

MASTER'S THESIS

The chemistry of organometallic derivatives of oligoacetylenic silanes

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The Chemistry of Organometallic Derivatives of Oligoacetylenic Silanes

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for the degree of Master of Philosophy

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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 $R_2Si(C\equiv CH)_2$ units ($R = Me, Ph$). Novel silole-based and alkynylgermane ligand precursors were also prepared. Full characterization of these molecules was accomplished by FTIR, NMR ($^1H, ^{13}C, ^{29}Si$) and UV/Vis spectroscopies and FAB mass spectrometry. The single-crystal X-ray structure of $HC\equiv C(p-C_6H_4)C\equiv CSi(Ph)_2C\equiv C(p-C_6H_4)C\equiv CSi(Ph)_2C\equiv C(p-C_6H_4)C\equiv CH$ 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 *trans*- $[M(dppm)_2Cl(C\equiv CRC\equiv CH)]$ ($M = Ru, Os$; $R = SiMe_2-O-SiMe_2, SiPh_2$) 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 $R_2Si(C\equiv CH)_2$ and $R_4Si_2(C\equiv CH)_2$ units ($R = Me, Ph$). 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≡C-Pt(Ph)(PEt₃)₂] and *trans*-[Pt(Ph)(PEt₃)₂C≡CRC≡C-Pt(PBu₃)₂C≡CRC≡C-Pt(Ph)(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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