finally, we argue that use of a neutral Ni(II) center might facilitate the polymerization of functionalized comonomers, as compared to a more oxophilic cationic metal center.

Salicylaldimine ligands **2a**–**g** were prepared by condensation of the corresponding salicylaldehydes **1** and 2,6-diisopropylaniline in excellent yields (Scheme 1).[12] The salicyladehydes **1d** and **1e**, containing the bulky aromatic 9-phenanthrenyl and 9-anthracenyl groups, respectively, were synthesized in a manner analogous to the preparation of both the *t*-Bu- (**1b**) and Ph-substituted (**1c**)[13] compounds by formylation of the corresponding phenols[15] with paraformaldehyde/tin chloride in low yields.

The sodium salts **3a**–**g** were obtained upon treatment of **2a**–**g** with NaH in THF. By reaction of **3a**–**g** with *trans*-[NiCl(Ph)(PPh_3)$_2$],[15] the Ni(II) complexes **4a**–**g** were synthesized in good yields.[13] According to the NMR spectra, the diamagnetic Ni(II) complexes adopt a square-planar geometry, as seen by Klein.[10] In the ^{1}H NMR spectra of **4a**–**g** the imine protons show a characteristic ^{31}P ($J_{HP} \approx 9$ Hz) coupling, which corresponds to PPh_3 bound in a *trans* relationship to the ketimine. The signals for the triphenylphosphine ligand in the ^{31}P NMR spectra of complexes **4a**–**g** are observed between 21.9 and 25.9 ppm.

Table 1. Crystal Data and Structure Refinements of 4e·2C_7H_8[16]

empirical formula	$C_{71}H_{66}NNiOP$
fw	1038.93
cryst syst	monoclinic
a (Å)	20.397(9)
b (Å)	10.994(5)
c (Å)	26.028(13)
β (deg)	107.85(4)
V (Å^3)	5556(5)
Z	4
ρ_{calcd} (g cm^{-3})	1.24
space group	$P2_1/c$
F(000)	2200
μ(Mo $K\alpha$) (cm^{-1})	0.710 73
θ range (deg)	1.6–22.5
no. of rflns	7234
no. of variables	731
residuals: R; R_w	0.1126; 0.1069
data/param ratio	9.9
largest peak/ hole in final diff map (e Å^{-3})	+0.330/−0.298

In addition to the NMR data presented above, the structure of the salicylaldiminato complexes was further confirmed by a single-crystal X-ray structure analysis of complex **4e**.[16–18] The data collection and refinement data of the analysis are summarized in Table 1, and the ORTEP diagram is shown in Figure 1. In the solid state, the molecule adopts a nearly ideal square-planar coordination geometry with the Ni displaced approximately 0.03 Å from the plane of its ligands. The bulky 2,6-diisopropylbenzimine occupies the position *trans* to the triphenylphosphine ligand with a nearly linear P–Ni–N angle (172.16(12)°). The phenyl group attached to Ni lies *trans* to O with an O–Ni–C31 angle of 166.2(2)°. The Ni–O, Ni–N, and Ni–C31 bond distances are similar to those in known nickel complexes.[2,6d,7b,8a] The Ni–PPh_3 bond of **4e** (2.172(2) Å) is less than 0.01 Å longer than in Cavell's [Ni(PPh_3)(*o*-tolyl)(N~O)] complexes with the N~O bidentate pyridinecarboxylate ligands (d(Ni–P) = 2.163(2) Å),[8a] suggesting that in the solid state there is little or no steric interaction between the anthracene moiety and the triphenylphosphine ligand. The anthracene unit swings out of the plane of the phenolato fragment, forming an approximately 80° angle between the planes of the aryl moieties.

The polymerization of ethylene by complexes **4a**–**g** was accomplished by dissolving the corresponding cata-

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[11] Bulky substituents blocking the axial faces of the metal center should also retard the rate of chain termination due to rapid associative displacement, as proposed by Brookhart.[1a]

[12] Experimental details are given in the Supporting Information.

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[16] Crystals suitable for X-ray structure determination were grown from a solution of **4e** in toluene at −20 °C over a few days. The yellow crystal used for data collection had dimensions 0.48 × 0.10 × 0.07 mm. The X-ray diffraction data were collected by using a CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were determined by a least-squares analysis of 25 automatically centered reflections in the range 8.6° < Θ < 10.9°. Data were collected at 160 K in the range Θ = 1.6–22.5°. A total of 16 164 reflections were collected, 7238 of which were independent. A set of 4691 reflections with $F_o^2 > 2\sigma(F_o^2)$ were observed. The structure was solved by direct methods using the SHELXS-86 program. Hydrogen atoms appeared in the difference Fourier map. They were restrained to these positions during refinement, and their U_{iso} values were fixed at 1.1 times the U_{eq} value of the attached atom. Refinement was full-matrix least squares on F^2 using SHELXL-93.

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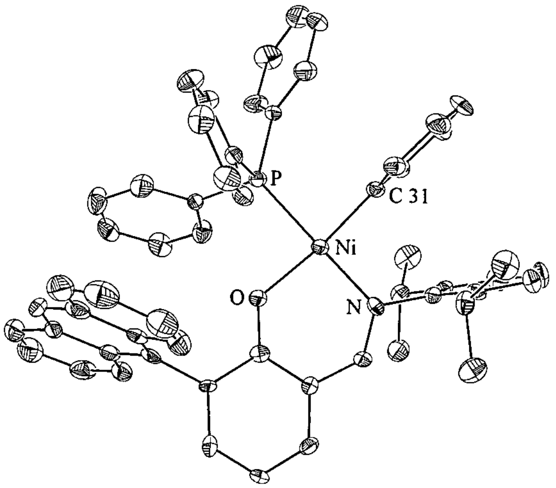

Figure 1. ORTEP of **4e**.

Table 2. Polymerization Data for 4a−g[a]

entry no.	catalyst/ cocatalyst	polymer yield (g)	M_w[b]	M_w/ M_n	branches/ 1000C	catalyst productivity[c]
1	**4a**/Ni(COD)$_2$	2.0	4 000	1.5	45	26.7
2	**4a**/Ni(COD)$_2$ [d]	2.4	10 000	1.4	20	32.0
3	**4b**/Ni(COD)$_2$	3.5	11 400	1.8	55	46.7
4	**4c**/Ni(COD)$_2$	6.1	23 500	2.3	40	81.3
5	**4c**/ Ni(COD)$_2$ [e]	9.9	24 2000	2.1	5	132.0
6	**4d**/Ni(COD)$_2$	7.0	37 700	3.8	30	93.3
7	**4d**/B(C$_6$F$_5$)$_3$	7.0	49 500	6.8	35	93.3
8	**4e**/Ni(COD)$_2$	7.4	54 000	6.4	30	98.7
9	**4f**/Ni(COD)$_2$	1.0	7 300	1.7	53	13.3
10	**4 g**/Ni(COD)$_2$[f]	19.0	360 000	12.4	22	253.3

[a] Polymerizations were carried out with 75 μmol of catalyst and 2 equiv of cocatalyst without temperature control for 40 min (except **4d** and **4e**; 15 min) in 90 mL of toluene at 7 atm ethylene pressure. [b] Determined by GPC vs polyethylene standards, uncorrected. [c] kg of polyethylene/(mol of Ni). [d] Reaction at 14 atm ethylene pressure. [e] Reaction at 0 °C. [f] More solvent added during the reaction.

lyst in toluene, followed by injection of a toluene solution of the appropriate phosphine scavenger (Ni(COD)$_2$ or B(C$_6$F$_5$)$_3$). The phosphine scavengers bind PPh$_3$ more strongly than the nickel(II) catalysts, effectively removing phosphine from the solution. The results of several representative polymerizations are summarized in Table 2.[12] Attempts to polymerize ethylene with **4a** and no phosphine sponge gave little uptake of ethylene and yielded no polyethylene. However, when **4a** was combined with a phosphine scavenger (entry 1), a 5−8 min induction period was followed by rapid ethylene uptake and a rise in the reaction temperature. It has been proposed for the SHOP system that the induction period is due to the slow insertion of ethylene into the Ni−Ph bond, followed by β-hydride elimination to generate the active "Ni-H" species.[7b,c] To date, low-temperature NMR studies of ethylene consumption by **4a** have shown neither a "Ni-H" species nor the formation of styrene, leading us to believe that the induction period may be due to the relatively slow abstraction of PPh$_3$ from the Ni(II) center. The resultant polyethylene demonstrated a fairly low molecular weight and moderate branch content. Increasing the pressure of the polymerization with **4a** (14 atm, entry 2) yielded polyethylene with a higher M_w value. This is consistent with observations made using the SHOP system, where higher pressure reduces the rate of chain termination.[7b]

As outlined above, chain migratory processes (which control branching) and also chain termination reactions (which control M_w) were expected to be suppressed by bulky substituents in the 3-position of the salicylaldiminato ring.[1] When complexes **4b**−**4e** were used as catalysts, no induction period was observed. The polymerizations were highly exothermic, with reaction temperatures rising up to 95 °C. These catalysts produced higher molecular weight polyethylene than did **4a**, with M_w values of 11 400 to 54 000, and exhibited a slight decrease in the total number of branches (except **4b**, entry 3). Entry 5 demonstrates that temperature has a direct influence on both the molecular weight and branch content of the resultant polymer.

The effect of various electronic substitutents on the catalysts' activities was investigated by simple *para* substitution of the salicylaldimine ligand. Electron-deficient systems such as **4g** were found to be the most active, while catalyst activity was found to diminish in relatively electron-rich complexes such as **4f**. Polymerization with complex **4g** occurs with a relatively long induction period of approximately 20 min. This observation is consistent with a mechanism in which phosphine dissociation is the rate-limiting step, since an electron-withdrawing ligand strengthens the Ni−PPh$_3$ bond. Although complex **4g** exhibits greater activity, it is not clear at this point why it gives a broad molecular weight distribution.

In conclusion, several Ni(II) salicylaldiminato systems have been developed which are highly active for the polymerization of ethylene. Bulky substituents in the 3-position of the salicylaldiminato ring were found to enhance the activity of the catalyst and lower the number of branches in the resulting polyethylene. An electron-withdrawing group in the 5-position of the salicylaldiminato ring also increases catalyst activity. With these systems, moderately high molecular weight polymer with about 10−50 branches per 1000 carbons can be obtained. As observed in other late-metal systems, branching can be controlled by the variation of both the temperature and pressure.[1,2,5−8] Rational design of new ligands to further control branching, obtain polymer with higher molecular weights, and decrease or eliminate the requirement for a cocatalyst is currently under investigation and will be reported soon.

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Supporting Information Available: Text giving experimental details, NMR data, and analytical data for the compounds prepared in this work and tables of crystal and intensity collection data, positional and thermal parameters, and all bond distances and angles for **4e** (19 pages). Ordering information is given on any current masthead page.

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