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Regioselective competition between the formation of seven-membered and five-membered cyclometalated platinacycles preceded by C_{sp2}–C_{sp3} reductive elimination

Craig M. Anderson [a, *], Matthew W. Greenberg [a], Lucia Spano [a], Labeeby Servatius [a], Joseph M. Tanski [b]

[a] Department of Chemistry, Bard College, 30 Campus Road, Annandale-on-Hudson, NY 12504, USA
[b] Department of Chemistry, Vassar College, Poughkeepsie, NY 12604, USA

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ABSTRACT

A mixture of seven-membered and five-membered platinacycle complexes are eventually formed after a series of substitution, oxidative addition, and reductive elimination reactions between the platinum dimer, *cis*-[$Pt_2Me_4(\mu$-$SMe_2)_2$] and the naphthyl-derived C^N chelate ligands, (8-$XC_{10}H_6CH$ = N-R), X = I, Br; R = phenyl and 4-Cl-benzyl. From the tethered ligand, either an sp^2 C–H bond can be activated forming a five-membered ring or an sp^3 C–H bond can be activated forming a seven-membered ring. All compounds have the imine included in the platinacycle. The ratio of complexes as a function of ring size varies depending on ligand architecture of the chelate ligand and the nature of other ligands in the coordination sphere. The cyclometalated platinum complexes have been characterized by NMR spectroscopy. One complex with a seven-membered ring was characterized crystallographically. Reductive elimination reactions of isolated and/or identified cyclometalated, six-membered platinum(IV) compounds [$PtMe_2Br\{C_{10}H_6CH$ = $NCH_2(4$-$ClC_6H_4)\}L$] and [$PtMe_2Br\{C_{10}H_6CH$ = $N(C_6H_5)\}L$] (L = SMe_2) to form C_{sp3}–C_{sp2} bonds, followed by competition between C_{sp2}–H and C_{sp3}–H bond activation are also reported.

1. Introduction

Reductive Elimination (RE)/Oxidative Addition (OA) are fundamental reactions in organometallic chemistry in both stoichiometric processes and catalytic cycles and involve the addition and elimination of a large variety of bond types [1–11]. Some contend that reductive elimination is of paramount importance as it is often the step where the desired product is formed in essentially an irreversible step [12–14]. However oxidative addition should be considered no less important as it is often a preliminary step in a set of reactions that generates a carbon-metal bond allowing for future functionalization [15]. C–C bond formation by the reductive elimination of two ligands or fragments from a metal center, and C–H bond activation by oxidative addition are two important examples of reactions of these types. C–H activation being particularly interesting as it has generated much study over the years in the area of specialty chemicals, C–H functionalization, and the use of ubiquitous hydrocarbons as fuel stock [16–19].

As noted, reductive elimination from metal centers is one way in which C–C bonds may be formed. Reductive elimination from platinum centers has centered on sp^2-sp^2 and sp^3-sp^3 couplings [20–25] as well as other types, including C–O, C–H, and C–X [12,26–29]. Recently reported are some mixed C_{sp2}–C_{sp3} bond couplings but they are much more rare in nature [30–32]. In this work, we have studied a system in which either C_{sp2}–C_{sp3} or C_{sp2}–C_{sp2} bond forming RE from a Pt (IV) metal center may occur, ultimately, exclusively the former is observed. This leads to the possibility of two different intramolecular C–H activation reactions resulting in two different cyclometalated platinum complexes. These potential reaction pathways are illustrated in Equation (1) and Scheme 1. The selectivity of the C–C forming step thus plays a role in the competition of the subsequent steps involving ring-size formation of the newly formed cyclometalated species.

Cyclometalated complexes, often formed by oxidative addition or C–H activation, have many practical applications in materials science and as artificial photosynthetic devices [33–36]. The ring size of the cyclometalated platinacycle has been of interest in

* Corresponding author.
E-mail address: canderso@bard.edu (C.M. Anderson).

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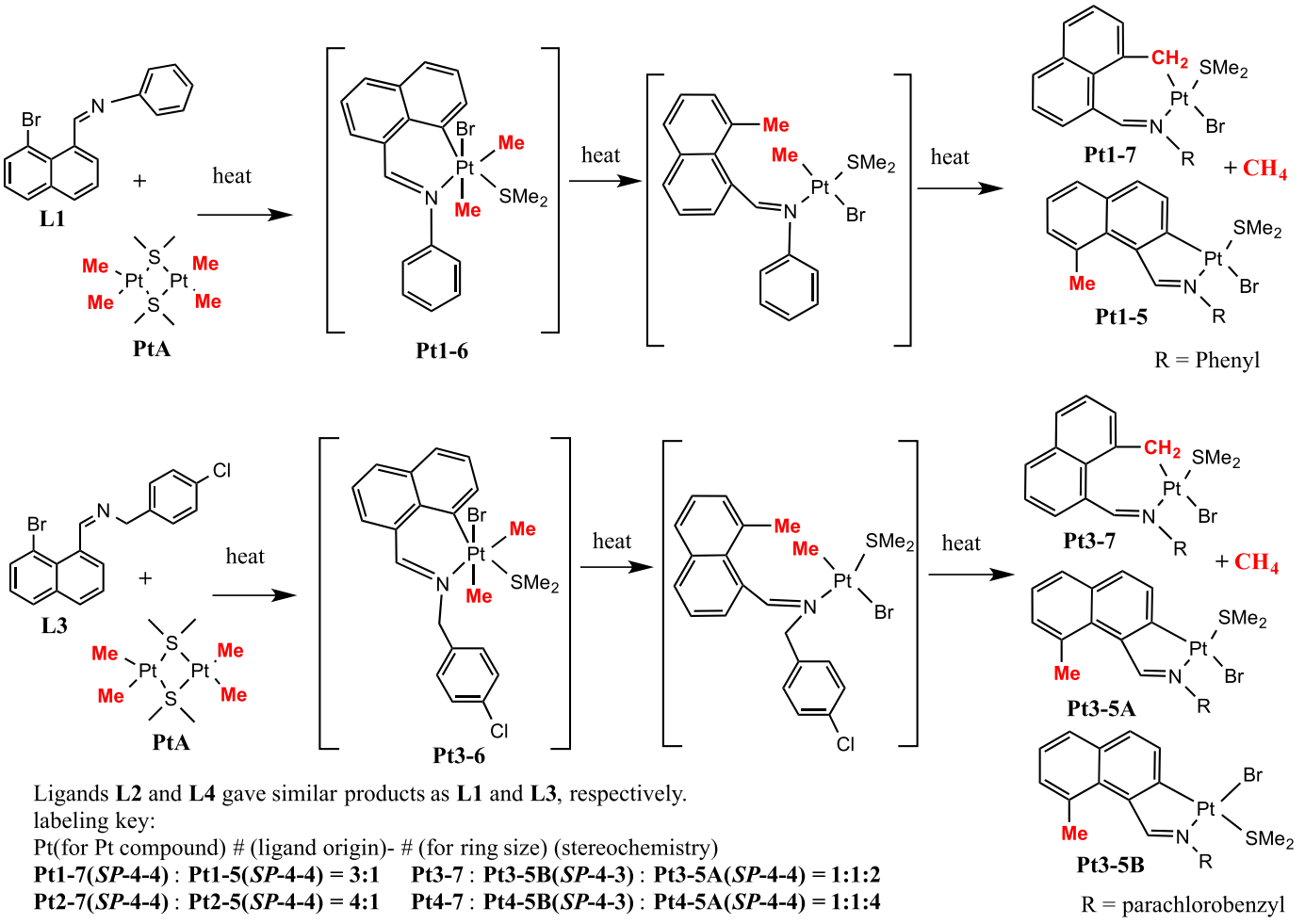


Scheme 1. Synthesis of platinum(II) products by thermolysis of ligands with PtA.

recent years. Habitually, five-membered rings predominate overwhelmingly over any other size [37]. Recently larger platinacycle rings have been reported by us and others, including six-membered rings [38–43], and some seven-membered rings [44]. It can be speculated that different ring sizes may lead to different reactivities due to subtle changes in ligand architecture. Consequently, the regioselectivity of cylometalation reactions by C–H activation is an important subject of study, since knowing the factors which influence this regioselectivity will enable different ring-sizes to be selectively targeted. In this report we have managed to regioselectively synthesize seven-membered platinacycles using naphthyl-based ligands. The reaction of the appropriately-designed ligands with a platinum-methyl precursor proceeds through several OA and RE reactions to afford the products.

The final ratio of products and/or isomers is determined by the "competitive choice" (in the next to final step), of activating either an sp^2 C–H bond on the naphthyl ring or activating an sp^3 C–H bond on a methyl that became available, dangling as it were, after the reductive elimination of the naphthyl and a methyl group (C–C bond formation) [45]. The regioselectivity of five-membered versus seven-membered rings in the final stages of the system are examined and shown to be a function of the ligand structure. Recently, five-membered ring versus seven-membered ring selectivity was studied with compounds containing C–H sp^2 aryl systems with the conclusion that the rate determining step depends on the nature of the aryl-Pt bond and ring size determined by the nature of the halide coordinated to the metal center [21,46,47].

The many reactions reported in this manuscript include a variety of OA and RE steps towards the final products. These OA addition reactions include C–X and C–H addition depending on the stage of the overall reaction. Many of the RE reactions are those where Csp^3–Csp^2 bonds are formed preferentially over Csp^3–Csp^3 bonds, as might be expected, whereas certain C–H activation reactions have Csp^3 bonds preferentially activated over Csp^2 bonds, contrary to the vast majority of reported cases [37]. Finally an attempt to explore the study of the speculated reaction intermediates by examining isolated platinum (IV) complexes formed in the overall proposed process was undertaken.

2. Results and discussion

$\{C_{10}H_6(8\text{-Br})CH{=}N(C_6H_5)\}$, **L1**, $\{C_{10}H_6(8\text{-I})CH{=}N(C_6H_5)\}$, **L2**, $\{C_{10}H_6(8\text{-Br})CH{=}NCH_2(4\text{-}ClC_6H_4)\}$, **L3**, $\{C_{10}H_6(8\text{-I})CH{=}NCH_2(4\text{-}ClC_6H_4)\}$, **L4** were synthesized from condensation reactions between the appropriate aldehydes and amines. All were characterized by ^1H and ^{13}C NMR spectroscopies. The NMR spectra clearly indicate the formation of each of the four imine ligands. These ligands were designed to generate at first, a six-membered ring by oxidative addition. Our recent publications reported that C^N^N pincer complexes were inert to subsequent thermolysis reactions once a new Pt (IV) cyclometalated compound was formed, but C^N chelate-type compounds with five-membered rings were not

[41,42]. In addition, naphthyl derived ligands, when appropriately designed, could "force" the more rare six-membered cyclometalated ring [39].

L1 and **L2** differ from **L3** and **L4** mainly in the methylene group that separates the imine nitrogen from the pendant phenyl group (Chart 1). **L1** and **L3** have bromo at the 8-position on the naphthyl ring whereas **L2** and **L4** have an iodo substituent. It is speculated that the greater reactivity of C–X bonds over C–H bonds can be exploited to form, initially a six-membered platinacylce by oxidative addition of the C–X bond, resulting in a six-coordinate, Pt (IV) species, which then will undergo several subsequent reactions when subjected to thermolysis.

2.1. Reactions of ligands L1 and L2 with cis-[$Pt_2Me_4(\mu\text{-}SMe_2)_2$], *PtA*

The sets of products related to **Pt1** and **Pt2** were formed by refluxing *cis*-[$Pt_2Me_4(\mu\text{-}SMe_2)_2$], **PtA** and **L1** and **L2**, respectively, in anhydrous toluene for 2 h. Upon heating to reflux, the solution changed color from light yellow to dark red within 10 min, and a small of amount of black precipitate formed which was assumed to be the result of decomposition to metallic platinum. These products were determined to be platinum (II) products (Scheme 1) where several reactions must have occurred, including oxidative addition of an aromatic C–X from the naphthyl ring, reductive elimination to form a C–C sp^2/sp^3 bond, subsequent oxidative addition of C–H from the dangling, tethered ligand, finishing with reductive elimination of methane. The possible reaction sequence is shown in Scheme 1. However, with the naphthyl ligands, the second oxidative addition, the C–H activation step, has a "choice" to activate an aliphatic C–H bond or an aromatic C–H bond, each rendering an *endo* metalacycle (containing the imine double bond), which are known to preferentially form [41,48], thus giving products with either a seven or a five membered ring, respectively (Fig. 1). Spectroscopic data indicates that both possibilities occur for both **L1** and **L2**.

An ORTEP from an XRD study of the seven-membered ring, **Pt2-7(*SP*-4-4)** is included in Fig. 2. The structure has one puckered seven-membered ring (the chelate C^N ligand), with the coordination sphere being completed with the dimethyl sulfide (dms) and an iodide. The iodide is trans to the strong sigma donor carbon ligand. The angles and bonds lengths about the metal center are in the accepted range for platinum (II) cyclometalated complexes [49].

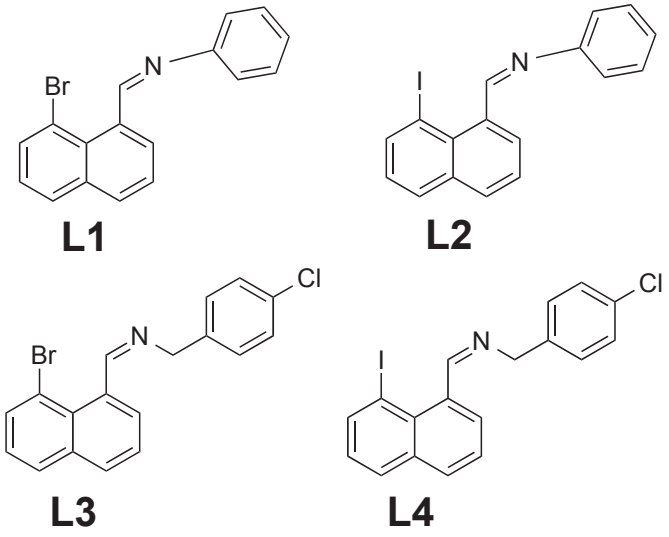


Chart 1. Structures of the four ligands.

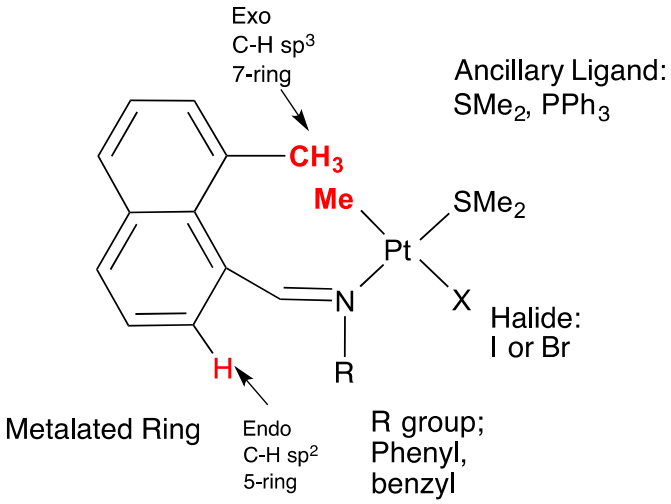


Fig. 1. Ligand design and possible sites for C–H metalation.

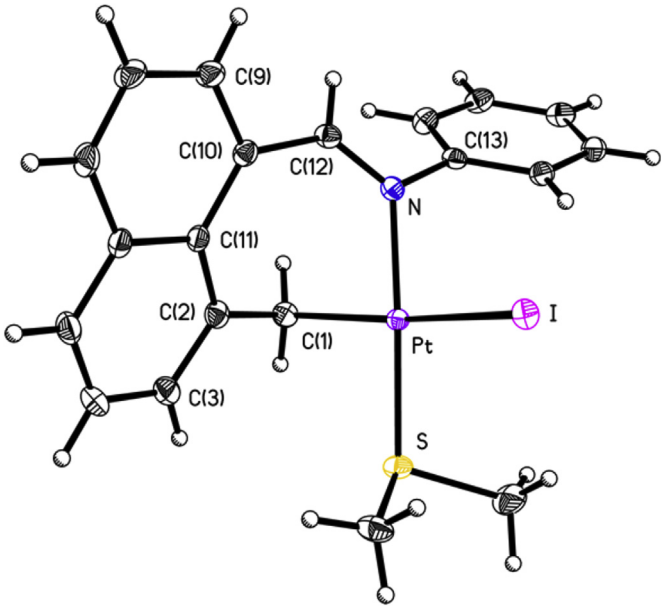


Fig. 2. ORTEP of Compound **Pt2-7(*SP*-4-4)** (50% probability thermal ellipsoids). Selected bonds lengths (Å) and angles (°): Pt–N: 2.025(2); Pt–C(1): 2.063(2); Pt–I: 2.718(1); Pt–S: 2.267(1); N–C(12): 1.292(3); C(1)–C(2): 1.491(3); N–C(13): 1.441(2); C(1)–Pt–N: 82.12(8); C(1)–Pt–S: 89.25(7); N–Pt–S: 166.53(5); C(1)–Pt–I: 162.29(5); N–Pt–I: 95.45(6); Pt–C(1)–C(2): 99.8(1); C(3)–C(2)–C(1): 118.2(2); C(11)–C(2)–C(1): 123.6(2); C(9)–C(10)–C(12): 112.2(2); C(11)–C(10)–C(12): 128.2(2).

The pucker in the seven-membered ring is observed with the methylene angle of Pt–C(1)–C(2) = 99.8(1)°, clearly indicating sp^3 hybridization, but being strained to some degree. There are relatively very few known seven-membered C^N platinacycles that have been characterized crystallographically. To date we have found 16 such published structures [44,46,47,50–57].

The proton NMR spectra of the complexes derived from ligands **L1** and **L2** show the clean formation of both five-membered and seven-membered cyclometalated complexes, with the seven-membered complex forming as the major isomer, as determined by NMR integration, and show a product distribution of approximately 3:1 for **L1**, while **L2** shows a slight but appreciably different product distribution of approximately 4:1. Both isomers have no methyl ligands and possess characteristically large ^3J (H–Pt)

coupling constants for their SMe_2 and CHN platinum satellite resonances consistent with Pt (II) species [3]. The imine ^3J (H–Pt) coupling constants for **L1** were 124 Hz and 120 Hz for the seven-membered and five-membered isomers, respectively, while the dimethyl sulfide ^3J (H–Pt) coupling constants are 52 Hz for the five-membered ring and 52 Hz and 60 Hz for the two sets of S–Me protons on the seven-membered ring, which have been rendered inequivalent in this isomer.

Similar values for these coupling constants were observed for the platinum products of **L2**. The magnitude of these coupling constants is diagnostic of a Pt (II) oxidation state in our complexes, and these values compare favorably to those found in recent publications [41,49,58–61]. While these spectroscopic features of the proton NMR spectra allow us to conclude that we are observing two different Pt (II) complexes, the identity of the five vs. seven membered product as major or minor isomer was determined by relative integration of the different peaks in the upfield methyl/methylene region to the imine resonance in the NMR spectrum. The five-membered ring contains a methyl group attached to the naphthyl group as a result of the Csp^2–Csp^3 carbon-carbon bond forming reductive elimination, while the seven-membered ring has two methylene protons on the carbon bonded to the platinum. In the case of **Pt2-5**, the five membered ring, we observe a methyl peak and a dimethyl sulfide peak with a relative integrations of 0.75 and 1.50, respectively, with respect to the largest imine peak of the seven-membered ring (major isomer). For the seven-membered ring, **Pt2-7,** we observe two dimethyl sulfide peaks with relative integrations of 3.00 and two inequivalent methylene doublets with relative integrations of 1.00 (with respect to the imine) in which both ^2J (H–H) and ^2J (Pt–H) coupling is observed, such that each of these peaks appears as a doublet with satellites that are also doublets thus indicating the inequivalency of the methylene protons and the methyls of the dms. In order to confirm our structural assignments of the seven-membered ring, a 2-D COSY NMR experiment was run. In particular, we wanted additional support that the two doublets with (Pt–H) and (H–H) coupling could be assigned as the CH_2–Pt protons. In the spectra for **Pt1** and **Pt2**, strong cross-peaks are observed between the two doublets that have been assigned as the inequivalent methylene protons in our 1D spectra, thus supporting said assignment. In addition, cross peaks are observed between the inequivalent methylenes and methyls in the NOESY spectrum.

The mixtures of complexes were allowed to react with PPh_3 in order to substitute it for the labile dms ligand. Usually, the reaction is complete at room temperature within minutes. However heating the mixtures to reflux is needed to the drive the reaction to completion for the products **Pt1** and **Pt2** to give **Pt1**–**P** and **Pt2**–**P**, respectively (Scheme 2). The ^{31}P NMR spectra of these complexes have ^{195}Pt coupling constants consistent with Pt (II) species with the stereochemistry at the platinum center having phosphine trans to the imine [41]. For example for **Pt1**–**7P** and **Pt1**–**5P**, the ^1J (Pt–P) coupling constants are 4440 and 4190 Hz, respectively. Other side and/or unidentified products are observed as decomposition when phosphine is introduced. However, one product crystalized from the reaction mixture and was identified by XRD to be *trans*-$[PtBr_2(PPh_3)_2]$ [62,63]. A diagram of its structure is included in the S.I. (Fig. S1).

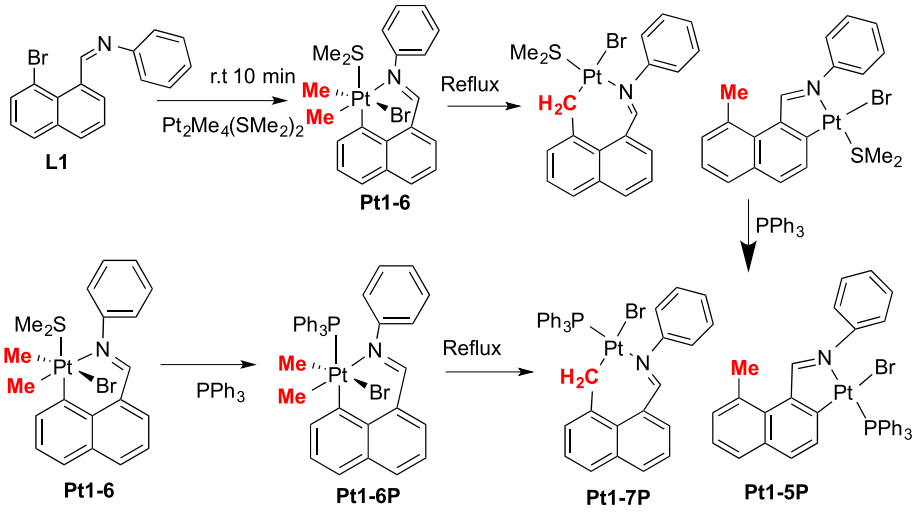
2.2. Reactions of ligands *L3* and *L4* with *PtA*

The driving force behind the observed regioselectivity is thought to be the proximity of the sterically bulky benzene ring to the coordination sphere. Stereoelectronic factors are thought to influence the selectivity of formation of different ring sizes and of intramolecular sp^3 versus sp^2 C–H activation [42,45,64]. In addition, aryl substitutions on an ancillary ligand can support either benzylic or aryl intermolecular C–H activation depending on whether the aryl substitutions point in towards or away from the coordination sphere of the metal [65]. However, a different means by which one could alter steric hindrance in the coordination sphere that might affect changes in the regioselectivity of the C–H activation step would be to simply employ a ligand with increased space between the bulky aryl substituent and the imine nitrogen. **L3** and **L4** (Chart 1) differ from **L1** and **L2** by the CH_2 "spacer" between the imine nitrogen and the aryl ring that is present in these ligands.

When **L3** or **L4** was reacted with **PtA**, using the same procedure used in the reaction of **L1** and **L2** with **PtA**, the result is that primarily a five-membered cyclometalated platinum complex from aromatic C–H activation is formed, reversing the regioselectivity observed for products derived from ligands **L1** and **L2**. Aside from this, another distinction of the products from ligands **L3** and **L4**, is that in these cases, both diastereomeric forms of the major isomer (five-membered ring) are observed in the proton NMR spectra. For example, the reaction of **L3** and **PtA** shows the formation of three Pt (II) products, in a ratio of 2:1:1 (**Pt3-5(*SP*-4-4): Pt3-5(*SP*-4-3): Pt3-7(*SP*-4-4)**), based on NMR peak integration (Scheme 1). The integration of the methyl group peak bound to the naphthalene ring, of the five-membered ring (major product) resulting from Csp^3–Csp^2 reductive elimination had a relative integration of three with respect to the largest imine, while each Pt–CH_2 doublet peak (of the seven-membered ring product) has a relative integration of 0.5 with respect to the largest imine peak. All imine peaks in these compounds showed characteristic Pt (II) ^3J (H–Pt) coupling constants of around 128 Hz. Furthermore, the SMe_2 resonances of the five-membered isomers show ^3J (H–Pt) coupling constants of around 50 Hz. The seven membered ring showed the same two Pt–CH_2 doublets as observed for **L1** and **L2**. However, the small relative abundance of these isomers in the overall product distribution, in this case, and the presence of substantial overlap of peaks in this region did not allow for determination of all possible coupling constants. Nevertheless, it is certainly clear from the proton NMR spectrum of the mixture of **Pt3** Pt (II) products that this reaction yields three different Pt (II) compounds. Additionally, the benzyl-methylene protons in the seven-membered cyclometalated complexes show up as two inequivalent doublets. 2D COSY NMR was a useful tool for assigning the resonances in the proton spectra. As expected, for the minor seven-membered isomer in **Pt3-7(*SP*-4-3),** both of the expected methylene cross-peaks are seen in 2D COSY NMR. For the five-membered ring, cross peaks can be seen between the imine proton and the benzyl methylene for both isomers of **Pt3-5**. **L4** also preferentially forms aromatic over aliphatic C–H activation products, and the product distribution in this case is even further weighted towards the five-membered cyclometalated compound resulting from aromatic C–H activation. We observe a distribution of approximately 4:1:1 (**Pt4-5(*SP*-4-4):Pt4-5(*SP*-4-3):Pt4-7(*SP*-4-4)**). Aside from the difference in distribution of products, the proton spectra associated with the products from the reactions with ligand **L4** are similar to those for **L3** vis-à-vis coupling constants and chemical shifts. Furthermore, a 2D COSY NMR successfully showed the expected methylene cross peaks for the seven-membered ring product, which shows that aliphatic C–H bond activation is still competitive to some degree in this system.

2.3. Characterization of Pt(IV) C–X oxidative addition intermediates

In order to identify the putative Pt (IV) C–X oxidative addition intermediates that would precede Csp^2–Csp^3 bond-forming



Scheme 2. Reactions of **L1**, **Pt1**, and **Pt1-6** at room temperature and with PPh_3. **Pt1-6** is a mixture of two diastereomers. For clarity, only one isomer is shown.

reductive elimination, the ligands were stirred with **PtA** overnight for 24 h in toluene. Identifiable Pt (IV) products from all of the ligands **L1**, **L2**, **L3**, and **L4** were observed. For example, stirring ligand **L1** with **PtA** afforded two six coordinate products as a result of C–Br oxidative addition in an approximate 1:1 ratio, identified by the dms and imine peaks. **L2** and **PtA** also gave a mixture of two diastereomers but in an approximate 3:1 ratio.

Mixtures of diastereomers are not always observed in similar systems, however, they have been reported [39,66]. For example, one of the isomers of **Pt1-6** was identified with the presence of two Pt–Me ligands, which are observed upfield at 0.98 and 1.38 PPM and the ^2J (H–Pt) coupling constants observed are reduced as expected for Pt (IV) as compared to Pt (II) [66,67]. Both Pt–S–Me and Pt–N=CH coupling constants are also reduced compared to Pt (II) products thus supporting the assignment. The assigned stereochemistry of the six coordinate compounds has all three strong carbon donors *fac* as supported by previous work [66,68]. Furthermore, when **Pt1-6** was refluxed in toluene, the products, **Pt1-5/Pt1-7** were generated, supporting the notion that mechanistically the Pt (IV) is indeed an intermediate in the overall reaction that eventually results in the final Pt (II) complex. The product distribution ratio in this case being essentially the same as compared to the original thermolysis reaction. Phosphine could be used to substitute for dms in the case of **Pt1-6** to generate only one diastereomer, **Pt1–6P**, from the mixture. The bulky phosphine ligand coordinates in the axial position, trans to a methyl and thus the bromide ligand is trans to the aryl ligand. A low quality crystal of **Pt1–6P**, the bromo/PPh_3 analogue, was obtained and subjected to X-ray diffraction study, from which only connectivity could be determined (SI, Fig. S2), which corroborates this stereochemical assignment.

In contrast, the room temperature reaction of platinum dimer **PtA** with **L3** and **L4** yielded a curious result; for both reactions a Pt (IV) complex with two methyl ligands was identified, but no dimethyl sulfide peaks were observed. All other expected peaks for the heteroatom-assisted oxidative addition product of **Pt3-6** or **Pt4-6** were accounted for, with Pt (IV) oxidation state-appropriate coupling constants. The structures of these complexes were assigned as platinum dimers with bridging halides (Scheme 3). Once again, a connectivity only (due to crystal quality) XRD study (SI, Fig. S3) was obtained supporting this assignment and corroborating the NMR data. When these Pt/halide dimers were subsequently heated to reflux, undetermined products of decomposition were observed and not the products observed when **PtA** was refluxed in toluene solution, with the ligands, in the one-pot synthesis. However, in the case of **Pt3-6dimer**, phosphine could be used to break the bromide-bridged dimer to give a monomeric Pt (IV) species (Scheme 3) with coordinated phosphine. Finally, when the ligands **L3** and **L4** were combined with **PtA** in toluene-d^8, and proton NMR spectra immediately taken, monomeric Pt (IV) products with coordinated dimethyl sulfide ligands were observed, analogous to products observed in reactions with ligand **L1**. The dms peak integrated to six protons with respect to the imine resonance as expected. In contrast to the halide-bridged dimers, when this solution with the observed product **Pt3-6** was refluxed in toluene-d^8, the result shows the formation of the products **Pt3-5** and **Pt3-7** analogous to the thermolysis of **Pt1-6** and reaction of **L1** and **PtA**. In this NMR tube experiment the halide bridged dimers were not observed within 4 h. We attribute this to the fact that the tube, being sealed would not allow evaporation of the dms from solution, which would drive the equilibrium to the dms-free dimers. Importantly, for these two ligands (**L3** and **L4**) a Pt (IV) C–X oxidative addition intermediate can be identified and made to undergo the same C–H activation reactivity that is witnessed in the one-pot synthesis where the ligand **PtA** are heated to reflux for an extended period of time. We therefore conclude that C–X oxidative addition is the initial mechanistic step following coordination of the imine ligand that eventually leads to aromatic or aliphatic C–H bond activation.

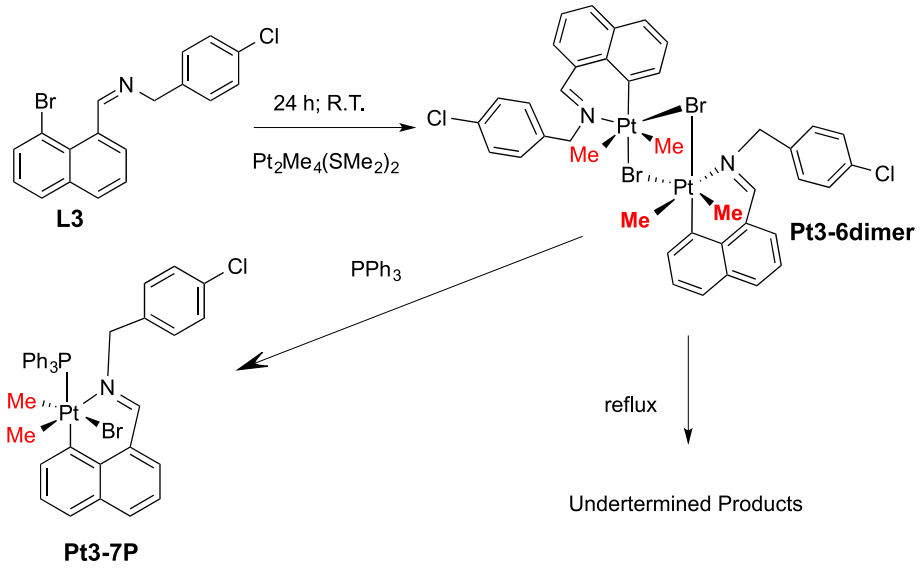
2.4. Concluding remarks

In summary, we have shown that the variation of ligand sterics in the coordination sphere can affect the regioselectivity of intramolecular platinum C–H activation. We have pursued the isolation of the Pt (IV) intermediates that we assumed must be part of this reactivity and have demonstrated their existence and ability to reductively eliminate towards the final C–H activation product.

3. Experimental section

3.1. General

The solvents and reagents were purchased from Sigma Aldrich unless otherwise noted. K_2PtCl_4 was purchased from the Pressure Chemical Company. NMR spectra were recorded at Bard College



Scheme 3. Reactions of **L3** at room temperature and substitution with triphenylphosphine.

using Varian MR-400 MHz spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{31}P-{^{1}H}, 161.8 MHz) and referenced to $SiMe_4$ (^{1}H, ^{13}C) and H_3PO_4 (^{31}P). δ values are given in ppm and J values in Hz. Abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet. Electrospray mass spectra were performed at Vassar College using an LC/MSD-TOF spectrometer. Reported yields refer to total mass of isolated solid mixture of all isomers present.

3.2. X-ray diffraction (XRD)

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα ($\lambda = 0.71073$ Å)) at 125 K Pt2-7(*SP*-4-4) was crystallized using vial-in-a-vial vapor diffusion. ~3 mg of a mixture of isomers of **Pt2-5** and **Pt2-7** was dissolved in 2 mL MeOH and filtered through diatomaceous earth into a 1 dram vial. This vial was placed into a 20 mL scintillation vial containing pentane, capped, sealed, and left undisturbed for approximately 2 weeks. A crystal was mounted in a nylon loop with Paratone-N cryoprotectant oil. The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL2014 [69]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. See Fig. 2 and the caption for ORTEP drawing, labels, bond lengths, and bond angles. CIF for compound Pt2-7(*SP*-4-4) is included in the supporting information.

3.3. Preparation of the compounds

Platinum dimer, *cis*-[Pt_2Me_4 (μ-SMe_2)$_2$], **PtA**, was prepared as reported elsewhere [70].

3.3.1. [($C_{10}H_6Br$)CH=N(C_6H_5)], ***L1***

Both 8-bromo-1-napthaldehdyde (0.508 g, 2.16 mmol) and aniline (0.201 g, 2.16 mmol) were dissolved in 10 mL anhydrous methylene chloride. $MgSO_4$ was added to the flask and the mixture was allowed to stir at room temperature for 24 h. The solution was then filtered and the solvent evaporated yielding an orange oil which was washed with 10. mL anhydrous pentane. The resulting compound crystallized into a yellow solid after one week. Final yield was 0.442 g of imine (1.42 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.47 (m, 6H), 7.57 (t, J(H–H) = 5.6 Hz, 1H) 7.88 (t, J (H–H) = 6.6 Hz, 2H), 7.94 (d, J (H–H) = 10.6 Hz, 1H), 8.08 (d, J (H–H) = 7.4 Hz, 1H), 9.81 (s, 1H, CHN). ^{13}C NMR (100.3 MHz, $CDCl_3$): δ = 118.9, 121.2, 126.0, 126.2, 126.4, 129.0, 129.2, 129.2, 130.0, 131.6, 133.1, 134.7, 135.9, 151.9, 161.6 (CHN).

3.3.2. [($C_{10}H_6I$)CH=N(C_6H_5)], ***L2***

L2 was prepared similarly to **L1** using 0.198 g of 8-iodo-1-napthaldehdyde (0.697 mmol) and 0.065 g of aniline (0.697 mmol). The yield was 0.185 g of resulting imine product (0.517 mmol, 74% yield) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, J = 7.9 Hz, 1H), 7.28 (dd, J = 8.6 Hz, 4.27, 1H), 7.43–7.46 (m, 4H), 7.56 (t, J = 7.2 Hz, 1H), 7.91 (dd,J = 8.0, 4.30 Hz, 2H), 8.06 (d, J = 7.6 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 10.00 (s, 1H, CHN). ^{13}C NMR (100.3 MHz, $CDCl_3$): 90.3 (C–I), 121.3, 126.1, 126.1, 127.0, 129.2, 129.8, 130.0, 132.0, 133.2, 135.2, 135.5, 141.2, 151.7, 160.4 (CHN).

3.3.3. [($C_{10}H_6Br$)CH=NCH$_2$(C_6H_4Cl)], ***L3***

L3 was prepared similarly to **L1** using 0.361 g of 8-bromo-1-napthaldehdyde (1.53 mmol) and 0.217 g of 4-chloro-1-benzylamine (1.53 mmol). The yield was 0.376 g of resulting imine product (1.05 mmol, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.85 (s, 2H), 7.28–7.37 (m, 5H), 7.51 (t, J = 7.8 Hz, 1H), 7.82–7.91 (m, 4H), 9.68 (s, 1H, CHN). ^{13}C NMR (100.3 MHz, $CDCl_3$): δ = 64.4 (CH_2), 118.9, 124.8, 126.1, 126.3, 128.5, 128.6, 129.0, 129.5, 129.8, 131.2, 133.0, 134.7, 135.8, 137.6, 143.9, 164.1 (CHN).

3.3.4. [($C_{10}H_6I$)CH=NCH$_2$(C_6H_4Cl)], ***L4***

L4 was prepared similarly to **L1** using 0.437 g (1.55 mmol) of 8-iodo-1-napthaldeyhde and 0.219 g of 4-chloro-1-benzylamine (1.55 mmol). The reaction mixture was filteredand the solvent evaporated to yield an off white solid. Final yield was 0.385 g of resulting imine product (0.94 mmol, 61.4% yield). ^{1}HNMR (400 MHz, CDCl3): δ = 4.87 (s, 2H), 7.13, (t, J = 8.6 Hz, 1H), 7.31–7.42 (m, 4H), 7.49 (t, J = 7.8 Hz, 1H), 7.83–7.89 (m, 3H), 8.24 (d, J = 7.4 Hz, 1H), 9.90 (s, 1H, CHN). ^{13}C NMR (100.3 MHz, $CDCl_3$): δ = 64.4 (CH_2), 90.3, 125.9, 126.0, 126.9, 128.5, 129.5, 129.8, 129.8, 131.6, 132.6, 132.7, 134.9, 135.4, 137.5, 141.2, 163.4 (CHN).

3.3.5. [PtMe$_2$Br{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}SMe$_2$], Pt1-6 (Pt1-6 (OC-6-54) and Pt1-6 (OC-6-54))

[PtMe$_2$Br{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}SMe$_2$] was obtained by dissolving 0.24 g (0.077 mmol) of **L1** and 0.022 g **PtA** (0.038 mmol) in 15 mL anhydrous toluene. The solution was then allowed to stir for 24 h. The resulting solution was light orange and the solvent was evaporated to yield an orange oil which was then washed with ice cold diethyl ether to yield a dark orange solid. Final yield was 0.034 g (0.057 mmol, 73%). ^{1}H NMR (400 MHz, CDCl$_3$): Major isomer: δ = 0.98, (s, ^2J (H–Pt) = 70.4 Hz, 3H, Pt–Me), 1.38 (s, ^2J (H–Pt) = 68.0 Hz, 3H, Pt–Me), 1.80, (s, ^3J (H–Pt) = 14.1 Hz, 6H, SMe$_2$), 7.12–7.78 (m, CH, aromatics), 8.11 (d, *J* = 8.4 Hz, CH, aromatic), 8.51 (s, ^3J(H–Pt) = 26.3 Hz, 1H, CHN). Minor isomer: δ = 2.08, (s, ^3J (H–Pt) = 11.3 Hz, 6H, SMe$_2$), 7.12–7.78 (m, CH, aromatics), 8.11 (d, *J* = 8.4 Hz, CH, aromatic), 8.67 (s, ^3J(H–Pt) = 22.7 Hz, 1H, CHN). HR-ESI-(+)-MS: *m/z* 454.1066 calcd for C$_{19}$H$_{18}$NPt; [M – Br, dms]$^+$ 454.1061. Anal. calcd for C$_{21}$H$_{24}$BrNPtS: C, 42.2; H, 4.05; N, 2.34. Found: C, 42.14; H, 3.89; N, 2.06.

*3.3.6. [PtMe$_2$Br{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}PPh$_3$], **Pt1–6P***

[PtMe$_2$Br{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}PPh$_3$] was obtained by adding [PtMe$_2$Br{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}SMe$_2$] (15.4 mg, 0.0258 mmol) and triphenylphosphine (6.7 mg, 0.023 mmol) together in toluene (10 mL) at room temperature and stirring for 1 h. The solvent was then evaporated to produce a brownish green powder. Yield: 11.3 mg (0.0137 mmol, 53.1%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.64 (d, 3H, ^3J (H–P) = 9.0, ^2J (H–Pt) = 66.5, Pt–Me); 1.69 (d, 3H, ^3J (H–P) = 7.4, ^2J (H–Pt) = 62.0, Pt–Me); 6.40–7.96 (aromatics); 8.35 (s, 1H, ^3J(H–Pt) = 25.1, CHN). ^{31}P NMR (161.8 MHz, CDCl$_3$): δ = −8.16 (s, ^1J (P–Pt) = 841). HR-ESI-(+)-MS: *m/z* 454.1066 calcd for C$_{19}$H$_{18}$NPt; [M – Br, PPh$_3$]$^+$ 454.1063. Anal. calcd for C$_{37}$H$_{33}$BrNPPt: C, 55.42; H, 4.17; N, 1.76. Found: C, 55.45; H, 4.27; N, 1.48.

3.3.7. [PtMe$_2$I{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}SMe$_2$], Pt2-6 (Pt2-6 (OC-6-54) and Pt2-6 (OC-6-54))

[PtMe$_2$I{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}SMe$_2$] was obtained by stirring a solution of **PtA** (25.0 mg, 0.044 mmol) and **L2** (31.4 mg, 0.088 mmol), in toluene, for 1 h, at room temperature. The solvent was then evaporated to produce a yellow solid. Yield: 34.1 mg (0.053 mmol, 60.1%). ^{1}H NMR (400 MHz, CDCl$_3$): Major isomer: δ = 1.17 [s, ^2J (Pt–H) = 68.3, 3H, Pt–Me]; 1.50 [s, ^2J (Pt–H) = 69.0, 3H, Pt–Me]; 2.13 [s, ^3J (Pt–H) = 13.7, 6H, SMe$_2$]; {7.14–7.82, aromatics}; 8.12 [d, *J* (H–H) = 8.33, 1H, aromatic]; 8.46 [s, ^3J (Pt–H) = 27.2, 1H, CHN]. Minor isomer: δ = 1.87 (s, ^3J (H–Pt) = 9.5 Hz, 6H, SMe$_2$), 7.12–7.78 (m, CH, aromatics), 8.27 (d, *J* = 8.0 Hz, CH, aromatic), 8.63 (s, ^3J(H–Pt) = 24.5 Hz, 1H, CHN). HR-ESI-(+)-MS: *m/z* 454.1066 calcd for C$_{19}$H$_{18}$NPt; [M – Br, dms]$^+$ 454.1062. Anal. calcd for C$_{21}$H$_{24}$INPtS: C, 39.14; H, 3.75; N, 2.17. Found: C, 40.37; H, 3.46; N, 2.22.

3.3.8. [PtMe$_2$-μ-Br{C$_{10}$H$_6$CH = NCH$_2$(4-ClC$_6$H$_4$)}]$_2$, Pt3-6dimer

[PtMe$_2$-μ-Br{C$_{10}$H$_6$CH = NCH$_2$(4-ClC$_6$H$_4$)}]$_2$ was obtained by dissolving 0.034 g (0.095 mmol) of **L3** and 0.027 g **PtA** (0.047 mmol) in 15 mL anhydrous toluene. The solution was then allowed to stir for 24 h. The resulting solution was light yellow and the solvent was evaporated to yield a bright yellow solid. Final yield was 0.048 g (87% yield, 0.041 mmol). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.41, (s, ^2J (H–Pt) = 78.0 Hz, 6H, Pt–Me), 1.97, (s, ^2J (H–Pt) = 68.2 Hz, 6H, Pt–Me), 5.48, (d, *J* (H–H) = 14.5 Hz, 2H, CH$_2$), 5.86, (d, *J* (H–H) = 15.3 Hz, 2H, CH$_2$), 7.10–8.04, (CH, aromatics), 8.53, (s, ^3J (H–Pt) = 19.6 Hz, 2H, CHN). HR-ESI-(+)-MS: *m/z* 502.0833 calcd for C$_{20}$H$_{19}$ClNPt; [M – Br, Br]$^+$ 502.0831. Anal. calcd for C$_{40}$H$_{38}$Cl$_2$Br$_2$N$_2$Pt$_2$: C, 41.1; H, 3.28; N, 2.40. Found: C, 40.02; H, 3.28; N, 1.73.

3.3.9. [PtMe$_2$-μ-I{C$_{10}$H$_6$CH = NCH$_2$(4-ClC$_6$H$_4$)}]$_2$, Pt4-6dimer

[PtMe$_2$-μ-I{C$_{10}$H$_6$CH = NCH$_2$(4-ClC$_6$H$_4$)}]$_2$, was obtained by dissolving 0.037 g (0.091 mmol) of **L4** with 0.026 g **PtA** (0.0452 mmol) in 15 mL anhydrous toluene. The solution was then allowed to stir for 24 h. The resulting solution was a cloudy orange which showed a precipitate which was filtered with diatomaceous earth. The solvent was then evaporated to yield a dark orange solid. Final yield was 0.038 g (66% yield, 0.030 mmol). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.55, (s, ^2J (H–Pt) = 77.4, 6H, Pt–Me), 2.34, (s, ^2J (H–Pt) = 70.0, 6H, Pt–Me), 5.74, (d, *J* (H–H) = 16.0, 2H, CH$_2$), 6.01, (d, *J* (H–H) = 14.0, 2H, CH$_2$), 7.12–8.05, (CH, aromatics), 8.41 (s, ^{3}J (H–Pt) = 21.9, 2H, CHN). HR-ESI-(+)-MS: *m/z* 502.0833 calcd for C$_{20}$H$_{19}$ClNPt; [M–I,I]$^+$ 502.0825. Anal. calcd for C$_{40}$H$_{38}$Cl$_2$I$_2$N$_2$Pt$_2$: C, 38.1; H, 3.04; N, 2.22. Found: C, 40.0; H, 3.03; N, 1.88.

*3.3.10. [PtMe$_2$Br{C$_{10}$H$_6$CH = NCH$_2$(4-ClC$_6$H$_4$)}]PPh$_3$], **Pt3–6P***

[PtMe$_2$Br{C$_{10}$H$_6$CH = NCH$_2$(4-ClC$_6$H$_4$)}]PPh$_3$], was obtained by stirring [PtMe$_2$-μ-Br{CH=NCH$_2$(4-ClC$_6$H$_4$)}]$_2$ (15.0 mg, 0.0128 mmol) and triphenylphosphine (6.9 mg, 0.026 mmol) in dry toluene for 1 h at room temperature. The solvent was then evaporated leaving a light brown solid. Yield: 12.2 mg (0.0137 mmol, 55.5%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.61 [d, ^2J (P–H) = 8.8, *J* (Pt–H) = 60.3, 3H, Pt–Me]; 1.62 [d, ^2J (P-H$_{d=}$) = 7.5, *J* (Pt–H) = 60.9, 3H, Pt–Me]; 4.89 [d, *J* (H–H) = 16.1, 1H, CH$_2$]; 5.97, *J* (H–H) = 16.3, 1H, CH$_2$]; {6.84–8.02, aromatics}; 7.77 [s, ^3J (Pt–H) = 25.6, 1H, CHN]. ^{31}P NMR (161.8 MHz, CDCl$_3$): δ = −7.6 (s, ^1J (P–Pt) = 853). HR-ESI-(+)-MS: *m/z* 764.1744 calcd for C$_{38}$H$_{34}$ClNPPt; [M–Br]$^+$ 764.1763. Anal. calcd for C$_{38}$H$_{34}$BrClNPPt: C, 53.94; H, 4.05; N, 1.66. Found: C, 54.96; H, 4.28; N, 1.33.

*3.3.11. [PtBr{CH$_2$C$_{10}$H$_6$CH = NC$_6$H$_5$}SMe$_2$]:[PtBr{8-MeC$_{10}$H$_5$CH = NC$_6$H$_5$}SMe$_2$], **Pt1-7**:**Pt1-5** (3:1)*

[PtBr{CH$_2$C$_{10}$H$_6$CH = NC$_6$H$_5$}SMe$_2$]:[PtBr{8-MeC$_{10}$H$_5$CH = NC$_6$H$_5$}SMe$_2$] (3:1) was obtained by dissolving 0.020 g (0.066 mmol) of **L1** and 0.019 g **PtA** (0.033 mmol) in 15 mL anhydrous toluene. The solution was then heated to reflux for 2 h. The resulting solution was dark red alongside whch contained some visible black platinum precipitate, which was filtered with diatomaceous earth. The solvent was removed under vacuum resulting in a red powder. Final yield was 0.023 g (59% yield, 0.039 mmol). Alternatively, [PtMe$_2$Br{C$_{10}$H$_6$CH = N(C$_6$H$_5$)}SMe$_2$], **Pt1-6**, when heated to reflux gave a similar mixture of products. ^{1}H NMR (400 MHz, CDCl$_3$): Major Isomer: δ = 2.19, (s, ^3J (H–Pt) = 52.3 Hz, 3H, SMe$_2$), 2.62 (s, ^3J (H–Pt) = 60.2 Hz, 3H, SMe$_2$), 3.21, (d, ^2J (H–H) = 9.7 Hz, ^2J (H–Pt) = 120.9 Hz,1H, CH$_2$), 3.50, (d, ^2J (H–H) = 7.3 Hz, ^{2}J (H–Pt) = 77.1 Hz, CH$_2$), 7.10–8.14 (CH, aromatics), 9.15 (s, ^{3}J(H–Pt) = 124.1 Hz, 1H, CHN); Minor Isomer: 2.75, (s, 3H, CH$_3$), 2.80, (s, ^3J (H–Pt) = 52.0 Hz, 6H, SMe$_2$), 7.10–8.70 (m, CH, aromatics), 9.27 (s, ^3J(H–Pt) = 120.2, 1H, CHN). ^{13}C NMR (100.3 MHz, CDCl$_3$): (Major Isomer Only) 15.8 (Pt–CH$_2$), 22.6 (S–Me), 23.5 (S–Me), 123.8, 123.9, 123.9, 124.6, 125.2, 126.9, 127.8, 127.9, 128.7, 128.9, 136.0, 138.1, 152.0, 153.1, 169.6 (CHN). (^{1}H–H)-2D-COSY-NMR-Cross Peaks-(3.27–3.60)-[Major Isomer Methylenes] (^{1}H–H)-2D-NOESY-NMR-Cross Peaks-(7.85–9.16)-[Major Isomer Methylenes], (2.20–2.63)-[Major Isomer SMe–SMe]. HR-ESI-(+)-MS: *m/z* 500.0943 calcd for C$_{20}$H$_{20}$NPtS; [M–Br]$^+$ 500.0956. Anal. calcd for C$_{20}$H$_{20}$BrNPtS: C, 41.3; H, 3.47; N, 2.41. Found: C, 40.3; H, 3.31; N, 2.15.

*3.3.12. [PtBr{CH$_2$C$_{10}$H$_6$CH = NC$_6$H$_5$}PPh$_3$]:[PtBr{8-MeC$_{10}$H$_5$CH = NC$_6$H$_5$}PPh$_3$], **Pt1–7P**: **Pt1–5P** (3:1)*

[PtBr{CH$_2$C$_{10}$H$_6$CH = NC$_6$H$_5$}PPh$_3$]:[PtBr{8-MeC$_{10}$H$_5$CH = NC$_6$H$_5$}PPh$_3$] (3:1) was obtained by refluxing an acetone solution of [PtBr{CH$_2$C$_{10}$H$_6$CH = NC$_6$H$_5$}SMe$_2$]:[PtBr{8-MeC$_{10}$H$_5$CH = NC$_6$H$_5$}SMe$_2$] (3:1) (15.0 mg, 0.0250 mmol) and

triphenylphosphine (6.8 mg, 0.026 mmol) under nitrogen for 1 h. The resulting solution was concentrated using rotary evaporation to produce a copper colored solid. Unidentified decomposition products were also present. Refluxing a toluene solution of **Pt1**–**6P** also resulted in a similar mixture of products. ^{1}H NMR (400 MHz, $CDCl_3$): Major Isomer: $\delta = 2.95$ [dd, J (H–H) = 8.8 hz, J (H–P) = 8.8 hz, 1H, Pt–CH_2], 3.13 [d, J (H–H) = 8.8 hz, 1H, Pt–CH_2], 5.70 [d, J (H–H) = 7.4 hz, 1H, Upfield Aromatic], 6.97–8.20, [aromatics], 9.20 [d, ^3J (Pt–H) = 85.3 hz, ^4J (P–H) = 10.3, 1H, CHN]. Minor Isomer: $\delta = 2.81$ [s, 3H, CH_3], 9.50 [d, ^3J (Pt–H) = 88.6, ^4J (P–H) = 9.0 hz, 1H, CHN]. ^{31}P NMR (161.8 MHz, $CDCl_3$): $\delta = 13.8$, [s, ^1J (P–Pt) = 4438 hz, Major Isomer], 23.4, [s, ^1J (P–Pt) = 4194, Minor Isomer]. (^{1}H–H)-2D-COSY NMR Cross Peaks-(3.13–2.98)-[Major Isomer Methylenes], (5.69–6.99)-[Upfield Aromatic-Aromatic]. HR-ESI-(+)-MS: m/z 779.0848 calcd for $C_{36}H_{29}BrNPPt$; $[M]^+$ 779.0822. Anal. calcd for $C_{36}H_{29}BrNPPt$: C, 55.3; H, 3.74; N, 1.79. Found: C, 54.0; H, 3.98; N, 1.60.

3.3.13. *[PtI{$CH_2C_{10}H_6CH = NC_6H_5$}$SMe_2$]:[PtI{8-$MeC_{10}H_5CH = NC_6H_5$}$SMe_2$], **Pt2-7**:**Pt2-5** (4:1)*

[PtI{$CH_2C_{10}H_6CH = NC_6H_5$}$SMe_2$]:[PtI{8-$MeC_{10}H_5CH = NC_6H_5$}$SMe_2$], (4:1) was obtained by dissolving 0.020 g (0.056 mmol) of **L2** and 0.016 g **PtA** (0.028 mmol) in 15 mL anhydrous toluene. The solution was then heated to reflux for 2 h. The resulting solution was black, which was filtered with diatomaceous earth to yield a dark brown solution. The solvent was evaporated to yield a dark brown solid. Final yield was 0.013 g (38%, 0.021 mmol). ^{1}HNMR (400 MHz, $CDCl_3$): Refluxing a toluene solution of **Pt2-6** also resulted in a similar mixture of products. Major Isomer: $\delta = 2.23$, (s, ^3J (H–Pt) = 49.6, 3H, SMe_2), 2.68 (s, ^3J (H–Pt) = 61.4, 3H, SMe_2), 3.27, (d, ^2J (H–H)=8.7, ^2J (H–Pt) = 118.2.1H, CH_2), 3.58, (d, ^2J (H–H) = 9.6, ^{2}J (H–Pt) = 77.1, CH_2), 7.15–8.15 (CH, aromatics), 9.16 (s, ^3J(H–Pt) = 119.3, 1H, CHN). Minor Isomer: $\delta = 2.76$, (s, 3H, CH_3), 2.88, (s, ^3J (H–Pt) = 53.8, 6H, SMe_2), 7.15–8.18 (CH, aromatics), 9.26 (s, ^3J(H–Pt) = 120.9, 1H, CHN). ^{13}C NMR (100.3 MHz, $CDCl_3$): (Major Isomer only) $\delta = 21.3$ (Pt–CH_2), 26.2 (S–Me), 26.7 (S–Me), 123.7, 123.8, 123.9, 124.0, 124.6, 125.1, 127.8, 128.0, 128.5, 129.4, 130.1, 141.2, 142.4, 153.6, 169.2 (CHN). (^{1}H–H)-2D-COSY-NMR Cross Peaks-(3.27–3.60)-[Major Isomer Methylenes]. (^{1}H–H)-2D-NOESY-NMR Cross Peaks-(3.27–3.60)-[Hc-Hd], (2.24–2.69)-[SMe_2–SMe_2]. HR-ESI-(+)-MS: m/z 500.0943 calcd for $C_{20}H_{20}NPtS$; $[M–I]^+$ 500.0962. Anal. calcd for $C_{20}H_{20}INPtS$: C, 38.2; H, 3.2; N, 2.23. Found: C, 39.66; H, 2.8; N, 1.92.

3.3.14. *[PtI{$CH_2C_{10}H_6CH = NC_6H_5$}$PPh_3$]:[PtI{8-$MeC_{10}H_5CH = NC_6H_5$}$PPh_3$], **Pt2**–**7P**:**Pt2**–**5P** (4:1)*

[PtI{$CH_2C_{10}H_6CH = NC_6H_5$}$PPh_3$]:[PtI{8-$MeC_{10}H_5CH = NC_6H_5$}$PPh_3$], (4:1) was obtained by refluxing a benzene solution of [PtI{$CH_2C_{10}H_6CH = NC_6H_5$}$SMe_2$]:[PtI{8-$MeC_{10}H_5CH = NC_6H_5$}$SMe_2$], (4:1) (15.0 mg, 0.0238 mmol) and triphenylphosphine (6.24 mg, 0.0238 mmol) for 1 h under nitrogen. The resulting solution was concentrated under rotary evaporation to produce a copper colored solid. Unidentified decomposition products were also present. ^{1}H NMR (400 MHz, $CDCl_3$): Major Isomer: $\delta = 3.10$ [dd, J (H–H) = 9, J (H–P) = 9, 1H, Major Isomer Methylene], 3.17 [d, J (H–H) = 9, 1H, Major Isomer Methylene], 5.80 [d, J (H–H) = 7.4, 1H, Upfield Aromatic], 6.97–8.20, [aromatics], 9.21 [d, ^3J (Pt–H) = 88.7, ^4J (P–H) = 10.4, 1H, CHN]. Minor Isomer: $\delta = 2.80$ [s, 3H, CH_3, Me], 9.54 [d, ^3J (Pt–H) = 88.5, ^4J (P–H) = 9.0, 1H, CHN]. ^{13}C NMR (100.6 MHz, $CDCl_3$): Major Isomer: $\delta = 25.4$ [CH_2–Pt], 123.9, 124.3, 124.7, 125.4, 127.2, 127.4, 127.7, [d, J (C–P) = 10.5, C^{meta}, PPh_3], 127.9, 128.5, 129.7, 130.1, [d, J (C–P) = 2.2, C^{para}, PPh_3], 130.6, 131.2, 135.5, 135.7, 135.3, [d, J (C–P) = 10.5, C^{ortho}, PPh_3], 137.3, 141.9, 153.3, 169.3 [CHN]. ^{31}PNMR (161.8 MHz, $CDCl_3$): $\delta = 13.65$, [s, ^1J (P–Pt) = 4388, Major Isomer], 22.86, [s, ^1J (P–Pt) = 4145, Minor Isomer]. (^{1}H–H)-2D-COSY NMR: Cross Peaks: (3.18–3.09)-[Methylenes], (5.80–7.07)-[Upfield Aromatic-Aromatic]. (^{1}H–H)-2D-NOESY NMR Cross Peaks: (2.79–9.54)-[methyl-imine], (3.11–3.17)-[Methylenes], (3.11–5.80)-[Methylene-Upfield Aromatic], (5.80–7.07), (5.80–7.07)-[Upfield Aromatic-Aromatic]. HR-ESI-(+)-MS: m/z 828.0730 calcd for $C_{36}H_{29}INPPt$; $[M]^+$ 828.0785. Anal. calcd for $C_{36}H_{29}INPPt$: C, 52.18; H, 3.53; N, 1.69. Found: C, 51.91; H, 3.78; N, 1.55.

3.3.15. *Pt3-5(SP-4-4): Pt3-5(SP-4-3): Pt3-7(SP-4-4); [PtBr{8-MeC10H5CH = NCH2(4ClC6H4)}SMe2] and [PtBr{CH2C10H6CH = NCH2(4-ClC6H4)}SMe2] (2:1:1)*

Pt3-5(SP-4-4): **Pt3-5(SP-4-3)**: **Pt3-7(SP-4-4)** (2:1:1) was obtained by dissolving 0.022 g (0.063 mmol) of L3 with 0.018 g **PtA** (0.032 mmol) in 15 mL anhydrous toluene. The solution was then heated to reflux for 2 h. The resulting solution was brownish with some black precipitate. The solution was filtered with diatomaceous earth and the solvent evaporated to yield a dark brown solid. Yield was 0.018 g (42%, 0.027 mmol). When an NMR tube containing a toluene-d8 solution of **Pt3-6** was heated at 100 °C for 2 h a similar mixture of products was observed. 1H NMR (400 MHz, CDCl3): Five-Membered Ring, Major Isomer: $\delta = 2.46$, (s, 3H, Me), 2.79, (s, ^3J (H–Pt) = 50.0 Hz, 6H, SMe2), 5.46, (s, 3J (H–Pt) = 23.6 Hz, 2H, CH2), 7.10–8.19, (CH, aromatics), 9.00 (s, ^3J (H–Pt) = 128.2, 1H, CHN). Five-Membered Ring, Minor Isomer: $\delta = 2.35$, (s, 3H, Me), 2.80, (s, ^3J (H–Pt) = 52.0 Hz, 6H, SMe2), 5.45, (s, 2H, CH2), 7.10–8.19, (CH, aromatics), 8.55 (s, ^3J (H–Pt) = 128.4 Hz, 1H, CHN). Seven-Membered Ring, Major Isomer: $\delta = 2.22$, (s, 3H, SMe2), 2.56, (s, 3H, SMe2), 2.63, (d, 1H, J (H–H) = 8.84, CH2), 3.10, (d, 1H, J (H–H) = 9.99, CH2), 5.07, (d, J (H–H) = 12.3 Hz, 1H, CH2), 6.08, (d, J (H–H) = 12.6 Hz, 1H, CH2), 7.10–8.19, (CH, aromatics), 9.09 (s, J (H–Pt) = 128.2 Hz, 1H, CHN). 13C NMR (100 MHZ, CD2Cl2) Major Isomer Only: δ = 15.0 [CH3], 23.8 [SMe2], 70.0 [CH2], 123.7, 124.5, 124.8, 127.7, 128.1, 128.5, 128.8, 129.7, 131.5, 132.7, 133.6, 135.5, 137.1, 143.0, 168.2 [CHN]. (1H–H)-2D-COSY-NMR Cross Peaks: (2.63–3.09)-[PtCH2–PtCH2], (6.09–5.07)-[CH2–CH2], (8.55–5.44)–(CHN–CH2), (9.00–5.46) –(CHN–CH2). HR-ESI-(+)-MS: m/z 548.0710 calcd for C21H21ClNPtS; [M–Br]+ 548.0722. Anal. calcd for C21H21BrClNPtS: C, 40.0; H, 3.36; N, 2.22. Found: C, 42.3, H, 3.19; N, 2.0.

3.3.16. *[PtI{8-MeC10H5CH = NCH2(4ClC6H4)}SMe2] and [PtI{CH2C10H6CH = NCH2(4-ClC6H4)}SMe2], **Pt4–5(SP-4-4):Pt4-5(SP-4-3):Pt4-7(SP-4-4)** (4:1:1)*

Pt4-5(SP-4-4):**Pt4-5(SP-4-3)**:**Pt4-7(SP-4-4)**, (4:1:1), was obtained by dissolving 0.022 g (0.054 mmol) of **L4** and 0.015 g (0.026 mmol) **PtA** in 15 mL anhydrous toluene. The solution was then heated to reflux for 2 h. The resulting solution was brown with black precipitate. The solution was filtered with diatomaceous earth and the solvent evaporated to yield a dark brown solid. Yield was 0.019 g (0.028 mmol, 52% yield). When an NMR tube containing a toluene-d8 solution of **Pt4-6** was heated at 100 °C for 2 h a similar mixture of products was observed. 1H NMR (400 MHz, CDCl3): Five-Membered Ring, Major Isomer: $\delta = 2.44$, (s, 3H, Me), 2.86, (s, ^3J (H–Pt) = 52.2 Hz, 6H, SMe2), 5.68, (s, ^3J (H–Pt) = 26.6 Hz, 2H, CH2), 7.11–8.11, (CH, aromatics), 9.02 (s, ^3J (H–Pt) = 128.8, 1H, CHN). Five-Membered Ring, Minor Isomer: $\delta = 2.34$, (s, 3H, Me), 2.87, (s, ^3J (H–Pt) = 51.76 Hz, 6H, SMe2), 5.64, (s, 2H, CH2), 7.11–8.11 (CH, aromatics), 8.63 (s, 3J(H–Pt) = 127.5 Hz, 1H, CHN). Seven-Membered Ring, Major Isomer: $\delta = 2.47$, (s, 3H, SMe2), 2.49, (s, 3H, SMe2), 2.67, (d, 1H, J (H–H) = 7.70, CH2), 3.16, (d, 1H, J (H–H) = 8.40, CH2), 5.13, (d, J (H–H) = 12.47 Hz, 1H, CH2), 6.19, (d, J (H–H) = 14.1 Hz, 1H, CH2), 7.11–8.11, (CH, aromatics), 9.11 (s, J (H–Pt) = 126.5 Hz, 1H, CHN). (1H–H)-2D-COSY-NMR Cross Peaks:

(2.67–3.11)-[PtCH2–PtCH2], (5.15–6.20)-[CH2–CH2], (8.63–5.65)–(CHN–CH2), (9.02–5.68)–(CHN–CH2). HR-ESI-(+)-MS: *m/z* 548.0710 calcd for C21H21ClNPtS; [M–I]+ 548.0721. Anal. calcd for C21H21ClINPtS: C, 37.3; H, 3.13; N, 2.07. Found: C, 39.2; H, 2.97; N, 1.75.

3.4. NMR tube experiments

3.4.1. [$PtMe_2Br\{C_{10}H_6CH = NCH_2(4\text{-}ClC_6H_4)\}SMe2$], ***Pt3–6***

Pt3-6 was obtained by dissolving 0.010 g of **L3** (0.028 mmol) and 0.008 g (0.014 mmol) of **PtA** in 5 mL of toluene-d8. This solution was transferred to an NMR tube. An 1H NMR spectrum of the reaction was taken approximately 10 min after making the solution and the formation of the product, **Pt3-6**, was observed. No halide-bridged dimer was observed. 1H NMR (400 MHz, toluene-d8): δ = 1.36, (s, 6H, SMe2), 1.61, (s, ^2J (H–Pt) = 67.5 Hz, 3H, PtMe), 1.86, (s, ^2J (H–Pt) = 69.7 Hz, PtMe), 5.59, (d, J (H–H) = 14.6 Hz, CH2), 5.73, (d, J (H–H) = 15.3 Hz, CH2), 6.78–7.59, (m, aromatics), 7.90 (s, ^3J (H–Pt) = 24.6, CHN).

3.4.2. [$PtMe_2I\{C_{10}H_6CH = NCH_2(4\text{-}ClC_6H_4)\}SMe2$], ***Pt4–6***

Pt4-6 was obtained by dissolving 0.026 g of **L4** (0.064 mmol) and 0.018 g (0.031 mmol) of **PtA** in 5 mL of toluene-d^8. This solution was transferred to an NMR tube. An ^{1}H NMR spectrum of the reaction was taken approximately 10 min after making the solution and the formation of the product, **Pt4-6**, was observed. No halide-bridged dimer was observed. ^{1}H NMR (400 MHz, toluene-d^8): δ = 1.40, (s, 6H, SMe_2), 1.77, (s, ^2J (H–Pt) = 73.3 Hz, 3H, Pt–Me), 2.07, (s, ^{2}J (H–Pt) = 73.4 Hz, Pt–Me), 5.79, (m, 2H, CH_2), 6.65–7.35 (m, aromatics), 7.84 (s, ^3J(H–Pt) = 22.2, CHN).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.06.018.

Notes

The authors declare no competing financial interest.

References

[1] N. Selander, K.J. Szabó, Catalysis by palladium pincer complexes, Chem. Rev. 111 (2011) 2048–2076, http://dx.doi.org/10.1021/cr1002112.
[2] L. Souillart, N. Cramer, Catalytic C–C bond activations via oxidative addition to Transition metals, Chem. Rev. 115 (2015) 9410–9464, http://dx.doi.org/10.1021/acs.chemrev.5b00138.
[3] L.M. Rendina, R.J. Puddephatt, Oxidative addition reactions of organo-platinum(II) complexes with nitrogen-donor ligands, Chem. Rev. 97 (1997) 1735–1754.
[4] P. Sehnal, R.J.K. Taylor, I.J.S. Fairlamb, Emergence of palladium(IV) chemistry in synthesis and Catalysis, Chem. Rev. 110 (2010) 824–889, http://dx.doi.org/10.1021/cr9003242.
[5] E.P.A. Couzijn, I.J. Kobylianskii, M.-E. Moret, P. Chen, Experimental gas-phase thermochemistry for alkane reductive elimination from Pt(IV), Organometallics 33 (2014) 2889–2897, http://dx.doi.org/10.1021/om500478y.
[6] M.J. Geier, M. Dadkhah Aseman, M.R. Gagné, Anion-dependent switch in C–X reductive elimination diastereoselectivity, Organometallics 33 (2014) 4353–4356, http://dx.doi.org/10.1021/om5006929.
[7] Y. Shiba, A. Inagaki, M. Akita, C–C bond forming reductive elimination from diarylplatinum complexes driven by visible-light-mediated photoredox reactions, Organometallics 34 (2015) 4844–4853, http://dx.doi.org/10.1021/om501080v.
[8] A.L. Liberman-Martin, D.S. Levine, W. Liu, R.G. Bergman, T.D. Tilley, Biaryl reductive elimination is dramatically accelerated by remote lewis acid binding to a 2,2′-bipyrimidyl–platinum complex: evidence for a bidentate ligand dissociation mechanism, Organometallics (2016), http://dx.doi.org/10.1021/acs.organomet.5b01003 acs.organomet.5b01003–6.
[9] R. Das, A. Hepp, C.G. Daniliuc, F.E. Hahn, Synthesis of complexes with protic NH,NH-NHC ligands via oxidative addition of 2-Halogenoazoles to zero-valent transition metals, Organometallics 33 (2014) 6975–6987, http://dx.doi.org/10.1021/om501120u.
[10] C. Tschersich, B. Braun, C. Herwig, C. Limberg, PBiP pincer complexes of platinum, palladium, and iridium featuring metal–metal bonds synthesized by oxidative addition of bismuth–halide bonds, Organometallics 34 (2015) 3782–3787, http://dx.doi.org/10.1021/acs.organomet.5b00439.
[11] J.A. Labinger, Tutorial on oxidative addition, Organometallics 34 (2015) 4784–4795, http://dx.doi.org/10.1021/acs.organomet.5b00565.
[12] J.M. Racowski, M.S. Sanford, Carbon–heteroatom bond-forming reductive elimination from palladium(IV) complexes, in: Topics in Organometallic Chemistry, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011, pp. 61–84, http://dx.doi.org/10.1007/978-3-642-17429-2_3.
[13] D.M. Crumpton, K.I. Goldberg, Five-coordinate intermediates in carbon–carbon reductive elimination reactions from Pt(IV), J. Am. Chem. Soc. 122 (2000) 962–963, http://dx.doi.org/10.1021/ja9912123.
[14] D.M. Crumpton-Bregel, K.I. Goldberg, Mechanisms of C–C and C–H alkane reductive eliminations from octahedral Pt(IV): reaction via five-coordinate intermediates or direct elimination? J. Am. Chem. Soc. 125 (2003) 9442–9456, http://dx.doi.org/10.1021/ja029140u.
[15] J.A. Labinger, J.E. Bercaw, The role of higher oxidation state species in platinum-mediated C–H bond activation and functionalization, in: Topics in Organometallic Chemistry, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011, pp. 29–59, http://dx.doi.org/10.1007/978-3-642-17429-2_2.
[16] M. Lersch, M. Tilset, Mechanistic aspects of C–H activation by Pt complexes, Chem. Rev. 105 (2005) 2471–2526, http://dx.doi.org/10.1021/cr030710y.
[17] R.H. Crabtree, Organometallic alkane CH activation, J. Organomet. Chem. 689 (2004) 4083–4091, http://dx.doi.org/10.1016/j.jorganchem.2004.07.034.
[18] J.A. Labinger, J.E. Bercaw, Understanding and exploiting C-H bond activation, Nature 417 (2002) 507–514, http://dx.doi.org/10.1038/417507a.
[19] R.J. Puddephatt, Platinum (IV) hydride chemistry, Coord. Chem. Rev. 219 (2001) 157–185.
[20] T. Wang, L. Keyes, B.O. Patrick, J.A. Love, Exploration of the mechanism of platinum(II)-catalyzed C–F activation: characterization and reactivity of platinum(IV) fluoroaryl complexes relevant to catalysis, Organometallics 31 (2012) 1397–1407, http://dx.doi.org/10.1021/om2007562.
[21] P.V. Bernhardt, T. Calvet, M. Crespo, M. Font-Bardía, S. Jansat, M. Martínez, New insights in the formation of five- versus seven-membered platinacycles: a kinetico-mechanistic study, Inorg. Chem. 52 (2013) 474–484, http://dx.doi.org/10.1021/ic3023584.
[22] M. Crespo, M. Font-Bardía, T. Calvet, Biaryl formation in the synthesis of endo and exo-platinacycles, Dalton Trans. 40 (2011) 9431–9438, http://dx.doi.org/10.1039/c1dt10664c.
[23] R. DiCosimo, G.M. Whitesides, Reductive elimination of a carbon-carbon bond from bis (trialkylphosphine)-3, 3-dimethylplatinacyclobutanes produces bis (trialkylphosphine) platinum (0), J. Am. Chem. Soc. 104 (1982) 3601–3607, http://dx.doi.org/10.1021/ja00377a011.
[24] G.S. Hill, G. Yap, R.J. Puddephatt, Electrophilic platinum complexes: methyl transfer reactions and catalytic reductive elimination of ethane from a tetramethylplatinum (IV) complex, Organometallics (1999), http://dx.doi.org/10.1021/om9809419.
[25] G.S. Hill, R.J. Puddephatt, Electrophilic platinum complexes: catalytic reductive elimination of ethane from a tetramethylplatinum (IV) complex, Organometallics 16 (1997) 4522–4524, http://dx.doi.org/10.1021/om970741h.
[26] A. Vigalok, Electrophilic halogenation–reductive elimination chemistry of organopalladium and -platinum complexes, Acc. Chem. Res. 48 (2015) 238–247, http://dx.doi.org/10.1021/ar500325x.
[27] N.A. Smythe, K.A. Grice, B.S. Williams, K.I. Goldberg, Reductive elimination and dissociative β-hydride abstraction from Pt(IV) hydroxide and methoxide complexes, Organometallics 28 (2009) 277–288, http://dx.doi.org/10.1021/om800905q.
[28] F. Zhang, E.M. Prokopchuk, M.E. Broczkowski, M.C. Jennings, R.J. Puddephatt, Hydridodimethylplatinum(IV) complexes with bis(pyridine) ligands: effect of chelate ring size on reactivity, Organometallics 25 (2006) 1583–1591, http://dx.doi.org/10.1021/om050982m.
[29] E.M. Prokopchuk, R.J. Puddephatt, Hydrido(methyl)carbene complex of platinum(IV), Organometallics 22 (2003) 563–566, http://dx.doi.org/10.1021/

om0205400.
[30] H.L. Buckley, A.D. Sun, J.A. Love, User-friendly precatalyst for the methylation of polyfluoroaryl imines, Organometallics 28 (2009) 6622–6624, http://dx.doi.org/10.1021/om9008229.
[31] B.L. Madison, S.B. Thyme, S. Keene, B.S. Williams, Mechanistic study of competitive sp^3-$sp^3$and sp^2-sp^3 carbon–carbon reductive elimination from a platinum (IV) center and the isolation of a C–C agostic complex, J. Am. Chem. Soc. 129 (2007) 9538–9539, http://dx.doi.org/10.1021/ja066195d.
[32] E.G. Bowes, S. Pal, J.A. Love, Exclusive Csp^3–Csp^3vs Csp^2–Csp^3 reductive elimination from Pt IV governed by ligand constraints, J. Am. Chem. Soc. 137 (2015) 16004–16007, http://dx.doi.org/10.1021/jacs.5b10993.
[33] S. Jamali, S.M. Nabavizadeh, M. Rashidi, Binuclear cyclometalated organoplatinum complexes containing 1,1′-Bis(diphenylphosphino)ferrocene as spacer ligand: kinetics and mechanism of MeI oxidative addition, Inorg. Chem. 47 (2008) 5441–5452, http://dx.doi.org/10.1021/ic701910d.
[34] J.H. Alstrum-Acevedo, M.K. Brennaman, T.J. Meyer, Chemical approaches to artificial photosynthesis. 2, Inorg. Chem. 44 (2005) 6802–6827, http://dx.doi.org/10.1021/ic050904r.
[35] J. Boixel, V. Guerchais, H. Le Bozec, D. Jacquemin, A. Amar, A. Boucekkine, et al., Second-order NLO switches from molecules to polymer films based on photochromic cyclometalated platinum(II) complexes, J. Am. Chem. Soc. 136 (2014) 5367–5375, http://dx.doi.org/10.1021/ja4131615.
[36] J. Kalinowski, V. Fattori, M. Cocchi, J.A.G. Williams, Light-emitting devices based on organometallic platinum complexes as emitters, Coord. Chem. Rev. 255 (2011) 2401–2425, http://dx.doi.org/10.1016/j.ccr.2011.01.049.
[37] M. Albrecht, Cyclometalation using d-block transition metals: fundamental aspects and recent trends, Chem. Rev. 110 (2010) 576–623, http://dx.doi.org/10.1021/cr900279a.
[38] L. Keyes, T. Wang, B.O. Patrick, J.A. Love, Pt mediated C-H activation: formation of a six membered platinacycle via Csp^3-H activation, Inorg. Chim. Acta 380 (2012) 284–290, http://dx.doi.org/10.1016/j.ica.2011.09.030.
[39] C.M. Anderson, M.W. Greenberg, T.A. Balema, L.M. Duman, N. Oh, A. Hashmi, et al., Regioselective formation of six-membered platinacycles by C-X and C-H oxidative addition, Tetrahedron Lett. 56 (2015) 6352–6355, http://dx.doi.org/10.1016/j.tetlet.2015.09.121.
[40] C.M. Anderson, M. Crespo, J.M. Tanski, Synthesis and reactivity of coordination and six-membered, cyclometalated platinum complexes containing a bulky diimine ligand, Organometallics 29 (2010) 2676–2684, http://dx.doi.org/10.1021/om100068j.
[41] C.M. Anderson, M. Crespo, N. Kfoury, M.A. Weinstein, J.M. Tanski, Regioselective C–H activation Preceded by C sp^2–C sp^3 reductive elimination from cyclometalated platinum(IV) complexes, Organometallics 32 (2013) 4199–4207, http://dx.doi.org/10.1021/om400398g.
[42] M. Crespo, C.M. Anderson, N. Kfoury, M. Font-Bardía, T. Calvet, Reductive elimination from cyclometalated platinum(IV) complexes to form Csp^2–Csp^3Bonds and subsequent Competition between C sp2–H and C sp3–H bond activation, Organometallics 31 (2012) 4401–4404, http://dx.doi.org/10.1021/om300303a.
[43] K.A. Grice, J.A. Kositarut, A.E. Lawando, R.D. Sommer, Intramolecular C-H activation by air-stable Pt(II) phosphite complexes, J. Organomet. Chem. 799–800 (2015) 201–207, http://dx.doi.org/10.1016/j.jorganchem.2015.09.031.
[44] R. Cascante, M. Crespo, L. Davin, R. Martín, J. Quirante, D. Ruiz, et al., Seven-membered cycloplatinated complexes as a new family of anticancer agents. X-ray characterization and preliminary biological studies, Eur. J. Med. Chem. 54 (2012) 557–566, http://dx.doi.org/10.1016/j.ejmech.2012.06.002.
[45] S.H. Crosby, G.J. Clarkson, J.P. Rourke, A delicate balance between $sp^2$and sp^3C–H bond activation: a Pt(II) complex with a dual agostic interaction, J. Am. Chem. Soc. 131 (2009) 14142–14143, http://dx.doi.org/10.1021/ja905046n.
[46] M. Crespo, M. Font-Bardía, M. Martínez, Kinetico-mechanistic studies on the formation of seven-membered [C,N]-platinacycles: the effect of methyl or fluoro substituents on the aryl ancillary ligands, Dalton Trans. 44 (2015) 19543–19552, http://dx.doi.org/10.1039/C5DT01926E.
[47] G. Aullón, M. Crespo, M. Font-Bardía, J. Jover, M. Martínez, J. Pike, A combined kinetico-mechanistic and computational study on the competitive formation of seven- versus five-membered platinacycles; the relevance of spectator halide ligands, Dalton Trans. 44 (2015) 17968–17979, http://dx.doi.org/10.1039/C5DT02657A.
[48] M. Crespo, M. Martinez, J. Sales, X. Solans, Syntheses and mechanistic studies in the formation of endo-and exo-cyclometalated platinum compounds of N-benzylidenebenzylamines, Organometallics 11 (1992) 1288–1295, http://dx.doi.org/10.1021/om00039a038.
[49] C.M. Anderson, M.A. Weinstein, J. Morris, N. Kfoury, L. Duman, T.A. Balema, et al., Biscyclometalated platinum complexes with thiophene ligands, J. Organomet. Chem. 723 (2013) 188–197, http://dx.doi.org/10.1016/j.jorganchem.2012.10.027.
[50] R. Martín, M. Crespo, M. Font-Bardía, T. Calvet, Five- and seven-membered metallacycles in [C, N,N′] and [C,N] cycloplatinated compounds, Organometallics 28 (2009) 587–597, http://dx.doi.org/10.1021/om800864f.
[51] A. Capap, M. Crespo, J. Granell, A. Vizcarro, J. Zafrilla, M. Font-Bard a, et al., Unprecedented intermolecular C-H bond activation of a solvent toluene molecule leading to a seven-membered platinacycle, Chem. Commun. (2006) 4128, http://dx.doi.org/10.1039/b608666g.
[52] M. Crespo, M. Font-Bardía, X. Solans, Compound $[PtPh_2(SMe_2)_2]$ as a versatile metalating agent in the preparation of new types of [C, N,N'] cyclometalated platinum compounds, Organometallics 23 (2004) 1708–1713, http://dx.doi.org/10.1021/om030674t.
[53] M. Crespo, M. Font-Bardía, T. Calvet, Biaryl formation in the synthesis of endo and exo-platinacycles, Dalton Trans. 40 (2011) 9431, http://dx.doi.org/10.1039/c1dt10664c.
[54] S. Anabuki, H. Shinokubo, N. Aratani, A. Osuka, A meso-spiro[cyclopentadiene-isoporphyrin] from a phenylethynyl porphyrin platinum(II) pincer complex, Angew. Chem. Int. 51 (2012) 3174–3177, http://dx.doi.org/10.1002/anie.201109091.
[55] M. Font-Bardía, C. Gallego, M. Martínez, X. Solans, Unexpected formal aryl insertion in a cyclometalated diphenylplatinum(IV) complex: the first seven-membered cyclometalated platinum compound structurally characterized, Organometallics 21 (2002) 3305–3307, http://dx.doi.org/10.1021/om020260k.
[56] C.R. Baar, M.C. Jennings, J.J. Vittal, R.J. Puddephatt, Activation of imines by platinum(II) to give aminoalkyl complexes: scope and limitations of the reaction, Organometallics 19 (2000) 4150–4158, http://dx.doi.org/10.1021/om000401n.
[57] A. Escolà, M. Crespo, J. Quirante, R. Cortés, A. Jayaraman, J. Badia, et al., Exploring the scope of $[Pt_2(4\text{-}FC_6H_4)_4(\mu\text{-}SEt_2)_2]$ as a precursor for new organometallic platinum(II) and platinum(IV) Antitumor agents, Organometallics 33 (2014) 1740–1750, http://dx.doi.org/10.1021/om5000908.
[58] M. Crespo, C.M. Anderson, J.M. Tanski, Synthesis of platinum (II) cyclometallated compounds derived from imines containing pyridyl or pyrimidyl groups, Can. J. Chem. (2009) 80–87, http://dx.doi.org/10.1139/v08-084.
[59] C. Anderson, M. Crespo, Cyclometallated platinum complexes with heterocyclic ligands, J. Organomet. Chem. 689 (2004) 1496–1502, http://dx.doi.org/10.1016/j.jorganchem.2004.01.026.
[60] C. Anderson, M. Crespo, J. Morris, J.M. Tanski, Reactivity of cyclometallated platinum complexes with chiral ligands, J. Organomet. Chem. 691 (2006) 5635–5641, http://dx.doi.org/10.1016/j.jorganchem.2006.09.012.
[61] C. Anderson, M. Crespo, F.D. Rochon, Stereoselective oxidative addition of methyl iodide to chiral cyclometallated platinum (II) compounds derived from (R)-(+)-1-(1-naphthylethylamine), J. Organomet. Chem. 631 (2001) 164–174, http://dx.doi.org/10.1016/S0022-328X(01)01043-9.
[62] L. Rigamonti, A. Forni, M. Manassero, C. Manassero, A. Pasini, Cooperation between cis and trans influences in cis-PtII(PPh_3)$_2$ complexes: structural, spectroscopic, and computational studies, Inorg. Chem. 49 (2010) 123–135, http://dx.doi.org/10.1021/ic901510m.
[63] L. Rigamonti, M. Rusconi, C. Manassero, M. Manassero, A. Pasini, Quantification of cis and trans influences in $[PtX(PPh_3)_3]^+$ complexes. A ^{31}P NMR study, Inorg. Chim. Acta 363 (2010) 3498–3505, http://dx.doi.org/10.1016/j.ica.2010.07.002.
[64] M. Crespo, T. Calvet, M. Font-Bardía, Platinum-mediated aryl–aryl bond formation and sp^3 C–H bond activation, Dalton Trans. 39 (2010) 6936, http://dx.doi.org/10.1039/c0dt00631a.
[65] H.A. Zhong, J.A. Labinger, J.E. Bercaw, C–H bond activation by cationic platinum(II) complexes: ligand electronic and steric effects, J. Am. Chem. Soc. 124 (2002) 1378–1399, http://dx.doi.org/10.1021/ja011189x.
[66] C.M. Anderson, M. Crespo, M.C. Jennings, A.J. Lough, G. Ferguson, R.J. Puddephatt, Competition between intramolecular oxidative addition and ortho metalation in organoplatinum (II) compounds: activation of aryl-halogen bonds, Organometallics 10 (1991) 2672–2679.
[67] C.M. Anderson, M. Crespo, G. Ferguson, A.J. Lough, R.J. Puddephatt, Activation of aromatic carbon-fluorine bonds by organoplatinum complexes, Organometallics 11 (1992) 1177–1181.
[68] M. Lashanizadehgan, M. Rashidi, J.E. Hux, R.J. Puddephatt, S.S.M. Ling, The synthesis, characterization and reactions of a binuclear tetramethylplatinum complex, J. Organomet. Chem. 269 (1984) 317–322.
[69] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. A, Found. Crystallogr. 64 (2008) 112–122, http://dx.doi.org/10.1107/S0108767307043930.
[70] J.D. Scott, R.J. Puddephatt, Ligand dissociation as a preliminary step in methyl-for-halogen exchange reactions of platinum (II) complexes, Organometallics (1983) 1643–1648.