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Copper-free Sonogashira reactions catalyzed by a palladium(II) complex bearing pyrenealdehyde thiosemicarbazonate under ambient conditions

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ABSTRACT

Convenient synthesis of a new square-planar mononuclear palladium(II) complex bearing N,S-donor 1-pyrenaldehyde 4-methyl-3-thiosemicarbazonate (L^-) as ligand is described. The identity of the complex has been established as $[Pd(L)Cl(PPh_3)]$ by elemental analysis, ESI-MS, FT-IR, NMR and single crystal X-ray crystallographic measurements. The complex has been found to be an active and efficient homogeneous catalyst for the copper free Sonogashira coupling reactions of phenylacetylene with various aryl halides (bromides and chlorides) at room temperature under aerobic conditions.

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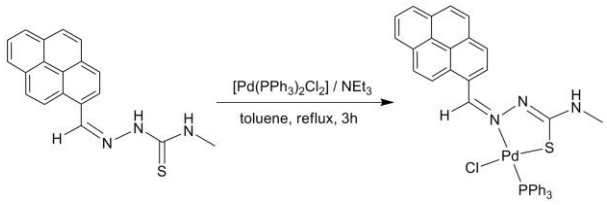
The Sonogashira cross-coupling reaction between an aryl halide and a terminal alkyne has emerged as one of the most widely used carbon-carbon bond forming reactions in organic chemistry. The reaction has been utilized as an efficient methodology to synthesize dendrimers,[1] conjugated oligomers and polymers,[2] substituted alkynes,[3] intermediates in natural products, pharmaceuticals,[4] optical materials,[5] etc. Since its discovery in 1975,[6] the original procedure has been modified from time to time by varying the palladium-source, ligand, solvent, base, additive, reaction temperature and catalyst loading to expand the scope of the reaction.[7] The most common catalytic systems used for this coupling reaction include $[PdCl_2(PPh_3)_2]$, $PdCl_2/PPh_3$, and $[Pd(PPh_3)_4]$ together with copper(I) salt as the co-catalyst. However, if the reactions are not performed under oxygen free conditions copper salts can induce Glaser-Hay type homocoupling of terminal alkynes to yield diynes, which are difficult to separate from the desired products due to their similar chromatographic mobility[8] and in addition, potentially explosive copper acetylides can also be formed. Hence development of copper-free systems has received considerable attention.[7,9] Significant progresses in this direction have been made using palladium nanoparticles,[10] palladacycles[11] and a variety of palladium complexes with Schiff bases,[12] pincers,[13] carbenes[14] and N-[15] and P-donor[16] ligands.

Thiosemicarbazones containing N- and S-donor atoms act as versatile ligands for transition metal ions and exhibit a wide range of coordination modes in their metal complexes.[17] Though there are plenty of reports related to the biological applications of thiosemicarbazones and their metal complexes,[18] research into their role in catalysis is still a relatively new area of interest. In recent years, some palladium(II) thiosemicarbazone complexes have been employed as effective catalysts for carbon-carbon and carbon-heteroatom coupling reactions.[19] Though there are a few reports on the use of such complexes as catalysts for Sonagashira cross-coupling reactions under aerobic conditions,[20] there is ample scope for developing new air-stable palladium(II) thiosemicarbazonate complexes that can act as efficient catalysts for the room temperature copper-free Sonogashira reaction of aryl bromides and the more challenging aryl chlorides in air. In continuation of our research on transition metal complexes with Schiff bases derived from acid- and thioacid-hydrazides and thiosemicarbazide,[21] herein we report a new air-stable palladium(II) complex with 1-pyrenaldehyde 4-methyl-3-thiosemicarbazone and its application as catalyst in the copper-free, homogeneous Sonogashira cross-coupling reactions of phenylacetylene with aryl bromides and also with aryl chlorides at room temperature in air.

Condensation of 4-methyl-3-thiosemicarbazide with 1-pyrenaldehyde in acidic ethanol affords the Schiff base 1-pyrenaldehyde 4-methyl-3-thiosemicarbazone (HL, where H represents the dissociable thioamide proton).[21a,22] The square-planar palladium(II) complex, $[Pd(L)Cl(PPh_3)]$ (**1**), was synthesized in ~67% yield by refluxing equimolar amounts of $[Pd(PPh_3)_2Cl_2]$ and HL in toluene in presence of triethylamine (Scheme 1). The elemental analysis (Calc.: C, 61.67; H, 4.06; N, 5.83%. Found: C, 61.56; H, 4.12; N, 5.75%) and ESI-MS spectroscopic (m/z $\{M+H\}^+$ Calc.: 720.0622; Found: 720.0619) data of **1** are in good agreement with the proposed molecular formula of **1**. The complex is non-hygroscopic and air stable in both solid and liquid states at room temperature. It is soluble in organic solvents such as chloroform, dichloromethane, toluene, acetonitrile, methanol, dimethyl sulphoxide, dimethylformamide, etc., producing intense orange coloured solution.



Scheme 1. Synthesis of $[Pd(L)Cl(PPh_3)]$ (**1**).

In the infrared spectra, the lowering of the C=N stretching frequency of **1** (1577 cm^{-1}) compared to that of the free HL (1600 cm^{-1}) indicates coordination of the azomethine-N to the metal centre in **1**. The thioamide N–H (3150 cm^{-1}) and C=S (833 cm^{-1}) stretches displayed by free HL are not observed in the spectrum of **1**. The nonappearance of these bands suggests deprotonation of the thioamide moiety and subsequent coordination of the thioamidate-S to the metal centre in **1**.[19a-c,20d,23]

In the ^{1}H NMR spectra, the azomethine proton of L^- in **1** and that of the free HL resonates as a singlet at δ 10.22 and 9.23 ppm, respectively. The downfield shift of the signal in the complex suggests deshielding of the –CH=N– proton due to coordination of the N-atom to the palladium(II) centre. In case of **1**, the absence of the singlet that appeared at δ 11.5 ppm for the thioamide proton of the free HL supports the deprotonation of thioamide and thioamidate-S coordination to the palladium(II) centre.[19a-c,20b,24] The chemical shifts of the other protons of the coordinated PPh_3 and thiosemicarbazonate ligands are unexceptional. In the ^{13}C NMR spectrum of **1**, a downfield shift of the azomethine-C (δ 153.0 ppm) relative to that of the free HL (δ 140.1 ppm) substantiates the coordination of the azomethine-N to the metal centre. The signal due to the thioamide-C in free HL (δ 178.1 ppm) moves upfield in **1** (δ 166.5 ppm) indicating coordination of the thiolate-S to the palladium(II) ion.[19a-c,25] A singlet resonance observed at δ 28.0 ppm in the ^{31}P NMR spectrum of **1** is in agreement with the existence of one PPh_3 ligand.[19b,26]

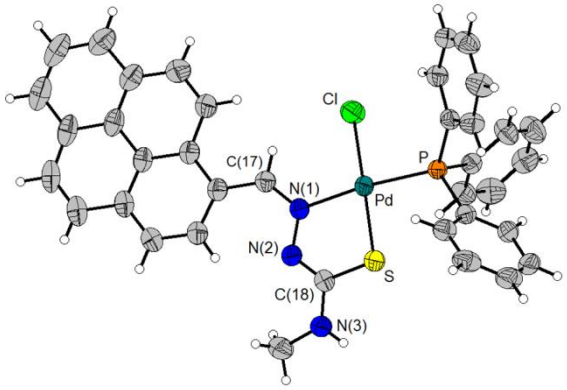
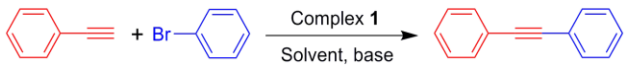


Figure 1. ORTEP of **1** at the 50% probability level. Some selected atoms are labeled for clarity. Selected bond lengths (Å) and angles (º): Pd–N(1) 2.0983(16), Pd–S 2.2584(6), Pd–P 2.2703(5), Pd–Cl 2.3472(6), N(1)–C(17) 1.292(3), N(1)–N(2) 1.391(2), N(2)–C(18) 1.290(3), C(18)–S 1.758(2), C(18)–N(3) 1.349(3), N(1)–Pd–S 82.61(5), N(1)–Pd–Cl 94.09(5), S–Pd–P 91.863(19), P–Pd–Cl 91.029(19), N(1)–Pd–P 173.79(5), S–Pd–Cl 171.95(2).

The molecular structure of **1** has been determined by single crystal X-ray diffraction to confirm the coordination mode of the ligand and the geometry of the complex. The ORTEP view of **1** is shown in Figure 1. In **1**, the metal centre is tetracoordinated. The five-membered chelate ring forming thiosemicarbazonate (L^-) coordinates to the metal centre via the azomethine-N and the thioamidate-S atoms and the remaining two coordination sites are occupied by the P-atom of the PPh_3 and a chloride ion. Consequently the palladium(II) centre resides in a NSClP coordination environment which is distorted from the ideal

square-planar geometry as manifested in the bond parameters around it. The N(2)–C(18) and C(18)–S bond lengths of 1.290(3) and 1.758(2) Å, respectively are consistent with the deprotonation of the thioamide functionality in L^-. All the metal centred bond lengths and bond angles in **1** are consistent with those found in structurally characterized related square-planar palladium(II) complexes containing thiosemicarbazonate ligands.[19a-c,20b,24–26]

Table 1
Optimization of reaction conditions[a]



Entry	Solvent	Base	Yield[b] (%)
1	Toluene	Et_3N	<20
2	p-Xylene	Et_3N	<20
3	Acetone	Et_3N	<20
4	THF	Et_3N	<20
5	MeCN	Et_3N	57
6	DMSO	Et_3N	77
7	DMF	Et_3N	85
8	DMF	NaOAc	30
9	DMF	KOH	<20
10	DMF	$NaHCO_3$	46
11	DMF	K_2CO_3	58

[a] Bromobenzene (1.0 mmol), phenylacetylene (1.5 mmol), **1** (1 mol%), solvent (5 ml), base (3.0 mmol), room temperature, 12 h.
[b] Isolated yield after column chromatography.

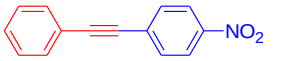
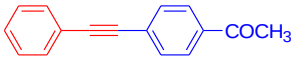
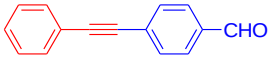
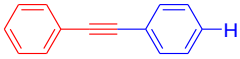
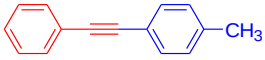
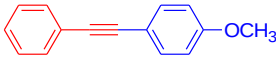
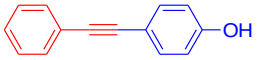
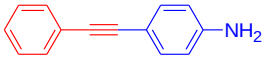
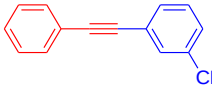
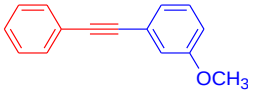
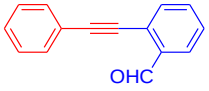
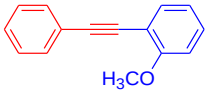
Among the various cross-coupling reactions, Sonogashira reaction of aryl halides with phenylacetylenes has emerged as a practical and efficient method for the preparation of diaryl acetylenes. It is very apparent from the available literature reports that the reaction conditions such as solvent, base and the amount of catalyst loading influence the yield of product formed, though there is no well-defined rule that a specific solvent or a certain base can be used to attain highest efficiency. Thus to determine the effectiveness of **1** as catalyst in the Sonogashira cross-coupling reaction optimization of the reaction condition was performed. As a model system, the reaction of bromobenzene with phenylacetylene in the presence of **1** as catalyst under various reaction conditions was examined at room temperature under aerobic conditions (Table 1). Various solvents were screened in the beginning (entries 1-7). As can be inferred from the scrutiny of the obtained results, the reaction proceeded relatively well in polar solvents when compared with non-polar hydrocarbons and DMF emerged as the solvent of choice with excellent isolated yield of diphenylacetylene at room temperature. Significant sensitivity to base in DMF was also noted. Among the various bases screened (entries 7-11), Et_3N gave excellent results at room temperature. Other bases such as NaOAc, KOH, $NaHCO_3$ or K_2CO_3 were less active or inactive under the studied conditions. When the coupling reaction was carried out at 50 °C, the yield of diphenylacetylene was slightly higher (90%, 10 h). However, at elevated temperatures in addition to the desired product, the undesired biphenyl (10% at 80 °C, 10 h; 15% at 110 ˚C, 8 h) was also obtained due to the homocoupling of bromobenzene, thereby decreasing the yield of the diphenylacetylene. Hence, the coupling reactions were performed at room temperature. It may also be noted that reactions those proceed at room temperature have significant practical advantages relative to those that require elevated temperatures. In addition, the formation of the inactive palladium-black was not observed during the reaction. Controlled experiments showed that the absence of the catalyst or the base resulted in no detectable cross-coupling product. In order to achieve maximum conversion, the yield of the target product was verified with different catalyst loadings (Table 2). Good isolated yields of diphenylacetylene were obtained when 1.0 or 0.5 mol % of the catalyst (entries 1 and 2) was used. The yield significantly dropped with catalyst loading of 0.2 or 0.1 mol % (entries 3 and 4). For further room temperature reactions with various substrates, DMF as solvent, Et_3N as base and catalyst loading of 0.5 mol % were used as optimized conditions.

Table 2
Effect of catalyst loading[a]

Entry	mol % of **1**	Yield[b] (%)
1	1.0	85
2	0.5	81
3	0.2	56
4	0.1	23

[a] Bromobenzene (1.0 mmol), phenylacetylene (1.5 mmol), DMF (5 ml), Et_3N (3.0 mmol).
[b] Isolated yield after column chromatography.

Table 3
Sonogashira reaction of aryl bromides with phenylacetylene[a]

Entry	Product	Yield[b] (%)	TON[c]
1		99	198
2		92	184
3		90	180
4		81	162
5		77	154
6		74	148
7		72	144
8		67	134
9		88	176
10		73	146
11		78	156
12		68	136

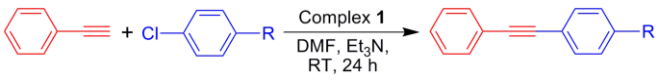
[a] Aryl bromide (1.0 mmol), phenylacetylene (1.5 mmol), **1** (0.5 mol %), DMF (5 ml), Et_3N (3.0 mmol).
[b] Isolated yield after column chromatography.
[c] TON = ratio of moles of product formed to moles of catalyst used.

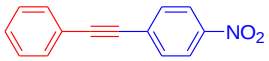
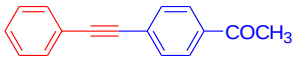
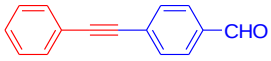
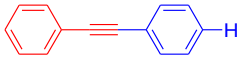
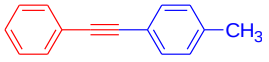
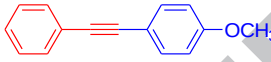
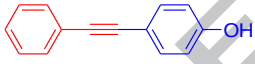
By using the above mentioned optimized reaction conditions the copper free room temperature Sonogashira coupling reactions of phenylacetylene with activated (electron-withdrawing

substituents), non-activated (unsubstituted) and deactivated (electron-donating substituents) aryl bromides were investigated (Table 3). All the reactions were carried out under identical conditions to allow comparison of the results. Notwithstanding the variation of the electronic nature of the substituents, all the aryl bromides coupled rather smoothly with phenylacetylene and the corresponding internal alkynes were obtained in moderate to excellent yields. It was observed that aryl bromides containing electron-withdrawing groups (4-nitro, 4-acetyl and 4-formyl) could effectively couple (entries 1–3) and provide the corresponding products in excellent isolated yields in 12 h. Bromobenzene (entry 4) and aryl bromides containing electron-donating groups (4-methyl, 4-methoxy, 4-hydroxy and 4-amino) (entries 5–8) gave moderate amount of the corresponding internal alkynes. Coupling of *meta*-bromo benzaldehde (entry 9) is less effective than that of the corresponding *para* substituted derivative (entry 3). Notably, sterically hindered *ortho*-bromo benzaldehde also participated in the reaction and the desired product was obtained in satisfactory yield (entry 11). A similar trend was observed in the case of *ortho*-, *meta*- and *para*-bromo anisoles (entries 6, 10 and 12).

Table 4

Sonogashira reaction of aryl chlorides with phenylacetylene[a]



Entry	Product	Yield[b] (%)	TON[c]
1		90	90
2		82	82
3		78	78
4		64	64
5		58	58
6		54	54
7		50	50

[a] Aryl chloride (1.0 mmol), phenylacetylene (1.5 mmol), **1** (1 mol %), DMF (5 ml), Et_3N (3.0 mmol).
[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 complex **1** catalyzed Sonogashira reactions of phenylacetylene with various aryl bromides at room temperature, the catalytic efficacy of **1** in the coupling of phenylacetylene with electronically diverse aryl chlorides was examined at room temperature (Table 4). It was observed that here also **1** can act as an active catalyst. As observed in the case of aryl bromides, the electronic nature of the substituents on the aryl ring affected the yields of the products. The yields were more with substrates having electron-withdrawing substituents (entries 1-3) than those with substrates having electron-donating substituents (entries 5-7), while the yield with the unsubstituted phenyl chloride (entry 4) is somewhere in between the higher and the lower ranges. However, when compared to the bromo analogue, a decreased reactivity was observed in the case of the corresponding chloro derivative and a higher catalyst loading (1 mol %) as well as longer reaction time (24 h) were required to obtain satisfactory to good isolated yield of the product. The stronger C–X bond in the aryl chloride than in the aryl bromide is expected to be the primary reason for the variation of their reactivities.

In conclusion, a mononuclear square-planar palladium(II) complex of formula $[Pd(L)Cl(PPh_3)]$ (L^- = 1-pyrenaldehyde 4-methyl-3-thiosemicarbazonate) has been synthesized and characterized by elemental analysis and spectroscopic (ESI-MS, FT-IR, NMR) measurements. Single crystal X-ray diffraction analysis revealed the coordination of the thiosemicarbazonate ligand through the azomethine-N and the thioamidate-S atoms and a distorted square planar geometry around the metal centre. The utility of the new complex as an effective catalyst for the copper-free room temperature Sonogashira cross-coupling reaction of activated, neutral and deactivated aryl bromides and also chlorides with phenylacetylene under aerobic conditions has been demonstrated.

Acknowledgments

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Supplementary Material

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1408691. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Other supplementary material associated with this article includes experimental procedures; ^1H, ^{13}C and ^{31}P NMR spectra of the complex; ^1H and ^{13}C NMR data for all the coupling products.

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1. (a) Kozaki, M.; Okada, K. Org. Lett. **2004**, 6, 485; (b) Agou, T.; Kojima, T.; Kobayashi, J.; Kawashima, T. Org. Lett. **2009**, 11, 3534.
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Graphical Abstract

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Copper-free Sonogashira reactions catalyzed by a palladium(II) complex bearing pyrenealdehyde thiosemicarbazonate under ambient conditions

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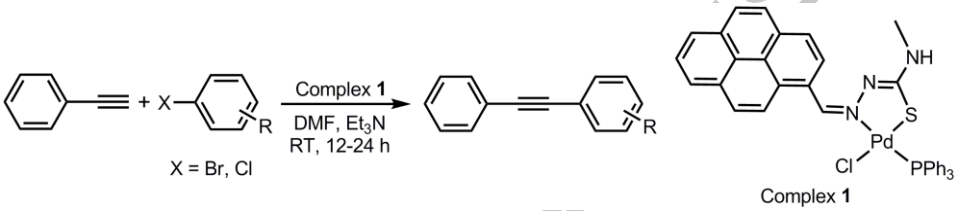

Highlights

- A Pd(II) complex catalyst with precise structure for Sonogashira reactions is reported.
- The catalyst was used at room temperature under aerobic conditions.
- This catalytic process displays good functional group tolerance and high reactivity.