

PREPARATION OF TWO NEW BIS(2-PYRIDYL)SILANE LIGANDS AND THE COPOLYMERIZATION OF
MESI(2-PYRIDYL)₂(CH=CH₂) WITH STYRENE AND DIVINYLBENZENE.

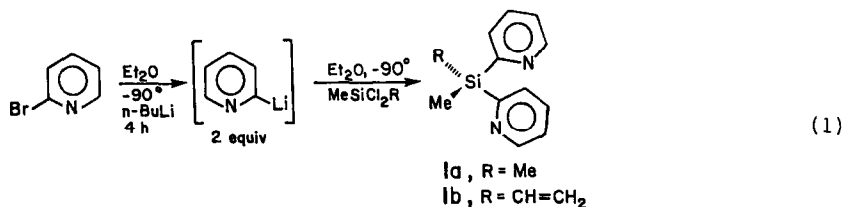
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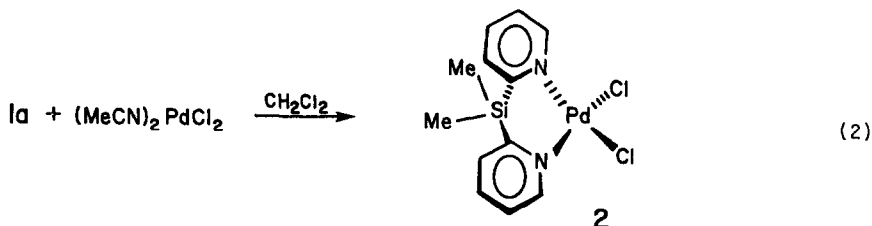
Summary: Reaction of two equiv of 2-(lithio)pyridine with one equiv of RMeSiCl₂ [R= Me(**1a**) & vinyl(**1b**)] produces the corresponding bis(2-pyridyl)silane in good yield. Compound **1a** forms an air stable complex with PdCl₂ in which the bis(2-pyridyl)silane ligand is held in a rigid conformation. The suspension copolymerization of **1b** with styrene and divinylbenzene is reported.

Chelating ligands are ubiquitous in the literature and are utilized in countless applications. The 2,2'-bipyridine ligands have commanded a considerable share of the attention over several decades. In more recent years, the interest in polymer-supported ligands has prompted the synthesis of 2,2'-bipyridine derivatives which contain a polymerizable vinyl group.¹ In this paper we wish to describe a synthesis of two new bis(2-pyridyl)silane ligands which are easily prepared in a one-pot, two step procedure. In addition, the new ligands are shown to readily coordinate to palladium and the vinyl derivative can be incorporated with modest success into a polystyrene copolymer.

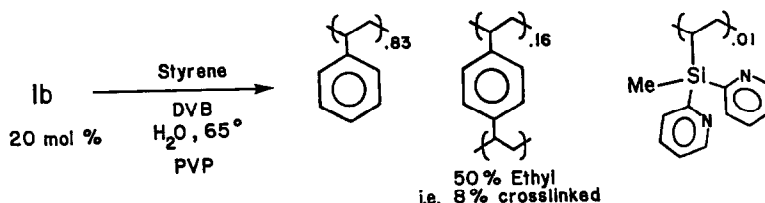
Reaction of 2-(lithio)pyridine² with either Me₂SiCl₂ or Me(CH₂=CH)SiCl₂ produces the corresponding bis(2-pyridyl)silanes, **1a** (75%) and **1b** (65%), respectively, in good yield after purification by distillation at reduced pressure.³



Treatment of (CH₃CN)₂PdCl₂ with one equiv of **1a** in methylene chloride for 30 min produces the one:one complex **2** in quantitative yield (eq 2).⁴



Interestingly, the palladium complex displays two signals in the NMR spectra for the silyl methyl groups which we believe can best be rationalized in terms of a rigid chelate ring. In order for the ligand to accommodate the palladium the pyridine rings rotate about the pyridine-Si bond, which then destroys the C_2 axis and one of the mirror planes of symmetry. In the complex both pyridine rings are magnetically equivalent in 1H and ^{13}C NMR spectra which indicates a plane of symmetry remains which is defined by the Pd, Si, and the silyl-methyl groups. Heating a 1H NMR sample of **2** to $65^\circ C$ showed no line broadening of the methyl resonances, indicating the energy barrier between the two possible isomers is reasonably large.



Suspension copolymerization⁵ of **1b** (20 mol-%) with styrene and divinylbenzene gave polymer beads (20–50 μm) containing approximately 1 mol-% of the silane monomer as determined by nitrogen analysis. The lack of incorporation of the silyl monomer in the polymerization process indicates that the reactivity ratio is quite small in comparison to styrene and/or the silane monomer is destroyed under the polymerization conditions.

References

- 1) Abruna, H. D.; Breikss, A. I.; Collum, D. B. *Inorg. Chem.* **1985**, *24*, 987. Kelly, J. M.; Long, C.; O'Connell, C. M.; Vos, J. G.; Tinnemans, A. H. *A. Inorg. Chem.* **1983**, *22*, 2818 and references therein.
- 2) Yale, H. L. *Pyridine and Its Derivatives*, Part 2, Interscience, New York, 1961, Chapter 5.
- 3) **1a** (bp $100^\circ/1.3$ mm) 1H NMR(CDCl_3) 8.80 (ddd, $J=1.5$ Hz, 4.6 Hz, 2H), 7.56 (m, 4H), 7.20 (ddd, $J=5.9$, 4.6, 3.2 Hz, 2H), 0.67 (s, 6H); ^{13}C NMR(CDCl_3) 165.5, 150.1, 133.9, 129.9, 122.9 (pyridine ring), -3.5 (SiCH₃). Anal Calcd. for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Si}$: C, 67.25; H, 6.58. Found: C, 67.55; H, 6.72. **1b** (bp $115^\circ/1.2$ mm) 1H NMR(CDCl_3) 8.81 (m, 2H), 7.58 (m, 4H), 7.2 (m, 2H), 6.59 (dd, $J=14.6$, 20.3 Hz, 1H), 6.26 (dd, $J=3.5$, 14.6 Hz, 1H), 5.95 (dd, $J=3.5$, 20.3 Hz, 1H), 0.77 (s, 3H); ^{13}C NMR(CDCl_3) 164.0 (py C-2), 150.1, 150.2 (CH's), 135.6 (=CH₂), 133.9, 130.5, 129.9 (CH's), -5.5 (SiCH₃).
- 4) The complex was precipitated with ether, filtered, washed with cold chloroform, and dried at 40° under reduced pressure. **2**: 1H NMR (CDCl_3) 9.23 (ddd, $J=5.7$, 1.5, 0.9 Hz, 2H), 7.79 (apparent dt, $J=8.0$, 1.5 Hz, 2H), 7.63 (ddd, $J=7.4$, 1.7, 0.8 Hz, 2H), 7.37 (ddd, $J=7.6$, 5.9, 1.7 Hz, 2H), 1.70 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (CDCl_3) 161.2 (py C-2), 155.7, 137.0, 130.5, 125.4 (pyridine CH's), -0.4, -4.5 (SiCH₃).
- 5) The cross-linked copolymer was prepared using the procedure of: Parrinello, G.; Deschenaux, R.; Stille, J. K. *J. Org. Chem.* **1986**, *51*, 4189.

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