Stereoselective C-X and Regioselective C-H activation to, and selective $C(sp^2)$-$C(sp^3)$ reductive elimination from, platinum compounds with thiophene-derived ligands

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Stereoselective C-X and Regioselective C-H activation to, and selective C(sp^2)-C(sp^3) reductive elimination from, platinum compounds with thiophene-derived ligands.

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ABSTRACT

Several thiophene-based N^C ligands were synthesized. Strategically, a bromide was incorporated on the 2-position of the thiophene ring. When allowed to react with the platinum tetramethyl dimer, [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], platinum(IV) platinacycles were formed by oxidative addition of the C(sp^2)-X bond. These platinum(IV) compounds were characterized by NMR and HRMS. The platinum (IV) compounds were subsequently subjected to thermolysis. A series of reactions occurred, including selective C-C reduction elimination and selective C-H oxidative addition, giving mixtures of platinum(II) products with varying degrees of regioselectivity.

Fundamental organometallic reactions, including oxidative addition and reductive elimination are known to be important in catalytic cycles.[1,2] Carbon-carbon coupling, by reductive elimination, is often the crucial step where the desired product is formed in many catalytic and stoichiometric reactions, which then dissociates from the metal center irreversibly. In addition, this elimination step may also be viewed as model for the reverse step of C-C bond activation.[3-5] Specifically, oxidative addition of platinum(II) to platinum(IV) using chelate-assisted hetero atom ligands is an extremely useful strategy for forming metallacycles and affecting C-H and C-X bond activation.[6-8] Selectivity in C-H bond activation reactions is always an important aspect to study and trying to control regio- and stereoselectivity can often be difficult, as most organic substrates have many carbon-hydrogen bonds with similar bond dissociation energies.[9] Our previous studies have found thiophenes to be very reactive with regard to C-H/C-X activation. C-X bonds (where X=Cl, Br, I) have been founded to be more reactive than C-H bonds and correlate to bond dissociation energies.[10,11] The cyclometalated products of many of these reactive systems are studied for many reasons, including in material science as sensors and in artificial photosynthetic devices. [12-14] Therefore, we have appropriately designed a set of thiophene based ligands to study their oxidative addition and reductive elimination reactivity with the platinum dimer, [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], **Pt1**.[15] The tetramethyl platinum dimer is known to be reactive towards C-X bond oxidative addition leading to Pt(IV) complexes that may subsequently undergo further reactions to afford cyclometalated products. In our case, reductive elimination was afforded by thermolysis of the platinum(IV) species generated from the initial oxidative addition reaction,[16] which was then followed by a series of reactions outlined below including a second oxidative addition of an available C-H bond followed by elimination of methane. We have deduced the following selectivity/activity trend for these systems: C-X > C(sp^2)-H > C(sp^3)-H. [17,18] We have observed that in some cases five-membered rings are formed almost exclusively in the second oxidative addition thus exhibiting a very high degree of regioselectivity.

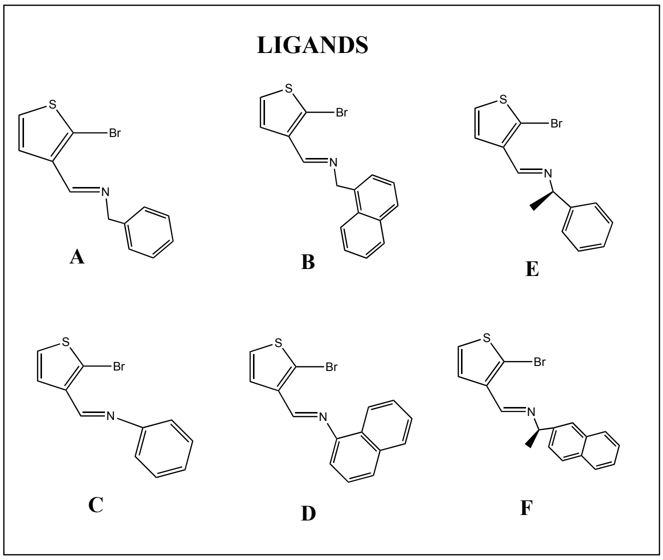
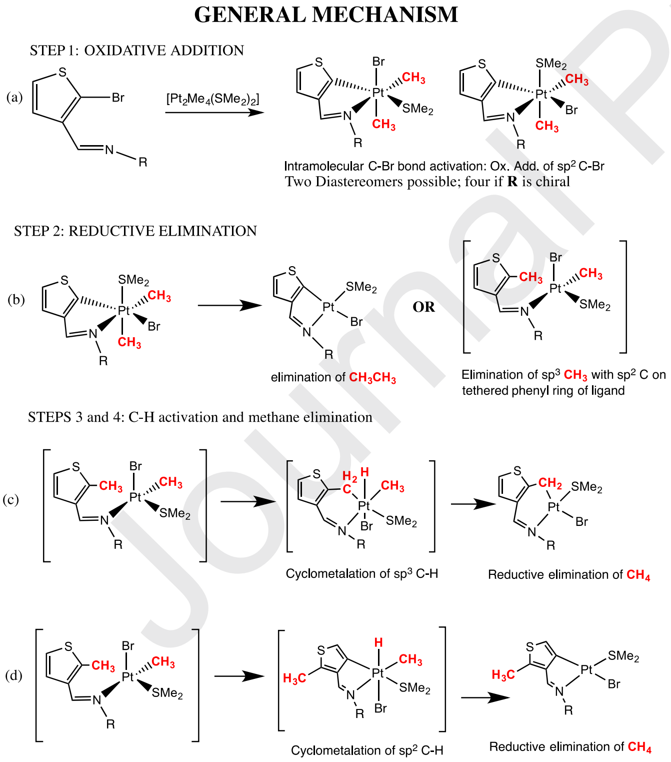


Chart 1: Ligand Structures

substituent at the 2-position were synthesized by simple condensation reactions of a thiophene aldehyde and a primary amine (see Scheme SI#1 for details). Ligands **A** and **B** are similar while the nature of the R group dangling from the imine is different. **A** and **B** differ from **C** and **D** in that there is no methylene spacer group between the nitrogen and the aromatic ring. **A** and **B** differ from **E** and **F** in that **E** and **F** have a methyl group off the carbon attached to the imine nitrogen rendering the ligand chiral (Chart 1). Each of these ligands when allowed to react with the platinum tetramethyl dimer $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, **Pt1**, afforded monomeric platiunum(IV) species. The imine nitrogen substituted for one of the labile dimethylsulfide ligands and subsequent chelate-assisted oxidative addition of the C-Br bond gave a six-coordinate species that included two methyl ligands in the coordination sphere. Given the chelate nature of the ligand, this necessarily renders the N^C ligand *cis*, while the three carbon donors are assumed to have a *fac* preference due to the strong trans influence of the carbon ligands. Thus, for compounds formed with ligands **A-D,** a maximum of two possible diastereomers are expected to be observed, not including their enantiomers, as the six-coordinate platinum center is also chiral. However, for the complexes with the chiral ligands, **E** and **F**, four possible diastereomers are possible given the parameters listed above. The complexes were characterized by multi-nuclear NMR spectroscopy. The platinum(IV) compounds were then reacted with triphenylphosphine, **TPP**, as **TPP** quite readily substitutes for the remaining dimethylsulfide ligand. Armed with several variations of thiophene/platinum (IV) species, we then examined the thermolysis of these species.



Scheme 1: General Mechanism for Reactions

Ligands **E** and **F** and their reactions with **Pt1** were studied and interestingly, they showed the greatest product selectivity in their thermolysis reactions. Generally, the thermolysis of dimethylplatinum(IV) species may generate a variety of products, usually as a result of carbon-carbon bond formation. Ethane elimination is possible and would yield a product with no methyl

tive intermediate with a dangling group still tethered to the metal by the imine ligand. The dangling group would still be in very close proximity allowing for a chelate assisted C-H bond activation. There are two possible C-H bonds (sp^3 methyl or sp^2 thienyl) available to give a putative platinum(IV) intermediate that quickly eliminate methane to give the final platinum(II) product. The selectivity of the C-C bond formation (reductive elimination) step as well as the subsequent C-H activation step exhibit selective regiochemistry.

The ligands **E** and **F** have a chiral carbon next to the imine nitrogen. Therefore, their reactions with **Pt1** to give **PtIVE** may result in a mixture of four possible diastereomers, however a mixture of two major isomers was observed as concluded from analysis of the proton spectra (Scheme 2). The samples were difficult to characterize as there are many overlapping peaks in the proton NMR spectrum. However, essentially two sets of peaks were observed with a small degree of stereoselectivity of approximately 1:1.2. Two dimethylsulfide (**DMS**), two methines, two alpha-methyls, and four platiunum-methyls, with their respective platinum satellites, were observed indicative of two platinum(IV) species. The ^{2}J(Pt-H) of 66-69 Hz is characteristic of platinum (IV) species.[19] In each case, the entire mixture was subsequently subjected to thermolysis in a refluxing solution of toluene and interestingly, only one major product was observed presumably through a series of reactions, including reductive elimination (RE), C-H activation, and reductive elimination of methane (Schemes 1 & 2). Scheme 1 gives the overall general mechanism of the reactions including speculative or putative intermediates. For example, **PTIIE**, was deduced to have formed a five-membered platinacycle as a result of sp^2 C-H activation at the 3-position of the thienyl ring resulting in an almost exclusive regioselective reaction (Scheme 2). Essentially one product was observed even in the crude material. No platinum-methyl resonances remained. The imine proton was observed at 7.81 ppm with ^{3}J(Pt-H) = 119 Hz; the methine at 6.57 ppm and alpha methyl at 1.75 ppm. The methyl group, originally a ligand on the platinum, after thermolysis, became attached to the thienyl ring and was observed at 2.54 ppm with its assignment being confirmed by its NOSEY cross peak with the imine proton (Scheme 2). When this platinum(II) product was reacted with one equivalent of **TPP** a single product was observed thus retaining the regioselectivity and only one geometric isomer with the phosphine trans to the nitrogen as concluded from the ^{31}P NMR spectrum that contained a single resonance at 16.5 ppm with ^1J(Pt-P) of 4108 Hz. The imine proton was shifted slightly downfield with a reduction in the coupling constant compared to the DMS analogue and was observed at 8.04 ppm with ^3J(Pt-H) = 89 Hz. The thienyl methyl was observed at 2.47 ppm and once again was corroborated by a NOESY cross peak with the imine proton. The *sp*^{2} C-H activation is of interest as the C-H bond is at the 3-position (B-position) of the thiophene ring, which is considered less reactive. In other systems, we have obtained C-H activation only at the two position of the thiophene ring not at the 3-position.[10]

An alternate route to study this selectivity would be to choose to substitute the dimethylsulfide with **TPP** before the thermolysis of the platinum(IV) compound. Thus, in order to examine the reactivity difference as a result of the ancillary ligand **DMS** and **TTP** the original mixture of diastereomers of **PTIVE** was reacted with **TPP** and unsurprisingly, two diastereomers were observed, with essentially the same degree of stereoselectivity as the original **DMS** mixture of isomers of 1:1.2. The structures are deduced to be those with **TTP** in the axial position trans to a methyl, probably as a result of **TTP**'s large size. Two resonances are 8.5 and 8.1 ppm with ^{1}J(Pt-P) of 999 and 963 Hz, respectively, in the accepted range for this type of platinum(IV) compound. The methyl trans to the phosphine has a much-reduced ^{2}J(Pt-H) of 59 Hz, as expected when trans to a ligand with a large trans influence, such as a phosphine ligand. When this mixture of two diastereomers was heated in a refluxing solution of toluene and thus subjected to thermolysis, once again, essentially only a single product was obtained, **PtIIBTPP**, one platinum(II) regioisomer and stereoisomer with the **TPP** ligand trans to the imine nitrogen, identical to the product formed from the reactions done in reverse order (Scheme 2). Thus, once again, a highly selective C-H activation reaction was observed. Ligand **F** gave very similar reactivity as ligand **E**. Notable was the high degree of selectivity for the C-H activation step during thermolysis (Scheme1).

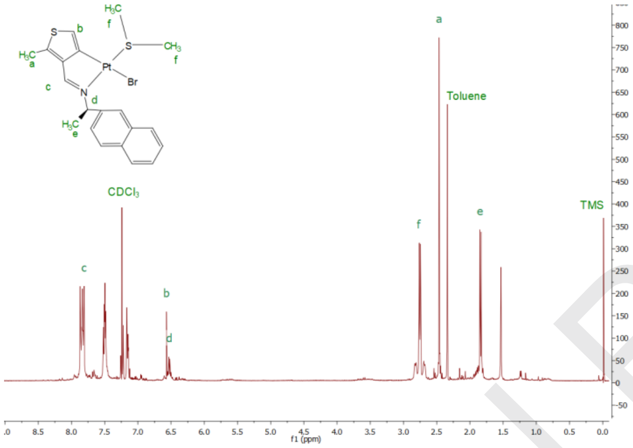
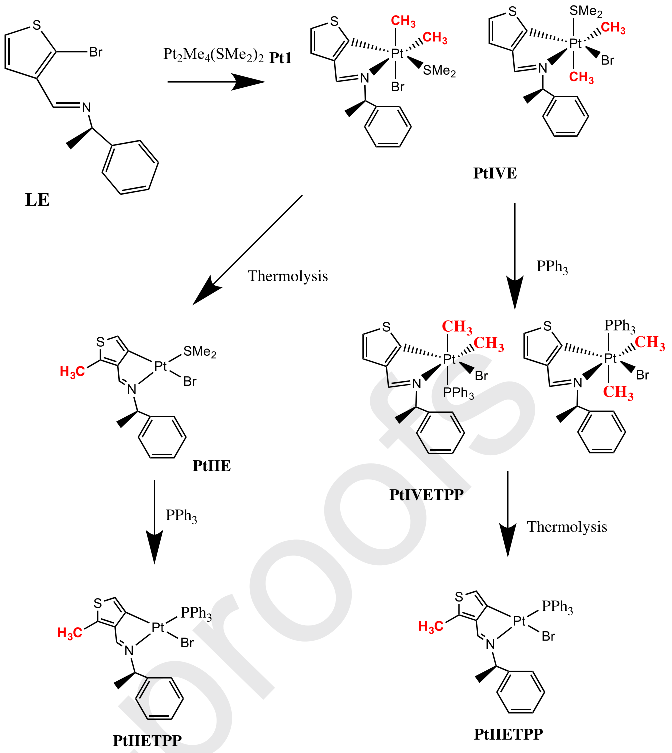


Figure 1: Proton NMR spectrum of **Pt(II)F** (400 MHz)



Scheme 2: Reaction for Ligand **LE.** Compounds are named as followed: Metal/oxidation state/ligand. **TPP** is added to the phosphine derivatives.

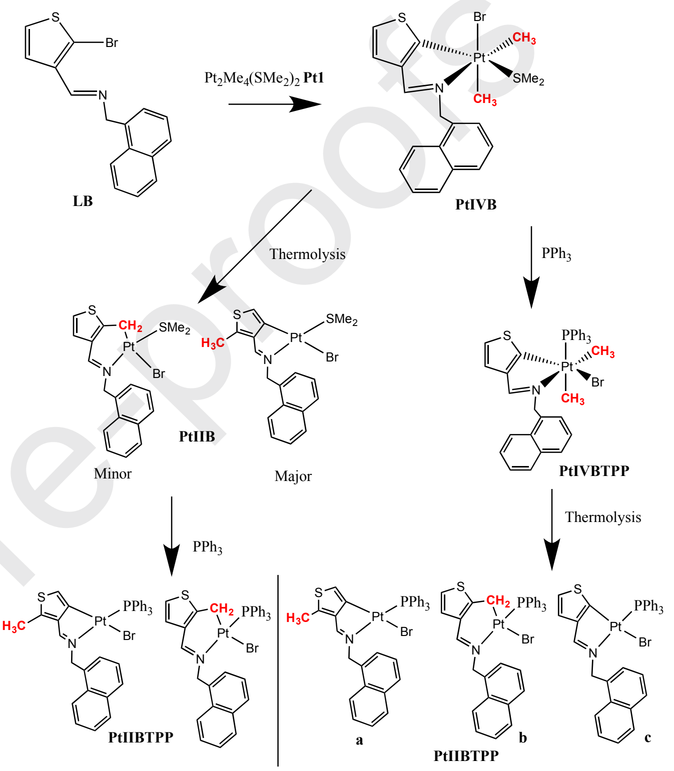
Ligands **A** and **B** (similar to **E** and **F** without the methyl at the alpha position) each gave essentially one single platinum(IV) diastereomer product for the initial reaction with **Pt1**. On occasion, it appeared the other isomer might be present in small amounts estimated at around 10% as determined from the NMR spectrum of the crude material. We assume the isomer with the bromide trans to the thiophene-carbon ligand to be the diastereomer formed. The platinum(IV) compounds were characterized by proton NMR spectra. The expected two methyl peaks are observed with ^{2}J(Pt-H) coupling constants characteristic of platinum(IV) species as a result of oxidative addition of C-Br. For example, **PtAIV** has methyl resonances at shifts of 1.19 and 1.51 ppm with ^{2}J(Pt-H) = 68 and 67 Hz, respectively. The imine resonance and the dimethylsulfide resonance are also useful for the characterization of the compounds. They were observed at 8.04 and 2.00 ppm with ^{3}J(Pt-H) of 45 and 12 Hz, respectively. As mentioned **TPP** easily substitutes for the dimethylsulfide ligand, thus once again we also synthesized the **TPP** derivative of the platinum(IV) species that gave one diastereomer in each case, with **TPP** in the axial position. Each platinum(IV) species was then heated and this resulted in the observation of new platinum(II) species, formed once again, presumably through a series of reactions, including C-C reductive elimination (RE), C-H activation, and reductive elimination of methane (Schemes 1&3). Interestingly, the thermolysis reactions of these compounds were not as clean as those with the seemingly more sterically demanding compounds with ligands **E** and **F**, as mixtures of products, including decomposition and unknown side reactions, were observed. These mixtures or side reactions often made it was difficult to determine the outcome. Table 1 lists the number of region or stereoisomers of the products observed in each case.

	Pt(IV)	Pt(II) Therm	Pt(II) TPP	Pt(IV)TPP	Pt(IV)TPP Therm
LA	1	2	2	1	1
LB	1	2	1	1	2+1*
LC	2	N/A	N/A	1	N/A
LD	2	N/A	N/A	1	N/A
LE	2	1	1	2	1
LF	2	1	1	2	1

Table 1: Number of Diastereomers or Constitutional Isomers (also see Schemes 1, 2, and 3 for Structures). *Including ethane elimination product.

The thermolysis of ligands **A** and **B** gave a major product analogous to those when utilizing ligands **E** and **F** but under certain conditions minor product(s) could be observed (Scheme 3 and Table 1). In addition, interestingly, the order of the reactions had an effect on the overall outcome of product distribution when utilizing ligands **A** and **B**, which did not occur with ligands **E** and **F**. For example, when utilizing ligand **LB**, two regioisomers were observed when heating the platinum(IV) species, **PtBIV,** with the major product being **PtIIBc** (Scheme 3). However, three products (Scheme 3), the two expected regioisomers along with the compound where ethane had been eliminated, were speculated to have formed when "thermolysizing" the **TPP** analogue, **PtBIVTTP** with the major thermolysis product, **PtIITPPa,** formed as a result of C-C reductive elimination followed by sp^2 C-H activation. Other minor products of the reaction were observed and assigned from the NMR data, and deduced to be **PtIITPPb**, formed as a result of C-C RE and sp^3 C-H activation, with the third being **PtIITPPc**, our first observation of product as result of sp^3-sp^3 ethane elimination. Whereas the proton NMR results were complex and gave overlapping peaks and thus were not very useful in the assignments of the minor products, the ^{31}P NMR spectrum showed three distinct resonances, each with appropriate coupling constants for P trans to N; one major peak and two significantly minor products. Mass spectrometry data also confirmed the presence of **PtIITPPa** formed by elimination of ethane (sp^3-sp^3 RE) along with that for the other products. Conversely, when any of the other Pt(IV) species were thermolyzed, we did not observe any sp^3/sp^3 coupling (ethane elimination). This was concluded by analysis of the final products by NMR spectroscopy and HRMS. The product ratio from the thermolysis of the Pt(IV) species for these reactions was not always identical under the reaction condition, but we concluded that both sp^3 and sp^2 C-H activation were observed in the final steps in the formation of the square planar compound to some extent for most cases with ligands **A** and **B**. As mentioned, the major product being similar to those for ligands **E** and **F**; the result of sp^2 C-H activation to give the more common five-membered platinacycle and the minor product as a result of sp^3 C-H activation with the formation of a six-membered ring. The minor product that can deduced from NMR data, but was often removed during routine washings with pentane during reaction workup, as the concentration of the minor product is much lower than the major product. For example, the NMR spectral data clearly show a methyl group on the thiophene ring at the 5-position to support the assignment of the major product, including the NOSEY shows a cross peak with the methyl and the imine. The minor six-membered platinacycle, was assigned from NMR data analogously to seven-membered ringed structures observed for naphthyl derivatives and six-membered species observed with phenyl derivatives, especially the Pt-CH_2 resonance around 3 ppm. Given the mixture of products observed for the final Pt(II) compounds resulting from ligands **A** and **B**, in comparison to ligands **E** and **F,** the chiral center and an alpha methyl group, apparently allowed for greater regioselectivity in the thermolysis reactions.

REACTION SCHEME for LB



Scheme 3: Reactions for Ligand **LB.** Compounds are named as followed: Metal/oxidation state/ligand. **TPP** is added to the phosphine derivatives.

Finally, ligands **C** and **D** and their reactions with **Pt1** were explored as they differ from ligands **A** and **B** in that they do not have a methylene spacer leaving the large aromatic rings closer to the metal center. These ligands gave six-coordination platinum(IV) products similar to those for ligands **A** and **B** (scheme 1) except in these cases two diastereiomers were observed deduced to be those where the **DMS** and bromide ligands switch coordination sites. Presumably the lack of a methylene spacer might cause more steric hindrance in the compound bringing the naphthyl group or the phenyl group closer to the coordination sphere. In any event, the two must be closer in energy as both are both observed and are stable at room temperature. The spectroscopic observation of two diastereomers of presumably comparable energy in the case of **C** and **D**, which was not observed in the case of **A** and **B**, is consistent with Density Functional Calculations, *vide infra*. **TPP** was substituted for **DMS** to form new Pt(IV) species and only one diastereomer resulted with the **TPP** ligand in the axial position. The thermolysis reactions were studied and resulted in a mixture of

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products and thus their study was discontinued.

DFT calculations using the Schrodinger Suite[20,21] were performed to determine the thermodynamic differences between sets of two constitutional isomers observed in the Pt(II) products obtained by thermolysis in addition to the Pt(IV) products obtained by initial C-X oxidative addition. The calculated Gibbs Free Energy of the diastereomeric Pt(IV) products that form from oxidative addition of ligand **C** show a smaller difference in Free Energy than those that are formed from ligand **A**. In particular, this difference in Free Energy for the pair of Pt(IV) diastereomers resulting from oxidative addition of ligand **A** is ~3.7 kcal/mol in contrast to ~1.4 kcal/mol for **C** that corresponds to a Boltzmann population ratio of 500:1 and 10:1 respectively at 298.15 K. In both cases the stable diastereomer is seen to be the product with the bromide ligand trans to the 2 position of the thiophene ring as might be expected from steric considerations as is illustrated for ligand **A** in Figure 2.[21] This is consistent with experimental results where two diastereomers are observed in ^{1}H NMR spectroscopy for the oxidative addition products of ligand **C** but not for ligand **A** assuming the observed product ratios represent a thermodynamic equilibrium of diastereomers in each case.

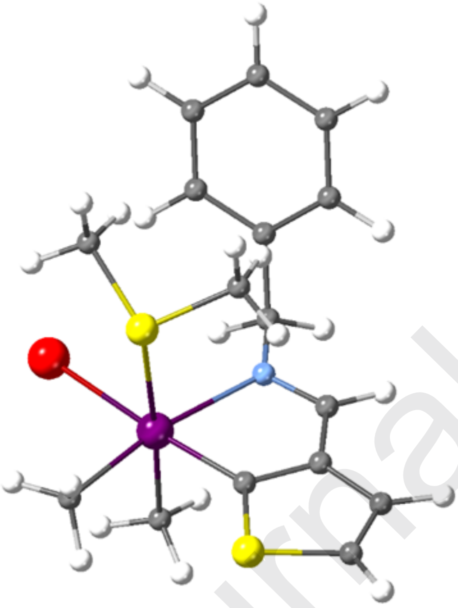

Figure 2: LACVP**/B3LYP DFT optimized structure of the more stable diastereomer resulting from C-Br oxidative addition of ligand **A** to $Pt_2Me_4(\mu\text{-}SMe_2)_2$

DFT calculations were also performed to examine the thermodynamic preference for the Pt(II) five-membered platinacycle resulting from sp^2 C-H activation at the 3-position of the thienyl ring over sp^3 C-H activation. Using ligand **A** as a model system, a strong thermodynamic preference is observed for the observed five membered ring product with a calculated Gibbs Free Energy difference of ~5.4 kcal/mol for the more stable cis/trans diastereomer of each regioisomer. For both five and six membered Pt(II) regioisomeric products, a smaller thermodynamic preference (< 1.5 kcal/mol Gibbs Free Energy difference in each case) was observed for the diastereomer where the bromide ligand is trans to nitrogen. However, the regioisomeric thermodynamic preference for the five membered
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regardless of what cis/trans diastereomer of each regioisomer is compared. This thermodynamic preference is consistent with the regioselective preference for aromatic versus aliphatic C-H activation and five membered versus six membered platinacycle formation that is generally observed in the literature. [22,23]

In summary, we have synthesized a variety of platinum(IV) compounds contain C^N chelate, thiophene-based ligands. These compounds, when subjected to thermolysis, give selective C-C coupling followed by highly regionselective C-H activation reactions, as observed by analysis of the final platinum(II) products. The final compounds were characterized by NMR spectroscopy and mass spectrometry. Slight stereoselectivity was observed in the oxidative addition step for the chiral ligands **E** and **F**.

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Supplementary Material Available Supplementary data associated with this article, including experimental and spectral data for compounds can be found online.

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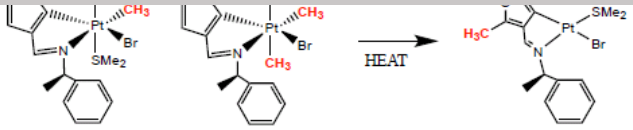
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Regioselective cyclometalated platinum complexes with five-membered rings have been synthesized and characterized
DFT calculations have been performed to support observation of platinum(IV) isomers
Small degree of stereoselectivity is observed for oxidative addition of C-Br bonds