Preparation, Structure, and Olefin Polymerization Behavior of Functionalized Nickel(II) N-Heterocyclic Carbene Complexes[†]

Xin Wang, Shuang Liu, and Guo-Xin Jin*

Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200 433, China

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Picolyl-functionalized N-heterocyclic carbene complexes have been synthesized by a route involving carbene transfer from Ag(I) carbene precursors. The Ag complexes undergo facile reaction with $Ni(PPh_3)_2Cl_2$ to yield the carbene complexes $Ni(C{\wedge}N)_2Cl_2$ ($C{\wedge}N$ = 3-methyl-1-picolylimidazolin-2-ylidene (**2a**), 3-benzyl-1-picolylimidazolin-2-ylidene (**2b**)). Complexes **2a**,**b** have been characterized by IR and ^1H and ^{13}C NMR spectra and elemental analyses. The molecular structures of complexes **2a**,**b** have been confirmed by X-ray single-crystal analyses. The carbene complex **2a** shows high catalytic activities of up to 2.6×10^7 g of PNB (mol of Ni)$^{-1}$ h^{-1} for the addition polymerization of norbornene in the presence of methylaluminoxane (MAO) as cocatalyst and exhibits moderate catalytic activity (3.3×10^5 g of PE (mol of Ni)$^{-1}$ h^{-1}) for ethylene polymerization. Catalytic activities, polymer yield, molecular weights, and molecular weight distributions of polynorbornene have been investigated under the various reaction conditions.

Introduction

Since the first isolation of a free carbene by Arduengo,[1] N-heterocyclic carbenes (NHCs) have attracted increasing attention as ancillary ligands in organometallic catalysis, such as hydrogenation,[2] hydroformylation,[3,4] C−C coupling,[5−12] olefin metathesis,[13] hydrosilylation,[14] and hydroamination,[15] among many others,[16] but few are used as catalysts for olefin polymerization. Among the known N-heterocyclic carbene complexes, none can catalyze vinyl addition polymerization of norbornene, and only one Ti compound has been used to successfully catalyze the polymerization of ethylene.[17]

Bidentate or polydentate ligands containing both strong and weak donor groups (hemilable ligands) have found widespread use in homogeneous catalysis.[18,19] The hemilabile arm in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle; at the same time, the strong donor moiety remains connected to the metal center. The possibility of functionalized nitrogen groups in heterocyclic carbenes makes them suitable for the generation of hemilabile ligands. Recently there have been a few reports of metal

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* To whom correspondence should be addressed. Fax: +86-21-65641740. Tel: +86-21-65643776. E-mail: gxjin@fudan.edu.cn.

[†] Dedicated to Professor Hemult D. Alt on the occasion of his 60th birthday.

(1) (a) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363. (b) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530−5534.

(2) Lee, H. M.; Smith, D. C.; He, Z. J.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794−797.

(3) Poyatos, M.; Uriz, P.; Mata, J. A.; Claver, C.; Fernandez, E.; Peris, E. *Organometallics* **2003**, *22*, 440−444.

(4) Chen, A. C.; Ren, L.; Decken, A.; Crudden, C. M. *Organometallics* **2000**, *19*, 3459−3461.

(5) (a) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201−202. (b) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93−96.

(6) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700−706.

(7) (a) Poyatos, M.; Marquez, F.; Peris, E.; Claver, C.; Fernandez, E. *New J. Chem.* **2003**, *27*, 425−431. (b) Schwarz, J.; Bohm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *61*, 1773−1780.

(8) (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371−2374. (b) Herrmann, W. A.; Brossmer, C.; Ofele, K.; Reisinger, C. P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844−1848.

(9) (a) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617*, 546−560. (b) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741−748. (c) Grundemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485−5488.

(10) (a) Boehm, V. P. W.; Herrmann, W. A. *Chem. Eur. J.* **2000**, *6*, 1017−1025. (b) Boehm, V. P. W.; Gstottmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *595*, 186−190. (c) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G. *Organometallics* **1999**, *18*, 4082−4089.

(11) Tulloch, A. A. D.; Danopoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenz, S. *Chem. Commun.* **2000**, 1247−1248.

(12) Lebel, H.;, Janes, M. K.; Charette, A.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046−5047.

(13) (a) Chatterjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Org. Lett.* **2002**, *4*, 1939−1942. (b) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247−2250. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (d) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490−2493.

(14) (a) Poyatos, M.; Mas-Marza, E.; Mata, J. A.; Sanau, M.; Peris, E. *Eur. J. Inorg. Chem.* **2003**, 1215−1221. (b) Mas-Marza, E.; Poyatos, M.; Sanau, M.; Peris, E. *Inorg. Chem.* **2004**, 2213−2219.

(15) Burling, S.; Field, L. D.; Li, H. L.; Messerle, B. A.; Turner, P. *Eur. J. Inorg. Chem.* **2003**, 3179−3184.

(16) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

(17) Aihara, H.; Matsuo, T.; Kawaguchi, H. *Chem. Commun.* **2003**, 2204−2205.

(18) Drent, E.; Arnoldy, P.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1994**, *475*, 57−63.

(19) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235−244.

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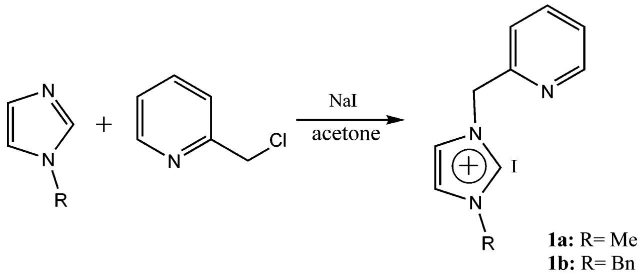
Scheme 1



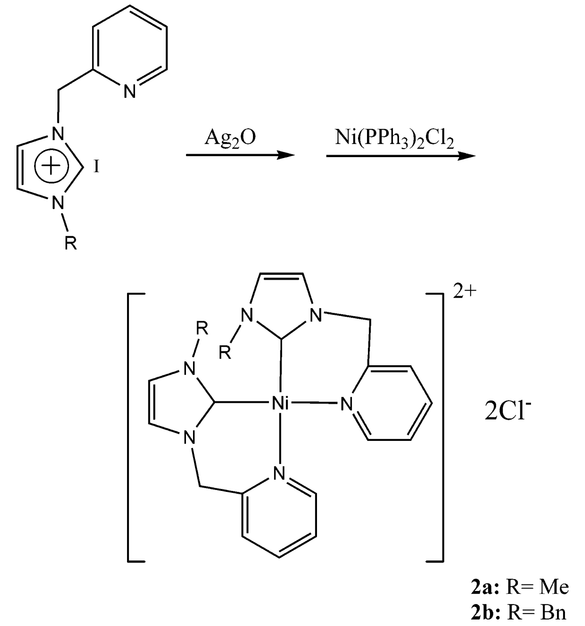
complexes containing pyridine-functionalized carbene ligands and their use as catalyst precursors for C−C coupling[9b] and copolymerization of CO/norbornene.[20] The properties of such hemilabile ligands and the growing importance of nickel complexes as olefin polymerization catalysts[21] led us to develop new olefin polymerization catalysts containing a hemilabile picolylcarbene ligand.

We report here the synthesis of Ni complexes of picolyl-functionalized carbenes generated via Ag carbene species by carbene transfer routes. Preliminary studies show that the complex $[Ni(C\wedge N)_2]Cl_2$ ($C\wedge N$ = 3-methyl-1-picolylimidazolin-2-ylidene (**2a**)) is active in the polymerization of norbornene and the polymerization of ethylene.

Results and Discussion

The functionalized imidazolium salts were synthesized by reacting picolyl chloride with the corresponding substituted imidazole according to Scheme 1. Attempts to prepare the free carbenes by deprotonation of the imidazolium salts failed due to the high acidity of the methylene protons in **1a**,**b**. Since Wang and Lin[22] reported that simple imidazolium salts react with Ag_2O to yield Ag(I) bis(carbene) complexes, which were then used as transfer agents to synthesize Pd(II) carbene complexes, the use of Ag_2O has been successfully employed by many groups to prepare carbene complexes of late transition metals,[23−26] including the palladium complexes of hemilabile carbene ligands reported by McGuiness and Cavell.[9b] We report the synthesis of nickel complexes by transmetalation from the corresponding silver carbene derivatives by a two-step process. The first involves deprotonation of the imidazolium salt with silver oxide to form the silver carbene species. These can be isolated as white powders, although we used them in situ after filtering the reaction mixture through Celite to remove unreacted silver oxide and other solids. The addition of $Ni(PPh_3)_2Cl_2$ to the filtrate immediately gave the desired product and a white suspension of silver iodide. The reaction was allowed to continue for 16 h to achieve completion. Complexes **2a**,**b** were isolated in good yield (Scheme 2).

Scheme 2



The ^{1}H NMR spectra of complexes **2a**,**b** do not exhibit a signal at 10−11 ppm, where the imidazolium C_2−H signals of the precursors are found (10.32 ppm for **1a** and 10.31 ppm for **1b**), and the chemical shifts of the other hydrogen substituents are similar to those in the NMR spectra of the corresponding precursors. In the ^{13}C NMR spectra the signals for the carbene carbon atoms of complexes **2a**,**b** appear at 161.9 and 161.7 ppm, respectively, which is characteristic for a metal carbene signal.[23−25]

All described nickel complexes are excellently soluble in CH_3OH, sparingly soluble in CH_2Cl_2 and THF, and insoluble in diethyl ether and hydrocarbon solvents. The complexes are moderately stable in dry air.

The crystallographic data for complexes **2a**,**b** are given in Tables 1 and 4. The ORTEP drawings of compounds **2a**,**b** (Figures 1 and 2) show that the two complexes have similar structures. The structure differences between the two compounds are due to the steric hindrance of the substituent group of the ligand: a benzyl group exerts greater steric hindrance than a methyl group. The molecular structure of the cationic $[Ni(C\wedge N)_2]^{2+}$ reveals that the geometry at the nickel atom is essentially square planar (maximum deviations 0.1739 Å (**2a**) and 0.0213 Å (**2b**)). The two chelates adopt a cis arrangement around the nickel atom, such that there is a C_2 symmetry at the nickel center. The two cis carbenes have relatively short Ni−C bonds (**2a**,

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(20) Chen, J. C. C.; Lin, I. J. B. *Organometallics* **2000**, *19*, 5113−5121.

(21) (a) Zhang, D.; Jin, G.-X. *Orgnometallics* **2003**, *22*, 2851−2854. (b) Zhang, D.; Jin, G.-X.; Weng, L. H.; Wang, F. S. *Organometallics* **2004**, *23*, 3270−3275.

(22) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.

(23) (a) Bildstein, B.; Malaun, M.; Kopacka, H.; Wurst, K.; Mitterboeck, M.; Ongania, K. H.; Opromolla, G.; Zanello, P. *Organometallics* **1999**, *18*, 4325−4336. (b) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340−2341. (c) Caballero, A.; Diez-Barra, E.; Jalon, F. A.; Merino, S.; Tejeda, J. *J. Organomet. Chem.* **2001**, *617*, 395−398. (d) Garrison, J. C.; Simons, R. S.; Talley, J. M.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2001**, *20*, 1276−1278. (e) Garrison, J. C.; Simons, R. S.; Kofron, W. G.; Tessier, C. A.; Youngs, W. J. *Chem. Commun.* **2001**, 1780−1781. (f) Pytkowicz, J.; Roland, S.; Mangeney, P. *J. Organomet. Chem.* **2001**, *631*, 157−163. (g) Lee, K. M.; Wang, H. M. J.; Lin, I. J. B. *Dalton* **2002**, 2852−2856. (h) Lee, C. K.; Lee, K. M.; Lin, I. J. B. *Organometallics* **2002**, *21*, 10−12.

(24) Tulloch, A. A. D.; Danopoulos, A. A.; Tizzard, G. J.; Coles, S. J.; Hursthouse, M. B.; Hay-Motherwell, R. S.; Motherwell, W. B. *Chem. Commun.* **2001**, 1270−1271.

(25) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2002**, *327*, 116−125.

(26) (a) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663−1667. (b) Mata, J. A.; Chianese, A. R.; Crabtree, R. H. *Organometallics* **2004**, *23*, 1253−1263.

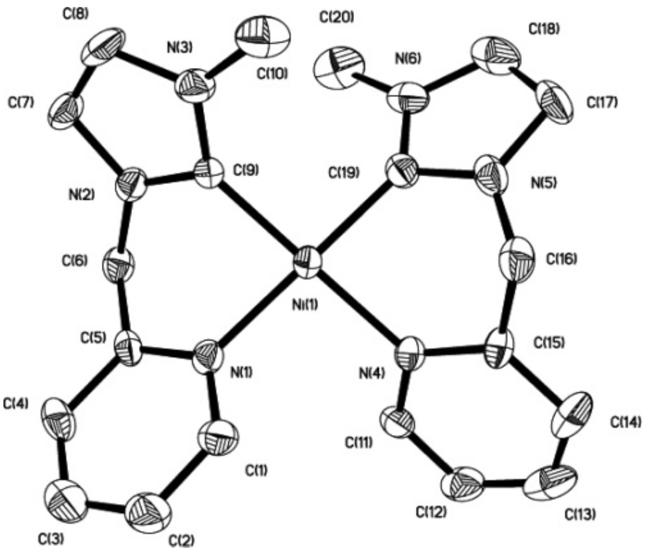

Figure 1. Crystal structure of complex **2a** showing 30% probability ellipsoids (cation only). The hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a,b

Compound **2a**			
Ni(1)−C(9)	1.863(6)	Ni(1)−C(19)	1.872(6)
Ni(1)−N(1)	1.931(5)	Ni(1)−N(4)	1.948(5)
C(9)−Ni(1)−C(19)	91.8(3)	C(9)−Ni(1)−N(1)	87.8(2)
C(19)−Ni(1)−N(1)	179.5(3)	C(9)−Ni(1)−N(4)	179.4(3)
C(19)−Ni(1)−N(4)	87.8(3)	N(1)−Ni(1)−N(4)	92.6(2)
C(1)−N(1)−Ni(1)	119.9(5)	C(5)−N(1)−Ni(1)	121.1(5)
C(11)−N(4)−Ni(1)	120.9(5)	C(15)−N(4)−Ni(1)	121.7(4)
N(3)−C(9)−Ni(1)	134.7(5)	N(2)−C(9)−Ni(1)	120.0(4)
N(6)−C(19)−Ni(1)	134.6 (5)	N(5)−C(19)−Ni(1)	119.6(5)
N(5)−C(16)−C(15)	107.1(6)	N(2)−C(6)−C(5)	110.3(5)
Compound **2b**			
Ni(1)−C(23)	1.851(4)	Ni(1)−C(7)	1.861(4)
Ni(1)−N(1)	1.948(4)	Ni(1)−N(4)	1.957(3)
C(23)−Ni(1)−C(7)	91.25(18)	C(23)−Ni(1)−N(1)	176.24(16)
C(7)−Ni(1)−N(1)	88.74(16)	C(23)−Ni(1)−N(4)	87.00(17)
C(7)−Ni(1)−N(4)	177.66(16)	N(1)−Ni(1)−N(4)	92.90(15)
C(1)−N(1)−Ni(1)	119.9(3)	C(5)−N(1)−Ni(1)	122.0(3)
C(21)−N(4)−Ni(1)	121.1(3)	C(17)−N(4)−Ni(1)	120.5(3)
N(3)−C(7)−Ni(1)	134.6(3)	N(2)−C(7)−Ni(1)	120.4(3)
N(6)−C(23)−Ni(1)	134.2(3)	N(5)−C(23)−Ni(1)	120.0(3)
N(5)−C(22)−C(21)	108.6(4)	N(2)−C(6)−C(5)	110.1(3)

1.863(6) and 1.872(6) Å; **2b**, 1.851(4) and 1.861(4) Å) as compared with bis[1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene]nickel(II) diiodide (1.909(2) Å)[27] and [Ni($^{\mathrm{tBu}}$CC$^{\mathrm{meth}}$)$_2$]Br$_2$ ($^{\mathrm{tBu}}$CC$^{\mathrm{meth}}$ = 1,1′-methyl-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene; 1.936(4) and 1.928(4) Å)[28] but these values are similar to the value for a cyclophane−nickel complex (1.870(8) and 1.862(2) Å)[29] that has been reported recently. The formation of the six-membered chelate ring of the picolyl-functionalized carbene distorts the coordination geometry of the nickel only slightly, with the C−Ni−N bite angle being reduced to 86.64(9)° (**2a**) and 87.00(17)° (**2b**). The dihedral angles of the N-heterocyclic carbene planes with the planes of the nickel (N(1)−C(9)−C(19)−N(4) and (N(1)−C(7)−C(23)−N(4)) are 44.59(0.25)° (**2a**) and 46.67(0.15)° (**2b**), respectively, which are much smaller compared with those ina bis(monodentate)nickel complex (dichlorobis(1,3-dicyclohexylimidazol-2-ylidene)nickel(II); 75.64(65) and 77.98(13)°)[30] and are similar to those in a bis(chelate)nickel complex (bis{1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}nickel(II) diiodide; 36.94(9), 40.85(8)°).[27] The dihedral angles between the two carbene planes are 61.93(0.30)° (**2a**) and 65.84(0.20)° (**2b**), respectively. The C−C and C−N bond distances within the imidazline-2-ylidene-based ring systems and the Ni−C bond distances are consistent with both contributions from σ and π donation to the metal center and π stabilization of the carbene onto the adjacent nitrogens.

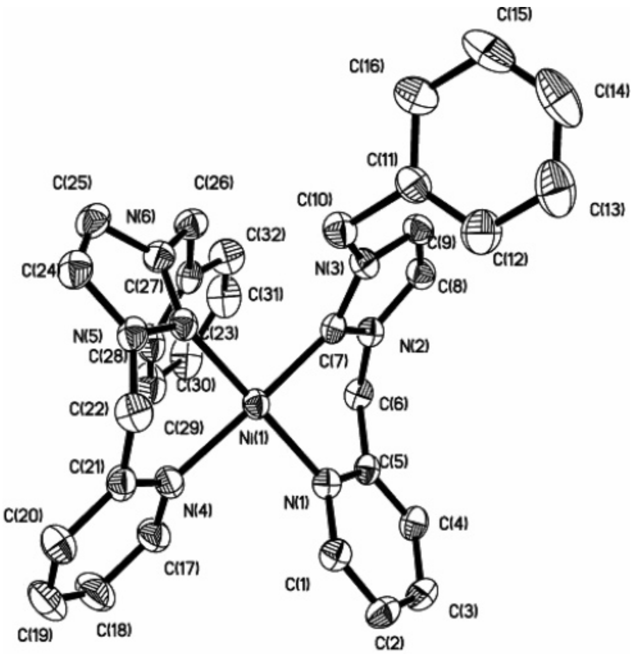

Figure 2. Crystal structure of complex **2b** showing 30% probability ellipsoids (cation only). The hydrogen atoms are omitted for clarity.

Preliminary experiments indicated that the nickel-based catalyst precursor **2a** can be activated for norbornene polymerization by treatment with MAO to afford addition-type polynorbornene (PNB) with high activities (10^7 g of PNB (mol of Ni)$^{-1}$ h^{-1}). The resulting PNBs have high molecular weight ($M_{\mathrm{w}} = 10^6$) and a moderate molecular weight distribution ($M_{\mathrm{w}}/M_{\mathrm{n}}$ = 2.3−3.5). Under the same conditions, the complex along with MAO and MAO alone did not produce any polymer (runs 7 and 8). The norbornene polymerization results are collected in Table 2. We found that complex **2a** showed the highest activity at 80 °C (2.6×10^7). The activity of **2a** increased rapidly when the temperature of polymerization rose from 20 to 80 °C. This is because the concentration of active centers activated by MAO increases as the temperature is increased. At the same time **2a** usually becomes unstable at high temperature. The highest activity at 80 °C is the result of the compromise of two factors. The decomposition rate of the active center increased and the activity dropped at

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(27) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239−247.

(28) Douthwaite, R. E.; Haussinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A. *Organometallics* **1999**, *18*, 4584−4590.

(29) Baker, M. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *Organometallics* **2002**, *21*, 2674−2678.

(30) Herrmann, W. A.; Gerstberger, G.; Spiegler, M. *Organometallics* **1997**, *16*, 2209−2212.

Table 2. Addition Polymerization of Norbornene with Nickel Complex 2a Activated by Methylaluminoxane (MAO)[a]

run	complex	T (°C)	yield (%)	activity[b]	M_w [c]	M_w/M_n [c]
1	**2a**	20	12.3	3.5		
2	**2a**	30	14.6	4.0	42.0	2.4
3	**2a**	40	55.5	15.6		
4	**2a**	60	59.0	16.5	26.2	2.3
5	**2a**	80	92.0	26	13.2	2.6
6	**2a**	100	77.0	21.7	11.1	3.5
7[d]	**2a**	30	0	0		
8[e]	none	30	0	0		

[a] Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; nickel complex (**2a**), 0.4 μmol; 1.2 mL of MAO (10%) (Al/Ni(molar) = 4500); norbornene, 1.88 g (norbornene/Ni(molar) = 68 000); reaction time, 10 min. [b] In units of 10^6 g of PNB (mol of Ni)$^{-1}$ h^{-1}. [c] M_w ($\times 10^{-5}$) and M_w/M_n values were determined by GPC. [d] Without cocatalyst MAO. [e] Without nickel complex but with MAO present.

Table 3. Influence of Reaction Time for Norbornene Polymerization with Nickel Complex 2a Activated by Methylaluminoxane (MAO)[a]

run	complex	T (°C)	time (min)	yield (%)	activity[b]
1	**2a**	30	10	15	3.5
2	**2a**	30	30	32	3.0
3	**2a**	30	60	48	2.3
4	**2a**	30	120	56	1.3

[a] Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; nickel complex (**2a**), 0.4 μmol; 1.2 mL of MAO (10%) (Al/Ni(molar) = 4500); norbornene, 1.88 g (norbornene/Ni(molar) = 68 000); temperature, 30 °C; [b] In units of 10^6 g of PNB (mol of Ni)$^{-1}$ h^{-1}.

100 °C. The temperature also showed similar effects on polymer yields. An increase of the molecular weight of the derived polymer was observed when the reaction temperatures were decreased. A molecular weight of 4.2 $\times 10^6$ was obtained at a reaction temperature of 30 °C.

The variation of the reaction time showed that the conversion increases with longer reaction time, and the catalytic activities decrease due to the decreasing monomer concentration during the reaction (Table 3).

The polymers obtained were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and by GPC analyses. The resonances of PNB appear at 0.9−2.6 (m, maxima at 1.35, 1.75, and 2.46 ppm). The absence of bands at 1680−1620 cm^{-1} in the IR spectra indicated that no double bonds were present, which was different from the case for the polymers of norbornene ring-opening metathesis polymerization.[31] The ^{13}C NMR spectrum of PNB shows the main four groups of resonances at δ 27.9−48.1 ppm (m, maxima at 27.9, 32.3, 40.05, 48.04), attributed to the vinyl addition polymer structure of polynorbornene, bridge carbon, bridgehead carbon, and the backbone carbon, respectively.[32] Therefore, the polymerization took place exclusively in a vinyl addition manner. The GPC molecular weights M_w of polymers were very high, indicating that the normal mode of chain transfer (β-hydride elimination) was not possible in PNB, given the geometry of the growing active center. The DSC study of the PNB obtained did not show an endothermic signal upon heating to the decomposition temperature (above 450 °C), and the TGA scans suggested that these polymers are very stable up to 400 °C.

A preliminary ethylene polymerization study showed that complex **2a** is a moderately active precatalyst for the polymerization of ethylene. For example, ethylene was polymerized under MAO activation of **2a** (polymerization conditions: solvent, 50 mL of toluene; nickel complex **2a**, 2 μmol; 1.2 mL of MAO(10%) (Al/Ni(molar) = 1000); ethylene; pressure, 1 atm; reaction time, 60 min; temperature, 30 °C) with an activity of 3.3 $\times 10^5$ g mol^{-1} h^{-1}. A molecular weight distribution (M_w/M_n = 12.8) was observed centered at 67 213 (M_{pk}s). In the high-temperature ^{13}C NMR spectrum of the polyethylene produced, methyl branches were identified by the resonances at 30.1 (CH_2), 20.1 (CH_3), 30.3 (CH), 37.7 (α-CH_2), 30.5 (γ-CH_2), and 27.6 ppm (β-CH_2), which was affirmed in the entire spectrum.[33] Methyl branches predominate, with ca. 3.4 methyl branches per 1000 carbon atoms in the polyethylene chain. No other kinds of short branches could be observed through the ^{13}C NMR research.

Conclusion

We have synthesized two nickel carbene complexes by the transmetalation method. Our preliminary study shows that the new cationic nickel carbene complex **2a**, containing a hemilabile picolyl carbene ligand, shows high activity as a catalyst precursor in ethylene polymerization and norbornene polymerization. Although the detailed mechanism of the catalytic olefin polymerization is not clear, we suggest that a cationic methyl nickel complex is formed in the presence of cocatalyst (MAO) and that a vacant site (active site) for coordination of the olefin must be generated. To our best knowledge, this is the first report that this kind of N-functionalized carbene late-transition-metal complex exhibits high activity toward vinyl addition polymerization of norbornene and polymerization of ethylene. Further investigations of the olefin polymerization of such complexes and of the polymerization mechanism are ongoing.

Experimental Section

General Procedures. All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Methanol was dried over Mg, CH_2Cl_2 and chlorobenzene were dried over CaH_2, and norbornene was dried over Na; all were then distilled under nitrogen immediately prior to use. Methylaluminoxane (MAO), 1-methylimidazole, and 2-picolyl chloride hydrochloride were purchased from Witco and Acros, respectively. Other solvents were used as received as technical grade solvents. $Ni(PPh_3)_2Cl_2$ [34] and 1-benzylimidazole[35] were prepared according to the literature. ^{1}H and ^{13}C NMR spectra were recorded on a VAVCE-DMX 500 spectrometer in $CDCl_3$, CD_3OD, and o-dichlorobenzene-d_4; for polyethylene, ^{13}C NMR spectra of polyethylene were obtained using o-dichlorobenzene as a solvent on an FX-100 NMR spectrometer at 130 °C. Elemental analysis was performed on an Elementar Vario EL III analyzer. IR (KBr) spectra were recorded on a Nicolet FT-IR spectrophotometer. Average molecular weight (M_w) and

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(31) (a) Sacchi, M. C.; Sonzogni, M.; Losio, S.; Forlin, F. *Macromol. Chem. Phys.* **2001**, *202*, 2052−2058. (b) Barnes, D. A.; Benedikt, G. M.; Goodall, B. L.; Huang, S. S. *Macromolecules* **2003**, *36*, 2623−2632.

(32) (a) Huang, W. J.; Chang, F. C.; Chu, P. P. *J. Polym. Sci.* **2000**, *38*, 2554−2563. (b) Mi, X.; Ma, Z.; Cui, N. *J. Appl. Polym. Sci.* **2003**, *88*, 3273−3278.

(33) (a) Linderman, L. P.; Adams, N. O. *Anal. Chem.* **1971**, *43*, 1245. (b) Dorman, D. E. *Macromolecules* **1972**, *5*, 574.

(34) Venanzi, L. M. *J. Chem. Soc.* **1958**, 719−724.

(35) *Chem. Abstr.* **1966**, *68*, 59583; Ger. Appl. May 4, 1966, 9.

molecular weight distribution (M_w/M_n) values of PBN products and polyethylene were determined with a PL GPC-220 permeation chromatograph at 150 °C, using a narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10 m MIXED-BLS). Trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL/min.

3-Methyl-1-picolyimidazolium Iodide (1a). To a solution of picolyl chloride (5.85 mmol, prepared by neutralizing 0.96 g of picolyl chloride hydrochloride) in 20 mL of acetone were added 1-methylimidazole (0.470 mL, 5.89 mmol) and NaI (0.88 g, 5.9 mmol). After it was stirred for 48 h, the solution was filtered through Celite and the solvent was removed under vacuum to afford a thick brown syrup. The syrup was redissolved in 15 mL of CH_2Cl_2, and the solution was filtered to remove residual NaCl. Addition of 25 mL of ether caused an oil to separate out. The solvent was decanted off, and then the resulting oil was taken up in 8 mL of CH_2Cl_2 and 20 mL of ether was added to precipitate the product. The oily solid that formed was triturated for 2 h and the resultant powder was washed with 10 mL of ether. Yield: 1.22 g (69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 1H, NC(H)N), 8.64 (s, 1H, pyridyl), 7.91 (m, 1H, pyridyl), 7.80 (s, 1H, HCCH), 7.75 (s, 1H, HCCH), 7.55 (m, 1H, pyridyl), 7.4 (s, 1H, pyridyl), 5.58 (s, 1H, NCH_2), 3.90 (s, 3H, NCH_3).

3-Benzyl-1-picolyimidazolium Iodide (1b). Analogous to the synthesis of **1a** but using picolyl chloride (5.85 mmol), 1-benzylimidazole (0.925 g, 5.85 mmol) and NaI (0.88 g, 5.9 mmol) in 20 mL of acetone, give **1b** as a red solid. Yield: 1.32 g (60%). 1H NMR(500 MHz, $CDCl_3$):δ10.32 (s, 1H, NC(H)N), 8.56 (m, 1H, pyridyl), 7.80 (d, 2H, HCCH), 7.66 (d, 1H, pyridyl), 7.43 (m, 7H, pyridyl, Ph), 5.66 (s, 4H, NCH_2).

Ni(3-methyl-1-picolyimidazolin-2-ylidene)$_2$Cl$_2$ (2a). A mixture of **1a** (300 mg, 1 mmol) and silver(I) oxide (119 mg, 0.5 mmol) was taken up in 30 mL of CH_2Cl_2 and was stirred for 2 h. The solution was filtered through Celite, and then $Ni(PPh_3)_2Cl_2$ (654 mg, 1 mmol) was added; the solution was stirred at room temperature overnight and filtered, and the resulting solid was washed with CH_2Cl_2 and then dried under vacuum. The product was recrystallized from MeOH/ether to give yellow crystals. Yield: 0.38 g (80%). ^{1}H NMR (500 MHz, CD_3OD): δ 8.09 (m, 4H, pyridyl), 7.97 (d, 2H, pyridyl), 7.63 (s, 2, HCCH), 7.41 (m, 2H, pyridyl), 7.27 (s, 2H, HCCH), 6.88 (d, 2H, NCH_2), 5.80 (s, 2H, NCH_2), 4.75 (m, 6H, CH_3). ^{13}C NMR (500 MHz, CD_3OD): δ 161.9 (Ni−C), 159.1 (pyridyl, C2), 157.1 (pyridyl, C6), 145.3 (pyridyl, C4), 129.5 (pyridyl, C3), 129.2 (pyridyl, C5), 128.9 (NCCN), 127.2 (NCCN), 52.2 (NCH_2), 39.8 (NCH_3). Anal. Calcd for $C_{20}H_{22}Cl_2N_6Ni$: C, 50.40; H, 4.62; N, 17.66. Found: C, 50.62; H, 4.60; N, 17.53.

Ni(3-benzyl-1-picolyimidazolin-2-ylidene)$_2$Cl$_2$ (2b). This complex was prepared in a manner analogous to that described above, using **1b** (377 mg, 1 mmol), silver(I) oxide (119 mg, 0.5 mmol), and $Ni(PPh_3)_2Cl_2$ (654 mg, 1 mmol) in 30 mL of CH_2Cl_2, and then recrystallized from MeOH/ether to yield orange crystals. Yield: 0.39 g (62%). ^{1}H NMR (500 MHz, CD_3OD): δ 8.08 (m, 2H, pyridyl), 7.84 (m, 4H, HCCH), 7.65 (d, 2H, pyridyl), 7.39−7.28 (m, 14H, pyridyl, Ph), 5.66 (m, 4H, NCH_2 pyridyl), 5.12 (m, 4H, NCH_2). ^{13}C NMR (500 MHz, CD_3OD): δ 161.7 (Ni−C), 158.8 (pyridyl, C2), 156.4 (pyridyl, C6), 145.6 (pyridyl, C4), 140.4 (Ph, C1), 133.5 (Ph, C3), 132.8 (Ph, C4), 130.9 (Ph, C2), 129.9 (pyridyl, C3), 129.5 (pyridyl, C5), 129.3 (NCCN), 127.8 (NCCN), 57.5 (NCH_2 pyridyl), 52.6 (NCH_2). Anal. Calcd for $C_{32}H_{30}Cl_2N_6Ni$: C, 61.17; H, 4.78; N, 13.38. Found: C, 61.04; H, 4.63; N, 13.32.

X-ray Crystallography. Suitable crystals for X-ray analysis of **2a**,**b** were obtained by slow diffusion of diethyl ether into methanol solutions of the corresponding compound. None showed signals of decomposition during the X-ray data collection, which was carried out at room temperature. Details of the data collection and refinement are summarized in Table 4. Selected bond lengths and angles are given in Table 1. The structures were solved by direct methods using SHELX-97 and refined by full-matrix least-squares calculations, using the program system SHELXTL-97.

Table 4. Summary of Crystallographic Data for 2a,b

	2a	2b
chem formula	$C_{22}H_{30}Cl_2N_6NiO_2$	$C_{35}H_{44}Cl_2N_6NiO_4$
formula wt	540.13	741.36
temp (K)	298(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
unit cell dimens		
a (Å)	8.301(3)	11.861(4)
b (Å)	33.766(10)	12.744(4)
c (Å)	9.622(3)	13.811(4)
α (deg)	90	95.772(4)
β (deg)	109.788(4)	105.255(4)
γ (deg)	90	115.401(4)
V (Å^3)	2537.6(13)	1763.9(9)
Z	4	2
D_{calcd} (Mg/m^3)	1.414	1.396
abs coeff (mm^{-1})	1.006	0.749
F(000)	1128	778
cryst size (mm)	0.25 × 0.20 × 0.10	0.25 × 0.15 × 0.10
θ range for data collecn (deg)	1.21−25.01	1.58−25.01
limiting indices	$-9 \le h \le 9$ $-34 \le k \le 40$ $-11 \le l \le 11$	$-14 \le h \le 13$ $-15 \le k \le 9$ $-16 \le l \le 16$
no. of rflns collected	10 540	7406
no. of indep rflns	4472 (*R*(int) = 0.0509)	6108 (*R*(int) = 0.0223)
completeness to θ (deg)	25.01 (99.9%)	25.01 (98.2%)
max, min transmissn	0.9061, 0.7871	0.9289, 0.8349
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	4472/0/304	6108/4/408
goodness of fit on F^2	1.005	1.040
final R indices ($I > 2\sigma(I)$)	R1 = 0.0733 wR2 = 0.1986	R1 = 0.0625 wR2 = 0.1785
largest diff peak, hole (e/Å^3)	1.125, −0.555	0.801, −0.582

Norbornene Polymerization. In a typical procedure, 0.4 μmol of nickel complex **2a** in 2.0 mL of chlorobenzene, 1.88 g of norbornene in 4.0 mL of chlorobenzene, and another 3.0 mL of fresh chlorobenzene were added into a flask (20 mL) with strong stirring under an Ar atmosphere. After the mixture was kept at the desired temperature for 10 min, 1.2 mL of MAO (10%) was charged into the polymerization system via syringe, and the reaction was started. Ten minutes later, acidified ethanol ($V_{methanol}$:$V_{concd\ HCl}$ = 20:1) was added to terminate the reaction. The PNB was isolated, washed with methanol, and dried at 80 °C for 48 h under vacuum. For all the polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by variation of the added chlorobenzene when necessary. IR (KBr): 2946 (vs), 2869 (vs), 1473 (m), 1451 (s), 1375 (m), 1295 (m), 1258 (m), 1222 (m), 1148 (m), 1108 (m), 1040 (w), 943 (w), 893 (m) cm^{-1}. ^{1}H NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ 0.9−3.03 (m, maxima at 1.35, 1.75, 2.46). ^{13}C NMR (o-dichlorobenzene-d_4, 500 MHz): δ 29.7−48.1 (m, maxima at 29.7, 32.3, 40.05, 48.04).

Ethylene Polymerization. Ethylene polymerization was performed in a 200 mL Schlenk-type glass reactor fitted with a mechanical stirrer. After being flame-dried three times, the flask was back-filled with ethylene. Then the reactor was charged with 45 mL of toluene and 1.2 mL of MAO (10%) via syringe under an atmosphere of nitrogen. Subsequently, the catalyst in 5 mL of solvent was introduced into the polymerization bottle via syringe, stirring was begun, and the polymerization reaction mixture was kept at 30 °C. The reaction flask was immersed in a certain temperature water bath for 15 min prior to injection of the catalyst. After 60 min, the reaction mixture was quenched with ethanol/HCl and the polymer was isolated by filtration and dried under vacuum at 40 °C for 10 h.

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Supporting Information Available: CIF files for **2a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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