# Regioselective C–H Activation Preceded by C sp 2 –C sp 3 Reductive Elimination from Cyclometalated Platinum(IV) Complexes

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# Regioselective C−H Activation Preceded by $C_{sp^2}$−$C_{sp^3}$ Reductive Elimination from Cyclometalated Platinum(IV) Complexes

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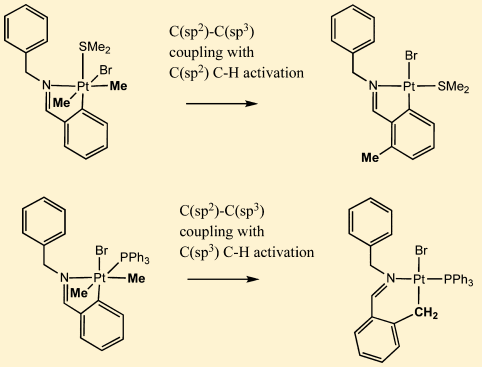
Supporting Information

**ABSTRACT:** Reductive elimination reactions of the cyclometalated platinum(IV) compounds $[PtMe_2Cl\{C_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)\}L]$ and $[PtMe_2Br\{C_6H_4CH{=}NCH_2(C_6H_5)\}L]$ (L = $SMe_2$, $PPh_3$) to form $C_{sp^3}$−$C_{sp^2}$ bonds, followed by either exclusive $C_{sp^2}$−H bond activation (L = $SMe_2$) or competition between $C_{sp^2}$−H and $C_{sp^3}$−H bond activation (L = $PPh_3$), are reported. Isomerization to give *endo* products instead of the expected *exo* complex was observed for the ligand $C_6H_4CH{=}NCH_2(2\text{-}BrC_6H_5)$, and formation of an *endo* six-membered platinacycle occurs for the ligand $2,4,6\text{-}Me_3C_6H_2CH{=}NCH_2(2\text{-}BrC_6H_4)$.




## INTRODUCTION

Reductive elimination is often viewed as the most important step in a catalytic cycle or in stoichiometric processes, as it often is the step where the desired product is formed, usually in an irreversible reaction of C−C or C−H bond formation. There has been much interest in reductive eliminations where $C_{sp^3}$−$C_{sp^3}$ elimination is concerned[1] and many others where competition between C−C bond formation and C−O,[2] C−N,[3] and C−I[4] bond formation exists. Methane elimination of a methyl group and a hydrido ligand is yet another much studied reaction,[5] the reverse of which has been studied in the area of C−H activation and which has gained a great deal of attention in recent decades. Reductive elimination studies have also been performed for arylplatinum(IV) compounds, including $C_{sp^2}$−H bond formation[6] and competition between $C_{sp^2}$−$C_{sp^2}$ and $C_{sp^2}$−halide bond formation.[7] In addition, $C_{sp^2}$−$C_{sp^2}$ coupling from cyclometalated platinum(IV) compounds leading to five-, six-, or seven-membered platinacycles containing a biaryl linkage has also been reported.[8] Examples of $C_{sp^2}$−$C_{sp^3}$ reductive elimination are more rare than those listed above.[9] Recently, a catalytic process for conversion of a $C_{sp^2}$−F bond into a $C_{sp^2}$−$C_{sp^3}$ bond involving reductive elimination from platinum(IV) compounds has been reported.[10] With respect to the reverse reaction, oxidative addition, many reports have included the use of chelate-assisted additions where an appropriately designed ligand has first a heteroatom coordinated to the metal, allowing for the C−X or C−H bond to be added to be in close proximity to the metal and hence facilitating the reaction.[11] Regioselective bond activation, specifically in the case of C−H bonds, is a subject of paramount importance in the area of obtaining value-added products from inexpensive fuel stocks and in the organic synthesis of complex molecules: for example, in the area of pharmaceuticals. In this study, which is an extension of our recently published communication,[12] we examined the reductive elimination of $C_{sp^2}$−$C_{sp^3}$ bonds from Pt(IV) intermediates, which are then held tethered to the metal center by the ligand's nitrogen atom. This allows for subsequent competitive regioselective C−H bond formation to give the final Pt(II) cyclometalated product. Figure 1 shows the molecular structures of the ligands which were examined in this study along with structures of the platinum(IV) intermediates either isolated or suspected to be part of an overall mechanism. The intramolecular oxidative addition of C−X bonds (X = Br, Cl) of these appropriately chosen nitrogen ligands to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) gives initially cyclometalated Pt(IV) products with *fac* carbon stereochemistry,[11] which then can be studied for reductive elimination reactions. We have probed the factors affecting the products in the elimination reactions and the subsequent C−H activation step. The final products have three variables that are important in their formation: $C_{sp^3}$−H or $C_{sp^2}$−H bond activation, *endo* (ring contains the imine double bond) versus *exo* (ring does not contain the double bond) platinacycle formation, and five-membered versus six-membered platinacycle ring formation.

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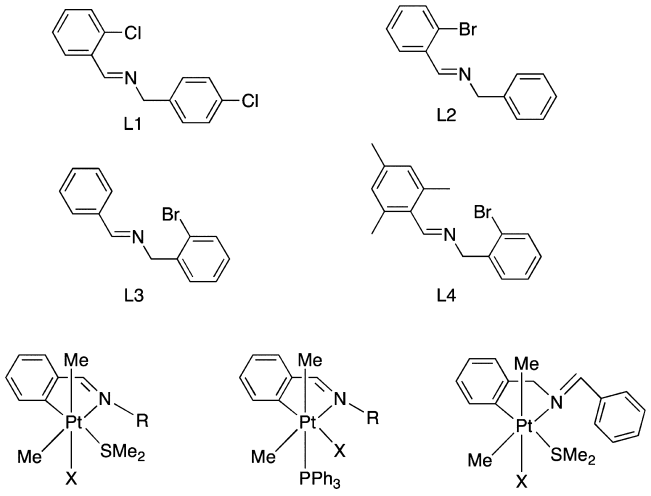


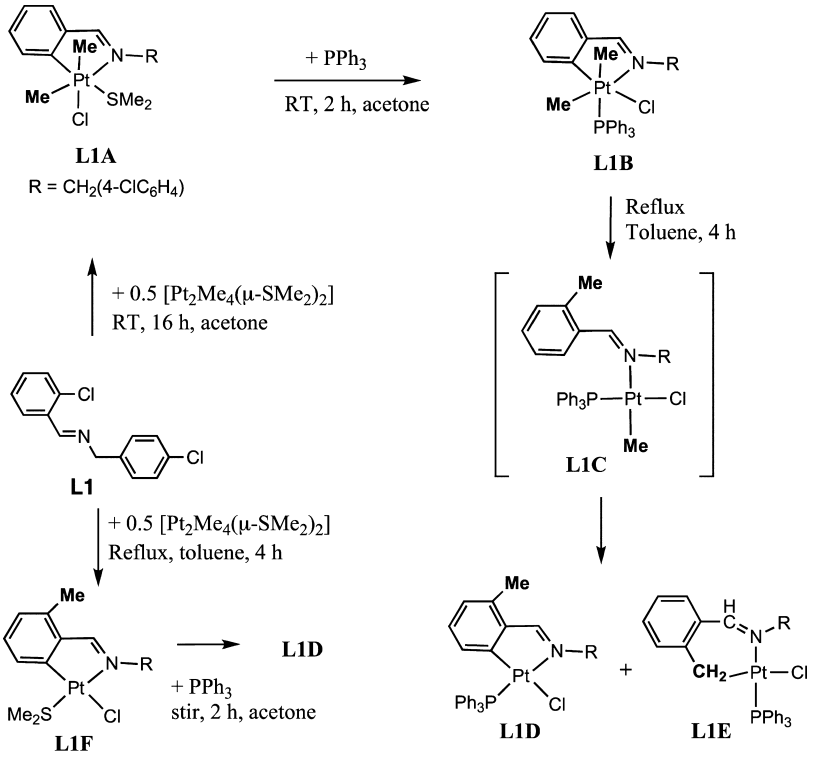

**Figure 1.** (top) Ligands used in this study. (bottom) Platinum(IV) intermediates.

## RESULTS AND DISCUSSION

**Reactions Related to Ligand L1.** In this report we present results for the thermolysis reactions of platinum(IV) compounds containing different cyclometalated ligands. To begin, 2-$ClC_6H_4CH{=}NCH_2(4\text{-}C_6H_4Cl)$ (**L1**; see Figure 1 for ligands) was studied in its reactions with the platinum(II) dimer $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**). Scheme 1 summarizes the reactions and conditions investigated for ligand **L1**. The reaction is assumed to go through a platinum(IV) intermediate by oxidative addition of the C−Cl bond followed by a C−C coupling reaction of the *ortho* carbon on the ring and one of the methyl ligands. The original chelate C^N ligand would remain attached to the metal through the Pt−N bond after the C−C coupling; thus, it would be in position to activate a second bond, in this case a C−H bond, which would allow for a choice between an $sp^3$ C−H of the methyl on the ring or an $sp^2$ C−H bond on the phenyl ring itself.

Scheme 1 shows the two routes examined, both generating the formation of complexes with $C_{sp^3}$−$C_{sp^2}$ coupling: one route includes the isolation of the Pt(IV) intermediate **L1B**, and the other route, that through **L1F**, consists of a one-pot synthesis where only the platinum(II) final products were isolated. The reaction was also run at room temperature, under very mild conditions, in order to isolate the platinum(IV) intermediate **L1A**. In any case the labile dimethyl sulfide ligand can be easily substituted by triphenylphosphine. This varies the sterics and electronics of the ancillary ligand as well as allowing for better crystallization. Scheme 1 includes many of the reactions observed. In addition to the compounds resulting from $C_{sp^3}$−$C_{sp^2}$ coupling, minor products, tentatively assigned to those resulting from either $C_{sp^3}$−$C_{sp^3}$ (elimination of ethane) or $C_{sp^2}$−Cl reductive elimination, were observed in the $^1$H NMR spectra of the crude reaction mixtures and were not pursued. Recent papers have reported on both $C_{sp^3}$−Cl and $C_{sp^2}$−Cl coupling from platinum(IV) cyclometalated compounds.[13] In the case involving cleavage of the metallacycle through $C_{sp^3}$−$C_{sp^2}$ reductive elimination (**L1C**, a suspected intermediate), subsequent cyclometalation at the available *ortho* position of the aryl ring or cyclometalation of the $C_{sp^3}$−H of the methyl group from the newly formed bond (followed by reductive elimination of methane) was observed. The results for **L1** are analogous to those obtained for the ligand 2-$BrC_6H_4CH{=}$

**Scheme 1. Syntheses of the Cyclometalated Platinum(II) and -(IV) Compounds using L1**[a]




[a]Proposed intermediates are given in brackets. In order to follow the fate of the methyl groups initially bound to platinum, these are indicated in boldface.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$NCH_2(4\text{-}C_6H_4Cl)$, reported in our recent communication.[12] Once the bulky phosphine was added to a solution of **L1A**, a platinum(IV) species was observed. With the chloro analogue, in contrast to the bromo analogue, we were able to isolate and characterize the Pt(IV) intermediate **L1B** by XRD (Figure 2),

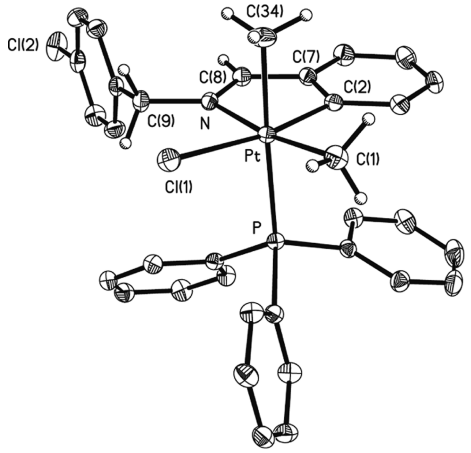


**Figure 2.** Molecular structure of compound **L1B.** Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt–C(2), 2.0073(17); Pt–C(1), 2.0704(17); Pt–C(34), 2.0923(19), Pt–N, 2.1467(14); Pt–P, 2.4150(4); Pt–Cl(1), 2.4298(4); N–C(8), 1.284(2); N–C(9), 1.474(2); C(8)–N–C(9), 122.41(15); C(8)–N–Pt, 112.82(12); C(9)–N–Pt, 124.40(11); C(2)–Pt–C(1), 93.47(7); C(2)–Pt–C(34), 87.13(7); C(1)–Pt–C(34), 86.79(8); C(2)–Pt–N, 80.21(6).

thus confirming its structure and indicating that the mechanism likely goes through an initial oxidative addition intermediate, even in the one-pot synthesis generating **L1F**, shown in Scheme 1. The platinum atom displays an octahedral coordination with a *fac*-$PtC_3$ arrangement and the bulky triphenylphosphine in the less hindered position, which is *trans* to a methyl group. This arrangement is consistent with previous studies indicating that the intramolecular oxidative addition of a C–Cl is initially *cis* and is followed by an isomerization process upon substitution of $SMe_2$ for the bulkier $PPh_3$.[14] We were also able to characterize one of our final platinum(II) products by XRD for the reactions with **L1**. The structure of **L1E** (Figure 3) indicated that the methyl group that had been eliminated by the C–C coupling with the phenyl group had then had one of its $sp^3$ C–H bonds activated. In addition to the six-membered platinacycle containing the imine functionality, a chloride and a $PPh_3$ ligand complete the square-planar coordination around the platinum(II). This was the major product (Scheme 1) as determined by NMR integration, in agreement with the previously reported results[12] indicating that the presence of the bulky triphenylphosphine ligand favors $C_{sp^3}$–H versus $C_{sp^2}$–H bond activation.

**Reactions Related to Ligands L2 and L3.** $2\text{-}BrC_6H_4CH{=}NCH_2(C_6H_5)$ (**L2**), when refluxed in toluene for several hours, gave results similar to those reported in our earlier communication for the ligand $2\text{-}BrC_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)$, and the isolated products were characterized by NMR spectroscopy.

Suitable crystals for XRD were not obtained for this product, with this ligand and reaction conditions, and the results observed were straightforward. However, surprisingly, a very unexpected result occurred with ligand **L3**. In this system,

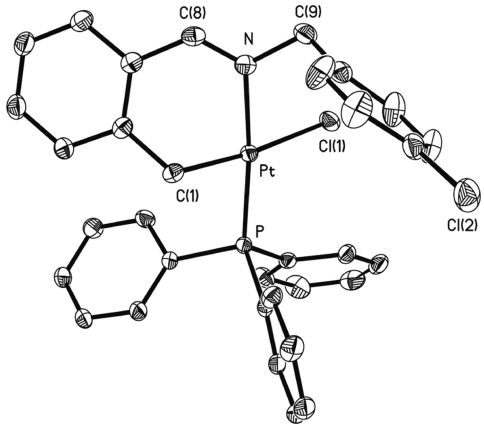


**Figure 3.** Molecular structure of compound **L1E**. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt–C(1), 2.057(3); Pt–N, 2.105(2); Pt–P, 2.2159(7); Pt–Cl(1), 2.4139(6); N–C(8), 1.288(3); N–C(9), 1.470(3); C(1)–Pt–N, 83.99(10); C(1)–Pt–P, 88.90(8); N–Pt–P, 172.85(6); C(1)–Pt–Cl(1), 173.83(7); N–Pt–Cl(1), 90.15(6); P–Pt–Cl(1), 96.98(2); C(8)–N–C(9), 117.9(2); C(8)–N–Pt, 123.44(19); C(9)–N–Pt, 118.36(18).

suitable crystals of the product *expected for* ***L2*** were obtained when using $C_6H_5CH{=}NCH_2(2\text{-}C_6H_4Br)$ (**L3**) (after phosphine substitution for dimethyl sulfide). **L3** was originally employed in our study in order to force the initial oxidative addition away from the imine double bond, thus giving an *exo* intermediate, which was to be studied in order to compare the elimination reactions to the known *endo* cases. The reaction of **1** with **L3** was followed under various conditions. Initially, the reaction was run under mild conditions and the $^1H$ and $^{31}P$ NMR data for the compound obtained after reaction with $PPh_3$ were consistent with the formation of a platinum(IV) cyclometalated compound (**L3B**). Although formation of this type of compound containing an *exo*-metallacycle had been previously described and characterized only by NMR,[15] the molecular structure determination indicated formation of an *endo*-platinacycle. Crystals of this Pt(IV) product were studied by XRD and shown clearly to have the *endo* structure with the imine double bond included in the platinacycle with an arrangement analogous to that observed for **L1B** (Figure 4). This is clearly evident from the lengths of the carbon–nitrogen bonds. The ligand **L3**, once coordinated, either subsequent to the initial oxidative addition reaction that produced the Pt(IV) species or immediately thereafter, isomerizes to give the *endo* product. Scheme 2 details the reactions and illustrates a possible mechanism for the transformation where, immediately after the C–Br oxidative addition, the isomerization occurs. The presence of a bromo substituent in the saturated arm of the free *N*-benzylidenebenzylamine mandates initial formation of an *exo*-platinacyle arising from C–Br bond activation, followed by isomerization to a more stable *endo*-platinacycle, which can take place before or after the substitution of $SMe_2$ by $PPh_3$. In principle, the isomerization could take place either through a 1,3-proton shift mechanism as described for *N*-benzylamines[16] or through an intramolecular exchange reaction as described for cyclopalladated compounds.[17] The second mechanism is more likely, since the ligand itself did not isomerize when left in solution for days or when refluxed for several hours with no metal complex.


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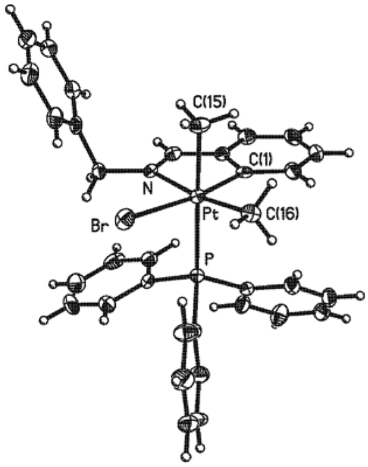



**Figure 4.** Molecular structure of compound **L3B**. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt–C(1), 2.017(3); Pt–C(16), 2.075(3); Pt–C(15), 2.080(3); Pt–N, 2.151(3); Pt–P, 2.4265(8); Pt–Br, 2.5791(4); N–C(7), 1.287(4); N–C(8), 1.486(4); C(1)–Pt–C(16), 94.66(13); C(1)–Pt–C(15), 85.65(13); C(16)–Pt–C(15), 85.24(14); C(1)–Pt–N, 80.25(11); C(16)–Pt–N, 172.16(12); C(15)–Pt–N, 88.41(12); C(1)–Pt–P, 93.77(9); C(16)–Pt–P, 93.73(10); C(15)–Pt–P, 178.77(10); N–Pt–P, 92.57(7).

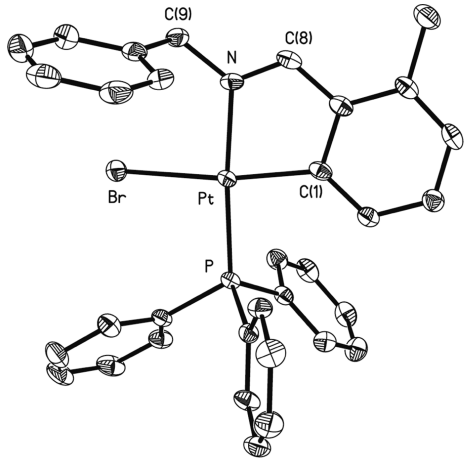
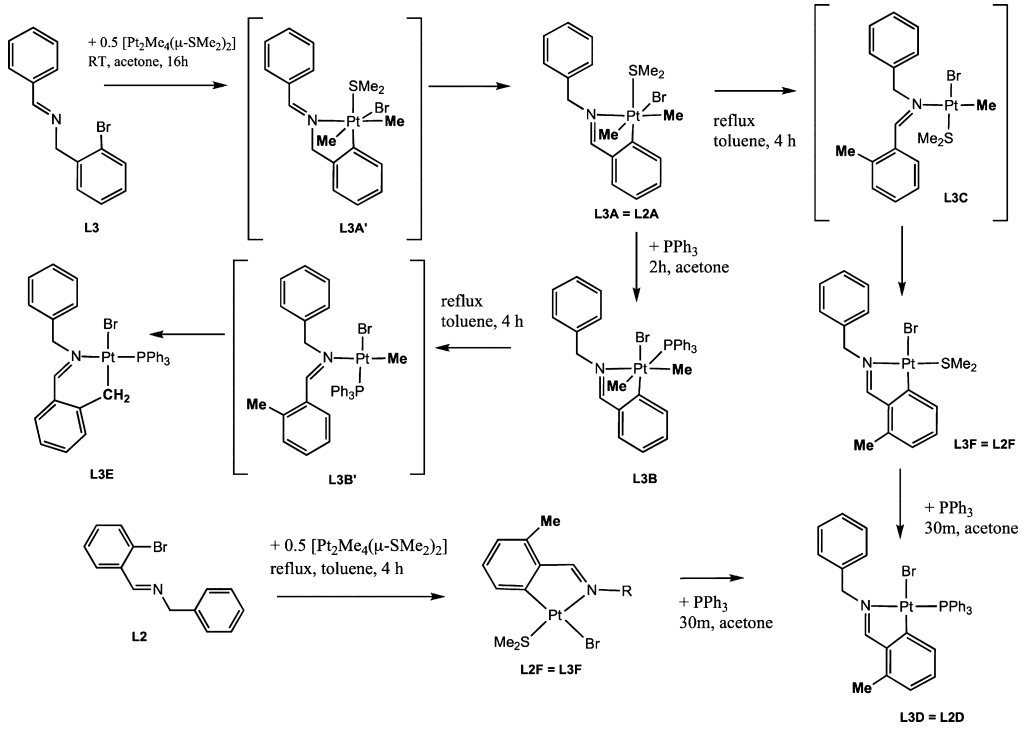



**Figure 5.** Molecular structure of compound **L3D**. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt–C(1), 2.020(3); Pt–Br, 2.4968(3); Pt–N, 2.077(2); Pt–P, 2.2298(7); N(1)–C(8), 1.287(4); N(1)–C(9), 1.468(4); N–C(8)–C(7), 117.7(3); N–C(9)–C(10), 111.3(2); C(8)–N–C(9), 119.1(3); C(8)–N–Pt, 114.6(2); C(9)–N–Pt, 126.11(19); C(1)–Pt–N, 80.16(11); C(1)–Pt–P, 94.62(8); N–Pt–P, 174.69(7); C(1)–Pt–Br, 170.68(8).

A one-pot procedure from ligand **L3** followed by reaction with $PPh_3$ produced crystals of **L3D**. The NMR spectra of these crystals matched the spectra of those from **L2D**; thus, the two different ligands eventually gave the same product. The compound was characterized by XRD (Figure 5), and once again the C=N bond, easily identified by its length, is included in the five-membered platinacycle and the methyl group is attached to the remaining *ortho* $C_{sp^2}$ of the benzyl ring.

The thermolysis of compound $[PtMe_2Br\{C_6H_4CH_2N{=}CHC_6H_5\}PPh_3]$ (**L3B**) was carried out in refluxing toluene for 4 h and gave, in addition to *trans*-$[PtMeBr(PPh_3)_2]$, the single cyclometalated platinum(II) compound $[PtBr\{CH_2C_6H_4CH{=}NCH_2(C_6H_5)\}PPh_3]$ (**L3E**) containing a six-membered metallacycle, which was also characterized by XRD (Figure 6) and showed features analogous to those of **L1E**. This result indicates that $C_{sp^3}$–$C_{sp^2}$ reductive elimination followed by a fast cyclometalation, with subsequent loss of methane, takes place. The cyclometalation step consists of

**Scheme 2. Proposed Mechanism and Reaction for L2 and L3**





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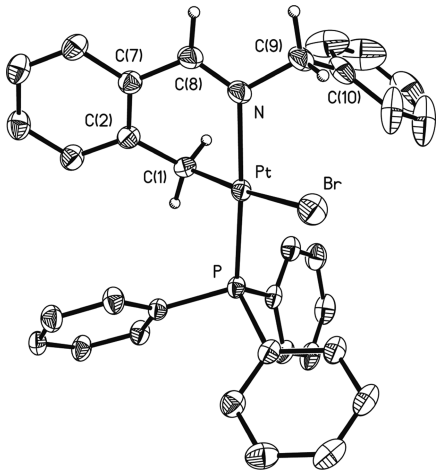


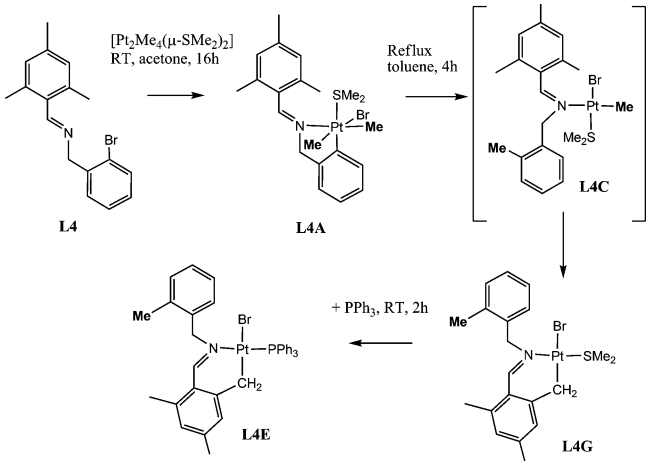

**Figure 6.** Molecular structure of compound **L3E**. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt–C(1), 2.072(3); Pt–N, 2.099(3); Pt–P, 2.2168(8); Pt–Br, 2.5193(4); N–C(8), 1.284(4); N–C(9), 1.481(4); C(1)–C(2), 1.496(4); C(1)–Pt–N, 82.10(7); C(1)–Pt–P, 89.03(9); N–Pt–P, 172.49(8); C(1)–Pt–Br, 173.11(9); N–Pt–Br, 90.32(8); P–Pt–Br, 97.15(2); C(8)–N–C(9), 117.5(3); C(8)–N–Pt, 124.2(2); C(9)–N–P, 118.0(2); C(2)–C(1)–Pt, 108.5(2).

activation of a $C_{sp^3}$–H bond of the methyl group previously reductively eliminated, leading to the six-membered platinacycle. As stated above, when an alternative reaction was run, where **L3** and **1** were refluxed for several hours and the Pt(IV) intermediate was not isolated, the final Pt(II) product isolated, after phosphine substitution and recrystallization, was the product shown in Scheme 2, which included the isomerization of the ligand but instead the $C_{sp^2}$–H had been activated to form the five-membered platinacycle **L3D**. As indicated above for ligand **L1**, the presence of the triphenylphosphine ligand favors cyclometalation at the $C_{sp^3}$–H bond over cyclometalation at the $C_{sp^2}$–H bond.

**Reactions Related to Ligand L4.** Finally, the ligand 2,4,6-$C_6H_2(CH_3)_3C{=}NCH_2(2\text{-}C_6H_4Br)$ (**L4**) was studied in order to examine a ligand which was predicted to give a product with the reductively eliminated methyl group not included in the final platinacycle and would be predicted not to isomerize due to the two *ortho* methyl groups poised to form an *endo*, six-membered platinacycle. Therefore, the predicted product was in this case, given the propensity for these systems to form *endo* products, an *endo* six-membered ring resulting from the $C_{sp^3}$–H activation. This ligand reacts according to Scheme 3: that is, oxidative addition of C–Br, followed by C–C bond coupling/reductive elimination, ending with a $C_{sp^3}$–H bond activation of a mesityl methyl group to give the *endo* six-membered platinacycle ring. No isomerization was observed in this case. In this system, it is one methyl group of the mesityl ligands that had its C–H activated to give the desired *endo* product, without the need for *exo* to *endo* isomerization, as was observed for ligand **L3**, which had the methyl originally on the platinum that was activated. XRD study of a single crystal clearly shows the original platinum/methyl group attached to the phenyl of the benzyl ring (Figure 7), even though the ring shows a slight disorder. The same product was observed whether the platinum(IV) intermediate was isolated prior to reflux or in a one-pot synthesis from the platinum dimer and ligand **L4**.

**Concluding Remarks.** Given our results for these systems, it appears that *endo* formation is the paramount driving force

**Scheme 3. Reactions of Ligand L4**



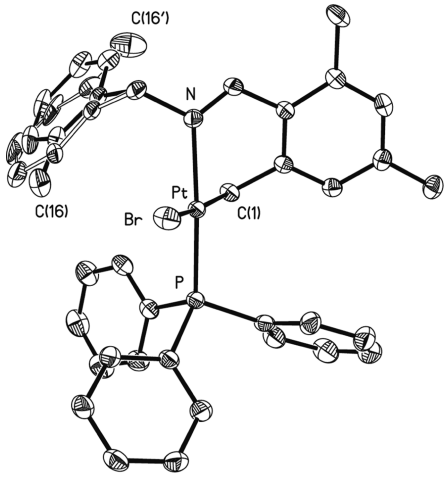




**Figure 7.** Molecular structure of compound **L4E**. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt–C(1), 2.0460(18); Pt–N, 2.0957(15); Pt–P, 2.2074(5); Pt–Br, 2.5421(2); N–C(8), 1.290(2); N–C(9), 1.484(2); C(1)–C(2), 1.495(3); C(1)–Pt–N, 82.10(7); C(1)–Pt–P, 88.19(5); N–Pt–P, 167.84(5); C(1)–Pt–Br, 168.39(5); N–Pt–Br, 90.70(4); P–Pt–Br, 100.000(14); C(8)–N–C(9), 118.08(16); C(8)–N–Pt, 123.35(13); C(9)–N–Pt, 117.61(12); C(2)–C(1)–Pt, 104.58(12).

for determining the final product. Generally, previous reports have stated that five-membered rings form more readily than six-membered rings[18] and that six-membered platinacycles are somewhat of a rarity.[19] A recent example has been reported for a fluorinated ligand.[19f] Furthermore, $C_{sp^2}$–H bonds are preferred over $C_{sp^3}$–H bonds on activation by a metal center. However, our results indicate that a six-membered ring with $C_{sp^3}$–H activation is preferred over a $C_{sp^2}$–H five-membered *exo* ring, overriding both of these accepted rules in order to form an *endo* product with the imine bond in the platinacycle. Therefore, of the three variables for the final C–H activation that are covered in this study (*endo* vs *exo*, $sp^2$ vs $sp^3$, five-membered ring vs six-membered ring), the most important appears to be formation of the platinacycle ring including the imine double bond, thus rendering the *endo* structure. This feature appears to override the other variables.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## EXPERIMENTAL SECTION

**General Considerations.** The solvents and reagents were purchased from Sigma Aldrich unless otherwise noted. $K_2PtCl_4$ was purchased from the Pressure Chemical Co. NMR spectra were performed at Bard College using a Varian MR 400 MHz spectrometer ($^1$H, 400 MHz; $^{13}$C, 100.6 MHz; $^{31}$P{$^1$H}, 161.8 MHz) or at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Varian Unity 300 ($^{31}$P{$^1$H}, 121.4 MHz) and Mercury 400 ($^1$H, 400 MHz; $^1$H−$^1$H NOESY) spectrometers, referenced to $SiMe_4$ ($^1$H, $^{13}$C) and $H_3PO_4$ ($^{31}$P). $\delta$ 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 and at the Servei d'Espectrometria de Masses (Universitat de Barcelona) using an LC/MSD-TOF spectrometer and 1/1 $H_2O/CH_3CN$ to introduce the sample. The labeling scheme for selected compounds is given in Figure 8.

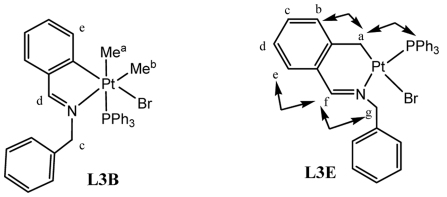


**Figure 8.** Labeling scheme for selected compounds. The arrows indicate the most relevant NOE interactions.

**X-ray Diffraction.** X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo K$\alpha$ ($\lambda$ = 0.71073 Å)) at 125 K. Crystals were 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 SHELXTL (version 6.14).[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. See Figures 2−7 and their captions for ORTEP drawings, labels, bond lengths, and bond angles. CIFs for all six structures are included in the Supporting Information.

**Preparation of the Compounds.** The platinum dimer *cis*-$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, ligands **L1**−**L4**, and compounds **L2A** and **L3A** were prepared as reported elsewhere.[8e,15,21,22]

*$PtMe_2Cl\{C_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)\}SMe_2$]* ***(L1A)***. A 50 mg portion (0.087 mmol) of **1** and 44 mg (0.17 mmol) of **L1** were combined in acetone (15 mL), and the mixture was stirred at room temperature for 16 h. The solution was filtered and the solvent evaporated to afford an oil which was triturated with pentane to afford a reddish powder. Yield: 84 mg (87%).

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 0.96 (s, $^2J$(H−Pt) = 69.6, 3H, $CH_3$); 1.26 (s, $^2J$(H−Pt) = 67.2, 3H, $CH_3$); 1.93 (s, $^3J$(H−Pt) = 12, 6H, $SMe_2$); {5.18 (d, $^2J$(H−H) = 15.0), 5.25 (d, $^2J$(H−H) = 15.0), *AB* system, 2H, $CH_2$}; 7.10 (t, $J$(H−H) = 9.2, 1H); 7.20−7.42 (m, 7H); 8.20 (s, $^3J$(H−Pt) = 45.6, 1H, CH═N). $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ 171.86 ($J$(C−Pt) = 54, CHN); 143.86 ($J$(C−Pt) = 970, $C^{metalated}$); 132.52 ($J$(C−Pt) = 65); 131.52 (2C); 129.86 ($J$(C−Pt) = 33); 129.07 (2C); 124.35 ($J$(C−Pt) = 7); 59.23 ($CH_2$); 18.43 ($SCH_3$); 1.52 ($J$(C−Pt) = 620, $PtCH_3$); −3.53 ($J$(C−Pt) = 662, $PtCH_3$). Anal. Calcd for $C_{18}H_{23}Cl_2NPtS$: C, 39.21; H, 4.20; N, 2.54. Found: C, 39.61; H, 3.72; N, 3.26. HR-ESI-(+)-MS: $m/z$ 499.0565; calcd for $C_{17}H_{19}ClNPtS$, $[M - Cl - CH_3 - H]^+$ 499.0575. Mp (°C): 73−77.

*$[PtMe_2Cl\{C_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)\}PPh_3]$* ***(L1B)***. An 83 mg amount (0.15 mmol) of **L1A** and 39 mg (0.15 mmol) of $PPh_3$ were combined in acetone, and the mixture was stirred at room temperature for 30 min. The solution was filtered and the solvent evaporated to afford an oil which was triturated with pentane to afford a gray-green powder. Yield: 64%. Crystals were obtained by recrystallization from dichloromethane/methanol.

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 0.88 (d, $^3J$(H−P) = 8.0, $^2J$(H−Pt) = 58.4, 3H, $CH_3$); 1.41 (d, $^3J$(H−P) = 8.0; $^2J$(H−Pt) = 68.8, 3H, $CH_3$); {4.51 (d, $^2J$(H−H) = 17.8), 5.23 (d, $^2J$(H−H) = 17.8), *AB* system, 2H, $CH_2$}; 6.61 (d, $J$(H−H) = 7.6, 1H); 6.76 (t, $J$(H−H) = 7.6, 1H); 6.84 (d, $J$(H−H) = 8.4, 2H); 6.92 (t, $J$(H−H) = 7.2, 1H); 7.10 (d, $J$(H−H) = 7.6, 1H); 7.28−7.37 (m, 11H); 7.46 (t, $J$(H−H) = 9.2, 6H); 7.69 (s, $^3J$(H−Pt) = 48.4, 1H, CH═N). $^{31}$P NMR ($CDCl_3$, 161.8 MHz): $\delta$ −4.04 (s, $^1J$(P−Pt) = 999.8). Anal. Calcd for $C_{34}H_{32}Cl_2NPPt$: C, 54.33; H, 4.29; N, 1.86. Found: C, 53.54; H, 3.31; N, 1.96. Mp (°C): 112−116 dec.

*$[PtCl\{2\text{-}MeC_6H_3CH{=}NCH_2(4\text{-}ClC_6H_4)\}PPh_3]$* ***(L1D)***. A 12 mg amount (0.022 mmol) of **L1F** and 6 mg (0.022 mmol) of $PPh_3$ were combined in acetone (10 mL), and the mixture was stirred at room temperature for 30 min. The solvent was evaporated and the brownish yellow solid washed with pentane and vacuum-dried. Yield: 9.1 mg (55%).

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.39 (s, 3H, $CH_3$); 5.37 (s, 2H, $CH_2$); 6.43 (t, $J$(H−H) = 7.6, 1H); 6.62 d, $J$(H−H) = 7.2, 1H); 7.31−7.41 (m, 14H); 7.70−7.76 (m, 6H); 8.53 (d, $^4J$(H−P) = 9.2, $^3J$(H−Pt) = 96, 1H, CH═N). $^{31}$P NMR (161.8 MHz, $CDCl_3$): $\delta$ 23.11 (s, $^1J$(P−Pt) = 4189). Anal. Calcd for $C_{33}H_{28}Cl_2NPPt$: C, 53.89; H, 3.84; N, 1.90. Found: C, 54.46; H, 3.80; N, 1.99. HR-ESI-(+)-MS: $m/z$ 699.1289; calculated for $C_{33}H_{28}ClNPPt$, $[M - Cl]^+$ 699.1296. Mp (°C): 164−168 dec.

*$[PtCl\{CH_2C_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)\}PPh_3]$* ***(L1E)***. Compound **L1B** was dissolved in toluene (10 mL), and the solution was refluxed for 4 h. The solvent was evaporated, and the residue was washed with pentane and cold diethyl ether to afford a yellow solid. The initial $^1$H NMR spectrum showed the presence of both **L1D** and **L1E** in an approximate 1/3 ratio. Crystals of **LIE** were obtained by recrystallization from acetone/hexane.

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.34 (d, $^3J$(H−P) =3.2, $^2J$(H−Pt) = 78.4, 2H, $CH_2Pt$), 5.60 (s, 2H, $CH_2$); 6.26 (m, 1H); 7.05 (m, 2H); 7.14 (m, 1H); 7.36−7.40 (m, 9H); {7.50 (d, $J$(H−H) = 8.4), 7.66 (d, $J$(H−H) = 8.4), *AB* system, 4H}; 7.71−7.75 (m, 6H); 8.14 (d, $^4J$(H−P) = 12.8, $^3J$(H−Pt) = 52, 1H, CH═N). $^{31}$P NMR (161.8 MHz, $CDCl_3$): $\delta$ 17.36 (s, $^1J$(P−Pt) = 4470.3). HR-ESI-(+)-MS: $m/z$ 699.1292; calcd for $C_{33}H_{28}ClNPPt$, $[M - Cl]^+$ 699.1296.

*$[PtCl\{2\text{-}MeC_6H_3CH{=}NCH_2(4\text{-}ClC_6H_4)\}SMe_2]$* ***(L1F)***. A 100 mg portion (0.17 mmol) of **1** and 92 mg (0.35 mmol) of **L1** were combined in toluene (15 mL), and the mixture was refluxed for 4 h. The solvent was evaporated, and the residue was washed with pentane and vacuum-dried to afford an orange solid. Yield: 134 mg (72%). Alternatively, compound **L1F** could be obtained by refluxing **L1A** (46 mg) in toluene for 4 h. Yield: 24 mg (49%).

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.41 (s, 3H, $CH_3$); 2.68 (s, $^3J$(H−Pt) = 52.8, 6H, $SMe_2$); 5.27 (s, 2H, $CH_2$); 6.81 (d, $J$(H−H) = 7.6, 1H); 7.01 (t, $J$(H−H) = 8, 1H); 7.16−7.40 (m, 5H); 8.29 (s, $^3J$(H−Pt) = 124.8, 1H, CH═N). $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ 176.62 (CHN); 133.06; 130.18 (2C); 128.97 (2C); 128.13; 125.83; 60.91 ($CH_2$); 22.93 ($J$(C−Pt) = 12, $SCH_3$); 19.69 ($CH_3$). HR-ESI-(+)-MS: $m/z$ 499.0564; calcd for $C_{17}H_{19}ClNPtS$, $[M - Cl]^+$ 499.0574. Anal. Calcd for $C_{17}H_{19}Cl_2NPtS$: C, 38.14; H, 3.58; N, 2.62, Found: C, 38.82; H, 3.21; N, 2.77. Mp (°C): 84−89 dec.

*$[PtMe_2Br\{C_6H_4CH{=}NCH_2(C_6H_5)\}SMe_2]$* ***(L2A)***. A 100 mg portion (0.17 mmol) of **1** and 96 mg (0.35 mmol) of **L2** were combined in acetone, and the mixture was stirred at room temperature for 16 h. The solution was filtered and the solvent evaporated to afford a yellow oil. Yield: 195 mg (75%). The NMR spectra were identical with those obtained for **L3A** and that previously reported.[22]

*$[PtBr\{2\text{-}MeC_6H_3CH{=}NCH_2(C_6H_5)\}PPh_3]$* ***(L2D)***. A 62 mg portion (0.11 mmol) of **L2F** and 30 mg (0.11 mmol) of $PPh_3$ were dissolved in acetone (12 mL), and the mixture was stirred at room temperature for 30 min. The solvent was evaporated and the residue washed with pentane and vacuum-dried to afford a brown solid. Yield: 63 mg (74%). The NMR spectra were identical with those obtained for **L3D**; see below.

*$[PtBr\{2\text{-}MeC_6H_3CH{=}NCH_2(C_6H_5)\}SMe_2]$* ***(L2F)***. A 100 mg portion (0.17 mmol) of **1** and 96 mg (0.35 mmol) of **L2** were dissolved in toluene (20 mL), and the solution was refluxed for 4 h. The solvent


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was evaporated and the residue washed with pentane and cold diethyl ether and vacuum-dried to afford a brown solid. Yield: 137 mg (72%). Alternatively, compound **L2F** could be obtained by refluxing **L2A** in toluene for 4 h. Yield: 90 mg (48%). The NMR spectrum was identical with that obtained for **L3F**; see below.

*[PtMe$_2$Br{C$_6$H$_4$CH$_2$N=CHC$_6$H$_5$}PPh$_3$] (**L3B**).* This compound was obtained from 95 mg (0.35 mmol) of imine 2-BrC$_6$H$_4$CH$_2$N=CHC$_6$H$_5$ and 100 mg (0.17 mmol) of *cis*-[Pt$_2$Me$_4$($\mu$-SMe$_2$)$_2$] in 20 mL of acetone. The mixture was stirred at room temperature for 16 h. **L3A** was formed and characterized as reported.[22] After this time, 90 mg (0.34 mmol) of PPh$_3$ was added and the mixture was stirred for 2 h at room temperature. The solvent was removed, and the residue was recrystallized in CH$_2$Cl$_2$/MeOH. Yield: 140 mg (53%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.67 (d, $^4J$(H−P) = 4.0, $^3J$(H−Pt) = 52.0, 1H, H$^d$); 7.47−7.42 (m, 6H); 7.35−7.30 (m, 6H); 7.24−7.22 (m, 6H); 7.10 (dd, $^3J$(H−H) = 8.0; $^4J$(H−H) = 2.0, 1H); 6.93 (t, $^3J$(H−H) = 7.0, 1H); 6.90 (m, 2H); 6.79 (td, $^3J$(H−H) = 7.0; $^4J$(H−H) = 2.0, 1H); 6.58 (d, $^3J$(H−H) = 8.0, $^3J$(H−Pt) = 44.0, 1H, H$^e$); {5.37 (dd, $^2J$(H−H) = 16.0; $^3J$(H−H) = 4.0); 4.60 (dd, $^2J$(H−H) = 16.0; $^3J$(H−H) = 4.0), *AB* system, 2H, H$^c$}; 1.49 (d, $^3J$(H−P) = 8.0, $^2J$(H−Pt) = 72.0, 3H, Me$^b$); 1.04 (d, $^3J$(H−P) = 8.0, $^2J$(H−Pt) = 60.0, 3H, Me$^a$). $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta$ 170.59 (CHN); 141.90; 135.97; 134.07 (d, $J$(C−P) = 13, C$^{ortho}$ PPh$_3$); 132.18; 131.00; 130.61; 130.41; 129.82 (C$^{para}$ PPh$_3$); 129.02; 128.86; 128.41; 128.07; 127.95 (d, $J$(C−P) = 6, C$^{meta}$ PPh$_3$); 123.20 ; 59.90 (CH$_2$); 10.35 (PtCH$_3$); −4.94 (PtCH$_3$). $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta$ −5.80 (s, $^1J$(P−Pt) = 1005.2). HR-ESI-(+)-MS: $m/z$ 681.1993, calcd for C$_{34}$H$_{33}$NPPt, [M − Br]$^+$ 681.1998. Anal. Calcd for C$_{34}$H$_{33}$BrNPPt: C, 53.62; H, 4.37; N, 1.84. Found: C, 53.93; H, 3.72; N, 2.01. Mp (°C): 91−95 dec.

*[PtBr{2-MeC$_6$H$_3$CH=NCH$_2$(C$_6$H$_5$)}PPh$_3$] (**L3D**).* A 15 mg portion of (0.028 mmol) of **L3F** and 10 mg (0.028 mmol) of PPh$_3$ were combined in acetone (10 mL), and the mixture was stirred at room temperature for 30 min. The solvent was evaporated and the residue washed with pentane to afford a yellow solid. Recrystallization from acetone/hexane gave single crystals, which were studied by XRD and, when redissolved, were shown to be identical with compound **L2D** by NMR characterization.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.32 (s, 3H, CH$_3$); 5.56 (s, 2H, CH$_2$); 6.41 (t, $J$(H−H) = 8, 1H); 6.58 (d, $J$(H−H) = 8, 1H); 7.34−7.44 (m, 12H); 7.53−7.57 (m, 3H); 7.70−7.75 (m, 6H); 8.44 (d, $^4J$(H−P) = 9.2; $^3J$(H−Pt) = 95.2, 1H, CH=N). $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta$ 175.83 (CHN); 137.68; 135.48 (d, $J$(C−P) =11, C$^{ortho}$ PPh$_3$); 132.12; 130.06 (br, C$^{para}$ PPh$_3$); 129.40 (2C); 128.74 (2C); 127.80 (d, $J$(C−P) = 13, C$^{meta}$ PPh$_3$); 124.96; 122.99; 62.55 (CH$_2$); 20.11 (CH$_3$). $^{31}$P NMR (161.8 MHz, CDCl$_3$): $\delta$ 22.87 (s, $^1J$(P−Pt) =4153). HR-ESI-(+)-MS: $m/z$ 665.1667, calcd for C$_{33}$H$_{29}$NPPt, [M − Br]$^+$ 665.1685. Anal. Calcd for C$_{33}$H$_{29}$BrNPPt·0.5C$_5$H$_{12}$: C, 54.55; H, 4.51; N, 1.79. Found: C, 54.19; H, 4.57; N, 1.83. Mp (°C): 95−100.

*[PtBr{CH$_2$C$_6$H$_4$CH=NCH$_2$(C$_6$H$_5$)}PPh$_3$] (**L3E**).* This compound was obtained from 50 mg of [PtMe$_2$Br{C$_6$H$_4$CH$_2$N=CHC$_6$H$_5$}PPh$_3$] (**L3B**) in 20 mL of toluene. The solution was refluxed for 4 h, the solvent was removed in a rotary evaporator, and $^1$H and $^{31}$P NMR spectra of the residue indicated the presence of equimolar amounts of the expected compound **L3E** and *trans*-[PtMeBr(PPh$_3$)$_2$]. Recrystallization in CH$_2$Cl$_2$/MeOH yielded 25 mg (51%) of the yellow solid **L3E**. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.10 (d, $^4J$(H−P) = 16.0, $^3J$(H−Pt) = 60.0, 1H, H$^f$); 7.72 (dd, $^3J$(H−H) = 8.0, $^4J$(H−H) = 4.0, 2H); 7.60−7.53 (m, 6H, PPh$_3$); 7.45−7.30 (m, 12H); 7.20 (m, 1H, H$^e$); 7.03 (m, 2H, H$^{c,d}$); 6.17 (m, 1H); 5.71 (d, $^4J$(H−P) = 4.0, 2H, H$^g$); 2.37 (d, $^4J$(H−P) = 4.0, $^2J$(H−Pt) = 80.0, 2H, H$^a$). NOESY cross peaks: H$^a$, H$^b$; H$^a$, Ar$^{PPh3}$; H$^f$, H$^g$; H$^e$, H$^f$. $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta$ −17.92 (s, $^1J$(P−Pt) = 4476.0). $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta$ 162.89 (CHN); 137.29; 134.78 (d, $J$(C−P) =10, C$^{ortho}$ PPh$_3$); 132.28; 130.75; 130.27 (d, $J$(C−P) = 2, C$^{para}$ PPh$_3$); 129.99 (2C); 128.58 (2C); 127.79 (d, $J$(C−P) = 13, C$^{meta}$ PPh$_3$); 126.76; 124.11; 67.00 (CH$_2$); 14.64 (PtCH$_2$). HR-ESI-(+)-MS: $m/z$ 665.1673, calcd for C$_{33}$H$_{29}$NPPt, [M − Br]$^+$ 665.1685. Anal. Calcd for C$_{33}$H$_{29}$BrNPPt: C, 53.16; H, 3.92; N, 1.88. Found: C, 53.73; H, 3.85; N, 1.81. Mp (°C): 71−76.

*[PtBr{2-MeC$_6$H$_3$CH=NCH$_2$(C$_6$H$_5$)}SMe$_2$] (**L3F**).* A 50 mg portion (0.087 mmol) of **1** and 48 mg (0.17 mmol) of **L3** were combined in toluene (15 mL), and the mixture was refluxed for 4 h. The solvent was evaporated and the residue was washed with pentane and vacuum-dried to afford a brown solid. Yield: 87 mg (90%). Alternatively, compound **L3F** can be obtained by refluxing compound **L3A** in toluene (15 mL) for 4 h. Yield: 92 mg (49%).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.37 (s, 3H, CH$_3$); 2.76 (s, $^3J$(H−Pt) = 51.6, 6H, SMe$_2$); 5.47 (s, 2H, CH$_2$); 6.82 (d, $J$(H−H) = 7.6, 1H); 7.09 (t, $J$(H−H)= 7.6); 7.34−7.43 (m, 6H); 8.26 (s, $^3J$(H−Pt) = 126.0, 1H, CH=N). $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta$ 176,43 ($J$(C−Pt) = 102, CHN); 132.85; 129.04 (2C); 128.83 (2C); 127.91; 127.51; 125.95; 63.54 ($J$(C−Pt) = 45, CH$_2$); 24.06 ($J$(C−Pt) = 16, SCH$_3$); 19.83 (CH$_3$). HR-ESI-(+)-MS: $m/z$ 465.0951, calcd for C$_{17}$H$_{20}$NPtS, [M − Br]$^+$ 465.0964. Anal. Calcd for C$_{17}$H$_{20}$BrNPtS·0.4C$_5$H$_{12}$: C, 39.74; H, 4.35; N, 2.44. Found: C, 40.12; H, 3.52; N, 2.72. Mp (°C): 78−83 dec.

*[PtMe$_2$Br{2,4,6-(CH$_3$)$_3$C$_6$H$_2$CH=NCH$_2$(C$_6$H$_4$)}SMe$_2$] (**L4A**).* A 50 mg portion (0.087 mmol) of **1** and 55 mg (0.17 mmol) of **L4** were combined in acetone, and the mixture was stirred at room temperature for 16 h. The solution was filtered and the solvent evaporated to afford a whitish- green powder. Yield: 43 mg (39%).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 0.75 (s, $^2J$(H−Pt) = 73.6, 3H, Me); 1.38 (s, $^2J$(H−Pt) = 71.2, 3H, Me); 2.12 (s, 3H, Me); 2.31 (m, 6H, Me); 2.43 (s, $^3J$(H−Pt) = 78, 6H, SMe$_2$); {4.83 (d, $^2J$(H−H) = 10.4), 6.00 (d, $^2J$(H−H) = 10.4), 2H, CH$_2$}; 6.83 (s, 1H); 6.91 (s, 1H); 7.02−7.17 (m, 3H); 9.08 (s, $^3J$(H−Pt) = 29.6, 1H, CH=N). $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta$ 168.55 (CHN); 130.54; 128.35; 127.64; 126.71 ($J$(C−Pt) = 65); 124.70; 122.06 ($J$(C−Pt) = 30); 73.27 (CH$_2$ $J$(C−Pt) = 13); 22.35 (CH$_3$); 21.11 (SCH$_3$); 20.24 (CH$_3$); 17.49 (CH$_3$); −0.41 (PtCH$_3$); −0.73 (PtCH$_3$). Anal. Calcd for C$_{21}$H$_{30}$BrNPtS: C, 41.79; H, 5.01; N, 2.32. Found: C, 40.67; H, 4.06; N, 2.44. Mp (°C): 68−74 dec.

*[PtBr{CH$_2$-2,4-(CH$_3$)$_2$C$_6$H$_2$CH=NCH$_2$(2-CH$_3$C$_6$H$_4$)}PPh$_3$] (**L4E**).* A 20 mg portion (0.034 mmol) of **L4F** and 9 mg (0.034 mmol) of PPh$_3$ were dissolved in acetone (10 mL), and the mixture was stirred at room temperature for 30 min. The solvent was evaporated, and the residue was washed with pentane and vacuum-dried to afford a gray solid. Yield: 11.5 mg (44%).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.04 (s, 3H, Me); 2.17 (s, 3H, Me); 2.31 (d, $^4J$(H−P) = 4.8, $^3J$(H−Pt) = 82, 2H, CH$_2$Pt); 2.47 (s, 3H, CH$_3$); 5.68 (d, $^4J$(H−P) = 8.4, 2H, CH$_2$); 6.60 (s, 1H); 7.26−7.42 (m, 13H); 7.55−7.59 (m, 6H); 7.72 (d, $^3J$(H−H) = 7.6, 1H); 8.07 (d, $^4J$(H−P) = 13.2, $^3J$(H−Pt) = 61.6, 1H, CH=N). $^{31}$P NMR (161.8 MHz, CDCl$_3$): $\delta$ 18.48 (s, $^1J$(P−Pt) = 4147.7). HR-ESI-(+)-MS: $m/z$ 707.2145; calcd for C$_{36}$H$_{35}$NPPt, [M − Br]$^+$ 707.2155. Anal. Calcd for C$_{36}$H$_{35}$BrNPPt: C, 54.90; H, 4.48; N, 1.78. Found: C, 54.45; H, 3.78; N, 1.68. Mp (°C): 95−100 dec.

*[PtBr{CH$_2$-2,4-(CH$_3$)$_2$C$_6$H$_2$CH=NCH$_2$(2-CH$_3$C$_6$H$_4$)}SMe$_2$] (**L4G**).* A 70 mg portion (0.12 mmol) of **1** and 78 mg (0.25 mmol) of **L4** were dissolved in toluene (15 mL), and the mixture was refluxed for 4 h. The solution was evaporated and the residue washed with pentane and cold diethyl ether to afford a grayish brown solid. Yield: 80 mg (55%). Alternatively, compound **L4F** can be obtained by refluxing **L4A** in toluene for 4 h. Yield: 43 mg (40%).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.05 (s, 3H, CH$_3$); 2.21 (s, 3H, CH$_3$); 2.41 (s, 3H, CH$_3$); 2.53 (s, $^3J$(H−Pt) = 52.0, 6H, SMe$_2$); 2.87 (s, $^2J$(H−Pt) = 92.4, 2H, CH$_2$Pt); 5.57 (s, 2H, CH$_2$); 6.65 (s, 1H); 6.83 (s, 1H); 7.21−7.25 (m, 3H); 7.44 (d, $^3J$(H−H) = 7.2, 1H); 7.78 (s, $^3J$(H−Pt) = 87.6, 1H, CH=N). $^{13}$C NMR (CDCl$_3$, 100.6 MHz): $\delta$ 160.23 (CHN); 130.93; 130.67; 128.93; 126.34; 65.88 (CH$_2$); 23.89 (SCH$_3$); 21.57 (CH$_3$); 19.58 (CH$_3$); 18.64 (CH$_3$); 11.97 (CH$_2$Pt). HR-ESI-(+)-MS: $m/z$ 507.1421; calce for C$_{20}$H$_{26}$NPtS, [M − Br]$^+$ 507.1434. Anal. Calcd for C$_{20}$H$_{26}$BrNPtS: C, 40.89; H, 4.46; N, 2.38. Found: C, 41.71; H, 3.59; N, 2.88. Mp (°C): 105−110 dec.


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## ■ ASSOCIATED CONTENT

### Supporting Information

CIFs giving crystallographic data for the six complexes characterized by XRD. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


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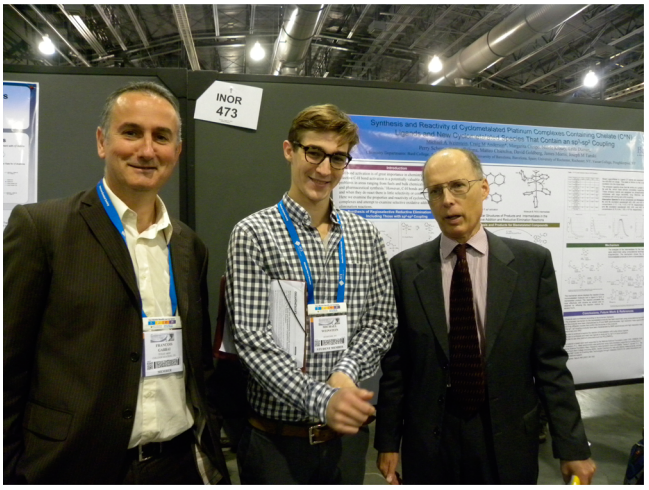
### Notes

The authors declare no competing financial interest.

### Biographies




Poster presentation of Michael Weinstein (center, Bard College), with François P. Gabbaï (left) and John A. Gladysz (right)

This article is based upon a poster presented by Michael Weinstein and coauthored by Craig M. Anderson, Margarita Crespo, Nicole Kfoury, and Joseph M. Tanski at the first Organometallics Symposium at the ACS meeting in Philadelphia, PA, on August 21, 2012. Michael Weinstein will receive his B.A. from Bard College this year. He is currently working under the direction of Craig Anderson, the corresponding author of this manuscript. Michael Weinstein's research interests encompass the synthesis of cyclometalated organoplatinum complexes by C−H activation and the study of their photophysical properties. After his undergraduate degree is complete, Mike will attend Tufts University to obtain an M.S. in biomedical engineering. After obtaining his graduate degree, he plans to open up his own engineering concern in the greater New York area.

Craig Anderson published his first paper in *Organometallics* in 1987 when he was an undergraduate student with Dick Puddephatt at UWO in London, ON, Canada. At Western University Craig met Margarita Crespo. They share a common interest in organoplatinum chemistry and have been working together for many years. Michael Weinstein represents the 44th undergraduate student he has mentored over a 12-year academic career at Bard College (an undergraduate college with no graduate program, but a strong undergraduate research program in chemistry). Professor Anderson is the Wallace Benjamin Flint and L. May Hawver Professor of Chemistry at Bard College and is currently a Henry Dreyfus Teacher-Scholar, which was awarded for his research with undergraduates at Bard College.

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