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Graphical Abstract

A new square planar nickel(II) complex bearing 2-((3-methylthiophen-2-yl)methylene)-*N*-phenylhydrazinecarbothioamide was synthesized and characterized by elemental analysis, FT-IR, NMR and single crystal X-ray crystallographic technique. The complex acts as an effective homogeneous catalyst for the Sonogashira reaction of phenylacetylene with various aryl halides (iodides and bromides) under optimized conditions.





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Square-planar Ni(II) thiosemicarbazonato complex as an easily accessible and convenient catalyst for Sonogashira cross-coupling reaction

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ABSTRACT

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Keywords: Thiosemicarbazone ligand Nickel(II) complex Crystal structure Sonogashira reaction A simple route for the synthesis of a new square-planar nickel(II) complex bearing 2-((3methylthiophen-2-yl)methylene)-*N*-phenylhydrazinecarbothioamide ligand has been described. The composition of the complex has been established by elemental analysis, FT-IR, NMR and single crystal X-ray crystallographic technique. The complex acts as an active homogeneous catalyst for the Sonogashira reaction of phenylacetylene with electron deficient (activating) and electron rich (deactivating) aryl halides (iodides and bromides) under optimized conditions.

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Diaryl acetylenes play an important role as intermediates for substituted alkynes,¹ dendrimers,² optical and electrical materials,³ intermediates in natural products, pharmaceuticals,⁴ conjugated oligomers and polymers,⁵ etc. Among the various cross-coupling reactions, palladium catalyzed Sonogashira reaction of aryl halides with phenylacetylenes has emerged as a practical and efficient method for the preparation of diaryl acetylenes.⁶ Though palladium complexes show high catalytic activities, one obvious drawback is the prohibitive cost of palladium which has resulted in the exploration of less costly transition metals as alternatives to palladium systems for crosscoupling reactions while still preserving high levels of efficiency and functional group tolerance. Nickel appears to be the most promising alternative for palladium as catalysts in Sonogashira coupling reaction.⁷ The low cost, low toxicity and high reactivity of nickel is attractive, and a range of substrates has been shown to undergo nickel-catalyzed C-C coupling reactions, although so far no nickel catalyst has been able to rival palladium for the Sonogashira coupling reaction.

Thiosemicarbazones are unique and multifaceted N- and Sdonor Schiff bases for transition metal ions that possess synthetic flexibility and exhibit a wide range of coordination modes in their metal complexes.⁸ Though there are several reports related to the biological applications of thiosemicarbazone complexes of nickel,⁹ research into their role in catalysis however, is still a relatively new area of interest. In recent years, though a few nickel(II) thiosemicarbazonato complexes have been developed as effective catalysts for various cross-coupling reactions,¹⁰ there is still ample scope for developing new air-stable nickel(II) thiosemicarbazonato complexes that can act as efficient catalysts for the Sonogashira reaction of the highly reactive aryl iodides, moderately reactive aryl bromides and the more challenging aryl chlorides. In addition, to the best of our knowledge the use of square planar nickel(II) thiosemicarbazonato complex as catalyst for the Sonogashira coupling reaction has not been explored so far.

In continuation of our research on the synthesis, structural characterization and catalytic applications of transition metal complexes containing multidentate ligands,11 herein, we have chosen a new square-planar nickel(II) thiosemicarbazonato complex to assess the suitability of the complex as a homogeneous catalyst in the synthesis of substituted diaryl acetylenes by the Sonogashira reaction of phenylacetylene with aryl halides (iodides and bromides) containing different electronic effect. The Schiff base, 2-((3-methylthiophen-2yl)methylene)-N-phenylhydrazinecarbothioamide (HL, where H represents the dissociable proton) was prepared by the condensation of 4-phenyl-3-thiosemicarbazide with 3-methylthiophene-2-carboxaldehyde.¹² The new neutral square-planar nickel(II) complex, [Ni(L)₂] (1), was synthesized in ~85% yield by the reaction of Ni(OAc)₂·4H₂O and HL in 1:2 ratio in ethanoldichloromethane at room temperature (Scheme 1). The complex is sparingly soluble in methanol, ethanol, chloroform, dichloromethane or acetonitrile and is readily soluble only in

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solvents such as dimethylformamide, dimethyl sulphoxide etc., producing intense brown solutions. The complex is electrically non-conductive in solution which is consistent with its molecular formula as neutral species. The complex is non-hygroscopic and air stable in both the solid and the liquid states at room temperature. The observed elemental analysis data of **1** (Calc. C, 51.41; H, 3.98; N, 13.83; S, 21.11%. Found: C, 51.32; H, 4.06; N, 13.80; S, 21.07%) is consistent with its composition and it appears from the formulation that each Schiff base coordinate to the nickel(II) ion in a monobasic bidentate fashion.



Scheme 1. Synthesis of Ni(II) thiosemicarbazonato complex

In the FT–IR spectroscopy, the $v_{C=S}$ (842 cm⁻¹) and v_{N-H} (3206 cm⁻¹) of the N-NH-C=S group present in the free HL disappeared in 1 suggesting enolization and subsequent coordination through the thioamidate sulfur to the Ni(II) ion. The $v_{C=N}$ absorption is observed at a lower frequency in the 1 (1583) cm^{-1}) when compared to that of the free HL (1605 cm^{-1}), indicating the coordination of azomethine-N to the metal centre.^{10a,13} In the ¹H NMR spectra, the signal due to the azomethine proton in 1 (δ 9.1 ppm) is slightly downfield when compared to that of the free Schiff base (δ 8.2 ppm), suggesting deshielding on coordination of the azomethine-N to Ni(II) ion. The singlet that appeared for the N-NH-C=S proton of the free HL (δ 11.4 ppm) is absent in **1**, supporting enolisation and coordination of the thioamidate-S to the metal centre.^{10a,14} In 1, the multiplets observed in the region δ 7.6-6.9 ppm are assigned to the aromatic protons (phenyl and thiophenyl ring) of the coordinated ligand. The singlet at δ 2.3 ppm is due to the resonance of the methyl protons of the thiophenyl ring.



Figure 1. ORTEP of **1** with 50% probability. The solvent (DMF) is omitted for clarity. Selected bond lengths (Å): Ni–Ni 9050(17), Ni–S2 2.1720(9), N1–N2 1.391(2), N2–C7 1.303(3), S2–C7 1.735(2); Selected bond angles (°): N1–Ni–N1a 180.000(1), S2–Ni–S2a 180.0, N1–Ni–S2 85.17(5), Ni–S2–C7 96.03(7), Ni–N1–N2 121.23(12), N1–N2–C7 112.04(16), N2–C7–S2 122.64(15).

The molecular structure of the complex 1 has been determined by single crystal X-ray diffraction to confirm the coordination mode of the ligand and geometry of the complex. The ORTEP view of 1 is shown in Figure 1. The nickel(II) ion is tetracoordinated in a square-planar geometry by two ligand molecules, each acting as monoanionic bidentate N,S-donor. The ligands are in trans position with respect to the azomethine nitrogen and the complex is centrosymmetric around the nickel centre. The N(2)-C(7) and C(7)-S(2) bond lengths of 1.303(3) and 1.735(2) Å respectively are consistent with the deprotonation the thioamide functionality in the coordinated of thiosemicarbazonate ligand.^{10a,15} The bond lengths and bond angles are in good agreement with those found in related thiosemicarbazonato complexes.^{10a,15} nickel(II)

Table 1. Optimization of reaction conditions^a



Entry	Solvent	Base	Temp. (°C)	Yield ^b (%)
1	Toluene	Et ₃ N	110	<20
2	Acetone	Et ₃ N	55	<20
3	THF	Et ₃ N	65	<20
4	MeCN	Et ₃ N	80	54
5	DMSO	Et ₃ N	80	80
6	DMF	Et ₃ N	80	>99
7	DMF	NaOAc	80	33
8	DMF	KOH	80	<20
9	DMF	NaHCO ₃	80	50
10	DMF	K_2CO_3	80	61
11	DMF	Et ₃ N	50	90
12	DMF	Et ₃ N	30	40
13	DMF	Et ₃ N	80	N.R. ^c
14	DMF	Et ₃ N	80	<20 ^d

 $[^]a$ 4'-Iodoacetophenone (1.0 mmol), phenylacetylene (1.5 mmol), 1 (121.5 ppm), CuI (5 μ mol), Solvent (5 ml), Base (3.0 mmol), N_2 atm, 2 h.

^b Isolated yield after column chromatography.

^c Without $\mathbf{1}$, for 6 h. N.R. = No reaction.

^d Without CuI, for 6 h.

In recent years, nickel complexes have attracted immense attention as catalysts for various carbon-carbon cross-coupling reactions and this prompted us to explore the catalytic efficacy of 1 in the Sonogashira cross-coupling reaction. The initial tests involved the optimization of solvent, base and reaction temperature. The reaction between 4'-iodoacetophenone and phenylacetylene to furnish 1-(4-(phenylethynyl)phenyl)ethanone in the presence of 1 as catalyst and CuI as cocatalyst was first selected and various reaction conditions such as solvent, base and temperature were sequentially varied to ascertain the optimum reaction condition for this coupling reaction (Table 1). In the beginning, various solvents were screened (entries 1-6). From the inspection of the obtained results, it can be inferred that the reaction proceeded relatively well in polar solvents and DMF was found to be the solvent of choice (entry 6) with excellent isolated yield of the expected internal olefin. In DMF, significant sensitivity to base was also noted. Among the various bases screened (entries 6-10), Et₃N gave excellent results. Inorganic bases such as NaOAc, KOH, NaHCO3 or K2CO3 resulted in much lower yields under the studied conditions. In DMF-Et₃N, excellent isolated yield of the desired product was obtained at 80 °C (entry 6). Decrease in temperature, resulted in reduced yield of the product (entries 11,12). Hence, further reactions were carried out using DMF as solvent and Et₃N as base at 80 °C. In

addition, control experiments revealed that the reaction completely shut down without the addition of 1 (entry 13), whereas the yield fell to below 20% if CuI was not added (entry 14).

Under the above optimized conditions the coupling reaction was then performed at different catalyst loadings in order to discover the effectiveness of 1 (Table 2). Good isolated yields of desired coupling product were obtained when 121.50 or 60.75 ppm of 1 (entries 1,2) was used. The yield of the product significantly dropped when a lower catalyst loading of 12.15 or 6.08 ppm were used (entries 3,4). Interestingly, the coupling reaction can be carried out even with a very low catalyst loading of 0.12 ppm (entry 5) with high turnover number (TON). The isolated yields are good with appreciable TON when 60.75 ppm of the catalyst was used and consequently, this catalyst loading was used for further studies.

Table 2. Effect of catalyst loading^a



^a 4'-Iodoacetophenone (1.0 mmol), phenylacetylene (1.5 mmol), 1 (121.50-0.12 ppm), CuI (5 μ mol), DMF (5 ml), Et₃N (3.0 mmol), 80 °C, N₂ atm, 2 h. ^b Isolated yield after column chromatography.

^c TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

After establishing the optimal reaction conditions, the Sonogashira coupling reaction of phenylacetylene with activated (electron-withdrawing substituents), unsubstituted (electronneutral) and deactivated (electron-donating substituents) aryl iodides was investigated to examine the electronic and steric effects of aryl iodides on the efficiency of the catalytic reaction (Table 3). All the reactions were carried out under identical conditions to allow comparison of results. It was inferred that aryl iodides with varying electronic nature of the substituents coupled smoothly with phenylacetylene and the corresponding internal alkynes were obtained in good to excellent yields. In general, it was observed that aryl iodides containing electronwithdrawing groups (4-nitro, 4-acetyl, 4-formyl) coupled effectively with phenylacetylene (entries 1-3) and the corresponding products were obtained in excellent isolated yield. Iodobenzene (entry 4) and aryl iodides containing electrondonating groups (4-methyl, 4-methoxy, 4-hydroxy, 4-amino) (entries 5-8) gave good amount of the desired product when coupling with the phenylacetylene. Aryl iodides with methoxy substituent on the meta position (entriv 9) underwent coupling reaction efficiently, whereas when the methoxy substituent was

present on the ortho position (entry 10), a slightly reduced reactivity than the corresponding para substituted derivative (entry 6) was observed which may be due to steric effect.

 Table 3.
 Sonogashira
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 a Aryl iodide (1.0 mmol), phenylacetylene (1.5 mmol), 1 (60.75 ppm), CuI (5 μ mol), DMF (5 ml), Et_3N (3.0 mmol), 80 °C, N_2 atm, 2 h.

^b Isolated yield after column chromatography.

^c TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

Encouraged by the facile Sonogashira reactions of various aryl iodides with phenylacetylene catalyzed by **1** in presence of CuI, the catalytic efficacy of **1** in the coupling of phenylacetylene with aryl bromides was then evaluated (Table 4). As observed in the case of aryl iodides, the electronic nature and the steric effect of the substituents on the aryl ring affected the yield of the products. However, it was observed that when compared to the iodo analogue, the coupling reactions of the bromo derivative was slower and a higher catalyst loading (121.50 ppm) as well as longer reaction time (8 h) were required to obtain good to excellent isolated yield of the product. The stronger C–X bond in the aryl bromide than in the aryl iodide is expected to be the main reason for the variation of their reactivities. The ultimate objective in designing the catalyst for Sonogashira coupling reaction is to form an active species that can catalyze the

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coupling of the more difficult aryl chlorides. However, no catalytic activity was observed in the coupling of 4'chloroacetophenone with phenylacetylene even after using larger amount of 1 (2400 ppm) in DMF/Et₃N after 24 h. This trend is consistent with the increasing strength of carbon–halide bonds from aryl bromide to aryl chloride. Though nickel(II) thiosemicarbazone complexes have been used earlier as effective catalysts for the Sonogashira reaction,¹⁰ a direct comparison with the present nickel(II) thiosemicarbazonato complex (1) is difficult due to the difference in the reaction conditions such as solvents, base, reaction temperature, reaction time and catalyst loading.



Entry	Product	Yield ^b (%)	TON ^c
1		99	990
2	Сосн3	97	970
3	СНО	94	940
4	— ———————————————————————————————————	91	910
5	СН3	88	880
6		87	870
7	ОН	85	850
8		84	840
9		92	920
10	ОСНа	83	830
11		82	820
12	OHC H ₃ CO	79	790

 a Aryl bromide (1.0 mmol), phenylacetylene (1.5 mmol), 1 (121.50 ppm), CuI (5 μ mol %), DMF (5 ml), Et_3N (3.0 mmol), 80 °C, N_2 atm, 8 h.

^b Isolated yield after column chromatography.

 c TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

In conclusion, a new square-planar nickel(II) complex containing 2-((3-methylthiophen-2-yl)methylene)-N-

phenylhydrazinecarbothioamide ligand has been synthesized and characterized by elemental analysis and spectral (FT-IR, NMR) methods. Single crystal X-ray diffraction study evidenced the coordination of each thiosemicarbazonate ligand through the azomethine-N and the thioamidate-S atoms and reveals the presence of a distorted square planar geometry around the Ni(II) ion. The utility of the new complex as excellent catalyst for the Sonogashira reaction has been highlighted by the coupling reaction of activating, neutral and deactivating aryl halides (iodides and bromides) with phenylacetylene under the optimized conditions of solvent, base, reaction temperature and catalyst loading. When compared with the aryl iodides, the reaction was slower in the case of the corresponding aryl bromo analogues, consistent with the strength of the C-X bond in Ar-I and Ar-Br. The desired products were obtained in good to excellent isolated vields.

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with Cambridge crystallographic center, CCDC No. 897455. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union roads, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk). The summary of the data collection and refinement parameters for the complex; Experimental procedures; ¹H NMR spectra of the complex; ¹H and ¹³C NMR data for all the coupling products.

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Highlights

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1. New Ni(II) thiosemicarbazone complex is

synthesised

2. X-ray structure indicates the presence of a

Acctebrace

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