Reactivity of Nickel metal Precursors towards Amido linked N-heterocyclic Carbenes and their catalytic studies for cross coupling reactions

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Abstract:

The refluxing of chloroacetamide derivatives with n-butyl imidazole resulted in their corresponding salt of composition 1-(*n*-butyl)-3-N-(2-Ar)acetamido-1, 3-imidazolium chloride (Ar = furylmethyl (**1a**); phenylmethyl (**1b**)). The latter salt on treatment with DBU followed by the addition of chalcogen atom resulted into a compound [(1-(*n*-butyl)-3-N-(2-Ar)acetamido-1,3-imidazol-3-ylidine)E] (Ar = furylmethyl; E = S (**2a**); Ar = phenylmthyl; E = Se (**2b**)). Similarly, the reaction of the imidazolium salts with, excess K_2CO_3 and $NiCl_2.6H_2O$ yielded compounds $[(1\text{-}(n\text{-butyl})\text{-}3\text{-}N\text{-}(2\text{-Ar})\text{acetamido-}1,3\text{-imidazol-}3\text{-ylidine})]_2Ni$ (Ar = furylmethyl (**3a**); phenylmethyl (**3b**)). The latter complexes have also been isolated by using Ni(II) phosphine precursors $[NiCl_2(P\text{-}P)]$ (P-P = PPh_3, dppf). The molecular structure of [(1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazol-3-ylidine)]$_2$Ni and [(1-(*n*-butyl)-3-N-(2-

phenylmethyl)acetamido-1, 3-imidazol-3-ylidine)]$_2$Ni were established by single crystal X-ray diffraction analysis. The catalytic property of complex **3a** and **3b** for cross coupling reactions has been studied.

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1. Introduction:

The chemistry of N-heterocyclic carbenes (NHC) has become popular due to its applicability in various organic transformations [1-4]. These broad prospective interest in NHCs is mainly attributed to their rich structural diversity as well as strong metal carbon bond [5-7]. Within the field, internally functionalized amido-linked carbenes have drawn interest due to their catalytic utility for the formation of C-X bonds (X = C, N, P) [8-10], biological importance [11, 12] and rich coordination chemistry [13,14].

The reaction of [1-R-3{N-(Arylacetamido)imidazolium}chloride] (R = Me, isopropyl, benzyl, menthyl, pinamyl, isboronyl; Aryl = phenyl, benzyl, furyl) with $NiCl_2.6H_2O$ in the presence of K_2CO_3 yielded a complex of type {1-R-3[N-(Arylacetamido)]imidazol-2-ylidene}$_2$Ni where nickel embedded in core of carbene [8, 10, 15]. Even the reaction with 1, 2, 4-triazole derived amido functionalized ligand also resulted in a similar type of compound [16, 17]. However, the reaction of nickel chloride with symmetrical substituted carbenes afforded [Ni(NHC)$_2$] (NHC = 1, 3-disubstituted imidazol-2-ylidenes) complex which are air stable robust catalyst for cross coupling reactions [18, 19]. This type of complex has also been reported by Hermann et.al. by the treatment of [$NiX_2(PPh_3)_2$] (X = Cl, Br) with NHCs, displacing the phosphine ligands with the carbene [20, 21] and Matsubara et al. have carried out similar reactions to isolate both [$NiX_2(NHC)_2$] (X = Cl, Br) and the mixed complex, containing both triphenyl phosphinne and NHC; [$NiX(PPh_3)_2(NHC)$] (X = Cl, Br; NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-

ylidene) [22]. These complexes showed a prominent catalytic reactivity for Grignard cross coupling reactions.

2. Experimental:

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents used in the reactions were distilled applying standard procedures. The precursor compound N-benzyl and N-furyl 2-chloroacetamide,[23] $[NiCl_2(P\text{-}P)]$ (P-P = PPh_3, dppf),[24] and 1-butylimidazole [25] were prepared according to literature methods. Starting materials were procured from Sigma-Aldrich. The ^{1}H and $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ NMR spectra were recorded on a Bruker AVANCE--II spectrometer operating at 300, 75.47 and 57.23 MHz, respectively. Chemical shifts are relative to internal chloroform peak for ^{1}H, $^{13}C\{1H\}$, and external Ph_2Se_2 (δ 463 ppm) in $CDCl_3$ for $^{77}Se\{^{1}H\}$ NMR spectra. Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer.

The electrochemical experiments were performed using a VERSATAT potentiostat/galvanostat with a three-electrode cell using Au disk as working electrode, a Pt gauze as the counter electrode, and a Saturated Calomel electrode as reference electrode. Measurements were made in water with a concentration of 3.0 mmole L^{-1} for the nickel complexes. Tetrabutylammonium tetrafluoroborate salt served as electrolyte (concentration 0.12 mmole L^{-1}). Potentials were recorded at mV s^{-1}.

The molecular structure of compound [1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazol-3-ylidine)]$_2$Ni (**3a**) and [1-(*n*-butyl)-3-N-(2-phenylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3b**) were collected at 173K on using a Rigaku FR-XUltrahigh Brilliance Microfocus RA generator/confocal optics and XtaLAB P200 diffractometer [Mo-K_α radiation (λ = 0.71075 Å)]. Intensity data were collected using ω steps accumulating area detector images

spanning at least a hemisphere of reciprocal space. Data were collected using Crystal Clear [26] and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro. The structures were solved by charge-flipping methods (Superflip),[27] and refined by full-matrix least-squares against F^2 (SHELXL-2018/3). The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Molecular structures were drawn using ORTEP.[28] Crystallographic and structural determination data are listed in Table 1. CCDC 1913414–1913415 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

2. Synthesis of complexes:

2.1 Preparation of 1-(n-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazolium chloride (*1a*)

To a toulene solution of 2-chloro-N-(2-furylmethyl)acetamide (1.5gm, 9.1mmol), n-butyl imidazole (1.2 ml, 9.1 mmol) was added. The reaction mixture was refluxed for 20 hours at 100 ºC which resulted black sticky precipitate. The precipitate was dissolved in minimum volume (5 mL) of dichloromethane which on addition of diethyl ether (20 mL) yielded a black solid of expected product (yield: 1.2 gm, 53%; m.p: 62ºC) (scheme **1**). Anal Calc. for $C_{14}H_{20}N_3O_2Cl$: C, 56.46; H, 6.76; N, 14.10%. Found: C, 56.68; H, 6.86; N, 14.40 %. ^{1}H NMR ($CDCl_3$) δ: 9.68 (s, 1H, NC(2)*H*N), 9.45 (br, 1H, N*H*CO), 7.66 (br, 1H, C_4H_3O), 7.39 (s, 1H, NC(4)*H*C), 7.28 (d, J = 4.6Hz, 1H, NC(5)*H*C), 6.25 (d, *J* = 7.5 Hz, 2H, C_4H_3O), 5.35 (s, 2H, CH_2), 4.36 (d, *J* = 4.8 Hz, 2H, CH_2NH), 4.24 (t, *J* = 6.9 Hz, 2H, -$CH_2CH_2CH_2CH_3$) 1.86-1.81 (m, 2H, -$CH_2CH_2CH_2CH_3$), 1.37-1.30 (m, 2H, -$CH_2CH_2CH_2CH_3$), 0.92 (t, *J* = 7.4 Hz, 3H,-$CH_2CH_2CH_2CH_3$).

2.2 Preparation of 1-(n-butyl)-3-N-(2-phenylmethyl)acetamido-1,3-imidazolium chloride **(1b)**

In a method similar to compound **1a,** compound **1b** was prepared by using the n-butyl imidazole (2.0 ml, 15 mmol) and 2-chloro-N-(phenylmethyl)acetamide (2.8 gm, 14.9 mmol) giving a white precipitate (yield: 2.4 gm, 66%; m.p: 146ºC). Anal Calc. for $C_{16}H_{22}N_3OCl$: C, 62.42; H, 7.20; N, 13.65%. Found: C, 62.96; H, 7.12; N, 13.96%. ^{1}H NMR ($CDCl_3$) δ: 9.92 (s, 1H, NC(2)*H*N), 9.75 (br, 1H, N*H*CO), 7.34-7.16 (m, 7H, C_6H_5), 5.37 (s, 2H, CH_2), 4.39 (d, J = 6.0 Hz, 2H, CH_2NH), 4.1(t, J = 4.5 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.86-1.81(m, 2H, $CH_2CH_2CH_2CH_3$), 1.39-1.32 (m, 2H, -$CH_2CH_2CH_2CH_3$), 0.95 (t, J = 7.5 Hz, 3H, -$CH_2CH_2CH_2CH_3$); ^{13}C{^{1}H} NMR ($CDCl_3$): 164.8 (<u>*C*</u>=O), 138.0 (N<u>*C*</u>N), 137.3 (N-<u>*C*</u>(3)-N), 128.4 (Ph), 127.8 (Ph), 127.1 (Ph), 123.8 (Ph), 120.7 (N-<u>*C*</u>(5)-N), 51.6 (<u>*C*</u>$H_2CH_2CH_2CH_3$), 49.9 (CO-<u>*C*</u>H_2), 43.4 (NH-<u>*C*</u>H_2), 31.9 (-CH_2<u>C</u>$H_2CH_2CH_3$), 19.4 (CH_2CH_2<u>C</u>H_2CH_3), 13.3 ($CH_2CH_2CH_2$<u>*C*</u>H_3).

2.3 ***Preparation of [(1-(<u>n</u>-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-ylidine)S]*** **(2a)**

An acetonitrile solution of 1-(<u>*n*</u>-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazolium chloride (261 mg, 1 mmol), on treatment with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 0.3 ml, 2 mmol) and sulfur powder (64 mg, 2 mmol) at 50ºC for 12 hours under inert atmosphere resulted a brown solution. The latter solution was concentrated under reduced pressure which on washing with dichloromethane-acetone mixture afforded **2a** (yield: 150 mg, 51%; m.p.: 88ºC) (scheme **1**). Anal. Calcd. for $C_{14}H_{18}N_3O_2S$: C, 57.51; H, 6.21; N, 14.37; S, 10.97%; Found: C, 57.43; H, 6.25; N, 14.11; S, 10.74%. IR (KBr, cm^{-1}): 3720 (m), 3173 (w), 3106 (w), 2953 (w), 2926 (w), 2866 (w), 1650 (s), 1547 (s), 1417 (s), 1372 (m), 1336 (m), 1228 (s), 1189 (m), 1143 (m), 1068 (m), 1012 (m), 951 (w), 907 (m), 800 (w), 757 (s), 706 (m), 670 (s), 630 (m), 602 (w), 571(w), 528(m). ^{1}H NMR ($CDCl_3$): 7.46 (br, 1H, N*H*CO), 7.34 (s, J = 2.0 Hz, 1H, C_4H_3O), 6.89 (d, J = 4.0 Hz, 1H, NC(4)*H*C), 6.74 (d, J = 2.0 Hz, 1H, NC(5)*H*C), 6.30 (d, J = 2.0 Hz, 1H,

C_4H_3O), 6.21 (dd, J = 3.0 Hz each, 1H, C_4H_3O), 4.76 (s, 2H, CH_2), 4.41 (d, J = 6.0 Hz, 2H, CH_2NH), 4.05 (t, J = 6.9 Hz, 2H, -$CH_2CH_2CH_2CH_3$) 1.69-1.84 (m, 2H, -$CH_2CH_2CH_2CH_3$), 1.29-1.44 (m, 2H, -$CH_2CH_2CH_2CH_3$), 0.93 (t, J = 6 Hz, 3H,-$CH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 167.0 (S-N<u>C</u>N), 161.7 (<u>C</u>=O), 151.0 (<u>C</u>$_4H_3O$), 141.7 (<u>C</u>$_4H_3O$), 117.5 (N-<u>C</u>(3)-N), 116.6 (N-<u>C</u>(5)-N), 110.4 (<u>C</u>$_4H_3O$), 107.1 (<u>C</u>$_4H_3O$), 51.5 (<u>C</u>$H_2CH_2CH_2CH_3$), 48.1 (CO-<u>C</u>H_2), 36.5 (NH-<u>C</u>H_2), 30.9 (CH_2<u>C</u>$H_2CH_2CH_3$), 19.9 (CH_2CH_2<u>C</u>H_2CH_3), 13.5 ($CH_2CH_2CH_2$<u>C</u>H_3).

2.4 *Preparation of [(1-(butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-ylidine)Se]* (2b)

Prepared similar to above method by using 1-(butyl)-3-N-(furylmethyl)acetamido-1,3-imidazolium chloride (261 mg, 1 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.3 ml, 2 mmol) and selenium powder (157.8 mg, 2 mmol), giving brown powder (yield: 189 mg, 45%; m.p.: 106ºC). Anal. Calcd. for $C_{14}H_{18}N_3O_2Se$: C, 49.56; H, 5.35; N, 12.39%; Found: C, 49.54; H, 5.31; N, 12.19%. IR (KBr, cm^{-1}): 3271 (m), 3171 (w), 3142 (w), 3104 (w), 2956 (w), 2926 (m), 2864 (w), 1654 (s), 1561 (s), 1544 (s), 1457 (m), 1408 (s), 1373 (m), 1343 (m), 1235 (s), 1139 (m), 1070 (m), 1012 (m), 959 (w), 924 (w), 879 (w), 796 (w), 733 (s), 707 (s), 666 (s), 600 (w), 568 (m). ^1H NMR ($CDCl_3$): 7.45 (br, 1H, C_4H_3O), 7.34 (d, J = 2.0 Hz, 1H, NC(4)HN), 7.07 (s, J = 2.0 Hz, 1H, NC(5)HN), 6.89 (d, J = 2.2 Hz, 1H, C_4H_3O), 6.28 (dd, J = 2.8 Hz, 1H, C_4H_3O), 6.21 (d, J = 3.2 Hz, 1H, C_4H_3O), 4.87 (s, 2H, CH_2), 4.43 (d, J = 6.0 Hz, 2H, CH_2NH), 4.14 (t, J = 7.8 Hz 2H, -$CH_2CH_2CH_2CH_3$), 1.69-1.87 (m, 2H, -$CH_2CH_2CH_2CH_3$). 1.31-1.45 (m, 2H, -$CH_2CH_2CH_2CH_3$), 0.98 (t, J = 7.2 Hz, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 166.4 (Se-N<u>C</u>N), 166.4 (<u>C</u>=O), 156.0 (<u>C</u>$_4H_3O$), 150.7 (<u>C</u>$_4H_3O$), 119.5(N-<u>C</u>(3)-N), 119.3 (N-<u>C</u>(5)-N), 110.3 (<u>C</u>$_4H_3O$), 107.4 (<u>C</u>$_4H_3O$), 53.1 (<u>C</u>$H_2CH_2CH_2CH_3$), 50.0 (CO-<u>C</u>H_2), 36.5 (NH-<u>C</u>H_2), 31.11 (-

$CH_2\underline{C}H_2CH_2\mathit{CH_3}$), 19.7(-$CH_2CH_2\underline{C}H_2\mathit{CH_3}$), 13.66 (-$CH_2CH_2CH_2\underline{\mathit{C}}\mathit{H_3}$). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 6.69 ppm.

2.5 *Preparation of [1-(n-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni* (3a)

(i) Treatment of an acetonitrile solution of 1-(*n*-butyl)-3-*N*-(2-furylmethyl)acetamido-1,3-imidazolium chloride (261 mg, 1 mmol) with K_2CO_3 (1.3 gm, 10 mmol) and $NiCl_2.6H_2O$ (119 mg, 0.5 mmol) at 100℃ for 20 hours resulted in a yellow solution which was concentrated and kept for crystallization under refrigerated conditions to afford a yellow crystalline product (yield: 138 mg, 27%, m.p.: 175℃). Anal. Calcd. for $C_{28}H_{36}N_6O_4Ni$: C, 58.05; H, 6.26; N, 14.50%; Found: C, 58.05; H, 6.13; N, 14.21%. IR (KBr, cm^{-1}) : 3084 (w), 2958 (w), 2873 (w), 1678 (m), 1581 (s), 1462 (m), 1427 (m), 1375 (w), 1297 (m), 1241 (w), 1171 (m), 1144 (w), 1070 (w), 1001 (w), 967 (w), 930 (w), 884 (w), 803 (w), 738 (s), 679 (m), 630 (w), 599 (m). ^1H NMR ($CDCl_3$): 7.26 (s, 2H, NC(4)*H*C), 7.03 (d, *J* = 2.0 Hz, 2H, NC(5)*H*C), 6.69 (d, *J* = 1.0 Hz, 2H, C_4H_3O), 6.27 (dd, *J* = 2.0 Hz, 2H, C_4H_3O), 6.03 (d, *J* = 4.0 Hz, 2H, C_4H_3O), 5.25 (d, *J* = 14 Hz, 2H, CH_2), 4.86 (d, *J* = 4.0Hz ,2H, CH_2), 4.40 (d, *J* = 14 Hz, 2H, CH_2), 3.6 (d, *J* = 14 Hz, 2H, CH_2), 3.20-3.10 (m, 4H, -$CH_2CH_2CH_2CH_3$). 2.79-2.65 (m, 4H, -$CH_2CH_2CH_2CH_2CH_3$), 1.26-1.49(m, 4H, -$CH_2CH_2CH_2CH_3$), 1.09 (t, 6.0 Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 169.4 (Ni-N$\underline{C}$N), 167.9($\underline{C}$=O), 156.6 ($\underline{C_4}H_3O$), 140.8 ($\underline{C_4}H_3O$), 122.1 (N-$\underline{C}$(3)-N), 120.1 (N-$\underline{C}$(5)-N), 110.2 ($\underline{C_4}H_3O$), 105.9 ($\underline{C_4}H_3O$), 56.6 ($\underline{C}H_2CH_2CH_2CH_3$), 49.3 (CO-$\underline{C}H_2$), 41.6 (NH-$\underline{C}H_2$), 32.9 ($CH_2\underline{C}H_2CH_2CH_3$), 19.9 ($CH_2CH_2\underline{C}H_2CH_3$), 13.4 ($CH_2CH_2CH_2\underline{C}H_3$).

(ii) To an acetonitrile solution of 1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazolium chloride (130mg, 0.5 mmol), K_2CO_3(1.3 gm, 10 mmol) along with [$NiCl_2$(dppf)] (342 mg, 0.5 mmol) were added in the same solvent. The reaction mixture was refluxed at 100℃ for 14 hours

and pass through a sintered glass funnel to remove the un-reacted starting materials. The solvent was removed from the filtrate under reduced pressure, and the residue was extracted with dichloromethane-hexane mixture to afford yellow crystals (yield: 105mg, 22%; m.p.: 175℃). Anal. Calcd. for $C_{28}H_{36}N_6O_4Ni$: C, 58.05; H, 6.26; N, 14.50%; Found: C, 58.22; H, 6.07; N, 14.36%. ^{1}H}NMR ($CDCl_3$): 7.26-7.24 (m, 2H, NC(4)*H*N), 6.94 (d, 2.0 Hz, 2H, NC(5)*H*C),6.66 (d, *J* = 2.0 Hz, 2H, C_4H_3O), 6.27 (q, *J* = 4.0 Hz, 2H, C_4H_3O), 6.05 (d, *J* = 4.0 Hz, 2H, C_4H_3O), 5.21 (d, *J* = 14 Hz, 2H, CH_2), 4.84 (d, *J* = 16.0 Hz, 2H, CH_2), 4.35(m, 2H, CH_2), 3.6 (m, 4H, CH_2), 3.24-3.14 (m, 4H, -$CH_2CH_2CH_2CH_3$). 2.77-2.66 (m, 4H, -$CH_2CH_2CH_2CH_3$), 1.57-1.08 (m, 4H, -$CH_2CH_2CH_2CH_3$), 0.84(t, *J* = 6.0 Hz, 6H, CH_2CH_3); ^{13}C{^{1}H}NMR ($CDCl_3$): 169.2 (Ni-NCN), 168.4 (C=O), 156.8 (C_4H_3O), 140.7 (C_4H_3O), 121.9 (N-C(3)-N), 119.9 (N-C(5)-N), 110.2 (C_4H_3O), 105.9 (C_4H_3O), 56.7 (-$CH_2CH_2CH_2CH_3$), 49.3 (CO-CH_2), 41.6 (NH-CH_2), 32.9 (-$CH_2CH_2CH_2CH_3$), 19.9 (-$CH_2CH_2CH_2CH_3$), 13.4 (-$CH_2CH_2CH_2CH_3$).

(iii) Treatment of an acetonitrile solution of 1-(*n*-butyl)-3-N-(phenyl-methyl) acetamido-1, 3-imidazolium chloride (130 mg, 0.5 mmol) with K_2CO_3 (1.3 gm, 10 mmol), followed by the addition of [$NiCl_2(PPh_3)_2$] (327 mg, 0.5 mmol), and heating at 100℃ for 14 hours resulted I a yellow solution. On passing through a sintered glass filtrate was collected, and solvent was removed under reduced pressure, to obtain yellow powder (yield: 115 mg, 25%, m.p.: 175℃). Anal. Calcd. for $C_{28}H_{36}N_6O_4Ni$: C, 58.05; H, 6.26; N, 14.50%; Found: C, 58.18; H, 6.27; N, 14.41%. ^{1}H NMR ($CDCl_3$): 7.34-7.29 (m, 2H, NC(4)*H*C), 6.97 (d, *J* = 2.0 Hz, 2H, NC(5)*H*C), 6.67 (d, *J* = 2.0 Hz, 2H, C_4H_3O), 6.30 (q, *J* = 4.0 Hz, 2H, C_4H_3O), 6.09 (d, *J* = 4.0 Hz, 2H, C_4H_3O), 5.25 (d, *J* = 14 Hz, 2H, CH_2), 4.88 (d, *J* = 14.0 Hz, 2H, CH_2NH), 4.39 (d, *J* = 7.0 Hz, 2H, -CH_2), 3.61(d, *J* = 4.0 Hz, 2H, CH_2NH), 3.27-3.12 (m, 4H, -$CH_2CH_2CH_2CH_3$). 2.83-2.69

(m, 4H, -CH_2*CH_2*CH_2CH_3), 1.41-1.05(m, 4H, -CH_2CH_2*CH_2CH_3) 0.91 (t, *J* = 6.0 Hz, 6H, -$CH_2CH_2CH_2$*CH_3); $^{13}C\{^1H\}$NMR signals are consistent with those noted above.

2.6. ***Preparation of [1-(n-butyl)-3-N-(phenyl-methyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni*** **(3b)**

(i) Prepared in a similar manner to complex **3a**, using method (i),with 1-(*n*-butyl)-3-N-(phenyl-methyl)acetamido-1,3-imidazolium chloride (274 mg, 1 mmol), K_2CO_3 (1.3 gm, 10 mmol) and $NiCl_2.6H_2O$ (119 mg, 0.5 mmol), giving a yellow powder (yield: 110 mg, 20%, m.p.: 225ºC). Anal. Calcd. for $C_{32}H_{40}N_6O_2Ni$: C, 64.11; H, 6.72; N, 14.02%; Found: C, 63.86; H, 6.60; N, 14.06%. IR (KBr, cm^{-1}) : 3117 (w), 2929 (w), 1678 (w), 1578 (s), 1493 (w), 1453 (m), 1425 (m), 1378 (m), 1338 (w), 1298 (m), 1237 (m), 1212 (w), 1175 (w), 1068 (w), 1029 (w), 967 (w), 913 (w), 806 (w), 737 (m), 694 (m), 622 (w). ^1H NMR ($CDCl_3$) : 7.33-7.08 (m, 10H, C_6*H_5), 6.95 (s, 2H, NC(4)*H*C), 6.66 (d, *J* = 2.0 Hz, 2H, NC(5)*H*C), 5.0(d, *J* = 14 Hz, 2H, C*H_2*), 4.6 (d, *J* = 14 Hz, 2H, C*H_2*), 4.40 (d, *J* = 16 Hz, 2H, C*H_2*) , 3.6(d, *J* = 16 Hz, 2H, C*H_2*), 3.07-2.92 (m, 4H, C*H_2*$CH_2CH_2CH_3$), 2.80–2.66 (m, 4H, -CH_2C*H_2*CH_2CH_3), 1.54–1.28 (m, 4H, CH_2CH_2C*H_2*CH_3), 1.20-0.78 (m, 6H, $CH_2CH_2CH_2$C*H_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 168.9 (Ni-N*C*N), 168.8 (*C*=O), 144.1 (N-*C*(3)-N), 128.6 (Ph), 127.9 (Ph), 125.9 (Ph), 121.9 (Ph), 119.5 (N-*C*(5)-N), 56.7(*C*$H_2CH_2CH_2$C*H_3), 49.1 (CO-*C*H_2), 49.0 (NH-*C*H_2), 32.2 (-CH_2*C*H_2CH_2*CH_2CH_3), 19.9 (CH_2CH_2*C*H_2*CH_3), 13.6 ($CH_2CH_2CH_2$*C*H_3).

(ii) Prepared in a similar to compound **3a**, using method (ii),with1-(*n*-butyl)-3-N-(phenyl-methyl)acetamido-1,3-imidazolium chloride (137 mg, 0.5 mmol), K_2CO_3 (1.3 gm, 10 mmol) and [$NiCl_2$(dppf)] (342 mg, 0.5 mmol), giving a yellow powder, which was re-crystallized from dichloromethane-hexane (yield: 87 mg, 18%, m.p.: 225ºC) (scheme **2**). Anal. Calcd. for

$C_{32}H_{40}N_6O_2Ni$: C, 64.11; H, 6.72; N, 14.02%; Found: C, 64.32; H, 6.41; N, 14.11%. ^1H and $^{13}C\{^1H\}$ NMR signals are consistent with those noted above.

(iii) Prepared in a similar to compound **3a**, using method (iii), with 1-(*n*-butyl)-3-N-(phenyl-methyl)acetamido-1,3-imidazolium chloride (137 mg, 0.5 mmol), K_2CO_3 (1.3 gm, 10 mmol) and $[NiCl_2(PPh_3)_2]$ (327 mg, 0.5 mmol), and heating for 20 hours at 100℃.This gave a yellow powder which was re-crystallized from dichloromethane-hexane to obtain yellow crystals (yield: 97 mg, 21%, m.p. 225ºC). Anal. Calcd. for $C_{32}H_{40}N_6O_2Ni$: C, 64.11; H, 6.72; N, 14.02%; Found: C, 64.22; H, 6.68; N, 13.98%. $^{13}C\{^1H\}$ NMR signals are consistent with those noted above.

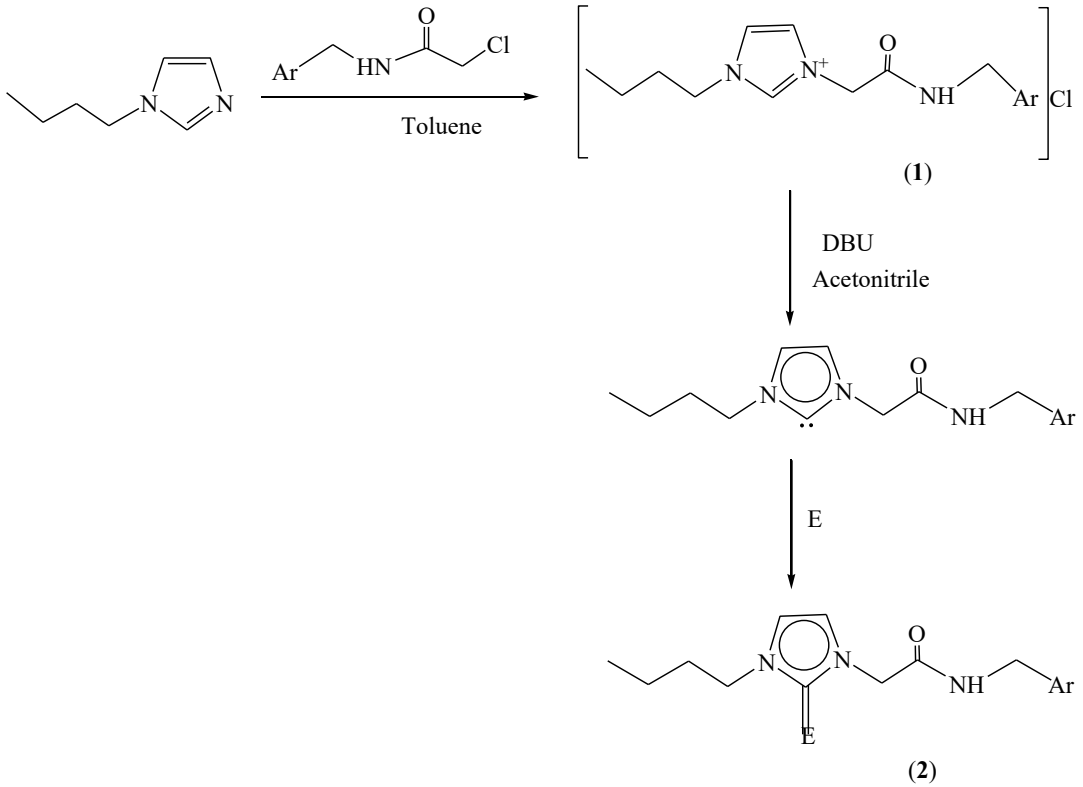
3. Result and Discussion

The widening utility of amido functionalized N-heterocyclic carbene as catalysts for base-free Michael addition has led us to prepare our functionalized carbenes [15, 23]. Refluxing of n-butyl imidazole with 2-chloro-N-(phenylmethyl)acetamide or 2-chloro-N-(furylmethyl)acetamide resulted the formation of the 1-(*n*-butyl)-3-N-(2-phenylmethyl/furylmethyl)acetamido-1, 3-imidazolium chloride salts in moderate yields (Scheme 1). The formation of the imidazolium salts was verified through ^1H NMR by the presence of downfield resonance of protons at 7.28 and 6.25 ppm of 4 and 5 position of the imidazole ring. A blue solution of the free carbene has been generated from these imidazolium salt by the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which on treatment with chalcogens atom afforded a compound of type [(1-(*n*-butyl)-3-N-(2-Ar)acetamido-1,3-imidazol-3-ylidine)E] (Ar = furyl methyl, E = S (**2a**); Se (**2b**)) (Scheme 1). The $^{13}C\{^1H\}$ NMR of compounds **2a** and **2b** showed a signature resonance of E-$C_{carbene}$ compounds, at ~167 ppm. The $^{77}Se\{^1H\}$ NMR of compound [(1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-

ylidine)Se] (**2b**) displayed a singlet at 6.69 ppm which is comparable to selenium adducts of imidazo[1, 5a]pyridine-3-ylidenes [29]. Recently, Ganter et.al. have documented a correlation between the ^{77}Se NMR chemical shift and donor properties of carbene [30]. The reports mentioned that de-shielded resonance corresponds to π-acidic nature of carbene due to the weak interaction of nitrogen lone pair and vacant p orbital of carbon. However, the selenium adducts **2b** resulted a shielded resonance with respect to 1, 3 dialkylimidazole-2-selenone (alkyl = isopropyl, mesityl, fluorophenyl) which resembles poor π-acceptor ability as well as good donor property of carbene [31]. The IR spectrum of the chalcogen-carbene compounds also demonstrated a characteristic stretching frequency at 1427 and 1570 cm^{-1} which correspond to the presence of both $E=C_{carbene}$ (E= S, Se) and CO bonds respectively.

The reaction of the substituted carbenes with $NiCl_2.6H_2O$ in the presence of excess K_2CO_3 yielded complex of composition [1-(*n*-butyl)-3-N-(Ar)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3**) (Ar = Phenylmethyl, (**3a**); furylmethyl, (**3b**)) (Scheme 2). It is noteworthy to mention that the similar reaction with d^8 system of Pd(II) precursor results the isolation of complex type [1-(*R*)-3-N-benzylacetamido-1,3-imidazol-3-ylidine)]$_2PdCl_2$ (R = isopropyl, -CH_2Ph) [32] where amido linked does not get coordinated with palladium center. The latter discussed outcomes can be rationalized by considering the fact that nickel precursors required quite harsh and stringent condition for the reaction with respect to palladium. Even theoretical calculation of amido linked NHC carbene corresponds 10:1 ratio of σ donor/π acceptor property which reflects rich contribution of charge from NHC ligand to metal system [10]. A substantial donor nature aroused due to simultaneous chelation of -NHC carbon to nickel as well as amido nitrogen to nickel center. This chelation through carbon and nitrogen granted an extra stability to the resulting complex. The coordination of nickel is confirmed by the ^1H NMR resonances at

4.96 and 4.63 ppm of imidazole protons. Another prominent characteristic of ^{1}H NMR spectra is the disappearance of proton signal at second position (-NCHN-) of imidazole ring. Additionally, the $^{13}C\{^{1}H\}$ NMR signals correspond to the presence of all expected carbon atoms, similar to those that have been seen previously [8, 10]. By comparison to the spectra of the free-ligand, a presence of de-shielded resonance at 169 ppm in $^{13}C\{^{1}H\}$ NMR is indicative of the formation of the Ni-$C_{carbene}$ bond. The IR spectrum of compounds **3a** and **3b** displayed all vibrations from 3010-550 cm^{-1}. Nevertheless, the intense peaks at 631 and ~ 690 cm^{-1} are indicative of the existence of Ni-N and Ni-$C_{carbene}$ bonds respectively [33-36].



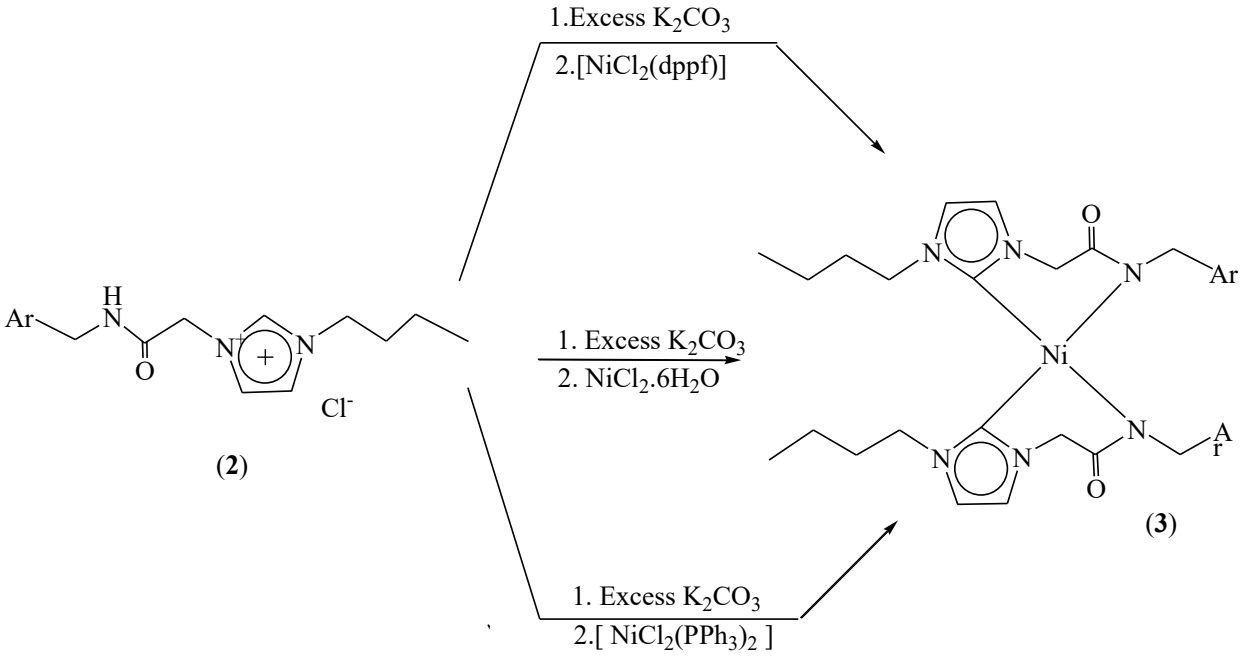
E	Ar	
S	Furyl	2a
Se	Furyl	2b

Scheme 1

In a similar manner, the reaction of one equivalent of 1-(*n*-butyl)-3-N-(2-Ar)acetamido-1, 3-imidazolium chloride (Ar = Phenylmethyl, furylmethyl) with excess K_2CO_3 and $[NiCl_2(P\text{-}P)]$ (P-P= PPh_3, dppf) also yielded the same compounds **3a** and **3b**, respectively. It appears that chelating ring formed by carbon and nitrogen with strong *trans* effect consequences the substitution of phosphine under the basic condition. The liberation of phosphine due to chelated cyclic ring formed by pyridyl nitrogen and chalcogen center is very well documented whether strong interaction between hard acid -hard base (pyridyl nitrogen) insist the ring formation by removing phosphine in to oxide.[37] An analogous pattern of reactivity has been noted by Grubbs et.al., where various ruthenium carbene complexes having NHC and PR_3 show loss of phosphine ligand under ambient reaction conditions [38, 39]. In another example, the reaction of $[NiCl_2(PPh_3)]$ with 1, 3 di-substituted imidazol-2-ylidenes resulted the substitution of triphenyl phosphine with free carbene. However, partial substitution of PPh_3 is also been reported where a reaction of $[NiCl_2(PPh_3)]$ with one equivalent of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (I^iPr) isolated a compound of type $[NiCl_2(PPh_3)(I^iPr)]$ which on keeping for more than one day in solution transformed to $[NiCl_2(I^iPr)_2]$ [22, 40].

Ar	

Furyl	3a
Phenyl	3b



Scheme 2

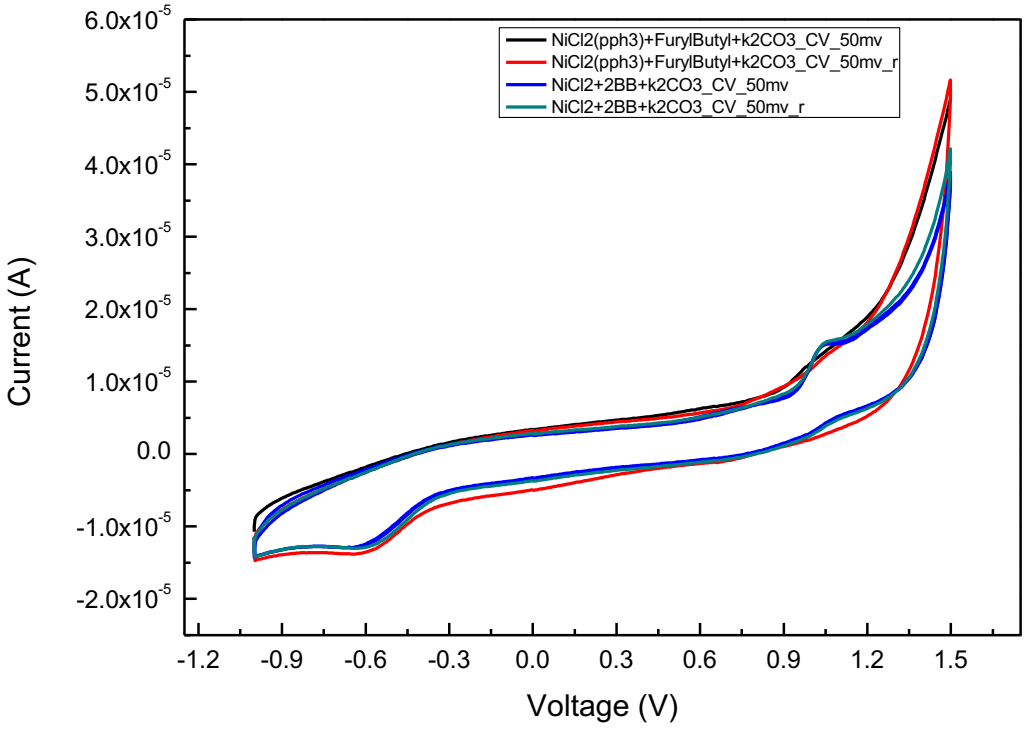


Figure 1: Cyclic voltammogram of complex [1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3a**) and [1-(*n*-butyl)-3-N-(2-phenylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3b**)

The electrochemical behaviour of the Ni(II) complexes was investigated in H_2O by cyclic voltammetry (CV). The nature of cyclic voltammogram is reversible in nature and reduction potential at approx. -0.6 V is related to the redox Ni centre in the catalyst, and it may be inferred that the catalytic activities of the catalysts are due to the presence of Ni(II). With consecutive scans, it was found that the redox centre was stable, and this accounts for the sustained catalytic activity of the complexes.

The solid state structures of [1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3a**) (figure 2) and [1-(*n*-butyl)-3-N-(2-phenylmethyl)acetamido-1,3-imidazol-3-

ylidine)]$_2$Ni (**3b**) (figure 3) show similar square planar geometries, with a C_2N_2 coordination environment, the imidaozle rings placed *cis* to each other. The bond lengths of Ni-$C_{carbene}$ in complex **3a** and **3b** is [1.8658(13) Å and 1.861(2)/1.859(2) Å], are comparable to the related compound {1-[(2-furanylmethyl)aminocarbonylmethyl]-3-methylimidazol-2-ylidene}$_2$Ni [1.865(4) Å, 1.867(5) Å] and longer than [1-(benzyl)-3-N-(benzylacetamido)imidazol-2-ylidene]$_2$Ni [1.841(4) Å and 1.858(4) Å] [8, 10]. The Ni-N bond lengths [1.9297(11) Å and 1.9306(19)/1.9367(19) Å] are in good agreement with previously reported values from related complexes [7, 10, 15, 16]. The bond angles around the nickel in compound **3a** and **3b** varies from 86.58(5)º - 93.12(12)º, comparable to the analogous compound [1-(benzyl)-3-N-(benzylacetamido)imidazol-2-ylidene]$_2$PdCl$_2$ [90.4(8)º and 90.6(2)º] [32] and [1-(benzyl)-3-N-(benzylacetamido)imidazol-2-ylidene]$_2$Ni [8].

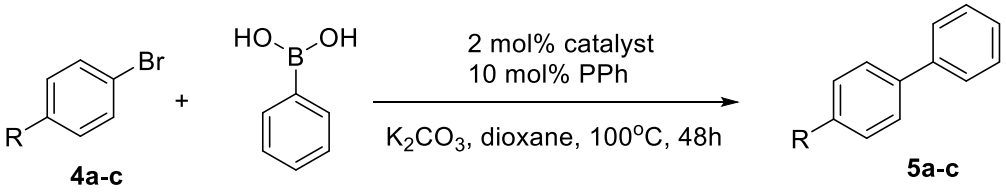
4. Catalytic activities of 3a and 3b in Suzuki cross coupling reactions

To a stirred solution of the substrate (1 mmol, Table 2) in dioxane (4 mL) was added phenylboronic acid (0.30 g, 2.5 mmol), K_2CO_3 (0.41 g, 3 mmol), PPh_3 (10 mol%) and **3a**/**3b** (2 mol%), and was refluxed for 48 h. The reaction mixture was concentrated in vacuo, and the residue was subjected to column chromatography (silica gel, 0-5% EtOAc/hexane) to obtain respective products. The yields of the products are depicted in Table 2.

i) Biphenyl (**5a**): white solid (m.p. 70 ºC; lit. 70.5-72 ºC) [41]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29-7.50 (m, 6H), 7.55-7.66 (m, 4H).

ii) 4-Methoxy-1,1'-biphenyl (**5b**). white solid (m.p. 91 ºC; lit. 91.1-92.3 ºC) [41]; 1H NMR (200 MHz, $CDCl_3$) δ 3.97 (d, J = 4.86 Hz, 3H), 7.03-7.18 (m, 1H), 7.31-7.40 (m, 1H), 7.45-7.65 (m, 4H), 7.67-7.82 (m, 3H)

iii) 4-Methyl-1,1'-biphenyl (**5c**). white solid (m.p. 45ºC; lit. 45-50 ºC) [41]; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.33-7.42 (m, 4H), 7.43-7.60 (m, 5H).



Scheme 3.

Table 2. Suzuki coupling of aryl bromides with phenylboronic acid.[a]

Substrate	R	Product	Catalyst	Yield[b]
4a	H	**5a**	**3a**	60
			3b	55
4b	-OCH_3	**5b**	**3a**	65
			3b	68
4c	-CH_3	**5c**	**3a**	54
			3b	58

[a]Reaction conditions: 1 mmol aryl bromide, 2.5 mmol phenylboronic acid, 10 mol% PPh_3, 3 mmol K_2CO_3 in 4 mL solvent refluxed with 2 mol% catalyst. [b]Isolated yield.

Finally, the catalytic activity of the Ni(II) complexes **3a** and **3b** in a Suzuki cross coupling reaction were evaluated using less active bromoarenes and phenyl boronic acid (**Scheme 3**, Table 2). In the absence of a catalytic amount of PPh_3, the yields of the reactions were very low (6-9%, data not shown). However, in presence of 10 mol% PPh_3, the yields of the desired product were satisfactory. Such a key role of PPh_3 in Ni(II) catalyzed Suzuki-Miyura cross coupling reaction is not unprecedented.[42]

5. Conclusion

In summary, we have synthesized 1-(*n*-butyl)-3-N-(2-furylmethyl/phenylmethyl)acetamido-1, 3-imidazolium chloride which in the presence of base and a Ni(II) precursor yielded the complexes [1-(*n*-butyl)-3-N-(furylmethyl/phenyl-

methyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni. The latter complexes have also been obtained through phosphine derived nickel precursors in which substitution of phosphine takes place by N-heterocyclic carbene. These complexes showed moderate catalytic activities in Suzuki cross coupling reactions.

Acknowledgement:

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Supporting Information

CCDC 1913414 for **3a** and 1913415 for **3b** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures.

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Table 1: Selected **c**rystallographic data for[1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3a**) and [1-(*n*-butyl)-3-N-(2-phenylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3b**)

Complex	**3a**	**3b**
Chemical formula	$C_{28}H_{36}N_6NiO_4$	$C_{32}H_{40}N_6NiO_2$
Formula wt.	579.33	599.41
Crystal size (mm^3)	0.15×0.10×0.08	0.070×0.030×0.020
Crystal system	Orthorhombic	Monoclinic
Space group	*Pccn*	*P21/n*
a (Å)	10.1795(2)	9.8093(4)
b (Å)	16.4812(3)	16.8345(6)
c (Å)	16.6731(4)	17.7177(5)
β (°)	90.0	95.204(3)
Volume ($Å^3$)	2797.25(10)	2913.75(18)
ρ_{cacld}, g cm^{-3}	1.376	1.366
Z	4	4
μ (mm^{-1})/F(000)	0.738/1224	0.707/1272
No of reflections collected	22516	37529
No of independent reflection (R_{int})	3210 (0.0245)	6757 (0.0975)
Data/restraints/parameters	3210/0/178	6757/38/391
Final R_1, wR_2 indices ($I>2\sigma I$)	0.0275/0.0709	0.0480/0.0825

R_1, wR_2 (all data)	0.0347/0.0736	0.1280/0.0990
Goodness of fit on F^2	1.054	0.983

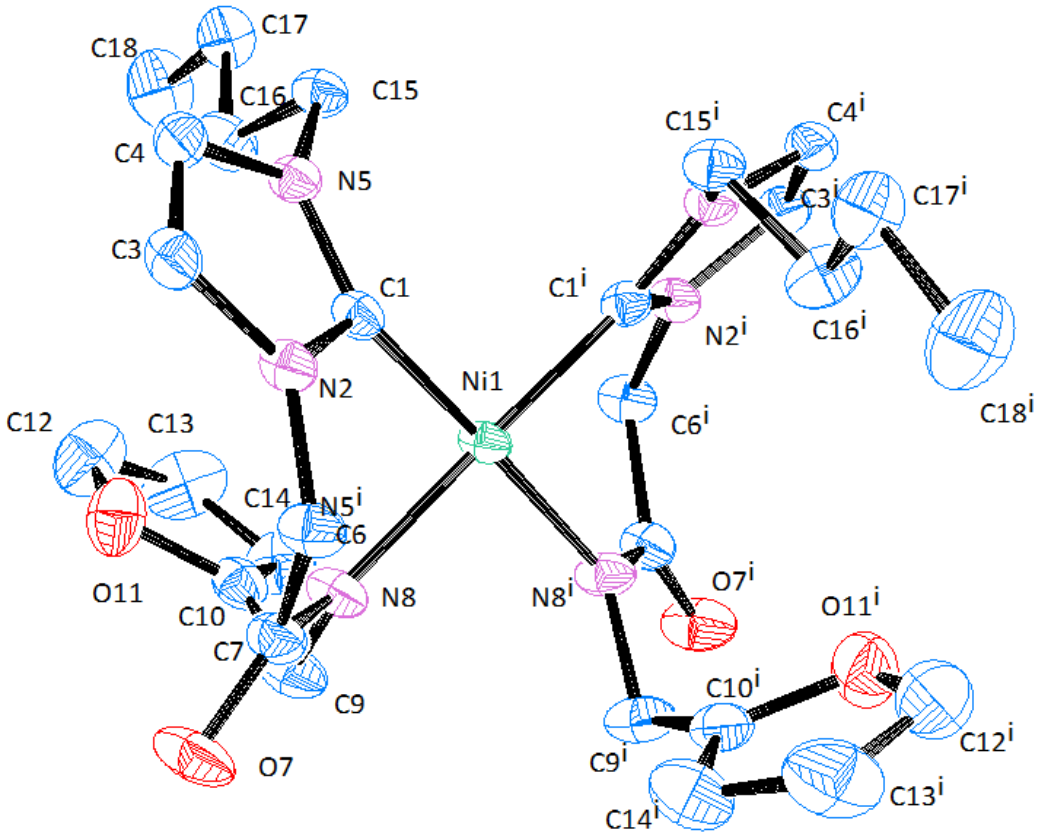

Figure 2: ORTEP diagram of [1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3a**) with 50% probability level. Selected bond lengths (Å) and bond angles (°): Ni(1)-C(1) 1.8658(13), Ni(1)-N(8)- 1.9297(11); C(1)-Ni(1)-C(1) 96.05(8), C(1)-Ni (1)-N(8) 176.55(5), C(1)-Ni(1)-N(8) 86.58(5), N(8)-Ni(1)-N(8) 90.87(7).

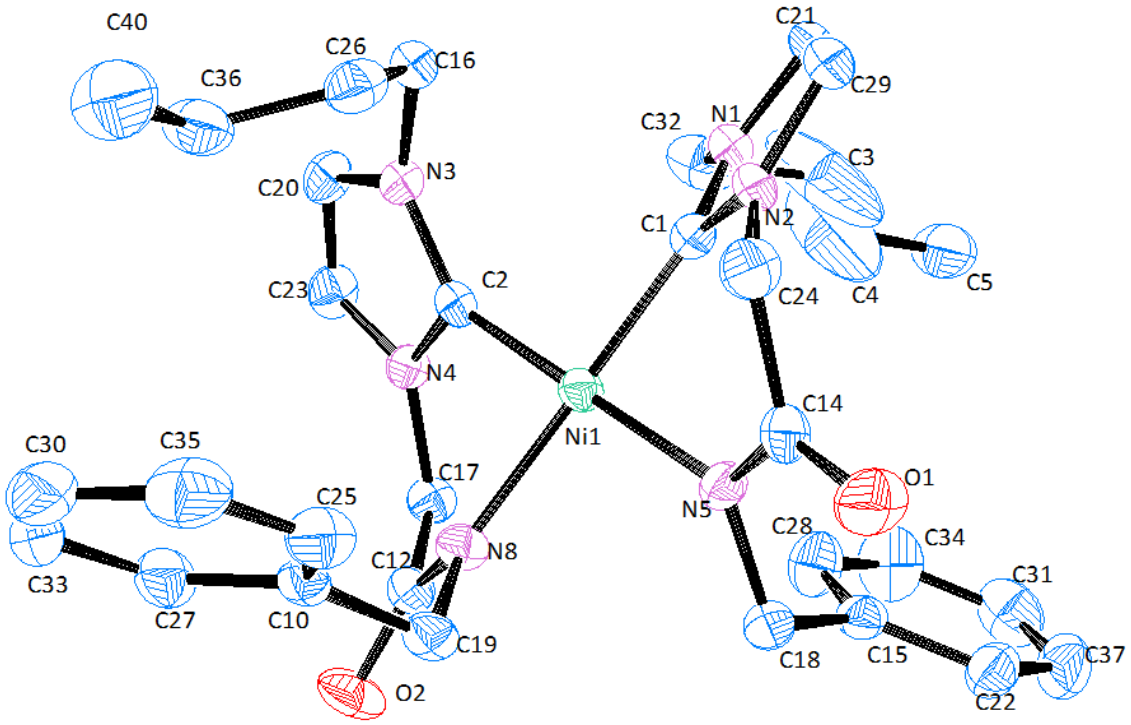

Figure 3: ORTEP diagram of [1-(*n*-butyl)-3-N-(2-phenylmethyl)acetamido-1,3-imidazol-3-ylidine)]$_2$Ni (**3b**) with 50% probability level. Selected bond lengths (Å) and bond angles (°): Ni(1)-C(1) 1.861(2), Ni(1)-C(21) 1.859(2), Ni(1)-N(8) 1.9306(19), Ni(1)-N(28) 1.9367(19); C(1)-Ni(1)-C(21) 92.33(10), N(8)-Ni(1)-N(28) 93.13(8), C(1)-Ni(1)-N(8) 87.35(9), C(21)-Ni(1)-N(28) 87.21(10), C(21)-Ni(1)-N(8) 178.90(9), C(1)-Ni(1)-N(28) 179.32(19).