The Chemistry of Organometallic Derivatives of Oligoacetylenic Silanes

WONG Chun Kin

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Philosophy

Principal Supervisor: Dr. WONG Wai Yeung, Raymond

Hong Kong Baptist University

September 2002
Abstract

The molecular design, synthesis, characterization, structural studies and optical spectroscopy of some metal-containing oligo- and poly(alkynylsilanes) are discussed.

Chapter 1 contains a brief review on metal acetylide complexes and polymers with reference to their preparations, characterization as well as their applications in the materials industry.

Chapter 2 presents the synthesis and characterization of a series of new oligoacetylenic silanes containing $R_2\text{Si}(C≡\text{CH})_2$ units ($R = \text{Me}, \text{Ph}$). Novel silole-based and alkynylgermane ligand precursors were also prepared. Full characterization of these molecules was accomplished by FTIR, NMR ($^1\text{H}, ^{13}\text{C}, ^{29}\text{Si}$) and UV/Vis spectroscopies and FAB mass spectrometry. The single-crystal X-ray structure of $\text{HC}=\text{C}(p-$C$_6\text{H}_4)\text{C}=\text{CSi(Ph)}_2\text{C}=\text{C}(p-$C$_6\text{H}_4)\text{C}=\text{CSi(Ph)}_2\text{C}=\text{C}(p-$C$_6\text{H}_4)\text{C}=\text{CH}$ has been determined, showing that two silicon atoms and six acetylenic units constitute the backbone of the molecule.

Chapter 3 describes the synthesis and characterization of a range of Groups 8 and 9 metal complexes bearing alkynylsilane ligands. In the first place, some novel mononuclear acetylide complexes $\text{trans-}[\text{M(dpmm)}_2\text{Cl}(\text{C≡CRC≡CH})] (\text{M} = \text{Ru, Os}; R = \text{SiMe}_2$–$\text{O}$–$\text{SiMe}_2$, $\text{SiPh}_2$) were prepared and structurally characterized and their electrochemical properties were investigated by cyclic voltammetry. Attempts were then made to synthesize a series of homometallic and heterometallic carbonyl clusters incorporating $R_2\text{Si}(C≡\text{CH})_2$ and $R_4\text{Si}_2(C≡\text{CH})_2$ units ($R = \text{Me}, \text{Ph}$). In most cases, the structures of these new compounds were unequivocally identified by X-ray crystallography.
A full account of the synthesis, characterization, electrochemistry and optical spectroscopy of some platinum(II)-containing oligo- and poly(alkynylsilanes) is presented in Chapter 4. Soluble and thermally stable platinum(II) poly(alkynylsilanes) trans-[−Pt(PBu₃)₂C≡CRC≡C−]ₙ (R = SiPh₂, (p-C₆H₄)C≡C-Si(Ph)₂C≡C(p-C₆H₄)) were successfully synthesized in good yields by CuI-catalyzed condensation polymerization of trans-[PtCl₂(PBu₃)₂] with HC≡CRC≡CH. The regiochemical structure of these polymers was studied by NMR (¹H, ¹³C, ²⁹Si and ³¹P) spectroscopy. We report the optical absorption and photoluminescence spectra of such metal-based organosilicon polymers and compare the data with their mono-, di- and triplatinum(II) acetylide model complexes: trans-[Pt(Ph)(PEt₃)₂C≡CRC≡CH], trans-[Pt(Ph)(PEt₃)₂C≡CRC≡CPh(PEt₃)₂] and trans-[Pt(Ph)(PEt₃)₂C≡CRC≡C-Pt(PBu₃)₂C≡CRC≡CPh(PEt₃)₂] (R = SiPh₂, (p-C₆H₄)C≡CSi(Ph)₂C≡C(p-C₆H₄)).

Our studies indicate that such organometallic poly(alkynylsilanes) shows a strong triplet emission with a very high efficiency of intersystem crossing from the S₁ singlet excited state to the T₁ triplet excited state. The dependence of intersystem crossing and the spatial extent of singlet and triplet excitons as a function of the central spacer group is discussed in polymetallaynes possessing SiPh₂, p-C₆H₄ and Pt(PR₃)₂ (R = Et, Bu) linkers.

Chapters 5 and 6 present the concluding remarks and the experimental details of the work presented in Chapters 2–4.
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