Ligand-Mediated C–Br Oxidative Addition to Cycloplatinated(II) Complexes and Benzyl-Me C–C Bond Reductive Elimination from a Cycloplatinated(IV) Complex

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ABSTRACT: Reaction of the Pt(II) complexes [PtMe2(pbt)], 1a, (pbt = 2-(2-pyridyl)benzothiazole) and [PtMe(C=N)(PPh2Me)] (C=N = deprotonated 2-phenylpyridine (ppy), 1b, or deprotonated benzo[h]quinoline (bhz), 1c) with benzyl bromide, PhCH2Br, is studied. The reaction of 1a with PhCH2Br gave the Pt(IV) product complex [PtBr(CH2Ph)Me2(pbt)]. The major trans isomer is formed in a trans oxidative addition (2a), while the minor cis products (2a′ and 2a″) resulted from an isomerization process. A solution of Pt(II) complex 1a in the presence of benzyl bromide in toluene at 70 °C after 7 days gradually gave the dibromo Pt(IV) complex [Pt-(Br)2Me2(pbt)] 4a, as determined by NMR spectroscopy and single-crystal XRD. The reaction of complexes 1b and 1c with PhCH2Br gave the Pt(IV) complexes [PtMeBr(CH2Ph)(C=N)(PPh2Me)] (C=N = ppy; 2b; C=N = bhq, 2c), in which the phosphine and benzyl ligands are trans. Multinuclear NMR spectroscopy ruled out other isomers. Attempts to grow crystals of the cycloplatinated(IV) complex 2b yielded a previously reported Pt(II) complex [PtBr(ppy)(PPh2Me)], 3b, presumably from reductive elimination of ethylbenzene. UV–vis spectroscopy was used to study the kinetics of reaction of Pt(II) complexes 1a−1c with benzyl bromide. The data are consistent with a second-order S2,2 mechanism and the first order in both the Pt complex and PhCH2Br. The rate of reaction decreases along the series 1 a ≫ 1 c > 1 b. Density functional theory calculations were carried out to support experimental findings and understand the formation of isomers.

INTRODUCTION

There is a great current interest in the chemistry of cyclometalated organometallic compounds on the basis of their applications in stoichiometric and catalytic organic synthesis,7−9 optoelectronic devices,7−9 therapeutic agents,10−12 chemical sensors,13 and luminescent probes for biomolecules because of their photophysical properties.14−16 Investigations of the cycloplatinated compounds have given rise to many interesting complexes and new mechanistic insights into their reactions.17−40 Cyclometalation proceeds by the reaction of Pt(II) precursor complexes, [Pt(aryl)2(SMe2)]2 or [PtMe2(μ-SMe2)]2, with ligands such as 2-phenylpyridine or benzo[h]quinoline. The C–halide bonds, along with other C–X bonds with large electronegativity differences, are considered as polar substrates in the oxidative addition reactions.40,41 Among distinct mechanisms suggested for C–X bond activation, the S2,2 mechanism is quite common. Because oxidative addition reactions are key steps in many catalytic reactions, they are extensively investigated.42−45 Although the kinetics and mechanism of organic halide addition to organoplatinum(II) complexes of the general formula [PtR2(NN)] (R = Me or aryl and NN = 2,2′-bipyridine or 1,10-phenanthroline) are well established,40,45,46,47 related reactions with cycloplatinated(II) complexes have been less studied.40,41−48

C–C bond-forming reductive elimination is well recognized as the last step in many catalytic cycles used in organic synthesis.41−44 Such processes have been studied extensively including Pt(IV) complexes.45−49 Although there are some reports on C–C bond formation from the organoplatinum(IV) complex involving Me−Me or acyl-Me,40,46,50,51 a limited number of studies on the intramolecular C–C reductive elimination from Pt(IV) complexes, especially C–C benzyl-methyl reductive elimination, are reported.46−50 Gold-
berg and Crumpton reported C–C reductive elimination reactions from Pt(IV) complexes. Also, we have recently reported on homocoupling of benzene.

Because our interests lie in the reactivity of cycloplatinated complexes, here, we show that although the cycloplatinated(II) complex [PtMe(C^N)(PPh2Me)] (C^N = deprotonated 2-phenylpyridinium (ppy), 1b, or deprotonated benzoli[3]-quinoxine (bq)), 1c) reacts with benzyl bromide, PhCH2Br to give exclusively the trans addition product, the previously reported complex [PtMe(pbt)], 1a, (pbt = 2-(2-pyridyl)-benzothiazole) reacts uniquely with PhCH2Br to give a mixture isomeric products. The reactivity of Pt(II) centers in these complexes as a nucleophile toward PhCH2Br is compared. Our kinetic and mechanistic study suggests that the reactions proceed through a bimolecular S_{N}2 pathway. The resulting cycloplatinated(IV) complex [PtMeBr(CH2Ph)(ppy)(PPh2Me)] undergoes a benzyl-Me C–C bond-forming reductive elimination to give the cycloplatinated(II) complex [PtBr(ppy)(PPh2Me)]. The experimental findings are also computationally investigated, and the optimized structures of the possible transition states and intermediates were determined.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of the Complexes.

The routes to prepare the new organoplatinum(IV) complexes are described in Scheme 1.

![Scheme 1](image)

The reaction of a solution of [PtMe(C^N)(PPh2Me)] (1b; C^N = ppy, 1c; C^N = bq) with benzyl bromide at room temperature gave the complexes [PtMeBr(CH2Ph)(C^N)-(PPh2Me)] (2b; C^N = ppy, 2c; C^N = bq) in good yields through oxidative addition of PhCH2Br. Both complexes were characterized using multinuclear 1H, 31P, and 13C NMR spectroscopy (see Table 1) and elemental analysis. The characteristic signal in the 1H NMR spectrum of [PtMeBr(CH2Ph)(ppy)(PPh2Me)], 2b (see Figure 1), is the methylene protons of the benzylplatinum group, which are diastereotopic and appeared as two doublets of doublets at δ = 2.77 and 3.88 ppm. In the 13C NMR spectrum of 2b, the signal for the C atom of the Me group in PPh2Me as a doublet appeared in a low field at δ = 11.2 with J_{PtC} = 807 Hz and J_{PtC} = 437 Hz, respectively, indicating that they are located trans to the C atom of the benzyl group. A doublet with Pt satellites at δ = 31.6 was assigned to the C atom of CH2 in the benzyl group, which was further confirmed by DEPT 13C NMR analysis (see Figure 1). The coupling constants mentioned above are typical values for Pt(IV) complexes.

Attempts to grow suitable crystals of the Pt(IV) complex [PtMeBr(CH2Ph)(ppy)(PPh2Me)], 2b, for a single-crystal X-ray diffraction experiment in solvents such as acetone and benzene were not successful. During the crystallization process in CH2Cl2/hexane at room temperature, a benzyl-Me C–C bond reductive elimination from cycloplatinated(IV) complex 2b occurred to give the complex [PtBr(PPh2Me)(ppy)], 3b, whose structure was confirmed by single-crystal analysis.

![Figure 1](image)

In the reaction of 1a with PhCH2Br, the product [PtBr(CH2Ph)Me2(pbt)] was shown to be a mixture containing all three possible isomers, 2a (PhCH2 being trans to Br), 2a′ (the PhCH2 ligand being trans to N of the benzothiazole group), and 2a″ (the PhCH2 ligand being trans to N of the pyridyl group). When the reaction was performed for 2 h, the ratio of the three isomers 2a/2a′/2a″ was found to be equal to 77:17:6, while after 24 h, the ratio changed to 90:10:0, indicating that the isomers 2a′ (significantly) and 2a″ (completely) returned back to isomer 2a, being both the kinetic and thermodynamic products. Our density functional theory (DFT) calculations (see the Theoretical Investigation of the Suggested Mechanisms section) are consistent with these experimental results.

The trend of stability follows 2a > 2a′ > 2a″.

In the 1H NMR spectrum of the isomer mixture of [PtBr(CH2Ph)Me2(pbt)] (see Table 1 and Figure 2), the major isomer 2a displays two doublets at δ = 2.90 and 3.11 ppm for the PtCH2 diastereotopic protons, as observed for similar compounds. 31,41 For the minor isomer 2a′, the two singlet signals at δ = 1.71 and 1.98 are assigned to the two different methyl ligands being trans to Br and N of the pyridyl ligand, respectively. The isomer 2a′ shows two doublets for diastereotopic protons of the methylene group at δ = 2.87 and 3.10. In the 1H NMR of isomer 2a″, two singlets at δ = 1.65 and 1.93 are assigned to the Me ligands trans to Br and N of the benzothiazole ligand, respectively.

In the 13C NMR spectrum (see Table 1 and Figure 3), for 2a, two singlets with Pt satellites are observed for the two different methyl groups directly connected to Pt, trans to N of pyridyl and benzothiazole rings. 31,41 The J_{PtC} values (see Table 1) are smaller than the corresponding values reported for the methyl groups of complex 1a (J_{PtC} = 807 Hz and 844 Hz), confirming the oxidation of Pt(II) to Pt(IV) by benzyl bromide. The CH2 of benzyl appears at δ = 22.8 and was confirmed by DEPT 13C analysis. 31,41 2a″ also shows the two singlet resonances for two different methyl ligands being trans to N of the pyridyl ligand and Br. Similar to 2a, the isomer 2a″ displays a singlet C atom of CH2, which was confirmed by DEPT 13C NMR experiments. The resonances for isomer 2a″ were not resolved in the 13C NMR spectrum.
Table 1. NMR Data (Chemical Shifts in ppm and J in Hz) for Pt(IV) Complexes

| Compound | δ_n (ppm) | J_m (Hz) | J_c (Hz) | δ_c (ppm) | J_m (Hz) | J_c (Hz) | δ_n (ppm) | J_m (Hz) | J_c (Hz) |
|----------|-----------|----------|----------|-----------|----------|----------|-----------|----------|----------|
| Me^a     | 1.78      | 76.0     | 1.98     | 72.2      | 1.65     | 72.4     | 1.36      | 68.1     | 7.9      |
|          | -6.4      | 680      | -5.8     | 718       | n.r.*    |          | -3.4      | 645      | 4        |
| Me^b     | 2.05      | 76.1     | 1.71     | 72.0      | 1.93     | 74.0     |          | ---      |          |
|          | -0.2      | 712      | -0.2     | n.r.*     |          |          |          |          |          |
| CH_2=Ph  | 2.90      | 85.0     | 3.11     | 96.3      | 2.87     | 85.2     |          | 2.77     | 49.8     |
|          | 3.10      | 97.3     | 18.6     | 648       | 3.80     |          | 3.92      | 101.2    | 9.3      |
|          | 22.8      | 639      |          |          | 31.6     | 447      | 3.92      | 101.2    | 9.3      |
| PPh_3Me  |          |          |          |          |          |          | 1.81      | 11.6     | 9.1      |
|          |          |          |          |          |          |          | 11.2      | 16       | 29       |
|          |          |          |          |          |          |          | -18.5     | 1063     |          |
|          |          |          |          |          |          |          | -18.0     | 1064     |          |

^n.r. = Not resolved.

Figure 1. (A) ^1^H (aliphatic region), (B) ^3^P, (C) ^1^C (aliphatic region), and (D) DEPT ^1^C (aliphatic region) NMR spectra of complex 2b in CDCl_3.

Scheme 2. Suggested Mechanism for Benzyl-Me C−C Bond Reductive Elimination from 2b
It should be noted that the reaction of complex 1a with excess of benzyl bromide in toluene at 70 °C for 6 days gave the dibromoplatinum(IV) complex [Pt(Br)₂Me₂(pbt)], 4a. Its ¹H NMR spectrum and X-ray crystal structure (Figure S1) are reported in the Supporting Information.

**Kinetic Study.** The kinetic study of oxidative addition reactions of Pt(II) complexes 1a−c with PhCH₂Br (and in one case with MeI in order to study the effect of alkyl halide on the rate of reaction) was carried out in acetone (and toluene to investigate the solvent effect). The rate of the oxidative addition reactions was studied by dissolving complexes 1a−c in the selected solvent followed by rapid mixing with a known excess of PhCH₂Br. Typical examples of the observed spectral changes and kinetic traces (Abs−time curves) are shown in Figures 4 and S5 respectively. The kinetic traces recorded for these reactions displayed excellent fits to eq 1 (for the pseudo-first-order condition) or eq 2 (for the 1:1 stoichiometric condition).
The activation parameters (enthalpy and entropy of activation) were obtained from the temperature dependence of $k_2$ by applying Eyring plots (see Figure 6), and the kinetic data are collected in Table 2. The large negative values of entropy of activation for the reactions studied in the present work are typical of oxidative addition by a common $S_N2$ mechanism, which involves nucleophilic attack of the Pt center at the methylene group of PhCH₂Br and the formation of a five-coordinate cationic intermediate (see the next section).

The order of the reaction rates of PhCH₂Br with Pt(II) complexes in aceton is $1a > 1c > 1b$. The slightly observed increase in rate on going from $[\text{PtMe(PPh}_2\text{Me)(ppy)}]$, $1b$, to $[\text{PtMe(PPh}_2\text{Me)(bhq)}]$, $1c$, by a factor of about 1.5 is probably due to more electron releasing character of the bhq ligand as compared to that of the ppy ligand, which makes the Pt(II) center in $1c$ more electron rich than the Pt(II) center in $1b$, toward oxidative addition reactions. The same behavior has been reported for the reactions of $\text{H}_2\text{O}_2$,$^{66}$ $\text{PhI(OAc)}_2$,$^{45}$ and $\text{MeF}^+$ with complexes $1b$ and $1c$. The rate of reaction of dimethylplatinum(II) complex $1a$ with PhCH₂Br was considerably higher than those obtained for complexes $1b$ and $1c$. For example, at $25 ^\circ \text{C}$, the values of $k_2$ are 11.95 and 0.31 $\times 10^{-2}$ L mol⁻¹ s⁻¹, respectively, for complexes $1a$ and $1b$. Thus, 3 orders of magnitude difference ($10^3$) can be attributed to the presence of an extra methyl group (a very strong σ-donor) in $1a$ versus an electron-withdrawing phosphine ligand in $1b$ and $1c$.

As shown in Table 2, the rates of reaction of complex $1a$ in toluene were some 18–20 times slower than those in aceton. We found that probably because the intermediate is ionic, as expected in the classical $S_N2$ mechanism, reactions are sensitive to the solvent polarity, and consequently, the reactions are faster in acetone than toluene.

The rates of reaction of complex $1b$ with MeI in aceton are faster than those with PhCH₂Br. Two factors can explain this observation. First, the halogen effect in which the rate of the reactions decreases in the order I > Br (generally ascribed to “iodide being a better leaving group than bromide”). Second, the effect of the R group. In $S_N2$ reactions, the rate of reaction is dependent on the steric of the R group. The bulkier R group (in this instant, benzyl vs Me) has a slower reaction rate. With due attention to the R group and the halogen effect, the Pt(II) complex $1b$ must react faster with MeI as compared to PhCH₂Br. Also, given that these reactions follow second-order kinetics with remarkable reproducibility and the fact that radical scavengers did not affect the rate would rule out the possibility of any radical mechanism.$^{30,70}$ Thus, the above-mentioned observations strongly suggest an $S_N2$ mechanism of oxidative addition of the benzyl bromide to Pt(II) complexes $1a$–$1c$. Also, the large negative entropies of activation are typical values for oxidative addition by the $S_N2$ mechanism (see Table 2). It should be noted that PhCH₂Br at $25 ^\circ \text{C}$ reacted nearly 1.3 times slower with the unsymmetric benzothiazol complex $1a$ ($k_2 = 11.95 \times 10^{-2}$ L mol⁻¹ s⁻¹) than the symmetric 2,2'-bipyridine (ppy) derivative, $[\text{PtMe}_2\text{(ppy)}]$ $^{37}$ ($k_2 = 15.60 \times 10^{-2}$ L mol⁻¹ s⁻¹). The same mechanism for the reaction of benzyl bromide with $[\text{PtMe}_2\text{(ppy)}]$ has been suggested and supported by the kinetic isotope effect.$^{37}$

**Theoretical Investigation of the Suggested Mechanisms.** To get more insight into the suggested mechanism and perform a reliable molecular modeling of the new Pt complexes

![Figure 5](image-url)

**Figure 5.** (A) Abs–time curves for the reaction of $[\text{PtMe}_2\text{(pbt)}]$, $1a$, ($5 \times 10^{-4}$ M) with PhCH₂Br ($0.006–0.015$ M, concentration increases reading downward) in toluene at $25 ^\circ \text{C}$. (B) Plots of first-order rate constants ($k_2$/s⁻¹) versus concentration of benzyl bromide for the reaction of (a) $[\text{PtMe}_2\text{(pbt)}]$, $1a$, with PhCH₂Br in toluene; (b) $[\text{PtMe(PPh}_2\text{Me)(ppy)}]$, $1b$, with MeI in acetone; (c) $[\text{PtMe(PPh}_2\text{Me)(bhq)}]$, $1c$, with PhCH₂Br in acetone; and (d) $[\text{PtMe(PPh}_2\text{Me)(bhq)}]$, $1c$, with PhCH₂Br in acetone at $T = 40 ^\circ \text{C}$.

![Figure 6](image-url)

**Figure 6.** Eyring plots for the reactions of (a) $[\text{PtMe}_2\text{(pbt)}]$, $1a$, with PhCH₂Br, in acetone; (b) $[\text{PtMe}_2\text{(pbt)}]$, $1a$, with PhCH₂Br, in toluene; (c) $[\text{PtMe(PPh}_2\text{Me)(ppy)}]$, $1b$, with PhCH₂Br, in acetone; (d) $[\text{PtMe(PPh}_2\text{Me)(bhq)}]$, $1c$, with PhCH₂Br, in acetone; and (e) $[\text{PtMe(PPh}_2\text{Me)(bhq)}]$, $1c$, with PhCH₂Br in acetone.$^{30,70}$

| complex | λmax/nm | $k_2$/L mol⁻¹ s⁻¹ at different temperatures | $\Delta H^\ddagger$/kJ mol⁻¹ | $\Delta S^\ddagger$/K mol⁻¹ |
|---------|---------|------------------------------------------|-------------------------------|------------------------------|
| $1a^b$  | 520, (562) | 7.66, (0.38) 10.44, (0.47) 11.95, (0.63) 14.29, (0.75) 21.47, (1.17) | 22.5 ± 1.7, (31.5 ± 1.1) | −148 ± 6, (−143 ± 4) |
| 1b$^c$  | 358 | 0.10 0.15, (3.75) 0.20, (5.05) 0.31, (6.55) 0.51, (11.00) 0.51 0.51 0.51 | 45.9 ± 2.0, (38.2 ± 0.4) | −142 ± 7, (−141 ± 2) |
| 1c      | 390 | 0.51$d$ 0.83$^3$ 0.31 0.39 0.61 | 35.8 ± 1.7 | −172 ± 6 |

$^a$Estimated errors in $k_2$ values are ±5%. $^b$Values in parenthesis are for toluene. $^c$Values in brackets are for MeI. $^d$At $35 ^\circ \text{C}$. $^e$At $45 ^\circ \text{C}$. 

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containing the pbt ligand, a suitable DFT method should be used. DFT calculations have proven to be useful methods for calculations of structures of transition-metal complexes. Among methods and basis sets used for metal complexes, the B3LYP/6-31G(d) level (LANL2DZ potential for Pt) is shown to be a good candidate between accuracy and CPU time of calculations, and therefore, they have been used for mechanistic study and structural optimizations of the Pt complexes. The reactions studied in the present work, shown in Scheme 1, have been considered with an emphasis on the differences between the Pt complexes (1a, 1b, and 1c), alkyl halides (MeI and PhCH2Br), and the reaction medium, solvent. The suggested mechanism is presented in Scheme 3.

The reaction of PhCH2Br with the Pt(II) complex 1a in acetonitrile is initiated by nucleophilic attack by the 5a,79,81 HOMO of 1a on the σ* LUMO of benzyl bromide (Figure 7). The most significant changes in bond distances of TSa are computed for the Br–CH2 and Pt–CH2 bonds. The computed bond length of 2.108 Å for Br–CH2Ph increases to 2.589 Å in TSa, while the Pt–CH2 distance decreases from far apart in the reactants to 2.788 Å. The formation of TSa is followed by completely breaking the Br–CH2 bond and forming the Pt–CH2 bond, to give intermediate IMa, which can abstract bromide to form the isomer 2a or undergo pseudorotation to give IMa and IMa. The coordination of bromide to these intermediates can then give isomers 2a and 2a with an octahedral geometry. As expected, the bond lengths of the starting cyclopentadienyl(II) complex 1a are shorter than those of the corresponding Pt(IV) complex 2a. For example, the Pt–Npy and Pt–Nbz bonds in 1a are shorter (2.200 and 2.250 Å, respectively) than those in 2a (with the values of 2.280 and 2.308 Å, respectively). The energy barrier for the formation of TSa in acetonitrile is calculated by DFT to be 23.8 kJ mol\(^{-1}\) (see Figure 8), which is in excellent agreement with the experimental value of 22.5 kJ mol\(^{-1}\) (see Table 2). The oxidative addition of similar Pt(II) complexes had been also performed using DFT calculations by us and others. For example, the computed energy barrier for oxidative addition of [PtMe2(bpy)] with benzyl bromide was found to be 23.0 kJ mol\(^{-1}\), which is lower than the calculated value of 1a. This is in agreement with experimental findings where the rate of the reaction of benzyl bromide with 1a is lower than that for [PtMe2(bpy)]. There are, in principle, seven possible isomers for the complex [PtBr(CH2Ph)Me2(pbt)]. We can quickly delete four of the possible isomers, that is, those having two C atoms in trans positions to one another, because we would have seen only one resonance at the same chemical shift for the two Pt–Me groups (when they are in trans arrangement) or two resonances for the two Pt–Me groups with very different coupling constants (one trans to the PhCH2 group and another cis because of different trans influences of C and other atoms) in the \(^1\)H NMR, whereas only two signals with close \(^3\)J(HH) values (see Figure 2) are observed. A series of DFT calculations was performed on the remaining three isomers, 2a, 2a, and 2a, depicted in Figure 8 with their relative energies. The enthalpy values obtained from the calculations show the order 2a < 2a < 2a with the lowest lying isomer being that the larger PhCH2 group is located in the axial position as compared with the equatorial position in 2a and 2a isomers. This agrees with NMR experimental findings where the product ratio of 2a/2a/2a is 77:17:6. The reaction of 1a with PhCH2Br was also computationally investigated in toluene with lower polarity compared to acetonitrile to understand the effect of the solvent on the energy barrier of oxidative addition reaction. The calculated enthalpy of activation in toluene is 40.5 kJ mol\(^{-1}\) (in good agreement with the experimental value of 45.9 kJ mol\(^{-1}\)). This solvent effect once again is consistent with an S2 mechanism. It was experimentally found that complex 1b reacts with MeI faster than benzyl bromide (see Table 2). As shown in Figure 9, the computational investigations show that the Δ\(\Delta H^f\) for the
oxidative addition reactions of complex 1b with PhCH₂Br and MeI in acetone are 41.2 and 36.1 kJ mol⁻¹, respectively. These observations are also consistent with the experimental values of 45.9 and 38.2 kJ mol⁻¹. As explained above, one possible interpretation for the higher energy barrier observed for PhCH₂Br versus MeI is that in SN₂-type reactions, the rate of reaction is dependent on the sterics of the R group: the bulkier the R group, the slower the reaction. Also, the iodide is a better leaving group than bromide.

**EXPERIMENTAL SECTION**

**General Remarks.** ¹H, ¹³C, and ³¹P NMR spectra in CDCl₃ were recorded using a Bruker Ultrashield 400 spectrometer (with TMS or 85% H₃PO₄ as references). The chemical shifts and coupling constants are in ppm and Hz, respectively. The microanalyses were performed using a ThermoFinigan Flash EA-1112 CHNSO rapid elemental analyzer, and melting points were recorded on a Buchi 530 apparatus. Kinetic studies were carried out using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. Benzyl bromide and 2-(2-pyridyl)benzothiazole (abbreviated as pbt) were purchased from commercial sources, and the precursor complexes [Pt₂Me₄(μ-SMe₂)], [PtMe₂(pbt)], [PtMe₂(pypy)(PPh₂Me)], [PtMe₂(bhq)(PPh₂Me)] and [PtMe₂(pppy)(PPh₂Me)] were prepared as reported.

**Synthesis of Platinum Complexes.** Preparation of [PtBr(CH₂Ph)Me₂(pbt)], 2a + 2a’ + 2a”. Benzyl bromide (0.014 mL, 0.12 mmol) was added to a solution of [PtMe₂(pbt)], 1a (0.05 g, 0.11 mmol) in dichloromethane, and the mixture was stirred at room temperature for 2 h. The solvent was evaporated from the solution, and the residue was washed with ether and n-hexane. The product as a light green solid was dried under vacuum. Yield: 0.063 g; 91%, mp 204 °C.
Preparation of [PtMeBr(CH2Ph)(ppy)(PPh2Me)], 2b. This compound as a white solid was made similarly using benzyl bromide (0.014 mL, 0.12 mmol) and [PtMe2(pbt)] (0.03 g, 0.069 mmol) in toluene was added an acetone and toluene as solvents, as implemented in the Gaussian program. The electronic core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was chosen to describe Pt and Br. The 6-31G(d) basis set was used for all other atoms.87 Frequency calculations were carried out at the same level of theory to identify whether the calculated stationary point is a minimum (zero imaginary frequency) or a transition-state structure (one imaginary frequency). All data were calculated at standard temperature and pressure (298.15 K and 1.0 atm.). We have also checked that imaginary frequencies exhibit the expected motion.

Kinetic Studies of the Oxidative Addition Reactions. In a typical experiment, a solution of the Pt(II) complex in a cuvette was thermostated at 25 °C in acetone, and a known concentration of PhCH2Br was added using a microsyringe. After rapid stirring, the absorbance at the corresponding wavelength was collected with time. The Abs−time curves were analyzed by pseudo-first-order methods ([PhCH2Br]0 ≫ [1b] or [1c]) or under second-order 1:1 stoichiometric conditions ([PhCH2Br]0 = [1a]). Under pseudo-first-order conditions, the pseudo-first-order rate constants (kabs) were evaluated by nonlinear least-squares fitting of the absorbance−time profiles to a first-order equation (eq 1). Then, the slope of the linear plot of kabs versus [PhCH2Br] gave the second-order rate constant (k2).

Abs = Abs∞ + (Abs0 − Abs∞) exp(−kabs t)

Abs = Abs∞ + (Abs0 − Abs∞) /

The same method was used at other temperatures, and activation parameters were obtained from the Eyring equation (eq 3).

∆Hf

Computational Details. Gaussian 09 was used84 to fully optimize the compounds using the B3LYP level of DFT. The starting structures were created by the Gaussian View program and optimized using the CPCM solvation method85 considering aceton and toluene as solvents, as implemented in the Gaussian program. The effective core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was chosen to describe Pt and Br. The 6-31G(d) basis set was used for all other atoms.87 Frequency calculations were carried out at the same level of theory to identify whether the calculated stationary point is a minimum (zero imaginary frequency) or a transition-state structure (one imaginary frequency). All data were calculated at standard temperature and pressure (298.15 K and 1.0 atm.). We have also checked that imaginary frequencies exhibit the expected motion.

Associated content 
Supporting information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03573.

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Characterization and crystallographic data for complex 4a, qualitative frontier molecular orbitals for 1a, T5a, and 2a, and Cartesian coordinates for computed structures (PDF)
CCDC 2011477 contains the supplementary crystallographic data for complex 4a (CIF)

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Notes
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