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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

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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*-$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and the naphthyl-derived C^N chelate ligands, (8-$XC_{10}H_6CH = N\text{-}R$), 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 $[PtMe_2Br\{C_{10}H_6CH = NCH_2(4\text{-}ClC_6H_4)\}L]$ 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

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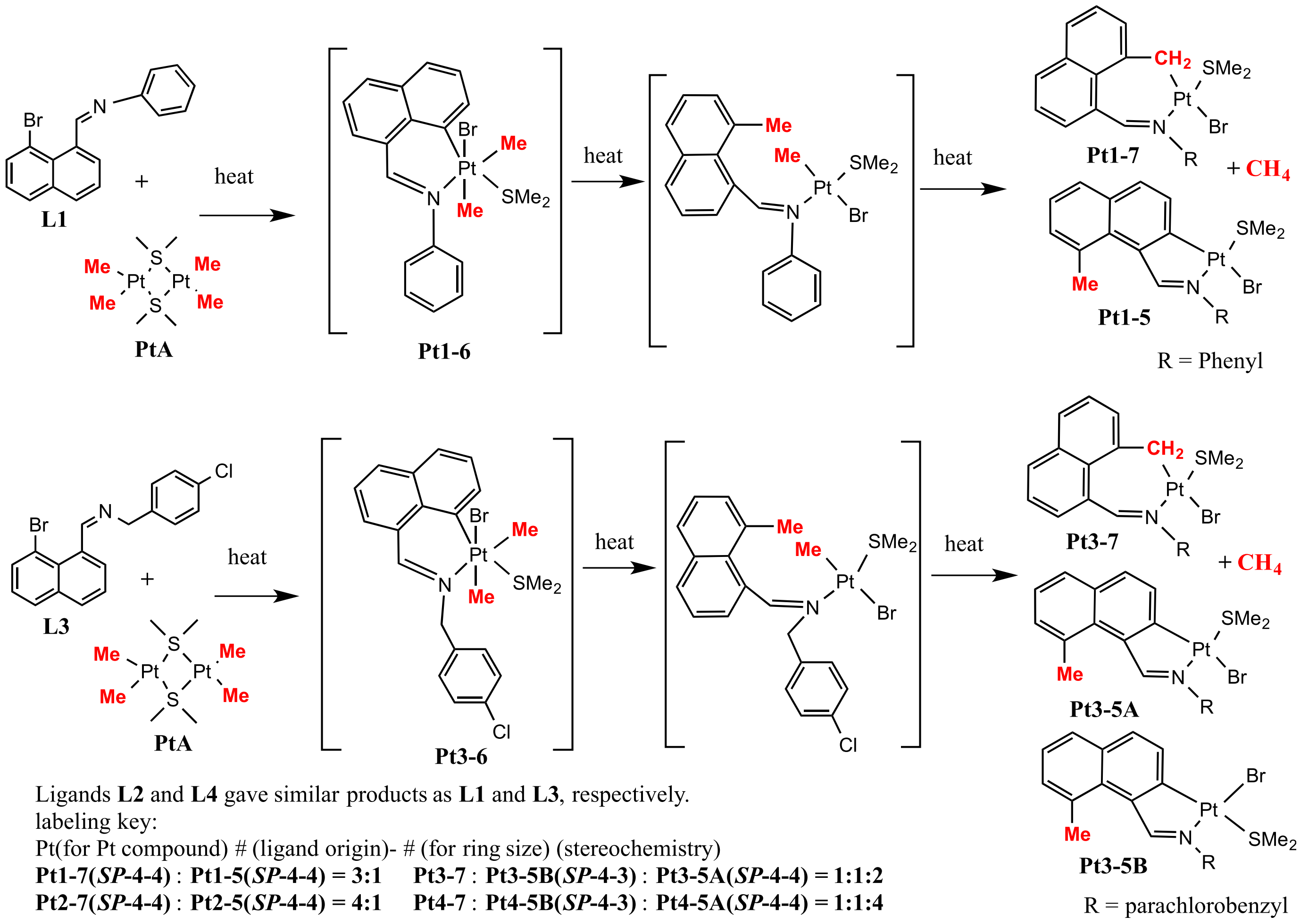

Ligands **L2** and **L4** gave similar products as **L1** and **L3**, respectively.
labeling key:
Pt(for Pt compound) # (ligand origin)- # (for ring size) (stereochemistry)
Pt1-7(*SP*-4-4) : Pt1-5(*SP*-4-4) = 3:1 Pt3-7 : Pt3-5B(*SP*-4-3) : Pt3-5A(*SP*-4-4) = 1:1:2
Pt2-7(*SP*-4-4) : Pt2-5(*SP*-4-4) = 4:1 Pt4-7 : Pt4-5B(*SP*-4-3) : Pt4-5A(*SP*-4-4) = 1:1:4

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-Br)CH═N(C_6H_5)}, **L1**, {$C_{10}H_6$(8-I)CH═N(C_6H_5)}, **L2**, {$C_{10}H_6$(8-Br)CH═NCH$_2$(4-ClC$_6$H$_4$)}, **L3**, {$C_{10}H_6$(8-I)CH═NCH$_2$(4-ClC$_6$H$_4$)}, **L4** were synthesized from condensation reactions between the appropriate aldehydes and amines. All were characterized by ^{1}H 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