Journal of Organometallic Chemistry xxx (2017) 1–8

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, characterization and catalytic application of some novel PNP-Ni(II) complexes: Regio-selective [2+2+2] cycloaddition reaction of alkyne

Masilamani Tamizmani, Chinnappan Sivasankar*

Catalysis and Energy Laboratory, Department of Chemistry, Pondicherry University (A Central University), Puducherry, 605014, India

ARTICLE INFO

Article history:
Received 26 January 2017
Received in revised form
20 February 2017
Accepted 25 February 2017
Available online xxx

Keywords:
Ni(II) complexes
PNP pincer ligands
Alkyne trimerization
Regioselectivity
[2+2+2] cycloaddition reaction

ABSTRACT

Some novel Ni(II) complexes of PN(H)P^{Ph}, PN(Me)P^{iPr} and PN(Me)P^{tBu} ligands have been synthesized and characterized using standard analytical and spectroscopic methods such as ^{1}H NMR, ^{31}P NMR, elemental analysis, ESI-MS, UV-Visible spectroscopy and single-crystal X-ray crystallography. In the presence of silver triflate, complex [PN(H)P^{Ph}NiBr]$_2$NiBr$_4$ **(5)** activated the C–Cl bond of dichloromethane at room temperature and afford complex [PN(H)P^{Ph}NiCl]OTf **(6)**. We have also performed alkyne [2+2+2] cycloaddition reaction using Ni(II) complexes and observed high regioselectivity of the products. The observed selectivity is well correlating with the electronic feature of alkynes. The [2+2+2] cycloaddition of electron rich alkynes produced 1,3,5-substituted benzene derivatives as a major product whereas the electron deficient alkynes produced 1,2,4-substituted benzene derivatives as a major product.

1. Introduction

The PNP pincer ligands based metal complexes play a vital role in the modern organometallic chemistry [1–4]. Several pyridine based PNP pincer ligands have been synthesized and extensively studied their chemistry with various metal ions [5,6]. The PNP ligand based transition metal complexes are found to be superior catalysts for several chemical transformations such as hydrogenation, dehydrogenation, hydroamination, C-F bond activation, Si-H bond activation, hydrogen production, dinitrogen activation, C-N bond forming reaction, C-S bond forming reaction and CO_2 reduction [7–12]. In this line, aliphatic PNP pincer ligands drawn much attention owing to the nature of their flexible binding to the transition metal ions [13–18]. Recently Schneider et al. have found that the [Ir(COE)(HN($CH_2CH_2P^tBu_2$)$_2$)]BPh_4 (COE = cyclooctene) pincer complex is capable of activating the C-H bond of tetrahydrofuran [19]. The [($^tBu_2PCH_2SiMe_2$)$_2$N]-Ni(II) complex synthesized by Caulton et al. cleaves the dihydrogen via oxidative addition pathway [20]. The above mentioned reactions clearly revealed the importance of pincer type ligands and their respective transition metal complexes. In this regard, we were interested in synthesis and characterization of pincer ligands stabilized metal complexes and their catalytic applications towards C-C bond formation reactions [21].

Transition metal catalyzed cycloaddition reaction is one of the powerful synthetic tools to construct the building blocks for making natural products and biologically some important compounds [22–25]. In this regard, transition metal catalyzed [2+2+2] cycloaddition reaction of alkynes is one of the profound methodologies to make substituted benzenes. Nevertheless the transition metal catalyzed cyclooligomerization of the acetylene produces mixture of products (**A-F** in Scheme 1a) [26]. After the first report from Reppe et al. [27] for cyclooligomerization of phenyl acetylene to 1,2,4-triphenylbenzene and 1,3,5,8-tetraphenylcyclooctatetraene using Ni(acac)$_2$/CaC_2 as a catalyst (Scheme 1b), research related to selectivity of cyclooligomerization reaction products of phenyl acetylene has become more important.

Many transition metals such as Ni, Co, Rh, Fe, Pd, Ru, Ti, Zr, Mo and Ta with suitable ligands have been used for [2+2+2] cycloaddition of different alkynes [28–34]. Majority of the nickel complexes known for this reaction produced mixture of products (Scheme 1) however some catalysts produced one or two products as major products. Oligomerization of terminal alkynes with (^{iPr}NDI)Ni$_2$(C_6H_6) or (NNN)$NiCl_2$ type complexes produced **B** as a major product (Scheme 1c) [35,36]. However the [PNPRh(H_2)]

* Corresponding author.
E-mail address: siva.che@pondiuni.edu.in (C. Sivasankar).

http://dx.doi.org/10.1016/j.jorganchem.2017.02.039
0022-328X/

complex produced only dimerization product with similar substrates and produced **E** as a major product (Scheme 1d) [37]. The [PNPFeH]BH_4 complex was also used for the dimerization of the terminal alkynes and produced **D** as a major product (Scheme 1e) [38]. Most of the Ni(0) or Ni(II) salts catalyzed [2+2+2] cycloaddition reactions of alkyne produced only 1,2,4-substituted benzene derivatives as a major product [35,39]. Cycloaddition reaction of phenyl acetylene with [1,2-bis(4-methoxyphenylthio)-ethane]cobalt bromide complex produced **A** (Scheme 1) as a major product in dichloromethane whereas product **B** (Scheme 1) was isolated as a major product in acetonitrile [40]. Similar scenario was observed for the cycloaddition reaction of alkynes with [{$NbCl_2(C_4H_8S)$}$_2$(μ-Cl)$_2$(μ-C_4H_8S)] and [(Ar'O)$_2$Ti(C_4Et_4)] (Ar' = 2,6-diphenylphenoxide) complexes and produced 95% of trimer **A** [41,42]. The selectivity of this reaction was correlated with the features of ancillary ligands of the corresponding metal complexes and reaction conditions [43–50].

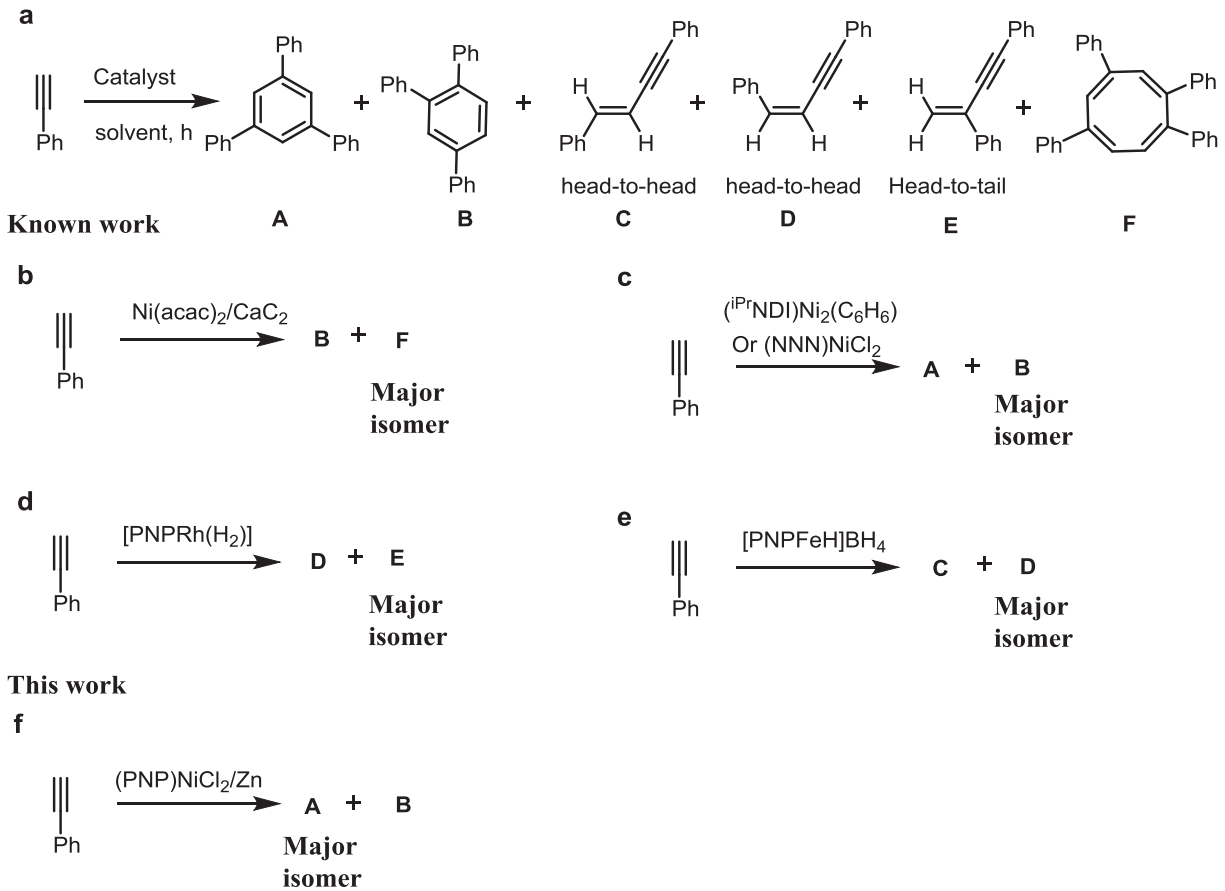
Based on the postulated reaction mechanism from the literature report [43] (Scheme 2), one can understand the product selectivity. The first step is the reduction of PNPNi(II) complex with zinc powder to give the possible intermediate with one equivalent of alkyne. Subsequently the intermediate **I** reacts with another equivalent of alkyne to produce intermediate **II**. The intermediate **II** undergoes oxidative addition followed by reductive coupling to give metallacyclopentadiene **III**. The metallacyclopentadiene **III** may react with one more equivalent of alkyne to produce the metallacycloheptatriene **IV** or **V** based on the orientation and insertion of third alkyne. Finally, reductive elimination of the metallacycloheptatriene **IV** or **V** afford the benzene derivatives.

All the above discussed studies clearly revealed that the selectivity is the major problem for Scheme 1 and only few complexes are known to produce compound **A** with moderate yield and selectivity. In this regard, we have synthesized a series of PNP^R pincer ligands stabilized Ni(II) complexes and characterized fully using standard analytical and spectroscopic methods and used them as catalysts to improve the regioselectivity of [2+2+2] cycloaddition reaction of various alkynes and presented the results.

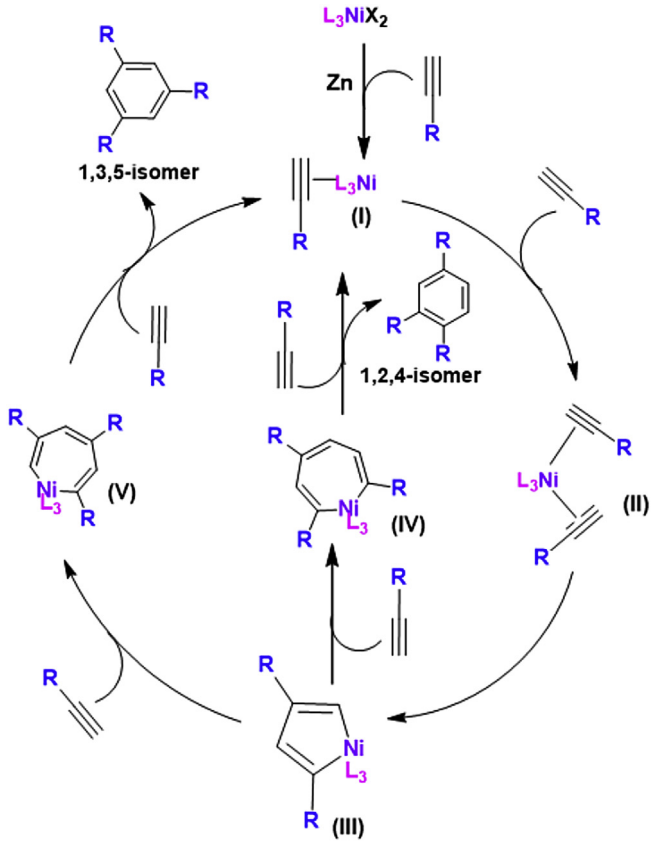
2. Results and discussion

The PNP pincer ligands **L1**-**L3** were prepared according to the modified literature procedure [51]. The reaction of **L1** and **L2** with $NiCl_2 \cdot 6H_2O$ in THF for 12 h at room temperature afforded desired complexes [(PN(Me)P^{iPr}NiCl)Cl] (**1,** 85%) and [(PN(Me)P^{tBu}NiCl)Cl] (**2**, 92%) respectively (Scheme 3). The ^{1}H NMR spectrum of complex **2** displayed a sharp peak at 4.38 ppm for N–Me protons and peaks around 1.83 ppm–1.69 ppm corresponds to the protons of $-P^tBu_2$. The complexes **1** and **2** displayed a single peak at 51.4 ppm and 50.4 ppm respectively in the ^{31}P NMR spectra for the coordinated phosphines. The observed ESI-MS (high resolution) values of complexes **1** (m/z = 412.16) and **2** (m/z = 468.22) are well correlating with the theoretically calculated ESI-MS values of the corresponding complexes.

Complex **2** is further confirmed by single-crystal X-ray analysis (Fig. 1). The Ni–Cl and Ni–N bond distances are found to be 2.169 Å and 1.955 Å respectively. The P1–Ni–P2 and N–Ni–Cl bond angles are found to be 169.14° and 169.17° respectively. One of the chloride ion is coordinated to the nickel center and other chloride ion is



Scheme 1. Representative examples for oligomerization of alkynes.



Scheme 2. The proposed catalytic cycle for alkynes [2+2+2] cycloaddition.

located in the lattice position.

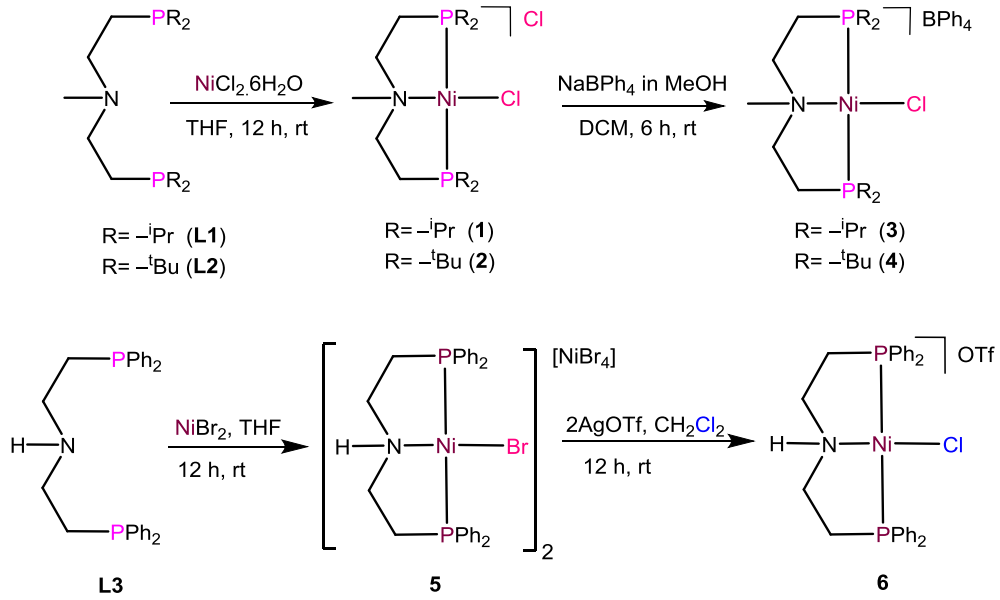
The complexes **3** and **4** have been synthesized by treating complexes **1** and **2** with a methanol saturated solution of $NaBPh_4$. The ^1H NMR spectrum of complex **3** displayed broad peaks at 2.21 ppm and also from 0.84 ppm to 1.52 ppm for N-Me, $-CH_2-$ and $-P^iPr_2$ protons. The ^1H NMR of complex **4** displays a single peak at 2.26 ppm for N-Me protons and a multiplet from 1.44 ppm to 1.55 ppm for the butyl protons of $-P^tBu_2$. The ESI-MS (high resolution) values of complexes **3** (m/z = 412.15) and **4** (m/z = 468.22) are well correlating with the theoretically calculated ESI-MS values of corresponding complexes. The molecular structure of complexes **3** and **4** are further confirmed by single-crystal X-ray analysis.

The Ni–Cl and Ni–N bond distances in complex **3** are found to be 2.151 Å and 1.953 Å respectively. The P1–Ni–P2 and N–Ni–Cl bond angles for complex **3** are found to be 167.44° and 174.54° respectively (Fig. 1). The Ni–Cl and Ni–N bond distances in complex **4** are found to be 2.151 Å and 1.967 Å respectively. The P1–Ni–P2 and N–Ni–Cl bond angles in complex **4** are found to be 170.06° and 169.07° respectively (Fig. 3). The structural analysis of complexes **3** and **4** indicate that the chloride ion is coordinated to the nickel center and the $-BPh_4^-$ ion is located in the lattice position, and the R group on the coordinated phosphine does not change the coordination environment of Ni center.

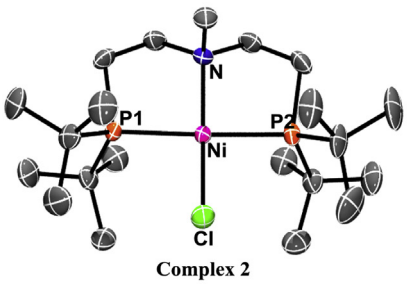
The reaction of alkyl $PN(H)P^{Ph}$ (**L3**) with $NiBr_2$ in THF at room temperature for 12 h produced $[(PN(H)P^{Ph}NiBr)_2(NiBr_4)]$ (**5**) as a red solid (yield 60%) (Scheme 3). The complex **5** shows a single peak at 33.5 ppm in ^{31}P NMR spectrum for coordinated phosphines. The formation of complex **5** was confirmed by single-crystal X-ray analysis (Fig. 2 and Fig. 3). The crystal structure of complex **5** revealed that the two monomeric $PNP^{Ph}NiBr$ units bridged through a $NiBr_4$ unit. The Ni–Br1 and Ni–N bond distances are found to be 2.3227 Å and 2.195 Å respectively. The P2–Ni–P1 and N–Ni–Br1 bond angles are found to be 165.84° and 176.53° respectively.

The reaction of complex **5** with two equivalents of silver triflate in a dichloromethane solution at room temperature for 12 h produced $[(PN(H)P^{Ph}NiCl)(OTf)]$ (**6**) (Scheme 3). The complex **5** activated the C–Cl bond of dichloromethane in the presence of silver triflate as observed in the literature [52]. The formation of complex **6** was confirmed by NMR and X-ray crystallography techniques. The ^1H NMR spectrum of complex **6** displays three multiplets at 3.36 ppm, 2.80 ppm and 2.40 ppm for $-CH_2-CH_2-$ methyl protons and a single peak at 4.86 ppm for N–Me protons. The $^{31}P\{^1H\}$ NMR spectrum of complex **6** displays a single peak at 27.6 ppm in $CDCl_3$ for coordinated phosphines. These spectral data indicates that the complex **6** is entirely different from complex **5**.

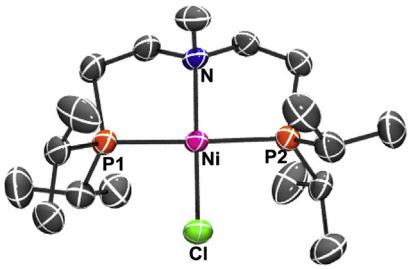
The solid state structure of complex **6** was determined using a



Scheme 3. Synthesis of complexes **1**–**6**.



Complex 2



Complex 3

Fig. 1. ORTEP drawing (50% probability ellipsoids) of the [PN(Me)P^{tBu}NiCl]Cl (**2**), and [PN(Me)P^{iPr}NiCl]BPh$_4$ (**3**). Omitted for clarity: solvent molecule, all H atoms. Selected bond distances (Å) and selected bond angles (°) for **2**, Ni-Cl, 2.1693(10); Ni-P1, 2.2454(9); Ni-P2, 2.2433(9); Ni-N1, 1.955(3): P1-Ni-P2, 169.14(4); P1-Ni-Cl, 93.46(4); P2-Ni-Cl, 93.49(4); N1-Ni-Cl, 169.17(9); for **3**: Ni-Cl, 2.151(0); Ni-P1, 2.212(0); Ni-P2, 2.194(1); Ni-N1, 1.953(2). P1-Ni-P2, 167.44(3); P1-Ni-Cl, 95.32(3); P2-Ni-Cl, 92.40(3); N1-Ni-Cl, 174.54(8).

single-crystal X-ray diffraction studies (Fig. 4). The Ni–Cl and the Ni–N bond distances are found to be 2.182 Å and 1.954 Å respectively. The P2–Ni–P1 and N–Ni–Cl bond angles are found to be 167.45° and 174.58° respectively. The structural parameters such as bond lengths, bond angles and dihedral angles of cationic part of complex **6** are found to be relatively similar to the structural features reported for [^{Ph}PNPNiCl]$^+$ by Walter et al.[56] Furthermore our solid state structure analysis confirmed the cleavage of C-Cl bond of dichloromethane. In complex **6**, the chloride ion is coordinated to the nickel center and the triflate ($^-$OTf) anion is found to be out of the primary coordination sphere. Selected bond distances and bond angles of complexes **2**–**6** are given in Table 1. The complexes **2**–**6** exhibits P2–Ni–P1 and N–Ni–X (X = Cl, Br) angles in the range of 165.84°–176.53° which is lower than the expected angle 180°. The geometry around the nickel center for complexes **2**–**6** is found to be slightly distorted square planar as observed in similar known PNP-NiX complexes [53–55]. Therefore the kind of distortion observed in complexes **1**–**6** is not unique. The Ni–Cl bond lengths of complex **2** (2.1693 Å) is longer than complexes **3** (2.151 Å) and **4** (2.151 Å). This indicates that the removal of chloride counter ion from complexes is responsible for shorting of N–Cl bond in **3** and **4**. The Ni–Br and N–Cl bond distances in complexes **5** and **6** are similar to previously reported Ni–Br (2.3036 Å) [55] and Ni–Cl (2.169(1) Å) bond distances in some PNP pincer nickel(II) complexes [56]. The average bond distance of Ni–P in complex **2** (2.244 Å) is found to be longer than that of Ni–P distance in other complexes **3**–**6** (**3**, 2.203 Å; **4**, 2.2366 Å; **5**, 2.1972 Å; **6**, 2.203 Å) and previously reported alkyl PNP-NiBr complex (2.024 Å) [55].

2.1. Electronic spectroscopy

The UV-Visible spectra of a dilute solution of complexes **1**–**6** have been recorded in acetonitrile (Fig. 5 and Fig. S1). The complex

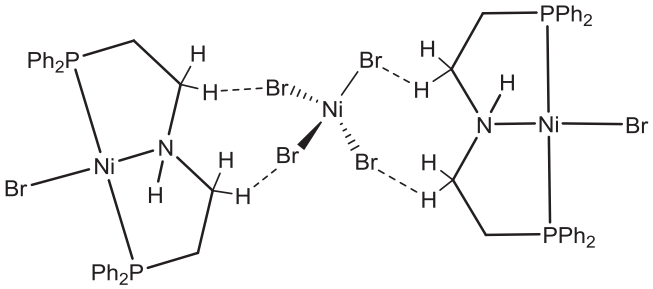
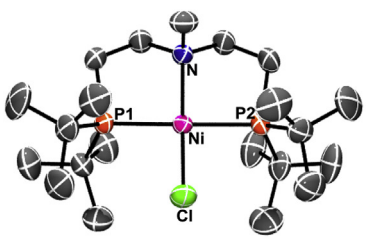


Fig. 3. Chemical structure of complex **5** as observed in the crystal structure.

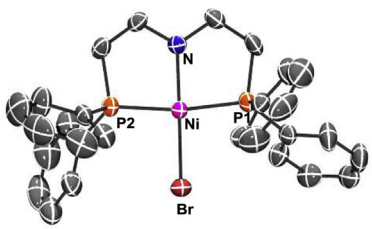
1 shows two strong absorption bands at 228 nm and 338 nm, and relatively a weak absorption band at 431 nm. The corresponding t-butyl substituted phosphine complex **2** shows two strong absorption bands at 239 nm and 355 nm, and relatively a weak absorption band at 505 nm. The complex **3** shows an intense absorption band at 204 nm and relatively weak intense bands at 334 nm and 474 nm. The complex **4** shows an intense absorption band at 238 nm and relatively weak intense bands at 358 nm and 510 nm. The absorption bands centered around 250–350 nm can be attributed to the ligand centered π-π* transition while the weak bands centered around 400–500 nm can be attributed to the d-d transition for the square planar geometry in their respective complexes **1**–**4**.

2.2. Catalysis: [2+2+2] cycloaddition reaction of alkyne

The [2+2+2] cycloaddition reaction of alkyne using already known Ni(II) complexes produces generally three products such as **A** (1, 3, 5-substituted benzene), **B** (1, 2, 4-substituted benzene) and **C** (dimer of alkyne) (Scheme 1a). We have optimized the [2+2+2] cycloaddition reaction with 1 mmol of phenyl acetylene in the



Complex 4



complex 5

Fig. 2. ORTEP drawing (50% probability ellipsoids) of the [PN(Me)P^{tBu}NiCl]BPh$_4$ (**4**) and [(PN(H)P^{Ph}NiBr)$_2$(NiBr$_4$)] (**5**). Omitted for clarity: solvated dichloromethane, all H atoms. Selected bond distances (Å) and selected bond angles (°) for **4:** Ni-Cl, 2.151(6); Ni-P1, 2.241(5); Ni-P2, 2.231(7); Ni-N1, 1.967(2). P1-Ni-P2, 170.06(4); P1-Ni-Cl, 93.41(3); P2-Ni-Cl, 93.41(3); N1-Ni-Cl, 169.07(8); for **5**: Ni-Br1, 2.3227(7); Ni-P1, 2.1950(14); Ni-P2, 2.1994(14); Ni-N1, 1.973(3). P1-Ni-P2, 165.84(5); P1-Ni-Br1, 94.03(4); P2-Ni-Br1, 94.21(4); N1-Ni-Br1, 176.53(12).

Please cite this article in press as: M. Tamizmani, C. Sivasankar, Journal of Organometallic Chemistry (2017), http://dx.doi.org/10.1016/j.jorganchem.2017.02.039

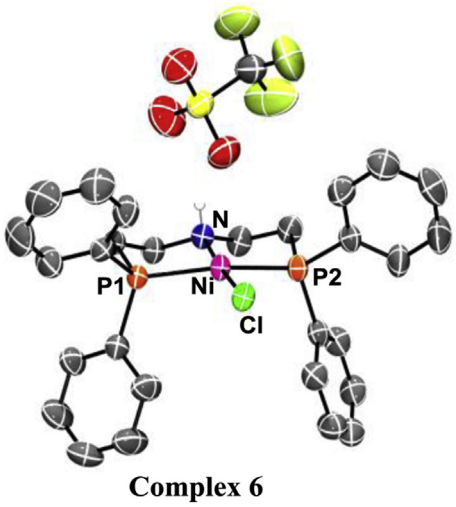


Fig. 4. ORTEP drawing (55% probability ellipsoids) of the [PN(H)P^{Ph}NiCl]OTf (**6**). Omitted for clarity: all H atoms. Selected bond distances (Å) and selected bond angles (°) for **6**: Ni-Cl, 2.1821(7); Ni-P1, 2.2122(8); Ni-P2, 2.1941(8); Ni-N1, 1.954(2). P1-Ni-P2, 167.45(3); P1-Ni-Cl, 95.33(3); P2-Ni-Cl, 92.39(3); N1-Ni-Cl, 174.58(9).

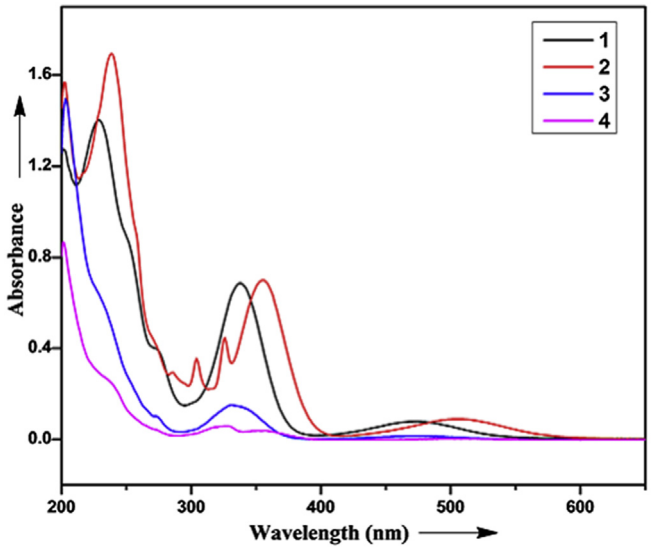


Fig. 5. UV-Visible spectra of complexes **1**–**4**.

presence of PNPNi(II) complexes (**1**–**6**) (2.5 mol%) using different reductant (5 mol%) in different solvents (Table 2). As mentioned in Table 2, complex **2** produced good yield in acetonitrile with two regio isomers and 1,3,5-substituted benzene (**A**) as a major product (Table 2, entry 1 and 2). In the presence of complexes **3**–**6**, the yield and selectivity of [2+2+2] cycloaddition product goes down (Table 2, entry 3–6). Furthermore the yield and selectivity have also been tested in different solvents, the dimerized product **C** is observed as a major product in DCM and THF solvents with low yields (Table 2, entry 7–8) and suggests that the solvent also plays a role in controlling the selectivity.

From Table 2, it can be noted that the complexes **2** and **4** shows better selectivity than complexes **1**, **3**, **5** and **6**. Since the complexes **2** and **4** have sterically bulky donor ligand **L2**, the bulkiness of the phosphine ligand seems to favors the formation of **A** isomer, however more detailed mechanism related experiments need to be carried out to fully understand the origin of the selectivity. The electronic and structural features of the complexes may also play significant role in controlling the reactivity of respective complexes. Nevertheless, the reduction of Ni(II) to Ni(0) in the presence of Zn is relatively more feasible in complexes **1** and **2** when compared to other complexes **3**–**6**. As the chloride ion present as a counter ion in complexes **1** and **2,** the formation of $ZnCl_2$ (lattice energy is more) is more feasible than the formation of other zinc salts such as $ZnCl(BPh_4)$ and $ZnBr_2$ from their respective complexes (**3**–**6**). As mentioned in Scheme 1, the formation of Ni(0) species is important to achieve the [2+2+2] cycloaddition reaction, hence concentration of Ni(0) complexes would be more in solution when we used complexes **1** and **2** whereas in case of complexes **3**–**6,** the concentration of Ni(0) species would be less and it may not even form.

In order to demonstrate the substrate scope of our newly synthesized complexes for [2+2+2] cycloaddition reaction, we have used different alkynes and isolated the product and characterized using standard analytical methods and compared with the reported analytical data of known compounds. The [2+2+2] cycloaddition of 3-ethynyltoluene produced 1,3,5-substituted benzene (85%) product (Table 3, entry 2) whereas 1-ethynyl-3,5-bis(trifluoromethyl) benzene offered 1,2,4- substituted benzene as a major product (Table 3, entry 7). These results revealed that the observed selectivity of the [2+2+2] cycloaddition of alkyne using complex **2** is also depends on the electronic nature of alkynes. We observed 1,3,5- substituted benzene as a major product while using simple alkyl substituted alkynes (Table 3, entry 3, 4 and 5). On the other hand, we observed 1,2,4-substituted benzene as a major product while using methyl propiolate and ethyl propiolate as substrates (Table 3, entry 8 and 9).

3. Conclusions

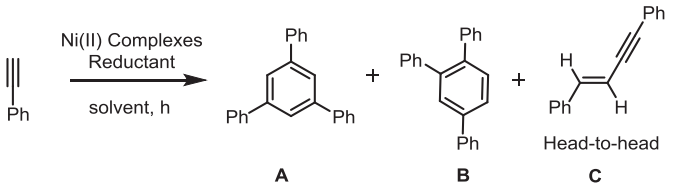
Some novel Ni(II) complexes **1**–**6** have been synthesized using pincer ligands **L1**-**L3**. Complexes **1**–**6** have been characterized using standard analytical and spectroscopic techniques such as ^{1}H NMR, ^{31}P NMR, ESI-MS and elemental analysis. The C-Cl bond cleavage in dichloromethane was observed with the complex **5** in the presence of silver triflate. The complex **2** acts as a good catalyst for regioselective [2+2+2] cycloaddition reaction of alkyne derivatives in the presence of zinc at low temperature while other complexes **1** and **3**–**6** produced relatively low yields.

Table 1
Selected bond distances (Å) and bond angles (°) from crystal structures of the nickel complexes.

Compound	**2**	**3**	**4**	**5**	6
Ni-X	2.1693	2.151	2.151(6)	2.3227(7)	2.1821
Ni-P1	2.2454(9)	2.212	2.241(5)	2.1950(1)	2.2122(8)
Ni-P2	2.2433(9)	2.194(1)	2.231(7)	2.1994(1)	2.194
Ni-N	1.9553	1.9532	1.967(2)	1.973(3)	1.954
P1-Ni-P2	169.14	167.44	170.06	165.84	167.45
N-Ni-X	169.17	174.54	169.07	176.53	174.58
P-Ni-X	93.46, 93.49	95.32, 92.40	93.41, 93.41	94.21, 94.03	95.33, 92.39

Please cite this article in press as: M. Tamizmani, C. Sivasankar, Journal of Organometallic Chemistry (2017), http://dx.doi.org/10.1016/j.jorganchem.2017.02.039

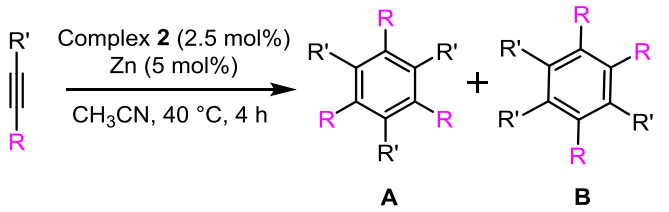
Table 2
Optimization of the reaction conditions for PNP-Nickel(II) complexes catalyzed [2+2+2] addition reaction.[a]



Entry	Complex	Solvent	Time (h)	Reductant	Yield[b] (%)	A: B: C[c]
1	**1**	CH_3CN	3	Zn	92	51:49:0
2	**2**	CH_3CN	3	Zn	95	75: 25:0
3	**3**	CH_3CN	12	Zn	30	50:50:0
4	**4**	CH_3CN	12	Zn	40	70:30:0
5	**5**	CH_3CN	12	Zn	40	52:48:0
6	**6**	CH_3CN	12	Zn	38	50:50:0
7	**2**	DCM	12	Zn	35	18:7:75
8	**2**	THF	12	Zn	40	18:7: 75
9	**2**	Toluene	5	Zn	25	34:66:0
10	**2**	Dioxane	12	Zn	40	50:50:0
11	**2**	CH_3CN	3	Sn	32	35:65:0
12	**2**	CH_3CN	12	Mg	–	–
13	**–**	CH_3CN	24	Zn	–	–
14	**2**	CH_3CN	24	–	–	–

[a] Reaction conditions: 2 mmol terminal alkyne, 2.5 mol % of [(PNP)NiCl]Cl, 5.0 mol % Zn in 3 mL of solvent.
[b] Isolated yield.
[c] The product ratio was determined by ^{1}H NMR spectra.

Table 3
[2+2+2] cycloaddition of various alkynes using complex **2**.[a]



Entry	R	R′	Yield[b] (%)	TON[c]	A: B[d]
1	Ph-	H	70	28.0	75: 25
2	3-MeC_6H_4-	H	82	32.8	85: 15
3	C_3H_5-	H	86	32.0	88: 12
4	C_8H_{17}-	H	86	32.0	90: 10
[e]5	$CyCH_2$-	H	72	28.8	66: 33
[f]6	Me_3Si-	H	60	24.0	–
7	3,5-$CF_3C_6H_3$-	H	95	38.0	5: 95
8	MeO_2C-	H	92	36.8	5: 95
9	EtO_2C-	H	92	36.8	5: 95
10	MeO_2C-	MeO_2C-	65	26.0	–

[a] Reaction conditions: 2 mmol terminal alkyne, 2.5 mol % [(PNP)NiCl]Cl (2), 5.0 mol% Zn in 3 mL of acetonitrile.
[b] Isolated yield of A for entry 1–4 and B for entry 7–9.
[c] TON calculated based on isolated product yield.
[d] Product ratio determined by ^{1}H NMR spectra.
[e] Combined isolated yield of A and B.
[f] Dimerized product only formed.

4. Experimental section

4.1. General considerations

Unless specified otherwise, all manipulations were performed under nitrogen atmosphere using standard Schlenk line techniques. Toluene and THF were dried and distilled over Na/Ph_2CO and stored in an N_2-filled solvent storage flask. $CDCl_3$, DCM and acetonitrile were dried and then distilled or vacuum transferred over CaH_2. Chlorodiphenylphosphine, chlorodiisopropylphosphine, chlorodi-*t*-butylphosphine and $NiBr_2$ were purchased from Aldrich and used without further purification. NMR spectra were recorded on a Bruker 400 MHz (^{1}H NMR, 400 MHz; ^{13}C NMR, 100.62 MHz; ^{31}P NMR, 161.822 MHz) spectrometer. For ^{1}H NMR and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm and ESI-MS was recorded on Agilent 6540 UHD Q-TOF mass spectrometer.

4.2. X-ray data collection and refinement

Data collections were performed on an OXFORD XCALIBUR diffractometer, equipped with a CCD area detector, using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation and a low-temperature device. All calculations were performed using SHELXS-97 and SHELXL-97 respectively using Olex 2–1.1 software package [57,58]. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F2). All non-hydrogen atoms were refined anisotropically. The crystallographic figures have been generated using Olex 2–1.1 software package (50% probability thermalellipsoids). CCDC files 1037672, 1031834, 1037671, 1440680 and 1005203 contain supplementary crystallographic data for the complexes **2, 3, 4, 5** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

4.2.1. Synthesis of $PN(Me)P^iPr_2$ (*L1*)

Under an atmosphere of argon, chlorodiisopropyl phosphine (4.56 g, 29.9 mmol) in tetrahydrofuran (10 mL) was added through a dropping funnel to a suspension of lithium granules (830 g, 120 mmol) in tetrahydrofuran (30 mL). The resulting solution was stirred vigorously at room temperature for 3 days to yield a lithium diisopropyl phosphide solution. The LiP^iPr_2 was transferred through a metal cannula from unreacted Li metal and the solution was cooled to −78 °C. A solution of $(ClCH_2CH_2)_2NMe{\cdot}HCl$ (2.84 g, 14.9 mmol) in tetrahydrofuran (30 mL) was neutralized with *n*-butyllithium (2.5 M in hexane, 6.0 mL, 15 mmol) at 0 °C. Then this solution was added to the above lithium diisopropyl phosphide solution at −78 °C with vigorous stirring. The mixture was then allowed to warm to room temperature and was refluxed for 10 h. Then the reaction mixture was cooled to room temperature, then degassed water (50 mL) was added to the reaction mixture. The aqueous layer was decanted through cannula and the organic layer was washed with two portions of degassed water (10 mL × 2). The organic layer was then dried with anhydrous magnesium sulfate. After stirring for an hour, the magnesium sulfate was filtered off through a pad of silica gel and the solvent was concentrated in vacuo. The residue was dissolved with pentane and filtered to yield a pale yellow liquid. (Yield: 3.3 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (b, 4H, $-NCH_2-$), 2.28 (s, 3 H, $-NCH_3$), 1.73 (b, 4H, $-PCH(CH_3)_2$), 1.53 (b, 4H, $-PCH_2$), 1.01 (bd, 24 H, $-PCH(CH_3)_2$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 1.6 ppm.

4.2.2. Synthesis of $PN(Me)P^tBu$ (*L2*)

Under an atmosphere of argon, chlorodi-*t*-butylphosphine (4.76 g, 4.76 mL, 31 mmol) in tetrahydrofuran (10 mL) was added through a dropping funnel to a suspension of lithium granules (0.85 g, 122 mmol) in tetrahydrofuran (30 mL). The resulting solution was stirred vigorously at room temperature for 3 days to yield a lithium di-*t*-butylphosphide solution. The LiP^tBu_2 was transferred through a metal cannula from unreacted Li metal and the solution was then cooled to −78 °C. To $(ClCH_2CH_2)_2NMe{\cdot}HCl$

(3 g, 15.6 mmol) in tetrahydrofuran (30 mL) was neutralized with *n*-butyllithium (2.5 M in hexanes, 6.24 mL, 15.6 mmol) at 0 °C. Then this solution was added to the above lithium di-*t*-butylphosphide solution at −78 °C with vigorous stirring. The workup was done as mentioned for **L1** synthesis. Bis(2-(di-*t*-butylphosphino)ethyl) methylamine. (yield: 3.8 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61–2.55 (m, 4H, $-CH_2CH_2-$), 2.33 (s, 3H, $-NCH_3$), 1.58–1.55 (m, 4H, $-CH_2CH_2-$), 1.14 (d, 18H, $-P(C(CH_3)_3)_2$), 1.11 (d, 18H, $-P(C(CH_3)_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 24.2 ppm.

4.2.3. Synthesis of $PN(H)P^{Ph}$ (**L3**)

Under an atmosphere of argon, chlorodiphenylphosphine (5.2 g, 23.6 mmol) in tetrahydrofuran (10 mL) was added through a dropping funnel to a suspension of lithium granules (0.65 g) in tetrahydrofuran (30 mL). The resulting solution was stirred vigorously at room temperature for 2 days to yield a lithium diphenylphosphide solution. The $LiPPh_2$ was transferred from unreacted Li metal through a cannula and the solution was cooled to −78 °C. The $(ClCH_2CH_2)_2NH\cdot HCl$ (2.25 g, 11.8 mmol) in tetrahydrofuran (30 mL) was neutralized with *n*-butyllithium (2.5 M in hexanes, 4.7 mL, 11.8 mmol) at 0 °C. Then this solution was added to the above lithium diphenylphosphide solution at −78 °C with vigorous stirring. The workup was done as mentioned for **L1** synthesis. (Yield:2.6 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (bs, 8H, Ph-H), 7.22 (bs, 12H, Ph-H), 2.64 (bs, 4H, $-CH_2CH_2-$), 2.14 (bs, 4H, $-CH_2CH_2-$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −20.66.

4.2.4. Synthesis of complex $PN(Me)P^{iPr}NiCl_2$ (**1**)

Under an atmosphere of nitrogen, $PN(Me)P^{iPr}$ **L1** (500 mg, 1.56 mmol) and $NiCl_2\cdot 6H_2O$ (372 mg, 1.56 mmol) were taken in THF (40 mL) and the reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuo, and the pink colour solid was dissolved in dichloromethane (25 mL) and filtered through a 1 cm^3 silica gel. The product was precipitated from the filtrate with hexane. The red brown product was filtered off, washed with hexane and dried under vacuum. (Yield: 0.6 g, 86%). ^{1}H NMR ($CDCl_3$): δ 3.8 (s, 3H, −NMe), 3.09 (m, 2H, −NC*H*2), 2.37 (m, 2H, $-PCH(CH_3)_2$), 2.22 (m, 6H, −PC*H*2(2), NCH_2(2), $-PCH(CH_3)_2$ (2)), 1.69 (m, 2H, $-PCH_2$), 1.55–1.35 (td, 24H, $-PCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 54.63 (t, NCH2), 24.89 (t, $-PCH(CH_3)_2$), 24.19 (t, $-PCH(CH_3)_2$), 21.25 (t, $-PCH_2$), 19.61, 19.13, 18.19 and 17.99 (s, $-PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.46 (s). ESI-MS: $[PN(Me)P^{iPr}NiCl]^+$ displays a peak at m/z = 412.16, calc. 412.16. Anal. Calcd. for $C_{17}H_{39}Cl_2NNiP_2$: C, 45.47; H, 8.75; N, 3.12. Found: C, 45.42; H, 8.67; N, 3.15.

4.2.5. Synthesis of $PN(Me)P^{tBu}NiCl_2$ (**2**)

Under an atmosphere of nitrogen, $PN(Me)P^{tBu}$ (**L2**) (500 mg, 1.33 mmol) and $NiCl_2\cdot 6H_2O$ (316 mg, 1.33 mmol) were taken in THF (40 mL) and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the pink colour solid was dissolved in dichloromethane (25 mL) and filtered through a 1 cm^3 silica gel. The product was precipitated from the filtrate with hexane. The pink colour product was filtered off, washed with hexane and dried under high vacuum. (Yield: 616 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60 (b, 2H), 4.38 (s, 3H), 3.83 (b, 2H), 2.93 (b, 2H), 2.53 (b, 2H), 1.83–1.69 (dt, 36H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 50.18 (s). ESI-MS: $[PN(Me)P^{tBu}NiCl]^+$ displays a peak at m/z = 468.22, calc. 468.22. Anal. Calcd. for $C_{21}H_{47}Cl_2NNiP_2$: C, 49.93; H, 9.38; N, 2.77. Found: C, 49.89; H, 9.32; N, 2.84.

4.2.6. Synthesis of $([PN(Me)P^{iPr}NiCl][BPh_4])$ (**3**)

Complex **1** (200 mg, 0.44 mmol) was dissolved in CH_3CN (5 mL). Upon addition of $NaBPh_4$ (183 mg, 0.53 mmol) in 2 mL MeOH, a red colour solution was slowly changed to orange solution. The reaction mixture was allowed to stirrer for 6 h at room temperature. The solvent was removed under vacuo, the solid was dissolved in dichloromethane and filtered through 1 cm^3 silica gel. The red-orange solid was dried under vacuum. (Yield: 283 mg, 88%). ^{1}H NMR ($CDCl_3$): δ 7.40 (bs, 8H), 7.07–7.04 (t, 8H), 6.94–6.91 (t, 4H), 2.21 (bs, 8H), 1.52–1.47 (b, 20H), 1.28 (b, 8H), 0.84 (b, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 54.8 (s). ESI-MS: $[PN(Me)P^{iPr}NiCl]^+$ displays a peak at m/z = 412.15, calc. 412.16. Anal. Calcd. for $C_{41}H_{59}BClNNiP_2$: C, 67.20; H, 8.12; N, 1.91. Found: C, 67.16; H, 8.15; N, 1.87.

4.2.7. Synthesis of $([PN(Me)P^{tBu}NiCl][BPh_4])$ (**4**)

Complex **2** (200 mg, 0.4 mmol) was dissolved in CH_3CN (5 mL). Upon addition of $NaBPh_4$ (164 mg, 0.48 mmol) in 2 mL of methanol, a red colour solution was slowly changed to orange solution. The reaction mixture was allowed to stir for 6 h at room temperature. The solvent was removed under vacuo, the solid was dissolved in dichloromethane and filtered through 1 cm^3 silica gel. The orange solid was dried under vacuum. (Yield: 285 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (bs, 8H, Ph-H), 7.07–7.03 (t, 8H, Ph-H), 6.94–6.90 (t, 3H, Ph-H), 2.26 (s, 3H, N-Me), 2.00 (s, 2H, $-CH_2-$), 1.70 (b, 2H, $-CH_2-$), 1.55–1.51 (t, 20H, $PC(CH_3)_3$ & $-CH_2-$), 1.48–1.44 (t, 20H, $-PC(CH_3)_3$ & $-CH_2-$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.4 (s). ESI-MS: $[PN(Me)P^tBuNiCl]^+$ displays a peak at m/z = 468.22, calc. 468.22. Anal. Calcd. for $C_{45}H_{67}BClNNiP_2$: C, 68.51; H, 8.56; N, 1.78. Found: C, 68.45; H, 8.55; N, 1.72.

4.2.8. Synthesis of $[PN(H)P^{Ph}NiBr]_2NiBr_4$ (**5**)

The complex **5** was prepared similar to complex **1** with $NaBr_2$ (123 mg, 0.56 mmol), $PN(H)P^{Ph}$ (250 mg, 0.56 mmol) as the starting compound. Yield: 130 mg (60%). Its paramagnetic nature failed to produce good ^{1}H NMR. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33.58 (s). ESI-MS: $[C_{28}H_{29}ClNNiP_2]^+$ displayed a peak at m/z = 579.2925, calc. 578.03. Anal. Calcd. for $C_{56}H_{58}Br_6N_2Ni_3P_4$: C, 43.72; H, 3.80; N, 1.82. Found: C, 43.65; H, 3.53; N, 1.80.

4.2.9. Synthesis of $[PN(H)P^{Ph}NiCl]OTf$ (**6**)

Silver triflate (129 mg, 0.5 mmol) was added to a solution of complex **3** (200 mg, 0.25 mmol) in 10 mL of dichloromethane with stirring and the colour of the solution immediately changed to orange, the reaction mixture was stirred for 12 h at room temperature. Then the mixture was filtered through celite and dried under vacuo. (Yield: 91.0 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.71 (m, 8H), 7.54–7.12 (m, 12H), 4.86 (s, br, 1H), 3.36–3.27 (m, 2H), 2.80–2.73 (m, 2H), 2.40–2.30 (m, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.6 (s). ESI-MS: $[C_{28}H_{29}ClNNiP_2]^+$ displays a peak at m/z = 535.632, calc. 535.638. Anal. Calcd. for $C_{29}H_{29}ClF_3NNiO_3P_2S$: C, 50.87; H, 4.27; N, 2.05. Found: C, 50.82; H, 4.11; N, 1.93.

4.2.10. General procedure for cycloaddition reaction of alkyne

To a 50 mL Schlenk flask acetylene derivatives (1 mmol), Ni(II) complex (2.5 mol%), Zn (5 mol%) and 3 mL acetonitrile were added. The reaction mixture was heated at 40 °C using an oil bath. After completion of the reaction, the crude reaction mixture was dried under vacuo and dissolved in diethyl ether and filtered through silica gel. The volatiles were removed under vacuo and column chromatography was performed to isolate the final product.

Acknowledgment

Dr. C. S gratefully acknowledges the Council of Scientific and Industrial Research, New Delhi, India for the financial support (No. 01(2535)/11/EMR-II) and Mr. Saraswatula Viswanadha G, Department of chemistry, Pondicherry University for the crystal data. We thank the Central Instrumentation Facility (CIF), Pondicherry University for NMR spectra and DST-FIST for the single-crystal X-ray

diffraction facility and ESI-MS facility.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.02.039.

References

[1] S. Chakraborty, P. Bhattacharya, H. Dai, H. Guan, Acc. Chem. Res. 48 (2015) 1995–2003.
[2] D. Benito-Garagorri, K. Kirchner, Acc. Chem. Res. 41 (2008) 201–213.
[3] M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750–3781.
[4] N. Selander, K.J. Szabó, Chem. Rev. 111 (2011) 2048–2076.
[5] M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759–1792.
[6] M. Asay, D. Morales-Morales, Dalton Trans. 44 (2015) 17432–17447.
[7] S. Werkmeister, J. Neumann, K. Junge, M. Beller, Chem. Eur. J. 21 (2015) 12226–12250.
[8] S. Chakraborty, J. Zhang, J.A. Krause, H. Guan, J. Am, Chem. Soc. 132 (2010) 8872–8873.
[9] M. Albrecht, M.M. Lindner, Dalton Trans. 40 (2011) 8733–8744.
[10] K. Arashiba, Y. Miyake, Y. Nishibayashi, Nat. Chem. 3 (2011) 120–125.
[11] G.T. Venkanna, H.D. Arman, Z.J. Tonzetich, ACS Catal. 4 (2014) 2941–2950.
[12] S.S. Rozenel, R. Padilla, J. Arnold, Inorg. Chem. 52 (2013) 11544–11550.
[13] K.L. Fillman, E.A. Bielinski, T.J. Schmeier, J.C. Nesvet, T.M. Woodruff, C.J. Pan, M.K. Takase, N. Hazari, M.L. Neidig, Inorg. Chem. 53 (2014) 6066–6072.
[14] Z.E. Clarke, P.T. Maragh, T.P. Dasgupta, D.G. Gusev, A.J. Lough, K. Abdur-Rashid, Organometallics 25 (2006) 4113–4117.
[15] C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa, F. Zanobini, Organometallics 15 (1996) 272–285.
[16] K.V. Vasudevan, B.L. Scott, S.K. Hanson, Eur. J. Inorg. Chem. 2012 (2012) 4898–4906.
[17] S. Schneider, J. Meiners, B. Askevold, Eur. J. Inorg. Chem. 2012 (2012) 412–429.
[18] B. Askevold, J.T. Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M.C. Holthausen, S. Schneider, Nat. Chem. 3 (2011) 532–537.
[19] J. Meiners, A. Friedrich, E. Herdtweck, S. Schneider, Organometallics 28 (2009) 6331–6338.
[20] T. He, N.P. Tsvetkov, J.G. Andino, X. Gao, B.C. Fullmer, K.G. Caulton, J. Am, Chem. Soc. 132 (2010) 910–911.
[21] M. Tamizmani, R. Kankanala, C. Sivasankar, J. Organomet. Chem. 763–764 (2014) 6–13.
[22] H.-W. Frühauf, Chem. Rev. 97 (1997) 523–596.
[23] M. Lautens, W. Klute, W. Tam, Chem. Rev. 96 (1996) 49–92.
[24] I. Ojima, M. Tzamarioudaki, Z. Li, R.J. Donovan, Chem. Rev. 96 (1996) 635–662.
[25] N.E. Schore, Chem. Rev. 88 (1988) 1081–1119.
[26] S. Pasynkiewicz, E. Olędzka, A. Pietrzykowski, J. Mol. Catal. A Chem. 224 (2004) 117–124.
[27] W. Reppe, O. Schlichting, K. Klager, T. Toepel, Eur. J. Org. Chem. 560 (1948) 1–92.
[28] M. Amatore, C. Aubert, Eur. J. Org. Chem. 2015 (2015) 265–286.
[29] S. Kotha, E. Brahmachary, K. Lahiri, Eur. J. Org. Chem. 2005 (2005) 4741–4767.
[30] D.L.J. Broere, E. Ruijter, Synthesis 44 (2012) 2639–2672.
[31] P. Kumar, J. Louie, Nickel-mediated [2 + 2 + 2] Cycloaddition, in: Transition-metal-mediated Aromatic Ring Construction, John Wiley & Sons, Inc, 2013, pp. 37–70.
[32] V.A. Rassadin, E. Nicolas, Y. Six, Chem. Commun. 50 (2014) 7666–7669.
[33] G.A. Ardizzoia, S. Brenna, S. Cenini, G. LaMonica, N. Masciocchi, A. Maspero, J. Mol. Catal. A Chem. 204–205 (2003) 333–340.
[34] M.I. Lipschutz, T. Chantarojsiri, Y. Dong, T.D. Tilley, J. Am. Chem. Soc. 137 (2015) 6366–6372.
[35] S. Pal, C. Uyeda, J. Am. Chem. Soc. 137 (2015) 8042–8045.
[36] S.K. Rodrigo, I.V. Powell, M.G. Coleman, J.A. Krause, H. Guan, Org. Biomol. Chem. 11 (2013) 7653–7657.
[37] C.J. Pell, O.V. Ozerov, ACS Catal. 4 (2014) 3470–3480.
[38] O. Rivada-Wheelaghan, S. Chakraborty, L.J.W. Shimon, Y. Ben-David, D. Milstein, Angew. Chem. Int. Ed. 55 (2016) 6942–6945.
[39] N. Mori, S.-i. Ikeda, K. Odashima, Chem. Commun. (2001) 181–182.
[40] G. Hilt, C. Hengst, W. Hess, Eur. J. Org. Chem. 2008 (2008) 2293–2297.
[41] M. Kakeya, T. Fujihara, T. Kasaya, A. Nagasawa, Organometallics 25 (2006) 4131–4137.
[42] J.E. Hill, G. Balaich, P.E. Fanwick, I.P. Rothwell, Organometallics 12 (1993) 2911–2924.
[43] C. Xi, Z. Sun, Y. Liu, Dalton Trans. 42 (2013) 13327–13330.
[44] R. Diercks, L. Stamp, J. Kopf, H. tom Dieck, Angew. Chem. Int. Ed. 23 (1984) 893–894.
[45] R. Diercks, L. Stamp, H.T. Dieck, Chem. Ber. 117 (1984) 1913–1919.
[46] N. Mori, S.-i. Ikeda, K. Odashima, Chem. Comm. (2001) 181–182.
[47] P. Chini, A. Santambrogio, N. Palladino, J. Chem. Soc. C (1967) 830–835.
[48] Y. Sato, T. Nishimata, M. Mori, J. Org. Chem. 59 (1994) 6133–6135.
[49] J.A. Teske, A. Deiters, J. Org. Chem. 73 (2008) 342–345.
[50] C. Müller, R.J. Lachicotte, W.D. Jones, Organometallics 21 (2002) 1975–1981.
[51] J.-H. Choi, N.E. Schloerer, J. Berger, M.H.G. Prechtl, Dalton Trans. 43 (2014) 290–299.
[52] Z. Csok, O. Vechorkin, S.B. Harkins, R. Scopelliti, X. Hu, J. Am, Chem. Soc. 130 (2008) 8156–8157.
[53] Q. Dong, M.J. Rose, W.-Y. Wong, H.B. Gray, Inorg. Chem. 50 (2011) 10213–10224.
[54] S. Kumar, G. Mani, S. Mondal, P.K. Chattaraj, Inorg. Chem. 51 (2012) 12527–12539.
[55] S.S. Rozenel, J.B. Kerr, J. Arnold, Dalton Trans. 40 (2011) 10397–10405.
[56] T.D.D. Walther, K. Heubach, O. Klobes, B. Schweder, H. Görls, Z. Anorg, Allg. Chem. 625 (1999) 923–932.
[57] G.M. Sheldrick, in: SHELXS-97 and SHELXL-97, University of Göttingen, Germany, 1997.
[58] A.L. Spek, Acta Crystallogr. Sect. D 65 (2009) 148–155.

Please cite this article in press as: M. Tamizmani, C. Sivasankar, Journal of Organometallic Chemistry (2017), http://dx.doi.org/10.1016/j.jorganchem.2017.02.039