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# Facile Heck coupling synthesis and characterization of a novel tris(4-(pyridine-4-vinyl)phenyl)methylsilane tridentate core

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## RESEARCH ARTICLE



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## ABSTRACT

Aromatic rigid ligands with carboxylate, phosphate, or pyridyl terminals are highly important today for application in the manufacturing of metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and other supramolecular structures. Aromatic rigid ligands give rigidity to MOFs and COFs materials. In addition, building units are important in that their judicious selection can result in a 2-D or 3-D framework with moderate or high surface area. Most aromatic linkers are based on carbon centres which are associated with a negative impact on the environment. However, in contrast, silicon-based centres are scarce and benign to the environment, even though they can be prepared facilely via metathesis. Here, we report the facile preparation of a new tris(4-(pyridine-4-vinyl)phenyl)methylsilane using the classical Heck coupling reaction. The bridging ligand was synthesized via the standard Heck coupling of 4-vinylpyridine with tris(4-bromophenyl)(methyl)silane.

## KEYWORDS

 Aromatic  
 Heck-coupling  
 4-Vinylpyridine  
 Silicon-based centre  
 Tris(4-Bromophenyl)(methyl)silane  
 Tris(4-(Pyridine-4-vinyl)phenyl)methylsilane

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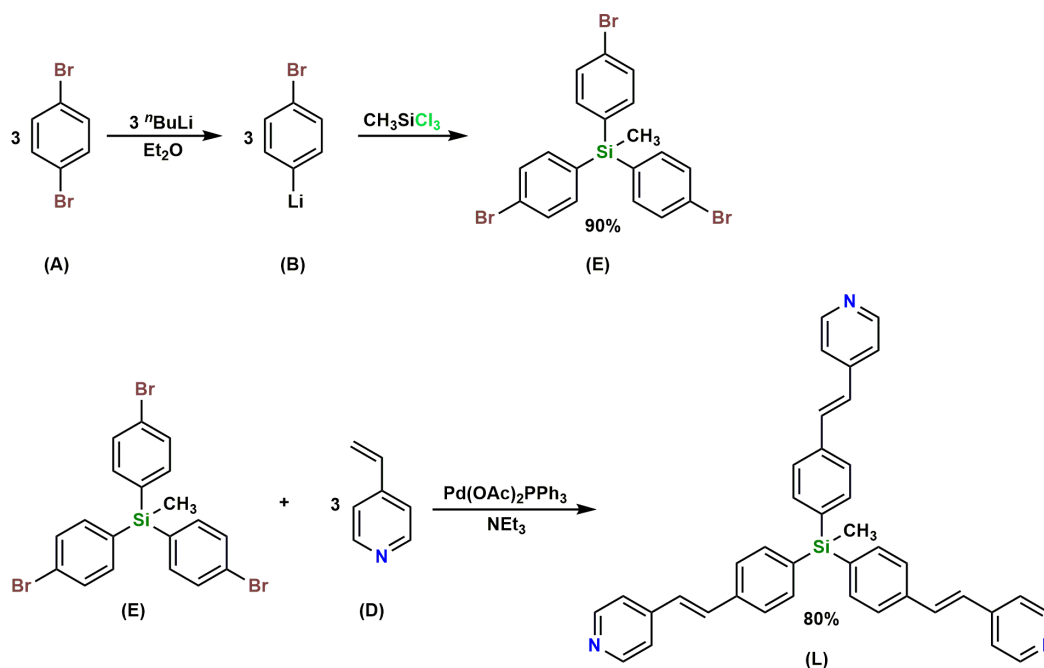
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## 1. Introduction

The importance of the availability of a wide range of ligands with the potential to bridge two remote metal centres cannot be overemphasized in coordination chemistry [1]. However, there are only a handful of ligands with three or more binding sites linked to a central spacer that can bind metal ions in a polygonal array [2]. Such ligands would be of considerable importance as precursors for the preparation of modern materials such as Metal Organic Frameworks (MOFs) [3-5] or Covalent Organic Frameworks (COFs) [6], which have been reported in the literature to have a variety of potential applications such as gas storage [7], gas purification [8], adsorption of heavy metals [9], catalysis [10,11], drug delivery [12], etc. as well as other supramolecular compounds [13]. Whether MOFs, COFs, or other supramolecular compounds, their preparation requires the presence of aromatic rigid ligands [14]. However, commercially available ligands are so small that the need for novel, tuneable, and functional materials to tackle the gamut challenges of the present day. Additionally, available linkers are carbon-based, which have been reported to be the culprit for a variety of environmental problems associated with a continuous and completely dependent on the carbon-centre linker [15]. One way to reduce such dependence on commercially available carbon-based linkers is to move in favour of silicon,

which is a congener of carbon. However, silicon is safer than carbon, and silicon centres can be easily prepared by metathesis [1,16]. To this end, it is still desirable to design new linkers with custom-designed dimensionality or pendant functional groups so as to have control of the physicochemical properties of the resulting framework materials [17]. Several synthetic routes have been used for the syntheses of varieties of rigid aryl systems based on silicon centres with pyridyl pendants [17,18]. Furthermore, after the preparation of the silicon centre linker, such linkers can be coupled to other rigid aromatic groups via the famous Heck coupling reaction [2]. The Heck reaction has not been fully used for the preparation of pyridyl pendants.

In this study, we report the preparation of a novel silicon-centred pyridyl ligand binding site linked via alkene bridges to phenyl spacers. This novel silicon-centre ligand has the potential to form 2-D or 3-D MOF with metals or COF with other non-metals. The preparation of tris(4-(pyridine-4-vinyl)phenyl)methylsilane (L) (a new linker), was analogous to the standard Heck reaction in the literature [2] as well as the preparation of tris(4-bromophenyl)(methyl)silane [1], as shown in Scheme 1.



Scheme 1. Pathway for the synthesis of tri(4-(pyridine-4-vinyl)phenyl)methylsilane (L).

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals, reagents, and solvents used in this work were commercially purchased from Sigma-Aldrich and used as received, unless otherwise noted. Spectroscopy:  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz spectrometer in  $\text{CDCl}_3$  solvent unless otherwise stated. The chemical shifts ( $\delta$ ) for  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  are quoted in ppm with reference to  $\text{Me}_4\text{Si}$ . The coupling constants are reported in Hz.

### 2.2. Preparation of tris(4-bromophenyl)(methyl)silane (E)

In a dry three-neck round bottom flask equipped with a magnetic stirrer bar, 1,4-dibromobenzene (7.5 g, 30 mmol) was dissolved in dry ether (100 mL) and the mixture was stirred and cooled to  $-76^\circ\text{C}$  under  $\text{N}_2$ .  $n\text{BuLi}$  (2.5 M in hexanes, 12 mL, 30 mmol) was taken using a dry syringe with needle and the content was carefully added into the solution dropwise while stirring. At the end of the addition, the mixture was stirred for 1 h. Then, methyltrichlorosilane (1.18 mL, 10 mmol) was taken using a dry syringe with needle and the content was carefully added dropwise at  $-76^\circ\text{C}$ . At the end of the addition, the reaction mixture was slowly increased to room temperature and stirred for 24 h. The reaction mixture was then quenched with 30 mL of  $\text{H}_2\text{O}$ , and the organic layer was separated and collected. The aqueous portion was washed twice with 30 mL of  $\text{Et}_2\text{O}$ , and the organic layer separated and collected. The two separate portions of the collected organic layers were combined, washed with brine, dried over anhydrous  $\text{MgSO}_4$ , and then filtered. Removal of the solvents under vacuum gave a crude product, which was recrystallized in hexane to give colourless crystals.

*Tris(4-Bromophenyl)(methyl)silane* (E): Color: White. Yield: 90%. M.p.:  $120.0\text{--}120.7^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.79 (s, 3H,  $\text{CH}_3$ ), 7.30 (d, 6H,  $J = 8.4$  Hz, Ar-H), 7.50 (d, 6H,  $J = 8.4$  Hz, Ar-H).

### 2.3. Preparation of tris(4-(pyridine-4-vinyl)phenyl)methylsilane (L)

In a clean dry round bottom flask, a mixture of tris(4-dibromophenyl)methylsilane (E) (1.70 g, 3.33 mmol), 4-vinylpyridine (D) (1.32 g, 12.53 mmol, 1.35 mL), stoichiometric base, trimethylamine (1.27 g, 12.53 mmol, 1.75 mL), which is generally needed to react with the acid produced to regenerate the active catalyst,  $[\text{Pd}(\text{OAc})_2]$  (0.023 g, 0.10 mmol),  $\text{PPh}_3$  (0.053 g, 0.20 mmol) and magnetic stirrer bar were mixed under  $\text{N}_2$  and then degassed to remove oxygen. The degassed mixture was heated under a gaseous flow of  $\text{N}_2$ , refluxed at  $100^\circ\text{C}$  for 48 h to keep the solution free of oxygen and water, which also helps for high conversion. The resulting solid mass was partitioned between  $\text{CH}_2\text{Cl}_2$  and water. The organic layer was separated and evaporated to dryness. The crude brown product was recrystallized from acetone to give the brown product.

*Tris(4-(Pyridine-4-vinyl)phenyl)methylsilane* (L): Color: Brown. Yield: 80%. M.p.:  $169.4\text{--}170.2^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.89 (s, 3H,  $\text{CH}_3$ ), 7.07 (d,  $J = 16$  Hz, 3H,  $\text{CHCH}$ ), 7.31 (d,  $J = 16$  Hz, 3H,  $\text{CHCH}$ ), 7.35–7.37 (m, 6H,  $m\text{-C}_5\text{H}_4\text{N}$ ), 7.54 (s, 12H,  $o,m\text{-C}_4\text{H}_4$ ), 8.46–8.58 (m, 6H  $o\text{-C}_5\text{H}_4\text{N}$ ).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -3.45, 120.90, 126.49, 126.83, 132.91, 135.74, 136.54, 137.31, 144.40, 150.24.  $^{29}\text{Si}$  NMR (79.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -11.09.

## 3. Results and discussion

Compound E, tris(4-dibromophenyl)(methyl)silane, was synthesized and characterized using standard analytical and spectroscopic methods. For example, the  $^1\text{H}$  NMR spectrum of the compound is comparable to the literature [17–19], and showed well-resolved resonances with aromatic proton signals found within the range  $\delta$  7.30–7.50 ppm, while nonaromatic methyl protons are found at  $\delta$  0.79 ppm.

Trichloro(methyl)silane ( $\text{CH}_3\text{SiCl}_3$ ) was added to the lithiation product, which resulted in the formation of tris(4-dibromophenyl)(methyl)silane as a colorless powder product after aqueous work in a 90% yield of the compound (Lit. 82%, 83.5%) [17,19]. At the end of the reaction, the reaction mixture was partitioned between aqueous and organic layers to give a

brown powder, which was washed with ethyl acetate to give an 80% yield of tris(4-(pyridine-4-vinyl)phenyl)(methyl)silane (L) as brown powder. The  $^1\text{H}$  NMR spectrum of compound L showed well-resolved resonances with aromatic proton signals found within  $\delta$  7.07-8.58 ppm, which are consistent with aromatic vinylpyridine compounds ( $\delta$  7.14-8.63 ppm) in the literature [2], while non-aromatic methyl protons were found at  $\delta$  0.89 ppm (starting material E =  $\delta$  0.79 ppm), (Lit.  $\delta$  0.94 ppm for similar Si-CH<sub>3</sub>) [17]. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of L shows signals for aromatic carbons in the range of  $\delta$  120.90-150.24 ppm, which is consistent with the values in the literature [2], while the methyl carbon signal was found at  $\delta$  -3.45 ppm, which is also consistent with similar compounds in the literature with values such as  $\delta$  -4.30 ppm, for tris(4-bromophenyl)(methyl)silane, and  $\delta$  -2.70 ppm, for tris(3,5-difluorophenyl)methylsilane [19]. Furthermore, the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of compound L shows a singlet at  $\delta$  -11.09 ppm. The Heck coupling reaction has thus been applied in this study to create novel silicon-centred pyridyl ligand binding sites linked via alkene bridges to phenyl spacers. The use of this novel ligand in the preparation of MOFs and COFs is being explored.

#### 4. Conclusion

A novel silicon-centre pyridyl ligand tris(4-(pyridine-4-vinyl)phenyl)methylsilane has been prepared by the Heck coupling reaction of 4-vinylpyridine with tris(4-bromophenyl)(methyl)silane. The product was made as a brown powder with a yield of 80%. Therefore, this ligand should be explored for the preparation of silicon-based MOFs, COFs, and other supramolecular structures.

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#### Disclosure statement


Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.

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