

Nickel(II) complexes containing ONS donor ligands: Synthesis, characterization, crystal structure and catalytic application towards C-C cross-coupling reactions

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Abstract. Nickel(II) complexes containing thiosemicarbazone ligands [Ni(L)₂] (**1-3**) (L = 9,10-phenanthrenequinonethiosemicarbazone (HL₁), 9,10-phenanthrenequinone-N-methylthio semicarbazone (HL₂) and 9,10-phenanthrenequinone-N-phenylthiosemicarbazone (HL₃)) have been synthesized and characterized by elemental analysis and spectroscopic (IR, UV-Vis, ¹H, ¹³C-NMR and ESI mass) methods. The molecular structures of complexes **1** and **2** were identified by means of single-crystal X-ray diffraction analysis. The analysis revealed that the complexes possess a distorted octahedral geometry with the ligand coordinating in a uni-negative tridentate ONS fashion. The catalytic activity of complexes towards some C–C coupling reactions (viz., Kumada-Corriu, Suzuki-Miyaura and Sonogashira) has been examined. The complexes behave as efficient catalysts in the Kumada-Corriu and Sonogashira coupling reactions rather than Suzuki-Miyaura coupling.

Keywords. Nickel(II) complexes; X-ray structure; Kumada-Corriu reaction; Suzuki reaction; Sonogashira reaction.

1. Introduction

Schiff bases are an important class of ligands in coordination chemistry and they find extensive applications in different fields. Schiff bases readily coordinate with a wide range of transition metal ions, yielding stable and intensely coloured metal complexes, which exhibit interesting physical, chemical, biological and catalytic properties.^{1–7} The Schiff bases derived from thiosemicarbazone are well known polydentate ligands which can bind to the transition metal ions either in its neutral or anionic form and the resulting transition metal complexes have been receiving considerable interest largely because of their bioinorganic relevance. Metal complexes with an ONS donor set are of much interest because of their potential applications in fundamental and applied sciences, especially in coordination chemistry, due to their diverse roles in metallo-enzymes, varied catalytic and pharmacological properties.^{8–10} There have been many reports on activity of Schiff base complexes in homogeneous and heterogeneous catalysis.^{11–14} The first-row late transition metals such as iron, cobalt, nickel and copper are now the most important transition metals used as catalysts in the

development of organic reactions,¹⁵ rather than the catalytically active noble metals such as ruthenium, rhodium and palladium.¹⁶

The carbon-carbon bond forming reaction is one of the simple and versatile method in organic synthesis. During the last three decades, advances in transition metal catalysis made it possible to couple an organic electrophile with an organometallic nucleophile with high efficiencies and broad substrate scopes. The Kumada-Corriu coupling of an aryl halide with Grignard reagents is the first cross-coupling reaction for forming a carbon-carbon bond which is a powerful method for constructing diverse variety of biaryl compounds.¹⁷ This is an important industrial approach applied for the synthesis of photonic materials, polymers, pharmaceuticals, agrochemicals and a variety of homogeneous ligands. Moreover, Kumada-Corriu reactions are performed at or near room temperature and thus reducing energy costs. Similarly, the transition metal catalyzed Suzuki-Miyaura coupling reaction in which phenylboronic acid and aryl halides are used to produce unsymmetrical biaryl units which have a wide range of applications such as drugs, herbicides, natural products as well as in engineering.^{18–22} On the other hand, the Sonogashira coupling of terminal alkyne with aryl and alkenyl halides is one of the most

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powerful and straightforward methods for the formation of C(sp)-C(sp²) bonds in organic synthesis. This method has been widely employed in the synthesis of natural products, biologically active molecules and materials science.^{23–25}

Based on the above facts and in continuation of our effort to develop efficient transition metal catalysts, herein we have chosen nickel as the metal centre to interact with thiosemicarbazones. One reason behind the choice of this particular metal centre is its ability to take up different coordination environments (such as octahedral, square-planar and tetrahedral), which makes its coordination chemistry very interesting and also may facilitate different steps of catalytic cycle. The other and more attractive reason is that the demonstrated ability of complexes to catalyze C–C cross-coupling reactions.^{26–30} Thus, the primary objective of the present work has been to prepare nickel complexes of thiosemicarbazones and find out the binding mode of thiosemicarbazones in the complexes. The other objective has been to explore catalytic properties of the complexes against Kumada-Corriu, Suzuki-Miyaura and Sonogashira coupling reactions.

2. Experimental

2.1 Materials and methods

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures. The ligands HL_{1–3} and starting complex [NiCl₂(PPh₃)₂] were prepared according to literature procedures.^{31,32} Microanalysis of carbon, hydrogen, nitrogen and sulfur was carried out using Vario EL III Elemental analyzer at SAIF - Cochin India. The IR spectra of the ligand and their complexes were recorded as KBr pellets on a Nicolet Avatar model spectrophotometer in 4000–400 cm^{–1} range. Electronic spectra of the complexes have been obtained in dichloromethane using a Shimadzu UV - 1650 PC spectrophotometer in 800–200 nm range. ¹H and ¹³C NMR spectra were measured in Jeol GSX - 400 instrument using DMSO-*d*₆ as the solvent. ¹H NMR and ¹³C NMR spectra were obtained at room temperature using TMS as the internal standard. The ESI-MS spectra were performed by LC-MS Q-ToF Micro Analyzer (Shimadzu) in the SAIF, Panjab University, Chandigarh. Melting points were checked on a Technico micro heating table and were uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness.

2.2 Synthesis of nickel(II) complexes

2.2a [Ni(L₁)₂].DMF (1): An ethanolic solution (10 mL) containing HL₁ (0.1 mmol) was added to [NiCl₂(PPh₃)₂] (0.1 mmol) in ethanol (10 mL) and the resulting red-coloured solution was refluxed for 4 h. On cooling the contents to room temperature through overnight, the coloured complex separated out. It was filtered off and recrystallized from ethanol. Red-coloured crystals, suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of DMF solution of compound. Yield: 88% M.p: 218°C. Anal. Calc. for C₃₃H₂₇N₇O₃NiS₂: C, 57.24; H, 3.93; N, 14.16; S, 9.26. Found: C, 57.47; H, 3.74; N, 14.33; S, 9.50% IR (KBr, cm^{–1}): 1605 (quinone C=O), 1578 (C=N), 1557 (C=N), 752 (C-S). UV-Vis (λ_{max}/nm): 524, 440, 331, 273. ¹H NMR (DMSO-*d*₆, ppm): 9.37 (s, 2H, NH₂), 7.30–8.02 (m, 16H, Ar-H). ¹³C NMR (DMSO-*d*₆, ppm): 180.2 (quinone C=O), 171.1 (C-S), 164.8 (C=N), 124.8–137.2 (Ar-C). ESI-MS (m/z) = 619.2 [M⁺].

2.2b [Ni(L₂)₂] (2): It was prepared using the same procedure as described for **1** with HL₂ (0.1 mmol) and [NiCl₂(PPh₃)₂] (0.1 mmol). Red coloured crystals, suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of DMF solution of compound. Yield: 85% M.p.: 212°C. Anal. Calc. for C₃₂H₂₄N₆O₂NiS₂: C, 59.37; H, 3.74; N, 12.98; S, 9.91. Found: C, 59.17; H, 3.59; N, 12.75; S, 9.78% IR (KBr, cm^{–1}): 1614 (quinone C=O), 1596 (C=N), 1566 (C=N), 754 (C-S). UV-Vis (λ_{max}/nm): 522, 437, 324, 265. ¹H NMR (DMSO-*d*₆ ppm): 8.38 (s, 1H, NH-CH₃), 6.92–8.08 (m, 16H, Ar-H), 2.96 (s, 3H, CH₃). ¹³C NMR (DMSO-*d*₆, ppm): 179.6 (quinone C=O), 169.8 (C-S), 160.2 (C=N), 124.2–138.1 (Ar-C), 30.4 (CH₃) ESI-MS (m/z) = 647.0 [M⁺].

2.2c [Ni(L₃)₂] (3): It was prepared using the same procedure as described for **1** with HL₃ (0.1 mmol) and [NiCl₂(PPh₃)₂] (0.1 mmol). Redcoloured solid obtained. Our efforts to obtain single crystal of the complex were unsuccessful. Yield: 80%, M.p: 215°C. Anal. Calc. for C₄₂H₂₈N₆O₂NiS₂: C, 65.38; H, 3.66; N, 10.89; S, 8.31. Found: C, 65.16; H, 3.86; N, 10.71; S, 8.54%. IR (KBr, cm^{–1}): 1602 (quinone C=O), 1572 (C=N), 1548 (C=N), 753 (C-S). UV-Vis (λ_{max}/nm): 499, 417, 314, 281. ¹H NMR (DMSO-*d*₆, ppm): 11.22 (s, 1H, NH-C₆H₅), 6.74–8.71 (m, 26H, Ar-H). ¹³C NMR (DMSO-*d*₆ ppm): 182.1 (quinone C=O), 171.4 (C-S), 161.1 (C=N), 123.5–135.8 (Ar-C). ESI-MS (m/z) = 771.2 [M⁺].

2.3 X-ray crystallography

Crystal data were collected on an Oxford/Agilent Gemini diffractometer. Structures were solved using the direct methods program SHELXL.³³ All non-solvent heavy atoms were located using subsequent difference Fourier syntheses. The structures were refined against F² with the program SHELXL,³⁴ in which all data collected were used including negative intensities. All nonsolvent heavy atoms were refined anisotropically. All non-solvent hydrogen atoms were idealized using the standard SHELXL idealization methods.

2.4 Aryl–aryl coupling reaction

2.4a Kumada-Corriu reaction: Aryl halide (10 mmol) was added to catalyst (0.2 mol%) in 5 mL diethyl ether. Phenylmagnesium chloride (10 mmol) was then added dropwise and the reaction mixture was stirred for 4 h at room temperature. Then the reaction was ended by addition of water. The mixture was extracted with ethyl acetate and the obtained organic layer was dried over MgSO₄. The crude mixture was analyzed by gas chromatography and then purified by column chromatography on silica gel to afford the desired product. The conversion percentage was determined against the remaining aryl halide. In addition, the isolated product was characterized by ¹H NMR.

2.4b Suzuki-Miyaura reaction: To a mixture of aryl halide (1 mmol), phenylboronic acid (1.5 mmol) and K₂CO₃ (1 mmol) in dimethylacetamide (4 mL) was added the catalyst (1 mol%) as a dimethylacetamide solution (1 mL). The resultant mixture was then heated at 90°C for 7 h. Then, the mixture was cooled, water was added and the product was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na₂SO₄, filtered, passed through celite, and analyzed by GC. GC yields were obtained based on corresponding aryl halide. The isolated yield was characterized by ¹H NMR.

2.4c Sonogashira coupling reaction: The aryl halide (1 mmol) and phenyl acetylene (1.5 mmol) were added to methanol solution (5 mL) of catalyst (0.5 mol%), copper(I) iodide (0.5 mol%) and pyridine (1 mmol) in a glass flask with vigorous stirring. The mixture was stirred at 70°C for 4 h under aerobic conditions. The mixture was cooled to room temperature, diluted with

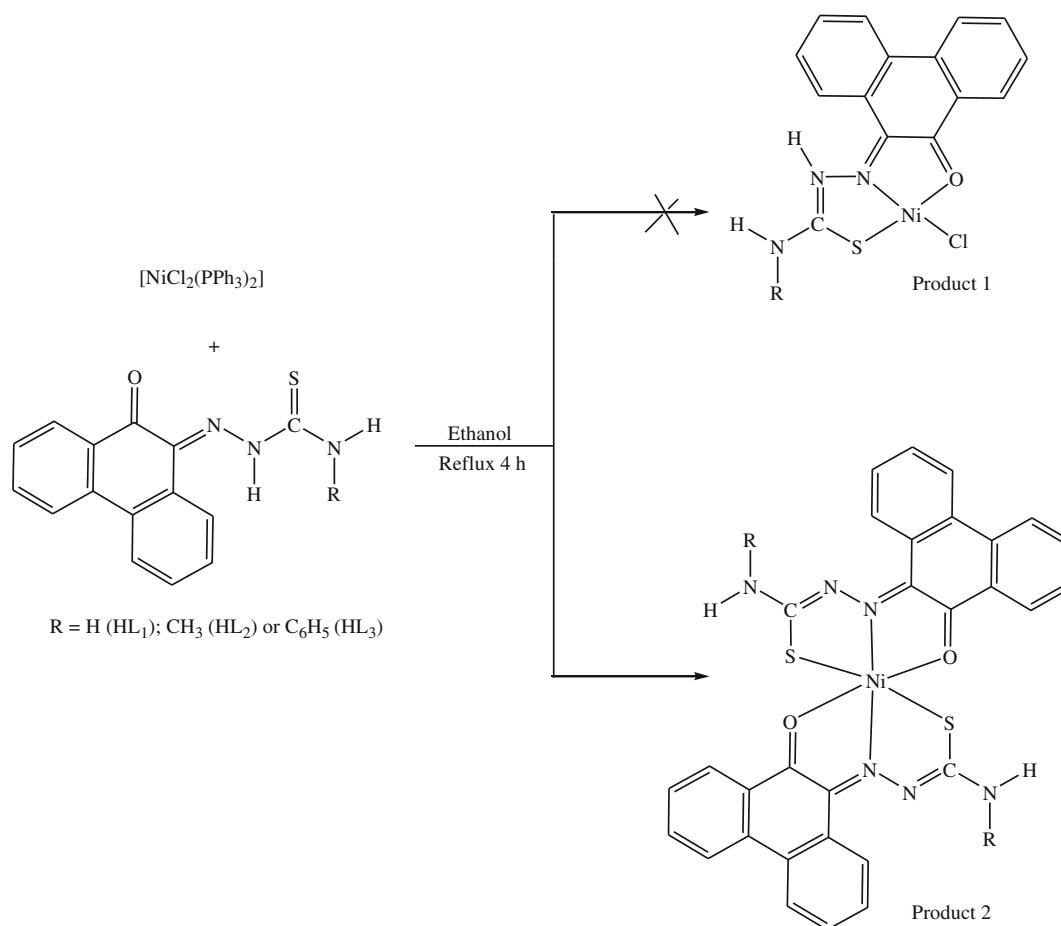
water and extracted with ether for three times. The organic phase thus collected was dried with Na₂SO₄, filtered and analyzed by GC. GC yield was determined based on the amount of aryl halide employed using n-dodecane as an internal standard.

3. Results and Discussion

Reactions of HL_{1–3} and [NiCl₂(PPh₃)₂] in 1:1 molar ratio (scheme 1) were carried out in ethanolic solution with the expectation that to yield a four coordinated complexes (product 1). Unexpectedly, the phenanthrenequinone N(4)-substituted thiosemicarbazone ligands (HL_{1–3}) involved in this work deceived all our expectations and formed stable six coordinated metal chelates with 1:2 metal-ligand stoichiometry (product 2). Reactions were also conducted changing solvents as well as the molar ratios of ligands in order to obtain the desired complexes, but in all the cases only [Ni(L)₂] was obtained. The complex [Ni(L₁)₂] was also obtained by the reaction of NiCl₂·6H₂O with HL₁ (molar ratio of NiCl₂·6H₂O:HL₁ = 1:2) in ethanol.³⁵ The isolated complexes were stable in air, in addition to being soluble in common organic solvents such as dichloromethane, chloroform, benzene, acetonitrile, ethanol, methanol, dimethylformamide and dimethylsulfoxide. All the complexes were structurally characterized by elemental analysis, IR, electronic, NMR and ESI-Mass spectra. In addition, single crystal of complexes **1** and **2**, used to determine its molecular structures by X-ray crystallographic analysis, which is shown in figure 1 and 2.

3.1 X-ray crystallography

The complexes **1** and **2** crystallize in a triclinic and monoclinic system with space group P-1, C2/c respectively. Crystal details, crystallographic data and refinement were summarized in table 1. Selected bond lengths and bond angles have been reported in table 2. In both the complexes, the nickel(II) atom was coordinated with two ligand molecules. The complex **1** was associated with one molecule of dimethylformamide solvent in the crystal lattice. The two ligand molecules in this complexes are deprotonated at the imino nitrogen N(2), resulting in two tridentate mono-anionic species coordinating to the central metal via the thiolato sulfur, imine nitrogen and the oxygen of the quinone carbonyl, resulting in a distorted octahedral moiety. Elongation of the C(15)–S(1) bond from 1.6705–1.6782 Å in the ligands to 1.6947–1.704 Å in the nickel complexes was indication of the deprotonation of ligands upon



Scheme 1. Synthesis of Ni(II) 9,10-phenanthrenequinone N-substituted thiosemicarbazone complexes.

complexation and charge delocalization in the thiosemicarbazone side chain. The Ni-N, Ni-S and Ni-O bond distances were comparable with those found in other nickel thiosemicarbazones.³⁶

3.2 Infrared spectra

The ligands behave as monoanionic tridentate, moiety forming two five-membered chelate rings around the

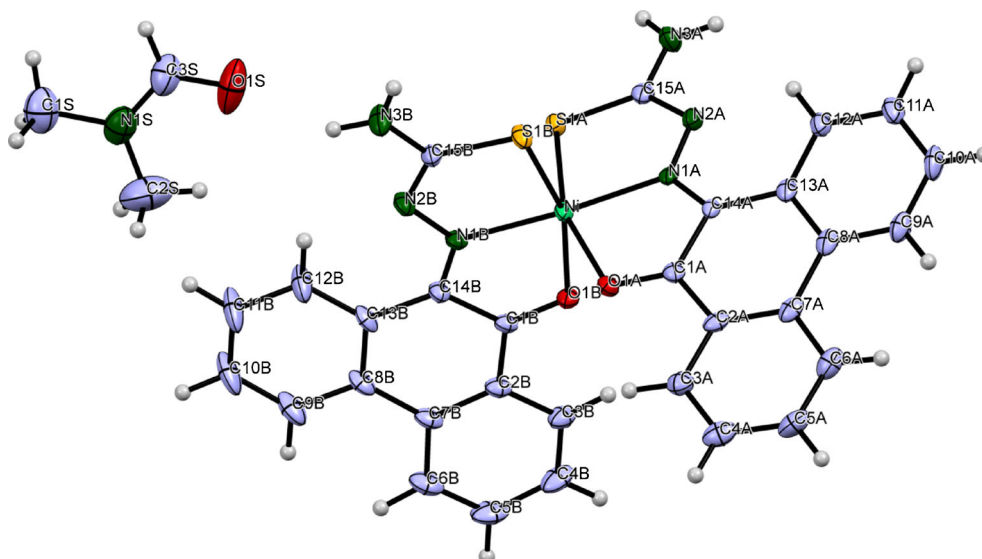


Figure 1. ORTEP view of complex 1

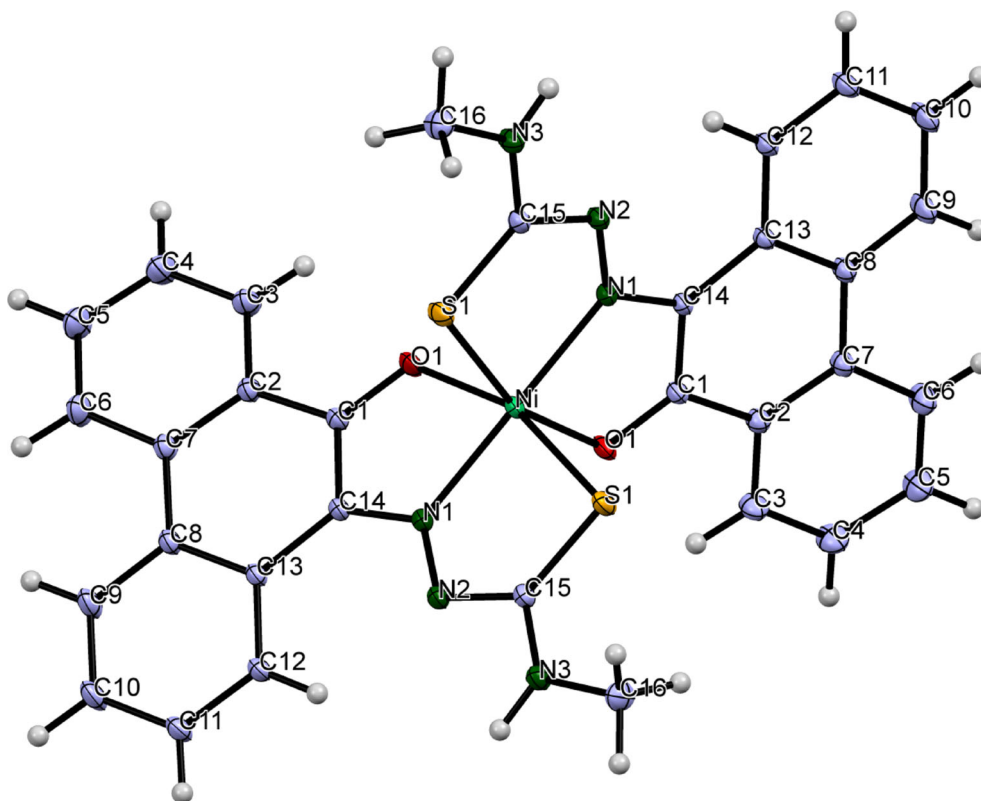


Figure 2. ORTEP view of complex 2

Table 1. Crystal data and structure refinement of the complexes 1 and 2.

	1	2
Empirical formula	C ₃₃ H ₂₇ N ₇ NiO ₃ S ₂	C ₃₂ H ₂₄ N ₆ NiO ₂ S ₂
Formula weight	692.44	647.40
Crystal dimensions (mm ³)	0.45x0.33x0.29	0.39x0.35x0.24
Temperature (K)	100(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
Unit cell dimensions (Å, °)	<i>a</i> = 10.3167(16) <i>b</i> = 11.0978(17) <i>c</i> = 13.564(2) α = 105.216(2) β = 90.618(2) γ = 96.006(2)	<i>a</i> = 20.5380(3) <i>b</i> = 11.5610(2) <i>c</i> = 13.5606(2) α = 90 β = 93.2193(14) γ = 90
Volume (Å ³)	1489.1(4)	3214.75(9)
<i>Z</i>	2	4
Calculated density (Mg/m ³)	1.544	1.338
Absorption coefficient (mm ⁻¹)	0.841	0.771
<i>F</i> (000)	716	1336
Theta range for data collection (°)	1.914 to 31.324	3.512 to 41.269
Absorption correction	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	8480/0/418	10544/0/200
Goodness-of-fit on <i>F</i> ²	1.063	1.088
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0524, <i>wR</i> 2 = 0.1250	<i>R</i> 1 = 0.0285, <i>wR</i> 2 = 0.0810
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0794, <i>wR</i> 2 = 0.1435	<i>R</i> 1 = 0.0340, <i>wR</i> 2 = 0.0844
Largest difference in peak and hole (e.Å ⁻³)	1.104 and -0.723	0.624 and -0.642

Table 2. Selected bond lengths (Å) and angles (°) of the complexes **1** and **2**

	1	2
Ni-N(1A)	2.012(3)	2.0243(5)
Ni-N(1B)	2.022(3)	2.0243(5)
Ni-O(1A)	2.073(3)	2.0832(5)
Ni-O(1B)	2.071(2)	2.0832(5)
Ni-S(1A)	2.3663(11)	2.37228(19)
Ni-S(1B)	2.3595(10)	2.37228(19)
C(15A)-S(1A)	1.704(4)	1.6947(6)
C(15B)-S(1B)	1.707(3)	1.6947(6)
C(15A)-N(2A)	1.370(5)	1.3859(8)
C(15B)-N(2B)	1.356(4)	1.3859(8)
N(1A)-Ni-N(1B)	175.91(10)	179.00(3)
N(1A)-Ni-O(1A)	78.90(11)	78.438(19)
N(1B)-Ni-O(1A)	104.01(11)	100.84(2)
N(1A)-Ni-O(1B)	104.42(11)	100.84(2)
N(1B)-Ni-O(1B)	78.85(11)	78.438(19)
O(1B)-Ni-O(1A)	84.78(9)	89.28(3)
N(1A)-Ni-S(1B)	94.35(8)	97.583(16)
N(1B)-Ni-S(1B)	82.79(8)	83.100(15)
O(1A)-Ni-S(1B)	91.04(8)	91.333(16)
O(1B)-Ni-S(1B)	159.55(8)	161.306(13)
N(1A)-Ni-S(1A)	83.33(9)	83.102(15)
N(1B)-Ni-S(1A)	94.17(9)	97.583(16)
O(1A)-Ni-S(1A)	160.45(8)	161.307(13)
O(1B)-Ni-S(1A)	91.87(8)	91.332(16)
S(1B)-Ni-S(1A)	98.41(3)	94.004(11)

central metal through a donor atom set comprising of the quinone carbonyl oxygen, imine nitrogen and the thiolate sulfur as revealed from the corresponding shifts in IR frequencies of the respective vibrations.³⁷ The bands assigned to azomethine (C=N) and quinone carbonyl (C=O) vibrations appeared at 1596–1598 and 1630–1634 cm⁻¹ respectively in the spectra of free ligands were shifted to lower wave numbers in the spectra of complexes while the bands at 3111–3148 and 807–843 cm⁻¹ ascribed to the ν (N-H), ν (C=S) stretching vibrations respectively in the spectra of ligands disappeared on metal complexation, confirming the thioenolization nature of the ligands and subsequent coordination through the deprotonated sulfur.^{38–40} This fact was further confirmed by the appearance of two new bands in the range 1572–1596 cm⁻¹ and 752–754 cm⁻¹ that corresponds to ν (C=N–N=C) and ν (C-S) stretching vibrations respectively.⁴¹

3.3 Electronic spectra

The electronic spectra of the nickel(II) complexes displayed four bands in the region around 260–533 nm. The bands at 260–281 nm can be ascribed to an intraligand transition (π - π^* and n - π^*). The band appeared in the region 308–440 nm has been assigned to an LMCT,

and the shoulder at 499–533 nm was attributed to a forbidden $d \rightarrow d$ transition.^{42,43}

3.4 NMR spectra

The ¹H NMR spectra of the ligands and the corresponding nickel(II) complexes were compared to confirm the presence of coordinated ligand in the complexes. The presence of singlet at 14.41–14.81 ppm was assigned to hydrazinic N-H proton which indicates that the ligands exist in thionic forms. The peak disappears in the spectra of complexes, which was consistent with deprotonation of these ligands upon metal complexation. The terminal NH₂ protons in the ligand HL₁ were magnetically non-equivalent and have two singlets at 9.07, 9.36 ppm. These protons became equivalent upon formation of complexes and were observed as singlet at 9.40 ppm. The ligands HL₂, HL₃ and their corresponding complexes showed singlet in the region 8.35–11.22 ppm which was assigned to terminal NH-CH₃ and NH-C₆H₅ protons. In the spectra of all the complexes, the multiplet observed around 6.74–8.81 ppm was assigned to aromatic protons of the ligands. Further, the methyl protons appeared at 2.96 ppm. The ¹H NMR spectra of complexes **1–3** was shown in figures S1–S3.

The ¹³C NMR spectra of the complexes have showed a peak at 179.6–182.1 ppm region which was assigned to quinone carbonyl (C=O) carbon. The azomethine (C=N) carbon exhibits peak in the region of 160.2–164.8 ppm. In addition, the presence of peak in the region 169.8–171.4 ppm was assigned to C-S carbon. The appearance of sharp singlet at 30.4 ppm was assigned to methyl carbon. The aromatic carbons appeared in the region of 123.5–138.1 ppm. The ¹³C NMR spectra of complexes **1–3** was shown in figures S4–S6.

3.5 Mass Spectra

ESI-Mass spectral analysis of the complexes was studied in order to confirm the molecular masses of the complexes. The m/z values of the molecular ion peaks for the complexes **1–3** were obtained at 619.2 [M-DMF]⁺, 647.0 and 771.2 [M]⁺ respectively. The calculated molecular masses corresponds to these complexes are 619.34, 647.40 and 771.53. The obtained molecular masses were in good agreement with that of the calculated molecular masses. The ESI mass spectra of complexes **1–3** was shown in figures S7–S9.

3.6 Kumada-Corriu coupling reaction

In order to find optimal reaction conditions, the influence of time, solvent and the catalyst concentration on

the yield were investigated. Our initial studies were carried out with 4-bromoanisole as standard substrate using complex **1** as catalyst. The first set reactions were run with constant concentration of catalyst (0.03 mmol) at various time intervals in different solvents. The best conversion was observed in diethyl ether and the least conversion was observed in benzene at 4 h (figure S10). Next, we focused the effect of catalyst concentration on the catalyst activity. The catalyst amount was varied

from 0.005 to 0.03 mmol in diethyl ether under similar reaction conditions. The yield increased with increase in catalyst loading and reaches to the highest value of 83% with 0.02 mmol of catalyst (figure S11).

Under the optimized conditions, we next tried to extend the Kumada-Corriu coupling reactions to various aryl halides and the results are summarized in table 3. The coupling reactions were performed well for all the substrates examined and gave moderate to

Table 3. Kumada-Corriu reaction of aryl halide with phenylmagnesium chloride by nickel(II) complexes.

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^aThe conversion is determined by GC.

^bIsolated yield is given in parenthesis.

excellent yields. As shown in table 3, aryl halide containing electron withdrawing substituents were found to proceed slightly higher yield than those with electron-donating substituents. For example, higher yield (entries 3–6) was obtained for aryl halide bearing electron withdrawing group relative to those of electron donating ones (entries 1, 2). In addition, hetero aromatic halides also undergo coupling reactions and provided the coupled products in higher yield (entries 7, 8). The coupling reaction of aryl halide bearing *ortho* substituents gave moderate conversions as a result of steric hindrance. For instance, the coupling reaction of 2-iodoanisole (entry 9) and 2-fluorobenzaldehyde (entry 10) with phenylmagnesium chloride gave the conversion of 55–64%. Remarkably, the conversion of aryl halides to biaryls proceeded efficiently in the present catalytic system. Moreover, the present catalytic system works at mild reaction conditions with low reaction time and the efficiency in terms of the yield of products was higher than the existing catalytic systems.^{26–30}

3.7 Suzuki-Miyaura coupling reaction

A brief optimization of experimental conditions for the reaction of 4-bromoanisole with phenylboronic acid using complex **1** as catalyst was given in table 4. First, the reaction was conducted with different catalyst:substrate (C:S) ratios. We started the C:S ratios from 1:25 to 1:100, the reaction proceeds with reasonable conversions (entries 1–4). When increasing the C:S ratio from 1:150 to 1:250, the reaction still proceeds by decrease in yield (entries 5–7). Thus, it concluded that

catalyst:substrate ratio of 1:100 was the best suitable for the catalytic C-C coupling reaction. We further evaluated the effect of solvents and bases on the reaction. The highest yield of coupled product was obtained in dimethylacetamide (DMAc) in presence of K₂CO₃ base (entries 8, 16). So, based on the results above, we selected K₂CO₃ as the base and DMAc as solvent with C:S ratio of 1:100 as the best conditions for the Suzuki-Miyaura reaction.

Under the optimized reaction conditions, coupling of various aryl halides with phenylboronic acid were carried out in presence of synthesized nickel complexes and the conversion of coupled products were given in table 5. As shown in table 5 (entries 1–6), many functional groups have been tolerated in the present catalytic system. The coupling reaction of aryl halides bearing an electron donating group, such as CH₃ and OCH₃, with phenylboronic acid produced biaryls in moderate yields (52–64%) (entries 1, 2). Similarly electron deficient aryl bromides, such as 4-bromobenzoinic acid, 4-chlorobenzaldehyde, 4-chlorobenzonitrile and 4-nitro-1-bromobenzene reacted with phenylboronic acid to produce biaryls in moderate yield, ranging from 47 to 61% (entries 3–6) under the same reaction conditions. Using this methodology, the coupling between phenylboronic acid and aryl halides that contain electron-donating as well as electron-withdrawing groups, proceeded moderately to afford the corresponding products. When heterocyclic aryl halides were used for cross-coupling with phenylboronic acid, a decrease in the yield of product (between 24% and 32%) was observed. For example, the lowest yield was

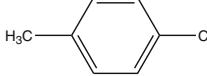
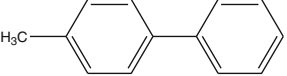
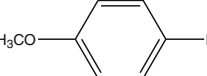
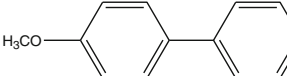
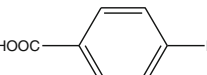
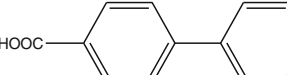
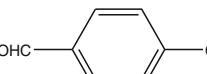
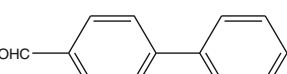
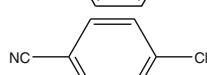
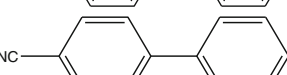
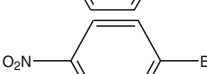
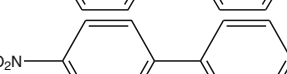
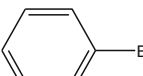
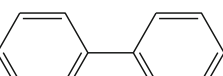
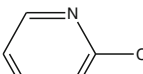
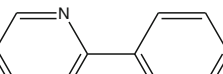
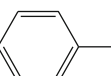
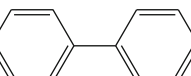
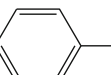
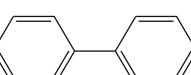
Table 4. Optimization of reaction conditions for the Suzuki-Miyaura coupling reaction.

Entry	Amount of substrate (mmol)	Solvent	Base	Conversion (%) ^b
1	0.25	DMF	Na ₂ CO ₃	61
2	0.5	DMF	Na ₂ CO ₃	58
3	0.75	DMF	Na ₂ CO ₃	56
4	1	DMF	Na ₂ CO ₃	55
5	1.5	DMF	Na ₂ CO ₃	39
6	2	DMF	Na ₂ CO ₃	22
7	2.5	DMF	Na ₂ CO ₃	10
8	1	DMAc	Na ₂ CO ₃	60
9	1	DMSO	Na ₂ CO ₃	48
10	1	Toluene	Na ₂ CO ₃	29
11	1	Methanol	Na ₂ CO ₃	22
12	1	THF	Na ₂ CO ₃	07
13	1	DMAc	–	–
14	1	DMAc	NaOH	48
15	1	DMAc	KOH	42
16	1	DMAc	K ₂ CO ₃	64

^aReaction conditions: Phenylboronic acid (1.5 mmol), 4-bromoanisole (1 mmol), base (1 mmol) and solvent (5 mL), stirring for 7 h at 90°C.

^bGC yield.

Table 5. Suzuki-Miyaura coupling reaction of aryl halides with phenylboronic acid by nickel(II) complexes.

$\text{C}_6\text{H}_5\text{B(OH)}_2 + \text{R-C}_6\text{H}_4\text{-X} \xrightarrow[\text{DMAc, 7 h, 90 } ^\circ\text{C}]{\text{Catalyst (1 mol\%), K}_2\text{CO}_3 \text{ (1 mmol)}} \text{R-C}_6\text{H}_4\text{-C}_6\text{H}_5$					
Entry	Aryl halide	Product	Yield (%) ^a		
			1	2	3
1			58 (50) ^b	55	52
2			64 (55) ^b	60 (50) ^b	57
3			56 (48) ^b	54	51
4			50	49 (38) ^b	47
5			58	55	53
6			61	57	53
7			28	31	30
8			32	27	24
9			29	24	21
10			24	23	20

^aGC yield.^bIsolated yield is given in parenthesis.

found in the reaction of 2-bromopyridine and 2-chloropyrimidine with phenylboronic acid (entries 7, 8). Similarly, the coupling reaction of aryl halide bearing *ortho* substituents gave lower conversions as a result of steric hindrance (entries 9, 10).

3.8 Sonogashira coupling reaction

The activity of the obtained nickel complexes was also examined in the Sonogashira coupling. In order to optimize the reaction condition with respect to time, base,

solvent and substrate concentration, we carried out the reaction of 4-bromoanisole with phenylacetylene using complex **1** as a test catalyst. First, several bases were screened for the Sonogashira coupling reaction (figure S12). The reaction works very well when organic bases, such as Et₃N, pyridine and piperidine were used, with the best result obtained in the case of pyridine as the base. However, the addition of inorganic bases such as K₂CO₃, Cs₂CO₃, KOH, NaOH and K₃PO₄ resulted in poor to moderate yields. These results indicate that organic bases were more favourable than

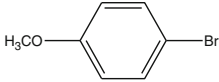
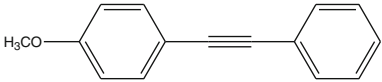
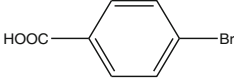
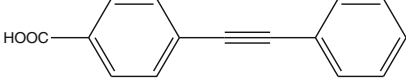
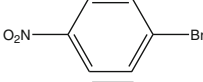
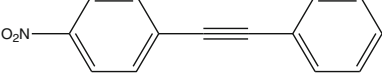
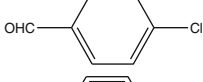
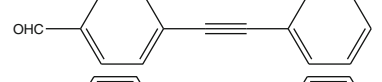
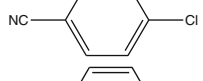
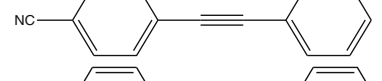
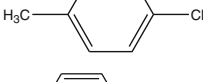
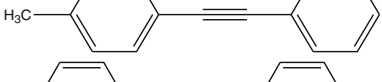
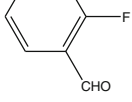

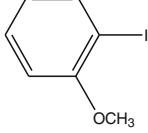
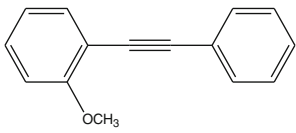
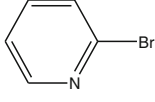
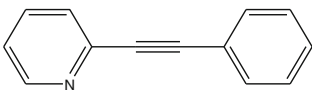
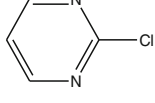
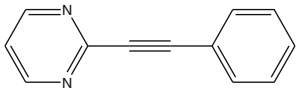
inorganic ones because they effectively trap hydrogen halide formed in the reaction.

Next, the solvent effect on the reaction rate of coupling has been studied. In the present study methanol was found to be more efficient for the conversion of coupling products. On the other hand, acetonitrile and 1,4-dioxane gave low yields while moderate yield was obtained when ethanol used as a solvent (figure S13). Finally, the reaction was carried out at different concentration of catalyst (figure S14). An excellent yield was obtained for 0.5 mol% of catalyst and it can be observed that even at very low catalyst loading of 0.25 mol%, the

moderate yield obtained. Moreover, there was no considerable change of yield observed when increasing the catalyst concentration beyond 0.5 mol%.

With the optimized reaction conditions in hand, the scope of the reaction with respect to other aryl halides was investigated (table 6). The electron-rich or electron-poor aryl bromides reacted with phenylacetylene to generate the corresponding cross-coupling products in high yields (entries 1–3). We next investigated the coupling of various aryl chlorides with terminal alkynes. As shown in table 6, moderate catalytic activity was observed in the coupling of aryl chlorides

Table 6. Sonogashira coupling reactions of phenylacetylene and aryl halides.

$\text{Phenylacetylene} + \text{R-Aryl-X} \xrightarrow[\text{MeOH, 70 } ^\circ\text{C, 4 h}]{\text{Catalyst (0.5 mol\%) CuI (0.5 mol\%) Pyridine (1 mol\%)}} \text{R-Aryl-Phenylacetylene}$					
Entry	Aryl halide	Product	Conversion (%) ^a		
			1	2	3
1			85	80	79
2			86	82	77
3			83	79	74
4			62	59	56
5			57	56	51
6			59	55	53
7			28	26	23
8			31	29	26
19			64	58	55
10			62	57	52

^aThe conversion is determined by GC.

possessing electron donating and electron withdrawing groups (entries 4–6). For *ortho* substituted aryl halides, relatively lower yields were obtained (entries 7, 8). Heteroaromatic compounds such as 2-bromopyridine and 2-chloropyrimidine also reacted with phenylacetylene to give moderate yield of cross-coupling products (entries 9, 10).

4. Conclusion

The present study shows that the N(4)-substituted thiosemicarbazones of phenanthrenequinone can readily bind to nickel as mononegative tridentate ONS-donors and afford stable mononuclear 1:2 (M:L) complexes. X-ray diffraction studies of the complexes **1** and **2** confirm the ONS coordination mode of thiosemicarbazone ligands and reveal a distorted octahedral geometry around the nickel(II) ion. The catalytic efficiency of the complexes was investigated towards the C-C coupling processes using different approaches namely Kumada-Corriu, Suzuki-Miyaura and Sonogashira coupling reactions. The results obtained in each method were compared in order to find the best catalytic system to C-C coupling. The comparison revealed that Kumada-Corriu C-C coupling to be the best among all followed by Sonogashira and Suzuki-Miyaura processes. The results also showed that steric effects in the ligands play a more important role than electronic effects in the catalytic activity of the complexes. That is, in all the reactions, complex **1** has been proven to be an efficient and versatile catalyst compared to complexes **2** and **3** due to the steric hindrance caused by the bulky methyl and phenyl groups on the terminal part of thiosemicarbazone ligands in **2** and **3**. Further, the present catalytic system is remarkably simple, convenient and efficient compared to the previous systems reported.

Supplementary Information

CCDC 999389, 979255 contain the supplementary crystallographic data for the complexes **1** and **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/datarequest/cif. The NMR (¹H and ¹³C), ESI-Mass spectra of complexes and optimized reaction conditions for Kumada-Corriu coupling and Sonogashira coupling are given as supplementary materials (figures S1–S14) and are available at www.ias.ac.in/chemsci.

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