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論文名	「Design, Synthesis, Characterization, and Luminescent Properties of Organosulfur/selenium-Functionalized Novel Platinum(II) Bis(alkenylarylalkynyl) Complexes （有機硫黄および有機セレンにより機能化された新規ビス（アルケニルアリアルキニル）白金(II) の設計、合成、性質と発光特性）」	
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論文要旨

The chemistry of metal-alkynyl conjugated systems has recently been advancing, because the optical properties of these systems are promising for materials chemistry. Therefore, it is important to develop new synthetic methods to make such novel metal-alkyne conjugated systems. In this research work, the author has designed and investigated the addition of organochalcogen moieties into the terminal alkyne of platinum(II) bis(alkynylarylalkynyl) complexes using photoirradiation or palladium catalyst to form new class of novel organometallic complexes where the platinum atom is stabilized with monodentate tertiary phosphine ligands. Several newly designed series of organochalcogen functionalized novel platinum(II) bis(alkenylarylalkynyl) complexes were successfully synthesized with the development of synthetic methods, and characterized by common spectroscopic techniques, and their optical absorption and emission properties.

This thesis consists of five chapters, and the contents of each chapter are as follows:

Chapter 1 includes a short discussion of research background, which also consists of purpose of the research work and a summary of this study.

In chapter 2, a convenient method has been developed for the addition of arenethiol into the terminal alkyne of platinum(II) bis(alkynylarylalkynyl) complexes (**1**), *trans*-[(R₃P)₂Pt{C≡C-Ar-C≡CH}₂] through photoirradiation technique for the synthesis of novel series of arenethiol functionalized platinum(II) bis(alkenylarylalkynyl) complexes (**2**), *trans*-[(R₃P)₂Pt{C≡C-Ar-CH=CH(SX)}₂] (Ar = phenylene or biphenylene, X = phenyl or *p*-tolyl, or 2-naphthalene, and R = ethyl). In this chapter, for the first time, the author focuses on photochemical synthesis, spectroscopic characterization and luminescent properties of a new class of *trans*-platinum(II) bis(alkenylarylalkynyl) complexes (**2**) containing one

arenethio moiety in each alkenyl backbone.

All the reactants were converted to thiolation adducts platinum(II) complexes **2** within 3 to 8 hours upon irradiation with UV light. All these newly synthesized compounds were isolated as pale yellow to yellow solids with yields ranging from good (70%) to excellent (90%) with good regioselectivity. All *trans*-platinum(II) complexes are air-stable, and they display good solubility in common organic solvents, but are insoluble in hexane. All *trans*-platinum(II) complexes (**2**) provided satisfactory microanalyses.

The exact three-dimensional solid state structure of complex (**2b**), *trans*-[(Et₃P)₂Pt{C≡C-C₆H₄-CH=CH(SC₆H₄CH₃-*p*)}₂] was established by single crystal X-ray analysis. Suitable single crystal of complex **2b** was obtained in order to determine the molecular structure. The platinum atom in **2b** sits on a crystallographic centre of symmetry, which imposes exact planarity at the metal centre, and requires the two alkynyl groups and the two phosphine ligands to occupy mutually *trans* positions. The platinum centre adopts a square planar geometry that is slightly distorted from its ideal geometry with the C-Pt-P bond angle in the range of 87-93°.

For the series of *trans*-platinum(II) complexes, the lowest energy absorption bands in the UV/Vis spectra in chloroform solution at room temperature occurred in the range 362-395 nm. As compared to the absorption band of platinum(II) complexes **1**, it was found that the position of the lowest energy absorption bands are red-shifted, in the platinum(II) complexes **2**, after the inclusion of arenethiol into the platinum(II) complexes **1**. The highest red-shift (27 nm) observed for the *trans*-platinum(II) complexes are recorded for complexes **2e** and **2f**. This reveals that π -conjugation is preserved through the metal site. The room temperature photoluminescence spectra in chloroform, for *trans*-platinum(II) complexes recorded under excitation at the wavelength of the absorption maximum ($\lambda_{\text{max}}=362\text{-}395$ nm), showed emission maxima in the region 399-426 nm. The series of *trans*-platinum(II) complexes displayed emission bands in the blue region of the electromagnetic spectra. The feature is attributable to emission from a singlet excited state, which is characterized as fluorescence, because of the small energy shift (Stokes shift).

In chapter 3, a convenient method has been developed to construct of novel series of platinum(II) bis(alkenylarylalkynyl) complexes having two phenylthio moieties in each alkenyl backbone. In this chapter, for the first time, the author reports the synthesis of novel examples of sulfur-containing platinum(II) bis(alkenylarylalkynyl) complexes, with general formula: *trans*-[(R₃P)₂Pt{C≡C-Ar-C(SPh)=CH(SPh)}₂] (**3**) (Ar = phenylene or biphenylene and R = Et or Ph), having two phenylthio moieties in each alkenyl backbone with good regioselectivity by palladium-catalyzed addition of diphenyl disulfide into the terminal carbon-carbon triple bond of platinum(II) bis(alkynylarylalkynyl) complexes (**1**).

All these newly synthesized compounds (**3**) were isolated as yellow solids with yields ranging from moderate (49%) to high (82%). All *trans*-platinum(II) complexes (**3**) are air-stable, and they display good solubility in common organic solvents, but are insoluble in hexane. All *trans*-platinum(II) complexes (**3**) provided satisfactory microanalyses.

The exact three-dimensional solid-state structure of model complex, *trans*-[(Et₃P)₂Pt{C≡C-C₆H₄-C(SC₆H₅)=CH(SC₆H₅)}₂] (**3a**) was established by single-crystal X-ray diffraction analysis. The platinum atom in **3a** sits on a crystallographic centre of

symmetry, which imposes exact planarity at the metal centre, and requires the two alkynyl groups and the two phosphine ligands to occupy mutually *trans* positions. The platinum centre adopts a square planar geometry that is a very little distorted from its ideal geometry with the C-Pt-P bond angle in the range of 89-91°.

For all platinum(II) complexes **3**, the lowest energy absorption bands in the UV/Vis spectra in chloroform solution at room temperature occurred in the range 363-376 nm. As compared to the absorption band of platinum(II) complexes **1**, it was found that the position of the lowest energy absorption bands are red-shifted, in the platinum(II) complexes **3**, after the functionalization of diphenyl disulfide into the platinum(II) complexes **1**. The highest red-shift (23 nm) observed for the *trans*-platinum(II) complexes is recorded for complex **3a**. The photoluminescence spectra recorded for the solutions of the *trans*-platinum(II) complexes **3** under excitation at the wavelength of the absorption maximum ($\lambda_{\text{max}} = 363\text{-}376$ nm), showed emission maxima in the region 411-415 nm. Platinum(II) complexes **3** displayed emission bands in the blue region of the electromagnetic spectra. The feature is attributable to emission from a singlet excited state, which is fluorescence, because of the small energy shift (Stokes shift).

In chapter 4, a convenient route has been developed to make a novel series of selenium-containing platinum(II) bis(alkenylarylalkynyl) complexes having two phenylseleno moieties in each alkenyl backbone. In this chapter, for the first time, the author reports the synthesis of novel example of selenium-containing *trans*-platinum(II) bis(alkenylarylalkynyl) complexes **4**, with general formula: *trans*-[(R₃P)₂Pt{C≡C-Ar-C(SePh)=CH(SePh)}₂], (where, Ar = phenylene or biphenylene, and R = ethyl or phenyl), by photoinduced addition of diphenyl diselenide into *trans*-platinum(II) bis(alkynylarylalkynyl) complexes **1**.

All the reactants were converted to selenation adducts within 1.5 to 5 hours upon irradiation with UV light. The new *trans*-platinum(II) complexes were isolated as yellow solids with yields ranging from good (76%) to excellent (92%). All *trans*-platinum(II) complexes are air-stable, and they display good solubility in common organic solvents, but are insoluble in hexane. All *trans*-platinum(II) complexes (**4**) provided satisfactory microanalyses.

For all platinum(II) complexes **4**, the lowest energy absorption bands in the UV/Vis spectra in chloroform solution at room temperature occurred in the range 363-375 nm. The absorption bands are slightly influenced by the presence of different organic spacers and phosphine groups. As compared to the absorption band of platinum(II) complexes **1**, it was found that the position of the lowest energy absorption bands are red-shifted in the newly synthesized platinum(II) complexes **4** after the functionalization of diphenyl diselenide into the platinum(II) complexes **1**. The highest red shift (18 nm) observed for the *trans*-platinum(II) complexes, is recorded for complex **4a**. The photoluminescence spectra recorded for the solutions of the *trans*-platinum(II) complexes under excitation at the wavelength of the absorption maximum ($\lambda_{\text{max}} = 363\text{-}375$ nm) showed emission maxima in the region 410-413 nm. Platinum(II) complexes **4** displayed emission band in the blue region of the electromagnetic spectra. This feature is attributable to emission from a singlet excited state (fluorescence), because of the small energy shift (Stokes shift).

The full characterization of the organometallic complexes has been carried out by using traditional methodologies such as elemental analysis, IR, ^1H , ^{13}C , ^{31}P and ^{77}Se NMR spectroscopic analysis. The molecular formula for the complexes were also established by the intense molecular ion $[\text{M}]^+$ or $[\text{M}+\text{Na}]^+$ peaks in the positive-ion ESI-HR mass spectra.

The scope of those reactions is quite general. The above methodologies are tolerated on platinum(II) bis(diethynylarylene) complexes, bearing different arene rings and different phosphine groups. Therefore, it is expected that the newly developed synthetic methods will be useful for the functionalization of metal containing conjugated materials.

Chapter 5 finally concludes this thesis by summarizing the previous chapters.

審査結果の要旨

本論文は、カルコゲン原子である硫黄、セレンに着目し、エチニル基を有する白金錯体に対する各カルコゲン原子の反応特性を活かした遷移金属触媒反応および光誘起ラジカル付加反応を開発するとともに、材料科学分野への展開を目的に、合成したカルコゲン含有白金錯体の光化学特性について研究したものであり、以下の成果を得ている。

(1) 両末端にエチニル基を有するビス(アルケニルアリールアルキニル)白金(II)錯体に対し、光誘起ラジカル反応を利用した芳香族チオール付加反応を行うことで、対応するアルケニルアリールアルキニル白金錯体を合成し、さらにフェニル、ビフェニル、p-トリルなどの汎用性の高い芳香族基を有するチオールについて反応を高位置選択的に進行させることに成功している。

(2) パラジウムを触媒とするジフェニルジスルフィドを用いた白金錯体の各エチニル基に対する2つのフェニルチオ基の導入反応が、位置および立体選択的に進行することを明らかにしている。

(3) ジフェニルジセレニドの導入反応について、光誘起反応を用い、白金の両末端エチニルの各部位に対し、2つのフェニルセレノ基が導入された新規ビス(アルケニルアリールアルキニル)白金(II)錯体の合成に成功している。

(4) 以上のように合成した新規ビス(アルケニルアリールアルキニル)白金(II)について、各分子の構造、および光吸収、発光特性を詳細に検討し、基本物性に関する機能特性を評価している。

以上の研究成果は、カルコゲン含有白金錯体の高選択的な構築法の開発と、その光化学特性について重要な知見を与えるものであり、本分野の学術的発展に貢献するところ大である。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。学位論文審査委員会は、本論文の審査な

らびに学力確認試験の結果から、博士(工学)の学位を授与することを適当と認める。