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<td>Rahman, Md. Mostafizur</td>
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Md. Mostafizur Rahman

February 2015

Doctoral Thesis at Osaka Prefecture University
Chapter 1

General Introduction

1.1 Research Background

There is a continuing interest in the scientific community in the search for novel conjugated organic and metal-organic molecular functional materials that might help to sustain the growth of opto-electronic research. These conjugated systems represent an interesting material exhibiting different material properties of the constituent molecules as well as intermolecular interactions.\(^1\) Although most of the work in this field has focused on conjugated materials that are comprised of organic building blocks, there has been an increasing interest in the properties of organometallic conjugated materials such as molecular wires, organogelators, and nonlinear optics.\(^2,3,4\) These interests are derived from the fact that incorporation of heavy metals into an organic conjugated framework can elicit large effects on the electronic and optical properties of the materials.\(^5\) In particular, conjugated polymers and their metallated derivatives show a wide domain of intriguing properties useful for the development of optoelectronic devices such as organic light-emitting diodes (OLEDs), photovoltaic cells, and field-effect transistors.\(^6,7,8\)

Among these, rigid-rod organometallic complexes and polyynes of late transition metals represent an important class of new materials for basic and applied research.\(^9\) Platinum acetylides, oligomers and polymers, \([\text{PtL}_2\text{C}≡\text{C}-\text{Ar}-\text{C}≡\text{C}]_n\) (where \(L = \) a phosphine ligand and \(\text{Ar} = \) a \(\pi\)-conjugated arylene unit), are a versatile platform for fundamental studies directed at understanding the effect of heavy metal centers on exciton structure and charge transport in \(\pi\)-conjugated systems.\(^10\) In particular, Pt-acetylides are of interest due to their excited state properties which are dominated by long-lived triplet excitons as well as their potential optoelectronic applications.\(^11\)

Therefore, it is important to develop new synthetic methods of such novel metal-alkynyl conjugated systems. Studies on synthesis and properties of transition metal \(\sigma\)-bonded ethynyl complexes, oligomers and polymers are growing considerably owing to their material and opto-electronic properties. Platinum \(\sigma\)-bonded ethynyl complexes were first synthesized by Hagihara et al. in the 1970s,\(^12\) and since then, many
new classes of materials have been extensively studied with the introduction of different group 8, group 9, group 10 and other transition metals.\textsuperscript{1,4,13} The relatively low oxidation states of late transition metals in the \( \sigma \)-bonded ethynyl complexes are usually stabilized by the presence of auxiliary ligands, and the complexes can exist in either a trans or a cis configuration.\textsuperscript{1,13} In group 10 systems, especially platinum, owing to the thermodynamic stability of the trans isomer, the majority of luminescent investigations have focused on the trans complexes with monodentate auxiliary ligands (L).\textsuperscript{12} The \( \sigma \)-bonded ethynyl complexes often exist as

\[
\begin{align*}
X-\text{Ar}\cdot-X & \xrightarrow{\text{Sonogashira coupling}} \text{Me}_3\text{SiC\equivC\equivAr-C\equivC\equivSiMe}_3 \xrightarrow{\text{MeOH-KOH}} \text{H\equivC\equivAr-C\equivCH} \\
\text{PR}_3 + \text{Cl}^{-}\text{M}^{-}\text{Cl} + 2\text{H\equivC\equivAr-C\equivCH} & \xrightarrow{\text{Cul/R}_3\text{N}} \text{H\equivC\equivAr-C\equivC\equivM\equivC\equivAr-C\equivCH} \text{PR}_3 \\
\text{PR}_3 & \text{PR}_3
\end{align*}
\]

Where, Ar = aromatic spacer; M = Pt, Pd, Ni; X = Br, I; and R = alkyl/aryl

**Figure 1.** Synthetic schemes for metal-alkynyl \( \sigma \)-bonded ethynyl complexes

the diterminal alkynes trans-\([\text{PtL}_2(\text{C\equivCR})_2]\) and polyynes trans-\([-\text{PtL}_2-\text{C\equivCRC\equivC-}]_n\) with a wide variety of aromatic ring systems (R).\textsuperscript{1,12,13} The conventional synthesis of group 10 metal-alkynyl \( \sigma \)-bonded ethynyl complexes are achieved by the reaction of metal halides with alkynes in presence of copper(I) catalyst in an amine solvent (Fig. 1).\textsuperscript{12}

Molecular orbital calculations on the Group 10 bis(acetylide) systems trans-\([\text{L}_2\text{M(}\text{C\equivCR})_2]\) (L=alkyl phosphines; M=Pt, Pd, Ni; R=H, alkyl, aryl) reveal that the lowest energy bands arise from the electronic transitions from \( \pi(\text{C\equivCR}) \) to \( \pi(\text{C\equivCR})^* \) orbitals.\textsuperscript{14} These transitions possess charge-transfer character as a result of overlap between the \( \pi(\text{C\equivCR})^* \) and metal p-orbitals.\textsuperscript{10} In the case of the platinum polymer, there is contact between the carbon \( \pi \) orbitals to either side of the platinum, this has been accounted for by the extended Hückel calculations which have shown that weak hybridization between \( \pi \) and the platinum 5d orbitals, and stronger hybridization between the \( \pi^* \) and the platinum 6p orbitals.\textsuperscript{15} Thus, the \( \pi \) conjugation of the ligand is preserved through the metal. The presence of the heavy metal enhances spin-orbit coupling, so that mixes the singlet and triplet excited states through efficient intersystem crossing (ISC), emission from the triplet excited state, i.e., phosphorescence, can be detected and measured easily.\textsuperscript{10,16} It is a very
attractive feature of this class of conjugated organometallic materials. Emission from a triplet excited state to a singlet ground state is forbidden by spin selection rules, but it can be rendered partially allowed by spin-orbit coupling induced by heavy atoms.\textsuperscript{10,16} However, the phosphorescence of some platinum(II) acetylide complexes has only been observed at low temperature.\textsuperscript{10a,17}

1.2 Aim of the Present Research Work

Researchers have started developing and searching for versatile building blocks for the construction of novel materials that will exhibit useful chemical, optical and electronic properties. Metal alkynyl complexes hold a fascination for synthetic chemists, structural chemists, and materials scientists alike. The methods needed for the synthesis of these materials are often well-established. There are many M-C≡C bond-forming reactions that are useful for synthesis of a wide variety of transition metal and alkynyl conjugated systems. Therefore, it is important to develop appropriate modifications for functionalization to synthesize such novel metal alkynyl conjugated systems. The linear geometry of alkynyl units and its $\pi$-unsaturated character made metal alkynyls to be attractive for synthetic organometallic chemistry. Among them, the platinum(II) bis(phosphine) bis(alkynyl) system, with its simple square planar geometry, has been widely explored.

Although the radical or metal-catalyzed addition of organochalcogen compounds into a terminal alkyl/arylacetylenes is well-precedented in synthetic organic chemistry, it has not been previously reported with regard to any compounds containing metal acetylide complexes.\textsuperscript{18}

Keeping this in mind, the author initiated a plan to investigate the possibility of introducing organochalcogeno moieties into \textit{trans}-platinum(II) bis(alkynylarylalkynyl) complexes to generate newly designed functionalized \textit{trans}-platinum(II) bis(alkenylnarylalkynyl) complexes having organochalcogeno moieties in each alkenyl backbone. In view of the fact that acetylides are ideal moieties for the synthesis of rigid-rod organometallic species, it is expected that, after the inclusion of organochalcogen into \textit{trans}-platinum(II) bis(alkynylarylalkynyl) complexes, the material properties may also be modified in the newly functionalized platinum(II) bis(acetylide) derivatives. Therefore, for the first time, three new classes of organochalcogen functionalized \textit{trans}-platinum(II) bis(alkenylnarylalkynyl) complexes have been
constructed using synthetic modification of photochemical method or palladium-catalyzed one (Fig. 2).

\[
\begin{align*}
\text{HC} & \equiv \text{C} \equiv \text{C} \equiv \text{M} \equiv \text{C} \equiv \text{C} \equiv \text{Ar} \equiv \text{C} \equiv \text{CH} \\
\text{PR}_3 & \text{PR}_3 \\
\text{PhS-SPh} & \text{[Pd(Ph}_3\text{P})_4]}
\end{align*}
\]

Where, \( R = \text{alkyl/aryl}; \ M = \text{Pt}; \ X = \text{phenyl, p-tolyl, 2-naphthalene}; \) and \( \text{Ar} = \text{aromatic spacer such as phenylene, biphenylene, 2,5-dimethylphenylene, 2,5-dimethoxyphenylene} \)

**Figure 2.** Synthetic schemes of new classes of novel series of platinum(II) bis(alkenylarylalkynyl) complexes having organochalcogeno moieties in each alkenyl backbone.

It is expected that the modified synthetic methods could be used for the functionalization of metal acetylide complexes, and thereby can be applied to materials science.

### 1.3 Thesis Structure

The thesis is structured as follows: Chapter 1 gives general introduction which includes research background and the aim of the present research work.

Chapter 2 describes the photochemical synthetic route, experimental techniques, spectroscopic characterization, structural characterization, and photoluminescence properties of a newly designed series of \textit{trans}-platinum(II) bis(alkenylarylalkynyl) complexes containing one arenethio moiety in each alkenyl backbone.

Chapter 3 deals with the palladium-catalyzed synthetic route to bis(dithiolation) of platinum(II) bis(alkynylarylalkynyl) complexes, experimental techniques, spectroscopic characterization, structural characterization, and photoluminescence properties of another new class of \textit{trans}-platinum(II)
bis(alkenylarylalkynyl) complexes containing two phenylthio moieties in each alkenyl backbone. It is noted that tetrakis(triphenylphosphine)palladium catalyst smoothly exhibited catalytic activity even in presence of transition metal platinum on platinum(II) bis(acetylide) complexes.

Chapter 4 presents the photochemical synthetic route for bis(diselenation) of platinum(II) bis(alkynylaryalkynyl) complexes, experimental techniques, spectroscopic characterization, and photoluminescence properties of another new class of trans-platinum(II) bis(alkenylarylalkynyl) complexes containing two phenylseleno moieties in each alkenyl backbone.

Chapter 5 provides general conclusions for all of the research works that are dealt with in this thesis.

1.4 References


Chapter 1: General introduction


Chapter 2

The Photochemical Synthesis, Characterization, and Photoluminescence Properties of a New Class of Thiolated Platinum(II) Bis(alkenylarylalkynyl) Complexes

2.1 Introduction

A great deal of interest has been devoted to the synthesis of novel $\pi$-conjugated systems in the materials chemistry, owing to their potential applications in electronic and electro-optical devices.\(^1\)\(^-\)\(^2\) In the past several decades, there has been a growing interest in the design of conjugated systems representing an interesting material which exhibits different material properties of the constituent molecules as well as intermolecular interactions. Although most of the work in this field has focused on conjugated materials that are comprised of organic building blocks, there has been increasing interest in conjugated organometallic materials and their material properties including nonlinear optical effects, organogelators, molecular wires, liquid crystallinity, electrical conductivity, and photovoltaic behaviour which differ from those of conventional organic materials.\(^1\)\(^-\)\(^8\) This interest derives from the fact that incorporation of heavy metals into organic conjugated framework can elicit large effects on the electronic and optical properties of the materials.\(^9\) In many cases the effects are predictable and tunable, allowing one to use structures to control the properties of desired materials.\(^5\) There are many M-C≡C bond-forming reactions that are useful for synthesis of a wide variety of transition metal-alkynyl conjugated systems.\(^10\)\(^-\)\(^12\) The linear geometry of alkynyl units and its $\pi$-unsaturated character made metal alkynyls to be attractive for synthetic organometallic chemistry. Among them, the platinum(II) bis(phosphine) bis(alkynyl) system, with its simple square planar geometry, has been widely explored.\(^13\)\(^-\)\(^16\)

Although the radical addition of hydrothiolation of terminal alkyl/arylacetylenes is well-precedented in synthetic organic chemistry\(^17\), it has not been previously reported with regard to any compounds containing metal acetylide complexes.
In this chapter, for the first time, the author has designed and developed a modified synthetic method for hydrothiolation of platinum(II) bis(alkynylarylalkynyl) complexes, and has also focused on the spectroscopic characterization and luminescent properties of a new class of trans-platinum(II) bis(alkenylarylalkynyl) complexes, trans-[(R_3P)_2Pt{C≡C-Ar-CH=CH(SX)}_2] (2) (Ar = phenylene or biphenylene, X = phenyl or p-tolyl, or 2-naphthalene, and R = ethyl), containing one arylthio moiety in each alkenyl backbone, which are stabilized by the presence of monodentate auxiliary phosphine ligands (Fig. 1). This series is the first example of platinum(II) bis(alkenylarylalkynyl) complexes containing one arenethio group in each alkenyl backbone.

Figure 1. The skeleton structure of novel trans-platinum(II) complexes 2

2.2 Results and Discussion

2.2.1 Syntheses and Scope

When a mixture of platinum(II) complex containing an extended alkynyl ligand trans-(Et_3P)_2Pt{C≡C-H_2C≡CH}_2 (1a) and benzenethiol in chloroform was irradiated, photochemically a novel thiolation product (2a), a sulfur-containing platinum(II) bis(alkenylarylalkynyl) complex, was obtained in good yield (82%, isolated yield, Table 1, entry 1; Scheme 1). To optimize reaction conditions, various solvents were used under identical conditions (Table 1). The reaction was completed within 3 hours in chloroform and benzene, while slightly prolonged reaction time (4 hours) in toluene did not improve the yield of 2a (Table 1, entry 3). Chloroform was found to be the best solvent for the addition of benzenethiol to platinum(II) bis(alkynylarylalkynyl) complexes 1. The starting material, platinum(II) bis(alkynylarylalkynyl) complex, is slightly better soluble in halogenated solvent such as chloroform than benzene and toluene. Probably, its effect slightly reflects in the yield of thiolation product, and thus better
yield is obtained in chloroform (82%, entry 1, Table 1). Its structure was characterized by UV/Vis, IR, multi-nuclear NMR spectroscopy, and ESI-HR mass spectrometry as well as elemental analysis.

Scheme 1. Photochemical addition of benzenethiol to trans-platinum(II) bis(alkynylarylalkynyl) complex

Table 1. Optimization of the photochemical addition reaction of benzenethiol with trans-platinum(II) acetylide (1a) in various solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pt-acetylide, 1</th>
<th>Solvent</th>
<th>Duration (h)</th>
<th>Yield(^{ii}) (%)</th>
<th>2a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>Chloroform-d</td>
<td>3</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>Benzene-d(_6)</td>
<td>3</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>Toluene-d(_6)</td>
<td>4</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>

[i] Reactions were carried out in 0.6 mL of deuterated solvent under photoirradiation by using 1a, trans-(Et\(_3\)P)\(_2\)Pt(C≡C-C\(_6\)H\(_4\)-C≡CH), (0.1 mmol) and benzenethiol (0.25 mmol). [ii] Isolated yield.

Under the optimized reaction conditions (Table 1, entry 1), several platinum(II) acetylides, trans-(Et\(_3\)P)\(_2\)Pt(C≡C-Ar-C≡CH), (1) (Ar = phenylene, biphenylene, 2,5-di-methylphenylene, and 2,5-dimethoxyphenylene) were also examined (Scheme 2) by adding various arenethiols (benzenethiol and \(p\)-toluenethiol). The results are summarized in Table 2. The scope of this reaction is quite general. The yields of the isolated addition products range from good to excellent with good regioselectivity. This methodology tolerates trans-platinum(II) acetylide complexes, with extended alkynyl ligand of diterminal acetylides, containing different arene ri-

Scheme 2. Photochemical addition of arylthiol to various trans-platinum(II) bis(alkynylarylalkynyl) complexes

Where, Ar = phenylene, biphenylene, 2,5-dimethylphenylene, and 2,5-dimethoxyphenylene; X = C\(_6\)H\(_5\) and 4-MeC\(_6\)H\(_4\)
Table 2. Optimized photochemical addition reactions of arenethiol with various trans-platinum(II) acetylides

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pt-acetylide, 1</th>
<th>Heteroatom reagent</th>
<th>Duration (h)</th>
<th>Isolated Yield(^{ii}) (%), 2, (E/Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>(\text{C}_6\text{H}_5\text{SH})</td>
<td>3</td>
<td>82 (2a) (60/40)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>4-Me(\text{C}_6\text{H}_4)\text{SH})</td>
<td>3</td>
<td>90 (2b) (70/30)</td>
</tr>
<tr>
<td>3</td>
<td>1b</td>
<td>(\text{C}_6\text{H}_5\text{SH})</td>
<td>4</td>
<td>90 (2c) (60/40)</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>4-Me(\text{C}_6\text{H}_4)\text{SH})</td>
<td>5</td>
<td>88 (2d) (60/40)</td>
</tr>
<tr>
<td>5</td>
<td>1c</td>
<td>(\text{C}_6\text{H}_5\text{SH})</td>
<td>3</td>
<td>85 (2e) (89/11)</td>
</tr>
<tr>
<td>6</td>
<td>1c</td>
<td>4-Me(\text{C}_6\text{H}_4)\text{SH})</td>
<td>3</td>
<td>83 (2f) (56/44)</td>
</tr>
<tr>
<td>7</td>
<td>1d</td>
<td>(\text{C}_6\text{H}_5\text{SH})</td>
<td>3</td>
<td>84 (2g) (94/6)</td>
</tr>
<tr>
<td>8</td>
<td>1d</td>
<td>4-Me(\text{C}_6\text{H}_4)\text{SH})</td>
<td>3</td>
<td>87 (2h) (81/19)</td>
</tr>
</tbody>
</table>

\(^{[i]}\) Reactions were carried out in chloroform solvent under irradiation by using 1, trans-(Et\(_3\)P)\(_2\)Pt\{C≡C-Ar-C≡CH\}_2; (0.1 mmol) and arenethiol (0.25 mmol. \(^{[ii]}\) Inseparable mixture of E/Z isomers were estimated by \(^1\)H NMR.

ngs and substituted arene rings, and also two arylthiols. Platinum(II) acetylide with phenylene rings provided good yield (82%, 2a, entry 1, Table 2) with benzenethiol, and excellent yield (90%, 2b, entry 2, Table 2) with \(p\)-toluenethiol, of thiolation products. Platinum(II) acetylide with biphenylene rings provided very good yield (88%, 2d, entry 4, Table 2) with \(p\)-toluenethiol, and excellent yield (90%, 2c, entry 3, Table 2) with benzenethiol, of thiolation products. Platinum(II) acetylide with methyl groups at 2 and 5 positions on the aryl rings provided good yield (83%, 2f, entry 6, Table 2) with \(p\)-toluenethiol, and very good yield (85%, 2e, entry 5, Table 2) with benzenethiol, of thiolation products. Platinum(II) acetylide with methoxy group at 2 and 5 positions on the aryl rings also provided good yield (84%, 2g, entry 7, Table 2) with benzenethiol, and very good yield (87%, 2h, entry 8, Table 2) with \(p\)-toluenethiol, of thiolation products.

Similarly, on the basis of the above results, the author also examined the addition reaction of 2-naphthalenethiol with several platinum(II) bis(acetylides), trans-(Et\(_3\)P)\(_2\)Pt(C≡C-Ar-C≡CH)\(_2\), (1) (where, Ar = phenylene, biphenylene, 2,5-dimethylphenylene, and 2,5-dimethoxyphenylene) under identical reaction conditions. The results are summarized in Table 3. The yields of the isolated addition products range from good to very good with good regioselectivity. Although, this methodology tolerates trans-platinum(II) acetylide complexes with extended alkynyl ligand of diterminal acetylides, containing different arene rings.
and substituted arene rings, it requires prolonged time (8 hours) to convert 2-naphthenethiol adduct.

![Scheme 3 - Photochemical addition of 2-naphthenethiol to various trans-platinum(II) bis(alkynylarylalkynyl) complexes](image)

Where, Ar = phenylene, biphenylene, 2,5-dimethylphenylene, and 2,5-dimethoxyphenylene

**Scheme 3.** Photochemical addition of 2-naphthenethiol to various trans-platinum(II) bis(alkynylarylalkynyl) complexes

| Table 3. Optimized photochemical addition reaction of 2-naphthenethiol with various trans-platinum(II) acetylides[^i]^ |
|---|---|---|---|---|
| Entry | Pt-acetylide, 1 | Heteroatom reagent | Duration (h) | Isolated Yield[^ii]^ (%) |
| 1 | 1a | C_{10}H_{7}SH | 8 | 75 (2i) (63/37) |
| 2 | 1b | C_{10}H_{7}SH | 8 | 70 (2j) (55/45) |
| 3 | 1c | C_{10}H_{7}SH | 8 | 83 (2k) (84/16) |
| 4 | 1d | C_{10}H_{7}SH | 8 | 78 (2l) (78/22) |

[^i]: Reactions were carried out in chloroform solvent under irradiation by using 1, trans-(Et_{3}P)$_{2}$Pt{(C≡C-Ar-C≡CH)$_{2}$} (0.1 mmol), and 2-naphthenethiol (0.25 mmol).[^ii]: Inseparable mixture of E/Z isomers were estimated by 1H NMR.

The stereochemistry of E/Z isomers were assigned on the basis of the observed values of the coupling constant of the vinylic proton by 1H NMR spectroscopic analysis; for example, trans-platinum(II) complex 2a observed values of coupling constant of the vinylic protons are 15.6 and 15.6 Hz for E isomer and 10.8 and 10.8 Hz for Z isomer. E isomer is also confirmed by single-crystal X-ray analysis of complex 2b (Fig. 2). E isomer is formed predominantly over Z isomer; probably owing to minimizing steric repulsion.

All the reactants were converted to thiolation adducts within 3 to 8 hours upon irradiation with UV light (Tables 2 and 3). All these newly synthesized compounds were isolated as pale yellow to yellow solids with yields ranging from 70 to 90%. They display good solubility in common organic solvents, but are insoluble in hexane. The trans-platinum(II) bis(alkenylarylalkynyl) complexes are air-stable. All trans-platinum(II)
complexes (2) provided satisfactory microanalyses. The identity of these newly synthesized trans-platinum(II) complexes (2) were performed based on their IR, ¹H and ³¹P NMR spectra and positive ESI-HR [M+Na]⁺ or [M]⁺ mass spectra.

### 2.2.2 Spectroscopic Characterization

The full characterization of the organometallic complexes has been performed using traditional methodologies: elemental analysis, IR, ¹H, ¹³C and ³¹P NMR spectroscopy and mass spectrometry (positive [M]⁺/[M+Na]⁺ ion ESI-HR MS). Table 3 summarizes basic spectroscopic data for all the new compounds (2a-2h) in this study.

In IR spectra, the ν(C≡C) stretching frequency is indicative of the characterization of the metal ethynyl complexes (M-C≡C) and the absence of the terminal ≡C-H confirms the completion of the reaction (=CH-). The platinum(II) bis(alkenylarylalkynyl) complexes display a single sharp ν(C≡C) absorption band in the range of 2090-2101 cm⁻¹, confirming the platinum-acetylenic carbon bond (Pt-C≡C) preserved on the newly formed platinum(II) complexes 2, for example, platinum(II) complex 2a displayed a sharp single absorption band at 2099 cm⁻¹, which is assigned to ν(C≡C) stretching vibration. The IR spectra of each platinum(II) complexes 2 shows no band in the range of 3200-3300 cm⁻¹, i.e., characteristic of ≡C-H stretching vibration, thus confirming that the terminal acetylenic groups (-C≡CH) selectively undergo the addition of arenethiols [-CH=CH(SX)]. So, the IR spectra of platinum(II) complexes 2 provided important information, confirming that the addition reaction proceeded only at the terminal alkyne bond of platinum(II) bis(alkynylarylalkynyl) complexes 1.

In the ¹H NMR spectra, the terminal acetylenic proton of each platinum(II) complexes 2 disappeared (about 3 ppm) and new peaks observed in each platinum(II) complexes 2 in the range of 6.37-7.03 ppm for the vinyl proton (Table 4), and in all cases, signals arising from the organic spacer such as aryl ring, arenethio moiety and ethyl phosphine protons also display peaks in the expected region. The characteristic feature of the trans-platinum(II) bis(alkenylarylalkynyl) complexes, trans-[(Et₃P)Pt{C≡C-Ar-CH=CH(SX)}₂], (2) is double doublet, because of their alkenyl backbone [-HC=CH(SPh)] in the ¹H NMR spectra. For instance, plat-
Chapter 2: Synthesis, characterization and luminescence properties of thiolated platinum(II) acetylides

Table 4. Selected spectroscopic data for the trans-platinum(II) bis(alkenylarylalkynyl) complexes 2a-2h

<table>
<thead>
<tr>
<th>Platinum(II) complexes (2)</th>
<th>IR (KBr) ν(C=C) (cm⁻¹)</th>
<th>¹H NMR (ppm)* [-CH=CH(SX)], vinyl proton (E/Z) (ppm)*</th>
<th>³¹P NMR</th>
<th>ESI-HR mass (Calc.) m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2099</td>
<td>6.80 (d, 15.6), 6.71 (d, 15.6), 6.54 (d, 15.6)</td>
<td>11.65 (2366)</td>
<td>924.2502 [M+Na⁺] (901.2633)</td>
</tr>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2101</td>
<td>6.76 (d, 15.6), 6.61 (d, 15.6), 6.47 (d, 15.6)</td>
<td>11.64 (2391)</td>
<td>930.2908 [M⁺] (930.0944)</td>
</tr>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2098</td>
<td>6.91 (d, 15.2), 6.75 (d, 15.2), 6.61 (d, 15.2)</td>
<td>11.70 (2367)</td>
<td>1076.2831 [M+Na⁺] (1053.3259)</td>
</tr>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2092</td>
<td>6.88 (d, 15.6), 6.66 (d, 15.6), 6.55 (d, 15.6)</td>
<td>11.73 (2371)</td>
<td>1082.3601 [M⁺] (1082.2863)</td>
</tr>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2090</td>
<td>6.95 (d, 14.8), 6.72 (d, 15.2), 6.66 (d, 15.2)</td>
<td>12.18 (2380)</td>
<td>980.3151 [M+Na⁺] (957.3259)</td>
</tr>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2091</td>
<td>6.88 (d, 15.6), 6.69 (d, 15.6), 6.60 (d, 15.6)</td>
<td>12.17 (2404)</td>
<td>986.3549 [M⁺] (986.2007)</td>
</tr>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2096</td>
<td>7.03 (d, 15.6), 6.89 (d, 15.6), 6.82 (d, 15.6)</td>
<td>11.81 (2367)</td>
<td>1044.2886 [M+Na⁺]</td>
</tr>
<tr>
<td>trans-[(Et₂P)₂Pt{C≡C-C≡C₁₅H₄-CH=CH(SX)}₂]</td>
<td>2094</td>
<td>6.96 (d, 15.6), 6.86 (d, 15.6), 6.80 (d, 15.6)</td>
<td>11.81 (2371)</td>
<td>1050.3336 [M⁺] (1050.1983)</td>
</tr>
</tbody>
</table>

[a] Referenced to internal TMS. [b] Referenced to external trimethylphosphite. [c] J₁₅₆ value (in Hz) is given in parenthesis, and d = doublet. [d] J₁₅₆ value (in Hz) is given in parentheses.

Platinum(II) complex 2a displayed four doublets at 6.80, 6.71, 6.54, and 6.42 ppm with coupling constants 15.6, 15.6, 10.8, and 10.8 Hz, respectively. The ³¹P NMR spectra of platinum(II) complexes 2 showed the expected signals consisting of three lines due to coupling of the ¹⁹⁵Pt with P³¹, for example, platinum(II) complex 2a displayed a sharp singlet at 11.65 ppm along with two satellites positioned at 18.96 and 4.33 ppm. The trans geometry around the platinum-diphosphine centre was confirmed by ³¹P NMR spectroscopy based on the Jₚₚₚ coupling constant. The trans geometry on platinum center is also confirmed by single-crystal X-ray analysis of model complex 2b (Fig. 2). E/Z intimate mixtures jointly displayed a sharp singlet in ³¹P NMR (Table 4), because in both cases (E/Z), geometry is retained up to (PEt₃)₂Pt{≡C-Ar-CH=CH-}₂ and only changed in the terminal alkyne, which converted to adduct of arenethiol {-CH=CH(SX)}. For instance, platinum(II) complex 2b displayed a sharp singlet at 11.64 ppm. The Jₚₚₚ values obtained - 2366, 2391, 2367, 2371, 2380, 2404, 2367, and 2371 Hz for the platinum(II) complexes 2a, 2b, 2c, 2d, 2e, 2f, 2g, and 2h, respectively.
respectively - are in agreement with the values previously reported for other square planar platinum(II) complexes with trans geometry.\(^{18}\) \(^{13}\)C NMR measurement was also performed in each complex and display signals at the expected region.

The molecular formulae for the complexes were also established by the intense molecular ion \([M+Na]^+\) peaks in the positive ion ESI-IR mass spectra, which were observed at \(m/z\) 924.2502 for \(2a\), at \(m/z\) 1076.2831 for \(2c\), at \(m/z\) 980.3151 for \(2e\), at \(m/z\) 1044.2886 for \(2g\). The \([M]^+\) peaks in the positive ion ESI-IR mass spectra were observed at \(m/z\) 930.2908 for \(2b\), at \(m/z\) 1082.3601 for \(2d\), at \(m/z\) 986.3549 for \(2f\), and at \(m/z\) 1050.3336 for \(2h\).

Similarly, 2-naphthalenethiol adducts, i.e., platinum(II) complexes \(2i\) to \(2l\) display IR, \(^1\)H NMR, and \(^{31}\)P NMR signals at the expected region (Table 5). Table 5 summarizes basic spectroscopic data for all the new compounds, \(2i\)-\(2l\), in this study. The molecular formulae for the complexes \(2i\) to \(2l\) were established by the intense molecular ion \([M+Na]^+\) peaks in the positive ion ESI-IR mass spectra, which was observed at \(m/z\) 1025.2781 for \(2i\). The \([M]^+\) peaks in the positive ion ESI-IR mass spectra were observed at \(m/z\) 1154.3609 for \(2j\), at \(m/z\) 1058.3519 for \(2k\), and at \(m/z\) 1122.3297 for \(2l\).

### Table 5. Selected spectroscopic data for the trans-platinum(II) bis(alkenylarylalkynyl) complexes \(2i\)-\(2l\)

<table>
<thead>
<tr>
<th>Platinum(II) complexes</th>
<th>IR (KBr) (\nu(C≡C)) (cm(^{-1}))</th>
<th>(^1)H NMR (ppm)(^a) [-CH=CH(SX)], vinyl proton ((E/Z))</th>
<th>(^{31})P NMR (ppm)(^b)</th>
<th>ESI-IR mass (Calc.) (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[Et(_3)P(<em>2)Pt(</em>{2})(C≡C-C(_6)H(<em>4)CH=CH(SC(</em>{10})H(_7)))] (2i)</td>
<td>2099</td>
<td>10.8(^f), 6.51 (d, 11.2(^f), (63:37)</td>
<td>10.70 (2366)(^d)</td>
<td>1025.2781 [M+Na](^+) (1002.1586)</td>
</tr>
<tr>
<td>trans-[Et(_3)P(<em>2)Pt(</em>{2})(C≡C-C(_6)H(_4)CH=CH)] (2j)</td>
<td>2098</td>
<td>7.00 (d, 15.2(^f), 6.81 (d, 15.6(^f)), 6.67 (d,</td>
<td>11.70 (2366)(^d)</td>
<td>1154.3609 [M](^+) (1054.3505)</td>
</tr>
<tr>
<td>trans-[Et(_3)P(<em>2)Pt(</em>{2})(C≡C-C(_6)H(_2)2,5-Me(_2))CH=CH] (2k)</td>
<td>2088</td>
<td>10.8(^f), 6.61 (d, 10.4(^f), (55:45)</td>
<td>12.21 (2384)(^d)</td>
<td>1058.3519 [M](^+) (1058.2649)</td>
</tr>
<tr>
<td>trans-[Et(_3)P(<em>2)Pt(</em>{2})(C≡C-C(_6)H(_2)2,5-OMe(_2))] (_2)</td>
<td>2093</td>
<td>7.09 (d, 15.6(^f), 6.98 (d, 15.2(^f)), 6.92 (d,</td>
<td>11.83 (2366)(^d)</td>
<td>1122.3297 [M](^+) (1122.2625)</td>
</tr>
</tbody>
</table>

\[a\] Referenced to internal TMS. \[b\] Referenced to external trimethylphosphite. \[c\] \(J_{\text{HeH}}\) value (in Hz) is given in parenthesis, and \(d\) = doublet. \[d\] \(J_{\text{PrP}}\) value (in Hz) is given in parentheses.

#### 2.2.3 X-ray Crystallography

The exact three-dimensional solid state structure of complex \(2b\) was established by single crystal X-ray
analysis (Fig. 2). Suitable single crystal of complex \( \text{trans-}[\text{(Et}_3\text{P})_2\text{Pt}\{\text{C}≡\text{C}-\text{C}_6\text{H}_4-\text{CH}≡\text{CH(SC}_6\text{H}_4\text{CH}_3-p)}\}_2 \) (2b) was grown from ethylacetate/hexane solution, and molecular structure was determined in order to confirm the molecular geometry. Selected bond structural parameters are presented in Table 6. To the best of my knowledge, this molecule represents the first structurally characterized example of platinum(II) bis(alkenylarylalkynyl) complex containing one arylthio moiety in each alkenyl backbone. 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(II)

![Figure 2. X-ray ORTEP diagram of complex 2b.](image)

| Table 6. Selected bond lengths (Å) and angles (°) for complex 2b |
|------------------|------------------|------------------|
| Bond length      | Bond angles      |                  |
| Pt(1)–P(1)       | 2.295(6)         | P(1)–Pt(1)–P'(1) |
| Pt(1)–C(1)       | 1.996 (3)        | P(1)–Pt(1)–C(1) |
| S(1)–C(10)       | 1.744 (4)        | P(1)–Pt(1)–C(1) |
| S(1)–C(11)       | 1.770 (3)        | P'(1)–Pt(1)–C(1) |
| P(1)–C(18)       | 1.823 (3)        | P'(1)–Pt(1)–C'(1) |
| P(1)–C(20)       | 1.820 (3)        | C(1)–Pt(1)–C'(1) |
| P(1)–C(22)       | 1.823 (4)        | C(10)–S(1)–C(11) |
| C(1)–C(2)        | 1.209 (3)        | Pt(1)–C(1)–C(2) |
| C(2)–C(3)        | 1.434 (4)        | S(1)–C(10)–C(9) |
| C(6)–C(9)        | 1.469 (5)        | C(1)–C(2)–C(3) |
| C(9)–C(10)       | 1.353 (6)        | C(6)–C(9)–C(10) |

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°. The Pt–C bond distance (ca. 1.99 Å) and the Pt–P bond distance (ca. 2.3 Å) are comparable to the literature values reported in typical platinum(II) phosphine bis(alkynyl) systems. The C≡C bond length (ca. 1.2 Å) is characteristic of metal-acetylide bonding. The Pt–C–C fragment is
essentially linear (ca 178.4°) such that the molecule affords a rigid C−C−Pt−C−C linear chain. The shortest contacts are present in the crystal structure involving non-covalent intermolecular interactions such as the arylthio carbon (C14,15,16) to proton of ethyl phosphine (H20B) (2.881, 2.786, and 2.878 Å for C14, C15, and C16, respectively, to H20B) in adjacent molecules, sulfur (S1) to methyl proton (H17A) of thiol moiety (2.872 Å) and alkenyl proton (H9) to aryl carbon (C15) of thiol moiety (2.827 Å) and carbon of arene ring (C4) to proton of ethyl phosphine (H21A) (2.804Å) in adjacent molecules, proton (H16) of arenethiol moiety to carbon (C4) of arene ring (2.797 Å) and proton (H13) of arenethiol moiety to carbon (C6) of arene ring (2.777 Å) in adjacent one to another molecule (Fig. 3).

2.2.4 Optical Absorption and Emission Spectroscopy

The investigation of UV/Vis absorption spectroscopy of all the platinum(II) complexes was carried out at room temperature. For all eight trans-platinum(II) bis(alkenylarylalkynyl) complexes 2a-2h, the lowest energy absorption bands in the UV/Vis spectra in chloroform solution, at room temperature, occurred in the range 362-395 nm, as shown in Fig. 4. The values of $\lambda_{\text{max}}$ are reported in Table 7. The absorption bands are slightly influenced by the presence of different organic spacers. The lowest energy band, in each case, was tentatively assigned to a predominantly $\pi$(C≡C) $\rightarrow$ $\pi^*$ (C≡C) transition by comparison with related systems\textsuperscript{20,27}, but they can be considered to have some LMCT character resulting from the possible admixture of a platinum (n+1) $p$ orbitals and a ligand $\pi^*$ orbital,\textsuperscript{21} and their position moves to longer wavelengths due to coordination of acetylides ligand. As compared to the absorption band of platinum(II) bis(alkynylarylalkynyl)

![Figure 4. UV/Vis absorption spectra of complexes 2a-2h in CHCl$_3$ at room temperature](image-url)
Table 7. Absorption and emission data for complexes 2a-2h

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\lambda_{\text{max}}$ (nm) absorption</th>
<th>$\varepsilon$ ($10^4$ 1 mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm) emission</th>
<th>Stokes shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>366</td>
<td>5.1</td>
<td>399</td>
<td>0.28</td>
</tr>
<tr>
<td>2b</td>
<td>366</td>
<td>5.2</td>
<td>401</td>
<td>0.29</td>
</tr>
<tr>
<td>2c</td>
<td>364</td>
<td>7.9</td>
<td>411</td>
<td>0.39</td>
</tr>
<tr>
<td>2d</td>
<td>365</td>
<td>7.7</td>
<td>409</td>
<td>0.36</td>
</tr>
<tr>
<td>2e</td>
<td>362</td>
<td>6.3</td>
<td>407</td>
<td>0.38</td>
</tr>
<tr>
<td>2f</td>
<td>362</td>
<td>4.8</td>
<td>425</td>
<td>0.50</td>
</tr>
<tr>
<td>2g</td>
<td>395</td>
<td>4.6</td>
<td>425</td>
<td>0.22</td>
</tr>
<tr>
<td>2h</td>
<td>394</td>
<td>6.3</td>
<td>426</td>
<td>0.23</td>
</tr>
</tbody>
</table>

[i] The concentration is $1\times10^{-5}$ M in chloroform at room temperature.

Figure 5. Normalized optical absorption and photoluminescence spectra of complexes 2a-2h in CHCl$_3$ at room temperature under excitation in the range 362-395 nm: (a) 2a-2b; (b) 2c-2d; (c) 2e-2f; (d) 2g-2h.

complexes 1, it was found that the position of the lowest energy absorption bands are red-shifted in the
platinum(II) bis(alkenylarylalkynyl) complexes 2, after the functionalization of arenethiols into the platinum(II) complexes 1. The highest red-shift (27 nm) is observed for trans-platinum(II) complexes 2e and 2f. The UV/Vis absorption maxima of complexes 1a, 1b, 1c, and 1d are observed at 345, 356, 335, and 377 nm, respectively, and those of their corresponding thiolation adduct complexes 2a, 2b, 2c, 2d, 2e, 2f, 2g, and 2h are observed at 366, 366, 364, 365, 362, 362, 395, and 394 nm, respectively. In each case, a small red-shift is observed, and the shifts are 21, 21, 8, 9, 27, 27, 18, and 17 nm for complexes 2a, 2b, 2c, 2d, 2e, 2f, 2g, and 2h, as compared to complexes 1a, 1a, 1b, 1b, 1c, 1c, 1d, and 1d, respectively. This reveals that π-conjugation is preserved through the metal site by mixing of the frontier orbitals of metal and the ligand acetylides along connected with alkenylaryl group which contain one arenethio moiety in alkenyl backbone. K. S. Schanze et al. reported butyl phosphine containing trans-platinum(II) bis(alkenylarylalkynyl) complex, trans-[(PBu₃)₂Pt{C≡C-C₆H₄-CH=CH(Ph)}₂], having one phenyl ring in each alkenyl backbone which showed absorption maxima at 370 nm. As compared to trans-[(PBu₃)₂Pt{C≡C-C₆H₄-CH=CH(Ph)}₂] complex, sulfur-containing trans-platinum(II) complexes 2g and 2h indicated red-shift (25 and 24 nm) but the other six complexes showed slightly blue-shift (4-8 nm) in their UV/Vis spectra. The room temperature photoluminescence spectra in chloroform for trans-platinum(II) bis(alkenylarylalkynyl) complexes, 2a-2h are shown in Fig. 5. The photoluminescence spectra of the trans-platinum(II) bis(alkenylarylalkynyl) complexes were recorded using excitation at the wavelength of their absorption maximum (λ_max= 362-395 nm) which showed emission maxima in the spectral region 399-426 nm (Table 7). The room temperature photoluminescence spectra in chloroform for trans-platinum(II) complexes 2a-2h 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). No phosphorescence is observed for any of these materials at room temperature.

2.3 Conclusions

The author has developed a convenient method for the synthesis of a novel series of trans-platinum(II) bis(alkenylarylalkynyl) complexes having one arenethio moiety in each alkenyl backbone regioselectively by
photochemical reaction. All these newly synthesized platinum(II) complexes 2a-2l were isolated as a pale yellow to yellow solid with good (70%) to excellent (90%) yields. Addition reaction occurred at the terminal alkyne bond of trans-platinum(II) bis(alkynylarylalkynyl) complexes, because internal triple bond is sterically hindered. The trans-platinum(II) bis(alkynylarylalkynyl) complexes 2a-2h show no absorption bands over 395 nm, so they are transparent in a very large region. The UV/Vis absorption and emission spectra, in solution, at room temperature, are influenced by the nature of acetylide along with its substituents on the aryl ring and alkenyl backbone containing one arenethio moiety. It was found that the position of the lowest energy absorption bands are red-shifted in the platinum(II) bis(alkynylarylalkynyl) complexes 2, after the functionalization of arenethiol into the platinum(II) complexes 1. Complexes 2a-2h displayed emission band in the blue region of the electromagnetic spectra. The synthesized trans-platinum(II) bis(alkynylarylalkynyl) complexes 2a-2l were fully characterized by spectroscopic techniques as well as elemental analysis. The trans square-planar arrangement at the platinum centre was further confirmed by the molecular structure of the model complex 2b by single crystal X-ray diffraction.

2.4 Experimental Section

General

Solvents were dried, distilled from appropriate drying agents and degassed before use. All chemicals, except where stated, were purchased from commercial sources and used as received without further purification. The compounds HC≡C·C₆H₄·C≡CH,HC≡C·C₆H₄·C≡C·C≡CH,HC≡C·C₆H₂(p·CH₃)₂·C≡CH,HC≡C·C₆H₂(OCH₃·p)₂·C≡CH,trans-[(Et₃P)₂Pt{C≡≡≡≡C/C₆H₄/C≡CH}₂],\(^{10}\) trans-[(Et₃P)₂Pt{C≡C·C₆H₄·C≡C·CH}₂]\(^{10}\), \((p·CH₃)₂·C≡CH\) \(^{10}\), and \((p·OCH₃)₂·C≡CH\) \(^{10}\) were prepared by literature methods. NMR spectra were recorded on JEOL JNM-ECX 400 or JEOL JNM-ECS 400FT NMR spectrometer in appropriate solvents. \(^{31}\)P NMR spectra were referenced to external trimethylphosphite. \(^1\)H NMR spectra were referenced to internal TMS, and \(^{13}\)C NMR spectra were referenced to solvents resonances. Infrared spectra were recorded on Shimadzu FTIR-8400 spectrometer by using KBr pellets, and ESI-HR mass spectra were recorded on JEOL
Chapter 2: Synthesis, characterization and luminescence properties of thiolated platinum(II) acetylides

JMS-T100LC spectrometer. Microanalyses were performed on the analytical section of Osaka University. Electronic absorption spectra were recorded on JASCO, V-560, UV/Vis spectrometer and emission spectra were recorded on JASCO, FT-6300 spectrofluorometer. Column chromatography was performed on silica gel.

Synthesis of Platinum(II) Bis(alkenylarylalkynyl) Complexes (2)

Trans-[(Et₃P)₂Pt{C≡C-C₆H₄-CH=CH(SPh)}₂] (2a)

A mixture of trans-[(Et₃P)₂Pt{C≡C-C₆H₄-C≡CH}] (1a) (0.068 gm, 0.1 mmol) and benzenethiol (0.027 gm, 0.25 mmol) in chloroform-d (0.6 mL) degassed under nitrogen atmosphere was placed to a sealed Pyrex tube. The resulting mixture was irradiated with tungsten lamp for 3 h. Upon irradiation with tungsten lamp (500 W), cool water was passed on the sealed tube to maintain room temperature. The completion of the reaction was determined by TLC and ¹H NMR. The solvent was removed in vaccuo, and the resulting residue was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2a as a pale yellow solid in 82% yield (0.074 gm), E/Z ratio: 60/40. IR (solid state, KBr): ν 2099 cm⁻¹ (C≡C); ¹H NMR (400 MHz, CDCl₃): (E/Z ratio: 60/40): δ 7.45-7.18 (m, 18H, Ar/H, SPh), 6.80 (d, 1.20H, J_H/H = 15.6 Hz), 6.71 (d, 1.20H, J_H/H = 15.6 Hz), 6.54 (d, 0.80H, J_H/H = 10.8 Hz), 6.42 (d, 0.80H, J_H/H = 10.8 Hz), 2.21-2.13 (m, 12H, CH₂) and 1.27-1.17 (m, 18H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 8.23, 16.27, 109.73, 109.85, 121.66, 121.69, 124.57, 124.60, 125.68, 126.70, 127.05, 127.33, 128.27, 128.42, 129.06, 129.10, 129.44, 129.92 130.69, 131.08, 132.41, 133.14, 135.59 and 136.37 ppm; ³¹P NMR (161.83 MHz, CDCl₃): δ 11.65 (J_{Pt/P} = 2366 Hz) ppm; ESI-HRMS [M+Na]⁺ m/z = 924.2502 (100%), Calc. mass: 901.2633, Anal. Calc. for C₄₄H₃₂P₂PtS₂: C, 58.59; H, 5.81%. Found: C, 58.55; H, 5.88%; UV/Vis: λ_{max} (CHCl₃) = 366 nm, ε = 51688 (l mol⁻¹ cm⁻¹).

Similarly, the reaction was performed in toluene-d₈ and benzene-d₆ under the same conditions. The isolated yields were obtained in toluene-d₈ and benzene-d₆ as 66% (0.0597 gm) and 77% (0.0695 gm), respectively.

Trans-[(Et₃P)₂Pt{C≡C-C₆H₄-CH=CH(SC₆H₄CH₃-p)}₂] (2b)

A mixture of trans-[(Et₅P)₂Pt{C≡C-C₆H₄-C≡CH}] (1a) (0.068 gm, 0.1 mmol) and p-toluenethiol (0.031 gm, 22
0.25 mmol) in chloroform (0.6 mL) was degassed under nitrogen atmosphere and added to a sealed Pyrex tube. The resulting mixture was irradiated with tungsten lamp for 3 h. Upon irradiation with tungsten lamp (500 W), cool water was passed on the sealed tube to maintain room temperature. The completion of the reaction was determined by TLC and $^1$H NMR. The reaction product was evaporated to dryness. The crude product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2b as a yellow solid in 90% yield (0.084 gm), $E/Z$ ratio: 70/30. IR (solid state, KBr): ν 2101 (C≡C) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$); ($E/Z$ ratio: 70/30): δ 7.40-7.12 (m, 16H, Ar/H, SAr/H ), 6.76 (d, 1.40H, $J_{H-H} = 15.6$ Hz), 6.61 (d, 1.40H, $J_{H-H} = 15.6$ Hz), 6.47 (d, 0.60H, $J_{H-H} = 10.4$ Hz), 6.37 (d, 0.60H, $J_{H-H} = 10.8$ Hz), 2.33 (s, 6H, SAr/CH$_3$/p), 2.20/2.12 (m, 12H, CH$_2$) and 1.25/1.16 (m, 18H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 8.31, 16.28, 21.04, 109.42, 109.56, 109.70, 109.85, 122.73, 122.77, 125.55, 125.66, 126.54, 127.49, 127.97, 128.36, 129.86, 130.19, 130.36, 130.66, 131.04, 131.11 131.48, 132.78, 133.27, 136.99, and 137.24 ppm; $^{31}$P NMR (161.83 MHz, CDCl$_3$): δ 11.64 ($J_{Pt/P} = 2391$ Hz) ppm; ESI-HRMS [M]$^+$ m/z = 930.2908 (100%), Calc. mass: 930.0944, Anal. Calc. for C$_{46}$H$_{56}$P$_2$PtS$_2$: C, 59.40; H, 6.07%. Found: C, 59.40; H, 6.13%; UV/Vis: $\lambda_{max}$ (CHCl$_3$) = 366 nm, $\varepsilon$ = 52640 (l mol$^{-1}$ cm$^{-1}$).

**Trans-[{Et$_3$P)$_2$Pt\{C≡C-C$_6$H$_4$-C$_6$H$_4$-CH=CH(SPh)}$_2$]** (2c)

The synthetic procedure was the same as for the synthesis of platinum(II) complex 2a, but platinum(II) bis(acetylide) complex 1b, trans-[(Et$_3$P)$_2$Pt\{C≡C-C$_6$H$_4$-C$_6$H$_4$-C≡CH\}$_2$], was used instead of trans-[(Et$_3$P)$_2$Pt\{C≡C-C$_6$H$_4$-C≡CH\}$_2$], 1a, and reaction was carried out for 4 hours. The crude product was purified by column chromatography on silica gel eluting with hexane and dichloromethane, and gave the title complex 2c as a pale yellow solid in 90% yield (0.095 gm), $E/Z$ ratio: 60/40. IR (solid state, KBr): ν 2098 (C≡C) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$); ($E/Z$ ratio: 60/40): δ 7.63-7.24 (m, 26H, Ar/H, SPh), 6.91 (d, 1.20H, $J_{H-H} = 15.2$ Hz), 6.75 (d, 1.20H, $J_{H-H} = 15.2$ Hz), 6.61 (d, 0.80H, $J_{H-H} = 10.8$ Hz), 6.51 (d, 0.80H, $J_{H-H} = 10.8$ Hz), 2.21-2.18 (m, 12H, CH$_2$) and 1.28-1.20 (m, 18H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 8.36, 16.33, 109.42, 123.15, 125.92, 126.35, 126.39, 126.46, 126.54, 126.81, 126.91, 127.20, 128.05, 129.15, 129.74, 130.06, 131.23, 131.43, 135.15, 135.24, 136.18, 136.88, 137.03, 139.58 and 140.13 ppm; $^{31}$P NMR (161.83 MHz, CDCl$_3$): δ 11.70 ($J_{Pt-P} = 2391$ Hz) ppm; ESI-HRMS [M+Na]$^+$ m/z = 1076.2831 (20%), Calc.
mass: 1053.3259, Anal. Calc. for C_{56}H_{60}P_{2}PtS_{2}: C, 63.80; H, 5.74%. Found: C, 63.89; H, 5.92%; UV/Vis: \( \lambda_{\text{max}} \) (CHCl\(_3\)) = 364 nm, \( \varepsilon = 79751 \) (l mol\(^{-1}\) cm\(^{-1}\)).

**Trans-[(Et\(_3\)P)\(_2\)Pt{C≡C-C\(_6\)H\(_4\)-C\(_6\)H\(_4\)-CH≡CH(SC\(_6\)H\(_4\)-p-CH\(_3\)-)}\(_2\)] (2d)**

The same procedure as one for platinum(II) complex 2b was applied for the synthesis of 2d, but platinum(II) bis(acetylide) complex 1b, _trans-[(Et\(_3\)P)\(_2\)Pt{C≡C-C\(_6\)H\(_4\)-C\(_6\)H\(_4\)-C≡CH} \(_2\)]_, was used instead of _trans-[(Et\(_3\)P)\(_2\)Pt{C≡C-C\(_6\)H\(_4\)-C≡CH} \(_2\)], 1a, and the reaction was carried out for 5 hours. The crude product was purified by column chromatography on silica gel eluting with hexane and dichloromethane, and gave the title complex 2d as a pale yellow solid in 88% yield (0.095 gm), E/Z ratio: 60/40. IR (solid state, KBr): \( \nu \) 2092 (C≡C) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): (E/Z ratio: 60/40): \( \delta \) 7.62/7.14 (m, 24H, Ar/H, SAr/H), 6.88 (d, 1.20H, \( J_{H-H} = 15.6 \) Hz), 6.66 (d, 1.20H, \( J_{H-H} = 15.6 \) Hz), 6.55 (d, 0.80H, \( J_{H-H} = 10.8 \) Hz), 6.46 (d, 0.80H, \( J_{H-H} = 11.2 \) Hz), 2.34 (s, 6H, SAr/CH\(_3\)/p), 2.21/2.17 (m, 12H, CH\(_2\)) and 1.28/1.19 (m, 18H, CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 8.34, 16.30, 21.07, 109.09, 109.18, 109.23, 109.42, 124.23, 126.05, 126.26, 126.31, 126.43, 126.51, 126.85, 126.95, 127.98, 129.09, 129.93, 130.08, 130.47, 130.51, 131.12, 131.21, 132.61, 135.24, 135.28, 136.91, 137.04, 137.23, 137.38, 139.42 and 139.88 ppm; \(^{31}\)P NMR (161.83 MHz, CDCl\(_3\)): \( \delta \) 11.73 (\( J_{Pt-P} = 2371 \) Hz) ppm; ESI-HRMS [M]\(^+\) \( m/z = 1082.3601 \) (100%), Calc. mass: 1082.2863, Anal. Calc. for C\(_{58}\)H\(_{64}\)P\(_2\)PtS\(_2\): C, 64.37; H, 5.96%. Found: C, 63.42; H, 6.29%; UV/Vis: \( \lambda_{\text{max}} \) (CHCl\(_3\)) = 365 nm, \( \varepsilon = 77905 \) (l mol\(^{-1}\) cm\(^{-1}\)).

**Trans-[(Et\(_3\)P)\(_2\)Pt{C≡C-C\(_6\)H\(_2\)(CH\(_3\)-p)-CH≡CH(SPh)}\(_2\)] (2e)**

The same procedure as one for platinum(II) complex 2a was followed for the synthesis of 2e, but platinum(II) bis(acetylide) complex 1c, _trans-[(Et\(_3\)P)\(_2\)Pt{C≡C-C\(_6\)H\(_2\)(p-CH\(_3\))\(_2\)-C≡CH} \(_2\)], was used instead of _trans-[(Et\(_3\)P)\(_2\)Pt{C≡C-C\(_6\)H\(_4\)-C≡CH} \(_2\)], 1a. The crude product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2e as a pale yellow solid in 85% yield (0.081 gm), E/Z ratio: 89/11. IR (solid state, KBr): \( \nu \) 2090 (C≡C) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): (E/Z ratio: 89/11): \( \delta \) 7.44-7.08 (m, 14H, Ar-H, SPh), 6.95 (d, 1.77H, \( J_{H-H} = 14.8 \) Hz), 6.72 (d, 1.77H, \( J_{H-H} = 15.2 \) Hz), 6.66 (d, 0.23H, \( J_{H-H} = 10.8 \) Hz), 6.45 (d, 0.23H, \( J_{H-H} = 10.0 \) Hz), 2.43 (s, 0.69H, Ar-p-CH\(_3\)), 2.37
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(s, 5.31H, Ar-p-CH₃), 2.26 (s, 6H, Ar-p-CH₃), 2.17-2.13 (m, 12H, CH₂) and 1.23-1.15 (m, 18H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 8.29, 16.24, 19.24, 19.38, 20.81, 20.93, 108.61, 113.50, 122.08, 124.92, 125.76, 126.26, 126.51, 126.79, 128.19, 129.10, 129.71, 130.73, 131.85, 131.89, 131.93, 132.73, 133.05, 135.64, 136.00, 136.23 and 136.57 ppm; ³¹P NMR (161.83 MHz, CDCl₃): δ 12.18 (Jₚt/P = 2380 Hz) ppm; ESI-HRMS [M+Na]⁺ m/z = 980.3151 (98%), Calc. mass: 957.3259, Anal. Calc. for C₄₈H₆₀P₂PtS₂: C, 60.17; H, 6.31%. Found: C, 59.80; H, 6.36%. UV/Vis: λᵢₜₐₜₕ(CHCl₃) = 362 nm, ε = 63492 (l mol⁻¹ cm⁻¹).

Trans-[{(Et₃P)₂Pt{C≡≡≡C-C₆H₂(OCH₃)₂-C≡CH(SPh)}₂]} (2f)

The synthetic procedure was the same as the synthesis of platinum(II) complex 2b, but platinum(II) bis(acetylide) complex 1c, trans-[(Et₃P)₂Pt{C≡≡≡C-C₆H₂(OCH₃)₂-C≡CH}₂], was used instead of trans-[(Et₃P)₂Pt{C≡≡≡C-C₆H₂(p-CH₃)₂-C≡CH}₂], 1a. The crude product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2f as a pale yellow solid in 83% yield (0.082 gm), E/Z ratio: 56/44. IR (solid state, KBr): ν 2091 (C≡C) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): (E/Z ratio: 56/44): δ 7.37/7.07 (m, 12H, Ar/H, SAr/H), 6.88 (d, 1.12H, Jₕ₁-H₁ = 15.6 Hz), 6.69 (d, 1.12H, Jₕ₁-H₁ = 15.6 Hz), 6.60 (d, 0.88H, Jₕ₁-H₁ = 10.4 Hz), 6.41 (d, 0.88H, Jₕ₁-H₁ = 10.8 Hz), 2.43 (s, 2.65H, Ar-CH₃-p), 2.36 (s, 3.35H, Ar-CH₃-p), 2.33 (s, 6H, SAr-CH₃-p), 2.24 (s, 6H, Ar-CH₃-p), 2.19-2.11 (m, 12H, CH₂) and 1.23-1.15 (m, 18H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 8.30, 16.24, 19.24, 19.39, 20.81, 20.94, 21.03, 108.56, 108.76, 112.60, 113.30, 113.49, 123.14, 123.20, 125.40, 125.87, 125.90, 127.68, 127.72, 127.98, 128.03, 128.90, 129.49, 129.52, 129.80, 130.19, 131.72, 131.76, 131.80, 132.02, 132.70, 133.02, 133.64, 136.20, 136.75 and 136.95 ppm; ³¹P NMR (161.83 MHz, CDCl₃): δ 12.17 (Jₚt-P = 2404 Hz) ppm; ESI-HRMS [M]⁺ m/z = 986.3549 (100%), Calc. mass: 986.2007, Anal. Calc. for C₅₀H₆₄P₂PtS₂: C, 60.89; H, 6.54%. Found: C, 60.82; H, 6.59%. UV/Vis: λᵢₜₐₕ(CHCl₃) = 362 nm, ε = 48829 (l mol⁻¹ cm⁻¹).

Trans-[{(Et₃P)₂Pt{C≡C-C₆H₄(OCH₃-p)₂-C≡CH(SPh)}₂]} (2g)

The same procedure as one for platinum(II) complex 2a was applied for the synthesis of 2g, but platinum(II) bis(acetylide) complex 1d, trans-[(Et₃P)₂Pt{C≡C-C₆H₄(p-OCH₃)₂-C≡CH}₂], was used instead of trans-[(Et₃P)₂Pt{C≡C-C₆H₄-p-C≡CH}₂], 1a. The crude product was purified by column chromatography on
silica gel eluting with hexane and ethyl acetate, and gave the title complex 2g as a yellow solid in 84% yield (0.086 gm), $E/Z$ ratio: 94/6. IR (solid state, KBr): $\nu$ 2096 (C≡C) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): ($E/Z$ ratio: 94/6): $\delta$ 7.47-7.20 (m, 10H, SPh), 7.03 (d, 1.88H, $J_{\text{H-H}} = 15.6$ Hz), 6.89 (d, 1.88H, $J_{\text{H-H}} = 15.6$ Hz), 6.82 (d, 0.12H, $J_{\text{H-H}} = 12.8$ Hz), 6.80 (s, 2H, Ar-H), 6.78 (s, 2H, Ar-H), 6.44 (d, 0.12H, $J_{\text{H-H}} = 10.4$ Hz), 3.85/3.77 (12H, Ar/OCH$_3$), 2.29/2.21 (m, 12H, CH$_2$) and 1.26/1.18 (m, 18H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.38, 16.09, 56.12, 105.41, 109.17, 115.91, 118.34, 122.32, 122.93, 126.44, 128.08, 128.98, 129.15, 129.91, 136.12, 150.47 and 154.39 ppm; $^{31}$P NMR (161.83 MHz, CDCl$_3$): $\delta$ 11.81 ($J_{\text{Pt-P}} = 2367$ Hz) ppm; ESI-HRMS [M+Na]$^+$ m/z = 1044.2886 (92%), Calc. mass: 1021.3056, Anal. Calc. for C$_{48}$H$_{60}$O$_4$P$_2$PtS$_2$: C, 56.40; H, 5.92%. Found: C, 56.33; H, 6.00%; UV/Vis: $\lambda_{\text{max}}$ (CHCl$_3$) = 395 nm, $\epsilon$ = 46124 (l mol$^{-1}$ cm$^{-1}$).

Trans-[($\text{Et}_3\text{P})_2\text{Pt}\{\text{C≡C-C}_6\text{H}_2(\text{OCH}_3)\}_2-\text{CH}]=\text{CH}(\text{SC}_6\text{H}_4\text{CH}_3\text{p}-\text{p})]_2$] (2h)

The same procedure as one for platinum(II) complex 2b was followed for the synthesis of 2g, but platinum(II) bis(acetylide) complex 1d, trans-[$($Et$_3P$)$_2$Pt{C≡C-C$_6$H$_2$(p-OCH$_3$)$_2$-C≡CH}$]$_2$, was used instead of trans-[$($Et$_3P$)$_2$Pt{C≡C-C$_6$H$_4$-C≡CH}$]$_2$, 1a. The crude product was purified by column chromatography on silica gel eluting with hexane and dichloromethane, and gave the title complex 2h as a yellow solid in 87% yield (0.091 gm), $E/Z$ ratio: 81/19. IR (solid state, KBr): $\nu$ 2094 (C≡C) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): (E/Z ratio: 94/6): $\delta$ 3.76-7.30 (m, 4H, SAr-H), 7.20-7.13 (m, 4H, SAr-H), 6.96 (d, 1.62H, $J_{H-H} = 15.6$ Hz), 6.86 (d, 1.62H, $J_{H-H} = 15.6$ Hz), 6.80 (d, 0.38H, $J_{H-H} = 9.2$ Hz), 6.79-6.76 (4H, Ar-H), 6.40 (d, 0.38H, $J_{H-H} = 11.2$ Hz), 3.85-3.76 (12H, Ar-OCH$_3$), 2.33 (s, 6H, SAr-CH$_3$), 2.29-2.21 (m, 12H, CH$_2$) and 1.26-1.17 (m, 18H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.39, 16.13, 21.03, 56.17, 56.24, 105.43, 105.57, 109.16, 111.90, 114.21, 114.35, 115.27, 115.99, 118.13, 121.40, 123.11, 123.16, 123.44, 123.48, 125.60, 126.85, 129.79, 129.92, 130.41, 132.14, 132.90, 136.72, 137.18, 150.07, 150.42, 154.00 and 154.43 ppm; $^{31}$P NMR (161.83 MHz, CDCl$_3$): $\delta$ 11.81 ($J_{\text{Pt-P}} = 2371$ Hz) ppm; ESI-HRMS [M]$^+$ m/z = 1050.3336 (100%), Calc. mass: 1050.1983, Anal. Calc. for C$_{50}$H$_{64}$O$_4$P$_2$PtS$_2$: C, 57.18; H, 6.14%. Found: C, 57.05; H, 6.22%; UV/Vis: $\lambda_{\text{max}}$ (CHCl$_3$) = 394 nm, $\epsilon$ = 63806 (l mol$^{-1}$ cm$^{-1}$).
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Trans-\{(Et_3P)_2Pt\{C≡C-C_6H_4-CH=CH(SC_{10}H_7)\}_2\} (2i)

A mixture of trans-\{(Et_3P)_2Pt\{C≡C-C_6H_4-C≡CH\}_2\} (1a) (0.068 gm, 0.1 mmol) and 2-naphthalenethiol (0.040 gm, 0.25 mmol) in chloroform (1 mL) was degassed under nitrogen atmosphere and added to a sealed Pyrex tube. The resulting mixture was irradiated with tungsten lamp for 8 h. Upon irradiation with tungsten lamp (500 W), cool water was passed on the sealed tube to maintain room temperature. The completion of the reaction was determined by TLC and \(^1\)H NMR. The reaction product was evaporated to dryness. The crude product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2i as a yellow solid in 75% yield (0.075 gm), \(E/Z\) ratio: 63/37. IR (solid state, KBr): \(\nu\ 2099\ (C≡C)\ \text{cm}^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(E/Z\) ratio: 63/37): \(\delta\ 7.89/7.73\ (m, 8H, SAr/H), 7.52/7.22\ (m, 14H, SAr/H, Ar/H), 6.88 (d, 1.25H, \(J_{H-H} = 15.6\ \text{Hz}\)), 6.76 (d, 1.25H, \(J_{H-H} = 15.6\ \text{Hz}\)), 6.59 (d, 0.75H, \(J_{H-H} = 10.8\ \text{Hz}\)), 6.51 (d, 0.75H, \(J_{H-H} = 11.2\ \text{Hz}\)), 2.21/2.12 (m, 12H, CH\(_2\)) and 1.27/1.17 (m, 18H, CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\ 8.32, 16.31, 109.74, 109.78, 109.85, 109.92, 121.35, 121.40, 124.27, 125.75, 125.93, 126.12, 126.63, 126.69, 127.19, 127.27, 127.30, 127.55, 127.58, 127.70, 127.81, 128.21, 128.32, 128.47, 128.63, 128.74, 130.71, 131.09, 132.04, 132.14, 132.82, 132.86, 132.99, 133.11, 133.61 and 133.73 ppm; \(^{31}\)P NMR (161.83 MHz, CDCl\(_3\)): \(\delta\ 11.67\ (J_{Pt-P} = 2366\ \text{Hz})\) ppm; ESI-HRMS \([\text{M+Na}]^+\ m/z = 1025.2781\ (100\%),\ \text{Calc. mass:} 1002.1586,\ \text{Anal. Calc. for} \ C_{52}H_{56}P_{2}PtS_{2}:\ C, 62.32; H, 5.63\%\). Found: C, 61.94; H, 5.52\%.

Trans-\{(Et_3P)_2Pt\{C≡C-C_6H_4C_6H_4-CH=CH(SC_{10}H_7)\}_2\} (2j)

The complex 2j was synthesized using similar procedure as described above for 2i, but platinum(II) bis(acetylide), trans-\{(Et_3P)_2Pt\{C≡C-C_6H_4C_6H_4-C≡CH\}_2\} (1b), was used instead of trans-\{(Et_3P)_2Pt\{C≡C-C_6H_4-C≡CH\}_2\} (1a). The crude product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2j as a yellow solid in 70% yield (0.081 gm), \(E/Z\) ratio: 55/45. IR (solid state, KBr): \(\nu\ 2098\ (C≡C)\ \text{cm}^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(E/Z\) ratio: 55/55): \(\delta\ 7.93/7.33\ (m, 30H, SAr/H, Ar/H), 7.00\ (d, 1.10H, \(J_{H-H} = 15.2\ \text{Hz}\)), 6.81 (d, 1.10H, \(J_{H-H} = 15.6\ \text{Hz}\)), 6.67 (d, 0.90H, \(J_{H-H} = 10.8\ \text{Hz}\)), 6.61 (d, 0.90H, \(J_{H-H} = 10.4\ \text{Hz}\)), 2.20-2.10 (m, 12H, CH\(_2\)) and 1.28-1.20 (m, 18H, CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\ 8.36, 16.34, 109.42, 122.89, 125.60, 126.06, 27
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126.36, 126.46, 126.56, 126.68, 126.74, 126.93, 127.26, 127.36, 127.50, 127.74, 128.03, 128.43, 128.73, 128.82, 129.21, 131.24, 131.84, 132.15, 132.22, 132.62, 133.46, 133.63, 133.75, 135.12, 136.86, 137.02, 139.68, and 140.22 ppm; $^{31}$P NMR (161.83 MHz, CDCl$_3$): $\delta$ 11.70 ($J_{Pt/P}$ = 2366 Hz) ppm; ESI-HRMS [M]$^+$ m/z = 1154.3609 (55%), Calc. mass: 1154.3505, Anal. Calc. for C$_{64}$H$_{64}$P$_2$PtS$_2$: C, 66.59; H, 5.59%. Found: C, 66.14; H, 5.60%.

**Trans-[(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_2$(CH$_3$)$_2$-CH=CH(SC$_{10}$H$_7$)}$_2$] (2k)**

The complex 2k was synthesized using similar procedure as described above for 2i, but platinum(II) bis(acetylide), *trans*-[{(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_2$(CH$_3$)$_2$-C≡CH}]$_2$] (1c) was used instead of *trans*-[{(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C≡CH}]$_2$} (1a). The crude product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2k as a pale yellow solid in 83% yield (0.088 gm), E/Z ratio: 84/16. IR (solid state, KBr): ν 2088 (C≡C) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): (E/Z ratio: 84/16): $\delta$ 7.88-7.74 (m, 8H, SAr/H), 7.51-7.42 (m, 6.34H, SAr/H, Ar/H), 7.28 (s, 1.67H, Ar/H), 7.14 (s, 0.33H, Ar-H), 7.10 (s, 1.67H, Ar-H), 7.03 (d, 1.67H, $J_{H-H} = 15.6$ Hz), 6.82 (d, 1.67H, $J_{H-H} = 15.6$ Hz), 6.73 (d, 0.33H, $J_{H-H} = 10.8$ Hz), 6.56 (d, 0.90H, $J_{H-H} = 10.4$ Hz), 2.46-2.28 (12H, Ar/CH$_3$), 2.18-2.12 (m, 12H, CH$_2$) and 1.23-1.15 (m, 18H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.32, 16.28, 19.28, 19.43, 20.83, 20.97, 108.64, 113.69, 121.78, 124.58, 125.84, 125.87, 125.99, 126.63, 126.78, 127.00, 127.07, 127.17, 127.28, 127.52, 127.73, 127.90, 128.35, 128.57, 128.63, 129.03, 130.36, 131.29, 131.64, 131.89, 131.97, 132.07, 132.79, 132.82, 133.10, 133.55, 133.66, 133.77, 133.94, 135.71 and 136.30 ppm; $^{31}$P NMR (161.83 MHz, CDCl$_3$): $\delta$ 12.21 ($J_{Pt-P}$ = 2384 Hz) ppm; ESI-HRMS [M]$^+$ m/z = 1058.3519 (100%), Calc. mass: 1058.2649, Anal. Calc. for C$_{56}$H$_{64}$P$_2$PtS$_2$: C, 63.56; H, 6.10%. Found: C, 63.58; H, 6.14%.

**Trans-[(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_2$(OCH$_3$)$_2$-CH=CH(SC$_{10}$H$_7$)}$_2$] (2l)**

The complex 2l was synthesized using similar procedure as described above for 2i, but platinum(II) bis(acetylide), *trans*-[{(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_2$(OCH$_3$)$_2$-C≡CH}]$_2$] (1d) was used instead of *trans*-[{(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C≡CH}]$_2$} (1a). The crude product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate, and gave the title complex 2l as a pale yellow solid in 78%
yield (0.087 gm), E/Z ratio: 78/22. IR (solid state, KBr): ν 2093 (C≡C) cm⁻¹; ^{1}H NMR (400 MHz, CDCl₃): (E/Z ratio: 78/22): δ 7.91-7.75 (m, 8H, SAr-H ), 7.54-7.42 (m, 6H, SAr-H), 7.09 (d, 1.55H, J₇₈-H = 15.6 Hz), 6.98 (d, 1.55H, J₇₈-H = 15.2 Hz), 6.92 (d, 0.35H, J₇₈-H = 10.8 Hz), 6.83-6.81 (m, 4H, Ar-H), 6.55 (d, 0.45H, J₇₈-H = 10.4 Hz), 3.88-3.79 (12H, Ar-OCH₃), 2.30-2.22 (m, 12H, CH₂) and 1.27-1.18 (m, 18H, CH₃) ppm; ^{13}C NMR (100 MHz, CDCl₃): δ 8.40, 16.13, 56.14, 56.17, 56.21, 105.46, 109.33, 111.97, 115.25, 115.93, 118.43, 122.10, 122.15, 122.76, 122.93, 124.23, 125.81, 126.08, 126.58, 126.67, 127.18, 127.21, 127.30, 127.60, 127.71, 128.22, 128.53, 128.60, 128.68, 131.98, 132.13, 133.58, 133.64, 133.75, 150.55, 150.58, 154.00 and 154.42 ppm; ^{31}P NMR (161.83 MHz, CDCl₃): δ 11.83 (JPt-P = 2366 Hz) ppm; ESI-HRMS [M]+ m/z = 1122.3297 (100%), Calc. mass: 1122.2625, Anal. Calc. for C₅₆H₆₄O₄P₂PtS₂: C, 59.93; H, 5.75%. Found: C, 60.01; H, 5.78%.

Single-Crystal Structure Determination for 2b: The crystal of C₄₆H₅₆P₂PtS₂ with approximate dimensions of 0.150 x 0.120 x 0.030 mm was mounted on a glass fiber. Crystal data, data collection parameters and refinement results of the analysis are listed in Table 8. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation. The data were collected at a temperature of -150 ±1°C to a maximum 2θ value of 55.0⁰. A total of 192 oscillation images were collected. The exposure rate was 30.0 sec./°. The crystal-to-detector distance was 127.40 mm. The exposure rate was 30.0 sec./°. The crystal-to-detector distance was 127.40 mm. The structure was solved by direct methods (SIR2011)²⁸ and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined with the riding model. The final cycle was subjected to full-matrix least-squares refinement (SHELXL-2013)²⁹ on F². All calculations were performed with the Crystal Structure crystallographic software package except for refinement, which was performed with SHELXL-2013.²⁹

<table>
<thead>
<tr>
<th>Table 8. Summary of crystal structure data for complex 2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
</tr>
</tbody>
</table>
Crystal dimensions (mm)  0.200 × 0.170 × 0.030
Crystal system  Monoclinic
Space group  \( P2_1/c \) (#14)
\( a \) (Å)  16.4001 (3)
\( b \) (Å)  10.1416 (2)
\( c \) (Å)  14.1993 (3)
\( \beta \) (°)  109.0620 (7)
Volume (Å\(^3\))  2232.18 (8)
\( Z \)  2
\( D \) (calc. g/cm\(^3\))  1.384
\( F \) (000)  944.00
\( \mu \) (Mo Kα) (cm\(^{-1}\))  33.248
Reflections collected  37681
Unique reflections  5110
\( R_{int} \)  0.0456
Number of parameters  236
Absorption correction  Empirical
Goodness-of-fit  1.086
\( R1 \)  0.0263
\( wR2 \)  0.0702
Largest diff. Peak and hole (e Å\(^3\))  2.27 and −0.86

### 2.5 References


Chapter 3

The Palladium-Catalyzed Dithiolated Novel Platinum(II) Bis(alkenylarylalkynyl) Complexes: Synthesis, Characterization and Photoluminescence Properties

3.1 Introduction

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 construct such novel metal-alkyne conjugated systems. There are many reactions for forming M-C≡C bonds that are useful for synthesis of a wide variety of conjugated systems containing transition metals and alkynyl groups.\(^1,2,3,4\) The linear geometry of the alkynyl unit and its π-unsaturated character make metal alkynyl compounds attractive for synthetic organometallic chemistry, because they exhibit numerous fascinating physical and chemical properties. A great deal of attention has been devoted to synthesis of new π–conjugated systems (complexes, oligomers, and polymers) involving σ–bonds between transition metals and alkynyl groups, because of their material and optoelectronic properties.\(^5,6,7\) Sulfur-rich π–conjugated metal complexes are also important as they exhibit good optical nonlinearity.\(^8\) Among these, the platinum(II) bis(phosphine) bis(alkynyl) system, with its simple square planar geometry, has been widely explored.\(^9,10\)

Insertion of carbon-carbon (CC) multiple bonds into a metal-heteroatom bond is a key-step of transition-metal-catalyzed heterofunctionalization of alkynes, and alkenes.\(^11\) An excellent model for the study of catalytic carbon-heteroatom bond formation is alkyne insertion into the metal-sulfur bond. Nowadays transition-metal-catalyzed S-S bond addition to alkynes is a versatile approach to vinyl sulfides, which combines 100% atom efficiency with excellent stereoselectivity and high yields. Convenient synthetic methods were developed to carry out stereoselective addition of S-S bond to terminal alkynes. The first study of [Pd(PPh\(_3\))\(_4\)]-catalyzed diaryl dichalcogenide addition to terminal alkynes leading to formation of
vinyl chalcogenide with high selectivity and yields was reported by Ogawa, Sonoda et al.\textsuperscript{11e} Catalytic activity of Rh complexes in this reaction was established by Yamaguchi et al.\textsuperscript{11f} For synthetic purposes microwave-assisted synthesis,\textsuperscript{11g} solvent-free reactions,\textsuperscript{11h} Ni catalyst,\textsuperscript{11i} and polymer-supported catalysts,\textsuperscript{11j} were developed for the addition reactions involving terminal alkynes.

In synthetic, organometallic, and materials chemistry, development of highly selective methods for introducing heteroatom groups into carbon-carbon unsaturated bonds of metal-alkynyl complexes is of special interest, because the newly designed organometallic compounds containing multifunctional systems may allow conjugation through a metal center to an organic spacer. Although the palladium-catalyzed 1,2-dithiolation of terminal alkyl/arylalkynes is well preceded in organic synthesis,\textsuperscript{11} it has not been previously reported with regard to any compounds containing metal ethynyl complexes or metal complexes.

In this chapter, for the first time, the author reports the synthesis of sulfur-containing platinum(II) bis(alkenylarylalkynyl) complexes, $\text{trans-}[\text{(R}_3\text{P})_2\text{Pt}(\text{C}≡\text{C}-\text{Ar}-\text{C(SPh)=CH(SPh)})_2]$ (3) (Ar = phenylene or biphenylene and R = Et or Ph), with two phenylthio moieties in each alkenyl backbone by palladium-catalyzed addition of diphenyl disulfide to platinum(II) bis(alkynylarylalkynyl) complexes (Fig. 1).

![Figure 1. The skeleton structure of novel trans-platinum(II) complexes 3](image)

### 3.2 Results and Discussion

#### 3.2.1 Syntheses and Scope

When diphenyl disulfide reacts with a platinum(II) complex containing an extended alkynyl ligand, $\text{trans-}(\text{Et}_3\text{P})_2\text{Pt}(\text{C≡C-C}_6\text{H}_4\text{-C≡CH})_2$, (1a) in the presence of a tetrakis(triphenylphosphine)palladium(0) catalyst, the addition reaction proceeded to afford a novel bis-disulfide addition product (3a), a sulfur-containing platinum(II) bis(alkenylarylalkynyl) complex, in good yield (73%, isolated yield, Scheme 1; entry 1, Table 1). Its structure was confirmed unambiguously by X-ray analysis and was also characterized by UV/Vis, IR, multi-nuclear NMR spectroscopy and ESI-HR mass spectrometry as well as elemental analysis.
Scheme 1. Palladium-catalyzed addition of diphenyl disulfide to platinum(II) bis(alkynylaryalkynyl) complex

Table 1. Optimization of the Pd-catalyzed addition reaction of diphenyl disulfide with platinum bis(acetylide) in various solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pt-acetylide, 1a (μmol)</th>
<th>(SPh)₂</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>2.2</td>
<td>Benzene</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>2.2</td>
<td>Toluene</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>2.2</td>
<td>1,2-Dichloroethane</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>2.2</td>
<td>Chloroform</td>
<td>0</td>
</tr>
</tbody>
</table>

[a] All the reactions were carried out at 90°C for 24 hours using 5 mol% of Pd(PPh₃)₄. [b] Isolated yield.

Furthermore, the effect of various solvents was examined under similar conditions (Table 1). Benzene was found to be the best solvent (isolated yield 73%, entry 1, Table 1), although the addition reaction also proceeded smoothly in toluene (isolated yield 72%, entry 2, Table 1). However, chloroform was not a suitable solvent for this addition reaction (entry 4, Table 1). Tetrakis(triphenylphosphine)palladium(0) catalyst could not perform well as a catalyst with this solvent due to the low boiling point of chloroform.

Under the optimized reaction conditions, bis-dithiolation of several platinum acetylides, trans-(R₃P)₂Pt(C≡C-Ar-C≡CH)₂ (where, Ar = phenylene or biphenylene and R = Et or Ph) were also examined (Scheme 2), and the results are summarized in Table 2. The scope of this reaction is quite general. This methodology tolerates platinum(II) acetylide complexes 1, with extended alkynyl ligands of diterminal acetylides, containing two different arene rings and two different phosphine groups. The yields of the isolated addition products range from moderate to high. Platinum(II) acetylides with ethyl phosphine groups on the platinum centre provided moderate (complex 3c, 55% isolated yield, entry 3, Table 2) to high yields (complex 3a, 73% isolated yield, entry 1, Table 2) of bis-disulfide addition product. Platinum(II) acetylides with phenyl phosphine groups on the platinum centre provided moderate (complex 3d, 49% isolated yield, entry 2, Table 2) to good yields (complex 3b, 82% isolated yield, entry 2, Table 2) of bis-disulfide addition.
product. The addition reaction proceeded preferentially toward the syn-addition at the terminal extended alkynes of platinum(II) complexes, because the internal triple bond is sterically hindered.

\[
\begin{align*}
\text{HCC} & \text{Ar} = \text{phenylene, biphenylene and R = Et, Ph} \\
\text{Scheme 2. Palladium-catalyzed addition of diphenyl disulfide to various platinum(II) bis(alkynylaryalkynyl) complexes}
\end{align*}
\]

**Table 2. Optimized Pd-catalyzed addition reaction of diphenyl disulfide with various platinum bis(acetylides)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>1, Ar in Pt-complex, trans-(R,P)Pt(C≡C-Ar-C≡CH)₂</th>
<th>1, R in Pt-complex, trans-(R,P)Pt(C≡C-Ar-C≡CH)₂</th>
<th>Yield (%)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenylene (1a)</td>
<td>C₂H₅</td>
<td>73 (3a)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Phenylene (1b)</td>
<td>C₆H₅</td>
<td>82 (3b)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Biphenylene (1c)</td>
<td>C₂H₅</td>
<td>55 (3c)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Biphenylene (1d)</td>
<td>C₆H₅</td>
<td>49 (3d)</td>
<td></td>
</tr>
</tbody>
</table>

[a] All reactions were carried out in 2 mL benzene, 6 mg of Pd(PPh₃)₄, 0.05 mmol platinum bis(acetylides), and 2.2 equivalents of (SPh)₂ at 90 °C for 24 h. [b] Isolated yield. [c] Syn-addition product along with anti-isomer (2:1, by ³¹P NMR).

All these newly synthesized compounds (3) were isolated as yellow solids with yields ranging from 49 to 82%. They display good solubility in common organic solvents but are insoluble in hexane. All trans-platinum(II) complexes (3) provided good satisfactory microanalyses. All of these trans-platinum(II) complexes are air-stable. The identity of these synthesized trans-platinum(II) complexes were based on their IR, ¹H and ³¹P NMR spectra and positive ESI-MS [M+Na]⁺ mass spectra.

### 3.2.2 Spectroscopic Characterization

The author has initially confirmed the structure of the addition product based on the basis of the absence of an acetylenic proton peak in the ¹H NMR spectrum. The IR spectrum of the platinum(II) complexes 3 provided important information, confirming that the addition reaction proceeded only at the terminal alkyne bond of the platinum(II) complexes 1. The IR spectrum of the platinum(II) complex 3a has no bands in the range 3200–3300 cm⁻¹, characteristic of acetylenic protons, but it has a strong peak at 2098 cm⁻¹, confirming
the bond between platinum and acetylenic carbon (Pt-C≡C) retained on the newly formed platinum complex 3a (Scheme 2). So, the IR spectra of platinum(II) complex 3a provided important information, confirming that the addition reaction proceeded only at the terminal alkyne bond of platinum(II) bis(alkynylarylalkynyl) complex 1a and internal triple bond is preserved on the newly formed platinum complex 3a. The $^{31}$P NMR spectrum of the platinum complex has the expected signal consisting of three lines due to coupling with $^{195}$Pt. The trans geometry around the platinum-diphosphine centre was confirmed by $^{31}$P NMR spectroscopy based on the basis of the $J_{Pt-P}$ coupling constant.\textsuperscript{12,13} The $J_{Pt-P}$ value obtained (2366 Hz) for complex 3a is in agreement with the values previously reported for other square-planar platinum(II) complexes with trans geometry; cis coupling constants are generally much larger (about 3500 Hz).\textsuperscript{12} The IR, $^1$H and $^{31}$P NMR spectra of the other three complexes display signals in the expected regions. In the $^{31}$P NMR spectrum of complex 3a, there are two singlets at 11.62 and 11.67 ppm, indicating that the reaction product contains a mixture of syn- and anti-addition products. The other three complexes (compounds 3b, 3c, and 3d) display only one singlet, indicating that the syn addition proceeded smoothly.\textsuperscript{13} C NMR spectroscopy was performed for all complexes, but, in the $^{13}$C NMR spectra, some peaks are merged together, because of the very close environment of the carbon atoms on different aromatic rings.

The molecular formula for the complexes were also established by the intense molecular ion [M+Na]$^+$ peaks in the positive-ion ESI-HR mass spectra, which were observed at $m/z$ 1141.2467 for 3a, at $m/z$ 1429.2299 for 3b, at $m/z$ 1293.3312 for 3c, and at $m/z$ 1581.2714 for 3d.

### 3.2.3 X-ray Crystallography

The exact three-dimensional solid-state structure of model complex 3a was established by single-crystal X-ray diffraction analysis (Figure 2). Suitable single crystal of complex trans-[((Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C(SC$_6$H$_5$)=CH(SC$_6$H$_5$)}$_2$] (3a) was grown from ethylacetate/hexane solutions, and crystal and molecular structure was resolved in order to confirm the molecular geometry. Selected bond structural parameters are presented in Table 3. To the best of my knowledge, this molecule represents the first structurally characterized example of platinum(II) bis(alkenylarylalkynyl) complex containing two phenylthio moieties.
Table 3. Selected bond lengths (Å) and angles (°) for complex 3a

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1)−P(1)</td>
<td>P(1)−P(1)−P(1)</td>
</tr>
<tr>
<td>2.305 (14)</td>
<td>180.00 (7)</td>
</tr>
<tr>
<td>Pt(1)−C(1)</td>
<td>P(1)−P(1)−C(1)</td>
</tr>
<tr>
<td>1.985 (5)</td>
<td>88.76 (15)</td>
</tr>
<tr>
<td>S(1)−C(9)</td>
<td>P(1)−P(1)−C(1)</td>
</tr>
<tr>
<td>1.771 (6)</td>
<td>91.24 (15)</td>
</tr>
<tr>
<td>S(1)−C(11)</td>
<td>P(1)−P(1)−C(1)</td>
</tr>
<tr>
<td>1.750 (6)</td>
<td>91.24 (15)</td>
</tr>
<tr>
<td>S(2)−C(10)</td>
<td>P(1)−P(1)−C(1)</td>
</tr>
<tr>
<td>1.728 (5)</td>
<td>88.76 (15)</td>
</tr>
<tr>
<td>S(2)−C(17)</td>
<td>C(1)−P(1)−C(1)</td>
</tr>
<tr>
<td>1.775 (6)</td>
<td>180.00 (3)</td>
</tr>
<tr>
<td>P(1)−C(23)</td>
<td>C(9)−S(1)−C(11)</td>
</tr>
<tr>
<td>1.822 (8)</td>
<td>102.9 (3)</td>
</tr>
<tr>
<td>P(1)−C(25)</td>
<td>C(10)−S(2)−C(17)</td>
</tr>
<tr>
<td>1.812 (7)</td>
<td>102.6 (3)</td>
</tr>
<tr>
<td>P(1)−C(27)</td>
<td>P(1)−C(1)−C(2)</td>
</tr>
<tr>
<td>1.848 (9)</td>
<td>178.0 (5)</td>
</tr>
<tr>
<td>C(1)−C(2)</td>
<td>S(1)−C(9)−C(10)</td>
</tr>
<tr>
<td>1.222 (7)</td>
<td>119.3 (4)</td>
</tr>
<tr>
<td>C(2)−C(3)</td>
<td>S(2)−C(10)−C(9)</td>
</tr>
<tr>
<td>1.438 (7)</td>
<td>124.9 (5)</td>
</tr>
<tr>
<td>C(6)−C(9)</td>
<td>C(1)−C(2)−C(3)</td>
</tr>
<tr>
<td>1.475 (6)</td>
<td>177.2 (3)</td>
</tr>
<tr>
<td>C(9)−C(10)</td>
<td>C(6)−C(9)−C(10)</td>
</tr>
<tr>
<td>1.342 (7)</td>
<td>127.0 (3)</td>
</tr>
</tbody>
</table>

in each alkenyl backbone. 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(II) centre adopts a square planar geometry that is a
Chapter 3: Synthesis, characterization, and photoluminescence properties of bis-dithiolated platinum(II) acetylides

very little distorted from its ideal geometry with the C−Pt−P bond angle in the range of 89-91°. The Pt−C bond distance (ca. 1.98 Å) and the Pt−P bond distance (ca. 2.3 Å) are consistent to the literature values reported in typical platinum(II) phosphine bis(alkynyl) systems. The C≡C bond length (ca. 1.22 Å) is characteristic of metal-acetylide bonding. The Pt−C−C fragment is essentially linear (ca 178.0°) such that the molecule affords a rigid C−C−C−Pt−C−C linear chain.

3.2.4 Optical Absorption and Emission Spectroscopy

For all four platinum(II) complexes, the lowest energy absorption bands in the UV/Vis spectra, in chloroform solution, at room temperature, occurred in the range 363-376 nm. The values of λ_{max} are reported in Table 4. The absorption bands are slightly influenced by the presence of different organic spacers and phosphine groups. The lowest energy band, in each case, was tentatively assigned to a predominantly π(C≡C)→π*(C≡C) transition by comparison with related systems but they can be considered to have some LMCT character resulting from the possible admixture of a platinum (n+1) p orbitals and a ligand π* orbital and their position moves to longer wavelengths due to coordination of acetylide ligand along connected with alkenylaryl group. The highest red-shift (23 nm) observed for the trans-platinum(II) complexes is recorded for complex 3a. The UV/Vis absorption maxima of complexes 1a, 1b, 1c, and 1d are

![Figure 3](image-url)  
**Figure 3.** UV/Vis absorption spectra of complexes 3a-3d in CHCl₃, at room temperature
Table 4. Absorption and emission data for complexes 3a-3d in CHCl₃, at room temperature

<table>
<thead>
<tr>
<th>Complexes²</th>
<th>λₓmax (nm) absorption</th>
<th>ε (10⁴ l mol⁻¹ cm⁻¹)b</th>
<th>λₓmax (nm) emission</th>
<th>Stokes shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>368</td>
<td>8.0</td>
<td>411</td>
<td>0.35</td>
</tr>
<tr>
<td>3b</td>
<td>376</td>
<td>5.7</td>
<td>412</td>
<td>0.29</td>
</tr>
<tr>
<td>3c</td>
<td>363</td>
<td>7.7</td>
<td>415</td>
<td>0.43</td>
</tr>
<tr>
<td>3d</td>
<td>375</td>
<td>7.6</td>
<td>414</td>
<td>0.31</td>
</tr>
</tbody>
</table>

[a] Concentration is 1.0×10⁻⁵ M. [b] Extinction coefficients ε (10⁴ l mol⁻¹ cm⁻¹).

Figure 4. Normalized optical absorption and photoluminescence spectra of complexes 3a-3d in CHCl₃, at room temperature

at 345, 361, 356, and 370 nm, respectively, and those of their corresponding bis-disulfide adduct complexes 3a, 3b, 3c, and 3d are at 368, 376, 363 and 375 nm, respectively. In each case, small red-shift is observed: 23, 15, 7, and 5 nm for complexes 3a, 3b, 3c, and 3d, respectively, as compared to complexes 1a, 1b, 1c, and 1d, respectively. This reveals that π-conjugation is preserved through the metal site by mixing of the frontier orbitals of metal and the ligands. Preliminary measurements concerning the luminescence properties were also performed. The photoluminescence spectra were recorded for the solutions of the trans-platinum(II) complexes under excitation at the wavelength of their absorption maximum (λₓmax = 363-376 nm), which showed emission maxima in the region 411-415 nm (Table 4). The room temperature photoluminescence spectra, in chloroform, for trans-platinum(II) complexes 3a-3d 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, 0.35, 0.29, 0.43, and 0.31 eV for 3a, 3b, 3c, and 3d, respectively).²²
3.3 Conclusions

The author has developed a convenient way for the synthesis of novel platinum(II) bis(alkenylnarylalkynyl) complexes with general formula \( \text{trans-}[\{(PR_3)_2Pt\{C\equiv C-Ar-C(SPh)=CH(SPh)\})_2] \) (Ar = phenylene, biphenylene, and R = ethyl, phenyl), having each alkenyl backbone containing two phenylthio moieties with good regioselectivity, by palladium-catalyzed simultaneous introduction of phenylthio moieties (organic disulfide) into terminal carbon-carbon triple bond of platinum(II) bis(alkynylarylalkynyl) complexes. The newly synthesized trans-platinum(II) bis(alkenylnarylalkynyl) complexes (3) have been fully characterized by spectroscopic techniques as well as elemental analysis, and the trans square-planar arrangement at the platinum center was confirmed by elucidating the molecular structure of model complex 3a using single crystal X-ray diffraction.

3.4 Experimental Section

General

Solvents were dried, distilled from appropriate drying agents and degassed before use. All chemicals, except where stated, were purchased from commercial sources and used as received without further purification. Compounds HC≡C-C_6H_4≡C≡CH, HC≡C-C_6H_4-C_6H_4≡C≡CH, \( \text{trans-}[(\text{Et_3P})_2Pt\{\text{C}≡\text{C}-\text{C}_6\text{H}_4-\text{C}≡\text{C}\}]_2 \), \( \text{trans-}[(\text{Et_3P})_2Pt\{\text{C}≡\text{C}-\text{C}_6\text{H}_4-\text{C}≡\text{C}\}]_2 \), \( \text{trans-}[(\text{Ph_3P})_2Pt\{\text{C}≡\text{C}-\text{C}_6\text{H}_4-\text{C}≡\text{C}\}]_2 \), and \( \text{trans-}[(\text{Ph_3P})_2Pt\{\text{C}≡\text{C}-\text{C}_6\text{H}_4-\text{C}≡\text{C}\}]_2 \) were prepared by literature methods. NMR spectra were recorded on JEOL JNM-ECX 400 or JEOL JNM-ECS 400FT NMR spectrometer in appropriate solvents. \(^{31}\text{P}\) NMR spectra were referenced to external trimethylphosphite. \(^1\text{H}\) NMR spectra were referenced to internal TMS, and \(^{13}\text{C}\) NMR spectra were referenced to solvents resonances. Infrared spectra were recorded by using KBr pellets with a Shimadzu FTIR-8400 instrument, and ESI-HR mass spectra were recorded with a JEOL JMS-T100LC spectrometer. Microanalyses were performed on the analytical section of Osaka University. Electronic absorption spectra were recorded with a JASCO V-560 UV/Vis spectrometer, and emission spectra were recorded with a JASCO FT-6300 spectrofluorometer. Column chromatography was performed either on silica gel or alumina.
Platinum(II) Bis(alkenylarylalkynyl) Complexes Synthesis (3)

**Trans-[(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C(SPh)=CH(SPh)}$_2$] (3a)**

Benzene (2 mL), tetrakis(triphenylphosphine)palladium(0) (0.006 gm, 5 mol%), diphenyl disulfide (0.024 gm, 0.11 mmol), and *trans*-bis(triethylphosphine)bis(1,4-phenyldiethynylene)platinum(II) 1a, (0.034 gm, 0.05 mmol) were added to a small double-neck flask, and the resulting mixture was stirred under reflux for 24 hours at 90 °C. Evaporation of the solvent under reduced pressure gave a solid residue. The crude product was purified by column chromatography, and 3a was obtained as yellow solid in 73% yield (0.041 gm). M. P.: 148-150 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.08-7.49 (m, 30 H), 2.08-2.15 (m, 12 H, CH$_2$) and 1.13-1.2 (m, 18 H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.23, 16.27, 109.43, 109.65, 125.71, 126.21, 126.46, 127.04, 127.43, 127.94, 128.19, 128.72, 128.85, 128.88, 129.12, 129.18, 129.23, 129.29, 129.52, 129.56, 130.44, 130.54, 130.86, 134.94, 135.26, 135.36 and 135.68 ppm; $^{31}$P NMR (161.83 MHz, CDCl$_3$): $\delta$ 11.62 ($J_{Pt-P}$ = 2366 Hz) and 11.67 ($J_{Pt-P}$ = 2366 Hz) ppm; IR (KBr): $\nu$ 3070, 3020, 2958, 2927, 2904, 2873, 2098, 1651, 1593, 1550, 1523, 1477, 1454, 1438 and 817 cm$^{-1}$; ESI-MS [M+Na]$^+$ $m/z$ = 1141.2467 (100%), FW: 1118.3651, Anal. Calc. for C$_{56}$H$_{60}$P$_2$PtS$_4$: C, 60.14; H, 5.41%. Found: C, 60.28; H, 5.42%.

Similarly, the reaction was performed in toluene, 1,2-dichloroethane and chloroform under the same conditions. The isolated yields of bis(disulfide) addition product, which were obtained in toluene, 1,2-dichloroethane and chloroform, as 72%, 52%, and 0%, respectively. As the reaction carried out in chloroform did not afford addition product, the starting material 1a, was recovered by column chromatography.

**Trans-[(Ph$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C(SPh)=CH(SPh)}$_2$] (3b)**

The synthetic procedure was the same for the synthesis of platinum(II) complex 3a, but platinum(II) bis(acetylide) complex 1b, *trans*-bis(triphenylphosphine)bis(1,4-phenyldiethynylene)platinum(II), was used instead of *trans*-bis(triethylphosphine)bis(1,4-phenyldiethynylene)platinum(II), 1a. The crude product was purified by column chromatography and gave the title complex 3b as yellow solid in 82% (0.0575 gm) yield.
Chapter 3: Synthesis, characterization, and photoluminescence properties of bis-dithiolated platinum(II) acetylides

M. P.: 192-193 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.72-7.76 (m, 12 H), 7.03-7.44 (m, 44 H) and 6.13 (d, 4H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 125.45, 125.63, 127.36, 127.76, 127.90, 128.01, 128.71, 129.17, 129.50, 130.17, 130.45, 130.83, 131.23, 131.53, 134.74, 134.99 and 135.41 ppm; \(^{31}\)P NMR (161.83 MHz, CDCl\(_3\)): \(\delta\) 19.23 (J\(_{Pt-P}\) = 2639 Hz) ppm; IR (KBr): \(\nu\) 3051, 2985, 2102, 1577, 1546, 1527, 1477, 1434 and 821 cm\(^{-1}\); ESI-HRMS [M+Na]\(^+\) \(m/z\) = 1429.2299 (100%), FW: 1406.6219, Anal. Calc. for C\(_{80}\)H\(_{60}\)P\(_2\)PtS\(_4\): C, 68.31; H, 4.30%. Found: C, 68.18; H, 4.42%.

\(\text{Trans-}[(\text{Et}_3\text{P})_2\text{Pt}\{\text{C}≡\text{C}-\text{C}_6\text{H}_4-\text{C}(\text{SPh})≡\text{CH(SPh)}\}_2] (3c)\)

The same synthetic procedure for platinum(II) complex 3a was followed for the synthesis of 3c, but platinum(II) bis(acetylide) complex 1c, \(\text{trans-bis(triethylphosphine)bis(4,4′-biphenyldiethynylene)platinum(II)}\), was used instead of \(\text{trans-bis(triethylphosphine)bis(1,4-phenyldiethynylene)platinum(II)}\), 1a. The crude product was purified by column chromatography and gave the title complex 3c as yellow solid in 55% (0.035 gm) yield. M. P.: 153-154 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.92-7.67 (m, 38 H), 2.14-2.22 (m, 12 H, CH\(_2\)) and 1.19-1.27 (m, 18 H, CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 8.36, 16.37, 125.85, 125.85, 126.35, 126.49, 126.63, 126.99, 127.14, 127.56, 128.05, 128.05, 128.78, 128.91, 129.17, 129.28, 129.47, 129.60, 129.79, 130.59, 131.21, 136.66 and 137.24 ppm; \(^{31}\)P NMR (161.83 MHz, CDCl\(_3\)): \(\delta\) 11.70 (J\(_{Pt-P}\) = 2370 Hz) ppm; IR (KBr): \(\nu\) 3051, 3024, 2962, 2931, 2904, 2873, 1596, 1581, 1542, 1485, 1438 and 813 cm\(^{-1}\); ESI-HRMS [M+Na]\(^+\) \(m/z\) = 1293.3312 (100%), FW: 1270.5570, Anal. Calc. for C\(_{68}\)H\(_{68}\)P\(_2\)PtS\(_4\): C, 64.28; H, 5.39%. Found: C, 64.55; H, 5.81%.

\(\text{Trans-}[(\text{Ph}_3\text{P})_2\text{Pt}\{\text{C}≡\text{C}-\text{C}_6\text{H}_4-\text{C}(\text{SPh})≡\text{CH(SPh)}\}_2] (3d)\)

The same synthetic procedure for platinum(II) complex 3a was applied for the synthesis of 3d, but platinum(II) bis(acetylide) complex 1d, \(\text{trans-bis(triphenylphosphine)bis(4,4′-biphenyldiethynylene)platinum(II)}\), was used instead of \(\text{trans-bis(triethylphosphine)bis(1,4-phenyldiethynylene)platinum(II)}\), 1a. The crude product was purified by column chromatography and gave the title complex 3d as yellow solid in 49% (0.038 gm) yield. M. P.: 209-210 °C. \(^1\)H NMR (400 MHz,
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CDCl₃: δ 7.78-7.84 (m, 12 H), 6.90-7.61 (m, 52 H) and 6.29-6.31 (m, 4 H) ppm; ¹³C NMR (100 MHz , CDCl₃): δ 125.42, 125.57, 125.84, 126.47, 126.92, 127.53, 127.81, 128.11, 128.87, 129.15, 129.26, 129.58, 129.86, 130.19, 130.58, 131.25, 131.38, 131.67, 135.09, 136.27 and 140.12 ppm; ³¹P NMR (161.83 MHz , CDCl₃): δ 19.31 (J_{Pt-P} = 2639 Hz) ppm; IR (KBr): ν 3055, 3024, 2106, 1581, 1542, 1481, 1434 and 813 cm⁻¹; ESI-HRMS (M+Na⁺)m/z = 1581.2714 (100%), FW: 1558.8138, Anal. Calc. for C₉₂H₆₈P₂PtS₄: C, 70.89; H, 4.40%. Found: C, 70.93; H, 4.55%.

**Single-Crystal Structure Determination for 3a:** A yellow block crystal of C₅₆H₆₀P₂PtS₄ with approximate dimensions of 0.150 x 0.120 x 0.030 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation. The summary of crystal analysis data are listed in Table 5. The data were collected at a temperature of -150 ±10°C to a maximum 2θ value of 55.0°. A total of 192 oscillation images were collected. The exposure rate was 24.0 [sec.]°. The crystal-to-detector distance was 127.40 mm. The structure was solved by direct methods¹⁹ and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle subjected to full-matrix least-squares refinement (SHELXL-97)²⁰ on F². All calculations were performed using the Crystal Structure crystallographic software package except for refinement, which was performed using SHELXL-97.²⁰

<table>
<thead>
<tr>
<th>Table 5. Summary of crystal structure data for complex 3a</th>
</tr>
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<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Crystal color</strong></td>
</tr>
<tr>
<td><strong>Temperature (°C)</strong></td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
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<tr>
<td><strong>Crystal dimensions (mm)</strong></td>
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<tr>
<td><strong>Space group</strong></td>
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<tr>
<td><strong>a (Å)</strong></td>
</tr>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>--------------------</td>
</tr>
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<td>( b (\text\AA) )</td>
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<tr>
<td>( c (\text\AA) )</td>
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<tr>
<td>( \alpha (^\circ) )</td>
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<tr>
<td>( \beta (^\circ) )</td>
</tr>
<tr>
<td>( \gamma (^\circ) )</td>
</tr>
<tr>
<td>Volume (\text\AA(^3))</td>
</tr>
<tr>
<td>( Z )</td>
</tr>
<tr>
<td>( D ) (calc. g/cm(^3))</td>
</tr>
<tr>
<td>( F (000) )</td>
</tr>
<tr>
<td>( \mu (\text{Mn Ka}) ) (cm(^{-1}))</td>
</tr>
<tr>
<td>Reflections collected</td>
</tr>
<tr>
<td>Unique reflections</td>
</tr>
<tr>
<td>( R_{int} )</td>
</tr>
<tr>
<td>Number of variables</td>
</tr>
<tr>
<td>Absorption correction</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
</tr>
<tr>
<td>( R1 )</td>
</tr>
<tr>
<td>( wR2 )</td>
</tr>
<tr>
<td>Largest diff. Peak and hole (e \text\AA(^3))</td>
</tr>
</tbody>
</table>

### 3.5 References


Chapter 4

The Photochemical Diselenated Novel Platinum(II) Bis(alkenylarylalkynyl) Complexes: Synthesis, Characterization and Photoluminescence Properties

4.1 Introduction

There is a continuing interest in the scientific community in the search for novel conjugated organic and metal-organic molecular functional materials that might help to sustain the growth of opto-electronic research. The most investigated systems have been metal-organic conjugated framework which contains multifunctional systems with high electron delocalization increased by the interaction between the metal centre and the organic spacers. This field has been stimulated by the large number of potential applications for conjugated materials in electronic and electro-optical devices. This interest derives from the fact that incorporation of heavy metals into an organic conjugated framework can elicit large effects on the electronic and optical properties of the materials. There are many M-C≡C bond-forming reactions that are useful for synthesis of a wide variety of transition metal and alkynyl conjugated systems. Among them, the platinum(II) bis(phosphine) bis(alkynyl) system, with its simple square planar geometry, has been widely explored. The linear geometry of alkynyl units and its π-unsaturated character was made metal alkynyls to be attractive for synthetic organometallic chemistry.

Radical addition of heteroatom compounds to carbon-carbon multiple bonds on the photoinduced homolytic cleavage of inter-element linkage is one of the most useful and highly atom-economical methods for selective introduction of heteroatom into organic/organometallic molecules/compounds to provide multifunctionalized organic/organometallic compounds. The absorption maximum of organic disulfides and diselenides lies in the ultraviolet and near-UV regions, respectively. Therefore, irradiation with the corresponding lights causes homolytic cleavage of the chalcogen-chalcogen bonds to generate the corresponding chalcogen-centered radicals. If the photolysis of dichalcogenide is performed in the presence of carbon-carbon unsaturated compounds, the formed chalcogen-centered radicals added to the unsaturated bonds, producing a variety of organic chalcogen functionalized compounds conveniently. In contrast to
the large amount of S-centered radical mediated cascade reactions, only few examples for radical cascades that are triggered by intermolecular Se-centered radical addition to alkynes have been reported.\textsuperscript{15} The most commonly used Se-centered radicals are phenylselenyl radicals which can be obtained from diphenyl diselenide through photochemically. An early example for a Se-centered radical induced addition to alkynes was reported by Back et al., who studied addition of PhSe\textsuperscript{+} to dimethyl acetylenedicarboxylate.\textsuperscript{14b} After that Ogawa and Sonoda et al. used the photoinitiated addition of diselenides to terminal alkynes.\textsuperscript{14c}

In the previous chapter, the palladium catalyzed bis-dithiolation of trans-platinum(II) bis(alkynylarylalkynyl) has been described. In this chapter, attention shall be focused on introducing diphenyl diselenide into the terminal alkynyl ligands of trans-platinum(II) bis(alkynylarylalkynyl) complexes to construct functionalized trans-platinum(II) bis(alkynylarylalkynyl) complex, having two phenylseleno moieties in each alkenyl backbone. It may expect that the newly designed organometallic compounds containing multifunctional systems may allow conjugation through a metal centre into organic spacers. Although, the photoinduced and metal-catalyzed addition of diphenyl diselenide into terminal arylacetylenes is reported,\textsuperscript{14-16} it has not been previously applied to any metal acetylide complexes or metal complexes. In this chapter, for the first time, the author reports the synthesis of novel examples of selenium-containing trans-platinum(II) bis(alkynylarylalkynyl) complexes (Fig. 1), trans-[(R\textsubscript{3}P)\textsubscript{2}Pt{C≡C-Ar-C(SePh)=CH(SePh)}\textsubscript{2}], (4) (Ar = phenylene or biphenylene, and R = ethyl or phenyl), by photoinduced addition of diphenyl diselenide into trans-platinum(II) bis(alkynylarylalkynyl) complexes.

Figure 1. The skeleton structure of novel trans-platinum(II) complexes 4
4.2 Results and Discussion

4.2.1 Syntheses and Scope

When a mixture of diphenyl diselenide and trans-platinum(II) complexes, trans-[(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C≡CH}]$_2$ (1a), in chloroform was irradiated, photochemically, a novel selenation product, a selenium-containing trans-platinum(II) bis(alkenylarylalkynyl) complex, trans-[(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C(SePh)=CH(SePh)}$_2$ (4a), was obtained in excellent yield (92%, isolated yield, entry 1, Table 1; Scheme 1). Its structure was elucidated by UV/Vis, IR, multi-nuclear NMR spectroscopy and ESI-HR mass spectrometry as well as elemental analysis.

To optimize reaction conditions, various solvents were examined under similar conditions (Table 1). Chloroform was found to be the best solvent (isolated yield 92%, entry 1, Table 1), although the addition reaction proceeded smoothly in benzene (isolated yield 89%, entry 2, Table 1) and toluene (isolated yield 85%, entry 3, Table 1). The starting material, platinum(II) bis(alkynylarylalkynyl) complex is slightly better soluble in halogenated solvent like chloroform, than benzene and toluene.

![Photoinduced addition of diphenyl diselenide to trans-platinum(II) bis(alkynylarylalkynyl) complex.](image)

**Scheme 1.** Photoinduced addition of diphenyl diselenide to trans-platinum(II) bis(alkynylarylalkynyl) complex.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pt-bis(acetylide)</th>
<th>Heteroatom reagent</th>
<th>Solvent</th>
<th>Duration (h)</th>
<th>Yield$^b$, 4a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>(SePh)$_2$</td>
<td>Chloroform-d</td>
<td>1.5</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>(SePh)$_2$</td>
<td>Benzene-d$_6$</td>
<td>1.5</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>(SePh)$_2$</td>
<td>Toluene-d$_6$</td>
<td>1.5</td>
<td>85</td>
</tr>
</tbody>
</table>

[a] Reactions were carried out in 0.8 mL of deuterated solvent under photoirradiation by using 1a, trans-(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C≡CH}]$_2$ (0.1 mmol), and diphenyl diselenide (0.25 mmol). [b] Isolated yield.
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Probably, its effect slightly reflects in the yield of selenation product, and thus better yield is obtained in chloroform (92%, entry 1, Table 1).

\[ \text{Scheme 2. Photoinduced addition of diphenyl diselenide to various } \text{trans-platinum(II)} \]
\[
\text{bis(alkynylarylalkynyl) complexes.}
\]

Table 2. Optimized photoinduced addition of diphenyl diselenide to various \text{trans-platinum(II)} \[
\text{bis(acetylides)}^{a}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pt-bis(acetylides)</th>
<th>Heteroatom reagent</th>
<th>Duration (h)</th>
<th>Yield$^b$, 4 (%) (anti/syn)$^c$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>(SePh)$_2$</td>
<td>1.5</td>
<td>92 (4a) (75/25)</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>(SePh)$_2$</td>
<td>2</td>
<td>85 (4b) (72/28)</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>(SePh)$_2$</td>
<td>2</td>
<td>90 (4c) (78/22)</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>(SePh)$_2$</td>
<td>5</td>
<td>76 (4d) (70/30)</td>
</tr>
</tbody>
</table>

$^{a}$Reactions were carried out in chloroform solvent under irradiation by using $1$, \text{trans-}(R_3P)_2Pt(C≡C-Ar-C≡CH)$_2$, (0.1 mmol), and diphenyl diselenide (0.25 mmol). $^{b}$Isolated yield. $^{c}$Inseparable \text{anti} (E) and \text{syn-addition} (Z) products were determined by $^1$H NMR spectroscopy.

Under the optimized reaction conditions, several platinum(II) bis(acetylides), \text{trans-}(R_3P)_2Pt(C≡C-Ar-C≡CH)$_2$, (1) (where, Ar = phenylene, biphenylene, and R = ethyl, phenyl) were also examined (Scheme 2). The results are summarized in Table 2. The scope of this reaction is quite general. This methodology tolerates two different arene rings and two different phosphine groups containing \text{trans-platinum(II)} bis(acetylides) with extended alkynyl ligands, and the corresponding bis-diselenation products were formed successfully. The yields of the isolated addition products range from good to excellent with good regioselectivity. Bearing ethyl phosphine groups on the \text{trans-platinum(II)} bis(acetylide) provided excellent yields, complex 4a (92% isolated yield, entry 1, Table 2) and complex 4c (90% isolated yield, entry 3, Table 2), of selenation product. Bearing phenyl phosphine groups on the \text{trans-platinum(II)} bis(acetylide) provided
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good (complex 4d, 76% isolated yield, entry 4, Table 2) to high yields (complex 4b, 85% isolated yield, entry 2, Table 2) of selenation product.

All the reactants were converted to selenation adducts within 1.5 to 5 hours upon irradiation with UV light (Table 2). The addition reaction proceeds preferentially toward anti-addition at the terminal extended alkynes of the trans-platinum(II) bis(alkynylarylalkynyl) complexes, because of the internal triple bond is sterically hindered. All these novel synthesized trans-platinum(II) bis(alkenylarylalkynyl) complexes were isolated as yellow solids with yields ranging from 76 to 92%. They display good solubility in common organic solvents but are insoluble in hexane. The trans-platinum(II) complexes are air-stable. All trans-platinum(II) complexes (4) provided satisfactory microanalyses. The identity of these synthesized trans-platinum(II) complexes were based on their IR, $^1$H, $^{31}$P, and $^{77}$Se NMR spectra and positive ESI-HR [M+Na]$^+$ mass spectra.

4.2.2 Spectroscopic Characterization

In IR spectra, the $\nu$(C≡C) stretching frequency is diagnostic of the characterization of the metal ethynyl complexes (MC≡C) and the absence of the terminal ≡C-H confirms the completion of the reaction. The trans-platinum(II) bis(alkenylarylalkynyl) complexes display a single sharp $\nu$(C≡C) absorption band in the range of 2098-2105 cm$^{-1}$, confirming the platinum-acetylenic carbon bond (Pt-C≡C) is preserved on the newly formed platinum(II) complexes 4. As for the example, platinum(II) complex 4a displayed a sharp single absorption band at 2101 cm$^{-1}$, which is assigned to platinum-ethynyl, $\nu$(Pt-C≡C), stretching frequency. The IR spectra of each platinum(II) complexes 4 shows no band in the range of 3200-3300 cm$^{-1}$, which is characteristic of $\nu$(≡C-H) stretching vibration. The result is confirming that the terminal acetylenic groups selectively undergo the addition of diphenyl diselenides. So, the IR spectra of platinum(II) complexes 4 provided important information, indicating clearly that the addition reaction proceeded only at the terminal alkyne bond of platinum(II) bis(alkynylarylalkynyl) complexes 1. In the $^1$H NMR spectra, the terminal acetylenic proton peak of each platinum(II) complexes 4, disappeared (about 3 ppm) and new peaks were observed in each platinum(II) complexes 4 at near 7.5 ppm (syn-addition product, Z isomer) and 7.0 ppm.
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(anti-addition product, E isomer) for their vinylic proton\textsuperscript{14c} for instance, platinum(II) complex 4a displayed singlet at 7.57 and 7.04 ppm for the vinyl proton, and in all cases, signals arising from the organic spacer, phenylseleno moiety and ethyl/phenyl phosphine protons also display peaks in the expected region. The\textsuperscript{31}P NMR spectra of platinum(II) complexes 4 showed the expected signal which consisting of three lines (a singlet and two satellites) due to coupling with \textsuperscript{195}Pt. The trans geometry around the platinum-diphosphine centre was confirmed by \textsuperscript{31}P NMR spectroscopy based on the $J_{Pt-P}$ coupling constant.\textsuperscript{17-18} The $J_{Pt-P}$ values obtained, i.e., 2366, 2640, 2391, and 2644 Hz for the platinum(II) complexes 4a, 4b, 4c, and 4d, respectively, are in agreement with the values previously reported for other square planar platinum(II) complexes with trans geometry; cis coupling constants are generally much larger (about 3500 Hz).\textsuperscript{17} In \textsuperscript{31}P NMR spectra, complexes 4a and 4b provides two singlets (E/Z isomers mixture), whereas complexes 4c and 4d provides only one singlet. Probably diphosphine centres in complexes 4c and 4d are somewhat far from the terminal selenation adduct. Measurement of \textsuperscript{77}Se NMR spectroscopy was performed for all complexes 4, and four peaks were displayed in each case due to E/Z isomers mixture, for example, platinum(II) complex 4a displayed four singlets at 383.92, 409.13, 437.61, and 504.53 ppm.\textsuperscript{14c} Four peaks in \textsuperscript{77}Se NMR spectra revealed that the addition reaction proceed preferentially toward anti-addition along with syn-isomer at the terminal extended alkynes of the trans-platinum(II) bis(alkynylarylalkynyl) complexes 1. Measurement of \textsuperscript{13}C NMR spectroscopy was performed in all complexes but, in the \textsuperscript{13}C NMR spectra, some peaks are merged together, because of very close environment of different aromatic ring carbons in the complexes.

The molecular formula for the complexes were also established by the intense molecular ion [M+Na]\textsuperscript{+} peaks in the positive ion ESI-HR mass spectra which were observed at $m/z$ 1329.0391 for 4a, at $m/z$ 1617.0550 for 4b, at $m/z$ 1481.0915 for 4c, and at $m/z$ 1769.1166 for 4d.

4.2.3 Optical Absorption and Emission Spectroscopy

UV/Vis characterization was carried out on all four platinum(II) complexes. For all four platinum(II) complexes, the lowest energy absorption bands in the UV/Vis spectra, in chloroform solution, at room temperature, occurred in the range 363-375 nm. The values of $\lambda_{\text{max}}$ are reported in Table 3. The absorption
Table 3. Absorption and emission data for complexes 4a-4d

<table>
<thead>
<tr>
<th>Complexes (4)</th>
<th>$\lambda_{\text{max}}$ (nm) absorption</th>
<th>$\varepsilon$ $(10^4$ L mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm) emission</th>
<th>Stokes shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>363</td>
<td>5.7</td>
<td>410</td>
<td>0.30</td>
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<tr>
<td>4b</td>
<td>375</td>
<td>4.5</td>
<td>412</td>
<td>0.29</td>
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<tr>
<td>4c</td>
<td>365</td>
<td>6.9</td>
<td>412</td>
<td>0.38</td>
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<td>4d</td>
<td>375</td>
<td>5.8</td>
<td>413</td>
<td>0.30</td>
</tr>
</tbody>
</table>

[a] The concentration is $1.0 \times 10^{-5}$ M in chloroform at room temperature.

Figure 3. Optical absorption for complexes 4a-4d in chloroform at room temperature

Figure 4. Normalized optical absorption and photoluminescence spectra of complexes 4a-4d in chloroform at room temperature
bands are slightly influenced by the presence of different organic spacers and phosphine groups. The lowest energy band, in each case, was tentatively assigned to a predominantly $\pi(C≡C) \rightarrow \pi^*(C≡C)$ transition by comparison with related systems\textsuperscript{1a,19} but they can be considered to have some LMCT character resulting from the possible admixture of a platinum (n+1) p orbitals and a ligand $\pi^*$ orbital,\textsuperscript{20} and their position moves to longer wavelengths due to coordination of acetylide ligand along connected with alkenylaryl group. The highest red shift (18 nm) was observed for the trans-platinum(II) complex 4a. The UV/Vis absorption maxima of complexes 1a, 1b, 1c, and 1d, are observed at 345, 361, 356, and 370 nm, respectively, and those of their corresponding organic diselenide adduct complexes 4a, 4b, 4c, and 4d, are observed at 363, 375, 365 and 375 nm, respectively. In each case, a small red-shift is observed, and the shifts are 18, 14, 9, and 5 nm for complexes 4a, 4b, 4c, and 4d, respectively as compared to complexes 1a, 1b, 1c, and 1d, respectively. This reveals that $\pi$-conjugation is preserved through the metal site by mixing of the frontier orbitals of metal and the ligand alkenylarylalkynyl groups. Preliminary measurements concerning the luminescence properties were also performed. The photoluminescence spectra were recorded for the solutions of the trans-platinum(II) complexes 4 using excitation at the wavelength of their absorption maximum ($\lambda_{\text{max}}$ = 363-375 nm) which showed emission maxima in the region 410-413 nm (Table 3). Complexes 4a-4d display emission band in the blue region of the electromagnetic spectra. The feature is attributable to emission from a singlet excited state, that is, fluorescence, because of the small energy shift (Stokes shift, 0.30, 0.29, 0.38, 0.30 eV for 4a, 4b, 4c, and 4d, respectively).\textsuperscript{21,22} No phosphorescence is observed for any of these complexes at room temperature.

4.3 Conclusions

The author has developed a synthetic method for the simultaneous introduction of phenylseleno moieties (from diphenyl diselenide) into terminal alkynyl ligands of trans-platinum(II) bis(alkynylarylalkynyl) complexes by photoirradiation to synthesize novel functionalized trans-platinum(II) bis(alkynylarylalkynyl) complexes, having two phenylseleno moieties in each alkenyl backbone, in good (76%) to excellent (92%) yields with good regioselectivity. As compared to the absorption band of platinum(II) complexes 1, the
position of the lowest energy absorption bands are red/shifted in the platinum(II) complexes 4, after the functionalization of diphenyl diselenide into the platinum(II) complexes 1. Complexes 4a-4d display emission band in the blue region of the electromagnetic spectra. The newly synthesized trans-platinum(II) bis(alkenylarylalkynyl) complexes (4) have been fully characterized by spectroscopic techniques as well as elemental analysis.

4.4 Experimental Section

General

Solvents were dried, distilled from appropriate drying agents and degassed under nitrogen before use. All chemicals, except otherwise stated, were purchased from commercial sources and used as received without further purification. The compounds HCC≡C-C₆H₄-C≡CH,²⁴ HCC≡C-C₆H₄-C≡CCH,²⁴ trans-[(Et₃P)₂Pt{C≡C-C₆H₄-C≡CH}],¹⁰ trans-[(Et₃P)₂Pt{C≡C-C₆H₄-C≡CCH}],¹⁰ trans-[(Ph₃P)₂Pt{C≡C-C₆H₄-C≡CCH}],¹⁰ and trans-[(Ph₃P)₂Pt{C≡C-C₆H₄-C≡CCH}],¹⁰ were prepared by literature methods. NMR spectra were recorded on JEOL JNM-ECX 400 or JEOL JNM-ECS 400FT NMR spectrometer in appropriate solvents. ³¹P NMR spectra were referenced to external trimethylphosphite. ⁷⁷Se NMR spectra were referenced to external dimethyl selenide. ¹¹H NMR spectra were referenced to internal TMS, and ¹³C NMR spectra were referenced to solvents resonances. Infrared spectra were recorded as KBr pellete using Shimadzu FTIR-8400 spectrometer and ESI-HR mass spectra were recorded on JEOL JMS-T100LC spectrometer. Microanalyses were performed on Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Electronic absorption spectra were recorded on JASCO, V-560, UV/Vis spectrometer and emission spectra were recorded on JASCO, FT-6300, spectrofluorometer. Column chromatography was performed on silica gel.

Platinum(II) Bis(alkenylarylalkynyl) Complexes Synthesis (4)

**Trans-**[(Et₃P)₂Pt{C≡C-C₆H₄-C(SePh)≡CH(SePh)}] (4a)

Chloroform (0.8 mL), trans-[(Et₃P)₂Pt{C≡C-C₆H₄-C≡CH}] (1a, 0.068 g, 0.1 mmol), and diphenyl diselenide (0.078 g, 0.25 mmol) were added in a sealed Pyrex tube and degassed under nitrogen, and the
resulting stirred solution was irradiated under tungsten lamp (500 W) for 1.5 hours. During irradiation, cool water was passed on the sealed Pyrex tube to maintain at room temperature. Completion of the reaction was indicated by TLC and $^1$H NMR. The solvent was removed in vaccuo, then the resulting residue was purified by column chromatography on silica gel and 4a was obtained as a yellow solid of title complex in 92% yield (0.120 g), $E:Z$ ratio: 75:25. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 (s, 0.5 H, $\equiv$CH), 7.11-7.47 (m, 28 H, SePh, Ar-H), 7.04 (s, 1.5 H, $\equiv$CH), 2.09-2.19 (m, 12 H, CH$_2$), 1.14-1.24 (m, 18 H, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.32, 16.27, 109.50, 109.72, 125.80, 126.45, 126.76, 127.22, 127.34, 127.75, 128.32, 128.87, 129.13, 129.20, 129.33, 130.38, 130.50, 130.65, 130.73, 131.05, 131.21, 131.32, 132.05, 132.63, 133.11, 135.53, 135.92, 136.98 ppm. $^{31}$P NMR (161.83 MHz, CDCl$_3$): $\delta$ 11.70 ($J_{Pt-P} = 2366$ Hz) and 11.78 ($J_{Pt-P} = 2366$ Hz) ppm. $^{77}$Se NMR (76.24 MHz, CDCl$_3$): $\delta$ 383.92, 409.13, 437.61, 504.53 ppm. IR (KBr): $\nu$ 3070, 3023, 2964, 2931, 2901, 2874, 2101, 1594, 1575, 1492, 1474, 1450, 1437, 1404, 1375, 1299, 835, 762, 737, 690 cm$^{-1}$. ESI-HRMS: $m/z$ (%) = 1329.0391 (59) [M+Na]$^+$. FW: 1305.9411. C$_{56}$H$_{60}$P$_2$PtSe$_4$ (1305.95): calc. C 51.50, H 4.63; Found: C 51.52, H 4.76.

Similarly, the reaction was performed in benzene and toluene under the same conditions. The isolated yields of the bis-diselenole addition product were obtained in benzene and toluene as 89% and 85%, respectively.

**Trans-[(Ph$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C(SePh)=CH(SePh)}=C(SePh)]$_2$** (4b)

The synthetic procedure was the same for the synthesis of platinum(II) complex 4a, but platinum(II) bis(acetylide) complex 1b, *trans*-bis(triphenylphosphine)bis(1,4-phenyldiethynylene)platinum(II), was used instead of *trans*-bis(triethylphosphine)bis(1,4-phenyldiethynylene)platinum(II) 1a, and the reaction was carried out for 2 hours. The crude product was purified by column chromatography and gave the title complex 4b as yellow solid in 85% (0.111 g) yield, $E:Z$ ratio: 72:28. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.83 (m, 12 H, PPh), 7.46 (s, 0.56 H, $\equiv$CH), 7.04-7.43 (m, 42 H, SePh, PPh, Ar-H), 6.96 (s, 1.44 H, $\equiv$CH), 6.13-6.25 (m, 4 H, Ar-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 113.20, 113.43, 124.95, 126.03, 126.39, 127.17, 127.28, 127.52, 127.78, 127.81, 127.86, 128.59, 128.98, 129.05, 129.16, 129.29, 130.18, 130.62,
Chapter 4: Synthesis, characterization, and photoluminescence properties of bis-diselenated platinum(II) acetylides

130.75, 130.92, 131.07, 131.13, 131.21, 131.42, 131.51, 131.64, 132.01, 132.72, 133.16, 134.40, 134.48, 134.98, 135.29, 136.39 ppm. $^{31}\text{P}$ NMR (161.83 MHz, CDCl$_3$): $\delta$ 19.26 ($J_{\text{Pt-P}} = 2640$ Hz) and 19.31 ($J_{\text{Pt-P}} = 2640$ Hz) ppm. $^{77}\text{Se}$ NMR (76.24 MHz, CDCl$_3$): $\delta$ 385.65, 409.05, 435.49, 504.07 ppm. IR (KBr): $\nu$ 3055, 3022, 2104, 1592, 1576, 1490, 1474, 1434, 841, 734, 690 cm$^{-1}$. ESI-HRMS: $m/z$ (%) = 1617.0550 (71) [M+Na]$^+$. FW: 1594.1979. C$_{80}$H$_{60}$P$_2$PtSe$_4$: (1594.2): calcd. C 60.27, H 3.79; Found: C 60.10, H 4.08.

$^{\text{Trans}}$-[(Et$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C$_6$H$_4$-C(SePh)=CH(SePh)}$_2$] (4c)

The same procedure for the synthesis of platinum(II) complex 4a was followed for that of 3c, but platinum(II) bis(acetylide) complex 1c, $^{\text{trans}}$-bis(triethylphosphine)bis(4,4′-biphenyldiethynylene)platinum(II), was used instead of $^{\text{trans}}$-bis(triethylphosphine)bis(1,4-phenyldiethynylene)platinum(II) 1a, and the reaction was carried out for 2 hours. The crude product was purified by column chromatography and gave the title complex 4c as yellow solid in 90% yield (0.132 g), $E$:Z ratio: 78:22. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.67 (s, 0.44 H, $\equiv$CH), 7.13-7.67 (m, 36 H, SePh, Ar/H), 7.10 (s, 1.56 H, $\equiv$CH), 2.14-2.23 (m, 12 H, CH$_2$), 1.19-1.28 (m, 18 H, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 8.35, 16.35, 109.29, 109.41, 126.31, 126.48, 126.60, 127.39, 127.44, 127.55, 127.86, 128.06, 128.16, 129.05, 129.20, 129.25, 129.39, 130.08, 130.41, 130.66, 130.86, 131.02, 131.20, 132.13, 132.56, 132.83, 133.22, 134.97, 136.39, 136.78, 138.07, 139.06, 139.99, 140.76 ppm. $^{31}\text{P}$ NMR (161.83 MHz, CDCl$_3$): $\delta$ 11.72 ($J_{\text{Pt-P}} = 2391$ Hz) ppm. $^{77}\text{Se}$ NMR (76.24 MHz, CDCl$_3$): $\delta$ 387.23, 409.17, 439.67, 507.92 ppm. IR (KBr): $\nu$ 3055, 3024, 2961, 2930, 2903, 2875, 2098, 1597, 1577, 1485, 1475, 1456, 1437, 1407, 1374, 824, 755, 734, 689 cm$^{-1}$. ESI-HRMS: $m/z$ (%) = 1481.0915 (22) [M+Na]$^+$. FW: 1458.1330. C$_{68}$H$_{68}$P$_2$PtSe$_4$ (1458.14): calcd. C 56.01, H 4.70; Found: C 55.75, H 4.80.

$^{\text{Trans}}$-[(Ph$_3$P)$_2$Pt{C≡C-C$_6$H$_4$-C$_6$H$_4$-C(SePh)=CH(SePh)}$_2$] (4d)

The same synthetic procedure for the platinum(II) complex 4a was applied for the synthesis of 4d, but platinum(II) bis(acetylide) complex 1d, $^{\text{trans}}$-bis(triphenylphosphine)bis(4,4′-biphenyldiethynylene)platinum(II), was used instead of $^{\text{trans}}$-bis(triethylphosphine)bis(1,4-
phenyldiethylnylene)platinum(II) 1a, and the reaction was carried out for 5 hours. The crude product was purified by column chromatography and gave the title complex 4d as yellow solid in 76% (0.132 g) yield, E:Z ratio: 70:30. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.85 (m, 12 H, PPh), 7.62 (s, 0.60 H, $\equiv$CH), 7.09-7.50 (m, 50 H, SePh, PPh, Ar-H), 7.08 (s, 1.40 H, $\equiv$CH), 6.29-6.34 (m, 4 H, Ar-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 112.63, 113.29, 125.42, 125.57, 126.18, 126.32, 126.36, 126.59, 127.37, 127.41, 127.46, 127.77, 127.81, 127.87, 128.96, 129.13, 129.16, 129.24, 129.38, 130.19, 130.40, 130.72, 130.82, 131.05, 131.24, 131.34, 131.64, 132.13, 132.37, 132.85, 133.22, 135.07, 136.00, 136.21, 137.86, 138.82, 139.99, 140.76 ppm. $^{31}$P NMR (161.83 MHz, CDCl$_3$): $\delta$ 19.33 ($J_{pt,p}$ = 2644 Hz) ppm. $^{77}$Se NMR (76.24 MHz, CDCl$_3$): $\delta$ 387.73, 409.39, 439.03, 507.73 ppm. IR (KBr): $\nu$ 3050, 3025, 2105, 1597, 1572, 1485, 1475, 1436, 823, 737, 689 cm$^{-1}$. ESI-HRMS: m/z (%) = 1769.1166 (20) [M+Na]$^+$. FW: 1746.3898. C$_{92}$H$_{68}$P$_2$PtS$_4$: (1746.39): calcd. C 63.27, H 3.92; Found: C 62.97, H 4.17.

4.5 References


Chapter 4: Synthesis, characterization, and photoluminescence properties of bis-diselenated platinum(II) acetylides

5. (a) S. R. Marder in *Inorganic Materials* (Eds.: D. W. Bruce and D. O’ Hare), Wily, Chichester, 1996, p 121; (b) D. W. Bruce in *Inorganic Materials* (Eds.: D. W. Bruce and D. O’ Hare), Wily, Chichester, 1996, p 429.


Chapter 5

General Conclusions

Development of novel conjugated organic and organometallic molecular functional materials is of great importance, because these conjugated molecular materials are expected to exhibit innovative properties in materials science. In this research work, the author has designed and investigated the photochemical and transition-metal catalyzed addition of organochalcogen moieties into the terminal triple bonds of platinum(II) bis(alkynylarylalkynyl) complexes, for the construction of novel organometallic complexes, in which the metal atom is stabilized with monodented tertiary phosphine ligands. The newly synthesized series of organochalcogen functionalized novel platinum(II) bis(alkenylarylalkynyl) complexes were characterized by common spectroscopic techniques, and their optical absorption and emission spectroscopy.

In chapter 2, the author has developed a convenient method for the addition of arenethiol into the terminal alkyne of platinum(II) bis(alkynylarylalkynyl) complexes (1), upon photoirradiation, which successfully affords a novel series of arenethiol functionalized platinum(II) bis(alkenylarylalkynyl) complexes (2). Furthermore, the author clarified spectroscopic characterization and luminescent properties of a new class of trans-platinum(II) bis(alkenylarylalkynyl) complexes, trans-[(R₃P)₂Pt{C≡C-Ar-CH=CH(SX)}₂], (2) (Ar = phenylene or biphenylene, X = phenyl or p-tolyl, or 2-naphthalene, and R = ethyl), containing one arenethio moiety in each alkenyl backbone (Fig. 1).

![Figure 1](image-url)  
**Figure 1.** The skeleton structure of novel trans-platinum(II) complexes 2

All the reactants were converted to hydrothiolated platinum(II) complexes within 3 to 8 hours upon irradiation with UV light. All these newly synthesized compounds were isolated as pale yellow to yellow solids, from good (70%) to excellent (90%) yields, with good regioselectivity. They display good solubility...
in common organic solvents, but are insoluble in hexane. The \textit{trans}-platinum(II) bis(alkenylarylalkynyl) complexes are air-stable. All \textit{trans}-platinum(II) complexes (2) provided satisfactory microanalyses. The identity of these newly synthesized \textit{trans}-platinum(II) complexes (2) were based on their IR, $^1$H and $^{31}$P NMR spectra and positive ESI-HR [M+Na]$^+$ or [M]$^+$ mass spectra.

The exact three-dimensional solid state structure of complex 2b was established by single crystal X-ray analysis. Suitable single crystal of complex \textit{trans}-[(Et$_3$P)$_2$Pt\{C≡C-C$_6$H$_4$-CH=CH(SC$_6$H$_4$CH$_3$-p)}$_2$] (2b) was obtained in order to confirm the molecular geometry. To the best of my knowledge, this molecule represents the first structurally characterized example of platinum(II) bis(alkenylarylalkynyl) complex containing one arythio moiety in each alkenyl backbone. 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 \textit{trans} positions. The platinum(II) centre adopts a square planar geometry that is a slightly distorted from its ideal geometry with the C−Pt−P bond angle in the range of 87-93°.

For the \textit{trans}-platinum(II) bis(alkenylarylalkynyl) complexes 2a-2h, the lowest energy absorption bands in the UV/Vis spectra, in chloroform solution, at room temperature, was observed in the range 362-395 nm. As compared to the absorption band of platinum(II) bis(alkynylarylalkynyl) complexes 1, the position of the lowest energy absorption bands are red-shifted, in the platinum(II) bis(alkenylarylalkynyl) complexes 2, after the inclusion of arenethiol into the platinum(II) complexes 1. The highest red-shift (27 nm) was observed for the \textit{trans}-platinum(II) complexes 2e and 2f. This reveals that \pi-conjugation is preserved through the metal site by mixing the frontier orbitals of the metal and ligand. The room temperature photoluminescence spectra, in chloroform, for \textit{trans}-platinum(II) bis(alkenylarylalkynyl) complexes 2a-2h were recorded under excitation at the wavelength of the absorption maximum ($\lambda_{\text{max}}$= 362-395 nm), which showed emission maxima in the region 399-426 nm. The \textit{trans}-platinum(II) complexes 2a-2h 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 3, the author has developed a convenient method for the synthesis of a novel series of platinum(II) bis(alkenylarylalkynyl) complexes containing two phenylthio moieties in each alkenyl backbone (Fig. 2). 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-\[((R_3P)_2Pt(C≡C-Ar-C(SPh)=CH(SPh))_2\] (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 bonds of platinum(II) bis(alkynylarylalkynyl) complexes.

All these newly synthesized compounds (3) were isolated as yellow solids with yields ranging from 49 to 82%. The trans-platinum(II) bis(alkenylarylalkynyl) complexes (3) have been fully characterized by spectroscopic techniques (IR, $^1$H, $^{13}$C and $^{31}$P NMR) as well as elemental analysis, and the trans square-planar arrangement at the platinum center was confirmed by elucidating the structure of model complex 3a by single-crystal X-ray diffraction. All trans-platinum(II) complexes (3) provided satisfactory microanalyses. They display good solubility in common organic solvents, but are insoluble in hexane, and are air-stable.

The exact three-dimensional solid-state structure of model complex trans-\[((Et_3P)_2Pt\{C≡C-C_6H_4-C(SC_6H_5)=CH(SC_6H_5)\}_2\] 3a was established by single-crystal X-ray diffraction analysis in order to confirm the molecular geometry. To the best of my knowledge, this molecule represents the first structurally characterized example of platinum(II) bis(alkenylarylalkynyl) complex containing two phenylthio moieties in each alkenyl backbone. 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 \textit{trans} positions. The platinum(II) centre adopts a square planar geometry that is a very little distorted from its ideal geometry with the \text{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, was observed in the range 363-376 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) bis(alkynylarylalkynyl) complexes 1, the position of the lowest energy absorption bands are red-shifted, in the platinum(II) bis(alkenylarylalkynyl) complexes 3, after the functionalization of diphenyl disulfide into the platinum(II) complexes 1. The highest red-shift (23 nm) was observed for the \textit{trans}-platinum(II) complex 3a. The photoluminescence spectra recorded for the solutions of the \textit{trans}-platinum(II) complexes 3 under excitation at the wavelength of the absorption maxima (\(\lambda_{\text{max}}=363-376\) nm), which showed emission maxima in the region 411-415 nm. The room temperature photoluminescence spectra, in chloroform, for \textit{trans}-platinum(II) complexes 3a-3d displayed emission bands in the blue region of the electromagnetic spectra. The feature is attributable to emission from a singlet excited state, fluorescence, because of the small energy shift (Stokes shift).

In chapter 4, a convenient synthetic method has been developed to construct 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 selenium-containing \textit{trans}-platinum(II) bis(alkenylarylalkynyl) complexes (Fig. 3), with general formula \textit{trans}[(R_3\text{P})_2\text{Pt}\{\text{C≡C-Ar}\text{-(SePh)=CH(SePh)\}_2}], (4) (Ar = phenylene or biphenylene, and R = ethyl or phenyl), by photoinduced addition of diphenyl diselenide into \textit{trans}-platinum(II) bis(alkynylarylalkynyl) complexes.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3}
\caption{The skeleton structure of novel \textit{trans}-platinum(II) complexes 4}
\end{figure}
All the reactants were converted to the corresponding selenation adducts within 1.5 to 5 hours upon irradiation with UV light. The addition reaction proceeds preferentially toward \textit{anti}-addition at the terminal extended alkynes of the \textit{trans}-platinum(II) bis(alkynylationalkynylnyl) complexes, because the internal triple bond is sterically hindered. All these novel \textit{trans}-platinum(II) bis(alkenylationalkynylnyl) complexes were isolated as yellow solids with yields ranging from good (76\%) to excellent (92\%). They display good solubility in common organic solvents, but are insoluble in hexane. The \textit{trans}-platinum(II) complexes are air-stable. The identity of these synthesized \textit{trans}-platinum(II) complexes were based on their IR, $^1$H, $^{31}$P, and $^{77}$Se NMR spectra and positive ESI-HR [M+Na]$^+$ mass spectra.

UV/Vis characterization was carried out on all platinum(II) complexes 4. For all platinum(II) complexes, the lowest energy absorption bands in the UV/Vis spectra, in chloroform solution, at room temperature, was observed 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, 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) was observed for \textit{trans}-platinum(II) complex 4a. The photoluminescence spectra were recorded for the solutions of the \textit{trans}-platinum(II) complexes under excitation at the wavelength of the absorption maxima ($\lambda_{\text{max}}$= 363-375 nm), which showed emission maxima in the region 410-413 nm. Complexes 4 display emission band in the blue region of the electromagnetic spectra. The feature is attributable to emission from a singlet excited state - fluorescence, because of the small energy shift (Stokes shift).

The scope of above mentioned reactions is quite general. These methodologies tolerate platinum(II) bis(diethynylarylene) complexes, containing different arene rings and different phosphine groups. Therefore, it is expected that the developed synthetic methods will be useful for functionalization of metal complexes for preparing new conjugated materials.
List of Publications and Academic Presentations

List of Publications

1. “Synthesis of the first sulphur-containing platinum(II) alkenylarylalkynyl complexes by photoirradiation”
   (Chapter 2)

2. “Palladium-catalyzed dithiolation of platinum(II) alkynylarylacetylides with diphenyl disulfide leading to construction of novel π-conjugated systems with platinum and thio groups”

3. “Synthesis of the first example of selenium-containing platinum(II) alkenylarylalkynyl complexes”
   (Chapter 4)
List of Academic Presentations

1. “The addition of benzenethiol into platinum phenylacetylide complex by photoirradiation”
   
   Md. Mostafizur Rahman, Akihiro Nomoto and Akiya Ogawa
   

2. “Synthesis and characterization of novel sulfur-rich platinum(II) alkenylarylacetylide complexes”
   
   Md. Mostafizur Rahman, Akihiro Nomoto and Akiya Ogawa
   
   Presented on poster session of the International Symposia on Advancing the Chemical Sciences, *ISACS*10, Challenges in Organic Materials and Supramolecular Chemistry, 18-21 June, 2013, Kyoto University, Japan.

3. “Synthesis and luminescent properties of selenium-containing platinum(II) alkenylarylalkynyl complexes”
   
   Md. Mostafizur Rahman and Akiya Ogawa
   
   Presented on poster session of the 4th International Conference on *MOF*-2014, 28 September to 1 October, 2014, Kobe, Japan.

4. “Synthesis and photophysical properties of sulfur-containing platinum(II) alkenylarylalkynyl complexes”
   
   Md. Mostafizur Rahman and Akiya Ogawa
   
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