Synthesis, structure, and olefin polymerization with nickel(II) N-heterocyclic carbene enolates†

Benjamin E. Ketz, Xavier G. Ottenwaelder and Robert M. Waymouth*

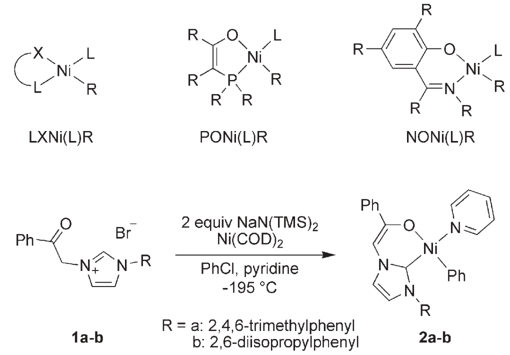
Received (in Berkeley, CA, USA) 4th August 2005, Accepted 26th September 2005
First published as an Advance Article on the web 20th October 2005
DOI: 10.1039/b511202h

Two novel N-heterocylic carbene enolate nickel complexes have been prepared and shown to be active for ethylene and propylene polymerization to yield linear polymers.

Neutral Ni(II) complexes supported by chelating anionic LX ligands are an important class of olefin oligomerization and polymerization catalysts.[1–9] The pioneering studies by Keim[5,10] formed the basis of the Shell Higher Olefin Process (SHOP) and stimulated the development of a variety of Ni complexes for ethylene oligomerization, polymerization, and copolymerization.[7,8,10,11] Brookhart's contributions with cationic Ni and Pd complexes sparked renewed interest in late transition metal catalysts for ethylene polymerization.[2,12,13]

The selectivity of neutral Ni catalysts for ethylene polymerization *versus* oligomerization depends on several interrelated factors including both the steric[1,3] and electronic[14,15] properties of the ligands, as well as the nature of the neutral L ligand.[9] Keim's studies implicating that dialkylphosphinoenolate Ni complexes of electron-donating alkyl phosphines lead to higher M_n polymers[14,15] stimulated us to investigate anionic enolate ligands based on N-heterocyclic carbenes (NHCs).[16] NHCs are versatile ligands that share many of the coordination properties of phosphines, but are more potent σ-donors.[17–20] To date, there are no known nickel complexes with monoanionic chelating NHC ligands, and neutral Ni catalysts based on NHCs have not been used for polymerization. However, two reports describe the structures of anionic NHC complexes of Pd,[16,21] and cationic Ni NHC complexes have been investigated for ethylene polymerization.[22,23] Herein, we describe the synthesis, structure, and polymerization behavior of two nickel carbene enolate complexes.

Initial attempts to prepare the nickel carbene complexes from singly or doubly deprotonated imidazolium salts **1a,b** and Ni halides were unsuccessful. Treatment of **1a,b** with $(Ph_3P)_2Ni(Ph)Cl$ in the presence of 2 equiv. of $NaN(TMS)_2$ yielded the Ph_3P-ligated Ni carbene phenyl complex, but removal of the excess Ph_3P proved difficult. After screening a number of reactions, we developed an expedient synthesis of the pyridine adduct, which we anticipated would be more labile than the phosphine adduct toward substitution by ethylene.[9] Complexes **2a,b** were prepared in high yield in a one pot procedure (eqn 1). The imidazolium salt, 1 equiv. of bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$), and 2 equiv. $NaN(TMS)_2$ were frozen in pyridine. As this mixture thawed, an excess of chlorobenzene was added and the mixture stirred for 1 h at 25 °C. Removal of the solvent *in vacuo* and recrystallization by slow diffusion of pentane into a CH_2Cl_2 solution of **2a** layered with Et_2O provided crystals suitable for X-ray diffraction.‡



LXNi(L)R PONi(L)R NONi(L)R

(1)

1a-b

R = a: 2,4,6-trimethylphenyl
b: 2,6-diisopropylphenyl

2a-b

The structure of **2a** (Fig. 1) reveals a square-planar coordination for Ni. The Ni–C1 bond length of 1.848 Å is shorter than that observed by Sigman in the complex (IPr)Ni(Cl)(allyl) (Ni–NHC = 1.903 Å, IPr = *N*,*N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidine),[24] and that of other known Ni–NHC complexes.[25–28] The Ni–O bond of 1.891 Å is slightly shorter than that of an analogous diphenylphosphinoenolate complex (Ni–O = 1.914 Å).[29] The bond angles and lengths within the carbene heterocycle are comparable to those of the analogous Pd carbene enolate.[16] The mesityl ring is nearly perpendicular to the NHC, with a C2–N2–C12–C13 dihedral angle of 99.6° for **2a**. The conformation of the chelate ring is slightly different between this structure and the analogous Pd complex, presumably due to the different covalent

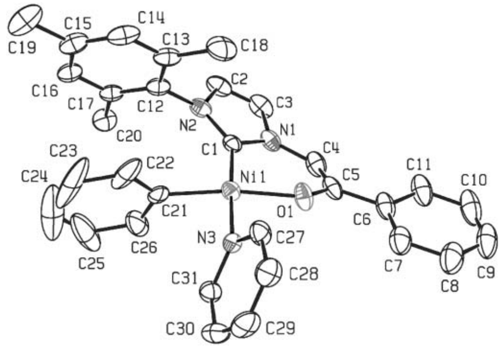


Fig. 1 ORTEP diagram of **2a**, selected bond lengths (Å) and angles (deg): Ni–C1, 1.848(3); Ni–C21, 1.891(2); Ni–N3, 1.934(2); Ni–O, 1.891(2); C1–N1, 1.375(4); C1–N2, 1.373(4); N1–C4, 1.406(4); C4–C5, 1.353(5); C5–O, 1.315(4); C1–Ni–C21, 93.17(12); C21–Ni–N3, 88.91(10); N3–Ni–O, 85.43(10); O–Ni–C1, 92.56(12); N1–C1–N2, 103.1(2); N1–C4–C5, 122.7(3); C4–C5–O, 122.7(3).

Department of Chemistry, Stanford University, Stanford, California, USA. E-mail: waymouth@stanford.edu; Fax: +01 650 736 2262; Tel: +01 650 723 4515

† Electronic supplementary information (ESI) available: experimental details, representative NMR spectra, and crystal structure data. See DOI: 10.1039/b511202h

radii. For the palladium complex, the atoms of the carbene enolate ligand are coplanar; but for the nickel complex, the ligand is puckered, as shown by the C1–Ni–O1–C5 dihedral angle of 27.3°.

Toluene solutions of complexes **2a,b** are active for ethylene polymerization (1–15 bar ethylene, 20–60 °C) in the absence of a co-catalyst to give linear polyethylenes (T_m = 123–132 °C) of modest molecular weights (M_n = 1000–7100 g mol^{-1}, Tables 1 and 2). Analysis of the endgroups reveals a high selectivity for terminal alpha olefins (95% to >98%). The productivities of these catalysts under these conditions range from 0.8–56 kg PE (mol Ni)$^{-1}$ h^{-1} (TOF = 28–2000 mol E (mol Ni)$^{-1}$ h^{-1}), which are comparable to the SHOP-type catalysts but lower than the neutral salicylaldimine,[3] or cationic diimine catalysts.[2] Complex **2b** is more active and yields higher M_n polymer than **2a**. For **2b**, the activity increases with temperature and ethylene pressure. Higher ethylene pressure also increases the M_n of the polymer produced, but the effect is modest (Table 2). The use of MAO as a co-catalyst leads to much lower activities and low M_n branched polymers. In contrast to the SHOP-type (PO)NiPhL complexes, there does not appear to be an extended induction period for ethylene polymerization.[8]

Studies at different reaction times and temperatures reveal that the catalyst rapidly decomposes to an inactive species. Increasing the time of polymerization has little effect on the yield; at 15 bar ethylene and 60 °C, similar amounts of polymer were obtained from **2b** after 20 min, 1 h, and 3 h. Even at 20 °C, there is a decrease in activity with an increase in time. Small amounts of nickel black were noted at the end of polymerizations, especially after longer runs. Monitoring a 1 bar polymerization in a glass vessel revealed a change in the color of the solution from brilliant yellow to yellowish brown after 12 min.

Analysis of the polymer endgroups provided some insight into the origin of catalyst deactivation. Signals characteristic of saturated methyl endgroups, α-olefin endgroups, and phenyl endgroups are observed in the ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum, a resonance at 2.59 ppm, characteristic of a benzylic methylene from a phenyl endgroup, and a resonance at 2.06 ppm, characteristic of an allylic methylene from an α-olefin endgroup, are observed. A significant fraction of phenyl endgroups were observed in the polyethylenes, especially at lower temperatures. The ^{1}H NMR spectrum of the polymer from run 2 (20°C) revealed a ratio of Ph/olefin endgroups of 1.43, suggesting that a fraction of the chains are living and are terminated by protonation upon workup with HCl. This ratio decreases at longer reaction times or higher temperatures. These results are consistent with the insertion of ethylene into the Ni–Ph bond to initiate chain growth. Similar observations have been made with SHOP-type catalysts, although rapid chain-transfer was proposed to generate styrene and ultimately a Ni–R which re-initiates chain grown to yield saturated alkyl endgroups.[1] The high fraction of phenyl endgroups relative to olefin endgroups suggests that following chain-transfer, the resultant species is unstable and decomposes rapidly, presumably by reductive elimination of the imidazolium salt. If chain-transfer occurs by β-H elimination, reductive elimination of the Ni–H would generate the imidazolium salt. Such reductive eliminations can be facile for group 10 metals as shown by Cavell.[27,30,31]

We did not observe alkylimidazolium endgroups, implying that reductive elimination from the Ni-alkyls does not occur under these conditions.[21] Thus, our results are most consistent with chain-transfer by β-H elimination to generate an unstable Ni–H.[32,33] Other catalyst decomposition pathways are possible

Table 1 Ethylene polymerization of **2** and effects of temperature, time, solvent, co-catalyst

Run	Precat.	Temp.	Time	Yield[a]	Activity[b]	T_m, °C[a]	M_n	M_w/M_n	Branches[c]	α-Olefins	Ph/Olefin[d]
1	2a	60 °C	20 min	415 mg	31	123	1490	2.5	<2	>98%	0.18
2	2b	20 °C	1 h	364 mg	9.1	131	5515	2.03	<2	>98%	1.43
3	2b	20 °C	3 h	545 mg	4.5	132	7100	2.48	<2	>98%	0.72
4	2b	40 °C	1 h	693 mg	17	130	5600	2.2	<2	>98%	0.42
5	2b	40 °C	3 h	757 mg	6.3	130	5750	2.24	<2	>98%	0.33
6	2b	60 °C	20 min	741 mg	56	129	3960	2.1	<2	98%	0.29
7	2b	60 °C	1 h	750 mg	19	130	4050	2.1	<2	98%	0.26
8	2b	60 °C	3 h	734 mg	6.1	130	4180	2.1	<2	97%	0.34
9	2b	80 °C	20 min	680 mg	51	129	3020	1.95	<2	95%	0.24
10	2b[e]	60 °C	1 h	478 mg	12	129	3920	2.18	<2	98%	0.25
11	2b[e]	60 °C	3 h	454 mg	3.8	130	4240	2.21	<2	98%	0.31
12	2b[f]	60 °C	3 h	96 mg	0.8	124	3410	2.42	11	89%	0.025

[a] All polymerizations were conducted at 15 bar ethylene with 40 μmol Ni in 80 mL toluene with no co-catalyst unless specified otherwise. Average of two runs. [b] kg PE (mol Ni)$^{-1}$ h^{-1}. [c] Branches per 1000 carbons; in the last entry only methyl branches are observed. [d] Ratio of phenyl/olefin endgroups by ^{1}H NMR. [e] 79 mL heptane, 1 mL toluene. [f] MAO co-catalyst used Al/Ni = 50.

Table 2 Effects of ethylene pressure variation in polymerization of **2b**

Run	Pressure	Yield [a]	Activity [b]	T_m, °C[a]	M_n	M_w/M_n	Branches [c]	α-Olefins	Ph/Olefin[d]
13	1.0 bar	360 mg	27	118	1000	2.44	<2	96 %	0.09
14	3.1 bar	409 mg	31	126	2190	2.46	<2	95 %	0.25
15	6.5 bar	500 mg	38	128	3460	2.4	<2	96 %	0.27
16	15 bar	741 mg	56	129	3960	2.1	<2	98 %	0.29

[a] All polymerizations were conducted at 60 °C with 40 μmol **2b** in 80 mL toluene with no co-catalyst. Average of two runs. [b] kg PE (mol Ni)$^{-1}$ h^{-1}. [c] Branches per 1000 carbons. [d] Ratio of phenyl/olefin endgroups by ^{1}H NMR.

and are the subject of ongoing investigations. These results suggest that the low productivity of these catalysts is not due to a low intrinsic activity for olefin insertion, but rather it is a consequence of the low turnover number in polymer chains resulting from the instability of the Ni–H.

The high linearity of the polyethylenes produced, particularly at low ethylene pressures (run 13) is noteworthy, especially in comparison to neutral salicylaldimine and cationic diimine Ni catalysts, which generate more highly branched polyethylenes.[2,13,34,35] One possible cause of the high selectivity for linear products is a low probability of chain-walking for these neutral Ni carbene complexes. Alternatively, if chain-walking does occur, the high selectivity for linear products could be a consequence of a higher rate of ethylene insertion into primary *versus* secondary metal carbon bonds. Trace amounts of internal olefins are observed, particularly at higher temperatures and lower ethylene pressures, suggesting that a small amount of chain walking is possible.

To test for chain-walking and to determine the ability of these catalysts to polymerize α-olefins, we investigated the propylene polymerization behavior of **2b**. Injection of a toluene solution of **2b** into a stirred stainless-steel reactor filled with liquid propylene at 40 °C generated low molecular weight ($M_n = 540$, $M_w/M_n = 2.68$) atactic propylene oligomers (4.1 kg PP (mol Ni)$^{-1}$ h^{-1}). The ^{13}C NMR spectrum of the polypropylene is consistent with a low molecular weight atactic polypropylene formed by both 1,2 and 2,1 insertions. Integration revealed equal amounts of methylene, methine, and methyl carbons. In contrast to the polypropylenes obtained from cationic Ni or Pd diimine catalysts, we did not observe a significant amount of 1,3 regio-errors or long ethylene sequences due to "chain-straightening" of propylene.[2,36]

These results suggest that the Ni carbene enolates exhibit a much lower preference for chain-walking compared to cationic Ni catalysts. The high linearity of these polyethylenes is thus likely a consequence of a minimal amount of chain-walking and a low turnover number in polymer chains. This linearity is consistent with observations that neutral Ni catalysts derived from more strongly donating PO ligands show a higher selectivity for linear ethylene enchainment than catalysts derived from NO ligands. Since carbenes are stronger donors than phosphines, these carbene enolate complexes may favor linear enchainment even more than PO complexes.

The low molecular weights observed are likely a consequence of the modest steric demands of the carbene enolate ligands in **2a** and **2b**. The higher molecular weights observed for **2b** relative to **2a** implies that more sterically hindered ligands might lead to higher molecular weights as observed for other neutral or cationic Ni catalysts.[2]

In conclusion, we have prepared two novel neutral Ni complexes derived from anionic N-heterocyclic carbene enolate ligands and shown that these complexes are capable of polymerizing ethylene in a highly linear fashion. Although the catalysts deactivate rapidly, endgroup analysis has provided a useful hypothesis for guiding future catalyst development. These complexes are also active for propylene oligomerization in the absence of co-catalysts; analysis of the oligopropylenes suggests that chain walking is minimal for this system. Ongoing efforts focus on improving catalyst lifetime and investigating the tolerance of this catalyst system to polar monomers.

We acknowledge the NSF (CHE-0305436) and LG Chem for financial support.

Notes and references

‡ *Crystal Data*. $C_{31}H_{29}N_3NiO$, M = 518.28, rhombic, $a = 9.742(1)$ Å, $b = 9.913(1)$ Å, $c = 13.653(2)$ Å, $V = 1299.1(3)$ Å^3, $\alpha = 81.520(2)°$, $\beta = 85.137(2)°$, $\gamma = 88.411(2)°$, $T = 150$ K, space group $P\bar{1}$, $Z = 2$, λ(0.71073 Å radiation), 6591 reflections measured, 4231 unique ($R_{int} = 0.0582$) which were used in all calculations. Residuals: $R1$; $wR2$ 0.0440; 0.1027. Substantial disorder was observed for C atoms (C22–C26) but was modeled at a single position, yielding a satisfactory solution. Other models of this positional disorder did not improve $R1$ and $wR2$ values. CCDC 280713. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511202h

1 W. Keim, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235–244.
2 S. Ittel, L. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169–1203.
3 T. Younkin, E. Conner, J. Henderson, S. Friedrich, R. Grubbs and D. Bansleben, *Science*, 2000, **287**, 460–462.
4 V. Gibson and S. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283–315.
5 R. Bauer, H. Chung, P. Glockner, W. Keim and H. Zwet, *US Patent*, 1972, 3635937.
6 J. Heinicke, M. Kohler, N. Peulecke and W. Keim, *J. Catal.*, 2004, **225**, 16–23.
7 K. A. Ostaja-Starzewski and J. Witte, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 63–64.
8 U. Klabunde and S. Ittel, *J. Mol. Catal.*, 1987, **41**, 123–134.
9 U. Klabunde, R. Mulhaupt, T. Herskovitz, A. Janowicz, J. Calabrese and S. Ittel, *J. Polym. Sci., Part A: Polym. Chem.*, 1987, **25**, 1989–2003.
10 J. Heinicke, M. Kohler, N. Peulecke, W. Keim and P. G. Jones, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1181–1190.
11 Z. Komon, X. Bu and G. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 12379–12380.
12 Z. B. Guan and W. J. Marshall, *Organometallics*, 2002, **21**, 3580–3586.
13 D. H. Camacho, E. V. Salo, J. W. Ziller and Z. B. Guan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1821–1825.
14 K. Hirose and W. Keim, *J. Mol. Catal.*, 1992, **73**, 271–276.
15 J. Heinicke, M. Kohler, N. Peulecke, M. Z. He, M. K. Kindermann, W. Keim and G. Fink, *Chem.–Eur. J.*, 2003, **9**, 6093–6107.
16 B. E. Ketz, A. P. Cole and R. M. Waymouth, *Organometallics*, 2004, **23**, 2835–2837.
17 R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff and S. P. Nolan, *J. Am. Chem. Soc.*, 2005, **127**, 2485–2495.
18 A. J. Arduengo, *Acc. Chem. Res.*, 1999, **32**, 913–921.
19 D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39–91.
20 W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309.
21 A. W. Waltman and R. H. Grubbs, *Organometallics*, 2004, **23**, 3105–3107.
22 X. Wang, S. Liu and G. X. Jin, *Organometallics*, 2004, **23**, 6002–6007.
23 M. Tilset, O. Andell, A. Dhindsa and M. Froseth, *WO Patent*, 1998, 0249758.
24 B. R. Dible and M. S. Sigman, *J. Am. Chem. Soc.*, 2003, **125**, 872–873.
25 D. Sellmann, W. Prechtel, F. Knoch and M. Moll, *Inorg. Chem.*, 1993, **32**, 538–546.
26 R. Douthwaite, D. Haussinger, M. Green, P. Silcock, P. Gomes, A. Martins and A. Danopoulos, *Organometallics*, 1999, **18**, 4584–4590.
27 D. Mcguinness, W. Mueller, P. Wasserscheid, K. Cavell, B. Skelton, A. White and U. Englert, *Organometallics*, 2002, **21**, 175–181.
28 S. Caddick, F. G. N. Cloke, P. B. Hitchcock and A. K. D. Lewis, *Angew. Chem., Int. Ed.*, 2004, **43**, 5824–5827.
29 W. Keim, F. Kowaldt, R. Goddard and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 466–467.
30 D. Mcguinness, N. Saendig, B. Yates and K. Cavell, *J. Am. Chem. Soc.*, 2001, **123**, 4029–4040.
31 D. Mcguinness, K. Cavell, B. Yates, B. Skelton and A. White, *J. Am. Chem. Soc.*, 2001, **123**, 8317–8328.
32 U. Mueller, W. Keim, C. Krueger and P. Betz, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1011–1013.
33 W. Keim, *New J. Chem.*, 1994, **18**, 93–96.
34 C. Wang, S. Friedrich, T. Younkin, R. Li, R. Grubbs, D. Bansleben and M. Day, *Organometallics*, 1998, **17**, 3149–3151.
35 Z. Guan, *J. Am. Chem. Soc.*, 2002, **124**, 5616–5617.
36 E. F. Mccord, S. J. Mclain, L. T. J. Nelson, S. D. Arthur, E. B. Coughlin, S. D. Ittel, L. K. Johnson, D. Tempel, C. M. Killian and M. Brookhart, *Macromolecules*, 2001, **34**, 362–371.