第 32 卷 第 5 期　　分　子　催　化　　Vol.32,No.5
2018 年 10 月　　JOURNAL OF MOLECULAR CATALYSIS(CHINA)　　Oct.　2018

Article ID: 1001-3555(2018)05-0397-08

Cross-Coupling Reaction of Aryl Halides with Grignard Reagents Catalyzed by Nickel Complexes Supported 2-pyrazolinyl-9-aryl-1,10-phenanthrolines

CUI Feng-juan*, WANG Huan-yu, DENG Qing-fang, JIANG Yan, CAO Yan-zhen, ZHAO Hua-ping
(*College of Chemistry and Chemical Engineering*, *Qiqihar University*, *Qiqihar* 161006, *China*)

Abstract: Four nickel complexes [$NiCl_2L$](**1-4**) supported by a tridentate pyrazolyl-based phenanthroline ligand (L^1-L^4) have been developed for C—C coupling reactions. The nickel complexes exhibited moderate catalytic activities for C—C coupling reactions of various aryl halides with Grignard reagent. Single-crystal X-ray diffraction analysis of the complex [$NiCl_2L^4$](**4**) reveal a distorted trigonal bipyramidal geometry at the Ni(II) center, which creates a reaction channel to facilitate C—C coupling reactions.

Key words: 2-pyrazolyl-9-aryl-1,10-phenanthrolines; nickel complexes; C—C cross coupling reactions

CLC number: O643.36　　**Document code**: A

Over the last three decades, late-transition metal complexes such as pincer-type metal complexes have attracted greatattention in catalytic chemistry[1-7]. The pincer-type metal complexes catalyzed cross-coupling reactions between ary/alkyl halide and organometallic reagents have been widely developed in the field of organic chemistry[8-12]. Among the most studied ligands are pincer DCD[13-14](D a donor atom such as P, N, or O, S) systems and NNN[15-16], PNP[17-19], SNS[20] NNO[21] and N-heterocyclic carbene (NHCs)[22-23], which have found wide applications in bond activation because of their unprecedented stability at high temperatures and catalytic activity. In addition, their ligand framework can be easily modified in order to tune the electronic properties of the metal and the steric hindrance around it.

In fact, among catalysts with metal ions as active sites, the Pd complexes are the most commonly used catalysts for cross-coupling reactions such as the Suzuki reaction, Negishi reaction, Kumada reaction, and Heck reaction because of their advantages that relatively mild reaction conditions, applicable to substrates of wide scope and displaying high turnover[24-26]. Despite their high utility, in the process of activation, precipitation of palladium black is harmful to the catalyst and leads to be inefficient, other drawbacks: palladium and the necessary ligands are expensive, palladium compounds are toxic and leaching of the palladium catalyst into final products can be problematic.

Compared with Pd, Ni catalysts are much cheaper and are the most promising alternative to palladium. Some nickel complexes[27-29] have been shown to be catalytically active for region-and stereo-selectivity and be tolerate to a wide range of functional groups, so the development of new nickel complexes with catalytic efficiency would be of practical importance for the synthetic industry. And thus the search for appropriate ligands for tuning the generation of highly active Ni catalyst precursors to catch up with or replace expensive Pd catalysts is of current interest.

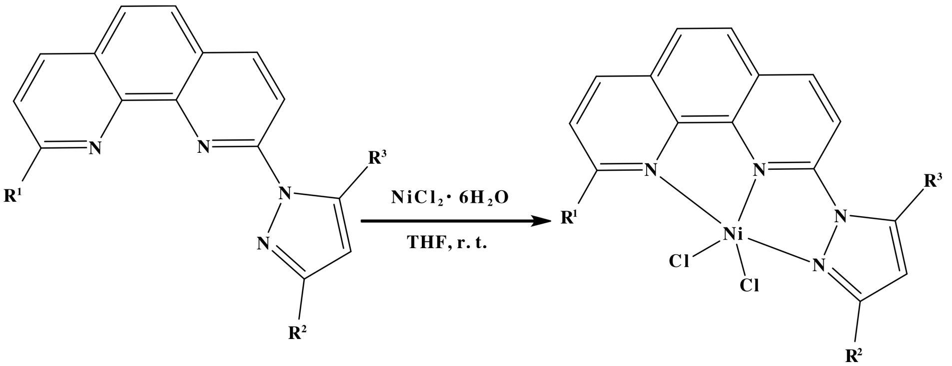
Received date: 2018-07-03; **Revised date**: 2018-08-10.

Foundation: This research was supported by the Natural Science Foundation of Heilongjiang Province of China (No. B2015015), the Post-doctoral Scientific Research Developmental Fund of Heilongjiang Province of China (No. LBH-Q14158) and the Program for Yong Teachers Scientific Research in Qiqihar University (No. 2014k-Z07).

First author: Cui Fengjuan (1983-), Famale, Doctor, Lecturer, Organic Catalysis.

Corresponding author: E-mail: cxf234@126.com(CUI Feng-juan); Tel. 0452-2742575.

Recently, a series of nickel halide complexes containing tridentate N^N^N ligands have been employed to catalyze ethylene oligomerization[30-31]. Upon activation with methylaluminoxane, the nickel complexes display good catalytic activities in ethylene oligomerization. And in the previous report the author suggested that the steric bulk of the aryl groups in the backbone created a reaction channel which made the ethylene coordination to the Ni atom more efficient and then makes the activity increase[24].Such an activity increase with increased steric bulk has also been observed in olefin polymerization reactions using zirconocene/MAO as catalysts[32]. Herein the activities of nickel complexes (Scheme 1) supported by tridentate [N^N^N] ligands with one phenanthroline linked to pyrazoly donors in C—C coupling reactions have been studied.



L^1 : R^1 = H, R^2 = R^3 = Me; L^2 : R^1 = H, R^2 = Me, R^3 = Ph;

L^3 : R^1 = H, R^2 = R^3 = Ph; L^4 : R^1 = Mes, R^2 = R^3 = Ph;

Scheme 1 Synthesis of the complexes [$NiCl_2$(L)] (1-4)

1 Experimental

1.1 General Procedures

All solvents and reagents were of analytical grade and were used as purchased without further purification. Unless otherwise mentioned, all non aqueous reactions and manipulations were carried out in a nitrogen atmosphere using standard Schlenk techniques, and chemicals were used as received without any further purification. Solvents were dried by sodium/benzophenone and distilled under nitrogen prior to use. GC analysis was performed with an SP-2100 gas chromatography spectrometer equipped with a flame ionization detector and an SE-30 silica capillary column. Retention times were compared to commercially obtained compounds. Decane was used as an internal standard.

1.2 Synthesis of the ligands L^1-L^4

2-(3-R^2-5-R^3-pyrazol)-9-R^1-1,10-phenanthroline ligands (L^1-L^4) were prepared according to the previously reported procedures[30]. In a typical experiment, a mixture of 2-hydrazine-1,10-phenanthroline or 2-hydrazine-9-aryl-1,10-phenanthroline (3.0 mmol) and the diketone (3.6 mmol), i.e. acetylacetone (for L^1), benzoylacetone (for L^2), or dibenzoylmethane (for L^3 and L^4), was stirred in dry methanol (15 mL) containing a few drops of acetic acid for 6~12 h. The solvent was removed and the residue was recrystallized from chloroform/activated charcoal to give the products.

1.3 Synthesis of the nickel complexes

The nickel(II) complexes were synthesized by the following general procedure: a solution of the ligand in THF was added to an equimolar amount of $NiCl_2 \cdot 6H_2O$ in THF. The reaction mixture was stirred at room temperature for 12 h. The resultant precipitate was collected, washed with THF and diethyl ether, and dried in vacuum. All of the complexes were prepared in high yield in this manner.

1.4 General Procedures for the C—C coupling reaction

The C—C coupling reactions were performed in 20 mL Schlenk tube in a nitrogen. In a typical experiment, required amount of catalyst, toluene and substrate were charged into the reactor and form a homogeneous solution. To the stirred solution was added dropwise a solution of PhMgBr in THF at room temperature. Stirring was continued at the desire reaction temperature within the desire reaction time. The reaction was ceased by addition of water (5 mL). The mixture was extracted with Et_2O (3 × 5 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. The Na_2SO_4 was removed by filtration and washed with Et_2O.

1.5 X-ray crystal structure determination

Diffraction data for the complexes were collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An empirical absorption correction using SADABS was applied for all data. The structures were solved by direct methods using the SHELXS program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F_2 by the use of the program SHELXL. The hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data for the complexes **4** are listed in Table 1.

2 Results and discussion

2.1 X-ray Crystallographic Study

Blue single crystals of complex **4** suitable for single crystal X-ray diffraction were obtained through slow diffusion of diethyl ether into its methanol solution. An ORTEP view of the molecular structure of complex **4** is presented in Figure 1 along with the selected bond lengths and angles. The complex **4** reveals a 1 ∶ 1 metal-to-ligand ratio with the metal center. And our catalysts are prepared in dry CH_2Cl_2, so the structure can represent the employed that of catalysts. The nickel center is coordinated a distorted trigonal bipyramidal geometry (The Addison τ = 0.16 for **4**) by two nitrogen atoms of phenanthroline, one pyrozely nitrogen, and two chlorine atoms in which N2 of the ligand and the two chlorine atoms define the equatorial plane, while the N1 and N2 atoms occupy the two coordination site of the axial. The center metal Ni(II) deviate from the equatorial 0.085 Å, the central Ni-N2 [1.973(2) Å]

Table 1 Crystallographic data and structure refinement details for 4

Empirical formula	$C_{222}H_{192}Cl_{12}N_{24}Ni_6O_8$
Fw	4101.66
Crystal color	Blue
Wavelength [Å]	0.71073
Temperature [K]	293(2)
Crystal system	Trigonal
Space group	R—3
a(Å)	37.3564(18)
b(Å)	37.3564(18)
c(Å)	12.8032(6)
A (°)	90.00
β(°)	90.00
γ (°)	120.00
V(Å^3)	15473.2(13)
Z	3
D_c(g cm^{-3})	1.321
F(000)	6384
μ (mm^{-1})	0.76
Crystal size(mm^3)	0.35 × 0.23 × 0.22
θrange (°)	1.09-26.00
Reflections collected	28986
Unique reflections	6771
Goodness of fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0401, $wR2$ = 0.1142
R indices (all data)	$R1$ = 0.0638, $wR2$ = 0.1320

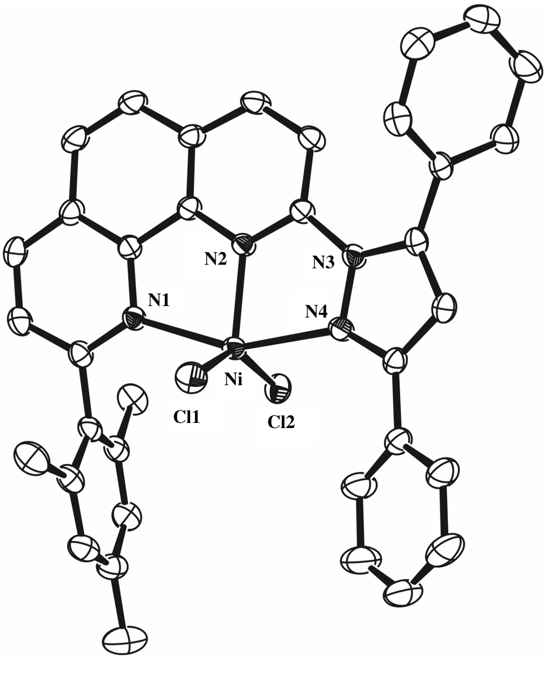


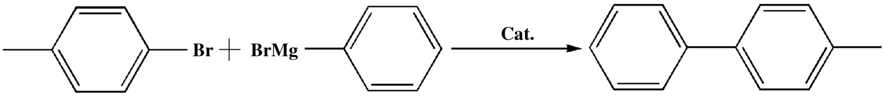
Fig.1 The molecular structure of **4** (thermal ellipsoids at the 30% probability level and hydrogen atoms are omitted for clarity)

bond is shorter than the terminal Ni-N1 [2.183(2) Å] and Ni-N4 [2.201(2) Å] bonds. In addition, compared with its analogue bromine (Ni-N2, 1.963(4) Å and Ni-N4, 2.199(4) Å)[23], clearly, the length of Ni-N2 and Ni-N4 in **4** are shorter. While the N1-Ni-N2 bite angle [79.50(8)°] is wider than the N2-Ni-N4 bite angle [75.72(8)°], the Cl-Ni-Cl angle in 4 [145.53(3)°] is similar to the analogue bromine [146.17(3)°]. And the mesityl group is nearly perpendicular to the phenanthroline plane in **4** (dihedral angle 89.5°), is also similar to the analogue bromine (89.2°), meanwhile the dihedral angle between the pyrazolyl ring and the phenanthroline plane is 15.1° in **4**, slightly smaller than the analogue bromine (17.0°). In the previous report, we found the skeleton of the chloride complexes with the formation of a more directional environment, bulkier aryl substituents can suppress chain-transfer reactions (typically-H elimination) and therefore increase the activity[30]. It suggests that if the steric bulk of the aryl groups create a reaction channel which also may makes the organometallic reagents coordination to the Ni atom more efficient and further easily reacted with other aryl halides.

2.2 Catalytic Properties

2.2.1 Optimization of reaction conditions With these considerations in mind, our initial work focused on the model reaction of p-MeC_6H_4Br with PhMgBr to optimize the reaction conditions. These results are summarized in Table 2. With toluene as the solvent and at room temperature, we first examined the effect of

Table 2 Optimization of the reaction conditions



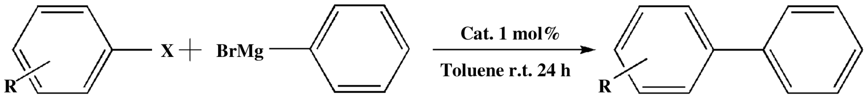
Entry[a]	Catal /mol%	Solvent /mL	Time /h	Yield /%[b]	Conversion /%	Selectivity /%
1	$NiCl_2L^1$(1)	toluene	24	39.1	76.3	51.2
2	L^1+$NiCl_2$(DME)	toluene	24	42.4	80.1	52.9
3	$NiCl_2L^1$+ 1 equiv. PPh_3	toluene	24	42.5	79.4	53.5
4	$NiCl_2L^1$+ 2 equiv. PPh_3	toluene	24	36.1	81.3	44.4
5	$NiCl_2L^1$+ 1 equiv. LiCl	toluene	24	20.0	34.1	58.6
6	$NiCl_2L^1$+ 1 equiv. Et_3N	toluene	24	10.0	33.7	29.7
7	$NiCl_2L^1$+ 1 equiv. Et_2NH	toluene	24	00	29.7	00
8	$NiCl_2L^1$(1)	THF	24	33.1	56.4	58.7
9	$NiCl_2L^1$(1)	toluene/THF	24	41.2	76.8	53.6
10	$NiCl_2L^1$(1)	dioxane	24	42.3	77.5	54.6
11	$NiCl_2L^1$(1)	Et_2O	24	36.7	67.4	54.4
12	$NiCl_2L^1$(1)	toluene	16	25.6	66.4	38.6
13[c]	$NiCl_2L^1$(1)	toluene	16	42.3	78.9	53.6
14	$NiCl_2L^1$(0.1)	toluene	24	35.7	47.8	74.7
15	$NiCl_2L^1$(2)	toluene	24	31.1	81.4	38.2
16	$NiCl_2L^1$(5)	toluene	24	21.9	86.6	25.3
17	$NiCl_2L^1$(10)	toluene	24	18.9	98.8	19.1
18	$NiCl_2L^2$(1)	toluene	24	47.9	76.7	62.5
19	$NiCl_2L^3$(1)	toluene	24	53.8	81.4	66.1
20	$NiCl_2L^4$(1)	toluene	24	60.7	84.9	71.5

a. Reaction conditions: aryl bromide 1.0 mmol, PhMgBr 1.2 mmol, solvent 5mL; b. GC yield; c. reflux catalyst precursors. To our delight, the C—C coupling reaction of *p*-MeC_6H_4Br with PhMgBr could proceed smoothly in the presence of $NiCl_2L^1$ complex (Table 2, entry 1). To achieve better results, various commercially available salt additives[33] were introduced to these systems, and the results proved that 1 equiv. PPh_3 was the best choice (Table 2, entry 3). Meanwhile, we conducted the experiment in situ by using ligand L^1 and (DME)$NiCl_2$, turning out to be the yield of *p*-MePh-Ph as well as $NiCl_2L^1$ complex (Table 2, entry 2). Subsequently, different solvents (non-polar or polar solvents) were examined. The results showed that toluene and dioxane were proved to be the best for the formation of *p*-MePh-Ph. After these optimized conditions were developed, the effects of dosage of $NiCl_2L^1$ complex and temperature were studied as well. Investigation of temperature revealed that getting the same yield needed to shorter time. Besides, with either an increase or decrease of the amount of the $NiCl_2L^1$ complex, inferior results were observed.

2.2.2 Effect of the ligand environment　Changes in the ligand environments led to different catalytic behaviors[30-31]. For example, Wang[18] group has recently reported that ligands containing electron-rich phosphorus atoms were suitable for the coupling reactions of aryl chlorides, the extent of which is strongly dependent upon the electronic nature of the phosphine ligand in the catalytic action. Based on above mentioned idea, We investigated the effect on the catalytic activities of these ligands coordinated environment in detail. The results are summarized in Table 2. The R^2 and R^3 substituents on the pyrazolinyl ring performed slight influence on their activities. It was observed that their catalytic activities increased with increasing the steric hindrance of their ligands, the regulation was easily confirmed in the catalytic systems of the complexes **1** (Me), **2** (Me, Ph) and **3** (Ph, Ph). Their activities increased in the order **1** >**2** >**3** (entries 1, 18 and 19 in Table 2). This case could be caused by electronic influences of ligands. Meanwhile, the results showed that the activity with the R^1 substituent as Mes on the phenanthroline backbone (**4**) was optimum (entry 20 in Table 2), This could be attributed to the more bulky groups at the 9-site of the phenanthroline backbone which may facilitate the course of oxidation addition and then reductive elimination.

2.2.3 Studies about the scope of substrates　With the optimized conditions in hand, the scope of aryl halides was investigated (Table 3). For example, complex **4** acted as an efficient catalyst for the substrate

Table 3 Substrate scope of complex $NiCl_2L^4$(4) catalyzed the C—C coupling Reactions



Entry[a]	R	X	Yield/%[b]	Conversion/%	Selectivity/%
1	*p*-Me	Cl	trace	trace	–
2	*o*-Me	Br	24.2	78.1	30.9
3	*p*-MeO	Cl	trace	trace	–
4	*p*-MeO	Br	13.4	89.8	14.9
5	*p*-MeO	I	63.5	99.1	64.1
6	*p*-Me	I	90.6	99.9	90.7
7	*p*-CF_3	I	98.1	99.3	98.8
8	*o*-Me	I	73.0	96.2	75.9
9	*o*-MeO	I	55.0	98.4	55.9

a. R and X mean substituents in aryl halides. The reactions were carried out using 1 mol% **4**, aryl halides 1.0 mmol, PhMgBr 1.2 mmol for 24 h at 20 ℃ in 5 mL toluene; b. GC yield of p-MeC_6H_4I, reaching 90% yield within 24 h at room temperature (Table 3, entry 6). Under same conditions, when p-$CF_3C_6H_4I$ as a substrate gave excellent conversations (yield up to 98%, Table 3, entry 7). On the same experimental conditions, complex **4** also applies to deactivated substrate such as 4-ioideanisol, but the yield of the corresponding product is a bit lower, reaching 63% yields for deactived aryl iodides over a period of 24 h (Table 3, entry 5). Probably because of the nature of the substituents (electron-withdrawing or electron-donating substituents) in the aromatic substrates, which play a key role on the activation of C—I bonds. Unfortunately, when deactivated substrates 4-bromotoluene and 4-bromoanisole were involved, only moderate or trace amounts of products were observed. In expectation, due to low reactivity of aryl chlorides, nickel complexes are almost inefficient even for the coupling reaction of activated 4-chlorotoluene and PhMgBr. It is easily explain that C—Cl bond (Ph—X bond dissociation energies (BDEs)[34]: Cl, 402 kJ/mol; Br, 339 kJ/mol; I, 272 kJ/mol) much stronger. In addition, the steric hindrance of the substituent has little influence on the product yield in the C—C coupling reaction.

2.2.4 Studies about the kind of products and catalytic action We also studied the products in the C—C cross coupling reactions. For example, Table 3, entry 5, apart from the desired product 4-methoxybiphenyl, homo-couplings and dehalogenation are observed in the reaction mixtures by GC. It is the by-products of the organic groups that occurred in the C—C coupling reactions, leading to difficulties in purification and yields of the main cross-coupled product. From the phenomenon of the experiments PhI with PhMgBr, we surmised that reaction firstly occurred between catalysts and PhMgBr (the color of reaction mixture immediately changed brown) but no reaction occurred between PhI by GC (no disappear). This is rationally understood since the generation of catalytically active species from the PhI would be more difficult than from the PhMgBr. It was in agreement with the mechanism for the alkyl-alkyl Kumada coupling catalyzed by a Ni(II) pincer complex recently proposed by Hu's group[15].

3 Conclusions

In summary, four Ni(II) dichloride complexes of 2,9-subtituted-1,10-phenanthrolin derivatives confirmed that Ni(II) complexes in apenta-coordinated fashion hold promise as catalysts for C—C coupling reactions. The steric bulk of the ligands significantly affected the catalytic behavior of the complexes. And complex **4** exhibited highly catalytic activities in the C—C coupling reaction of aryl iodide with aryl Grignard reagents at room temperature. As result, it is possible to enhance the catalytic activities by tuning the size of substituent on pyrazolyl of these complexes.

References:

[1] Di Franco T, Stojanovic M, Hu X, *et al.* A structure-activity study of nickel NNN pincer complexes for alkyl-alkyl kumada and suzuki-miyaura coupling reactions [J]. *Helv Chim Acta*, 2016, **99**(11): 830-847.

[2] a. Buono F G, Zhang Y, Tan Z, *et al.* Efficient iron-catalyzed kumada cross-coupling reactions utilizing flow technology under low catalyst loadings [J]. *Eur J Org Chem*, 2016, **2016**(15): 2599-2602.
b. Li Heng-yu(李恒宇), Bai Jie(白 杰), Wang Jun-zhong(王俊忠), *et al.* Ullmann-type coupling reactions catalyzed by SAPO-34 supported copper nanoparticles (SAPO-34 分子筛载铜催化剂催化 Ullmann 偶联反应) [J]. *J Mol Catal* (*China*) (分子催化), 2016, **30**(4): 317-323.
c. Yang Qin(杨 琴), Zhou Juan(周 娟), Yin Meng-yun(尹梦云), *et al.* Lysine-graphene oxideasa heterogeneous ligand applied in CuI-catalyzed C—N coupling reaction (赖氨酸修饰氧化石墨烯固体配体在 C—N 偶联中的应用研究) [J]. *J Mol Catal*(*China*)(分子催化), 2016, **30**(2): 99-104.

[3] Li X, Jiang Z X, Zhang X, *et al.* Nickel-catalyzed reductive cross-coupling of (hetero) aryl iodides with fluorinated secondary alkyl bromides [J]. *Org Lett*, 2015, **17**(22): 5570-5573.

[4] Franco T D, Epenoy A, Hu X. Synthesis of E-alkyl alkenes from terminal alkynes via Ni-catalyzed cross-coupling of alkyl halides with B-alkenyl-9-borabicyclo[3.3.1]nonanes [J]. *Org Lett*, 2015, **17**(19): 4910-4913.

[5] a. Frlan R, Sova M, Gobec S, *et al.* Cobalt-catalyzed cross-coupling of grignards with allylic and vinylic bromides: Use of sarcosine as a natural ligand [J]. *J Org*

Chem, 2015, **80**(15): 7803-7809.

b. Kang Zhen-wei(康振伟), Gao Zhan-chen(高占臣), Sun Wei-Peng(孙维朋), *et al.* Preparation of silicon nanosheet supported palladium as sustainable catalyst for suzuki reactions(硅纳米片负载钯催化剂的制备及其催化 Suzuki 反应研究)[J]. *J Mol Catal*(*China*)(分子催化), 2018, **32**(1): 18-26.

[6] Yang L, Huang H. Transition-metal-catalyzed direct addition of unactivated C-H bonds to polar unsaturated bonds [J]. *Chem Rev*, 2015, **115**(9): 3468-3517.

[7] Magano J, Dunetz J R. Large-scale applications of transition metal-catalyzed couplings for the synthesis of pharmaceuticals [J]. *Chem Rev*, 2011, **111**(3): 2177-2250.

[8] Petrone D A, Ye J, Lautens M. Modern transition-metal-catalyzed carbon-halogen bond formation [J]. *Chem Rev*, 2016, **116**(14): 8003-8104.

[9] Zhang X Q, Wang Z X. Cross-coupling of aryltrimethylammonium iodides with arylzinc reagents catalyzed by amido pincer nickel complexes [J]. *J Org Chem*, 2012, **77**(7): 3658-3663.

[10] Tamao K, Sumitani K, Kumada M. Selective carbon-carbon bond formation by cross-coupling of grignard reagents with organic halides. catalysis by nickel-phosphine complexes [J]. *J Am Chem Soc*, 1972, **94**(13): 4374-4376.

[11] Diederich F, Stang P J. *Metal-Catalyzed Cross-Coupling Reactions*[M]. Wiley-VCH, Weinheim, **1998**.

[12] Tsuji J. *Transition Metal Reagents and Catalysts: Innovations in Organic Synthesis*[M]. John Wiley & Sons, Chichester, **2000**.

[13] vander Boom M E, Milstein D. Cyclometalated phosphine-based pincer complexes: Mechanistic insight in catalysis, coordination, and bond activation [J]. *Chem Rev*, 2003, **103**(5): 1759-1792.

[14] Zhang Y, Song G, Ma G, *et al.* 1,3-dinitrone pincer complexes of palladium and nickel: Synthesis, structural characterizations, and catalysis [J]. *Organometallics*, 2009, **28**(11): 3233-3238.

[15] Breitenfeld J, Wodrich M D, Hu X. Bimetallic oxidative addition in nickel-catalyzed alkyl-aryl kumada coupling reactions [J]. *Organometallics*, 2014, **33**(20): 5708-5715.

[16] Vechorkin O, Hu X. Nickel-catalyzed cross-coupling of non-activated and functionalized alkyl halides with alkyl grignard reagents [J]. *Angew Chem Int Ed*, 2009, **48**(16): 2937-2940.

[17] Liang L, Chien P, Lin J, *et al.* amido pincer complexes of nickel(Ⅱ): Synthesis, structure, and reactivity [J]. *Organometallics*, 2006, **25**(6): 1399-1411.

[18] Wang Z X, Wang L. Amido pincer complex of nickel-catalysed kumada cross-coupling reactions [J]. *Chem Commun*, 2007, **2007**(23): 2423-2425.

[19] Sun K, Wang L, Wang Z X. Synthesis and characterization of amido pincer complexes of lithium and nickel and catalysis of the nickel complexes in the kumada cross-coupling [J]. *Organometallics*, 2008, **27**(21): 5649-5656.

[20] Bai S, Hor T S A. Isolation of an [SNS]Pd(Ⅱ) pincer with a water ladder and its Suzuki coupling activity in water [J]. *Chem Commun*, 2008, **2008**(27): 3172-3174.

[21] Wang Z X, Chai Z Y. Palladium(Ⅱ) and nickel(Ⅱ) complexes bearing N,N,O-chelate ligands: Syntheses, characterization and catalysis in heck and kumada coupling reactions [J]. *Eur J Inorg Chem*, 2007, **2007**(28): 4492-4499.

[22] Zhang J, Xu J, Xu Y, *et al.* Mixed NHC/Phosphine Ni (Ⅱ) complexes: Synthesis and their applications as versatile catalysts for selective cross-couplings of ArMgX with aryl chlorides, fluorides, and methyl ethers [J]. *Organometallics*, 2015, **34**(24): 5792-5880.

[23] Gu S, Chen W Z. Pincer complexes of palladium- and nickel-containing 3-butyl-1-(1, 10-phenanthrolin-2-yl) imidazolylidene as efficient aqueous sonogashira and kumada coupling reactions [J]. *Organometallics*, 2009, **28**(3): 909-914.

[24] Tsuji J. *Palladium Reagents and Catalysis: New Perspectives for the 21st Century*[C]. Wiley, Chichester, **2004**.

[25] Littke A F, Fu G C. Palladium-catalyzed coupling reactions of aryl chlorides [J]. *Angew Chem Int Ed*, 2002, **41**(22): 4176-4211.

[26] Consiglio G, Morandini F, Piccolo O. Asymmetric nickel, catalysis in the cross-coupling reaction of aryl halides with grignard reagentd. A study of the factors influencing asymmetric induction [J]. T*etrahedron*, 1983, **39**(16): 2699-2707.

[27] Terao J, Kambe N. Cross-coupling reaction of alkyl halides with grignard reagents catalyzed by Ni, Pd, or Cu complexes with π-carbon ligand(s)[J]. *Acc Chem Res*, 2008, **41**(11): 1545-1554.

[28] Zheng B, Tang F, Luo J, *et al.* Organometallic nickel (Ⅲ) complexes relevant to cross-coupling and carbon-heteroatom bond formation reactions [J]. *J Am Chem Soc*, 2014, **136**(17): 6499-6504.

[29] Schultz J W, Fuchigami K, Zheng B, *et al.* Isolated or-

ganometallic nickel(III) and Nickel(iv) complexes relevant to carbon-carbon bond formation reactions [J]. *J Am Chem Soc*, 2016, **138**(39): 12928-12934.

[30] Cui Feng-juan(崔凤娟), Yang Pei-ju(杨培菊), Wu Biao(吴彪), *et al.* Synthesis and catalytic ethylene oligomerization of nickel complexes with 2-pyrazolinyl-9-aryl-1,10-phenanthrolines, (2-吡唑啉-9-芳基邻菲咯啉配合物的合成及催化乙烯齐聚的研究) [J]. *J Mol Catal* (*China*)(分子催化), 2009, **23**(6): 534-540.

[31] Yang Y, Yang P, Zhang C, *et al.* Synthesis, structure, and catalytic ethylene oligomerization of nickel complexes bearing 2-pyrazolyl substituted 1,10-phenanthroline ligands [J]. *J Mol Catal A Chem*, 2008, **296**(1/2): 9-17.

[32] Janiak C, Lange K C H, Marquardt P. Alkyl-substituted cyclopentadienyl- and phospholyl-zirconium/MAO catalysts for propene and 1-hexene oligomerization [J]. *J Mol Catal A Chem*, 2002, **180**(1/2): 43-58.

[33] Krasovskiy A, Knochel P. A LiCl-mediated Br/Mg exchange reaction for the preparation of functionalized aryl- and heteroarylmagnesium compounds from organic bromides [J]. *Angew Chem Int Ed*, 2004, **43**(25): 3333-3336.

[34] Galli C, Pau T. The dehalogenation reaction of organic halides by tributyltin radical: The energy of activation vs. The BED of the C—X Bond [J]. *Tetrahedron*, 1998, **54**(12): 2893-2904.

2-吡唑啉-9-芳基邻菲咯啉镍配合物催化芳基卤化物和格氏试剂偶联反应的研究

崔凤娟*, 王环宇, 邓庆芳, 江艳, 曹艳珍, 赵桦萍
(齐齐哈尔大学 化学与化学工程学院, 黑龙江 齐齐哈尔 161006)

摘要: 4个基于2-吡唑啉-9-芳基邻菲咯啉(L^1-L^4)镍配合物[$NiCl_2L$](**1-4**)被开发用于芳基卤化物和格氏试剂偶联反应的研究, 表现出良好的催化活性. 对配合物(**4**)的结构进行了x-单晶衍射表征, 分析发现中心金属镍为五配位的四方锥构型利于C—C偶联反应. 讨论了配体空间位阻及反应条件对该偶联反应活性的影响, 发现邻菲咯啉的9位位阻对催化活性影响更明显.

关键词: 2-吡唑啉-9-芳基邻菲咯啉; 镍配合物; C—C偶联反应