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# 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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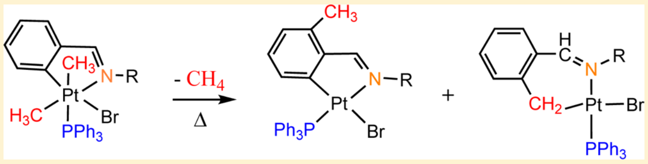
*Supporting Information*

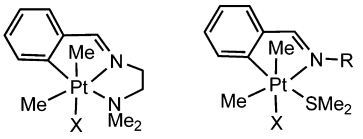
**ABSTRACT:** Reductive elimination reactions of the cyclometalated platinum(IV) compounds $[PtMe_2Br\{C_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)\}L]$ (L = $SMe_2$, $PPh_3$) to form $C_{sp^3}$–$C_{sp^2}$ bonds, followed by either exclusive $C_{sp^2}$–H bond activation (L = $SMe_2$) or competition between $C_{sp^2}$–H 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 product-forming 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 five-coordinate 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, N-donor, 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 $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ gives terdentate [C,N,N′] or bidentate [C,N] cyclometalated platinum(IV) compounds with the general formulas $[PtMe_2X(C_6H_4CH{=}NCH_2CH_2NMe_2)]$ (**I**)[12] and $[PtMe_2X(C_6H_4CH{=}NCH_2R)SMe_2]$ (**II**),[13] respectively (such as those shown in Chart 1).

**Chart 1**



**I** **II**

These compounds display a *fac*-$PtC_3$ 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 $2\text{-}BrC_6H_4CH{=}NCH_2(4\text{-}C_6H_4Cl)$. As shown in Scheme 1, these compounds could lead to $C_{sp^3}$–$C_{sp^3}$ (path *a*), $C_{sp^3}$–Br (path *b*), $C_{sp^3}$–$C_{sp^2}$ (path *c*), or $C_{sp^2}$-Br (path *d*) reductive elimination processes. In the two cases involving cleavage of the metallacycle (paths *c* and *d*), subsequent cyclometalation at the available ortho position of the aryl ring (with reductive elimination of methane) can be anticipated.[12,13]

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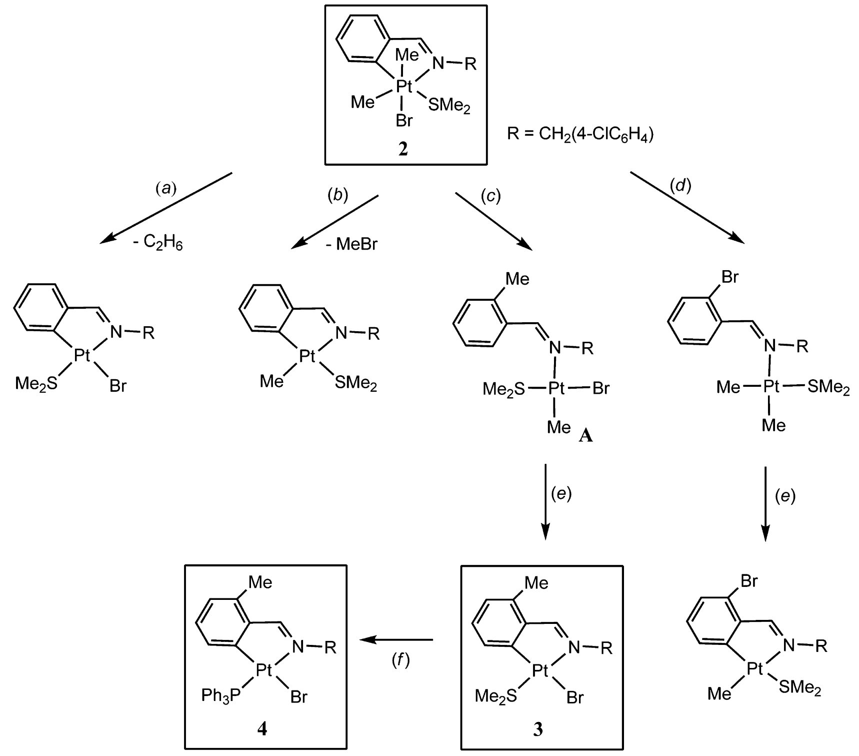
Scheme 1. Possible Reaction Paths from Cyclometalated Platinum(IV) Compound 2[a]



[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 $PPh_3$.

The reactivity of the [C,N,N′] platinum(IV) compound $[PtMe_2Br(C_6H_4CH{=}NCH_2CH_2NMe_2)]$ (**1**)[12a] was initially tested. The compound was recovered unaltered after refluxing in a toluene solution for 8 h. The lack of reactivity, under these conditions, was taken as an indication that ligand dissociation to yield a five-coordinate species, prior to the reductive elimination process, is required. Therefore, our next target was the compound $[PtMe_2Br\{C_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)\}SMe_2]$ (**2**) containing the labile $SMe_2$ ligand, which was prepared as a single isomer with a *fac*-$PtC_3$ arrangement, as previously reported for analogous compounds.[13]

When a toluene solution of compound **2** was refluxed for 4 h, the cyclometalated platinum(II) compound $[PtBr\{2\text{-}MeC_6H_3CH{=}NCH_2(4\text{-}ClC_6H_4)\}SMe_2]$ (**3**) shown in Scheme 1 was obtained as a single product. A one-pot procedure from a mixture of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and the ligand $2\text{-}BrC_6H_4CH{=}NCH_2(4\text{-}C_6H_4Cl)$ gave the same result. In the $^1H$ NMR spectrum, a single methyl resonance was observed at 2.42 ppm and showed NOESY interactions with both the imine and aromatic protons. A displacement reaction of dimethyl sulfide for triphenylphosphine produced the compound $[PtBr\{2\text{-}MeC_6H_3CH{=}NCH_2(4\text{-}ClC_6H_4)\}PPh_3]$ (**4**) (see Scheme 1), which was also characterized using one- and two-dimensional NMR spectroscopic techniques.

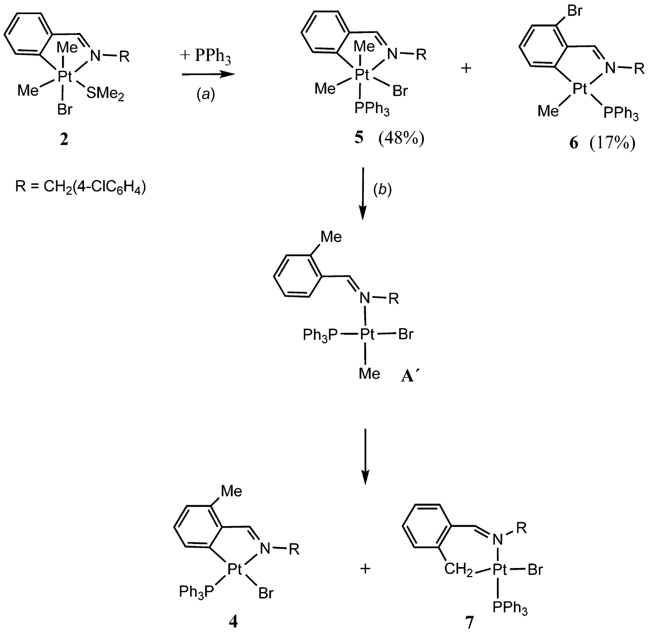
These results indicate that, under the conditions tried, $C_{sp^3}$−$C_{sp^2}$ reductive elimination is the most favored of the four possible processes (paths *a*−*d* indicated in Scheme 1). We speculate that the methyl reductively eliminates with the aryl ring but the ligand is still tethered to the metal by the nitrogen atom. Therefore, the aryl ring would be in close proximity to the metal and allow for a fast cyclometalation to occur, with subsequent loss of methane, as described for analogous compounds.[12,13] This reaction sequence is analogous to that reported for biaryl formation ($sp^2$−$sp^2$ coupling) from cyclometalated platinum(IV) compounds in which a final cyclometalation step occurs with release of an arene molecule.[9]

In order to explore this reaction type as a function of the stereoelectronic features of the ancillary ligand, the thermal behavior of $[PtMe_2Br\{C_6H_4CH{=}NCH_2(4\text{-}ClC_6H_4)\}PPh_3]$ (**5**) in refluxing toluene solution was also studied. As shown in Scheme 2, compound **5** was obtained from compound **2** in a substitution reaction of $SMe_2$ for $PPh_3$. Recrystallization of the resulting crude product gave, in addition to compound **5**, orange crystals of compound **6**, in a molar ratio of 3:1 for **5** and **6**. The NMR spectra of compound **5** indicate a *fac*-$PtC_3$ arrangement with the $PPh_3$ trans to a methyl ligand, as reported for analogous compounds.[12,13]

$[PtMe\{2\text{-}BrC_6H_3CH{=}NCH_2(4\text{-}ClC_6H_4)\}PPh_3]$ (**6**), formed as a byproduct in the synthesis of compound **5**, was fully characterized, including single-crystal X-ray diffraction analysis (Figure 1). The formation of this compound suggests that $C_{sp^2}$−Br reductive elimination and subsequent cyclometalation take place along with the substitution process.[14]

When a toluene solution of pure compound **5** was refluxed for 4 h, a mixture of compounds **4** and **7** in the ratio 1:2.5 was obtained. Compounds **4** and **7** both arise from $C_{sp^3}$−$C_{sp^2}$ reductive elimination from the platinum(IV) compound **5**, which is followed by subsequent cyclometalation and loss of methane. Competition between activation of either a $C_{sp^2}$−H bond, leading to a five-membered platinacycle (compound **4**), or activation of a $C_{sp^3}$−H bond in the methyl group previously reductively eliminated, leading to a novel six-membered platinacycle (compound **7**), takes place in the cyclometalation process. White crystals of compound **7** were obtained from the

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



[a]Yields of compounds **5** and **6** (see text) are given in parentheses.

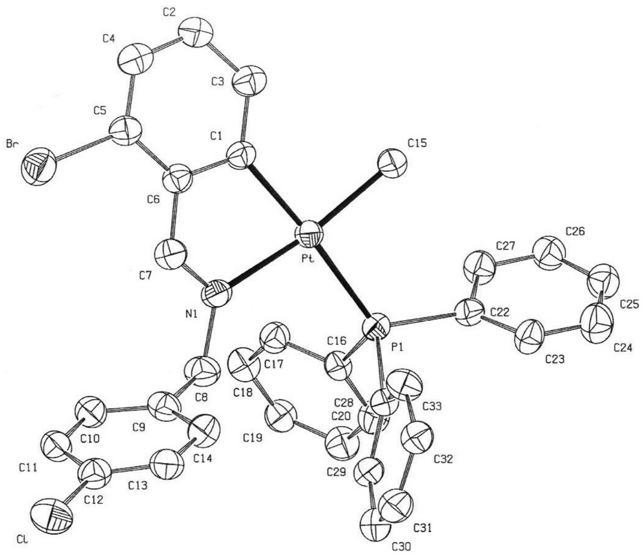


**Figure 1.** Molecular structure of compound **6**. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt−C(1), 2.040(8); Pt−C(15), 2.074(8); Pt−N(1), 2.141(7); Pt−P(1), 2.313(2); N(1)−C(7), 1.286(11); N(1)−C(8), 1.486(11); C(1)−C(6), 1.378(12); C(6)−C(7), 1.427(12); C(1)−Pt−C(15),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

initial crude product. The compound was fully characterized, including NMR spectroscopy and an X-ray diffraction study (Figure 2).

Formation of a six-membered platinacycle as a result of the activation of a $C_{sp^3}$−H bond is remarkable, since (i) a strong tendency to form five-membered rings over six-membered rings and (ii) a preference for the activation of $sp^2$ over $sp^3$ C−H bonds are generally observed in cyclometalation reactions.[15] Few examples of platinacycles formed through aliphatic C−H bond activation have been reported.[16] The results presented in this communication have some noteworthy features. First, the activated methyl was the methyl group initially bound to platinum that was transferred to the imine ligand through a reductive elimination process. Second, $C_{sp^3}$−H bond activation was only observed when $PPh_3$ was coordinated as the ancillary ligand to the platinum(IV) center, thus indicating that stereoelectronic factors are decisive in the competition between aromatic and aliphatic C−H bond activation. A recent example of a related process with formation of a six-membered platinacycle also involves a platinum(IV) precursor containing a $PPh_3$ ligand.[17] Moreover, it has been reported that the preference for aromatic versus aliphatic C−H bond activation in the reactions of methylbenzenes with platinum(II) complexes can be overridden under different conditions.[18]

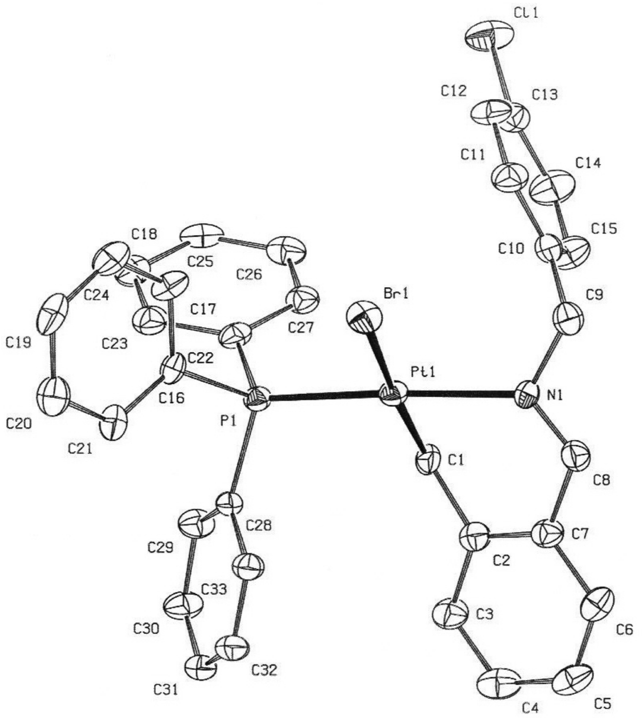


**Figure 2.** Molecular structure of compound **7**. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pt(1)−C(1), 2.059(3); Pt(1)−N(1), 2.114(3); Pt(1)−P(1), 2.2191(11); Pt(1)−Br(1), 2.5328(7); N(1)−C(8), 1.278(4); N(1)−C(9), 1.477(4); C(1)−C(2), 1.509(4); C(2)−C(7), 1.411(4); C(7)−C(8), 1.459(4); C(1)−Pt(1)−N(1), 84.38(12); 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); N(1)−Pt(1)−Br(1), 90.41(8); P(1)−Pt(1)−Br(1), 96.60(3).

In summary, our results show that reductive elimination from cyclometalated platinum(IV) compounds **2** and **5** takes place selectively to produce exclusively $C_{sp^3}$−$C_{sp^2}$ coupling, which is followed by cyclometalation and subsequent loss of methane. The latter metalation process produced $C_{sp^2}$−H bond activation for the compound containing a smaller $SMe_2$ ligand (**2**) and competition between $C_{sp^3}$−H and $C_{sp^2}$−H bond activation for the bulkier triphenylphosphine analogue (**5**). In addition, a C−Br reductive elimination process followed by cyclometalation has also been observed. Further work is in progress with the aim of exploring the scope and the mechanism of both the $C_{sp^3}$−$C_{sp^2}$ and $C_{sp^2}$−Br reductive elimination processes as well as the factors governing the competition between aliphatic and aromatic C−H bond activation.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Full experimental details and characterization data for compounds **2**−**7**, crystal data for compounds **6** and **7**, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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

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