



Synthesis and characterization of six-membered pincer nickelacycles and application in alkylation of benzothiazole[†]

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Abstract. Six-membered pincer nickelacycle complexes have been synthesized and employed for the catalytic C–H bond alkylation of benzothiazole. The pincer nickelacycle, $\{\kappa^P, \kappa^C, \kappa^P\text{-}(2\text{-}i\text{Pr}_2\text{POCH}_2\text{-C}_6\text{H}_3\text{-6-CH}_2\text{OP}^i\text{Pr}_2)\}\text{NiBr}$, $[(^i\text{Pr}_4\text{-POCCCOP})\text{NiBr}$ (**2**)] was synthesized by the reaction of $1,3\text{-}i\text{Pr}_2\text{POCH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{OP}^i\text{Pr}_2$ [$(^i\text{Pr}_4\text{-POCCCOP})\text{-H}$ (**1**)] with $(\text{CH}_3\text{CN})_2\text{NiBr}_2$ in the presence of Et_3N via the C(2)–H activation on ligand **1**. Treatment of $[(^i\text{Pr}_4\text{-POCCCOP})\text{NiBr}]$ (**2**) with AgOAc afforded the complex $[(^i\text{Pr}_4\text{-POCCCOP})\text{Ni}(\text{OAc})]$ (**3**) in good yield. Both the complexes **2** and **3** were characterized by ^1H , ^{13}C and ^{31}P -NMR spectral analysis. Further, the molecular structures of complexes **2** and **3** were established by X-ray crystallography. The complex **2** was found to be an active catalyst for the C–H bond alkylation of benzothiazole with alkyl halides containing β -hydrogen atoms.

Keywords. Pincer complex; six-membered nickelacycle; benzothiazole; C–H activation; alkylation.

1. Introduction

Pincer-based transition-metal complexes have attracted considerable attention because of their applications in diverse catalytic transformations and advanced materials.¹ The tridentate coplanar coordination of the pincer ligands to the transition metals largely provides strong metal-ligand bonds and robust structures, which contribute to the thermal, air and moisture stability of the pincer complexes.² The pincer nickel complexes based on bis(phosphine)[1,3-(R₂PCH₂)₂C₆H₄; (PCP)–H] and bis(amine)[1,3-(R₂NCH₂)₂C₆H₄; (NCN)–H] ligands were among the early reports demonstrated by Shaw³ and van Koten,⁴ respectively. Particularly, the PCP-⁵ and NCN-⁶-type pincer nickel complexes have been most extensively studied, which led to the discoveries of diverse applications. In the last two decades, a number of new pincer nickel complexes based on

electronically distinct ligand systems, such as POCOP,⁷ POCN,⁸ PNP,⁹ NNN,¹⁰ PC_{sp3}P,¹¹ POC_{sp3}OP^{5f, 7b, 12} were developed (Chart 1). In this context, the groups of Guan and Zargarian have reported the reactivity and catalytic activity of (POCOP)NiX in a wide range of reactions.^{7d, 13} Similarly, the unsymmetrical hybrid (POCN)NiX complexes have shown excellent activity for certain reactions compared to their symmetrical counterparts.^{8f, g}

In all the reported pincer nickel complexes, the ligating properties of the pincer ligand system were systematically tuned by changing the substituents on PR₂ and NR₂ (R = alkyl, aryl), and by changing the PR₂-linker. These developments have underscored the importance of ligand tuning that has a direct impact on the reactivities of pincer nickel complexes. Notably, all the described pincer-nickels (nickelacycles) constitute two five-membered rings (Chart 1). Unfortunately, the impact of nickelacycle ring size on the reactivity and catalytic activity has rarely been examined on a pincer nickel complex.¹⁴ This could

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[†]Dedicated to Professor K. C. Kumara Swamy on the occasion of his 60th birth anniversary.

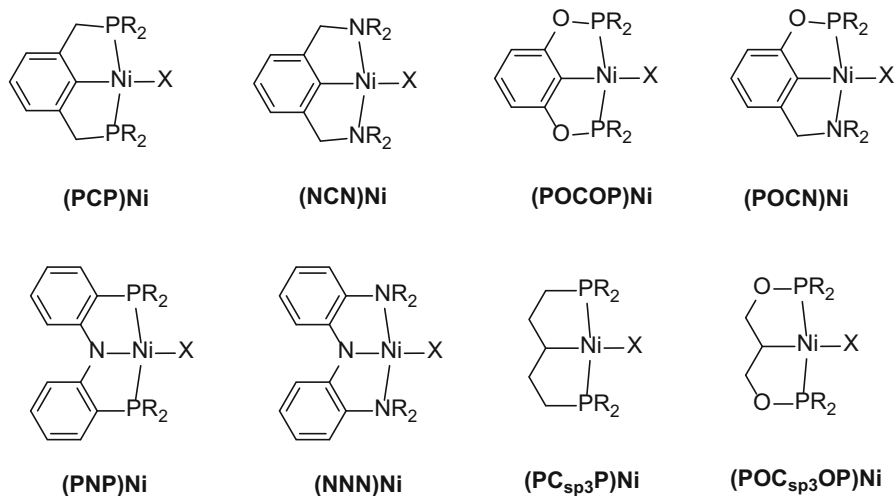


Chart 1. Pincer nickel complexes.

be partially due to the difficulties in synthesizing higher ring size (six- or seven-membered) or lower ring size pincer nickel complexes, because of the low stability of such nickelacycles. Nevertheless, Jensen demonstrated the six-membered ring palladacycle as an excellent catalyst for the Heck coupling reaction compared to the five-membered palladacycle counterpart.¹⁵ Encouraged by the Jensen observation, and as a part of our activity on the development of pincer-based nickel complexes for the C–H bond functionalization,^{10g, 16} herein, we report the synthesis and structural characterization of six-membered nickelacycles $\{\kappa^P, \kappa^C, \kappa^P-(2\text{-}^i\text{Pr}_2\text{POCH}_2\text{-C}_6\text{H}_3\text{-6-CH}_2\text{OP}^i\text{Pr}_2)\text{NiX}$, $[(^i\text{Pr}_4\text{-POCCOP})\text{NiX}]$, and demonstrate their catalytic activity for the alkylation of benzothiazole. Interestingly, various structural parameters of this phosphinite-based (POCCOP)NiX complexes are distinct from both the phosphine-based (PCP)NiX and phosphinite-based (POCOP)NiX system, though they are much akin to the (PCP)NiX complex. The (POCCOP)NiX complex acts as an active catalyst for the alkylation of benzothiazole with alkyl halides bearing β -hydrogen atoms.

2. Experimental

2.1 Materials and physical measurements

All manipulations were conducted under an argon atmosphere either in a glove box or using standard Schlenk techniques in pre-dried glasswares. The catalytic reactions were performed in flame-dried reaction vessels with Teflon screw cap. Solvents were dried over Na/benzophenone or CaH_2 and distilled prior to use. Liquid reagents were flushed with argon before use. The ligand, 1,3- $\text{C}_6\text{H}_4\text{-(CH}_2\text{-O-}^i\text{Pr}_2)_2$

$[(^i\text{Pr}_4\text{-POCCOP})\text{-H (1)}]$ was synthesized according to previously described procedure.¹⁵ All other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to the isolated compounds, estimated to be > 95% pure as determined by $^1\text{H-NMR}$. High resolution mass spectrometry (HRMS) mass spectra were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Büchi 540 capillary melting point apparatus was used, and the reported values are uncorrected. NMR (^1H , ^{13}C and ^{31}P) spectra were recorded at 500 MHz (^1H), 125 MHz (^{13}C , DEPT (distortionless enhancement by polarization transfer)) and 202 MHz (^{31}P) on Bruker AV 500 spectrometers in CDCl_3 or $\text{THF-}d_8$ solutions, if not otherwise specified; chemical shifts (δ) are given in ppm.

2.1a GC method: Gas Chromatography analyses were performed using a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20s autosampler and a Restek RTX-5 capillary column (30 m x 250 μm). The instrument was set to an injection volume of 1 μL , an inlet split ratio of 10:1, and inlet and detector temperatures of 250 and 320°C, respectively. UHP-grade argon was used as carrier gas with a flow rate of 30 mL/min. The temperature program used for all the analyses is as follows: 80°C, 1 min; 30°C/min to 200°C, 2 min; 30°C/min to 260°C, 3 min; 30°C/min to 300°C, 3 min. Response factors for all the required compounds with respect to standard *n*-dodecane were calculated from the average of three independent GC runs.

2.2 Synthesis of nickel complexes

2.2a Synthesis of $(^i\text{Pr}_4\text{-POCCOP})\text{NiBr (2)}$: To the mixture of bisphosphinite, 1,3- $\text{C}_6\text{H}_4(\text{CH}_2\text{OP}^i\text{Pr}_2)_2$ (0.272 g, 0.734 mmol) and $(\text{CH}_3\text{CN})_2\text{NiBr}_2$ (0.221 g, 0.735 mmol) in a Schlenk flask were added toluene (15 mL) and Et_3N (0.133 mL, 0.954 mmol). The resulted brown reaction mixture was stirred at 110°C for 3 h. At ambient temperature, the volatiles were evaporated under vacuum and the product was

extracted with pentane (20 mL x 3). Slow evaporation of the pentane solution at room temperature afforded the brownish-yellow crystalline compound of (*i*Pr₄-POCCCCOP)NiBr (**2**). Yield: 0.230 g, 62%. M.p.: 145°C (dec). ¹H NMR (500 MHz, CDCl₃): δ 6.95–6.84 (m, 3H, Ar–H), 5.10 (br s, 2H, CH₂), 4.86 (br s, 2H, CH₂), 3.04 (br s, 2H, CH), 1.91 (br s, 2H, CH), 1.50 (br s, 6H, CH₃), 1.21 (br s, 12H, CH₃), 0.41 (br s, 6H, CH₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 144.4 (t, *J*_{P–C} = 26.7 Hz, C_q), 142.8 (t, *J*_{P–C} = 6.2 Hz, 2C, C_q), 126.9 (2C, CH), 124.3 (CH), 78.9 (2C, CH₂), 27.5 (4C, CH), 18.1 (6C, CH₃), 15.9 (2C, CH₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 141.6 (s). HRMS (ESI): *m/z* calcd. for [C₂₀H₃₅O₂P₂BrNi+H]⁺ [M+H]⁺ 507.0722 and 509.0701; found 507.1698 and 509.1648; [C₂₀H₃₅O₂P₂BrNi – Br]⁺ [M – Br]⁺ 427.1460, found 427.1462. Anal. Calcd. for C₂₀H₃₅O₂P₂BrNi: C, 47.28; H, 6.94%. Found: C, 46.93; H, 6.77%.

2.2b Synthesis of (*i*Pr₄-POCCCCOP)Ni(OAc) (**3**):

To the solution of (*i*Pr₄-POCCCCOP)NiBr (**2**; 0.05 g, 0.098 mmol) in THF (10 mL) was added AgOAc (0.0197 g, 0.118 mmol). The reaction mixture in Schlenk flask was covered with aluminium foil, and was stirred at room temperature for 3 h. The reaction mixture was filtered through cannula filtration to remove the insoluble materials, and the filtrate was concentrated under vacuum to obtain nickel complex (*i*Pr₄-POCCCCOP)Ni(OAc) (**3**) as brown crystalline solid. Yield: 0.032 g, 67%. ¹H NMR (500 MHz, THF-*d*₈): δ 6.88–6.76 (br s, 3H, Ar–H), 5.53–5.32 (m, 2H, CH₂), 4.94–4.77 (m, 2H, CH₂), 2.22 (br s, 2H, CH), 1.86 (br s, 2H, CH), 1.71 (s, 3H, OCH₃), 1.42 (d, *J* = 5.7 Hz, 6H, CH₃), 1.22–1.10 (m, 12H, CH₃), 0.40 (d, *J* = 5.7 Hz, 6H, CH₃). ¹³C{¹H} NMR (125 MHz, THF-*d*₈): δ 176.5 (C_q, COCH₃), 144.4 (t, *J*_{P–C} = 6.2 Hz, 2C, C_q), 142.9 (t, *J*_{P–C} = 29.1 Hz, C_q), 126.9 (2C, CH), 124.3 (CH), 79.0 (2C, CH₂), 28.2 (t, *J*_{P–C} = 13.4 Hz, 2C, CH), 27.3 (t, *J*_{P–C} = 9.5 Hz, 2C, CH), 24.3 (CH₃), 18.0 (6C, CH₃), 16.2 (2C, CH₃). ³¹P{¹H} NMR (202 MHz, THF-*d*₈): δ 136.5 (s). HRMS (ESI): *m/z* calcd. for [C₂₂H₃₈O₄P₂Ni+H]⁺ [M+H]⁺ 487.1672, found 487.0840; [C₂₂H₃₈O₄P₂Ni – OAc]⁺ [M – OAc]⁺ 427.1460, found 427.1461. This compound is highly moisture and thermal sensitive; hence, a satisfactory elemental analysis was not obtained.

2.3 Representative procedure for alkylation reaction

2.3a Synthesis of 2-*n*-octylbenzo[*d*]thiazole (**6a**): To a flame dried screw cap tube equipped with magnetic stirrer bar was introduced catalyst **2** (0.006 g, 0.01 mmol, 5.0 mol%), CuI (0.001 g, 0.005 mmol, 2.5 mol%), LiO^tBu (0.032 g, 0.4 mmol), benzothiazole (**4**; 0.027 g, 0.2 mmol) and 1-iodooctane (**5a**; 0.096 g, 0.4 mmol) inside the glove box. To the above reaction mixture, 1,4-dioxane (1.0 mL) was added under an argon atmosphere, and the resultant reaction mixture was stirred at 100°C in a preheated oil bath for 24 h. At ambient temperature, the reaction mixture was quenched with distilled water (5 mL) and neutralized with 2 N HCl (0.5 mL).

The crude product was then extracted with ethyl acetate (10 mL x 3) and the organic extract was dried over Na₂SO₄. Then, *n*-dodecane (0.025 mL, internal standard) was added and the mixture was stirred vigorously. An aliquot of the sample was withdrawn to a GC vial and subjected to the GC analysis. The yield of the coupled product **6a** was found to be 91% (Note: The authenticity of all the coupled products was verified by comparing them with the isolated products).^{10g}

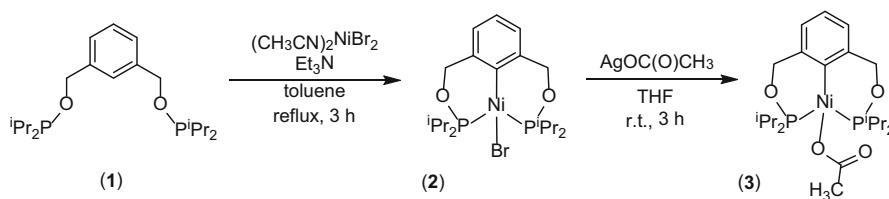
2.4 X-ray crystallography

Single crystal structures of compounds **2** and **3** were determined by measuring X-ray intensity data on a Bruker SMART APEX II single crystal X-ray CCD diffractometer having graphite-monochromatized (Mo-Kα = 0.71073 Å) radiation at room temperature (296 K) for **2** and at low temperature (100 K) for **3**. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from total 36 frames. Data were collected with ω scan width of 0.5° at eight different settings of φ and 2θ, keeping the sample-to-detector distance fixed at 5.00 cm for both the compounds. The X-ray data acquisition was monitored by the APEX2 program suit.¹⁷ All the data were corrected for Lorentz-polarization and absorption effects using SAINT and SADABS programs integrated into the APEX2 package.¹⁷ The structures were solved by direct methods and refined by full matrix least squares, based on *F*², using SHELX-97¹⁸ integrated in the program suite APEX2.¹⁷ All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on their parent atoms. The ORTEP III¹⁹ view of both the compounds were drawn with 30% probability displacement ellipsoids and H atoms are not included for the clarity. Crystal data for the structures have been deposited in the Cambridge Crystallographic Data Center with numbers (compound numbers) CCDC-1546876 (**2**), CCDC-1546875 (**3**).

3. Results and Discussion

3.1 Synthesis and characterization

The 1,3-*i*Pr₂POCH₂-C₆H₄-CH₂OP^{*i*}Pr₂ [(*i*Pr₄-POCCCCOP) – H, (**1**)] ligand was prepared by following the literature procedure.¹⁵ Treatment of the pro-pincer ligand **1** with (CH₃CN)₂NiBr₂ in the presence of triethylamine afforded the pincer complex, {κ^P, κ^C, κ^P-(2-*i*Pr₂POCH₂-C₆H₃-6-CH₂OP^{*i*}Pr₂)}NiBr, [(*i*Pr₄-POCCCCOP)NiBr] (**2**) via the C(2)–H bond activation on the ligand, (*i*Pr₄-POCCCCOP)–H (Scheme 1). The complex **2** was obtained as a brownish yellow solid. The ³¹P NMR spectrum of complex **2** shows a single resonance at 141.6 ppm, which is *ca.* 14 ppm more upfield shifted than the free ligand. In the ¹H NMR spectrum of **2**, the –CH₂ protons show two broad singlets against a single set for all the four protons in free-ligand **1**. Similarly, the



Scheme 1. Synthesis of $[(i\text{Pr}_4\text{-POCCCOP})\text{NiX}]$ complexes.

four methylene ($-\text{CH}$) protons displayed two broad singlets. The twenty four protons on eight methyl ($-\text{CH}_3$) groups displayed three sets of signals contrary to a single set in the ligand **1**. The HRMS analysis of complex **2** shows a molecular mass peak m/z 507.1698, which corresponds to the $[\mathbf{2}+\text{H}]^+$ ion. The molecular structure of complex **2** was further confirmed by the single crystal X-ray diffraction study.

The acetate derivative of nickel complex was synthesized by the reaction of complex **2** with AgOAc in quantitative yield. Hence, the treatment of **2** with AgOAc in THF afforded the complex $\{\kappa^{\text{P}}, \kappa^{\text{C}}, \kappa^{\text{P}}-(2-i\text{Pr}_2\text{POCH}_2-\text{C}_6\text{H}_3-6-\text{CH}_2\text{OP}^i\text{Pr}_2)\}\text{Ni}(\text{OAc})$, $[(i\text{Pr}_4\text{-POCCCOP})\text{Ni}(\text{OAc})]$ (**3**) as a brown crystalline solid (Scheme 1). The complex **3** shows a single peak at 136.5 ppm in the ^{31}P NMR spectrum. The ^1H NMR data of complex **3** is almost identical with that of **2**, except the methyl protons on acetate ($-\text{OC}(\text{O})\text{CH}_3$) displaying a singlet at 1.71 ppm. The mass spectrum of **3** displayed peaks at m/z 487.0840 and 427.1461 for the ions $[\mathbf{3}+\text{H}]^+$ and $[\mathbf{3}-\text{OAc}]^+$, respectively. The X-ray analysis further establishes the structure of compound **3**.

3.2 Structure of complexes

The ORTEP diagrams of complexes **2** and **3** are shown in Figures 1 and 2, respectively. Selected bond lengths and bond angles are given in Table 1. The coordination geometry around the nickel center in both the complexes **2** and **3** is square planar. Both the Ni–P bond distances (2.1951(6) Å) in **2** are exactly same and slightly longer than the corresponding bond distance in (2, 6- $(i\text{Pr}_2\text{PCH}_2)_2\text{C}_6\text{H}_3$)NiBr (2.1645(6) Å)^{11b} and (2, 6- $(i\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3$)NiBr (*ca.* 2.142–2.153 Å).²⁰ The Ni–C bond distance follows the same trend, being slightly longer in **2** (1.934(3) Å) than the PCP- (*ca.* 1.918 Å) and POCOP-analogue (*ca.* 1.885 Å). The Ni–Br bond distance in **2** (2.3416(6) Å) is comparable with that of PCP-analogue (*ca.* 2.344 Å),^{11b} whereas it is slightly longer than that observed in POCOP-analogue (*ca.* 2.323 Å).²⁰ This can be attributed to the similar σ -donor strength of the ligands (POCCCOP) and PCP towards nickel in the respective nickel complexes. The nickel center in complex **2** forms a perfect square plane

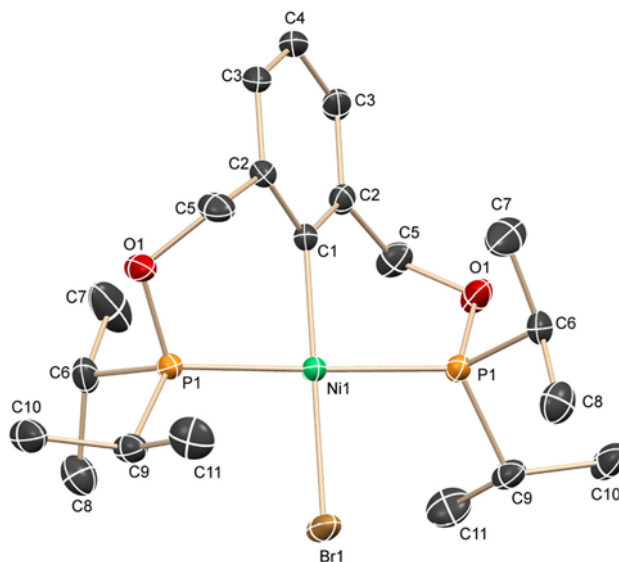


Figure 1. Thermal ellipsoid plot of $[(i\text{Pr}_4\text{-POCCCOP})\text{NiBr}]$ (**2**). All the hydrogen atoms are omitted for clarity.

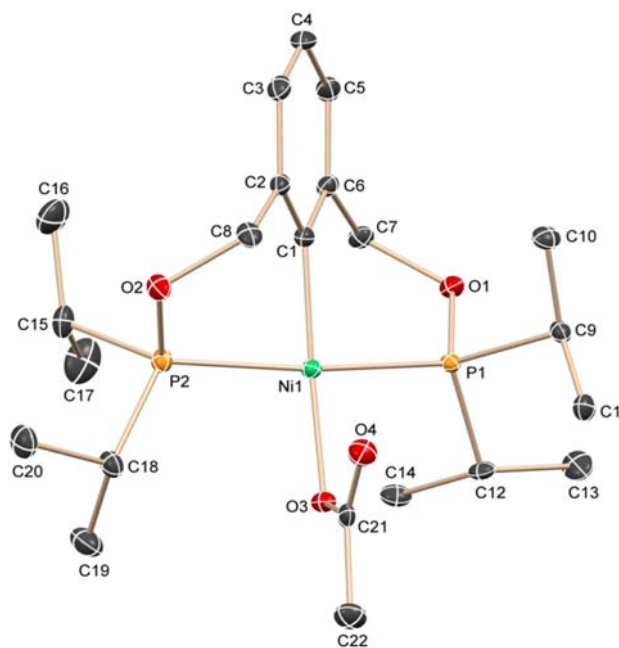
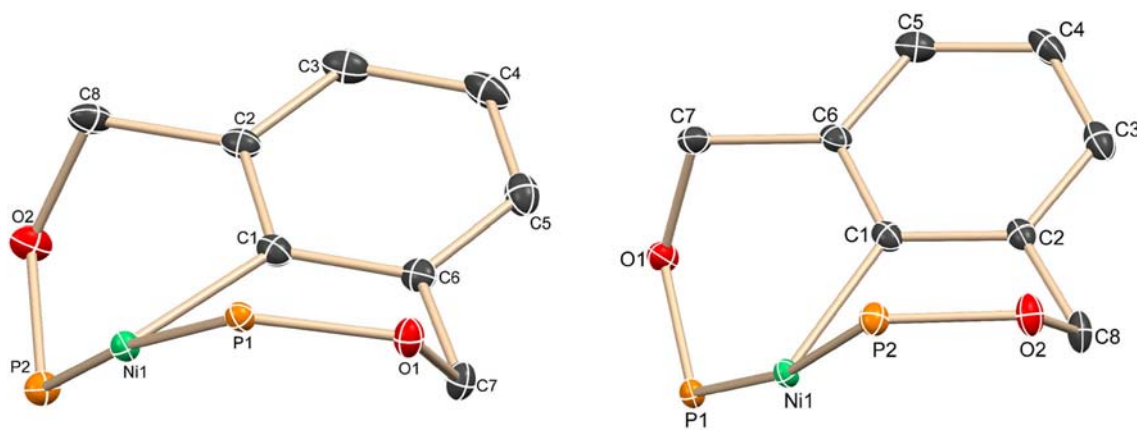


Figure 2. Thermal ellipsoid plot of $[(i\text{Pr}_4\text{-POCCCOP})\text{Ni}(\text{OAc})]$ (**3**). All the hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and bond angles (°) of compounds **2** and **3**.

	Bond lengths (Å)			Bond angles (°)	
	2	3		2	3
Ni(1)–C(1)	1.934(3)	1.910(3)	C(1)–Ni(1)–O(3)	–	173.99(9)
Ni(1)–O(3)	–	1.9445(17)	C(1)–Ni(1)–P(1)	89.254(17)	88.33(8)
Ni(1)–P(1)	2.1950(6)	2.1774(7)	C(1)–Ni(1)–P(2)	89.254(17)	85.69(8)
Ni(1)–P(2)	2.1950(6)	2.1955(7)	C(1)–Ni(1)–Br(1)	180.0	–
Ni(1)–Br(1)	2.3416(6)	–	P(1)–Ni(1)–O(3)	–	92.23(5)
			P(2)–Ni(1)–O(3)	–	94.48(5)
			P(1)–Ni(1)–Br(1)	90.746(17)	–
			P(2)–Ni(1)–Br(1)	90.746(17)	–
			P(1)–Ni(1)–P(2)	178.51(3)	170.59(3)

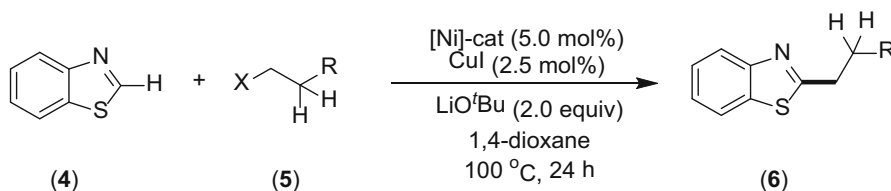
**Figure 3.** Thermal ellipsoid plot of [*i*Pr₄-POCCCOP)NiBr] (**2**) showing two different nickelacycle cores.

with the *cis* angles *ca.* 89.2 and 90.7° and the *trans* angles *ca.* 178.5 and 180.0°. The P–Ni–P bite angle of the POCCCOP ligand in complex **2** (178.51(3)°) is significantly larger than that in PCP-analogue (*ca.* 170.6°) and POCOP-analogue (*ca.* 164.9°). Similarly, the C–Ni–P bond angle in **2** (89.254(17)°) is larger than the corresponding bond angles in PCP-analogue (*ca.* 85.3°) and POCOP-analogue (*ca.* 82.3, 82.7°). The comparison of all the bond lengths and bond angles of **2** with (PCP)NiBr and (POCOP)NiBr shows that the structural features of complex **2** are closer to the (PCP)NiBr than with the (POCOP)NiBr complex. This could be due to the electronic density provided by the (POCCCOP)-moiety towards nickel in (POCCCOP)NiX is similar to that provided by (PCP)-moiety towards nickel in the complex (PCP)NiBr. The presence of methylene (–CH₂) group in the six-membered nickelacycle (POCCCOP)NiX might have a crucial role for this changes. The Ni–P and Ni–C bond lengths in complex **3** are comparable to that observed in complex **2**. However, the P–Ni–P bite angle in **3** (170.59(3)°) is significantly shorter than the corresponding bond angle in **2**. Both the six-membered nickelacycles containing Ni, P, O and C exist in a boat-like conformation, and they are anti to

each other (Figure 3). This is the first solid-state structure for a six-membered pincer nickelacycle complex.

3.3 C–H bond alkylation of benzothiazole

The C–H bond functionalization of sulphur containing azoles, such as benzothiazole, is very crucial as they are ubiquitous building blocks of several pharmaceutical and biologically active compounds.²¹ Particularly, the alkylation of benzothiazole with alkyl halides containing β-hydrogens is a very important and challenging reaction, due to the undesired β-elimination from these electrophiles at the active metal center after the oxidative addition of the same.²² In this regards, the newly developed six-membered nickelacycle (*i*Pr₄-POCCCOP)NiBr (**2**) was screened and employed for the alkylation of benzothiazole (**4**) with alkyl halides (**5**) to obtain the alkylated products **6** (Scheme 2; see Supporting Information for details). Notably, the alkylation reaction of benzothiazole with various alkyl halides afforded better yields while employing six-membered nickelacycle (*i*Pr₄-POCCCOP)NiBr (**2**) as a catalyst than with either (*i*Pr₄-PCP)NiBr or (*i*Pr₄-POCOP)Ni(OAc) catalysts (Table



Scheme 2. Nickel-catalyzed alkylation of benzothiazole.

S1, Supporting Information). However, the catalyst **2** is slightly inferior than earlier reported catalyst systems for the same reaction.^{10g, 23} This catalyst system requires further study to establish the actual activation path.

4. Conclusions

In summary, we have synthesized two six-membered pincer nickelacycle complexes and demonstrated their catalytic application for the alkylation of benzothiazole. Both the six-membered pincer nickelacycles, [(ⁱPr₄-POCCCOP)NiX; (X = Br, OAc)] were synthesized in good yields and structurally characterized. The electronic features of these bis(phosphinite)-nickelacycles are very similar to the bis(phosphine), (ⁱPr₄-PCP)Ni rather than the bis(phosphinite), (ⁱPr₄-POCOP)Ni complex. The complex, (ⁱPr₄-POCCCOP)NiBr catalyzed the alkylation of benzothiazole with alkyl iodides. The C–H alkylation by the six-membered nickelacycle (ⁱPr₄-POCCCOP)NiBr is superior to the five-membered nickel complexes, (ⁱPr₄-PCP)NiBr and (ⁱPr₄-POCOP)Ni(OAc). Further utilization of these six-membered pincer nickelacycles, (ⁱPr₄-POCCCOP)NiX in other C–H functionalization reactions is currently underway in our laboratory.

Supplementary Information (SI)

Crystallographic data for the structural analyses of complexes **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre having CCDC Nos. 1546876 and 1546875, respectively. Copy of this information is available on request at free of charge from CCDC, Union Road, Cambridge, CB21EZ, UK (e-mail: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>). Crystal data and structure refinement, HRMS spectra and NMR spectra of complexes **2** and **3** and Table S1 are available at www.ias.ac.in/chemsci.

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