Reductive Elimination from Cyclometalated Platinum(IV) Complexes To Form $C_{sp}^{2}-C_{sp}^{3}$ Bonds and Subsequent Competition between $C_{sp}^{2}-H$ and $C_{sp}^{3}-H$ Bond Activation

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Abstract

Reductive elimination reactions of the cyclometalated platinum(IV) compounds [PtMe$_2$Br{C$_6$H$_4$CH=NCH$_2$(4-ClC$_6$H$_4$)}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. Reductive elimination to form a C−Br bond is also reported.
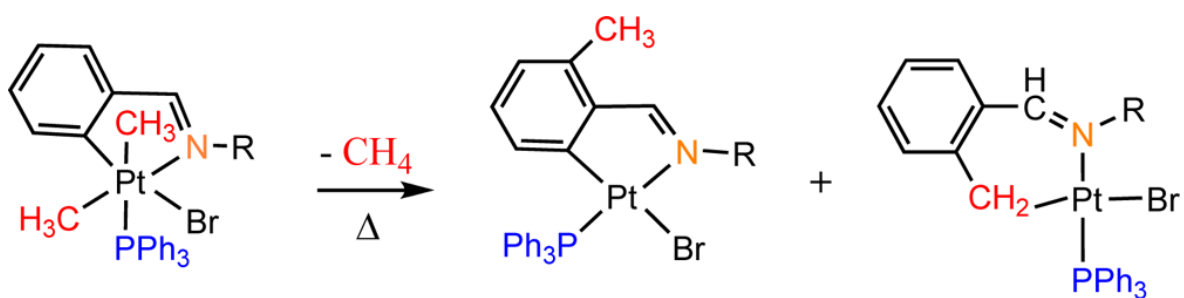
The reductive elimination reaction is often the productforming step in both catalytic cycles and stoichiometric transformations leading to formation of C−C, C−H, or C−X bonds. Much attention has been paid recently to reductive elimination from d^6 octahedral complexes, in particular those containing Pt(IV). These compounds readily undergo reductive elimination, often with initial loss of a ligand to generate a fivecoordinate intermediate. Most reported studies are concerned with reductive $C_{sp}{}^3$−$C_{sp}{}^3$ elimination leading to ethane either from trimethylplatinum(IV)[1] or tetramethylplatinum(IV)[2] compounds. Competition between C−C bond formation and C−O,[3] C−N,[4] and C−I[5] bond formation has also been studied for trimethylplatinum(IV) compounds containing O-donor, Ndonor, or halo ligands. Reductive elimination of methane from platinum(IV) compounds containing both methyl and hydrido ligands[6] has also been addressed. Analogous reductive elimination studies have been carried out for arylplatinum(IV) compounds, including $C_{sp}{}^2$−H bond formation[7] and competition between $C_{sp}{}^2$−$C_{sp}{}^2$ and $C_{sp}{}^2$−halide bond formation.[8] Moreover, $C_{sp}{}^2$−$C_{sp}{}^2$ coupling from cyclometalated platinum-(IV) compounds leading to five-, six-, or seven-membered platinacycles containing a biaryl linkage has also been reported.[9] Examples of $C_{sp}{}^2$−$C_{sp}{}^3$ reductive elimination are scarce.[10] However, 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.[11]

Intramolecular oxidative addition of C−X bonds (X = Br, Cl, F) of appropriately designed nitrogen ligands to [Pt₂Me₄(μ-SMe₂)₂] gives terdentate [C,N,N′] or bidentate [C,N] cyclometalated platinum(IV) compounds with the general formulas [PtMe₂X(C₆H₄CH=NCH₂CH₂NMe₂)] (I)[12] and [PtMe₂X(C₆H₄CH=NCH₂R)SMe₂] (II),[13] respectively (such as those shown in Chart 1).

These compounds display a *fac*-PtC₃ arrangement and are stable at room temperature both in solution and in the solid state. Although these compounds provide an opportunity to analyze the competition between different reductive elimination processes, such reactions have not yet been studied. In this communication we present preliminary results for the thermolysis reactions of platinum(IV) compounds containing the cyclometalated ligand 2-

73   BrC$_6$H$_4$CH=NCH$_2$(4-C$_6$H$_4$Cl). As shown in Scheme 1, these compounds could lead to

74   C$_{sp}^3$–C$_{sp}^3$ (path *a*), C$_{sp}^3$–Br (path *b*), C$_{sp}^3$–C$_{sp}^2$ (path *c*), or C$_{sp}^2$-Br (path *d*) reductive

75   elimination processes. In the two cases involving cleavage of the metallacycle (paths *c* and

76   *d*), subsequent cyclometalation at the available ortho position of the aryl ring (with reductive

77   elimination of methane) can be anticipated.[12,13]

78   The reactivity of the [C,N,N′] platinum(IV) compound

79   [PtMe$_2$Br(C$_6$H$_4$CH=NCH$_2$CH$_2$NMe$_2$)] (**1**)[12a] was initially tested. The compound was

80   recovered unaltered after refluxing in a toluene solution for 8 h. The lack of reactivity, under

81   these conditions, was taken as an indication that ligand dissociation to yield a five-coordinate

82   species, prior to the reductive elimination process, is required. Therefore, our next target was

83   the compound [PtMe$_2$Br{C$_6$H$_4$CH=NCH$_2$(4-ClC$_6$H$_4$)}-SMe$_2$] (**2**) containing the labile

84   SMe$_2$ ligand, which was prepared as a single isomer with a fac-PtC$_3$ arrangement, as

85   previously reported for analogous compounds.[13]

86   When a toluene solution of compound 2 was refluxed for 4 h, the cyclometalated

87   platinum(II) compound [PtBr{2-MeC$_6$H$_3$CH=NCH$_2$(4-ClC$_6$H$_4$)}SMe$_2$] (**3**) shown in

88   Scheme 1 was obtained as a single product. A one-pot procedure from a mixture of [Pt$_2$Me$_4$(

89   μ -SMe$_2$)$_2$] and the ligand 2-BrC$_6$H$_4$CH=NCH$_2$(4-C$_6$H$_4$Cl) gave the same result. In the ^{1}H

90   NMR spectrum, a single methyl resonance was observed at 2.42 ppm and showed NOESY

91   interactions with both the imine and aromatic protons. A displacement reaction of dimethyl

92   sulfide for triphenylphosphine produced the compound [PtBr{2-MeC$_6$H$_3$CH=NCH$_2$(4-

93   ClC$_6$H$_4$)}PPh$_3$] (**4**) (see Scheme 1), which was also characterized using one- and two-

94   dimensional NMR spectroscopic techniques.

95   These results indicate that, under the conditions tried, C$_{sp}^3$–C$_{sp}^2$ reductive

96   elimination is the most favored of the four possible processes (paths *a−d* indicated in Scheme

97   1). We speculate that the methyl reductively eliminates with the aryl ring but the ligand is

98   still tethered to the metal by the nitrogen atom. Therefore, the aryl ring would be in close

99   proximity to the metal and allow for a fast cyclometalation to occur, with subsequent loss of

100   methane, as described for analogous compounds.[12,13] This reaction sequence is analogous

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101 to that reported for biaryl formation (sp^2–sp^2 coupling) from cyclometalated platinum(IV)

102 compounds in which a final cyclometalation step occurs with release of an arene molecule.[9]

103   In order to explore this reaction type as a function of the stereoelectronic features of

104 the ancillary ligand, the thermal behavior of [PtMe$_2$Br{C$_6$H$_4$CH=NCH$_2$(4-ClC$_6$H$_4$)}PPh$_3$]

105 (**5**) in refluxing toluene solution was also studied. As shown in Scheme 2, compound **5** was

106 obtained from compound **2** in a substitution reaction of SMe$_2$ for PPh$_3$. Recrystallization of

107 the resulting crude product gave, in addition to compound **5**, orange crystals of compound

108 **6**, in a molar ratio of 3:1 for **5** and **6**. The NMR spectra of compound **5** indicate a *fac*-PtC$_3$

109 arrangement with the PPh$_3$ trans to a methyl ligand, as reported for analogous

110 compounds.[12,13]

111   [PtMe{2-BrC$_6$H$_3$CH=NCH$_2$(4-ClC$_6$H$_4$)}PPh$_3$] (**6**), formed as a byproduct in the

112 synthesis of compound **5**, was fully characterized, including single-crystal X-ray diffraction

113 analysis (Figure 1). The formation of this compound suggests that C_{sp^2}–Br reductive

114 elimination and subsequent cyclometallation take place along with the substitution

115 process.[14]

116   When a toluene solution of pure compound **5** was refluxed for 4 h, a mixture of

117 compounds **4** and **7** in the ratio 1:2.5 was obtained. Compounds **4** and **7** both arise from

118 C_{sp^3}–C_{sp^2} reductive elimination from the platinum(IV) compound **5**, which is followed by

119 subsequent cyclometalation and loss of methane. Competition between activation of either

120 a C_{sp^2}–H bond, leading to a five-membered platinacycle (compound **4**), or activation of a

121 C_{sp^3}–H bond in the methyl group previously reductively eliminated, leading to a novel six-

122 membered platinacycle (compound **7**), takes place in the cyclometallation process. White

123 crystals of compound **7** were obtained from the initial crude product. The compound was

124 fully characterized, including NMR spectroscopy and an X-ray diffraction study (Figure 2).

125   Formation of a six-membered platinacycle as a result of the activation of a C_{sp^3}–H

126 bond is remarkable, since (i) a strong tendency to form five-membered rings over six-

127 membered rings and (ii) a preference for the activation of sp^2 over sp^3 C–H bonds are

128 generally observed in cyclometalation reactions.[15] Few examples of platinacycles formed

129 through aliphatic C−H bond activation have been reported.[16] The results presented in this

130 communication have some noteworthy features. First, the activated methyl was the methyl

131 group initially bound to platinum that was transferred to the imine ligand through a reductive

132 elimination process. Second, C_{sp}^3−H bond activation was only observed when PPh$_3$ was

133 coordinated as the ancillary ligand to the platinum(IV) center, thus indicating that

134 stereoelectronic factors are decisive in the competition between aromatic and aliphatic C−H

135 bond activation. A recent example of a related process with formation of a six-membered

136 platinacycle also involves a platinum(IV) precursor containing a PPh$_3$ ligand.[17] Moreover,

137 it has been reported that the preference for aromatic versus aliphatic C−H bond activation in

138 the reactions of methylbenzenes with platinum(II) complexes can be overridden under

139 different conditions.[18]

140   In summary, our results show that reductive elimination from cyclometalated

141 platinum(IV) compounds **2** and **5** takes place selectively to produce exclusively C_{sp}^3−C_{sp}^2

142 coupling, which is followed by cyclometalation and subsequent loss of methane. The latter

143 metalation process produced C_{sp}^2−H bond activation for the compound containing a smaller

144 SMe$_2$ ligand (**2**) and competition between C_{sp}^3−H and C_{sp}^2−H bond activation for the

145 bulkier triphenylphosphine analogue (**5**). In addition, a C−Br reductive elimination process

146 followed by cyclometallation has also been observed. Further work is in progress with the

147 aim of exploring the scope and the mechanism of both the C_{sp}^3−C_{sp}^2 and C_{sp}^2−Br reductive

148 elimination processes as well as the factors governing the competition between aliphatic and

149 aromatic C−H bond activation.

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236 (14) Activation of a C−H bond upon reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with the imine 2-
237           $BrC_6H_4CH\text{=}NCH_2(4\text{-}C_6H_4Cl)$, followed by reaction with PPh_3, could also lead to
238   formation of compound 6. However, activation of a C−H bond was not observed in
239   the synthesis of compound 2, as confirmed by ^{1}H NMR spectra. Moreover, such a
240   process has not been observed previously for related ligands containing an o-
241   bromophenyl group.[12,13]

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248   M. Dalton Trans. 2010, 39, 6936. (f) Crespo, M.; Font-Bardia, M.; Calvet, T. Dalton

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258 **Figures Captions**

259 **Scheme 1**. Possible Reaction Paths from Cyclometalated Platinum(IV) Compound 2[a]

260 **Scheme 2**. Synthesis (Step a) and Thermolysis (Step b) of the Cyclometalated Platinum(IV)
261 Compound 5[a]

262 **Figure 1** Molecular structure of compound 6. Selected bond lengths (Å) and angles (deg)
263 with estimated standard deviations: Pt−C(1), 2.040(8); Pt−C(15), 2.074(8); Pt−N(1),
264 2.141(7); Pt−P(1), 2.313(2); N(1)−C(7), 1.286(11); N(1)−C(8), 1.486(11); C(1)−C(6),
265 1.378(12); C(6)−C(7), 1.427(12); C(1)−Pt−C(15), 92.5(3); C(1)−Pt−N(1), 78.4(3);
266 C(15)−Pt−N(1), 169.8(3); C(1)−Pt−P(1), 173.3(2); C(15)−Pt−P(1), 91.5(2); N(1)−Pt−P(1),
267 98.02(19).

268 **Figure 2**. Molecular structure of compound 7. Selected bond lengths (Å) and angles (deg)
269 with estimated standard deviations: Pt(1)−C(1), 2.059(3); Pt(1)−N(1), 2.114(3); Pt(1)−P(1),
270 2.2191(11); Pt(1)−Br(1), 2.5328(7); N(1)−C(8), 1.278(4); N(1)−C(9), 1.477(4); C(1)−C(2),
271 1.509(4); C(2)−C(7), 1.411(4); C(7)−C(8), 1.459(4); C(1)−Pt(1)−N(1), 84.38(12);
272 C(1)−Pt(1)−P(1), 88.65(9); N(1)−Pt(1)−P(1), 172.95(8); C(1)−Pt(1)−Br(1), 174.24(9);
273 N(1)−Pt(1)−Br(1), 90.41(8); P(1)−Pt(1)−Br(1), 96.60(3).
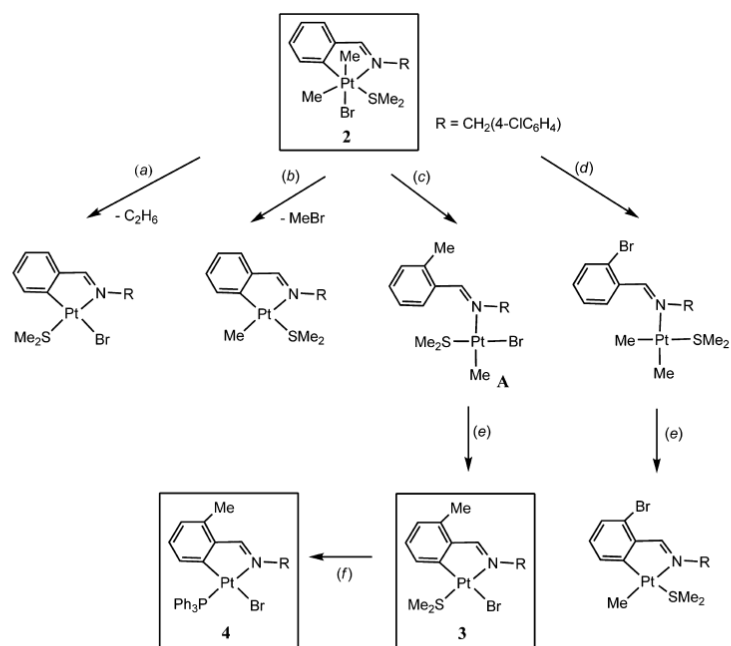
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275   **Chart 1.**
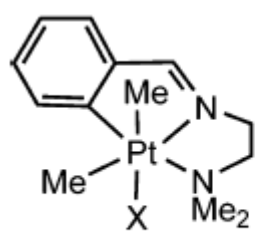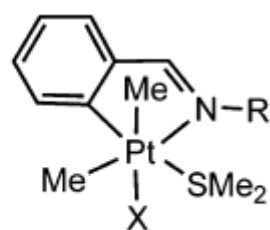
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279 **Scheme 1.**

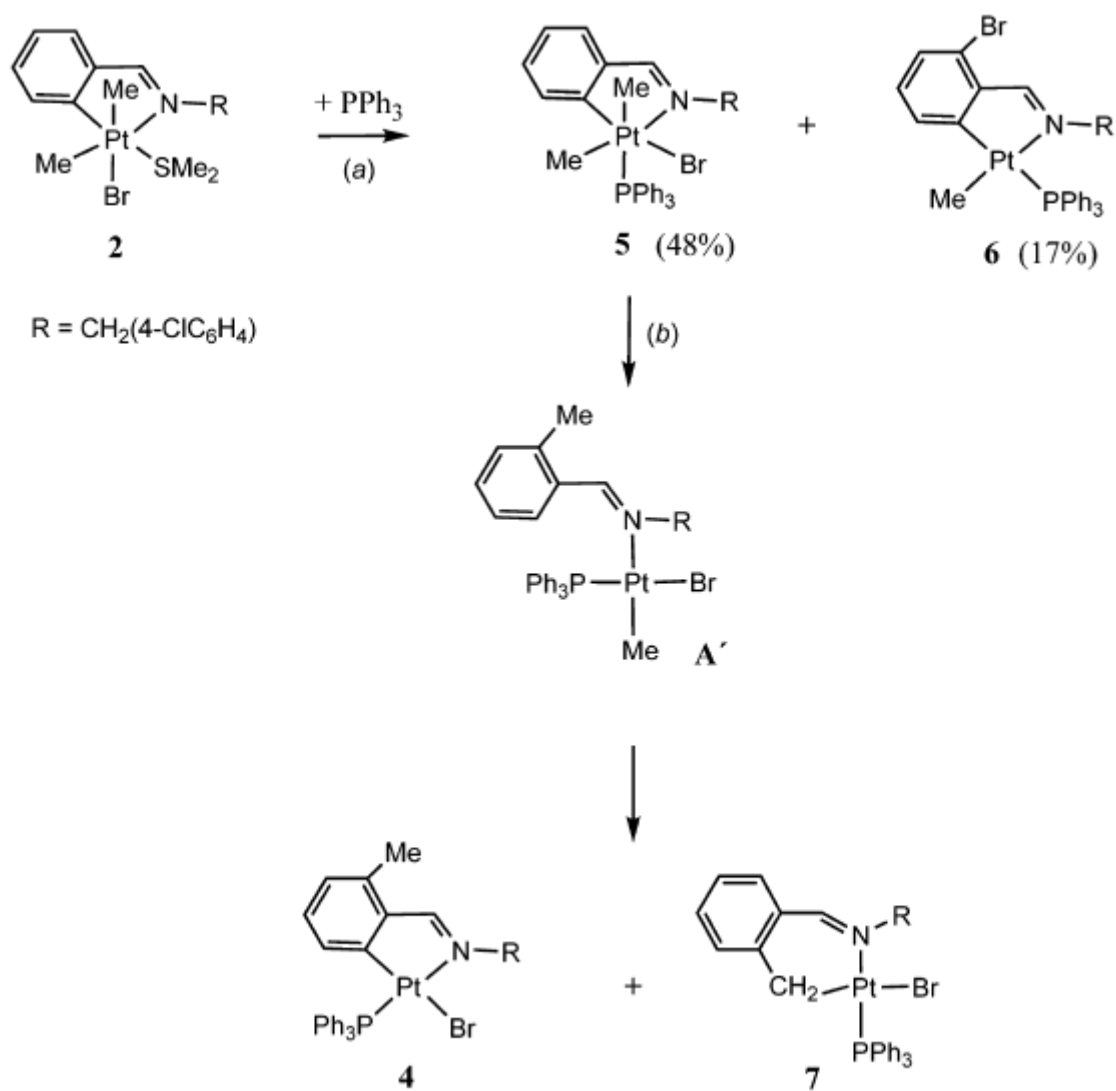280 ^{a}Isolated compounds are shown within a frame. Legend: (a−d) reductive elimination reactions from cyclometalated platinum(IV) complexes, C_{sp^3}−C_{sp^3} (a), C_{sp^3}−Br (b), C_{sp^3}−C_{sp^2} (c), C_{sp^2}−Br (d); (e) cyclometalation step with methane elimination; (f) substitution reaction of SMe$_2$ for PPh$_3$.

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283   **Scheme 2.**

R = CH$_2$(4-ClC$_6$H$_4$)

5 (48%)

6 (17%)

A′

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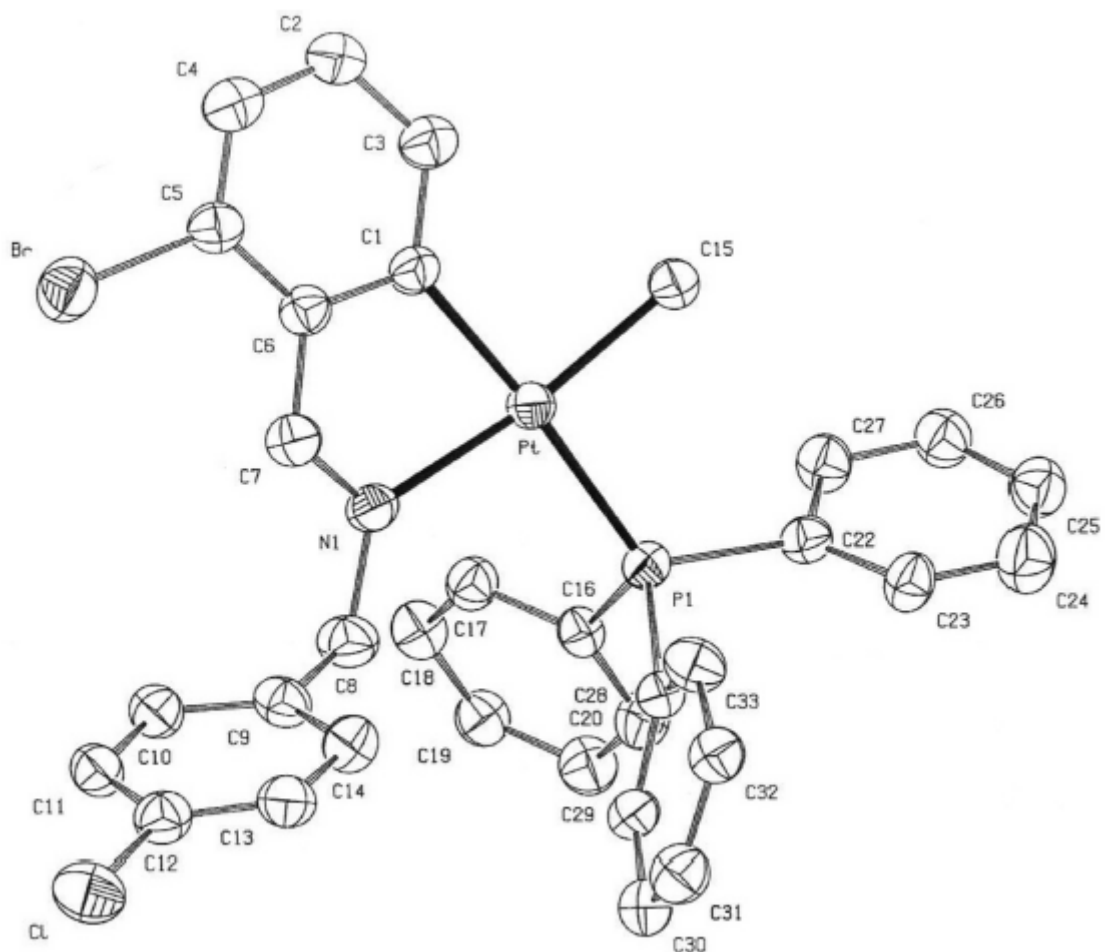^{a}Yields of compounds 5 and 6 (see text) are given in parentheses.

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287 **Figure 1**

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293   **Figure 2**

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