BROMINE PHOTOELIMINATION FROM ORGANOPLATINUM(IV) COMPLEXES

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the Faculty of the Graduate School
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
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The undersigned, appointed by the dean of the Graduate School, have examined the dissertation entitled

**BROMINE PHOTOELIMINATION FROM ORGANOPLATINUM(IV)
COMPLEXES**

presented by Alice Raphael Karikachery

a candidate for the degree of Doctor of Philosophy

and hereby certify that, in their opinion, it is worthy of acceptance.

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Prof. Steven W. Keller

Prof. Stephen J. Lombardo

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ABBREVIATIONS

1(Br)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₂
2(Br)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₄
1(cisBr)	<i>cis</i> -Pt(PEt ₃) ₂ (Br) ₂
2(cisBr)	<i>cis</i> -Pt(PEt ₃) ₂ (Br) ₄
1(depe)	Pt(depe)(Br) ₂
2(depe)	Pt(depe)(Br) ₄
1(COD)	Pt(COD)(Br) ₂
1(Ph)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(1-phenyl)
2(Ph)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (1-phenyl)
1(CF₃Ph)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(2-(trifluoromethyl)phenyl)
2(CF₃Ph)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (2-(trifluoromethyl)phenyl)
1(MeO₂Ph)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) (2,6-dimethoxyphenyl)
1(BrMeO₂Ph)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) (3,5-dibromo-2,6-dimethoxyphenyl)
2(BrMeO₂Ph)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (3,5-dibromo-2,6-dimethoxyphenyl)
1(NPh)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(2-aminophenyl)
1(BrNPh)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(3,5-dibromo-2-aminophenyl)
2(BrNPh)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (3,5-dibromo-2-aminophenyl)
1(iPrOPh)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(2-isopropoxyphenyl)
1(BriPrOPh)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(5-bromo-2-isopropoxyphenyl)
2(BriPrOPh)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (5-bromo-2-isopropoxyphenyl)
1(1-Nap)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(1-naphthyl)

2(1-Nap)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (1-naphthyl)
1(BrNap)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(4-bromo-1-naphthyl) / <i>trans</i> -Pt(PEt ₃) ₂ (Br)(4-BrNap)
2(BrNap)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (4-bromo-1-naphthyl) / <i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (4-BrNap)
2(BrNapBr)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (7,4-dibromo-1-naphthyl)
1(2-Nap)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(2-naphthyl)
2(2-Nap)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (2-naphthyl)
1(DiPt)	Di- <i>trans</i> -Pt(PEt ₃) ₂ (Br)(1,4-naphthyl)
2(DiPt)	Di- <i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (1,4-naphthyl)
2(DiBrPt)	Di- <i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (6,7-dibromo-1,4-naphthyl)
1(Phen)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(9-phenanthryl)
1(BrPhen)	<i>trans</i> -Pt(PEt ₃) ₂ (Br)(10-bromo-9-phenanthryl)
2(Phen)	<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₃ (9-phenanthryl)
3	2,3-dimethyl-2,3-dibromobutane
4	1-bromo-2,3-dimethyl-2-butene
5	2-bromo-2,3-dimethylbutane
6	3,4- <i>trans</i> -dibromohexane
7	1,2-dibromohexane
CH ₂ Cl ₂	Methylene chloride
COD	1,5-cyclooctadiene
DFT	Density functional theory
DMSO	Dimethyl sulfoxide
depe	1,2-bis(diethylphosphino)ethane
Et ₂ O	Diethyl ether

GC-MS	Gas chromatography-mass spectroscopy
Hr	hours
LED	Light emitting diodes
MeTHF	2-methyltetrahydrofuran
Min	minutes
PAC	Polycyclic aromatic carbon compounds
Ref	Reference
TME	2,3-dimethyl-2-butene
THF	Tetrahydrofuran
Uv-vis	Ultraviolet-visible

LIST OF COMPLEXES

1(Br)

2(Br)

1(cisBr)

2(cisBr)

1(depe)

2(depe)

1(Ph)

2(Ph)

1(1-Nap)

1(BrNap)

2(1-Nap)

2(BrNap)

2(BrNapBr)

1(2-Nap)

2(2-Nap)

1(Phen)

1(BrPhen)

2(Phen)

1(CF₃Ph)

2(CF₃Ph)

1(NPh)

2(BrNPh)

1(BrNPh)

1(MeO₂Ph)

2(BrMeO₂Ph)

1(BrMeO₂Ph)

1(iPrOPh)

2(BriPrOPh)

1(BriPrOPh)

1(2-Nap)

2(2-Nap)

1(DiPt)

2(DiPt)

1(DiPt)₂

2(DiBrPt)

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ABSTRACT

With burgeoning population growth and widespread economic development world energy consumption is constantly on the rise. Currently most of our energy requirements are met through fossil fuels which are non-renewable. The production and use of these fuels also raise significant environmental concerns. Hence, renewable energy exploration is crucial to satiate the global energy demand and achieve sustainable growth.

Coupling solar energy conversion storage cycle with small molecule activation promises renewable and greener fuel technology. Hence, there has been great interest in photochemical water splitting for the production of hydrogen and oxygen. But the four electron oxidation of water is difficult and currently not very economical. Alternatively, light driven endergonic hydrogen halide (HX) splitting, a more facile two electron process is also being explored. Photolytic halide elimination from high valent late transition metal centers like platinum (Pt), gold (Au) and rhodium (Rh) is a key step in designing HX splitting cycles. A high quantum yield (Φ) for the X_2 photoelimination step is crucial for designing efficient transition metal based HX splitting cycles. Endergonic

X₂ photoelimination from transition metal complexes is rare and poorly understood though.

We have discovered Br₂ photoelimination from σ -aryl platinum(IV) centers showing Φ as high as 82 %. Endothermic and endergonic Br₂ elimination is observed with a radical-like excited state platinum precursor. Solution Br₂ elimination is thermally reversible though and alkene traps are required. Insights and inferences gained from this research can be extended to understand the splitting of water and other small molecules using photon. Efficient and economical water splitting would be crucial for the realization of a hydrogen economy as well as providing us with clean energy in a sustainable fashion.

CHAPTER 1: INTRODUCTION

1.1 Solar energy and water splitting

Global energy consumption will double by midcentury.¹ Currently most of our energy requirements are fulfilled by fossil fuels. Higher energy efficiency and clean energy sources are imperative in reducing air pollution.² Hence, it is essential to find renewable and carbon neutral energy sources for future generations.³ In recent years research interest has been burgeoning in exploring viable and economical technology to harness solar power.³⁻⁵ Solar energy as a power supply will not be available to societies if it cannot be stored.^{5, 6} Storing the sun's abundant energy that falls on earth in chemical bonds by designing solar driven molecular machines to split water into hydrogen and oxygen would be key to a hydrogen economy.⁷ Hydrogen can be directly used or can be combined with carbon dioxide to generate methanol, a liquid fuel.⁸ It is clean, abundant and a zero-emission fuel. Hydrogen economy is crucial for securing our energy future. In fuel cells hydrogen combines with oxygen to form water and produce electrical or thermal energy. Production, storage, transportation and usage impediments have to be overcome before the realization of hydrogen economy cost effectively.⁹

1.2 Hydrogen halide splitting

Solar energy conversion storage cycle coupling with small molecule activation promises renewable and greener fuel technology. Hence, there has been great interest in photochemical water splitting for the production of hydrogen and oxygen. Water splitting

to H₂ and O₂ is neither facile nor economical currently. It is difficult and a complex four-electron four-proton process. Comparatively, hydrogen halide (HX: HCl and HBr) splitting is a relatively easier two-electron two-proton process. Understanding a simpler proton-coupled electron transformation can expand our knowledge of multi-electron processes with regards to electron and proton management. Overall, energy stored per electron in HX splitting is comparable to H₂O splitting. Further, the chemical energy can be recovered in a fuel cell as electricity. H₂/X₂ fuel cell literature is extensive and offers many advantages.¹⁰ Fuel cell efficiency for cells using H₂/O₂, H₂/Cl₂ and H₂/Br₂ are 50%¹¹, 70%¹² and 90%¹³, respectively. Hence, exploring organoplatinum(IV) photocatalysts for HBr splitting is very relevant. The overall reactions and energetics for H₂O and HX splitting are shown in Equations 1.2.1 to 1.2.3.^{14, 15}

1.3 Metal catalysts for HX splitting

Photolytic reductive halogen elimination from metal centers is significant because they can be utilized in solar energy conversion storage cycle. The photocatalytic HX splitting cycle involving a metal complex is shown in Scheme 1.3.1.^{16, 17} The metal complex is a

photocatalyst. By absorption of light L_nMX_2 reductively photoeliminates X_2 to form L_nM . The metal center is reduced and its oxidation state changes from a high-valent to a low-valent one. Photochemically generated X_2 should be removed soon as it is formed to prevent back reaction and reactions with catalytic intermediates as well. This removal can be achieved through experimental design or by using traps (solvent or alkenes).¹⁸⁻²⁰ Energy storage is eliminated by the use of X_2 traps though. By increasing the quantum efficiency of the X_2 photoproduction step maximum storage of energy can be achieved in the absence of traps.²¹ Oxidative addition of HX to L_nM leads to the formation of the hydrido-halide L_nMHX intermediate. With the introduction of the second HX molecule there is H_2 production and overall oxidative addition of X_2 to the metal center.

Scheme 1.3.1. Photocatalytic HX splitting cycle for a monometallic catalyst.^{16, 17, 22}

The HX splitting cycle for a bimetallic system is shown in Scheme 1.3.2. The oxidation and reduction half reactions are decoupled at two different metal centers. Depending on

the metal center electron richness, the hydrogen production step can happen photochemically or through an acid-base pathway from L_nMHX .¹⁷ Hence, photolytic reductive halogen elimination from metal center is significant and can be utilized in solar energy conversion storage cycle.

Scheme 1.3.2. Photocatalytic HX splitting cycle for a bimetallic catalyst.²³

For HX splitting, heterogeneous photocatalysis is advantageous from a feasibility and engineering perspective.²⁴ By exploring homogenous photocatalytic systems we can gain mechanistic insights and knowledge about molecular transformations. Also, tunability of steric and electronic factors in homogenous compounds is very helpful in studying these complexes.¹⁷

1.4 Homogenous catalysis and functionalization of PAC

Previously the Sharp group has been extensively investigating homogenous catalysis and functionalization of polycyclic aromatic carbon compounds (PAC). Our group had reported the very first platinaoxetane complex from the coupling reaction of an alkene and a metal oxo complex.²⁵ Also mechanistic probing of the reactions of platinum oxo and hydroxo complexes with alkenes helped in understanding the Wacker process.^{26, 27} Organometallic chemistry of σ -bonded PAC to late transition metals (especially the Ni triad) has led to novel synthetic precursors. Bond expansion on the edge of the PAC paves way for synthesis of fullerenes, nanotubes and related fragments which have diverse applications in electronics and catalysis for the modern world.²⁸

Whilst investigating the possibility of synthesizing novel halogenated PACs from corranulenyl, phenanthrenyl and naphthalenyl organoplatinum(IV) complexes, Dr. Han Baek Lee, a former group member, discovered facile room light-induced ring bromination of the PAC aryl C-H bond as shown in Scheme 1.4.1.

Scheme 1.4.1. Photolysis of **2(1-Nap)** and **2(Phen)**.

Moreover, photolysis in solvents with weak C-H (low bond dissociation energy) bonds like triphenylmethane and dihydroanthracene, led to **1(1-Nap)**, the non-ring brominated platinum(II) analogue along with the ring brominated **1(BrNap)** complex. HBr was also detected. The same result was observed in the case of the phenanthrenyl platinum (IV) complex, as shown in Table 1.4.1. Initially, these results were significant with regards to potential transition metal catalyzed photolytic halogenation of PACs, since conventional methods are tedious and non-selective.²⁹ This steered our group towards exploring photoelimination of Br₂ and Cl₂ from organoplatinum(IV) complexes.²⁹ Moreover, steric and electronic changes were easily achievable in these systems by changing the σ -bonded

PAC or phosphine ligands. Also, molecular transformations and reaction progress were easier to track using ^{31}P NMR spectroscopy.

Table 1.4.1. Photolysis product yields for **2**(1-Nap) and **2**(Phen) in toluene and with added bromine traps.^{29, 30}

Trap	1(1-Nap) 1(BrNap)		1(Phen) 1(BrPhen)	
No added trap	0%	100%	30%	70%
Triphenylmethane (0.2 M)	44%	56%	44%	15%
Dihydroanthracene (0.2 M)	62%	38%	62%	9%

1.5 Halogen elimination literature review

Halogen elimination from metal centers is not so common.²¹ Solution state photoelimination usually happens in the presence of halogen traps like alkenes.^{20, 31} Photoeliminated Cl_2 or Br_2 can add back to the metal center. The trap prevents the facile

back reaction. In the last decade, Nocera and coworkers have synthesized various rhodium, iridium, nickel, platinum and gold monometallic and bimetallic mixed-valent as well as uni-valent complexes for photolytic Br₂ and Cl₂ elimination.^{17, 20, 31-33} The metal d-electron count varied from d⁷ to d¹⁰ in these complexes. A bimetallic Pt₂(tfepma)₂Cl₆ (tfepma = bis(trifluoroethoxylphosphino)methylamine) complex showing 38% quantum yield (in the solution state) and trap free Cl₂ elimination in the solid state was reported as depicted in Scheme 1.5.1.³²

Scheme 1.5.1. Bimetallic platinum complex.

Dinuclear and mononuclear Au(III) complexes showing Cl₂ and Br₂ elimination with quantum yields varying from 10 to 25 % were also reported as shown in Scheme 1.5.2.²¹ These gold complexes were not thermally stable. Thermal halogen elimination at room temperature in the presence of alkene trap was seen.

Scheme 1.5.2. Bimetallic gold complex.

However, Cl_2 and Br_2 photoelimination yields for these complexes were not reported.

Moreover solid state photoeliminated Cl_2 was detected by mass spectroscopy only. Mass spectroscopy can detect very small amounts of Cl_2 . The Gabbai group has also been studying the dinuclear tellurium platinum (TePt) core for photoreductive elimination of Cl_2 as shown in Scheme 1.5.3.³⁴ They report a low 4% quantum yield and Cl_2 trap products based on GC-MS only.

Scheme 1.5.3. Dinuclear tellurium platinum complex.

Since in the literature there are fewer examples of complexes showing facile visible light induced halogen elimination more research is needed. Mechanistic understanding of halogen elimination from metal centers with regards to HX splitting is crucial for the design of photocatalysts.^{22, 30} Eventually insights from homogenous catalysis can be extended to heterogeneous trap-free catalysis for HX splitting. Hence our group's recent focus has been understanding halogen (Br₂, Cl₂), HOCl and H₂O₃ photoeliminations from platinum and iridium centers.^{30, 35-38}

1.6 Research summary

We have discovered Br₂ photoelimination from σ -aryl platinum(IV) centers showing quantum yield as high as 82 %. Synthesis, characterization and photolytic Br₂ elimination studies on a variety of phenyl, naphthyl and phenanthryl organoplatinum(IV) complexes were undertaken. Chelated and *cis* phosphine ligand modifications were also explored in our platinum(IV) complexes. Easy tunability of the ligand framework was crucial in designing platinum(IV) complexes with varied steric and electronic aspects. Solution state Br₂ photoelimination experiments were carried out in the presence of alkene traps. Solution Br₂ elimination is thermally reversible in the absence of traps. ³¹P NMR spectroscopy was an excellent tool in monitoring reductive elimination of Br₂ from Pt(IV) centers. Quantum yield measurements were undertaken to quantify the efficiency of photolytic Br₂ elimination. Alkene product profile and their respective yields were investigated. 2,3-dimethyl-2-butene (TME), a reactive trap showed radical pathway products. Reaction with *cis*-2-hexene, a less reactive and unsymmetrical trap, showed exclusive Br₂ *anti*-addition product. Evidence for molecular bromine (Br₂) as the

brominating agent was also found in a competition experiment with mixed alkene (*trans*-3-hexene and 1-hexene) as traps. 1-hexene Br₂ addition versus platinum(II) Br₂ addition rates were estimated. Calorimetric measurements by Prof. Carl D. Hoff's group and DFT calculations by Prof. Paul R. Sharp shows endothermic and endergonic Br₂ elimination with a radical-like excited state platinum precursor.

CHAPTER 2: BROMINE PHOTOELIMINATION FROM PLATINUM(IV) COMPLEXES

2.1 Background

Net Br₂ photoelimination was observed in our family of platinum(IV) bromo complexes in the solution state in the presence of traps (alkenes). Most of these compounds contain σ -bonded aryl mononuclear organoplatinum(IV) centers with phosphine and bromo ligands. Some complexes studied were exclusively phosphine and bromo ligand coordination frameworks only. A bimetallic diplatinum naphthalene system was also investigated. In comparison to existing literature, our systems showed very high quantum efficiency for Br₂ photoelimination. A quantum yield of 82% was measured for one of our complexes.³⁰ The work was supported by DFT calculations by Prof. Sharp and calorimetric measurements by Prof. Hoff's group. These results show that the Br₂ elimination process is endergonic (energy consuming) with energy storage varying from 2 kcal/mol to 22 kcal/mol. Bromine trapping experiments and kinetic studies show evidence for Br₂ elimination as shown in Equation 2.1.2. But with highly reactive trap like TME, a radical reaction product profile is also observed. This result suggests direct reaction of the trap with the radical character platinum excited state before molecular bromine elimination.

2.2 Synthesis and characterization

Scheme 2.2.1. Ortho-substituted phenyl and 2-naphthyl platinum(II) and platinum(IV) complexes.

Platinum(II) and platinum(IV) complexes shown in Scheme 2.2.1. were synthesized and characterized. These ortho-substituted phenyl and 2-naphthyl complexes were prepared to understand the effect of sterics in Br₂ photoelimination from platinum(IV) complexes.

By oxidative addition of the corresponding aryl halide to the tetrakis(triethylphosphine) platinum(0) complex (Pt(PEt₃)₄), platinum(II) complexes were prepared as shown in Scheme 2.2.2.^{29, 30, 39}

Scheme 2.2.2. Synthesis of substituted phenyl and 2-naphthyl platinum(II) complexes.

Most of our platinum(IV) (**2**) complexes were synthesized by direct bromination of the platinum(II) (**1**) complexes, as shown in Scheme 2.2.3. These bromination reaction rates were extremely fast. One of our group members Lasantha Wickramasinghe monitored the kinetics of Br₂ addition to platinum(II) using low temperature NMR in CH₂Cl₂ and

toluene. The rate of Br₂ oxidative addition to the platinum(II) center was faster than the NMR time scale.

Scheme 2.2.3. Synthesis of ortho-substituted phenyl and 2-naphthyl platinum(IV) complexes.

Subsequent to Br₂ addition to the metal center aryl ring bromination is observed. Thus, σ -aryl ring brominated platinum complexes **2**(BrNPh), **2**(BrMeO₂Ph) and **2**(BriPrOPh) were isolated. Br₂ photoelimination yields the corresponding **1**(BrNPh), **1**(BrMeO₂Ph) and **1**(BriPrOPh) platinum(II) complexes respectively. We observed that with electron-donating substituents such as -OCH₃, -OCH(Me)₂ and -NH₂ on the aryl ring, electrophilic bromine attack on the ring is favored. However, with an electron-withdrawing substituent such as -CF₃ no ring brominated **2**(CF₃Ph) products are observed. This observation is consistent with the electrophilic attack of aromatic ring systems discussed in general chemistry textbooks.⁴⁰

The phenyl, naphthyl and phenanthryl platinum(II) and platinum(IV) complexes shown in Scheme 2.2.4 were previously synthesized by Dr. Han Baek Lee.²⁹ Br₂ photoelimination studies, calorimetry, molar extinction coefficient and quantum yield measurements were further carried out for these complexes.

Scheme 2.2.4. Phenyl, naphthyl and phenanthryl Pt(II) and Pt(IV) complexes.

1(BrNap) and **2(BrNap)** were also synthesized by an alternative route using 1,4-dibromonaphthalene as shown in Scheme 2.2.5.³⁰ The ligand 1,4-dibromonaphthalene was synthesized from a procedure reported by Cakmak et al.⁴¹

Scheme 2.2.5. Synthesis of **1(BrNap)** and **2(BrNap)**.

Bimetallic platinum complexes were also prepared. The **1(DiPt)** complex was prepared by using a 2:1 ratio of $\text{Pt}(\text{PEt}_3)_4$ versus 1,4-dibromonaphthalene. Further, addition of two equivalence Br_2 gave the bimetallic platinum(IV) complex **2(DiPt)** as shown in Scheme 2.2.6.

Scheme 2.2.6. Synthesis of diplatinum complexes.

Photoelimination of Br_2 was investigated from platinum(IV) complexes $\mathbf{2}(\text{Br})$, $\mathbf{2}(\text{cisBr})$ and $\mathbf{2}(\text{depe})$ containing no aryl ligand. The complexes are shown in Scheme 2.2.7. These complexes have been reported previously. Br_2 photoelimination with alkene trap was studied.

Scheme 2.2.7. Platinum(II) and platinum(IV) phosphine complexes.

Addition of Br₂ to **1(Br)** yields **2(Br)** as shown in Scheme 2.2.8. Calorimetry, molar extinction coefficient and quantum yield measurements were further carried out for **2(Br)**.

Scheme 2.2.8. *trans*-phosphine platinum(IV) complex.

2(cisBr) was obtained by bromination of **1(cisBr)** as shown in Scheme 2.2.9. **2(cisBr)** left in solution, over the course of a day isomerizes to **2(Br)**. Correspondingly, **2(Br)** solutions do not show isomerization to **2(cisBr)** and are relatively stable.

Scheme 2.2.9. *cis*-phosphine platinum(IV) complex.

Chelated phosphine platinum(II) complex **2(depe)** was synthesized through an alternative route. Addition of 1,2-bis(diethylphosphino)ethane (depe) to $\text{Pt}(\text{COD})(\text{Cl})_2$ ⁴² yielded $\text{Pt}(\text{depe})(\text{Cl})_2$ through ligand exchange. **1(depe)** was then obtained from metathesis of $\text{Pt}(\text{depe})(\text{Cl})_2$ using KBr. Bromination of **1(depe)** yielded **2(depe)** as shown in Scheme 2.2.10. The **2(depe)** complex has poor solubility in CDCl_3 and CH_2Cl_2 . Hence photolysis was carried out in DMSO in which solubility was slightly better.

Scheme 2.2.10. Chelated phosphine platinum(IV) complex.

With huge excess Br_2 , the **1(BrNap)** and the bimetallic **1(DiPt)**, ring brominated to yield **2(BrNap)** and **2(DiBrPt)** respectively. This is shown in Scheme 2.2.11. These

dibrominated naphthyl platinum(IV) complexes could be significant synthetic precursors for unusually brominated naphthalene compounds.

Scheme 2.2.11. Dibrominated naphthyl platinum(IV) complexes.

^{31}P NMR spectra is crucial in identifying the various platinum oxidation states. The coupling constants and δ are the two main factors in following the oxidation state transformations at the platinum center. This has been an invaluable handle throughout the entire project. Singlets with satellites in the δ -8 to -10 region and coupling constants between 1400 Hz to 1650 Hz are indicative of the platinum(IV) species. Singlets with satellites in the δ 13 to 9 region and coupling constants between 2300 Hz to 2800 Hz are

indicative of the platinum(II) species. The corresponding ring-brominated analogues of both **2** and **1** show a small upfield shift in δ (<1 unit) and about a 50 Hz lowering of the coupling constant in comparison to the non-ring brominated ones.

Uv-vis spectra of **2** and **1** are characteristic of their ligand framework. Complexes **2** are red shifted in comparison to **1**. The absorbance in the uv region is very strong for both **1** and **2**. The platinum(IV) complexes are light orange to light red in color. They have broad and weak blue absorbance in the visible region. According to DFT calculations carried out by Prof. Sharp on the lowest-energy triplet pertaining to **2**, a charge transfer excited state with radical bromine character was observed.^{30, 43} The uv-vis spectra of **2**(BrNap) and **2**(Phen) measured in CH_2Cl_2 , hexane and dimethylformamide (DMF) were the same. Thus, band shifts associated with charge transfer transitions were not observed when solvent polarity was changed for the peaks in the visible region.⁴⁴ Since the blue absorbance is weak the shifts might not be significant enough to be detected probably. The naphthyl platinum(IV) complex shows strong vibronically coupled π - π^* bands.⁴⁵ The ring bromination in **2**(BrNap) and the diplatinum in **1**(DiPt) contribute to bathochromic shifts.⁴⁵

2.3 Photolysis

Complexes **2** are light sensitive. Conversions to complexes **1** were observed in the presence of 1-hexene alkene trap and 313 nm light in the solution state within a few minutes. Bromine addition product 1,2-dibromohexane was observed based on ^1H NMR

monitoring. Previously it was seen that photolysis of **2**(1-Nap) yielded mixtures of **1**(BrNap) and **1**(1-Nap). The ratios of these products varied according to solvents and traps used.²⁹ In Table 2.3.1 with *cis*-2-hexene trap, photolysis ratios are shown in CD₂Cl₂ and CDCl₃ for **2**(1-Nap). These results were important in synthesizing platinum(IV) complexes which promote net Br₂ photoelimination. Hence, **2**(BrNap), **2**(BrMeO₂Ph), **2**(Br_iPrOPh) and **2**(BrNPh) were synthesized for Br₂ photoelimination investigation. In these complexes, the possible ring bromination sites are protected by prior bromine substitution. Whilst brominating **1** to synthesize **2**, the possible ring bromination positions were also brominated.

Table 2.3.1. Photolysis product yields for **2**(1-Nap) with *cis*-2-hexene in CD₂Cl₂ and CDCl₃ at 313 nm.

Solvent	10 minutes Irradiation			>1 hour Irradiation
	2 (1-Nap)	1 (1-Nap)	1 (BrNap)	2 (1-Nap)	1 (1-Nap)	1 (BrNap)
CD ₂ Cl ₂	60%	20%	20%	-	38%	62%
CDCl ₃	60%	27%	17	-	55%	45%

The photolysis of **2**(BrNap) in the presence of an unsymmetrical alkene like *cis*-2-hexene gave 96% of *anti*-bromine addition product as shown in Equation 2.3.1. The ^1H NMR shows a racemic mixture of (2R, 3S)- and (2S, 3R)-2,3-dibromohexane and no *syn*-addition product is detected.⁴⁶ In the absence of trap **2**(BrNap) is only weakly photoactive and shows 8% formation of **1**(BrNap) with 10 min photolysis. Continued irradiation shows further formation of **1**(BrNap) and 1,4-dibromonaphthalene. Some other products containing phosphorus are also seen. Solvent or solvent impurities can act as traps. With alkene trap and 10 min irradiation, all the **2**(BrNap) converts to **1**(BrNap).

In the presence of 1-hexene trap **2**(Ph) and **2**(2-Nap) are nearly inactive. Prolonged irradiation (hours) does show conversion to **1**(Ph) and **1**(2-Nap) respectively. The quantum yields of **2**(Ph) and **2**(2-Nap) should be less than 1% as shown in Table 2.3.2. **2**(CF₃Ph) is highly light sensitive and all of it convert to **1**(CF₃Ph) very quickly. Similarly **2**(BrNPh), **2**(BrMeO₂Ph) and **2**(BriPrOPh) readily convert to **1**(BrNPh), **1**(BrMeO₂Ph) and **1**(BriPrOPh), respectively. No photo-induced ring bromination is observed for **2**(BrNPh), **2**(BriPrOPh), **2**(BrMeO₂Ph) and **2**(CF₃Ph).

Initial photolysis of **2**(cisBr) showed most of it isomerizing to **2**(Br) along with minor amounts of **1**(Br) and **1**(cisBr). Extended photolysis gave complete conversion to 66% **1**(Br) and 33% **1**(cisBr).

Photolysis of the diplatinum compound **2**(DiPt) with 1-hexene alkene trap yielded a mixed valent **1**(DiPt)**2** complex as shown in the Scheme 2.3.1. Based on ^1H and ^{31}P NMR no **1**(DiPt) was observed. 1,2-dibromohexane, the Br_2 addition product of 1-hexene was observed.

Scheme 2.3.1. Diplatinum complex photolysis.

Using a chemical actinometer (potassium ferrioxalate) quantum yields (Φ) were measured.^{47, 48} Thus, the Br_2 photoelimination step efficiency was quantified. The values are given in Table 2.3.2. **2**(CF_3Ph) shows a very high quantum yield of 82%. One of our former group member Dr. Mehdi Masjedi's synthesis of perylene coordinated platinum(IV) complexes, allowed the photolysis to be conducted in the visible (440 nm) rather than the uv region. Perylene's strong π - π^* transitions in the visible region enables

this. Hence depending on the ligand environment we can shift the photolysis into the visible region as well.³⁰

Table 2.3.2. Quantum yields (Φ) at 313 nm for conversion of **2** to **1** in the presence of 1-hexene.^a

R	Quantum Yield (Φ) (%)
Br	59
Ph	<1
CF ₃ Ph	82
Br ₂ NPh	5
1-Nap	13
BrNap	19
2-Nap	<1
Phen	13, 15 ^b

^a CH₂Cl₂ solvent, [1-hexene] = 0.13 M. ^b [1-hexene] = 1.0 M

Reactivity with other traps was investigated to further understand the Br₂ photoelimination process. A reactive trap like 2,3-dimethyl-2-butene (TME) unlike 1-hexene and *cis*-2-hexene had a different product profile. Photolysis products of **2**(Br) and **2**(BrNap) were investigated with various concentrations of TME and the results are

shown in Table 2.3.3 and Table 2.3.4, respectively. For **2**(BrNap) photolysis the corresponding **1**(BrNap) was seen. In the case of **2**(Br) we observed the isomers **1**(Br) and **1**(cisBr) as major and minor products, respectively. Photolysis of **2**(Br) at 313 nm in CDCl₃ with 1-hexene alkene trap also showed the same trend. Apart from the TME Br₂ addition product 2,3-dimethyl-2,3-dibromobutane (**3**),⁴⁹ we observe some allylic bromination product 1-bromo-2,3-dimethyl-2-butene (**4**)^{50, 51} as well. Also 2-bromo-2,3-dimethylbutane (**5**) is detected.⁴⁹ HBr generated from production of **4** reacts with TME to yield **5**. Yield of **4** increased with increasing trap (TME) concentrations. Similar reaction trends are observed for **2**(BrNap) as well as shown in Table 2.3.4. The alkene reaction product profile, depends on the reaction conditions and is very sensitive to impurities in solvents and traps. Hence, these experiments were carried out in drybox conditions and anhydrous solvents. In contrast, photolysis of an organoplatinum(IV) perylene derivative prepared by Dr. Masjedi, exclusively gave the Br₂ addition product **3** over TME concentrations varying from 22 to 560 mM.³⁰

Table 2.3.3. Photolysis product yields^a for *trans*-Pt(PEt₃)₂(Br)₄ (**2**(Br))^b with 2,3-dimethyl-2-butene (TME) trap at 313 nm in CDCl₃.

Products	[TME]		
	8 mM	34 mM	100 mM
<i>trans</i> -Pt(PEt ₃) ₂ (Br) ₂ (1 (Br))	89%	75%	70%
<i>cis</i> -Pt(PEt ₃) ₂ (Br) ₂ (1 (cisBr))	11%	25%	30%
3 2,3-dimethyl-2,3-dibromobutane ^c	73%	68%	62%
4 1-bromo-2,3-dimethyl-2-butene ^d	26%	34%	38%
5 2-bromo-2,3-dimethylbutane ^c	14%	39%	43%

^a Based on **2**(Br). ^b [**2**(Br)] = 4 mM. ^c Ref 49. ^d Refs 50 and 51.

Table 2.3.4. Photolysis product yields^a for *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) (**2**(BrNap))^b with 2,3-dimethyl-2-butene (TME) trap at 313 nm in CDCl₃.

Products	[TME]		
	17 mM ^c	50 mM	132 mM
1 (BrNap)	52%	100%	100%
2 (BrNap)	48%	—	—
3 2,3-dimethyl-2,3-dibromobutane ^c	33%	72%	65%
4 1-bromo-2,3-dimethyl-2-butene ^d	8%	27%	31%
5 2-bromo-2,3-dimethylbutane ^c	3%	32%	33%

^a Based on **2**(BrNap). ^b [**2**(BrNap)] = 7 mM. ^c Ref 49. ^d Refs 50 and 51, ^e [TME] not sufficient for conversion of all **2**(BrNap).

Evidence for molecular bromine (Br_2) as the brominating agent for the alkene trap was also found in a competition experiment. Photolysis of **2**(BrNap) with an excess 1:1 mixture of 1-hexene and *trans*-3-hexene was carried out at 313nm in CDCl_3 (Scheme 2.3.2).^{35, 52} Only *trans*-3-hexene brominated product 3,4-*trans*-dibromohexane (**6**) was seen. 1,2-dibromohexane (**7**) was not observed. Alternatively to an excess 1:1 mixture of *trans*-3-hexene and 1-hexene, when a solution of Br_2 in CDCl_3 was added, 3,4-*trans*-dibromohexane was only observed. The 1-hexene addition product 1,2-dibromohexane was not seen. The solution of Br_2 in CDCl_3 was added slowly with vigorous stirring to mimic the conditions of Br_2 photoelimination from **2**(BrNap).

Scheme 2.3.2. Alkene trap competition experiment.

2.4 HBr Photolysis

Gaseous HBr was added to platinum(II) complexes to check for oxidative addition and ring bromination products. This is illustrated in Scheme 2.4.1. Addition of gaseous HBr to CDCl₃ solutions of **1**(1-Nap) and **1**(Phen) showed no reaction. Further photolysis of the same solutions at 313 nm also showed no reaction. Neither photolytic oxidative addition of HBr to the platinum(II) center nor bromination of the naphthyl or phenanthryl ring is seen. HBr addition to the metal center photolytically or thermally is an important step in the realization of the HBr splitting cycle by a metal catalyst.

Scheme 2.4.1. HBr addition to platinum(II) complex.

2.5 Photokinetics

Photolysis kinetic measurements were carried out in the presence of 313 nm radiation. The reaction rate is zero order in terms of **2**(BrNap). The photon flux is rate limiting. The photolysis rate is affected by the reactivity of the traps. Measurements were carried out in TME and 1-Hexene as shown in Figures 2.5.1 and 2.5.2. The rate is doubled with TME as trap in comparison to 1-hexene. With TME the rate constant is $1.2(\pm 1) \times 10^{-3} \text{ Mmin}^{-1}$. The rate constant with 1-hexene is $6(\pm 1) \times 10^{-4} \text{ Mmin}^{-1}$. The error percentages are based on 4% error associated with ^{31}P integration.³⁶

Figure 2.5.1. Kinetic plot (table from ^{31}P) for the photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2**(BrNap) with TME (0.48 M) at 313 nm in CDCl₃.

Figure 2.5.2. Kinetic plot (from ^{31}P) for the photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) 2(BrNap) with 1-hexene (0.46 M) at 313 nm in CDCl₃.

The photolysis rate was unaffected by the presence of gaseous oxygen. 2(BrNap) photolysis (313 nm) with 1-hexene was monitored after the addition of O₂ gas as shown in Figure 2.5.3. The rate constant $6(\pm 1) \times 10^{-4} \text{ Mmin}^{-1}$ in the presence of oxygen was the same as in the absence of oxygen. The error percentages are based on 4% error associated with ^{31}P integration.³⁶ There is no quenching by O₂. Quenching by paramagnetic O₂ is significant in the case of triplet excited states usually.

Figure 2.5.3. Kinetic plot (from ^{31}P) for the photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2**(BrNap) with 1-hexene (0.46 M) at 313 nm in CDCl₃ in the presence of oxygen.

To check for photoelimination of Br₂, photokinetic monitoring of **2**(BrNap) at 380 nm was undertaken with trap in the presence and absence of **1**(BrNap). At 380 nm **1**(BrNap) has no absorption and **2**(BrNap) has a molar extinction coefficient of 2976 M⁻¹cm⁻¹. Br₂ molar extinction coefficient at 380 nm is ~106 M⁻¹cm⁻¹. **2**(BrNap) photolysis at 380 nm with excess 1-hexene follows zero order dependence on the concentration of **2**(BrNap). The photon flux is rate limiting. The rate constant was 7.9(8) X 10⁻⁵ Mmin⁻¹ as shown in Figure 2.5.4.

Figure 2.5.4. Kinetic plot (from ^{31}P and ^1H NMR) for the photolysis of *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Br})_3(4\text{-BrNap})$ **2**(BrNap) with 1-hexene (0.46 M) at 380 nm in CDCl_3 .

2(BrNap) photolysis at 380 nm with excess 1-hexene in the presence of **1**(BrNap) also follows zero order dependence with concentration of **2**(BrNap). The photon flux is rate limiting. But the rate constant is decreased almost by half and has a value of $4.1(3) \times 10^{-5} \text{ Mmin}^{-1}$ as shown in Figure 2.5.5 **1**(BrNap) competes with the trap (1-hexene) for the photogenerated Br_2 and hence probably we see the decrease in the rate.

Figure 2.5.5. Kinetic plot (from ^{31}P and ^1H NMR) for the photolysis of *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Br})_3(4\text{-BrNap})$ **2**(BrNap) with 1-hexene (0.46 M) in the presence of *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Br})(4\text{-BrNap})$ **1**(BrNap) at 380 nm in CDCl_3 . (Beginning **2**(BrNap):**1**(BrNap) ratio is 44:56)

2.6 Thermal reactions

Complexes **2** eliminate Br_2 and convert to **1** in the presence of traps through the thermal pathway as well. Thermal conversion happens at room temperature and shows first-order dependence with regards to **2**(CF_3Ph) as shown in Figures 2.6.1-2.6.3. The average rate constant is $1.4(2) \times 10^{-3} \text{ min}^{-1}$. The thermochemistry significance of this rate constant is explained in the discussion section. The reaction rate is independent of the alkene concentration. Experiments were carried out in the presence of 1-hexene ranging from 0.096 M to 0.38 M. Thermolysis rate is affected by solvent polarity. Reaction of **2**(CF_3Ph) in benzene with trap showed only 5 - 10% conversion to **1**(CF_3Ph) after nearly

four days. In comparison all of **2**(CF₃Ph) converted to **1**(CF₃Ph) within 2 days in CDCl₃. Hence, the rate determining step probably involves a polar transition state.

Figure 2.6.1. Kinetic plot (from ³¹P and ¹⁹F NMR) for the 1-hexene dark reaction of *trans*-Pt(PtEt₃)₂(Br)₃(CF₃Ph) **2**(CF₃Ph) (4.3 mM) at 300 K and [1-hexene] = 0.096 M in CDCl₃.

Figure 2.6.2. Kinetic plot (from ³¹P and ¹⁹F NMR) for the 1-hexene dark reaction of *trans*-Pt(PEt₃)₂(Br)₃(CF₃Ph) 2(CF₃Ph) (4.3 mM) at 300 K and [1-hexene] = 0.19 M in CDCl₃.

Figure 2.6.3. Kinetic plot (from ³¹P and ¹H NMR) for the 1-hexene dark reaction of *trans*-Pt(PEt₃)₂(Br)₃(CF₃Ph) 2(CF₃Ph) (4.2 mM) at 300 K and [1-hexene] = 0.38 M in CDCl₃.

The other **2** complexes are stable in the presence of the trap at room temperature. But conversion of **2** to **1** is seen at temperatures varying from 50 to 120 °C. Thermolysis kinetics of **2**(BrNap) conversion to **1**(BrNap) was monitored in the presence of trap in CDCl₃ at 325 K. The rate constant was $9(\pm 1) \times 10^{-4} \text{ min}^{-1}$. The thermochemistry significance of this rate constant is explained in the discussion section. The error percentage is based on 4% error associated with ³¹P integration.³⁶ The thermal reaction had first-order dependence in **2**(BrNap) concentration as shown in Figure 2.6.4. Thermolysis of **2**(1-Nap) with trap in CDCl₃, yields 59% of **1**(BrNap) and 41% of **1**(1-Nap). This ratio is the reverse of the photolysis ratio.

Figure 2.6.4. Kinetic plot (from ³¹P) for the 1-hexene dark reaction of trans-Pt(PEt₃)₂(Br)₃(4-BrNap) **2**(NapBr) (3.1 mM) at 325 K and [1-hexene] = 0.31 M in CDCl₃.

2.7 Br₂ addition to platinum(II) versus alkene

Bromination competition experiments were carried out to check the rate of Br₂ addition to **2**(BrNap) versus 1-hexene. This is shown in Equations 2.7.1 and 2.7.2.

Addition of Br₂ to a 1:1 ratio of **1**(BrNap):1-hexene reaction mixture showed bromination of **1**(BrNap). **2**(BrNap) was observed based on ¹H and ³¹P NMR. The 1-hexene addition product 1,2-dibromohexane (**7**) was not seen. Addition of Br₂ to a 1:10 ratio of **1**(BrNap):1-hexene reaction mixture also showed bromination of **1**(BrNap) only. **2**(BrNap) was observed rather than the alkene addition product **7**. Br₂ solution was added in one shot to the **1**(BrNap):1-hexene reaction mixture under constant stirring. This suggests that bromination of platinum(II) is at least 10 times faster than Br₂ addition to 1-hexene.

2.8 Low temperature photoemission

2(BrNap) and **2**(Br) in 2-methyltetrahydrofuran glass at 77 K showed no low-temperature photoemission. **1**(BrNap) in 2-methyltetrahydrofuran (MeTHF) glass at 77 K showed yellowish green colored low-temperature photoemission with excitation at 360 nm and

340 nm. Broad emission spectra with structured emission bands at 520 and 564 nm are observed as shown in Figure 2.8.1.

Figure 2.8.1. Photoemission spectrum of *trans*-Pt(PEt₃)₂(Br)(4-bromo-1-naphthyl) 1(BrNap) in 2-methyltetrahydrofuran glass at 77K with 360 nm excitation.

The emission at 520 nm shows exponential decay with a mean life time of 332 μ s as shown in figure 2.8. This decay is also visually observed. As soon as the solution is warmed to room temperature the yellowish green color quickly fades. The long life time is indicative of the phosphorescence of the naphthalenyl ring which shows emission at 471, 480, 483, 504, 506, 509, 510, 514, 518, 523 nm.^{53, 54} Photochemistry of **2**(Br) and **2**(BrNap) with trap at 77 K in MeTHF is very slow. The molecules are held rigidly in the frozen matrix.

Figure 2.8.2 Emission decay at 520 nm for *trans*-Pt(PtEt₃)₂(Br)(4-bromo-1-naphthyl) **1**(BrNap) in 2-methyltetrahydrofuran glass at 77K, lifetime = 332(1) μs, λ(excitation) = 360 nm, gate time = 0.1 ms and delay time = 0.1 ms.

2.9 Solid state photolysis

We see solid state conversion of **2**(NapBr) to **1**(NapBr) in the presence of 313 nm light. Photolysis of **2**(NapBr) deposited on the sides of a quartz NMR tube by solvent evaporation shows conversion to **1**(NapBr). This can be seen from the orange to yellow color change in some areas. When the volatiles were condensed onto a frozen solution containing 1-hexene, the bromine addition products were seen using ¹H NMR spectroscopy. Rate of photoconversion was affected by experimental conditions (deposit thickness and residual solvent). Interestingly, **2**(1-Nap) in the solid state over the course of a year yielded ring-brominated **1**(BrNap) exclusively. Further investigation and Br₂ elimination yield measurement is required. Previously solid state Br₂ and Cl₂ elimination

from gold and platinum systems were reported by the Nocera group.^{21, 32} No yields were reported though.

2.10 Calorimetry

The bromine reaction enthalpies of the four complexes **1**(Br), **1**(Ph), **1**(CF₃Ph) and **1**(BrNap) were determined in toluene by the Hoff group using calorimetry.³⁰ The gas-phase DFT calculations on **1'** (PMe₃ used in place of PEt₃) were carried out by Prof. Sharp and the theoretical enthalpy and free energy changes were calculated. The M06 functional gave values close to that of the experimental.³⁰ The results are shown in Table 2.10.1.

Table 2.10.1. Thermodynamic values (kcal/mol) for the bromination of **1** and **1'**.³⁰

R	ΔH			ΔG
	Exp ^a	B3LYP ^b	M06 ^b	M06 ^b
Ph	-38.3 ± 1.5	-20.7	-32.5	-21.8
Nap	-20.5 ± 1.5^c	-10.6	-23.6	-10.5
CF ₃ Ph	-17.5 ± 2	-2.7	-16.3	-4.7
BrMeO ₂ Ph	-	-	-16.8	-2.2
Br	-20.9 ± 1	-16.2	-27.4	-15.3

^a Toluene solvent. ^b Gas phase for *trans*-Pt(PMe₃)₂(R)(Br) **1'**. ^c R = BrNap, LANL2DZ basis set for Br, P and Pt (an added d function), 6-31G(d) basis set for all other atoms.

2.11 Structures

Using single crystal X-ray diffraction studies by Dr. Charles Barnes the solid-state structures of **2**(Br, BrNPh, BrMeO₂Ph, BrNap, BriPrOPh, DiBrPt, depe) were determined. **2**(BrNap), **2**(DiBrPt), **2**(depe), **2**(BriPrOPh), **1**(CF₃Ph) and **1**(DiPt) probability ellipsoidal drawings are shown in Figures 2.11.1-2.11.6, respectively. The effect of *peri*-hydrogen (R = BrNap) or a vicinal substituent on the aryl ring (R = BrNPh, DiBrPt, BrMeO₂Ph, BriPrOPh) leads to steric crowding at the platinum center and can be seen in the crystal structures. The Br and PEt₃ ligands *cis* to the aryl group are sterically hindered. The aryl group tilts about 45° with regards to the P-Pt-P axis. In this way the *peri*-hydrogen or the vicinal substituent on the aryl ring is nestled between a *cis* bromo and a PEt₃ ligand. The effect of sterics is clearly visible in the metrical parameters listed in Table 2.11.1. The probability ellipsoid drawing for **2**(BrNap) is shown in Figure 2.11.1. The Pt1-C1-C4 angle is 173° and not linear. Similarly the Pt1-C1-C9 and Pt1-C1-C2 are 127° and 116°, respectively, and deviant from the expected 120° for a sp² carbon. The *peri*-hydrogen on C8 introduces this strain and the Pt1-C1-C9 angle is larger than the Pt1-C1-C2. These steric interactions are also seen at the octahedral platinum(IV) center. The C1-Pt1-Br3 and C1-Pt1-P2 angles are 95°. Br3 and P2 are *cis* with regards to the aryl ring. Correspondingly, the C1-Pt1-Br2 and C1-Pt1-P1 are 89° and as expected.

Figure 2.11.1. XSeed/POV-Ray drawing of **2**(BrNap). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.³⁰

The probability ellipsoid drawing for **2**(DiBrPt) is shown in Figure 2.11.2. The **2**(DiBrPt) also show the above mentioned steric effects. The naphthalenyl ring lies between the P-Pt-P and Br-Pt-Br planes. The PEt_3 and bromo ligands on either platinum are in the *anti*-conformation with regards to each other.

Figure 2.11.2. XSeed/POV-Ray drawing of **2**(DiBrPt). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.

Figure 2.11.3. XSeed/POV-Ray drawing of **2**(depe). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.

In the case of **2**(BrMeO₂Ph) shown in Figure 2.11.4 with vicinal substituents on both sides of the aryl ring the steric strain is felt on all four (P1, P2, Br2 and Br3) ligands. More deviation is seen with regards to the PEt₃ ligands though. The probability ellipsoid drawing for **2**(BriPrOPh) is shown in figure 2.11.4. The **2**(BriPrOPh) parameters are similar to **2**(BrNap). In the case of 2-phenanthrenyl and 2-perylenyl platinum(IV)

analogues and DFT structures of the PMe_3 analogue **2'** calculated by Prof. Sharp also such steric effects were seen.³⁰

Figure 2.11.4. XSeed/POV-Ray drawing of **2**(BrPrOPh). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.

Using single crystal X-ray diffraction studies by Dr. Barnes the solid-state structures of **1**(CF_3Ph , NPh , MeO_2Ph , BrMeO_2Ph , DiPt) were also obtained. The aryl ring plane lies between the two *trans*- PET_3 ligands. The *peri*-hydrogen or vicinal substituents influence the parameters of the ligand *cis* to them. **1**(CF_3Ph) structure is interesting and shown in Figure 2.11.5. The Pt1 nestles between two of the CF_3 fluorine atoms. Hence the P-Pt-P angle on the CF_3 side is close to 188° and bent. The **1**(DiPt) structure is shown in figure 2.11.6.

Figure 2.11.5. XSeed/POV-Ray drawing of **1**(CF₃Ph). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.³⁰

Figure 2.11.6. XSeed/POV-Ray drawing of **1**(DiPt). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.

Table 2.11.1. Metrical parameters for **2** (R = BrNap, ^bBrMeO₂Ph, ^bBriPrOPh, DiBrPt).

Atoms ^a	2 (BrNap)	2 (BrMeO ₂ Ph)	2 (BriPrOPh)	2 (DiBrPt)
Pt1-C1	2.107(5)	2.104(2)	2.105(6)	2.104(3)
Pt1-C1-C4	172.8(4)	177.3(2)	170.07	171.54
Pt1-C1-C2	115.9(4)	121.9(2)	115.7(4)	116.8(2)
Pt1-C1-C9	127.4(4)	121.4(2)	126.1(4)	128.1(2)
C1-Pt1-P1	88.24(14)	93.72(6)	89.21(15)	89.06(9)
C1-Pt1-P2	94.93(14)	93.34(6)	93.86(15)	93.71(9)
C1-Pt1-Br2	89.38(14)	90.91(6)	89.95(15)	90.39(9)
C1-Pt1-Br3	95.10(14)	89.55(6)	93.69(15)	96.01(9)

^a Numbering from **2**(BrNap). Corresponding atoms in other structures may have different numbers. ^b Ref 30.

CHAPTER 3: DISCUSSION

3.1 Effect of sterics on photochemistry

Initially, halogen photoelimination from organoplatinum(IV) centers was investigated using sterically encumbered aryl ligands to probe the effects of sterics at the metal center. The idea was that steric bulk adjacent to the metal center spring loads the complex for Br₂ photoelimination. In complex **2**(BrNap) the *peri*-hydrogen is nestled between the bromo and phosphine ligand as shown in Scheme 3.1.1. In complexes **2**(CF₃Ph, BrNPh, BrMeO₂Ph, and BriPrOPh) also the vicinal substituent exercises steric effects similar to the *peri*-hydrogen. The solid-state X-ray structure and DFT calculations support steric interaction between the *peri*-hydrogen and the bromo ligand.³⁷ Thus, the initial inference was in complexes **2** halogen elimination can be turned on or off based on sterics.³⁰

Scheme 3.1.1. *Peri*-hydrogen sterics.

From literature we know that the *peri*-hydrogen atoms protect 1-naphthalenyl and 2-anthracenyl platinum(II) centers from Br₂ addition.^{29, 45} Previously our group had

reported novel polybromoanthracenes by addition of excess Br₂ to an anthracenyl platinum(II) complex as shown in Scheme 3.1.2.⁴⁵ Addition of bromine was not seen at the platinum center even with huge excess of Br₂. This was attributed to *peri*-hydrogen sterics.

Scheme 3.1.2. *peri*-hydrogen sterics in platinum(II) anthracenyl complex.

Correspondingly, the 1-phenyl and 2-naphthyl (**2**(2-Nap)) platinum(IV) complexes with no *peri*-hydrogen and vicinal substituents are nearly photoinactive. Also, it is known in aryl systems, the photoexcited state can be deactivated by rotation of the aryl ring.^{55, 56} Thus, if sterics prevent the facile rotation of the aryl ring, then deactivation of the excited state decreases, correspondingly, showing increase in the efficiency for the photoelimination process. Complex **2**(CF₃Ph) agrees with this trend and shows a very high quantum yield of 82%. Interestingly **2**(Br) shows a very high quantum yield of 59% for Br₂ photoelimination. This complex is relatively unhindered. Also the absence of the aryl ring in **2**(Br) decreases the deactivation pathways possible through facile rotation. Population, lifetime and decay of the excited state should be factors which should be explored in understanding the photoelimination process.

Hence, with regards to understanding the quantum yield measurements, no specific trends are observed. As discussed above sterics seem to play a role and is one of the aspects to be considered. **2**(1-Nap), **2**(BrNap) and **2**(Phen) show good quantum efficiencies of 13%, 19% and 13%, respectively. Correlating this to reaction free energies obtained from calorimetry and DFT calculations also does not show any specific trends.³⁰ Again the **2**(Br) with a high free energy change of 21 kcal/mol shows a very high quantum yield of 59%.³⁰ Hence, to consider the trends with regards to one specific aspect is not sufficient. Effects of sterics, electronics and photochemical deactivation pathways should be thoroughly explored.

3.2 Thermochemistry

Steric affects the thermochemistry of Br₂ addition to platinum(II) centers as well. Based on DFT calculations (by Prof. Sharp), calorimetry measurements (by Prof. Hoff) and X-ray crystal structure parameters, steric strain is revealed in platinum(IV) complexes.^{23, 28, 30} Correspondingly in the square planar platinum(II) complexes these effects are absent. Based on the DFT and calorimetry calculations, the **2**(CF₃Ph) complex shows the least stability for Br₂ elimination thermally. **2**(CF₃Ph) converts to **1**(CF₃Ph) at room temperature in the solution and solid state. A first and zero order dependence in **2**(CF₃Ph) and 1-hexene is seen respectively. A possible thermal Br₂ elimination mechanism for **2**(CF₃Ph) is shown in Scheme 3.2.1 The k_{obs} is $1.4(2) \times 10^{-3} \text{ min}^{-1}$ based on the kinetic measurement is comparable to the k_{re} . Based on the DFT calculations the free energy

change associated with the Br₂ addition to **2**(CF₃Ph) is ~5 kcal. Correspondingly the k_{ox} value should be at least 10 min⁻¹M⁻¹.³⁰

Scheme 3.2.1 Thermal Br₂ elimination mechanism for **2**(CF₃Ph).

The **2**(BrNap) converts to **1**(BrNap) at 325 K in the solution state. The possible thermal Br₂ elimination mechanism for **2**(BrNap) is shown in Scheme 3.2.2. A first order dependence in **2**(BrNap) is observed. Based on the above **2**(CF₃Ph) kinetics for Br₂ elimination a zero order dependence with 1-hexene for **2**(BrNap) is also assumed. k_{obs} is comparable to k_{re} and a value of 9(±1) X 10⁻⁴ min⁻¹ was obtained. Based on the DFT calculations the free energy associated with thermal Br₂ elimination from **2**(1-Nap) is ~ 11 kcal.³⁰ This should be comparable to **2**(BrNap) free energy change. Hence, the k_{ox} value should be at least 2 X 10⁴ min⁻¹M⁻¹ at 325 K. Based on these k_{ox} values of **2**(CF₃Ph) and **2**(BrNap), the rate of Br₂ addition to platinum(II) complexes seems very fast.

Scheme 3.2.2. Thermal Br₂ elimination mechanism for **2(BrNap)**.

Electronic factors also affect the thermochemistry of our platinum(II) complexes. Looking at the free energy change associated with the bromination of **1(Br)** and **1(Ph)**, we see that the **1(Ph)** free energy change is more negative. Possibly the phenyl ligand is more electron donating in **1(Ph)** compared to the bromo ligand in **1(Br)**.³⁰

3.3 Br₂ addition to platinum(II) versus alkene comparison

Based on literature and experimental results the alkene versus platinum(II) Br₂ addition rates were compared. At low Br₂ concentrations (< 10⁻³ M) and absence of bromide ions, the bromination rate expression is second order.⁵⁷ It is first order with both alkene and Br₂. Further, at high alkene concentrations the rate law is reduced to first order as shown in Scheme 3.3.1. From literature the second order rate constant for 1-hexene in CCl₄ was 0.015 min⁻¹M⁻¹.⁵⁸ For 1-pentene in acetic acid it was found to be 990(± 12) min⁻¹M⁻¹.⁵⁷ In the case of cyclohexene the second order rate constant was 684(13) min⁻¹M⁻¹ in CDCl₃.⁵⁹

At low Br_2 concentrations^a

$$\text{Rate} = k_{\text{alkene}}[1\text{-hexene}][\text{Br}_2]$$

$$\text{Rate} = k'_{\text{alkene}}[\text{Br}_2] \quad (\text{with excess alkene})$$

$$k'_{\text{alkene}} = k_{\text{alkene}}[1\text{-hexene}]$$

$$k_{\text{alkene}} = 0.015 \text{ min}^{-1}\text{M}^{-1} \text{ (CCl}_4 \text{ at 298 K)}^b$$

For 1-pentene

$$k_{\text{alkene}} = 990 (+/- 12) \text{ min}^{-1}\text{M}^{-1} \text{ (Acetic acid at 298 K)}^a$$

For cyclohexene

$$k_{\text{alkene}} = 684 (13) \text{ min}^{-1}\text{M}^{-1} \text{ (CDCl}_3 \text{ at 298 K)}^c$$

Scheme 3.3.1. Br_2 addition to alkene rates.^a Ref 57, ^b Ref 58, ^c Ref 59

Possible reaction rate expression for Br_2 addition to platinum(II) center is shown in Scheme 3.3.2. It is first order in both platinum(II) and Br_2 . Further, at high platinum(II) concentrations the rate law is reduced to a first order expression. Based on the thermochemistry and kinetic experiments the k_{ox} value should be at least $2 \times 10^4 \text{ min}^{-1}\text{M}^{-1}$ at 325 K. k_{ox} is the same as k_{PtII} in Scheme 3.3.2. According to the rate expression and experimental results the platinum(II) bromination rate is at least ten times greater than alkene bromination rate.

At low $[\text{Br}_2]$

$$\text{Rate} = k'_{\text{PtII}}[\text{Br}_2] \quad (\text{with excess PtII})$$

$$k'_{\text{PtII}} = k_{\text{PtII}}[\text{PtII}]$$

$$\text{Rate} = k_{\text{PtII}}[\text{PtII}][\text{Br}_2]$$

$$k_{\text{PtII}} \sim 2 \times 10^4 \text{ min}^{-1}\text{M}^{-1} \text{ at } 325 \text{ K}$$

$$k_{\text{PtII}} > 10k_{\text{alkene}}$$

Scheme 3.3.2. Br_2 addition to platinum(II).

3.4 Photochemical pathways

A simplified Jablonski diagram is shown in Scheme 3.4.1 to understand the various photoexcited pathways.³⁰ The strong $\pi-\pi^*$ singlet state transition ($S_0 \rightarrow S_x$) is significant in the case of organoplatinum (IV) complexes coordinated to aryl ligands. For **2(Br)** with a bromo and phosphine ligand framework there are no $\pi-\pi^*$ transitions. Further at 313 nm and 380 nm (absorption at the tail end in the uv-vis spectrum) **2(BrNap)** undergoes facile Br_2 photoelimination. This suggests that from a lower energy singlet excited state S_1 intersystem crossing (ISC) happens into the triplet (T_1) state. S_1 is probably the Br-Pt LMCT excited state involving the $n-\sigma^*$ transition where bromine lone pairs get excited to the σ^* orbital on the metal center. Based on DFT calculations in our group for Br_2 , Cl_2 and HOCl eliminations we see that T_1 is the lowest energy state from which the various

photochemical reaction pathways are accessed. The triplet excited state also has more radical character.^{37, 38} The triplet platinum excited state can be trapped by solvents and traps (*cis*-2-hexene, 1-hexene and TME). Self-trapping generates ring brominated products. The population of the T_1 state is crucial with regards to the quantum yield. The various processes affecting it are fluorescence (k_{fx} of $\pi-\pi^*$ and k_{f1} of $n-\sigma^*$), phosphorescence (k_p) and non-radiative decay. Non-radiative decay rates k_{nrs1} , k_{nrsx} , and k_{nrt} relating to $S_1 \rightarrow S_0$, $S_x \rightarrow S_1$, and $T_1 \rightarrow S_0$ transitions, respectively, also compete with the radiative decay pathways.

Scheme 3.4.1. Photoexcited pathways.

Photoelimination kinetic studies and investigation of the trap reaction products gives us insights with regards to net Br₂ photoelimination from our platinum(IV) complexes. Our results support Br₂ elimination as well as an excited state radical pathway. With less reactive traps like *cis*-2-hexene *anti*-bromination product is observed. Addition of Br₂ to alkene proceeds through a cyclic bromonium ion mechanism and *anti*-products are favored.⁶⁰⁻⁶² The mixed alkene bromination competition experiment also support elimination of molecular bromine (Br₂), whilst photolysis of **2**(BrNap). Only 3,4-*trans*-dibromohexane addition product is observed on photolysis of **2**(BrNap) with excess 1:1 mixture of *trans*-3-hexene and 1-hexene. 1,2-dibromohexane, the 1-hexene addition product is not seen. This result is in agreement with molecular Br₂ addition to excess 1:1 mixture of *trans*-3-hexene and 1-hexene. This also showed only the 3,4-*trans*-dibromohexane and no 1,2-dibromohexane is observed. Hence, the competition experiment suggests that the brominating agent is molecular bromine (Br₂).

Further the kinetic studies on **2**(BrNap) photoelimination in the presence and absence of **1**(BrNap) gave important insights. A decrease in **2**(BrNap) photolysis rate is observed when a 1:1 mixture of **2**(BrNap):**1**(BrNap) is photolysed at 380 nm with 1-hexene. Thus, the product **1**(BrNap) is competing with the alkene for the photoeliminated Br₂. **1**(BrNap) combines with Br₂ very quickly to form **2**(BrNap) decreasing the rate. Hence, there is support for Br₂ photoelimination from platinum(IV) centers based on these results.

3.5 Excited state platinum precursor

In the presence of a reactive trap like TME the alkene product profile is different in comparison to a less reactive alkene like 1-hexene. TME along with the bromine addition product yields alkene products which can only be accessed through the radical pathway. An increase in the trap concentration thus should increase the radical pathway products. With higher trap concentrations, the probability of trap molecules reacting with the excited state is higher. There was one exception seen, though. In the case of a perylene based σ -bonded platinum(IV) complex prepared by Dr. Masjedi, only the Br_2 addition product was observed even with a reactive trap like TME. The platinum excited state quickly eliminates Br_2 in comparison to the radical pathway. Also the radical excited state character could be more delocalized because of the ligand system.³⁰ Hence, Scheme 3.5.1 is given rationalizing the reactivity of the excited state platinum center with reactive and not so reactive traps.³⁰

Scheme 3.5.1 Reactivity of platinum excited state.

3.6 Bromo anion, bromo radical versus Br₂ elimination

To understand our system we looked at the [PtBr₆]²⁻ photochemistry. The Tarnovsky group using transient absorption spectroscopy measurements and computational modelling, had reported initial displacement of a bromo ligand to form [Pt(H₂O)Br₅]¹⁻ in aqueous solutions.⁶³ Previously also bromine anion,^{64, 65} bromine atom⁶⁶ and Br₂⁶⁷ eliminations were reported in the literature. Depending on the reaction conditions there have been reports of a radical like excited state platinum species.^{68, 69} Our platinum(IV) complexes are neutral species with non-aqueous solubility behavior. Hence, direct comparison to [PtBr₆]²⁻ is not feasible. Also phosphines and strong σ -donor aryl ligands add to the variation of the ligand environment at the platinum center. Hence CH₂Cl₂ soluble [NBu₄]₂[PtBr₆] was synthesized by our group member Andreas Ross and its photochemistry was studied.³⁰ It showed evidence for bromo ligand dissociation just like in [PtBr₆]²⁻. Hence, the corresponding differences in our platinum complexes behavior and [PtBr₆]²⁻ maybe based on charge or the variation in ligand environment. Bromo ligand dissociation is favored from an anionic [PtBr₆]²⁻ species versus our neutral platinum complexes. In the case of [PtBr₆]²⁻ the lowest energy triplet state is a metal centered, ligand field ³T_{1g} state with close lying Br-to-Pt charge transfer state.^{63, 70} Based on DFT calculations by Dr. Sharp we see that the lowest energy triplet state is a charge transfer excited state with bromine radical character. This directs us to the Br-to-Pt charge transfer state (LMCT) as the lowest energy triplet in our complexes. The Br₂ elimination proceeds from this triplet state.

3.7 *cis* photoelimination

Some additional insights of the photochemical process were gained from other group member's work. From studies done by Tharushi Perera and Lasantha Wickramasinghe, we see evidence for the photoelimination process to happen in the *cis* rather than the *trans* fashion.³⁷ This might have implications if the ligand coordination environment is too rigid around the metal center with regards to halogen photoelimination.

CHAPTER 4: EXPERIMENTAL SECTION

4.1 Materials and General Procedures

$\text{Pt}(\text{PEt}_3)_4$,³⁹ *cis*- $\text{Pt}(\text{PEt}_3)_2(\text{Cl})_2$,⁷¹ and 1,4-dibromonaphthalene,⁴¹ were prepared by reported procedures. Reagents were purchased from commercial sources (Aldrich or Acros) and used as received. Experiments performed under dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox or on a Schlenk line are specifically mentioned. Solvents for dinitrogen atmosphere experiments were dried, degassed and stored under dinitrogen over 4 Å molecular sieves or sodium metal. NMR spectra were recorded on Bruker AMX-250, -300, or -500 spectrometers at ambient probe temperatures except as noted. NMR shifts are given in δ with positive values downfield of TMS (^1H and ^{13}C), external H_3PO_4 (^{31}P), or external K_2PtCl_4 (aq) (^{195}Pt , δ -1630). ^{13}C and ^1H NMR spectra were recorded in proton-decoupled mode. Peaks assignment was assisted by ^{13}C dept-135 experiments. Desert Analytics performed the microanalyses. Uv-vis spectra were recorded on a Cary 50, Cary 100 or Hewlett-Packard 8452 diode array spectrophotometer in quartz cells. Photolysis was performed in quartz (uv or fluorescence) or borosilicate glass vessels using a 500 W halogen lamp, a 400 W medium pressure Hg lamp, a Philips PL-S 9W/01, 9 W lamp with a 300-380 nm band pass filter (313 nm emission), or LED's of the indicated wavelength. Emission spectra were obtained on a Varian Cary Eclipse fluorescence spectrophotometer with 1 cm path length quartz cells. For low temperature, emission spectra and lifetime were obtained on a Cary Eclipse Fluorescence spectrophotometer with samples in quartz (UV)/NMR tube at 77 K. Photolysis was also performed at 77 K in a quartz (UV)/NMR tube using LED's. For 380

nm irradiations, a home built tube photo-reactor was used and consisted of a short section of 4.2 cm PVC pipe lined with 24 LED's (superbrightleds.com, RL5-UV031 5mm UV LED) connected in series.³⁸

4.2 Syntheses

***trans*-Pt(PEt₃)₂(Br)₂ 1(Br).** Yellow-white waxy solid *cis*-Pt(PEt₃)₂(Cl)₂ (836.3 mg, 1.665 mmol) was dissolved in CH₂Cl₂ to yield a yellow clear solution. The solution was transferred to a 100 mL sealable tube and the volatiles were removed *in vacuo*. Absolute ethanol (10 mL) and finely ground KBr (12 g, 100 mmol) were added to form a cloudy light yellow solution. The tube was sealed and its contents were heated at 100 °C for 9 h with constant stirring. Within a few minutes of heating the mixture had changed to a deep yellow clear solution with KBr/KCl solid at the bottom. The mixture was cooled to room temperature and the volatiles were removed *in vacuo*. The residue was extracted with ~40 mL pentane and the extract was filtered through a diatomaceous earth pad to give a yellow clear solution. The volatiles were removed *in vacuo* to give 418.4 mg (43 %) of yellow crystalline solid of 1(Br). The residue from the pentane extraction was then extracted with CH₂Cl₂ to yield a clear yellow solution. The volatiles were removed *in vacuo* to give 349.7 mg (36 %) of light yellow crystalline solid *cis*-Pt(PEt₃)₂(Br)₂ 1(cisBr). Total yield was 79 %.

³¹P{¹H} NMR (101 MHz, CDCl₃): 8.2 (s with satellite, *J*_{PtP} = 2333 Hz); (101 MHz, C₆D₆): 8.4 (*J*_{PtP} = 2350 Hz); (101 MHz, DMSO-*d*₆): 10.1 (*J*_{PtP} = 2310 Hz); (101 MHz, toluene): 8.4 (*J*_{PtP} = 2360 Hz); (101 MHz, ethanol): 8.8 (*J*_{PtP} = 2400 Hz); (101 MHz,

diethyl ether): 9.0 ($J_{\text{PtP}} = 2350$ Hz); (101 MHz, pentane): 8.8 ($J_{\text{PtP}} = 2400$ Hz); (101 MHz, MeTHF): 8.75 ($J_{\text{PtP}} = 2362$ Hz).

^1H NMR (250 MHz, DMSO- d_6): 1.96 (asymmetric nine line pattern, $J_{\text{HH}} = 3.7$ Hz, 12H, CH_2CH_3), 1.07 (app q, $J_{\text{HH}} = 7.9$ Hz, 18H, CH_2CH_3); (C_6D_6): 1.87 (asymmetric nine line pattern, $J_{\text{HH}} = 3.7$ Hz, 12H, CH_2CH_3), 0.98 (app q, $J_{\text{HH}} = 7.9$ Hz, 18H, CH_2CH_3); (250 MHz, CDCl_3): 2.01 (asymmetric nine line pattern, $J_{\text{HH}} = 3.8$ Hz, 12H, CH_2CH_3), 1.13 (app q, $J_{\text{HH}} = 7.9$ Hz, 18H, CH_2CH_3).

***trans*-Pt(P Et_3) $_2$ (Br) $_4$ 2(Br).** This synthesis was conducted in air. Bromine (0.44 mL of a 584 mM CH_2Cl_2 solution) was added drop wise to a swirled yellow solution of *trans*-Pt(P Et_3) $_2$ (Br) $_2$ 1(Br) (140.4 mg, 0.2375 mmol) in ~7.5 mL CH_2Cl_2 . The resulting clear red solution was dried *in vacuo* to yield 150.7 g (85 %) of *trans*-Pt(P Et_3) $_2$ (Br) $_4$ 2(Br). The product was further washed with ~0.5 mL cold hexane, ~0.75 mL diethyl ether and 5 x 1 mL absolute ethanol, *in vacuo* to yield a powdery red solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (101 MHz, Toluene): -9.85 (s with satellite, $J_{\text{PtP}} = 1495$ Hz); (101 MHz, DMSO- d_6): -6.35 ($J_{\text{PtP}} = 1452$ Hz); (101 MHz, C_6D_6): -9.43 ($J_{\text{PtP}} = 1491$ Hz); (101 MHz, CDCl_3): -9.06 ($J_{\text{PtP}} = 1478$ Hz); (101 MHz, MeTHF): -9.95 ($J_{\text{PtP}} = 1496$ Hz).

^1H NMR (250 MHz, DMSO- d_6): 2.43 (asymmetric nine line pattern, $J_{\text{HH}} = 3.7$ Hz, 12H, CH_2CH_3), 1.23 (app q, $J_{\text{HH}} = 8.0$ Hz, 18H, CH_2CH_3); (250 MHz, C_6D_6): 2.29 (asymmetric nine line pattern, $J_{\text{HH}} = 3.7$ Hz, 12H, CH_2CH_3), 1.02 (app q, $J_{\text{HH}} = 8.0$ Hz, 18H, CH_2CH_3); (250 MHz, CDCl_3): 2.48 (asymmetric nine line pattern, $J_{\text{HH}} = 3.6$ Hz, 12H, CH_2CH_3), 1.28 (app q, $J_{\text{HH}} = 8.0$ Hz, 18H, CH_2CH_3).

***cis*-Pt(PEt₃)₂(Br)₂ 2(*cis*Br).** Check synthesis of **1(Br)**.

³¹P{¹H} NMR (101 MHz, CDCl₃): 9.60 (s with satellite, *J*_{PtP} = 3479 Hz); (101 MHz, DMSO-*d*₆): 11.97 (*J*_{PtP} = 3468 Hz).

¹H NMR (250 MHz, DMSO-*d*₆): 2.10 (asymmetric nine line pattern, *J*_{HH} = 7.5 Hz, 12H, CH₂CH₃), 1.08 (app q, *J*_{HH} = 8.1 Hz, 18H, CH₂CH₃); (250 MHz, CDCl₃): 2.13 (asymmetric nine line pattern, *J*_{HH} = 7.6 Hz, 12H, CH₂CH₃), 1.16 (app q, *J*_{HH} = 8.1 Hz, 18H, CH₂CH₃).

***cis*-Pt(PEt₃)₂(Br)₄ 2(*cis*Br).** This synthesis was conducted in air and *in situ*. Bromine (0.02 mL of a 567 mM CDCl₃ solution) was added drop wise to colorless solution of *cis*-Pt(PEt₃)₂(Br)₂ **1(cisBr)** (5.6 mg, 9.5 μmol) in ~1.2 mL CDCl₃. The resulting clear yellow solution yielded **2(cisBr)**.

³¹P{¹H} NMR (101 MHz, CDCl₃): 3.65 (*J*_{PtP} = 2029 Hz).

¹H NMR (250 MHz, CDCl₃): 2.48 (asymmetric nine line pattern, *J*_{HH} = 3.6 Hz, 12H, CH₂CH₃), 1.28 (app q, *J*_{HH} = 8.0 Hz, 18H, CH₂CH₃).

Pt(COD)(Br)₂ 1(COD). This compound has been previously reported via a different synthesis.^{72, 73} Outside the drybox to Pt(COD)(Cl)₂ (105 mg, 0.279 mmoles) in acetone (~7 mL) excess NaBr (~235 mg, 2.28 mmoles) was added and stirred for 5 hours at 29 °C. The reaction mixture was washed with water (3 X ~5 mL) and then dried *in vacuo* to yield 24.2 mg (19 %) of pale yellow **1(COD)**.

¹⁹⁵Pt NMR (64 MHz, CDCl₃): -3649 (s)

^1H NMR (250 MHz, CDCl_3): 5.66 (s with satellite, 4H, CH), 2.60 (b, 4H, CH_2), 2.23-2.04 (app d, 4H, CH_2)

Pt(depe)(Br) $_2$ 1(depe). This compound has been previously reported via a different synthesis.^{74, 75} Outside the drybox to a pale yellow cloudy solution of $\text{Pt}(\text{COD})(\text{Br})_2$ (7.5 mg, 16 μmoles) in toluene (~0.7 mL), depe (0.64 mL of a 25 mM toluene solution) was added under constant stirring. The resulting cloudy solution was stirred overnight and then dried *in vacuo*. The residue was extracted using CH_2Cl_2 (~5 mL) and further dried *in vacuo* to yield a pale yellow residue. This was washed with 3 X ~1 mL hexane and the volatiles were then removed *in vacuo* to yield 7.3 mg (80 %) of pale yellow **1(depe)**.

$^{31}\text{P}\{1\text{H}\}$ NMR (101 MHz, CDCl_3): 60.57 (s with satellite, $J_{\text{PtP}} = 3482$ Hz); (101 MHz, CD_2Cl_2): 60.80 (s with satellite, $J_{\text{PtP}} = 3486$ Hz); (101 MHz, DMSO-d_6): 63.53 (s with satellite, $J_{\text{PtP}} = 3484$ Hz).

^1H NMR (250 MHz, CD_2Cl_2): 2.53-1.65 (overlapping ms & app d, 8H & 4H, PCH_2CH_3 & $\text{PCH}_2\text{CH}_2\text{P}$), 1.34-1.09 (m, 12H, PCH_2CH_3)

Pt(depe)(Br) $_4$ 2(depe). Inside the drybox to a white suspension of $\text{Pt}(\text{COD})(\text{Cl})_2$ (35.3 mg, 94.3 μmoles) in 1mL CH_2Cl_2 , depe (19.0 mg, 92.1 μmoles) in 1mL CH_2Cl_2 was added under constant stirring. The depe vial was further washed with 3 mL CH_2Cl_2 . The washings were also added to the reaction mixture and the resulting pale yellow clear solution was taken out of the drybox. Then KBr (~300 mg) and absolute ethanol (~4 mL) was added to the solution. The resulting reaction mixture slurry was stirred for 30 minutes and dried *in vacuo*. The residue was extracted using CH_2Cl_2 (~ 1 mL) and then

filtered through a diatomaceous earth pad to give a pale yellow clear solution of **1**(depe). To this bromine (0.10 mL of a 0.93 M CH₂Cl₂ solution) was added drop-wise under constant stirring to yield an orange precipitate. The solution was separated and the orange residue was dried *in vacuo* to yield 34 mg (50%) **2**(depe).

³¹P{¹H} NMR (101 MHz, CH₂Cl₂): 50.94 (s with satellite, $J_{\text{PtP}} = 2050$ Hz); (101 MHz, DMSO-d₆): 57.09 (s with satellite, $J_{\text{PtP}} = 2032$ Hz).

¹H NMR (250 MHz, DMSO-d₆): 2.76-2.53 (m, 8H, PCH₂CH₃), 2.40 (app d, $J_{\text{HH}} = 17.51$ Hz, 4H, PCH₂CH₂P), 1.36-1.20 (m, 12H, PCH₂CH₃)

***trans*-Pt(PEt₃)₂(Br)(2-(trifluoromethyl)phenyl) 1(CF₃Ph).** A clear orange solution of Pt(PEt₃)₄ (128.6 mg, 0.1926 mmol) in THF (~10 mL) was added to a colorless THF (~4 mL) solution of 2-bromo(trifluoromethyl)phenyl (30 μL, 50 mg, 0.22 mmol). The resulting clear orange solution was stirred for 9.5 h at 127 °C in a sealed tube to yield a pale yellow solution. The mixture was cooled to ambient temperature and the volatiles removed *in vacuo*. The residue was washed with 2 x ~0.5 mL cold hexane and then extracted with 5 x ~2 mL CH₂Cl₂. The extract was filtered through a diatomaceous earth pad. The volatiles were then removed *in vacuo* to yield 96.8 mg (77 %) of pale yellow solid **1**(CF₃Ph).

³¹P {¹H} NMR (101 MHz, CDCl₃): 9.1 (s with satellites, $J_{\text{PtP}} = 2698$ Hz). A similar shift and coupling constant was observed in C₆D₆ and THF.

¹⁹F {¹H} NMR (235 MHz, CDCl₃): -59.74 (s with satellites, $J_{\text{PF}} = 17.42$ Hz).

¹H NMR (250 MHz, CDCl₃): 7.71 (d with satellites, $J_{\text{PtH}} = 75.79$ Hz, $J_{\text{HH}} = 7.50$ Hz, 1H, H6), 7.37 (dd with satellites, $J_{\text{FH}} = 25.01$ Hz, $J_{\text{HH}} = 7.63$ Hz, $J_{\text{HH}} = 1.63$ Hz, H3), 7.01-

6.88 (multiplet, 2H, H4 & H5), 1.79-1.50 (symmetric 20 line multiplet, 12H, CH₂CH₃), 1.02 (app quintet, $J = 7.82$ Hz, 18H, CH₂CH₃).

¹H NMR (250 MHz, C₆D₆): 7.83 (d with satellites, $J_{\text{PtH}} = 73.79$ Hz, 1H, H6), 7.53 (d, with satellites, $J_{\text{FH}} = 25.76$ Hz, $J_{\text{HH}} = 8.00$ Hz, 1H, H3), 6.85 (overlapping t, 2H, H4 & H5), 1.77-1.44 (symmetric 24 line multiplet, 12H, CH₂CH₃), 0.88 (app quintet, $J = 7.82$ Hz, 18H, CH₂CH₃).

***trans*-Pt(PEt₃)₂(Br)₃(2-(trifluoromethyl)phenyl) 2(CF₃Ph).** This synthesis was carried out in air. To 81.0 mg of 1(CF₃Ph) (0.123 mmol) in CH₂Cl₂ (~8 mL), 0.2 mL of 0.75 M bromine (0.15 mmol) in CH₂Cl₂ was added drop-wise. The resulting solution was stirred for 5 min and the volatiles were then removed *in vacuo* to give 106.9 mg (quantitative) of solid yellow 2(CF₃Ph). ³¹P { ¹H } NMR (101 MHz, CH₂Cl₂ or CDCl₃): -8.5 (s with satellites, $J_{\text{PtP}} = 1592$ Hz).

¹⁹F { ¹H } NMR (235 MHz, CDCl₃): -50.06 (s).

¹H NMR (250 MHz, CDCl₃): 8.72 (d with satellites, $J_{\text{PtH}} = 49.23$ Hz, $J_{\text{HH}} = 8.25$ Hz, 1H, H6), 7.49 (dd with satellites, $J_{\text{FH}} = 20.76$ Hz, $J_{\text{HH}} = 7.75$ Hz, $J_{\text{HH}} = 1.75$ Hz, H3), 7.18 (t, $J_{\text{HH}} = 7.38$ Hz, 1H), 7.02 (dt, $J_{\text{HH}} = 6.88$ Hz, 1H) 2.37-2.25 (symmetric nine-line pattern, $J = 3.63$ Hz, 12H, CH₂CH₃), 1.02 (app quintet, $J = 7.88$ Hz, 18H, CH₂CH₃).

***trans*-Pt(PEt₃)₂(Br) (2,6-dimethoxyphenyl) 1(MeO₂Ph).** A clear orange solution of Pt(PEt₃)₄ (205.0 mg, 0.3070 mmol) in C₆D₆ (~4 mL) was added to a pale yellowish brown C₆D₆ (~3 mL) solution of 2-bromo-1,3-dimethoxybenzene (69.2 mg, 0.319 mmol) drop-wise with constant stirring. The resulting clear orange solution was stirred for an

hour at room temperature and further heated for 18 h at 117 °C in a sealed tube to yield an orange yellow solution. The volatiles were then removed *in vacuo* to give a pale brownish yellow solid. To this ~5 mL of hexane was added and heated at 84 °C for 2 min. This yielded a yellow clear solution which was left for recrystallization. The colorless crystals were then washed with 3 x ~0.3 mL hexane. The volatiles were then removed *in vacuo* to yield a pale yellow crystalline solid. This was further washed with 2 x ~2 mL distilled water and heated at 84 °C for 10 min. This yielded a pale orange sticky solid. This was dissolved in CDCl₃ for ¹H and ³¹P NMR spectroscopy. Then the volatiles were removed *in vacuo* to yield 154.4 mg (78%) of crude **1**(MeO₂Ph). To this 0.3287 KBr and ~2 mL absolute ethanol was added and the yellow solution was heated for 1.5 hours at 84 °C. All the ethanol had evaporated and further ~2 mL of ethanol was added and the solution was left stirring overnight. Then the volatiles were removed *in vacuo* and **1**(MeO₂Ph) was extracted using CH₂Cl₂. The volatiles were further removed *in vacuo* to yield 132.4 mg (67%) of a pale yellow waxy solid **1**(MeO₂Ph). Anal. Calc. (found) for C₂₀H₃₉O₂PtP₂Br: C, 37.04 (37.23); H, 6.06 (6.50); N, 0.00 (0.07).

³¹P {¹H} NMR (101 MHz, C₆D₆ or CDCl₃): 12.7 (s with satellites, *J*_{PtP} = 2745 Hz).

¹H NMR (250 MHz, CDCl₃): 6.95 (t, *J*_{HH} = 8.0 Hz, 1H, H4), 6.25 (d with satellites *J*_{PtH} = 23.87 Hz, *J*_{HH} = 8.0 Hz, 2H, H5 & H3), 3.66 (s, 6H, OCH₃) 1.67-1.53 (symmetric 10 line pattern, *J* = 3.70 Hz, 12H, CH₂CH₃), 1.00 (app quintet, *J* = 7.84 Hz, 18H, CH₂CH₃).

***trans*-Pt(PEt₃)₂(Br)₃(3,5-dibromo-2,6-dimethoxyphenyl) 2(BrMeO₂Ph).** This synthesis was carried out in air. Bromine (22 mg, 0.14 mmol) in CDCl₃ (0.18 mL of a 0.77 M solution) was added drop-wise with constant stirring to a pale yellow solution of

1(MeO₂Ph) (24.0 mg, 37.0 μ mol) in CDCl₃ (~ 0.5 mL). The resulting orange red solution was further stirred for 1.5 h. The volatiles were then removed *in vacuo* to give 36.7 mg (quantitative) orange crystalline product.

³¹P {¹H} NMR (101 MHz, CDCl₃): -7.24 (s with satellites, $J_{\text{PtP}} = 1570$ Hz).

¹H NMR (250 MHz, CDCl₃): 7.61 (s, 1H, H4), 4.05 (s, 6H, OCH₃), 2.45 (broad multiplet, 12H, CH₂CH₃), 1.14 (broad app triplet, 18H, CH₂CH₃).

***trans*-Pt(PEt₃)₂(Br)(2-aminophenyl) 1(NPh).** A sealable tube was charged with a clear purple THF (~3 mL) solution of 2-bromophenylamine (51.4 mg, 0.299 mmol). A clear orange solution of Pt(PEt₃)₄ (195.4 mg, 0.2926 mmol) in THF (~4 mL) was added dropwise with stirring. ~5 mL more THF was added to the resulting clear yellowish orange solution. The tube was sealed and the mixture was stirred for 2.5 h at room temperature and then heated for 17 h at 117 °C to yield a yellow clear solution. After cooling to ambient temperature the volatiles were removed *in vacuo* to give a yellowish green residue. This was then extracted with 5 x ~2 mL CH₂Cl₂. The combined extracts were filtered through diatomaceous earth and dried *in vacuo* to yield a brown residue. To this ~5 mL of hexane was added and the mixture heated for 2 min and cooled. This yielded a clear yellow solution with a brown residue at the bottom. The yellow solution was decanted into a clean vial and left to evaporate. Pale yellow crystals and ~0.3 mL of pale brown mother liquor were obtained. The mother liquor was removed with a pipette and the crystals were washed with 2 x ~0.3 mL hexane and dried *in vacuo*. ³¹P NMR spectroscopy of the crystals indicated the presence of PEt₃O and possibly the chloro analogue of **1**(NPh). Hence the NMR sample was combined with the crystals and the

solvent removed in vacuo. The solid was then washed with 2 x ~2 mL distilled water and dried for ~10 min at 84 °C. After this, 0.30 g of KBr and ~2 mL of absolute ethanol was added to the solid and the mixture heated in an open vial for an hour at 84 °C. The solvent volume had reduced to ~1 mL. Another 1 mL of ethanol was added and the yellow solution was left stirring overnight at room temperature. ³¹P NMR spectroscopy showed complete conversion of the chloro compound to **1**(NPh). Ethanol was removed *in vacuo* and **1**(NPh) was extracted from the residue using 5 x ~2 mL of CH₂Cl₂. The combined extracts were filtered through diatomaceous earth and dried *in vacuo* to yield 91.4 mg (52 %) of a pale brown waxy solid.

³¹P {¹H} NMR (101 MHz, CDCl₃): 14.3 (s with satellites, *J*_{PtP} = 2674 Hz).

³¹P {¹H} NMR (101 MHz, THF): 14.3 (s with satellites, *J*_{PtP} = 2702 Hz).

¹H NMR (250 MHz, CDCl₃): 7.15 (d with satellites, *J*_{PtH} = 73.2 Hz, *J*_{HH} = 7.4 Hz, 1H, H6), 6.76 (t, *J*_{HH} = 8.1 Hz, 1H, H5), 6.46-6.33 (multiplet, 2H, H3 & H4), 4.01 (s, 2H, NH₂) 1.82-1.62 (symmetric 12 line pattern, 12H, CH₂CH₃), 1.04 (app quintet, *J* = 7.2 Hz, 18H, CH₂CH₃). ¹H NMR (500 MHz, CDCl₃): 7.15 (d with satellites, *J*_{PtH} = 71.0 Hz, *J*_{HH} = 7.5 Hz, 1H, H6), 6.76 (t, *J*_{HH} = 7.2 Hz, 1H, H5), 6.44-6.39 (multiplet, 2H, H3 & H4), 4.01 (s, 2H, NH₂) 1.80-1.63 (symmetric 9 line pattern, *J* = 3.7 Hz, 12H, CH₂CH₃), 1.05 (app quintet, *J* = 7.9 Hz, 18H, CH₂CH₃).

***trans*-Pt(PEt₃)₂(Br)₃(3,5-dibromo-2-aminophenyl) 2(BrNPh).** This synthesis was carried out in air. To 26.8 mg (44.4 μmol) of a clear brownish yellow solution of **1**(NPh) in CDCl₃ (~7 mL) was added 1.00 mL of 0.19 M bromine (190 μmol) with stirring. ³¹P NMR spectroscopy of the mixture indicated complete bromination of Pt but incomplete

ring bromination. Another 0.18 mL of 0.78 M bromine (140 μ mol) in CDCl_3 was added drop-wise with stirring to complete the reaction. The volatiles were then removed *in vacuo* to give a maroon oily residue. The residue was dissolved in ~ 3 mL of CDCl_3 and 0.45 g of NaHCO_3 was added. The orange solution was stirred for 30 min and filtered through diatomaceous earth. It was further dried *in vacuo* to yield 40.8 mg (quantitative) of a reddish orange solid **2(BrNPh)**.

^{31}P { ^1H } NMR (101 MHz, CDCl_3): -7.13 (s with satellites, $J_{\text{PtP}} = 1574$ Hz).

^1H NMR (250 MHz, CDCl_3): 7.89 (dd with satellites, $J_{\text{PtH}} = 51.28$ Hz, $J_{\text{HH}} = 2.00$ Hz, 1H, H6), 7.35 (dd, $J_{\text{HH}} = 2.00$ Hz, 1H, H4), 5.51 (s, 2H, NH_2) 2.46-2.32 (symmetric 10 line pattern, $J = 3.78$ Hz, 12H, CH_2CH_3), 1.13 (app quintet, $J = 7.94$ Hz, 18H, CH_2CH_3).

***trans*-Pt(PEt₃)₂(Br)(2-isopropoxyphenyl) 1(iPrOPh).** A clear orange solution of $\text{Pt}(\text{PEt}_3)_4$ (135.6 mg, 0.2031 mmol) in THF (~ 3 mL) was added to a clear solution of 2-isopropoxyphenyl ether (0.04 mL, 50 mg, 0.25 mmol) dissolved in THF (~ 2 mL). The resulting clear orange solution was stirred overnight at 126 $^\circ\text{C}$ during which time it turned a pale yellow. The mixture was cooled to room temperature and the volatiles were removed *in vacuo* to give a pale yellow solid. The solid was washed with 2 X ~ 0.5 mL cold hexane and dried *in vacuo* to yield 90 mg pale yellow **1(iPrOPh)** (69%).

^{31}P { ^1H } NMR (101 MHz, CDCl_3): 12.59 (s with satellites, $J_{\text{PtP}} = 2766$ Hz); (101 MHz, THF): 12.71 ($J_{\text{PtP}} = 2777$ Hz).

***trans*-Pt(PEt₃)₂(Br)₃(5-bromo-2-isopropoxyphenyl) 2(BriPrOPh).** This synthesis was carried out in air and the complex was not isolated. To 8.7 mg of **1(iPrOPh)** (13 μ mol) in

CDCl_3 (~0.6 mL), 0.21 mL of 0.19 M bromine (0.01 mL, 31 mg, 19 mmol) in CDCl_3 was added drop-wise resulting in a red clear solution of **2**(BriPrOPh).

^{31}P NMR (101 MHz, CDCl_3): -8.30 (s with satellites, $J_{\text{PtP}} = 1607$ Hz).

***trans*-Pt(PEt₃)₂(Br)(4-bromo-1-naphthyl) 1(BrNap).** This compound was previously synthesized from **1**(BrNap).⁴¹ A clear orange solution of Pt(PEt₃)₄ (623.7 mg, 0.9341 mmol) in THF (~7 mL) was added to a clear pale yellow solution of 1,4-dibromonaphthalene (270.6 mg, 0.9463 mmol) dissolved in THF (~6 mL). The resulting clear orange solution was stirred for 8 h at 120 °C during which time it turned a pale yellow. The mixture was cooled to room temperature and the volatiles were removed *in vacuo* to give a pale yellow oily residue. The residue was extracted with 5 x 3 mL of CH_2Cl_2 and the combined extracts were filtered through diatomaceous earth. The filtrate was dried *in vacuo* to yield a pale yellow waxy solid. The solid was dissolved in a minimum volume of CH_2Cl_2 and the solution was layered with CH_3OH . The resulting pale yellow crystals were isolated, washed with methanol (2 x 1.0 mL) and dried *in vacuo* to give 507.0 mg (76 %) of white solid.

^{31}P { ^1H } NMR (101 MHz, CDCl_3): 11.7 (s with satellites, $J_{\text{PtP}} = 2681$ Hz); (101 MHz, MeTHF): 12.35 ($J_{\text{PtP}} = 2692$ Hz).

^1H NMR (500 MHz, CDCl_3): 8.71 (dd with satellites, $J_{\text{HH}} = 7.3$ Hz, $J_{\text{HH}} = 2.3$ Hz, 1H, H8), 8.10 (d, $J_{\text{HH}} = 7.5$ Hz, $J_{\text{HH}} = 2.3$ Hz, 1H, H5), 7.47-7.31 (m, 4H, H2, H3, H6 and H7), 1.71-1.37 (symmetric 25 line multiplet, 12H, CH_2CH_3), 0.97 (app quintet, $J = 7.9$ Hz, 18H, CH_2CH_3).

***trans*-Pt(PEt₃)₂(Br)₃(4-bromo-1-naphthyl) 2(BrNap).** This synthesis was carried out in air. To a 134.7 mg of **1**(BrNap) (0.1878 mmol) in CDCl₃ (1 mL), 0.72 mL of 267.4 mM bromine (9.9 μL, 30.8 mg, 0.1925 mmol) in CH₂Cl₂ was added drop-wise resulting in an orange red clear solution. The volatiles were removed *in vacuo* to give 157.2 mg (95%) of orange solid **2**(BrNap).

³¹P NMR (101 MHz, CDCl₃): -8.41 (s with satellites, *J*_{PtP} = 1610 Hz); (101 MHz, MeTHF):

-9.66 (*J*_{PtP} = 1622 Hz).

¹H NMR (250 MHz, CDCl₃): 8.90 (d, *J*_{HH} = 9.7 Hz, 1H, H8), 8.17 (dd with satellites, *J*_{PtH} = 48.2 Hz, *J*_{HH} = 8.4 Hz, 2H, H2, H3), 7.52-7.36 (overlapping m & d, 3H, H7, H6 and H5), 2.32 (asymmetric 18 line splitting pattern, *J*_{HH} = 3.7 Hz, 12H, PCH₂CH₃), 1.01 (app q, *J*_{HH} = 7.9 Hz, 18H, PCH₂CH₃).

Di-*trans*-Pt(PEt₃)₂(Br)(1,4-naphthyl) 1(DiPt). A clear orange solution of Pt(PEt₃)₄ (19.5 mg, 29.2 μmol) in THF (~0.6 mL) was added to a clear pale yellow solution of 1,4-dibromonaphthalene⁴¹ (4.1 mg, 14 μmol) dissolved in THF (~0.6 mL). The resulting clear orange solution was stirred overnight at 128 °C during which time it turned a pale yellow. The mixture was cooled to room temperature and the volatiles were removed *in vacuo* to give a pale yellow solid. The solid was washed with 2 X ~0.5 mL cold hexane and dried *in vacuo* to yield 10.5 mg off-white **1**(DiPt) (64%).

³¹P {¹H} NMR (101 MHz, CDCl₃): 11.65 (s with satellites, *J*_{PtP} = 2778 Hz); (101 MHz, THF): 11.95 (*J*_{PtP} = 2783 Hz); (101 MHz, C₆D₆): 11.73 (*J*_{PtP} = 2781 Hz).

^1H NMR (500 MHz, C_6D_6): 8.86 – 8.84 (m, $J_{\text{HH}} = 3.50$ Hz, 2H), 7.33-7.30 (asymmetric m, $J_{\text{HH}} = 3.70$ Hz, 4H), 1.64 (asymmetric 9 line pattern, 12H, CH_2CH_3), 1.51 (asymmetric 9 line pattern, 12H, CH_2CH_3), 0.94 (app quintet, $J = 7.90$ Hz, 36H, CH_2CH_3).

Di-*trans*-Pt(PEt₃)₂(Br)₃(1,4-naphthyl) 2(DiPt). This synthesis was carried out in air and the complex was not isolated. To a 5.6 mg of **1**(DiPt) (4.9 μmol) in CDCl_3 (~0.6 mL), ~0.03 mL of 1.44 M bromine (0.08 mL, 249 mg, 1.6 mmol) in CDCl_3 was added drop-wise resulting in a red clear solution of **2**(DiPt).

^{31}P NMR (101 MHz, CDCl_3): -8.50 (s with satellites, $J_{\text{PP}} = 1631$ Hz).

^1H NMR (500 MHz, CDCl_3): 8.79 – 8.77 (m, $J_{\text{HH}} = 3.0$ Hz, 2H), 7.76 (s with satellites, $J_{\text{PH}} = 38.50$ Hz, 2H), 7.30 – 7.27 (m, $J_{\text{HH}} = 3.50$ Hz, 2H), 2.34 – 2.33 (m, 24H, CH_2CH_3), 1.05 (app quintet, $J = 7.50$ Hz, 36H, CH_2CH_3).

***trans*-Pt(PEt₃)₂(Br)₃(7,4-dibromo-1-naphthyl) 2(BrNapBr) and di-*trans*-Pt(PEt₃)₂(Br)₃(6,7-dibromo-1,4-naphthyl) 2(DiBrPt).** This synthesis was carried out in air. To a 54 mg mixture of containing 44% **1**(BrNap) (24 mg, 33 μmoles) and 56% **1**(DiPt) (30 mg, 26 μmoles) (ratios are based on ^{31}P NMR) in CDCl_3 (~2 mL), added ~ 6 g Br_2 (20 moles). The volatiles were removed *in vacuo* to yield a red oily residue. This was dissolved in CH_2Cl_2 (~2 mL) and layered with Et_2O (~2 mL) to yield red and orange crystals. The red and orange crystals were separated manually to yield 15 mg of **2**(BrNapBr) (47%) and 26 mg of **2**(DiBrPt) (62%) respectively. These crystals were used for single x-ray crystallography as well.

2(BrNapBr) (Red)

^{31}P NMR (101 MHz, C_6D_6): -9.24 ($J_{\text{PtP}} = 1599$ Hz).

^1H NMR (250 MHz, CDCl_3): 9.58 (d, $J_{\text{HH}} = 1.9$ Hz, 1H, H8), 8.30 (d with satellites, $J_{\text{PtH}} = 47.8$ Hz, 1H, H2), 8.09 (d, $J_{\text{HH}} = 9.0$ Hz, 1H, H3), 7.33 (dd, $J_{\text{HH}} = 9.0$ Hz, $J_{\text{HH}} = 1.9$ Hz, 1H, H5), 7.27 (d, $J_{\text{HH}} = 8.4$ Hz, 1H, H6), 2.17 (m, 12H, PCH_2CH_3), 0.75 (app q, $J_{\text{HH}} = 7.9$ Hz, 18H, PCH_2CH_3).

2(DiBrPt) (Orange)

^{31}P NMR (101 MHz, C_6D_6): -9.32 ($J_{\text{PtP}} = 1613$ Hz).

^1H NMR (250 MHz, C_6D_6): 9.60 (s, 2H, H8 and H5), 8.14 (s satellites, $J_{\text{PtH}} = 19.1$ Hz, 2H, H2, H3), 2.32 (m, 12H, PCH_2CH_3), 0.87 (app q, $J_{\text{HH}} = 7.9$ Hz, 18H, PCH_2CH_3).

***trans*-Pt(PEt₃)₂(Br)(2-naphthyl) 1(2-Nap).** A clear orange solution of Pt(PEt₃)₄ (446.2 mg, 0.6682 mmol) in THF (~9 mL) was added to a colorless THF (~6 mL) solution of 2-bromonaphthalene (139.9 mg, 0.6756 mmol). The resulting clear orange solution was stirred for 8 h at 120 °C in a sealed tube during which time it turned almost colorless. The mixture was cooled to ambient temperature and the volatiles removed *in vacuo*. The off-white solid residue was washed with cold hexane (2 x 0.5 mL) and dried *in vacuo* to give 391.9 mg (92 %) off-white solid product.

^{31}P NMR (101 MHz, CDCl_3 or C_6D_6): 12.8 (s with satellites, $J_{\text{PtP}} = 2754$ Hz).

^1H NMR (500 MHz, CDCl_3): 7.72 (s with satellites, $J_{\text{PtH}} = 70.0$ Hz, 1H, H1), 7.70 (d, $J_{\text{HH}} = 10.0$ Hz, 1H), 7.61 (d, $J_{\text{HH}} = 10.0$ Hz, 1H), 7.56 (dd with satellites partially overlapping other peaks, $J_{\text{PtH}} = 60$ Hz, $J_{\text{HH}} = 7.5$ & 2.5 Hz, 1H, H3), 7.41 (d, $J_{\text{HH}} = 10.0$ Hz, 1H), 7.37 (td, $J_{\text{HH}} = 7.5$ & 2.5 Hz, 1H), 7.32 (t, $J_{\text{HH}} = 7.5$ Hz, 1H), 1.67 (m, 12H, PCH_2CH_3), 1.67

(symmetric seventeen line pattern, $J = 3.4$ Hz, 12H, PCH_2CH_3), 1.07 (app quin, $J = 7.5$ Hz, 18H, PCH_2CH_3); (500 MHz, C_6D_6): 8.00 (s with satellites, $J_{\text{PtH}} = 75.0$ Hz, 1H, H1), 7.73 (dd with satellites partially overlapping other peaks, $J_{\text{PtH}} = 60$ Hz, $J_{\text{HH}} = 5.0$ & 1 Hz, 1H, H3), 7.69 (t, $J_{\text{HH}} = 5.0$ Hz, 1H), 7.50 (d, $J_{\text{HH}} = 10.0$ Hz, 1H), 7.30 (td, $J_{\text{HH}} = 5.0$ & 1 Hz, 1H), 7.24 (t, $J_{\text{HH}} = 7.5$ Hz, 1H), 1.56 (symmetric nineteen line pattern, $J = 3.9$ Hz, 12H, CH_2CH_3), 0.86 (apparent quin, $J = 8.8$ Hz, 18H, CH_2CH_3).

***trans*-Pt(PEt₃)₂(Br)₃(2-naphthyl) 2(2-Nap).** This synthesis was carried out in air. To 88.2 mg of **1**(2-Nap) (0.138 mmol) in CH_2Cl_2 (8 mL), 0.71 mL of 0.19 M bromine (0.14 mmol) in CH_2Cl_2 was added drop-wise. The resulting solution was covered with Al foil and stirred for 0.5 h at room temperature. CH_2Cl_2 (2 mL) was added to the solution whilst removing the stirbar. With the reaction vessel still covered with Al foil the volatiles were removed *in vacuo* to give 100.6 mg (91%) of orange solid **2**(2-Nap).

³¹P NMR (101 MHz, CDCl_3): -8.8 (s with satellites, $J_{\text{PtP}} = 1621$ Hz). ³¹P NMR (101 MHz, C_6D_6): -9.7 (s with satellites, $J_{\text{PtP}} = 1627$ Hz).

¹H NMR (500 MHz, CDCl_3): 8.48 (d with satellites, $J_{\text{PtH}} = 45.0$ Hz, $J_{\text{HH}} = 1$ Hz, 1H, H1), 8.25 (dd with satellites, $J_{\text{PtH}} = 38.5$ Hz, $J_{\text{HH}} = 9.3$ & 1.8 Hz, 1H, H3), 7.77-7.75 (m, 1H), 7.72-7.0 (m, 1H), 7.46-7.40 (overlapping m, 3H), 2.26 (symmetric nine line pattern, $J = 3.7$ Hz, 12H, PCH_2CH_3), 1.05 (apparent quin, $J = 8.0$ Hz, 18H, PCH_2CH_3); (C_6D_6): 8.85 (d with satellites, $J_{\text{PtH}} = 43.5$ Hz, $J_{\text{HH}} = 1.5$ Hz, 1H, H1), 8.54 (dd with satellites, $J_{\text{PtH}} = 37.8$ Hz, $J_{\text{HH}} = 9.0$ & 2.0 Hz, 1H, H3), 7.69 (d, $J_{\text{HH}} = 7.0$ Hz, 2H), 7.64 (d, $J_{\text{HH}} = 7.0$ Hz, 1H), 7.40 (d, $J_{\text{HH}} = 9.0$ Hz, 1H), 7.27-7.21 (m, 2H, H6 and H7), 2.10 (symmetric nine-

line pattern, $J = 3.7$ Hz, 12H, PCH_2CH_3), 0.77 (apparent quin, $J_{\text{HH}} = 7.9$ Hz, 18H, PCH_2CH_3).

4.3 Photolysis

Photolysis of $\text{Pt}(\text{depe})(\text{Br})_4$ **2(depe) with 1-hexene at 313 nm in CDCl_3 .** This was carried out in air. To 2.2 mg of **2(depe)** (3.1 μmol) in d_6DMSO (1.0 mL) added 50 μL 1-hexene (0.40 mmol). The NMR tube was capped and sealed with wax film. The tube was irradiated under 313 nm light for 20 minutes. ^{31}P (101 MHz) and ^1H NMR (250 MHz) spectra were recorded. After 10 minutes of irradiation 64 % of **2(depe)** converted to **1(depe)**. Further 10 minutes of irradiation converted all of the **2(depe)** to **1(depe)**. ^1H NMR spectroscopy indicated the formation of bromine addition product 1,2-dibromohexane (~65 %).

Photolysis of *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Br})_3(2\text{-naphthyl})$ **2(2-Nap).** 13.4 mg of **2(2-Nap)** was transferred to a quartz NMR tube using a micro spatula. The compound was washed down with 0.50 mL CDCl_3 . 30 μL of *cis*-2-hexene was added. The NMR tube containing 0.03 M **2(2-Nap)** and 0.46 M *cis*-2-hexene was capped and sealed with wax film. It was irradiated under the 313 nm light for 10 minutes, 20 minutes and 1 hour intervals. After each point ^{31}P NMR (101 MHz) and ^1H NMR (500 MHz) spectra were taken to monitor the reaction. Totally it was irradiated for 1 hour and 30 minutes after which 23% of *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{Br})(1\text{-bromo-2-naphthyl})$ and 10% of **1(1-Nap)** was formed. There was 62% of **2(1-Nap)** still remaining. There was also a minor (5%) peak at 8.27 ppm.

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(1-naphthyl), **2(1-Nap), with *cis*-2-hexene CD₂Cl₂.**

These procedures were carried out in a dark room with red lighting. Samples were covered with Al foil and kept in the dark except for brief exposure to dim light for NMR analysis. 13.1 mg (16.4 μmoles) sample of **2**(1-Nap) was transferred to a quartz NMR tube using a micro spatula. The solid was washed down with 0.5 mL CD₂Cl₂ and 30 μL of *cis*-2-hexene was added. The quartz NMR tube containing 0.031 M **2**(1-Nap) and 0.46 M *cis*-2-hexene, was capped and the top wrapped with parafilm. The tube was irradiated under 313 nm light initially for 10 min and then an hour. After each irradiation ³¹P (101 MHz) and ¹H NMR (500 MHz) spectra were recorded. After 10 minutes 20 % **1**(1-Nap) and 20 % **1**(BrNap) were seen with 60% of **2**(1-Nap) still remaining. An hour of irradiation further converted all the **2**(1-Nap) to 38 % **1**(1-Nap) and 62 % **1**(BrNap).

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(1-naphthyl), **2(1-Nap), with *cis*-2-hexene CDCl₃.**

These procedures were carried out in a dark room with red lighting. Samples were covered with Al foil and kept in the dark except for brief exposure to dim light for NMR analysis. 14.4 mg (18.0 μmoles) sample of **2**(1-Nap) was transferred to a quartz NMR tube using a micro spatula. The solid was washed down with 0.5 mL CD₂Cl₂ and 30 μL (0.24 mmoles) of *cis*-2-hexene were added. The quartz NMR tube containing 0.034 M **2**(1-Nap) and 0.46 M *cis*-2-hexene, was capped and the top portion wound with parafilm. The tube was irradiated under 313 nm light initially for 10 min and then 1.5 hours more. After each irradiation ³¹P (101 MHz) and ¹H NMR (500 MHz) spectra were recorded. After 10 minutes 27 % **1**(1-Nap) and 17 % **1**(BrNap) was seen with 60% of **2**(1-Nap) still

remaining. 1.5 hours more irradiation further converted all the **2**(1-Nap) to 55 % **1**(1-Nap) and 45 % **1**(BrNap).

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2(BrNap) with *cis*-2-hexene at 313 nm in CDCl₃.** Inside the drybox, **2**(BrNap) (30.6 mg, 34.9 μmol) was dissolved in CDCl₃ to make 5.00 mL of solution. (The CDCl₃ had been purified by treatment with Cl₂ followed by refluxing under a N₂ stream and vacuum transfer.) A 0.50 mL aliquot (3.5 μmol, 6.6 mM) of this solution was syringed into a quartz NMR tube. *Cis*-2-hexene (31 μL, 0.25 mmol) was added to the NMR tube. The NMR tube was capped and sealed with wax film. The tube was irradiated under 313 nm light for 10 min after which ³¹P (101 MHz) and ¹H NMR (250 MHz) spectra were recorded. All the **2**(BrNap) converted to **1**(BrNap). ¹H NMR spectroscopy indicated the formation of the *anti*-addition product (96%), a racemic mixture of (2R, 3S)- and (2S, 3R)-2,3-dibromohexane.⁴⁶

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2(BrNap) with 1-hexene at 313 nm in CDCl₃.** **2**(BrNap) (4.2 mg, 4.8 μmol) was dissolved in 0.5 mL CDCl₃. This solution was transferred to a quartz NMR tube. 1-hexene (50 μL, 0.40 mmol) was added to the NMR tube. The NMR tube was capped and sealed with wax film. The tube was irradiated under 313 nm light for 25 min after which ³¹P (101 MHz) and ¹H NMR (250 MHz) spectra were recorded. All the **2**(BrNap) converted to **1**(BrNap). ¹H NMR spectroscopy indicated the formation of the bromine addition product 1,2-dibromohexane (88%).⁷⁶

Photolysis of *trans*-Pt(PET₃)₂(Br)₃(4-BrNap) 2(BrNap) with TME at 313 nm in CDCl₃. Inside the drybox, 2(BrNap) (30.6 mg, 34.9 μmol) was dissolved in CDCl₃ to make 5.00 mL of solution. (The CDCl₃ had been purified by treatment with Cl₂ followed by refluxing under a N₂ stream and vacuum transfer). A 0.50 mL aliquot (3.49 μmoles, 6.98 mM) of this solution was syringed into three quartz NMR tubes. 1 μL (8 μmoles), 3 μL (25 μmoles) and 8 μL (67 μmoles) aliquots of TME was added to each tube. The quartz NMR tubes, containing 6.96 mM, 6.94 mM and 6.87 mM of 2(BrNap) and 17 mM, 50 mM and 132 mM of TME, respectively, were capped and sealed with wax film. The tubes were irradiated under 313 nm light for 10 min, 15 min and 15 min after which ³¹P (101 MHz) and ¹H NMR (250 MHz) spectra were recorded. All the 2(BrNap) converted to 1(BrNap) in the case of 50 mM and 132 mM TME concentrations. With only 52% of 2(BrNap) conversion to 1(BrNap) all the TME was consumed in the case of the 17 mM TME concentration. ¹H NMR spectroscopy indicated the formation of the addition product 2,3-dimethyl-2,3-dibromobutane (**3**),⁴⁹ 1-bromo-2,3-dimethyl-2-butene (**4**)^{50, 51} and 2-bromo-2,3-dimethylbutane (**5**).⁴⁹ Yield of the addition product decreased with increasing TME concentrations.

Photolysis of *trans*-Pt(PET₃)₂(Br)₃(4-BrNap) 2(BrNap) with 1-hexene at 380 nm in CDCl₃. Inside the drybox, 2(BrNap) (31.2 mg, 35.6 μmol) was dissolved in CDCl₃ to make 5.00 mL of solution. (The CDCl₃ had been purified by refluxing with MgSO₄ and then passing through activated neutral alumina.) A 0.50 mL aliquot (3.6 μmol, 7.1 mM) of this solution was syringed into a quartz NMR tube. 1-hexene (30 μL, 0.24 mmol) was added to the NMR tube and it was then capped and sealed with wax film. The tube was

irradiated under 380 nm with a 24 LED light source using 30 mA current. Using ^{31}P (101 MHz) and ^1H NMR (250 MHz) the photolysis was monitored. Based on the ^{31}P NMR 96 % of **2**(BrNap) converted to **1**(BrNap) after 98 min of irradiation. (Ratios are based on ^{31}P NMR).

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2(BrNap) with 1-hexene in the presence of *trans*-Pt(PEt₃)₂(Br)(4-BrNap) **1**(BrNap) at 380 nm in CDCl₃.** Inside the drybox, **2**(BrNap) (31.2 mg, 35.6 μmol) was dissolved in CDCl₃ to make 5.00 mL of solution. (The CDCl₃ had been purified by refluxing with MgSO₄ and then passing through activated neutral alumina.) A 0.50 mL aliquot (3.6 μmol , 7.1 mM) of this solution was syringed into a quartz NMR tube containing 3.3 mg (4.6 μmol , 9.2 mM) of **1**(BrNap) (previously weighed and dissolved in CH₂Cl₂, then transferred into the quartz NMR tube and dried *in vacuo*). 1-hexene (30 μL , 0.24 mmol) was added to the NMR tube and then it was capped and sealed with wax film. The tube was irradiated under 380 nm with a 24 LED light source using 30 mA current. Using ^{31}P (101 MHz) and ^1H NMR (250 MHz) the photolysis was monitored. Based on the ^{31}P NMR 94 % of **2**(BrNap) converted to **1**(BrNap) after 175 min of irradiation. (Ratios are based on ^{31}P NMR).

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2(BrNap) with 2,3-dimethyl-2-butene (TME) at 313 nm in CDCl₃.** Inside the drybox, **2**(BrNap) (31.2 mg, 35.6 μmol) was dissolved in CDCl₃ to make 5.00 mL of solution. (The CDCl₃ had been purified by refluxing with MgSO₄ and then passing through activated neutral alumina.) A 0.50 mL aliquot (3.6 μmol , 7.1 mM) of this solution was syringed into a quartz NMR tube. 2,3-

dimethyl-2-butene (30 μ L, 0.25 mmol) was added to the NMR tube and it was then capped and sealed with wax film. The tube was irradiated under 313 nm light. Using ^{31}P (101 MHz) and ^1H NMR (250 MHz) the photolysis was monitored. Based on the ^{31}P NMR 93 % of **2**(BrNap) converted to **1**(BrNap) after 6.5 min of irradiation. (Ratios are based on ^{31}P NMR).

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2(BrNap) with 1-hexene at 313 nm in CDCl₃.** Inside the drybox, **2**(BrNap) (31.2 mg, 35.6 μ mol) was dissolved in CDCl₃ to make 5.00 mL of solution. (The CDCl₃ had been purified by refluxing with MgSO₄ and then passing through activated neutral alumina.) A 0.50 mL aliquot (3.6 μ mol, 7.1 mM) of this solution was syringed into a quartz NMR tube. 1-hexene (30 μ L, 0.24 mmol) was added to the NMR tube and it was then capped and sealed with wax film. The tube was irradiated under 313 nm light. Using ^{31}P (101 MHz) and ^1H NMR (250 MHz) the photolysis was monitored. Based on the ^{31}P NMR 96 % of **2**(BrNap) converted to **1**(BrNap) after 13 min of irradiation. (Ratios are based on ^{31}P NMR).

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2(BrNap) with 1-hexene at 313 nm in the presence of Oxygen.** Inside the drybox, **2**(BrNap) (31.2 mg, 35.6 μ mol) was dissolved in CDCl₃ to make 5.00 mL of solution. (The CDCl₃ had been purified by refluxing with MgSO₄ and then passing through activated neutral alumina.) A 0.50 mL aliquot (3.6 μ mol, 7.1 mM) of this solution was syringed into a quartz NMR tube. 1-hexene (30 μ L, 0.24 mmol) was added to the NMR tube and it was then capped and sealed with wax film. It was taken out of the dry box and exposed to the atmosphere by

removing the cap. 7 X ~10 mL of oxygen gas was then syringed into the NMR tube above the solution. It was capped, sealed with wax film and shaken well to mix the solution with oxygen. The tube was irradiated under 313 nm light. Using ^{31}P (101 MHz) and ^1H NMR (250 MHz) the photolysis was monitored. Based on the ^{31}P NMR 94 % of **2**(BrNap) converted to **1**(BrNap) after 13 min of irradiation. (Ratios are based on ^{31}P NMR).

4.4 Low temperature photolysis

Low temperature photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) **2(BrNap) in 2-methyltetrahydrofuran at 380 nm.** **2**(BrNap) (3.1 mg, 3.6 μmol) was dissolved in 0.7 mL 2-methyltetrahydrofuran. This solution was transferred to a quartz NMR tube. The NMR tube was capped and sealed with wax film. The tube was frozen and irradiated at 77 K under 380 nm with a 24 LED light source using 30 mA current. Based on the ^{31}P NMR 4 % of **2**(BrNap) converted to **1**(BrNap) after 3 h and 40 min of irradiation. (Ratios are based on ^{31}P NMR).

Low temperature photolysis of *trans*-Pt(PEt₃)₂(Br)₄ **2(Br) in 2-methyltetrahydrofuran at 380 nm and 313 nm.** **2**(Br) (<5 mg, <5.8 μmol) in a quartz NMR tube was dissolved in 0.5 mL 2-methyltetrahydrofuran. The NMR tube was capped and sealed with wax film. The tube was frozen and irradiated for 15 h and 30 min at 77 K under 380 nm with a 24 LED light source using 30 mA current. Then the tube was frozen and irradiated for 1 h at 77 K under 313 nm. Using ^{31}P NMR (101 MHz) the photolysis

was monitored. Based on the ^{31}P NMR after 380 nm irradiation 33 % of **2**(BrNap) reacted. With further irradiation at 313 nm, 35 % of **2**(BrNap) converted to form 27 % of **1**(Br) and 7.5 % of an unknown product (4.709 ppm, ^{31}P NMR). (Ratios are based on ^{31}P NMR).

4.5 Quantum Yield

Quantum Yield Determinations. Irradiations were performed in 1 cm quartz cuvettes in the compartment of a Cary 50 UV-Vis spectrometer equipped with a magnetic stirrer and temperature control. A 313 nm Philips (PL-S 9W/01) 9 W lamp, with a 300-380 nm band pass filter, light source was positioned over the sample compartment allowing irradiations through the top of the uncovered cuvette.⁷⁷ The photon flux was measured (iron oxalate actinometry^{47, 48}) before and after each sample irradiation and the average of the before and after measurements was used as the photon flux during the sample irradiation. Sample solution concentrations were sufficiently high to assure complete photon absorption (absorbance ≥ 2 at the irradiation wavelength) over the ~3 cm depth of the solution. Reaction progress was monitored by the uv-vis absorbance of the starting Pt(IV) complex over a region where the Pt(II) product does not absorb and the Pt(IV) absorbance is ~1. The absorbance decrease at three wavelengths during 3 runs was used to calculate the quantum yield.

4.6 Thermal reactions

Dark reaction of *trans*-Pt(PEt₃)₂(Br)₃(2-trifluoromethylphenyl) 2(CF₃Ph) with 1-hexene in CDCl₃. Samples were covered with Al foil and kept in the dark (at room temperature) except for sample preparation and NMR analysis. Inside the dry box, 17.9 mg (21.9 μmoles) of 2(CF₃Ph) was made up to 5.00 mL using CDCl₃ (treated with Cl₂, refluxed under a stream of N₂ and vacuum transferred). A 1.00 mL aliquot (4.39 μmoles, 4.33 mM) of this solution was syringed into three quartz NMR tubes. An aliquot of 1-hexene, 12 μL (97 μmoles), 25 μL (0.20 mmol) and 50 μL (0.40 mmol) was added to each tube. The quartz NMR tubes, containing 4.3 mM, 4.3 mM and 4.2 mM of 2(CF₃Ph) and 0.096 M, 0.19 M and 0.38 M 1-hexene, respectively, were capped and sealed with wax film. ³¹P (101 MHz), ¹⁹F (235 MHz) and ¹H (250 MHz) NMR spectra were recorded at various time intervals as the reaction progressed at room temperature. Average first order rate constant (k_{obs}) = 1.4(1) x 10⁻³ min⁻¹.

Dark reaction of *trans*-Pt(PEt₃)₂(Br)₃(2-trifluoromethylphenyl) 2(CF₃Ph) with 1-hexene in C₆D₆. Sample was covered with Al foil and kept in the dark (at room temperature) except for sample preparation and NMR analysis. Inside the dry box, 3.7 mg (4.5 μmoles) of 2(CF₃Ph) was made up to 1.00 mL using C₆D₆ (passed through neutral Al₂O₃). Then this solution was transferred to a quartz NMR tube and 50 μL of 1-hexene (0.40 mmol) was added. The quartz NMR tube containing 4.3 mM of 2(CF₃Ph) and 0.38 M 1-hexene was capped and sealed with wax film. ³¹P (101 MHz), ¹⁹F (235 MHz) and ¹H (250 MHz) NMR spectra were recorded at various time intervals to monitor the reaction

progress at room temperature. After four days, only ~5 % of **2**(CF₃Ph) converted to **1**(CF₃Ph).

4.7 Bromination competition experiments

Bromine addition to *trans*-Pt(PEt₃)₂(Br)(4-BrNap) **1(BrNap) in the presence of 1-hexene in CDCl₃.** This addition was carried out in air. To 12.7 mg of **1**(BrNap) (17.7 μmol) in CDCl₃ (0.6 mL) was added 2.2 μL 1-hexene (18 μmol). Then under constant stirring, 20 μL of 100 mM bromine (5 μL, 20 mg, 100 μmol) in CDCl₃ was added. Color changed from colorless to pale yellow. The solution was transferred to a NMR tube, capped and sealed with wax film. Based on the ³¹P NMR 8 % of **1**(BrNap) converted to **2**(BrNap). ¹H NMR spectroscopy indicated no formation of the *anti*-addition product, 1,2-dibromohexane. (Ratios are based on ³¹P NMR).

Bromine addition to *trans*-Pt(PEt₃)₂(Br)(4-BrNap) **1(BrNap) in the presence of excess 1-hexene in CDCl₃.** This addition was carried out in air. To 5.7 mg of **1**(BrNap) (7.9 μmol) in CDCl₃ (0.6 mL) was added 10 μL 1-hexene (81 μmol). Then under constant stirring, 8 μL of 100 mM bromine (5 μL, 20 mg, 100 μmol) in CDCl₃ was added. Color changed from colorless to pale yellow. The solution was transferred to a NMR tube, capped and sealed with wax film. Using ³¹P (101 MHz) and ¹H NMR (250 MHz) bromine addition was monitored. Based on the ³¹P NMR 7 % of **1**(BrNap) converted to **2**(BrNap). ¹H NMR spectroscopy indicated no formation of the *anti*-addition product, 1,2-dibromohexane. (Ratios are based on ³¹P NMR).

Br₂ addition to a 1:1 mixture of 1-hexene and *trans*-3-hexene. Inside the glovebox, 1-hexene (0.02 mL, 0.2 mmol) and *trans*-3-hexene (0.02 mL, 0.2 mmol) were syringed into a vial containing 0.6 mL CDCl₃. The vial was taken out from the drybox. Then under constant stirring, 150 μ L of 0.1 M bromine (5 μ L, 20 mg, 100 μ mol) CDCl₃ solution was added to the vial containing the alkene mixture. ¹H NMR spectroscopy of the resulting solution indicated the formation of 3,4-*trans*-dibromohexane.

Photolysis of *trans*-Pt(PEt₃)₂(Br)₃(4-BrNap) 2(BrNap) with 1:1 mixture of *trans*-3-hexene and 1-hexene at 313 nm in CDCl₃. Inside the drybox, 2(BrNap) (3.1 mg, 3.6 μ mol) was dissolved in 0.6 mL CDCl₃ in a vial. Then 1-hexene (0.02 mL, 0.2 mmol) and *trans*-3-hexene (0.02 mL, 0.2 mmol) were syringed into the vial. The solution was transferred into a quart NMR tube, capped and sealed with wax film and taken out of the drybox. The tube was irradiated under 313 nm light. Using ³¹P (101 MHz) and ¹H NMR (250 MHz) the photolysis was monitored. Based on ³¹P NMR, 2(BrNap) converted to 1(BrNap) after 10 min of irradiation. ¹H NMR spectroscopy of the resulting solution indicated formation of 3,4-*trans*-dibromohexane.

4.8 Uv-visible spectroscopy

Figure 4.8.1 Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)₃(1-phenyl) **2**(Ph) in CH₂Cl₂.

Figure 4.8.2. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)₂ **1**(Br) in CH₂Cl₂.

Figure 4.8.3. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)₄ **2**(Br) in CH₂Cl₂.

Figure 4.8.4. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)(2-(trifluoromethyl)phenyl) **1**(CF₃Ph) in CH₂Cl₂.

Figure 4.8.5. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)₃(2-(trifluoromethyl)phenyl) **2**(CF₃Ph) in CH₂Cl₂.

Figure 4.8.6. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)(2-aminophenyl) **1**(NPh) in CH₂Cl₂.

Figure 4.8.7. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)₃(3,5-dibromo-2-aminophenyl) **2**(BrNPh) in CH₂Cl₂.

Figure 4.8.8. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br) (2,6-dimethoxyphenyl) **1**(MeO₂Ph) in CH₂Cl₂.

Figure 4.8.9. Electronic absorption spectrum of *trans*-Pt(PEt₃)₂(Br)₃(3,5-dibromo-2,6-dimethoxyphenyl) **2**(BrMeO₂Ph) in CH₂Cl₂.

Figure 4.8.10. Electronic absorption spectrum of **1**(1-Nap) in CH₂Cl₂.

Figure 4.8.11. Electronic absorption spectrum of **2**(1-Nap) in hexane.

Figure 4.8.12. Electronic absorption spectrum of **1**(BrNap) in CH_2Cl_2 .

Figure 4.8.13. Electronic absorption spectrum of **2**(BrNap) in CH₂Cl₂.

Figure 4.8.14. Electronic absorption spectrum of **2**(Phen) in CH₂Cl₂.

Figure 4.8.15. Electronic absorption spectrum of **1**(DiPt) in CH₂Cl₂.

Figure 4.8.16. Electronic absorption spectra of **1**(BrNap), **1**(1-Nap) and **1**(DiPt) in CH₂Cl₂.

Figure 4.8.17. Electronic absorption spectra of **2(1-Nap)**, **2(2-Nap)** and **2(BrNap)** in CH_2Cl_2 .

Figure 4.8.18. Electronic absorption spectra of **2(1-Nap)**, **2(Phen)**, **2(Ph)** and **2(Br)** in CH_2Cl_2 .

Figure 4.8.19. Electronic absorption spectra of **2**(1-Nap) in DMF and CH₂Cl₂.

Figure 4.8.20. Electronic absorption spectra of **2**(Phen) in hexane, CH₂Cl₂ and DMF.

4.9 Crystal Structures

Crystal Structure Determinations. These were mostly done by Dr. Charles Barnes. Few structures were determined by Dr. Morgan A Moody. Crystals were mounted by transferring the crystals from the crystallization vessel into a pool of heavy oil. A suitable crystal was selected and removed from the oil with a glass fiber. With the oil covered crystal adhering to the end of the glass fiber the sample was transferred to an N₂ cold stream on the diffractometer and data were collected at 100 °C. Data reduction and processing followed routine procedures. Prof. Sharp also carried out these procedures on few structures. Analytical absorption corrections were applied and provided adequate corrections. Structures were solved by direct methods. Details may be found in the CIF file³⁰ and in Tables 5.9.1-5.9.4.

Figure 4.9.1. XSeed/POV-Ray drawing of **1(NPh)**. Carbon bonded hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids. H1A and H1B were refined isotropically.³⁰

Figure 4.9.2. XSeed/POV-Ray drawing of **1**(BrMeO₂Ph). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.³⁰

Figure 4.9.3. XSeed/POV-Ray drawing of 1(BrMeO₂Ph). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.³⁰

Figure 4.9.4. XSeed/POV-Ray drawing of **2**(BrMeO₂Ph). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids.³⁰

Figure 4.9.5. XSeed/POV-Ray drawing of **2(Br)**. Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids. Named and unnamed atoms are inversion related.³⁰

Figure 4.9.6. XSeed/POV-Ray drawing of 2(BrNPh). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids. N1 and N1' are disordered positions of the NH₂ group and were refined to occupancies of 77% and 23%, respectively.³⁰

Figure 4.9.7. XSeed/POV-Ray drawing of **2**(BrNapBr). Hydrogen atoms omitted. Atoms are drawn as 50% probability ellipsoids. There is crystallographic disorder at C6.

Table 4.9.1. Crystal data and structure refinement for di-trans-Pt(PtEt3)2(Br)3(6,7-dibromo-1,4-naphthyl) **2**(DiBrPt).

Identification code	2 (DiBrPt)	
Empirical formula	C ₄₆ H ₇₆ Br ₈ P ₄ Pt ₂	
Formula weight	1782.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.5673(19) Å	α = 101.664(2)°.
	b = 14.476(2) Å	β = 90.484(2)°.
	c = 16.057(2) Å	γ = 110.6440(10)°.
Volume	2879.2(7) Å ³	
Z	2	
Density (calculated)	2.056 Mg/m ³	
Absorption coefficient	10.546 mm ⁻¹	
F(000)	1696	
Crystal size	0.40 x 0.35 x 0.15 mm ³	
Theta range for data collection	1.61 to 27.53°.	
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20	
Reflections collected	34034	
Independent reflections	13057 [R(int) = 0.0351]	
Completeness to theta = 27.53°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.30 and 0.12	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13057 / 0 / 553	
Goodness-of-fit on F ²	1.015	
Final R indices [I > 2σ(I)]	R1 = 0.0235, wR2 = 0.0528	
R indices (all data)	R1 = 0.0305, wR2 = 0.0550	
Largest diff. peak and hole	0.999 and -1.360 e.Å ⁻³	

Table 4.9.2. Crystal data and structure refinement for Pt(depe)(Br)₄ **2**(depe).

Identification code	2 (depe)	
Empirical formula	C ₁₀ H ₂₄ Br ₄ P ₂ Pt	
Formula weight	720.96	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 9.3145(11) Å	α = 90°.
	b = 11.9794(14) Å	β = 105.0420(10)°.
	c = 17.361(2) Å	γ = 90°.
Volume	1870.8(4) Å ³	
Z	4	
Density (calculated)	2.560 Mg/m ³	
Absorption coefficient	16.197 mm ⁻¹	
F(000)	1328	
Crystal size	0.30 x 0.15 x 0.10 mm ³	
Theta range for data collection	2.43 to 27.54°.	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22	
Reflections collected	10651	
Independent reflections	2145 [R(int) = 0.0265]	
Completeness to theta = 27.54°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.29 and 0.10	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2145 / 0 / 80	
Goodness-of-fit on F ²	1.120	
Final R indices [I > 2σ(I)]	R1 = 0.0173, wR2 = 0.0410	
R indices (all data)	R1 = 0.0196, wR2 = 0.0417	
Largest diff. peak and hole	1.117 and -0.932 e.Å ⁻³	

Table 4.9.3. Crystal data and structure refinement for *trans*-Pt(PEt₃)₂(Br)₃(5-bromo-2-isopropoxyphenyl) **2**(BriPrOPh).

Identification code	2 (BriPrOPh)	
Empirical formula	C ₂₁ H ₄₀ Br ₄ O P ₂ Pt	
Formula weight	885.20	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 12.761(3) Å	α = 90°.
	b = 13.456(3) Å	β = 102.127(2)°.
	c = 17.406(3) Å	γ = 90°.
Volume	2922.3(10) Å ³	
Z	4	
Density (calculated)	2.012 Mg/m ³	
Absorption coefficient	10.392 mm ⁻¹	
F(000)	1688	
Crystal size	0.45 x 0.35 x 0.15 mm ³	
Theta range for data collection	1.81 to 27.62°.	
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22	
Reflections collected	32793	
Independent reflections	6725 [R(int) = 0.0635]	
Completeness to theta = 27.62°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.30 and 0.12	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6725 / 2 / 300	
Goodness-of-fit on F ²	1.017	
Final R indices [I > 2σ(I)]	R1 = 0.0365, wR2 = 0.0673	
R indices (all data)	R1 = 0.0728, wR2 = 0.0799	
Largest diff. peak and hole	1.372 and -1.642 e.Å ⁻³	

Table 4.9.4. Crystal data and structure refinement for di-trans-Pt(PtEt3)2(Br)(1,4-naphthyl) 1(DiPt).

Identification code	1(DiPt)	
Empirical formula	C ₃₄ H ₆₆ Br ₂ P ₄ Pt ₂	
Formula weight	1148.75	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 23.456(4) Å	α = 90°.
	b = 12.643(2) Å	β = 99.486(2)°.
	c = 14.518(3) Å	γ = 90°.
Volume	4246.6(13) Å ³	
Z	4	
Density (calculated)	1.797 Mg/m ³	
Absorption coefficient	8.635 mm ⁻¹	
F(000)	2224	
Crystal size	0.30 x 0.20 x 0.05 mm ³	
Theta range for data collection	1.76 to 27.59°.	
Index ranges	-30 ≤ h ≤ 30, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	
Reflections collected	48984	
Independent reflections	9789 [R(int) = 0.0376]	
Completeness to theta = 27.59°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.67 and 0.38	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9789 / 0 / 391	
Goodness-of-fit on F ²	1.017	
Final R indices [I > 2σ(I)]	R1 = 0.0237, wR2 = 0.0553	
R indices (all data)	R1 = 0.0300, wR2 = 0.0580	
Largest diff. peak and hole	3.160 and -1.443 e.Å ⁻³	

CONCLUSION AND OUTLOOK

Overall, facile solution Br₂ photoelimination from platinum(IV) complexes is observed in the presence of a trap. Endergonic and endothermic processes with free energy variation from 2 to 22 kcal/mol are observed. Less reactive traps (1-hexene and *cis*-2-hexene) yield a Br₂ *anti*-addition product, indicating photolytic molecular bromine elimination. The mixed alkene bromination competition experiment with *trans*-3-hexene and 1-hexene support elimination of molecular bromine (Br₂). Photokinetic measurements in the presence of platinum(II) show a decreased rate supporting evolution of Br₂ as well. Product profiles with a highly reactive trap such as TME reveal an excited state radical-like platinum precursor.

Synthesis, characterization and Br₂ photoelimination studies have given some valuable insights with regards to the excited state photochemical pathways of the various platinum(IV) complexes. The ligand framework is crucial in deciding the sterics, electronics and excited state transitions in the platinum(IV) systems. In the case of organoplatinum(IV) complexes we see novel bromination of the aryl ring. The platinum activates the ring for electrophilic bromine substitution. This paves the way for novel brominated polycyclic aromatic carbon compounds.

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VITA

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