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Journal of Organometallic Chemistry 694 (2009) 1254–1258

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Communication

Neutral Ni(II) complexes based on keto-enamine salicylideneanilines active for selective dimerization of ethylene

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ARTICLE INFO

Article history:
Received 3 November 2008
Received in revised form 12 January 2009
Accepted 13 January 2009
Available online 20 January 2009

Keywords:
Neutral Ni(II) complexes
Keto-enamine salicylideneaniline ligand
Ethylene oligomerization
Selective dimerization

ABSTRACT

Single component organonickel(II)phosphino neutral complexes from salicylideneaniline based ligands bearing N–O chelate sites, were synthesized, which were found efficient in dimerizing ethylene selectively to various butene products.

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1. Introduction

Advances in synthesis of zero valent nickel complexes and the successive development of synthetic protocol for single component organonickel(II)phosphino neutral complexes from them have attained great academic interests [1–10]. These complexes produced dramatic changes in their catalytic properties when they are having properly designed organic ligands. Also they produced an opportunity for better understanding of the role of complexes in catalysis mechanisms. Fabrication of ligands for these single component organonickel(II)phosphino neutral complexes starts from the report of Klein et al. on the first ever acylnickel compound containing three monodentate neutral ligands [2]. It was followed by methylnickel salicylaldiminato complexes with trimethylphosphine minor ligand [3]. Based on such complexes, Grubbs and coworkers have developed neutral Ni(II) based complexes active in ethylene polymerization reaction [4]. Modification of this ligand environment was successfully carried out by Brookhart by introducing a keto-enamine scaffold [5]. Even though the keto-enamine structure was found promising, the advances in developing such new molecules as ligands are fewer in number [5–8]. In this regard we have developed a new neutral nickel complex (Scheme 1) with N–O chelates in keto-enamine form, capable to mediate an industrially important selective dimerization reaction of ethylene [9,10].

2. Results and discussion

2.1. Synthesis of the complexes and their characterizations

Ligands were synthesized from triformylphloroglucinol and 2,6-dialkyl aniline (see Appendix A, Supplementary material, for details). The ligands showed multiple peaks between δ 8.0–8.5 and 12.2–13.6 ppm in ^{1}H NMR spectrum indicating the presence of possible geometrical isomer **a** of C_{3h} symmetry and **b** of C_s symmetry (Fig. 1) for both **1** and **2**. Coupling of these multiplets in ^{1}H–^{1}H COSY spectra with multiplets at 8.0–8.5 ppm region clarifies structure of ligands as these couplings are the outcome of interaction between enamine protons and NH of a keto-enamine scaffold [11]. The two geometrical isomers of **2** were found in a ratio of 2.9:1 (C_{3h}:C_s) from proton NMR spectrum in $CDCl_3$. A BLYP/DNP DFT calculation on different forms of compound **2** predicts that keto-enamine tautomer is more favorable by 11.86 kcal/mol than enolate-imine and among the keto-enamine tautomers the geometrical isomer **2a** is more stable than **2b** by about 1.2 kcal/mol.

The complexes **3** and **4** were synthesized from the mono-sodium salts of **1** and **2** by treating them with one equivalent of *trans*-[NiBr(*o*-tolyl)(PPh_3)$_2$] in benzene (Scheme 1). According to the NMR spectra of the complexes, the diamagnetic Ni(II) complexes adopt a square planar geometry as in the case of salicylaldimine ligand based Ni complexes [4]. The repeated presence of multiple peaks between δ 8.0–8.5 and 12.2–13.6 ppm in ^{1}H NMR spectra and the coupling of doublets in these regions in ^{1}H–^{1}H COSY spectra (Fig. 2) of these complexes reveals that the keto-enamine core remains intact even after metallation. In addition the

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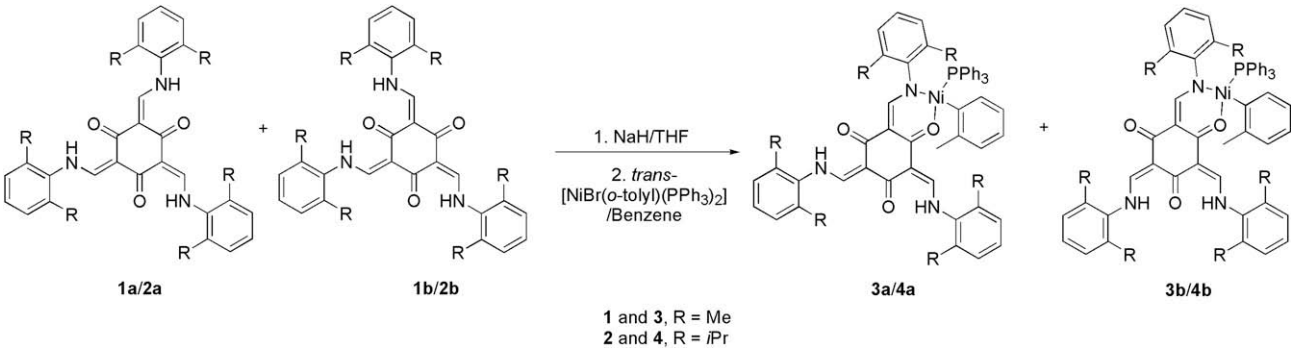
doi:10.1016/j.jorganchem.2009.01.017



Scheme 1. Synthesis of complexes **3** and **4**.

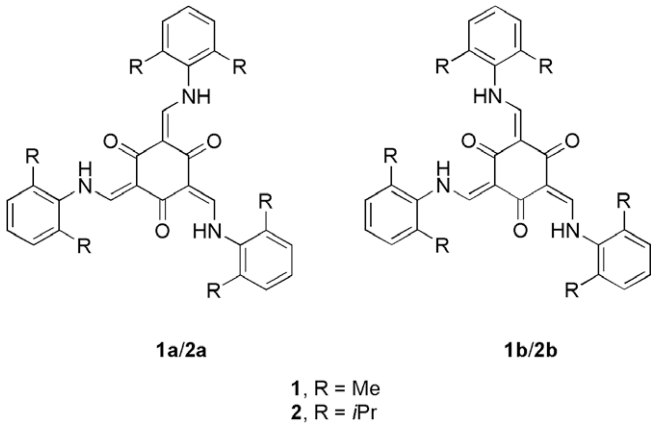


Fig. 1. The ligands **1a** and **2a** with the two possible geometric isomers **1b** and **2b**.

DFT calculations support keto-enamine structure of complex **4** by an energy factor of 7.45 kcal/mol. As the keto-enamine core remains unchanged, the two geometrical isomers **a** and **b** of **4** were found in a ratio of 2.4:1 from proton NMR spectrum in $CDCl_3$.

Single crystal XRD analysis of complex **4a** (Fig. 3) provided substantial evidences to prove that the ligand sustains keto-enamine structure in the complex. The bond length and bond angle values obtained from the DFT calculations for keto-enamine and enolate-imine forms were compared with that obtained for complex **4a** from its crystal structure. The values obtained for bond lengths O1–C2, C2–C3 and C3–C4 (1.281(5), 1.457(6) and 1.458(7) Å, respectively) from the crystal data are more close to the values obtained for NH form (1.271, 1.472 and 1.463 Å, respectively) than that obtained for OH form (1.343, 1.425 and 1.428 Å, respectively) from DFT calculations. The average C–C bond length 1.45 Å of central cyclohexanetrione core is considerably longer than the average bond length of 1.38 Å found in benzene. Conversion of a keto-enamine structure, originated from an imine reaction on triformylphloroglucinol, to an enolate-imine and its subsequent trapping with $BF_3 \cdot Et_2O$ had been reported along with its crystal structure for a tris(*N*-salicylideneaminoferrocene) type complex and this gives an excellent reference molecule for comparison [12]. For this enolate structure, bond length values reported for C2–C3 and C3–C4 in the core aromatic ring and O1–C2 of the enolate are 1.412(3), 1.408(3) and 1.318(3) Å, respectively from the single crystal XRD data. A comparatively shorter C–O and longer

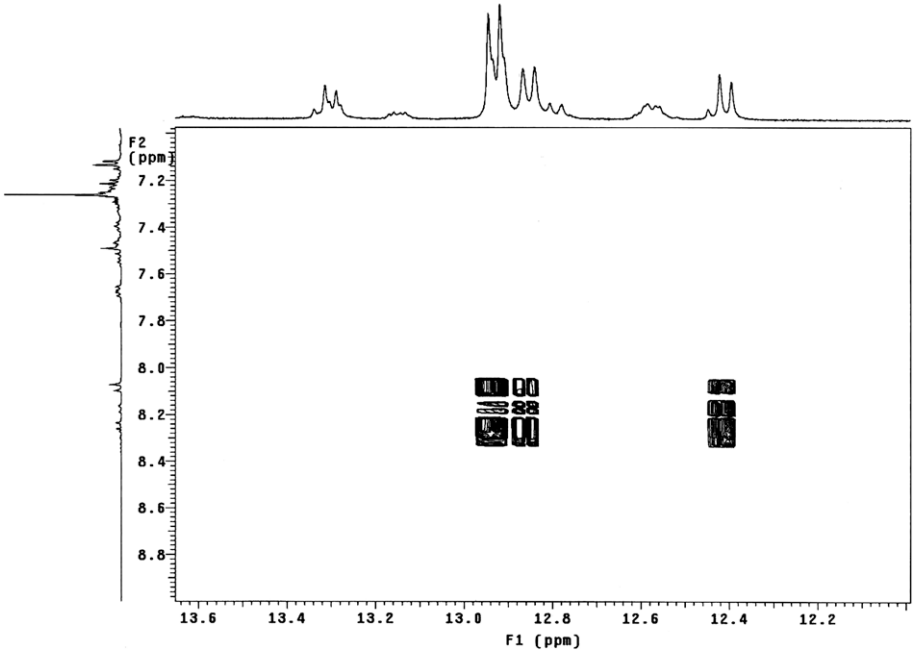


Fig. 2. ^1H–^1H COSY NMR spectrum ($CDCl_3$) of complex **4** showing the coupling between vinylic and NH protons.

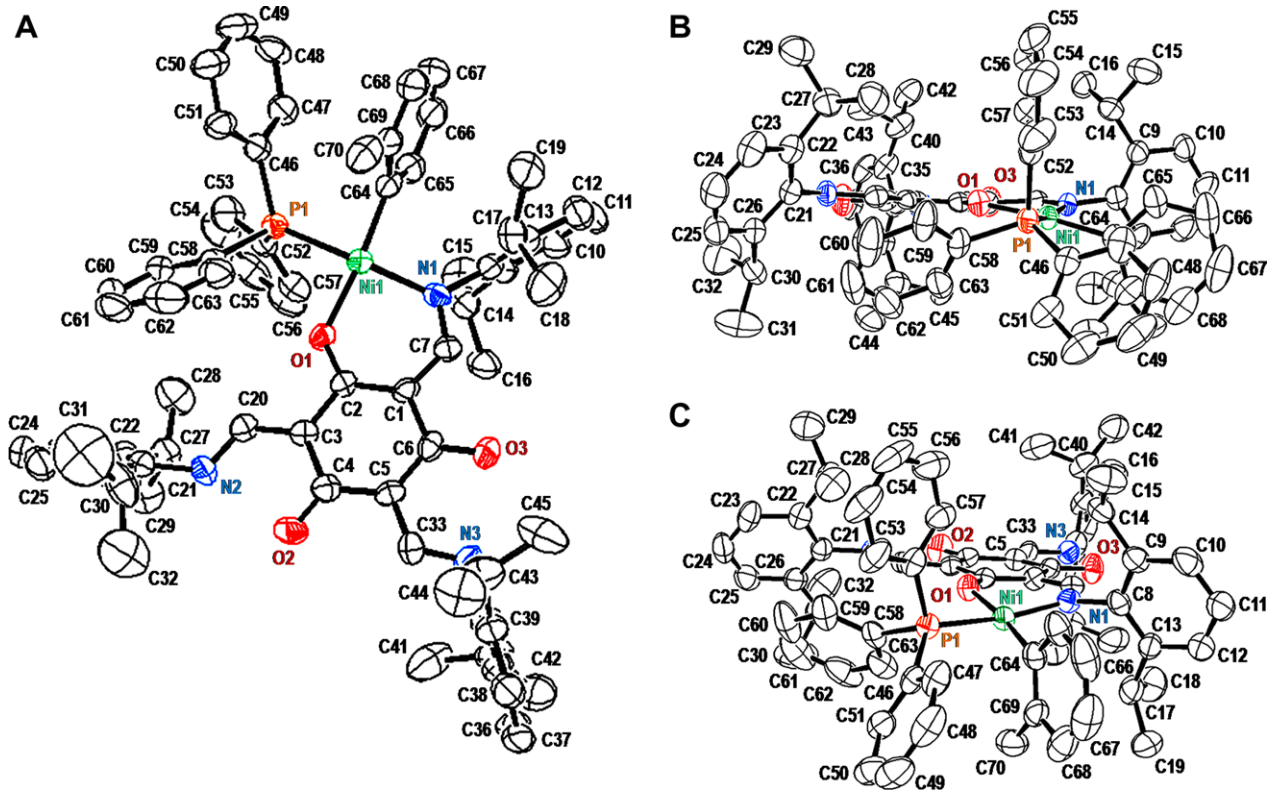


Fig. 3. ORTEP diagram representing the molecular structure of complex **4**. (A) Top view. (B) Side view detailing the PPh_3 on Ni. (C) Side view detailing the *o*-tolyl group on Ni. The hydrogen atoms and solvent entities are omitted for clarity.

C–C bond lengths of the central C_6O_3 core for complex **4a** justify the keto-enamine structure of ligands in these complexes.

It can be seen from Fig. 3 and Table 1 that the minor ligand, PPh_3, occupies the position *trans* to the bulky 2,6-diisopropyl-benzamino moiety. N(1)–Ni(1)–P(1) bond angle is 170.27(13)° and hence can be considered as positioned nearly linear. The C(64)–Ni(1)–O(1), that is the angle between *o*-tolyl group and O, through Ni, is more open and hence the bonds making this angle are arranged more close to be linear (173.67(18)°). The linear orientation of these angles, which are separated from each other at their intercept by an average angle value of 90.41°, makes the metal center more planar. The Ni(1)–N(1) and Ni(1)–C(64) bond distances are similar to those in known nickel complexes [4]. The Ni(1)–O(1) bond is 0.027 Å longer than that in neutral salicylaldiminato Ni(II) complexes [4], indicating the sp^2 hybridization of this oxygen and hence a reduced availability of electrons than a sp^3 hybridized oxygen of salicylaldiminato Ni(II) complexes. The Ni–P bond is considerably longer than that of neutral Ni(II) pyridine carboxylate complexes [13], but slightly longer than neutral salicylaldiminato Ni(II) complexes [4], suggesting a steric free atmosphere of the triphenylphosphine minor ligand. The central cyclohexanetrione ring consisting of six carbon atoms can be observed as flat within the error. It can be the fractional crystallization which produced the crystals only of **4a** exclusively.

Table 1
Selected bond distances and angles from crystallographic data.

Bond lengths (Å)		Bond angles (°)	
C1–C2	1.420(6)	O1–Ni1–C64	173.67(18)
C2–C3	1.457(6)	O1–Ni1–P1	89.07(10)
C3–C4	1.458(7)	O1–Ni1–N1	91.73(15)
C4–C5	1.436(6)	N1–Ni1–P1	170.27(13)
C5–C6	1.443(7)	N1–Ni1–C64	93.6(19)
C6–C1	1.469(7)	P1–Ni1–C64	86.25(15)
C2–O1	1.281(5)	Ni1–O1–C2	129.5(3)
C4–O2	1.264(6)	Ni1–N1–C7	123.2(3)
C6–O3	1.267(5)	C1–C2–C3	119.6(4)
C7–N1	1.311(6)	C2–C3–C4	121.3(4)
O1–Ni1	1.943(3)	C3–C4–C5	117.8(5)
N1–Ni1	1.932(4)	C4–C5–C6	121.9(5)
C64–Ni1	1.899(5)	C5–C6–C1	119.0(4)
P1–Ni1	2.1807(15)	C6–C1–C2	120.3(4)

The use of multinucleating ligands as a means to impose close spacial confinement on multimetal centers has been widely documented for a variety of naturally occurring metalloenzymes [14] and for catalysts with a range of metal-mediated processes [15–17]. For polymerization applications, good catalytic performances have been observed and cooperative effects by the neighboring active metal centers have been suggested [16,17]. In this sense, attempts to prepare bi and tri-sodium salts of ligands **1a** and **2a** were successful in high yields but the metallations using two and three equivalent of *trans*-[NiBr(*o*-tolyl)$(PPh_3)_2$] were found ineffective based on their FAB-mass spectra. A computational investigation showed that when a metal moiety is attached at only one N–O chelate the larger space filled by this metal moiety pushes the two nearby Ar(*i*Pr)$_2$ away. As a result, it makes the dihedral angle between the central $C_6O_3(CHNH)_3$ and Ar(*i*Pr)$_2$, i.e., the angle between the central plane and the edge plane, expanded at one center while contracting at the other. Accordingly, it reduces available volume for the two other centers, making any possible new intake of metal moiety into the complex difficult. The calculations on reaction energetics for the formation of mono-, bi-, and trinuclear complexes, with −263.8, −170.3 and −110.3 kcal/mol, respectively, revealed that the formation of bi- and trinuclear complexes are energetically more demanding than the mononuclear one. Details of the spatial confinements and related energy calculations are described in Appendix A, Supplementary material.

2.2. Ethylene oligomerizations

Reaction towards ethylene were carried out with complexes **3** and **4** in combination with methylalumoxane (MAO). Both complexes selectively gave dimerization of ethylene along with a little amount of trimerization product and trace amount of polymer (Table 2). At 30 °C both complexes **3** and **4** gave high butene content which is above 90% of the total oligomer content. A 96% of total butene content (Run No. 4 of Table 2) given by complex **4** at 30 °C records the highest. When temperature of oligomerization was increased the selectivity towards dimerization was found diminished. An 83% of total butene content by complex **3** (Run No. 3 of Table 2), at 70 °C is the lowest recorded value of butene content of this group. Fig. 4 shows the rate (R_o) versus time plots carried out at various temperatures. The profiles at 30 °C are stable with slight decay for both **3** and **4** (curves A and D), suggesting that the active species are stable under oligomerization conditions at 30 °C. Being less crowded, complex **3** shows higher activity (5.10×10^5 g-oligomer/mol-Ni h bar) than that of **4** (4.33×10^5 g-oligomer/mol-Ni h bar). Complex **3** and **4** show very high initial activities at higher temperatures (50 and 70 °C) and then the rate decreased monotonously, giving a reduced overall activities of 1.22×10^5 and 1.42×10^5 g-oligomer/mol-Ni h bar, respectively at 70 °C. These results indicate the active species become thermally unstable at high temperature. The low solubility of ethylene monomer and the accumulation of vapor pressure of the oligomer products are another factors to decrease the activity at high temperatures.

2.3. Conclusions

In summary, keto-enamine ligands with varying bulkiness directed towards the chelation sites have synthesized and the oxygen and nitrogen atoms of this molecule were exploited as chelations for a nickel complex with triphenyl phosphine and *o*-tolyl group as minor ligands. The ligands were proved to retain the keto-enamine structure even in the complex state. The metal center found to have a square planar structure from the single crystal XRD measurements. When activated with MAO, these complexes showed high activity towards ethylene giving selective dimerization with a minor amount of trimerization products.

3. Experimental

Synthesis of pre-ligands, ligands and their sodium salts are given in Appendix A, Supplementary material, with details of their characterizations.

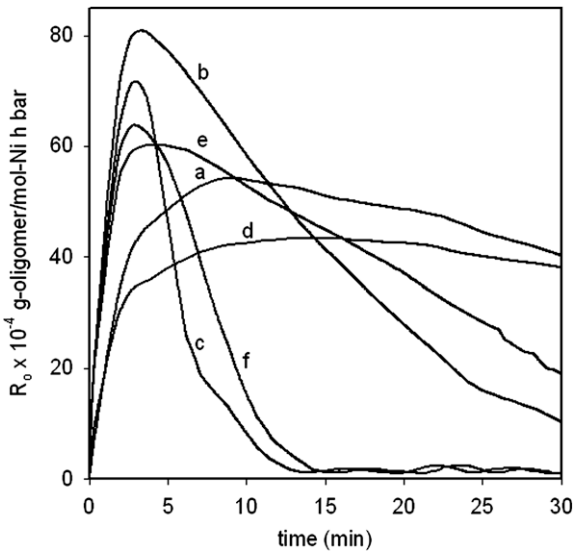


Fig. 4. Ethylene oligomerization profiles obtained by **3** at 30 (a), 50 (b) and 70 °C (c), and by **4** at 30 (d), 50 (e) and 70 °C (f). Conditions: catalyst = 2.5 μmol, [MAO]/[Ni] = 200, $P_{C_2H_4} = 5.5$ bar, and toluene = 40 mL.

3.1. General method for synthesis of tris(N-salicylideneaniline) substituted Ni complex (*3* and *4*)

Sodium salt of compound **1** (0.15 g, 0.27 mmol), and *trans*-[NiBr(*o*-tolyl)(PPh_3)$_2$] (0.20 g, 0.27 mmol) in a Schlenk flask were dissolved in dry benzene (20 mL) and stirred well at rt for 6 h. The reaction mixture was filtered using a Schlenk frit. The filtrate was concentrated to ~3 mL, and added dry pentane (30 mL). An orange-brown solid precipitated from solution and it was isolated by filtration using a Schlenk frit to yield complex **3** (0.19 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.18–12.30 (m, 2H, NH), 8.38–8.22 (m, 3H, HC-N), 7.73–7.14 (m, 28H, Ar), 2.31 (s, 18H, CH_3), 2.14 (s, 3H, *o*-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.1, 185.0, 184.0, 173.7, 168.0, 160.4, 157.8, 157.0, 156.8, 156.4, 149.4, 138.0, 137.4, 137.0, 135.0, 134.1, 133.9, 132.6, 132.3, 132.4, 131.1, 129.7, 129.2, 129.0, 128.4, 127.7, 127.2, 124.9, 124.2, 121.8, 29.0, 18.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.5. Anal. Calc. for $C_{58}H_{54}N_3NiO_3P$: C, 74.85; H, 5.85; N, 4.51. Found: C, 74.70; H, 5.64; N, 4.26%. MS(FAB+): *m*/*z* = 840 (M-tolyl).

Sodium salt of compound **2** (0.19 g, 0.27 mmol), and *trans*-[NiBr(*o*-tolyl)(PPh_3)$_2$] (0.20 g, 0.27 mmol) in a Schlenk flask were dissolved in dry benzene (20 mL) and stirred well at rt for 6 h. The reaction mixture was filtered using a Schlenk frit. The filtrate

Table 2
Summary of ethylene oligomerization results.[a]

Run No.	Complex	Temperature (°C)	Selectivity (%)[b]				Yield (g)	$R_{o,avg}$[e] × 10^{-5}
			$C_4^=$		$C_6^=$			
			α-[c]	$\sum C_4^=$[d]	α-[c]	$\sum C_4^=$[d]		
1	**3**	30	9	83	1	7	7.02	5.10
2	**3**	50	11	80	2	7	6.26	4.55
3	**3**	70	20	63	3	14	2.12	1.22
4	**4**	30	9	87	1	3	5.99	4.33
5	**4**	50	11	84	2	3	6.25	4.54
6	**4**	70	17	69	4	10	2.13	1.42

[a] *Oligomerization conditions*: catalyst = 2.5 μmol, [MAO]/[Ni] = 200, $P_{C_2H_4} = 5.5$ bar, toluene = 40 mL, and time = 30 min.
[b] Determined by GC.
[c] α-Olefin.
[d] Sum of internal olefins other than α-olefin.
[e] Average rate of oligomerization in g-oligomer/mol-Ni h bar.

was concentrated to ~3 mL, and added dry pentane (30 mL). A yellow solid precipitated from solution and it was isolated by filtration using a Schlenk frit to yield complex **4** (0.21 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.87–12.56 (m, 2H, NH), 8.4–8.0 (m, 3H, HC-N), 7.68–7.19 (m, 28H, Ar), 3.20 (sept, 6H, CH), 2.10 (s, 3H, *o*-CH_3), 1.24 (d, 36H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.1, 184.7, 183.1, 172.4, 167.6, 158.2, 157.1, 156.9, 156.2, 144.4, 137.5, 136.4, 135.9, 134.9, 134.0, 133.9, 132.3, 132.2,131.4, 130.1, 128.9, 128.7, 128.4, 127.6, 126.4, 124.1, 123.8, 123.2, 106.8, 105.9, 102.9, 29.8, 28.7, 24.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.4. Anal. Calc. for $C_{70}H_{78}N_3NiO_3P$: C, 76.50; H, 7.15; N, 3.82. Found: C, 76.90; H, 7.24; N, 3.54%. MS(FAB+): m/z = 1099 (M), 1007 (M-tolyl).

Acknowledgements

The authors thank H.J. Lee (KBSI, Jeonju) and R. Thomas (JNCASR, India) for assistance with X-ray crystallography and discussion. This work was supported by grants-in-aid for the *World Class University Program* (No. R32-2008-000-10174-0) and the *National Core Research Center Program* from MEST (No. R15-2006-022-01001-0), and the *Brain Korea 21 program* (BK-21).

Appendix A. Supplementary material

CCDC 690677 contains the supplementary crystallographic data for **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.01.017.

References

[1] Z. Zhang, Synlett 5 (2005) 877.
[2] H.-F. Klein, A. Bickelhaupt, B. Hammerschmitt, Organometallics 13 (1994) 2944.
[3] H-F. Klein, A. Bickelhaupt, Inorg. Chim. Acta 248 (1996) 111.
[4] C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149.
[5] F.A. Hicks, M. Brookhart, Organometallics 20 (2001) 3217.
[6] J.C. Jenkins, M. Brookhart, Organometallics 22 (2003) 250.
[7] L. Zhang, M. Brookhart, P.S. White, Organometallics 25 (2006) 1868.
[8] M. Okada, Y. Nakayama, T. Shiono, J. Organomet. Chem. 692 (2007) 5183.
[9] R.D. Broene, M. Brookhart, W.M. Lamanna, A.F. Volpe, J. Am. Chem. Soc. 127 (2005) 17194.
[10] M. Shiotsuki, P.S. White, M. Brookhart, J.L. Templeton, J. Am. Chem. Soc. 129 (2007) 4058.
[11] J.H. Chong, M. Sauer, B.O. Patrick, M.J. MacLachlan, Org. Lett. 5 (2003) 3823.
[12] Y.-K. Lim, S. Wallace, J.C. Bollinger, X. Chen, D. Lee, Inorg. Chem. 46 (2007) 1694.
[13] S.Y. Desjardins, K.J. Cavell, J.L. Hoare, B.W. Skelton, A.N. Sobolev, A.W. White, W. Keim, J. Organomet. Chem. 544 (1997) 163.
[14] A.L. Gavrilova, B. Bosnich, Chem. Rev. 104 (2004) 349.
[15] L.E. Breyfigle, C.K. Williams, V.G. Young Jr., M.A. Hillmyer, W. Tolman, Dalton Trans. (2006) 928.
[16] H. Li, L. Li, D.J. Schwartz, M.V. Metz, T.J. Marks, L. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 127 (2005) 14756.
[17] M.L.H. Green, N.H. Popham, J. Chem. Soc., Dalton Trans. (1999) 1049.