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NICKEL COMPLEXES OF CHELATING TRIDENTATE AMIDO DIPHOSPHINE LIGANDS

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ABSTRACT

This mini review summarizes the evolution of history about nickel complexes supported by tridentate pincer ligands in organometallic chemistry. The series of these pincer ligands have hybrid characteristic of hard and soft donor atoms, in order to coordinating with metals in the periodic table. The *o*-phenylene backbone of the ligands are rigid and robust to develop of reaction chemistry of these diarylamido diphosphine complexes beneficially. In this paper, we briefly discuss ligand preparation and corresponding nickel complexes, and reactivity studies.

Keywords: Tridentate pincer ligands; diarylamido diphosphine complexes.

1. INTRODUCTION

To design or research suitable ligands is an essential rule to control the stability and reactivity of metal complexes effectively in inorganic and organometallic chemistry. From precedent references, hybrid chelating ligands play an important role because of their potentials. It makes them increase attention between metal and ligands, and generate metal complexes with unusual reactivity (Fryzuk *et al.* 1997). The remarkable example is the chelating amido phosphine ligands that include $–SiMe_2CH_2$- backbone shown in Fig 1 (Fryzuk 1992; Fryzuk and Montgomery 1989; Fryzuk *et al.* 1990, 1996a, 1996b, 1998a, 1998b, 1999, 2001a, 2001b, 2002, 2003a; Schrock *et al.* 1999; Shaver and Fryzuk 2005). These compounds have shown extensive reactivity and developed significant results in the last 25 years. It is particularly that these coordinated dinitrogen molecules were successful hydrogenation (Basch *et al.* 1999; Fryzuk and Johnson 2000; Fryzuk *et al.* 1997, 2002; MacKay and Fryzuk 2004). However, it is a disadvantage of this ligand system. It has been observed that cleavage of both N-Si (Fryzuk *et al.* 2003b; Ozerov *et al.* 2002) and C-H (Fryzuk *et al.* 1991) bonds under some situations.

Subsequently, chemists developed *o*-phenylene-derived backbone and extensively investigate metal complexes of diarylamido phosphine ligands. These *o*-phenylene-derived ligands have more rigid and robust than those of $–SiMe_2CH_2$- derived ones (Liang *et al.* 2003b). Therefore, it would be expected to decrease unsuccessful reaction. It is worth noting that N-alkylated *o*-phosphinoaniline phenylene compounds are developed in the last 40 years (Fritz et al. 1965; Crociani *et al.* 1998; Hedden and Roundhill 1985; Rauchfuss *et al.* 1975). A series of diarylamine derivatives containing *o*-phosphine functionalized are unfamiliar until 2003 (Liang *et al.* 2003a, 2003b; Winter *et al.* 2003).

In this review, Silyl-derived ligand system has been changed to diarylamido diphosphine ones, as shown in Fig 2. The H[R-PNP] pincer ligand contains two aryl rings and bridges with the N atom to form undistort backbone. The Me[^{i}Pr-PNP^{E}] compound contains a tolylene backbone and the Me[^{i}Pr-PNP^{C2}] ligand includes N-methylated and two methylene bridges with two aryl rings as the backbone. These ligands have the similar preparation steps, and H[R-PNP] has the best stability and reactivity of the three. Because N-C_{sp2} bonds are more robust than N-Si bonds, the rigidity of the *o*-phenylene backbone promotes and restrains N donor atom separation from the metal center (Liang 2006). Therefore, the thermal stability of metal complexes in the diarylamido diphosphine system are enhanced. In addition, these diarylamido diphosphine ligands are constitution of a numerous of parameters, such as substituent groups at donor atoms, the bond strength, tuning hard and soft atoms, and etc (Liang 2006). Otherwise, the reactivity and stability of diarylamido diphosphine complexes are well controllable. Furthermore, it is convenient for ^{31}P (I = 1/2, natural abundance 100%) NMR detection that these ligands incorporated phosphorous donor atoms. It is an important evidence for characterization of these isolated compounds including the solution NMR spectroscopy and X-ray crystallography (Liang 2006).

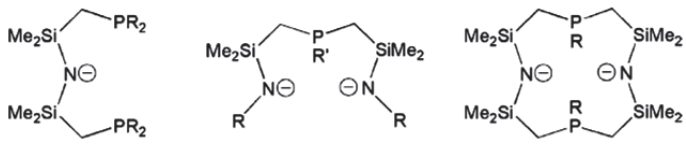

Fig. 1 The -$SiMe_2CH_2$- backbone with chelating amido phosphine ligands.

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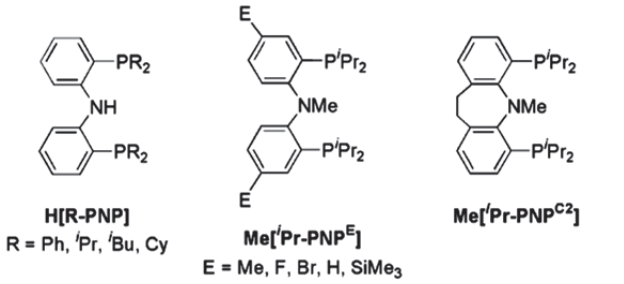
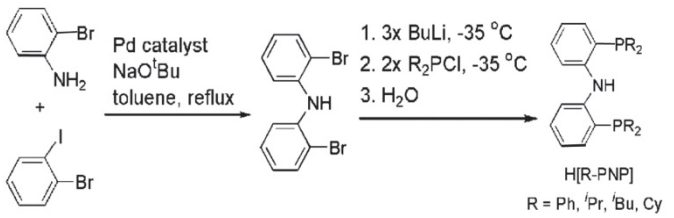


Fig. 2 Abbreviations employed for diarylamido diphosphine ligands.

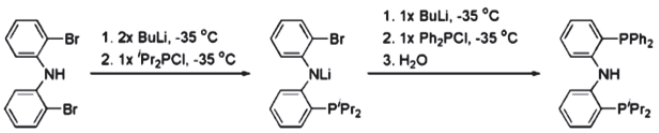
2. TRIDENTATE DIARYLAMIDO DIPHOSPHINE LIGANDS

The strategy of desired compounds has two steps and starting materials were received from chemical company commercially. It takes advantage of 2-bromoaniline and 2-bromoiodobenzene through the palladium catalyzed aryl amination reaction to produced *o*-bromo-substituted biphenyl amines (Liang 2006). Subsequently, adding of n-BuLi and R_2PCl (R = Ph, ^{i}Pr, Cy) to a diethyl solution of di(2-bromophenyl)amine at -35°C, and then quenched with ionic water generated the corresponding symmetrically neutral ligand H[R-PNP] (R = Ph, ^{i}Pr, Cy), as shown in Scheme 1 (Liang 2006). From solution NMR spectroscopic data indicated these molecules belonged C_{2V} symmetry. The NH proton in these compounds showed a triplet resonance with J_{HP} ca. 8 Hz because of proton coupling with two chemically equivalent phosphorus atoms. And X-ray crystallography data also appeared these results (Liang 2006).



Scheme 1 Synthesis of symmetric pincer ligands H[R-PNP] (R = Ph, ^{i}Pr, ^{t}Bu, Cy).

In order to investigate processes of transition-metal-catalyzed olefin polymerization clearly, the effective controlling regioselectivity of 1, 2- or 2, 1 α- olefin insertion is decisive (Liang *et al.* 2008a). It has been shown that regiospecificity was an impressive impact on polymer weights and indicated it was different between reactivity and durability of propagating species of 1, 2- olefin insertion and those of 2, 1- olefin insertion (Liang *et al.* 2008a). Therefore, a series of symmetrical H[R-PNP] (R = Ph, ^{i}Pr, Cy) and unsymmerical H[Ph-PNP-^{i}Pr] ligands were prepared (Liang *et al.* 2008a). Scheme 2 shows the protocol of synthesis of the unsymmerical H[Ph-PNP-^{i}Pr] ligand (Liang *et al.* 2008a). The synthetic protocol of unsymmetrical H[Ph-PNP-^{i}Pr] ligand was similar to symmetrical H[R-PNP] ones. It takes advantage of diethyl solution of *o*-bromo-substituted biphenyl amines with n-BuLi to promote the lithiation reaction, adding R_2PCl (R = Ph, ^{i}Pr, Cy) to progress phosphanylation, and then quenched with ionic water generated the corresponding unsymmetrically neutral ligand H[Ph-PNP-^{i}Pr] (Liang *et al.* 2008a). The symmetrical ligands have the same substituents on phosphorus atoms, but the unsymmetrical one has different substituents (one is phenyl and the other is isopropyl).



Scheme 2 The protocol of synthesis of the unsymmerical H[Ph-PNP-^{i}Pr] ligand (Liang *et al.* 2008a).

It has been characterized by ^{1}H, ^{13}C, and ^{31}P NMR data and X-ray crystallography. The amino proton appeared doublet of doublet at 8 ppm in the ^{1}H NMR spectrum. The ^{31}P {^{1}H} NMR spectra revealed two signals at -16.7 and -14.8 ppm for the diphenyl- and the diisopropyl- substituted phosphorous atoms, separately. It was interesting that these ^{31}P chemical shifts were approximate to those found for symmetrically substituted H[R-PNP] (R = Ph, ^{i}Pr), respectively. Table 1 indicated the ^{31}P {^{1}H} NMR spectra of diarylamido diphosphine ligands in d_6-benzene solution at room temperature. Fig. 3 presented the molecular structure of H[Ph-PNP-^{i}Pr] natural ligand.

Table 1 Selected spectroscopic data for diarylamido diphosphine ligands[a].

Compound	δ_P	Reference
H[Ph-PNP]	−18.6	23,29,32
H[*i*Pr-PNP]	−13.3	32
H[Cy-PNP]	−22.0	32
H[Ph-PNP-^{i}Pr]	-16.7 and -14.8	31

[a] All Phosphorus Thirty-One NMR spectra were recorded in C_6D_6 at room temperature, chemical shifts in ppm, and coupling constants in Hz.

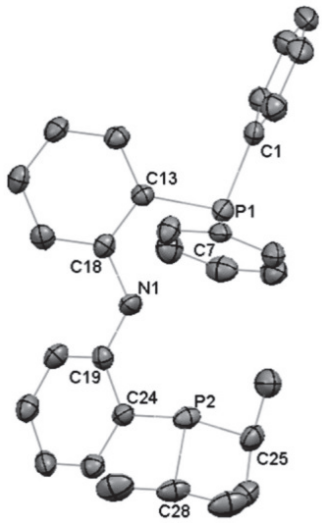
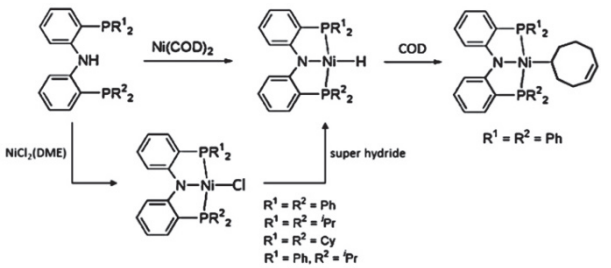


Fig. 3 The molecular structure of asymmetrical natural ligand H[Ph-PNP-^{i}Pr].

3. NICKEL COMPLEXES

3.1 Nickel Hydride and Nickel Chloride Complexes

A series of diamagnetic and square-planar nickel(II) complexes sustained by tridentate amido diphosphine ligands were synthesized. It took advantages of neutral ligand and $NiCl_2$(DME) in THF reaction solution at RT in the existence of a little bit triethylamine generated the corresponding [R-PNP]NiCl (R = Ph, ^{i}Pr, Cy) and [Ph-PNP-^{i}Pr]NiCl nickel chloride complexes (Liang 2006). They were all air and water stable in solution and solid state. The [R-PNP]NiH (R = Ph, ^{i}Pr, Cy) and [Ph-PNP-iPr]NiH nickel hydride complexes were produced from the reaction of nickel chloride complexes with super hydride in THF solution at −35°C or neutral ligands with Ni(COD)$_2$ by oxidative addition reaction, as shown in Scheme 3 (Liang 2006).



Scheme 3 Synthesis of nickel hydride and nickel chloride complexes (Liang 2006).

However, the reaction of Ni(COD)$_2$ with [Ph-PNP]H produced mixture complexes including [Ph-PNP]NiH and the cyclooct-4-en-1-yl complex which was COD insertion into the Ni-H bond (Liang 2006). Subsequently, adding quantitative COD to the mixture reaction formed the single complex [Ph-PNP]NiH. In contrast, there were no reactions of [R-PNP]NiH (R = ^{i}Pr, Cy) and [Ph-PNP-iPr]NiH with COD, respectively. These results from the phosphorus substituent effect which were related with electrophilicity and steric geometry influence on the divalent nickel center of these complexes. The phenyl-substituted phosphorus donors of nickel hydride complexes was more electrophilic and steric to induce COD coordination and insertion facilly (Liang 2006). Nevertheless, the nickel centers of [R-PNP]NiH (R = ^{i}Pr, Cy) and [Ph-PNP-^{i}Pr]NiH complexes were too bulky to coordinate with the eight-membered COD rings (Liang 2006). Fig 4 shows the molecular structure of asymmetrical nickel hydride complex, and Fig 5 displays the formation complex of symmetrical nickel COD insertion compound.

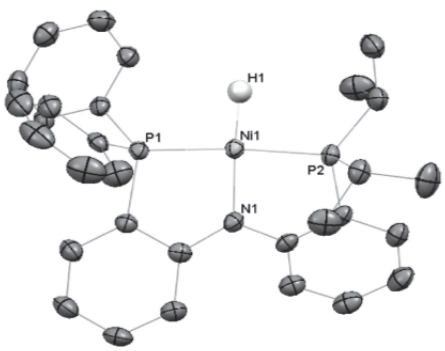


Fig. 4 The molecular structure of asymmetrical nickel hydride [^{i}Pr-PNP-Ph]NiH.

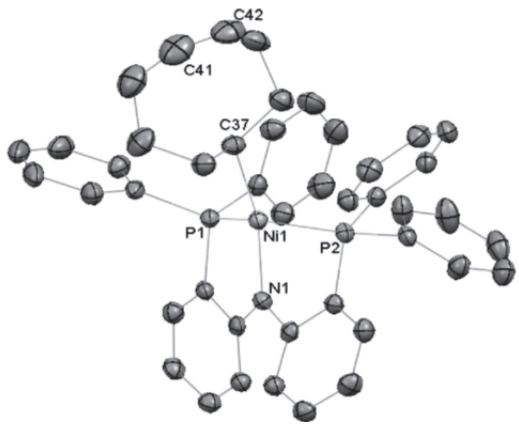
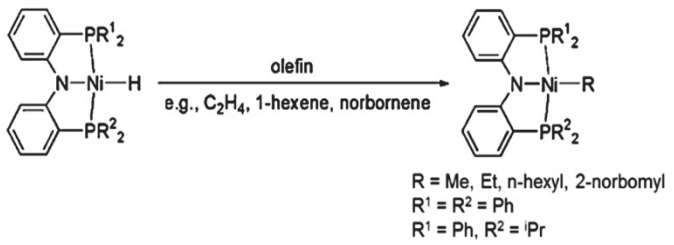


Fig. 5 The molecular structure of symmetrical nickel COD insertion complexe [Ph-PNP]Ni(η^1-C_8H_{13}).

3.2 Nickel Alkyl Complexes

It is particularly attractive to isolate nickel alkyl complexes bearing ß-hydrogen compounds because ß-hydrogen elimination reaction accesses automatically. The similar method was prepared for nickel alkyl complexes. It made use of nickel chloride complexes with Grignard reagents to receive the corresponding [R-PNP]NiR' and [Ph-PNP-^{i}Pr]NiR' nickel alkyl complexes (Liang *et al.* 2008a). These nickel alkyl complexes including ß-hydrogen compounds were thermally stable for 3 days. These results correspond to previous description of rigidity and robustness of tridentate amindo phosphine ligands (Liang *et al.* 2008a). There are uncommon examples of crystallographically characterized of single nuclear nickel alkyl complexes containing ß-hydrogen groups. It was notable that olefin insertion into the Ni-H bond of nickel hydride complexes containing ß-hydrogen alkyl groups occurred readily at RT (Liang *et al.* 2008a). ß-hydrogen elimination and olefin insertion are microscopic reversibility reactions in the principle and generously results (Liang *et al.* 2008a). However, these pincer ligands containing ß-hydrogen alkyl groups with nickel complexes were isolated and identified. Therefore, it was proposed that ß-hydrogen elimination of these complexes seemed to uphill therthermodynamically (Liang *et al.* 2008a). Nickel alkyl complexes reacted with halogenated hydrocarbon compounds to generate nickel halide complexes (Liang *et al.* 2008a).

Take advantage of the in situ prepared [Ph-PNP]NiH reacted with other olefins such as ethylene, 1-hexene, and norbornene to receive [Ph-PNP]NiEt, [Ph-PNP]Ni(n-hexyl), and [Ph-PNP]Ni (2-norbornyl), separately (Liang *et al.* 2008a). Similar reactions were found for [Ph- PNP-^{i}Pr]NiH. There were isolated pure compounds including [Ph-PNP-^{i}Pr]NiEt, [Ph-PNP-^{i}Pr]Ni(n-hexyl), and [Ph-PNP-^{i}Pr]Ni (2-norbornyl) (Liang *et al.* 2008a). However, there were no similar reaction for [R-PNP]NiH (R = ^{i}Pr, Cy). Therefore, [Ph-PNP]NiH and [Ph- PNP-^{i}Pr]NiH have more reactive in higher energy than [Ph- PNP]Ni(alkyl) and [Ph-PNP-iPr]Ni(alkyl) bearing ß-hydrogen alkyl complexes. The reactivity of [Ph-PNP-^{i}Pr]NiH occupied in the middle of [R-PNP]NiH (R = ^{i}Pr, Ph). These nickel alkyl complexes were all thermally stable. Scheme 4 shows the synthetic method of nickel alkyl complexes (Liang *et al.* 2008a).



Scheme 4 The method for synthesis of nickel alkyl complexes (Liang *et al.* 2008a).

On the basis of microscopic reverse between ß-hydrogen elimination and olefin insertion, nickel hydride species were ordinarily thermally more stable than nickel alkyl ones containing ß-hydrogen groups. The electrophilicity of nickel hydride complexes originated from phosphorous substituents. It played an important role that the distinction of insertion reactivity of these olefins, especially small size molecular (Liang *et al*. 2008a).

Figure 6 presented molecular structures of nickel alkyl complexes (Liang *et al.* 2008a). These symmetrical nickel complexes were suggested C_{2V} symmetry by solution NMR data, but the unsymmetrical one belonged C_S symmetry (Liang *et al.* 2008a). The *o*-phenylene carbon atoms of symmetrical nickel complexes was observed virtual-triplet resonances in the $^{13}C\{^1H\}$ NMR spectra, indicating a square planar geometry for these compounds (Liang *et al*. 2008a). The H_α and C_α atoms in nickel alkyl complexes and the hydride in symmetrical nickel hydride complexes were represented triplet resonances in the ^1H and $^{13}C\{^1H\}$ NMR spectra (Liang *et al.* 2008a). However, the Ni-H bound of unsymmetrical nickel complexes exhibited a doublet of doublets resonance at -18 ppm with two distinct $^2J_{HP}$ coupling constant for the two chemically inequivalent phosphorous atoms (Liang *et al.* 2008a). The NiCH_2 moiety of unsymmetrical nickel alkyl complexes presented two signals at 1.4 and 1.0 ppm in ^1H NMR spectra, indicating that these H_α were diastereotopic geometry (Liang *et al.* 2008a). This chemical nonequivalence of α-hydrogen atoms was ascribed to the lack of rotate symmetry in the α-methylene groups. In the $^{31}P\{^1H\}$ NMR spectra, unsymmetrical nickel complexes presented two doublet resonances for chemically inequivalent phosphorous atoms that chemical shifts were very closely symmetrical ones. The large $^2J_{PP}$ coupling constant indicated that two phosphorus atoms were in trans-orientation and bounding with meridional coordination mode (Liang *et al.* 2008a). These results were consistent with hindered rotation of Ni-C bounds, resistant ß-hydrogen elimination, and thermally stable for nickel insertion complexes (Liang *et al.* 2008a). The DEPT ^{13}C NMR spectra showed α-methine and ß-methyl groups for the nickel insertion complexes of ethylene derived olefins such as 1-hexene, styrene, and methyl acrylate (Liang *et al.* 2008a). There was no methylene signal observed. The results revealed regiospecificity effect for these nickel insertion complexes including electronically neutral olefins (Liang *et al.* 2008a). These data indicated that 1-hexene selected 1,2-insertion into Ni-H bound, but styrene and methyl acrylate selected 2,1-insertion into those (Liang *et al.* 2008a). This result originated from the olefin substituent effect. However, [R-PNP] NiH (R = ^{i}Pr, Cy) didn't react with electronically neutral olefins such as 1-hexene and styrene, they reacted with electronically activated olefin such as methyl acrylate and indicated 2,1-insertion into Ni-H bound in the DEPT ^{31}C NMR spectra (Liang *et al.* 2008a). This result implied that [R-PNP]NiH (R = ^{i}Pr, Cy) nickel hydride complexes enhanced back-π-acceptor capability of methyl acrylate to coordinate with nickel center (Liang et al. 2008a). Scheme 5 showed synthesis of electronically activated olefin inserted into nickel hydride bond (Liang *et al.* 2008a). All spectroscopic data were consistent with solid state structures. Fig. 7 presented molecular structures of nickel insertion complexes (Liang *et al.* 2008a).

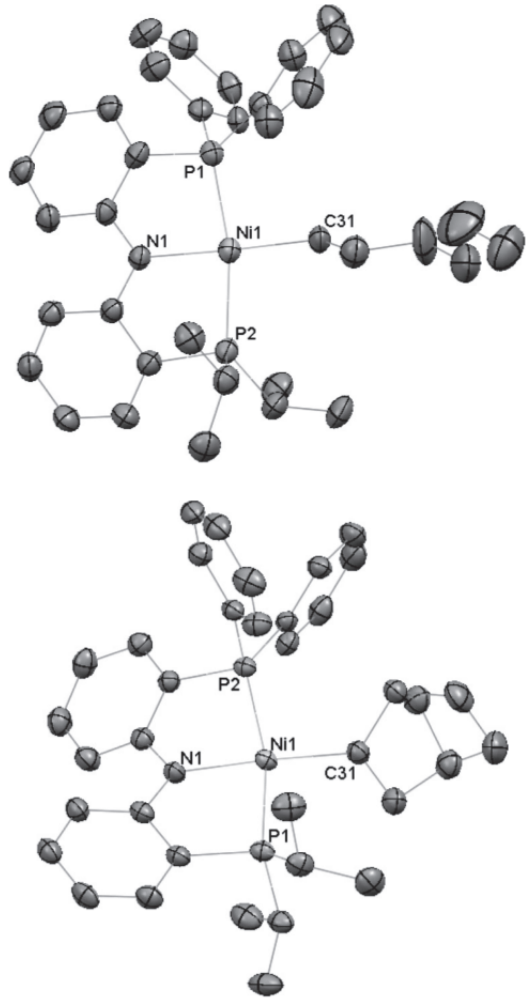
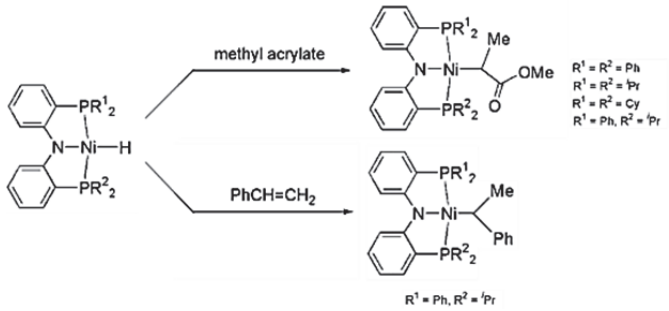


Fig. 6 Molecular structures of (a) [Ph-PNP-^{i}Pr]Ni(n-hexyl) (above) and (b) [Ph-PNP-^{i}Pr]Ni(2-norbornyl) (below).



Scheme 5 Insertion reaction of electronically natural olefins (Liang *et al.* 2008a).

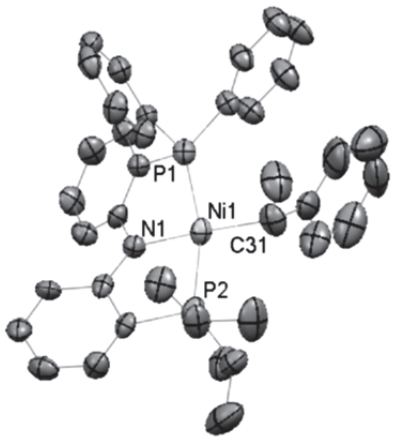


Fig. 7 The molecular structure of asymmetrical nickel styrene insertion complexes [Ph-PNP-^{i}Pr]NiCH(Me)Ph.

It is divergent regioselectivities of 1-hexene, styrene and methyl acrylate insertion for nickel insertion complexes. Figure 8 suggested two different cyclic transition states in these reactions. The former picture in Fig. 8 showed that electropositive charge of the coordinated olefins is favorably localized at the α-carbon atom, while it is at the ß-carbon on the latter picture in Fig. 8. This suppose is coherent with the expected electron-releasing character of an n-butyl group and electron-withdrawing property of a phenyl or ester substituent (Liang *et al.* 2008a).

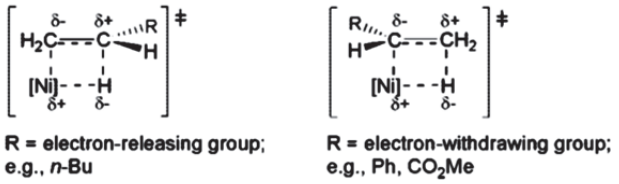
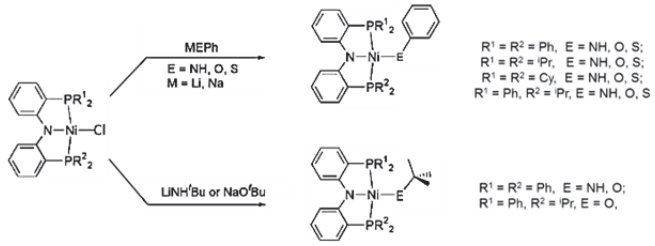


Fig. 8 Proposed cyclic transition states of the four-membered ring (Liang *et al.* 2008a).

3.3 Nickel-heteroatom complexes

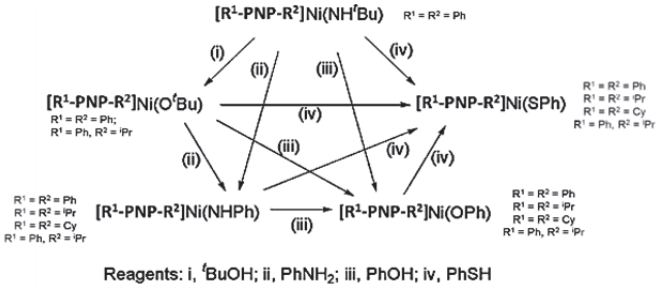
A collection of nickel alkyl and hydride complexes were thermally stable, incorporating those existing ß-hydrogen atoms. The chelating amido diphosphine ligands offered the rigid and robust behavior to induce unusual stability of nickel alkyl complexes. These complexes could endure C-R (R= H, alkyl) bound activation of intramolecular arene and produced metal-heteroatom bonds (Liang *et al.* 2008b). It was an important thing that late transition metal complexes attached π-donor ligands with covalent bonds such as amide, alkoxide, and thiolate in biology system and catalytic processes (Liang *et al.* 2008b).

Take the advantage of [R-PNP]NiCl (R = Ph, ^{i}Pr, Cy) with LiNHPh, NaOPh, or NaSPh, generated the relevanting anilide [R-PNP]Ni(NHPh), phenolate [R-PNP]Ni(OPh), and thiophenolate [R-PNP]Ni(SPh) derivatives, respectively (Liang *et al.* 2008b). The similar reaction of [Ph-PNP-^{i}Pr]NiCl with LiNHPh, NaOPh, NaSPh, or NaO^{t}Bu generated the conforming anilide [Ph-PNP-^{i}Pr]Ni (NHPh), phenolate [Ph-PNP-^{i}Pr]Ni(OPh), and thiophenolate [Ph-PNP-^{i}Pr]Ni(SPh), and tert-butoxide [Ph-PNP-^{i}Pr]Ni(O^{t}Bu) derivatives, respectively (Liang *et al.* 2008b). Treatment of [Ph-PNP]NiCl with either LiNH^{t}Bu or NaO^{t}Bu generated tert-butyl amide [Ph-PNP]Ni (NH^{t}Bu) and tert-butoxide [Ph-PNP]Ni (O^{t}Bu), separately (Liang *et al.* 2008b). In comparison, seeks to prepare analogous tert-butyl amide and tert-butoxide complexes of [^{i}Pr- PNP]$^{-}$ or [Cy-PNP]$^{-}$ were not successful, as shown in Scheme 6 (Liang *et al.* 2008b).



Scheme 6 The method for synthesis of nickel-heteroatom bond complexes.

Approach to study protonolysis of these nickel(II)–heteroatom complexes indicated the primary reactivity of these *p*-donor ligands. The basicity followed the order NH^{t}Bu > O^{t}Bu > NHPh > OPh > SPh. The activity sequence of nickel chloride complexes was [Ph-PNP]NiCl > [Ph-PNP-^{i}Pr]NiCl > [R-PNP]NiCl (R = ^{i}Pr, Cy), as shown in Scheme 7 (Liang *et al.* 2008b). The solution NMR spectroscopic data for all compounds were in Table 2, and X-ray structures of [^{i}Pr-PNP] Ni(NHPh) and [^{i}Pr-PNP] Ni (OPh) were evidenced in Fig 9 (Liang *et al.* 2008b).



Scheme 7 Summeried the protonolysis discussed of nickel-heteroatom complexes (Liang *et al.* 2008b).

Table 2 The selected NMR data of nickel covalented with p-donor ligand complexes[a]

Compound	δ_{31P}	δ_{NH}
[Ph-PNP]NiCl[b]	18.77	
[Ph-PNP]Ni(NHPh)	12.93	−1.10
[Ph-PNP]Ni(OPh)	8.77	
[Ph-PNP]Ni(SPh)	23.83	
[Ph-PNP]Ni(NH^{t}Bu)	12.77	−0.70
[Ph-PNP]Ni(O^{t}Bu)	−1.78	
[^{i}Pr-PNP]NiCl[b]	34.68	
[*i*Pr-PNP]Ni(NHPh)	29.25	−1.18
[*i*Pr-PNP]Ni(OPh)	28.13	
[*i*Pr-PNP]Ni(SPh)	33.82	
[Cy-PNP]NiCl[b]	26.77	
[Cy-PNP]Ni(NHPh)	21.53	−1.26
[Cy-PNP]Ni(OPh)	21.00	
[Cy-PNP]Ni(SPh)	26.62	

[a] All spectra were recorded in C_6D_6 at room temperature, chemical shifts in ppm.
[b] Data selected from Liang *et al.* (2006).

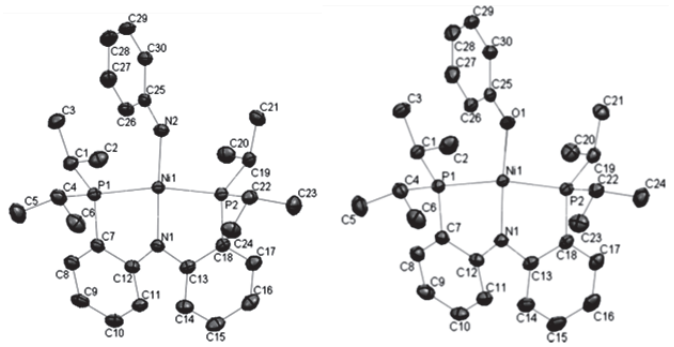
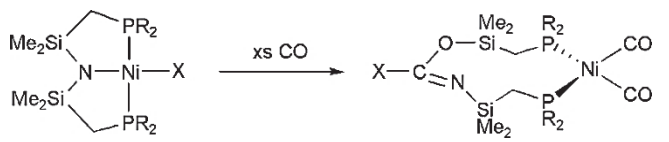


Fig. 9 Molecular structures of [^{i}Pr-PNP]Ni(NHPh) (left) and [^{i}Pr-PNP]Ni(OPh) (right).

3.4 Nickel Carbonyl Complexes

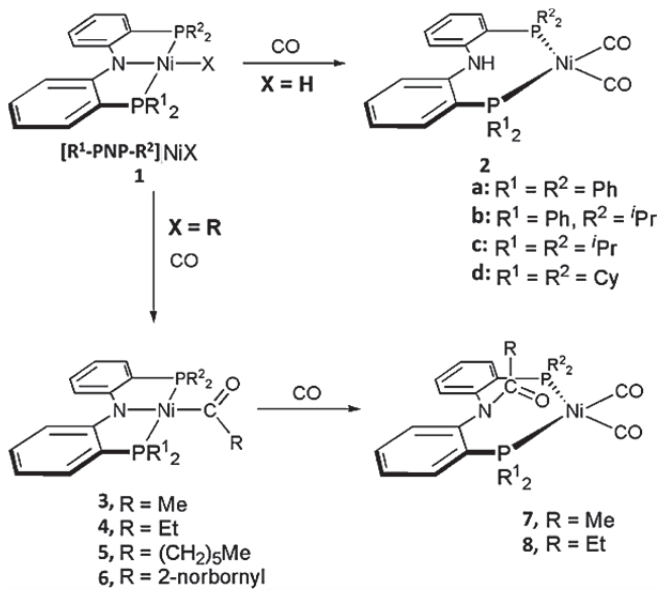
Owing to a collection of hydridonickel(II) complexes of symmetrical $[N(o\text{-}C_6H_4PR_2)_2]^-$ (R = Ph, ^{i}Pr, Cy) and asymmetrical $[N(o\text{-}C_6H_4PPh_2)(o\text{-}C_6H_4P^iPr_2)]^-$ were known to go through olefin insertion reactions, producing $[PNP]^-$ connected organonickel(II) derivatives that are thermally stable and restrain to β-elimination even at high temperatures. Extending to the applications of carbonylation for these nickel hydride, alkyl, and aniline complexes, it was interested in the reactivity studies of these complexes for migratory insertion of carbon monoxide (Liang *et al.* 2012). It was an important thing that a reactive transition-metal-ligand bond goes through migratory insertion of carbon monoxide for catalytic olefin hydroformylation, olefin/CO polymerization, and thioester constitution in acetyl coenzyme (Liang *et al.* 2012).

However, Fryzuk *et al*. have previously illustrated that hydrocarbylnickel(II) complexes $NiX[N(SiMe_2CH_2PR_2)_2]$ (R = Ph, X = Me, vinyl, allyl, Ph; R = Me, X = Ph) reacted with CO to give $Ni(CO)_2[R_2PCH_2SiMe_2OC(X)=NSiMe_2CH_2PR_2]$ after a procedure of continuous transmutations involving migratory insertion, reductive elimination, and rearrangement of N,O-silatropic atoms, as shown in Scheme 8 (Liang *et al.* 2012; Fryzuk and Macneil 1982, 1984; Fryzuk *et al.* 1987). Pay attention to that the procedure of the nickel(0) dicarbonyl products in these reactions is individual of the feature of R or X incorporated (Fryzuk and Macneil 1982, 1984; Fryzuk *et al.* 1987).



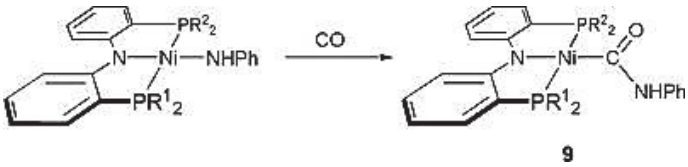
Scheme 8 Carbonylation of NiX $[N(SiMe_2CH_2PR_2)_2]$ (R = Ph, X = Me, vinyl, allyl, Ph; R = Me, X = Ph) complexes (Fryzuk and Macneil 1982, 1984; Fryzuk *et al.* 1987).

Therefore, a series of nickel(II) hydride bearing o-diarylamido diphosphine ligands with carbon monoxide under ambient conditions lead to reductive elimination of diarylamine to give zerovalent nickel dicarbonyl complexes [R-PNHP]Ni$(CO)_2$ (R = Ph, ^{i}Pr, Cy) and [Ph-PNHP-^{i}Pr]Ni$(CO)_2$ (Liang *et al.* 2012). Through the migratory insertion of CO into the Ni-X (X = Me, Et, n-hexyl, 2-norbornyl) bonds of [R-PNP]Ni-X (R = Ph, ^{i}Pr, Cy. X = Me, Et, n-hexyl, 2-norbornyl) and [Ph-PNP-^{i}Pr]Ni-X (X = Me, Et, n-hexyl, 2-norbornyl) afforded Ni(II)-acyl derivatives [R-PNP] NiC(O)X (R = Ph, ^{i}Pr, Cy; X = Me, Et, n-hexyl, 2-norbornyl) and [Ph-PNP- ^{i}Pr]NiC(O)X (X = Me, Et, n-hexyl, 2-norbornyl) (Liang *et al.* 2012). Interestingly, further carbonylation of acyl nickel complexes [Ph-PNP]NiC(O)X (X = Me, Et) generated [RC(O)N $(o\text{-}C_6H_4\ PPh_2)_2]Ni(CO)_2$ (R = Me, Et) as a result of C−N bond forming reductive elimination whereas no reaction occurs for [Ph-PNP- ^{i}Pr]NiC(O)X or [^{i}Pr-PNP]NiC(O) X (X = Me, Et) under similar conditions, as shown in Scheme 9 (Liang *et al.* 2012). Carbonylation of the nickel anilide complexes [R-PNP]NiNHPh (R = Ph, ^{i}Pr, Cy) and [Ph- PNP-^{i}Pr]NiNHPh produced carbamoyl nickel complexes [R-PNP]NiC(O)NHPh (R = Ph, ^{i}Pr, Cy) and [Ph-PNP-^{i}Pr]NiC(O) NHPh as the final products in Scheme 10 (Liang *et al.* 2012).



Scheme 9 Summarized the carbonylation of nickel hydride and nickel alkyl complexes (Liang *et al.* 2012).

Apart from solution NMR spectroscopic data for all nickel complexes were in Table 3, X-ray structures of [Ph-PNHP-^{i}Pr]Ni $(CO)_2$ (2b), [Ph-PNP-iPr]NiC(O)(Me) (3b), [Ph-PNP-^{i}Pr]NiC(O) (n-hexyl) (5b), [Ph-PNP-^{i}Pr]NiC(O)(2-norbornyl) (6b) and [Ph-PNP]NiC(O)NHPh (9a) were presented in Fig 10 and Fig 11 (Liang *et al.* 2012).



Scheme 10 Synthesis of nickel carbonyl anilide complexes (Liang *et al.* 2012).

Table 3 Selected solution NMR and IR data for nickel complexes[a] (Liang *et al.* 2012).

Compound	δ_{NH}	δ_{31P}	$^2J_{pp}$	$\delta_{C\alpha}$	$^2J_{PC\alpha}$	ν (C≡O)	ν (C=O)
2a	8.61	16.2		199.4	4.5	1993, 1924	
2b	9.99	23.7, 13.7		200.4	4.6	2004, 1948	
2c	10.65	19.3		201.6	5.0	2000, 1942	
2d	10.63	9.8		201.6	5.5	1997, 1937	
3a		18.8					
3b		37.8, 18.3	192	259.7	18.8		1621[c]
3c		35.8		259.2	20.5		1618
4a		16.0					
4b		36.9, 17.6	194	261.2	19.2		1622[c]
4c		35.6		259.3	20.6		1618[c]
5b		36.9, 17.9	193	260.8	18.8		1621[c]
6b		34.8, 18.2	194	264.1	18.3		1621[c]
7a		23.4, 22.2	5.6	197.2	4.5	2002, 1943[c]	1695[c]
8a		24.7, 23.5	5.5	197.9	6.0	1994, 1927	1693
9a	6.77	22.3		194.5	31.0		1558 (1573)[c]
9b	6.89[b]	42.8, 21.1[b]	222[b]	195.7[b]	27.0[b]		1572 (1585)[c]
9c	7.19	40.9		196.1	27.4		1572

[a] All NMR spectra were recorded in C_6D_6 at room temperature, chemical shifts in ppm, coupling constants in Hz; all IR spectra were recorded in Nujol at room temperature, stretching frequency in cm^{-1}.
[b] Data selected from Liang *et al.* 2011.
[c] Data recorded in THF.

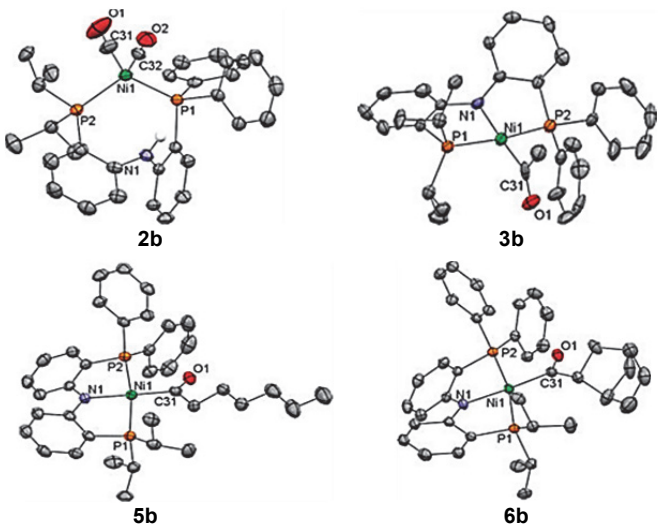


Fig 10 Molecular structures of asymmetrical nickel carbonyl insertion complexes [Ph-PNHP-^{i}Pr]Ni(CO)$_2$ (2b), [Ph-PNP-^{i}Pr]NiC(O)(Me) (3b), [Ph-PNP-^{i}Pr]NiC(O)(n-hexyl) (5b), and [Ph-PNP-^{i}Pr]NiC(O)(2-norbornyl) (6b).

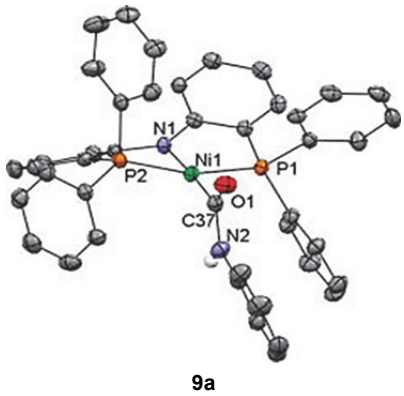


Fig 11 Molecular structure of symmetrical nickel carbonyl anilide complexes [Ph-PNP]NiC(O)NHPh (9a).

4. CONCLUSIONS

Nickel complexes containing diarylamido diphosphine ligands has become very popular (Liang 2006). The diarylamido diphosphine ligands with the *o*-phenylene backbone are rigid and robust and has been demonstrated in organometallic chemistry (Liang 2006). The various substituents such as alkyl and aryl at phosphorus atoms of the diarylamido diphosphine ligands may be well controlled for stability and reactivity of nickel complexes (Liang 2006). The catalytic activity of nickel complexes has been developed including the oxidative addition, insertion steps, and migratory insertion progresses (Liang 2006).

The olefin insertion into a Ni-H bond can be effectively controlled by the electronic and steric properties of substituents at the olefinic substrates, and the reactivity and regioselectivity of that can also related with phosphorus donors of the amido diphosphine ligands (Liang *et al.* 2008a). The derived nickel(II) hydride complexes bear with various substituents at the phosphorus donors are finely tunable by the electronic and steric characteristics (Liang *et al.* 2008a). The reactivity of unsymmetrical [Ph-PNP-^{i}Pr]NiH exhibited between [Ph-PNP]NiH and [^{i}Pr-PNP]NiH. [Ph-PNP]NiH is the best reactivity because its higher electrophilic and steric effect induced more approachable to nickel center (Liang *et al.* 2008a).

The remarkable results are that individual 1,2-insertion products were generated from reactions with 1-hexene, whereas selective 2,1-insertion reactions occur with styrene or methyl acrylate (Liang *et al.* 2008a). This is because that regioselectivity and electron-withdrawing groups are binding with olefin molecules such as styrene and methyl acrylate. However, the alkyl group which is binding with olefin ones such as 1-hexene belongs to electron-releasing substituents.

The insertion reactivity illustrated that nickel hydrocarbyl complexes involving ß-hydrogen atoms are all thermally stable and resistive ß-elimination, even at raising high temperatures (Liang *et al.* 2008a). These results imply that the nickel hydride species are higher in energy than their olefin insertion products on the foundation of the microscopic reverse between ß-elimination and olefin insertion (Liang *et al.* 2008a).

In the part of covalently bounded with π-donor ligands including anilide, phenolate, thiophenolate, tertbutylamide, and tert-butoxide derivatives to generate nickel-heteroatom complexes. The basicity of the π-donor ligands follows the order NH^{t}Bu > O^{t}Bu > NHPh > OPh > SPh (Liang *et al.* 2008b).

The nickel hydride complexes generated N-H bond formation undergo reductive elimination to generate zerovalent nickel dicarbonyl complexes in the presence of carbon monoxide (Liang *et al.* 2012). However, nickel anilide complexes prefer migratory insertion to approach [R-PNP]NiC(O)NHPh (R = Ph, ^{i}Pr, Cy) and [Ph-PNP-^{i}Pr]NiC(O)NHPh complexes. Interestingly, nickel alkyl complexes react with CO to produce nickel acyl complexes (Liang *et al.* 2012). Only [Ph-PNP]NiC(O)R (Me, Et) complexes are undergo N-C_{sp2} bond-formation and reductive elimination to generate [RC(O)N(*o*-$C_6H_4PPh_2$)$_2$]Ni(CO)$_2$ (R = Me, Et) complexes (Liang *et al.* 2012). These reactivity preferences involved a function of the

electrophilicity of the nickel center. These consequences are especially corresponding to the synthesis of carbonyl including organic molecules by means of continuous oxidative addition, CO migratory insertion, and reductive elimination (Liang *et al.* 2012).

According to the consequents received to date, it is distinct to anticipate the probability of a wide arrangement of new diarylamido diphosphine complexes and concering compounds that commit to generate exciting chemistry broadly and abundantly (Liang 2006).

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