Articles

Reactions of Platinum(II) Complexes with Chloride-Based Oxidants: Routes to Pt(III) and Pt(IV) Products

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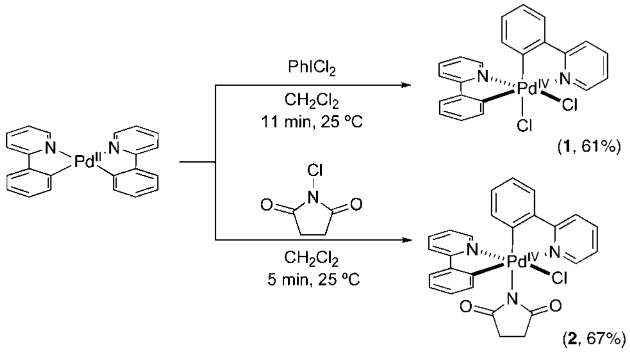
This paper describes the oxidation of $Pt^{II}(phpy)_2$ (phpy = 2-phenylpyridine) with two different electrophilic chlorinating reagents—$PhICl_2$ and *N*-chlorosuccinimide (NCS). $Pt^{II}(phpy)_2$ reacts with $PhICl_2$ to provide the Pt^{IV} complex $Pt^{IV}Cl_2(phpy)_2$ as a mixture of symmetrical and unsymmetrical isomers. In contrast, the reaction of $Pt^{II}(phpy)_2$ with NCS affords a mixture of the Pt^{III} dimer $[(phpy)_2(Cl)Pt^{III}]_2$ and $Pt^{IV}Cl_2(phpy)_2$, whose ratio varies as a function of reaction time, concentration, and the presence/absence of ambient light. The implications of these results for the mechanisms of the two reactions are discussed in detail.

Introduction

We have recently become interested in the isolation and reactivity of palladium(IV) chloride complexes that are potentially relevant to intermediates of Pd-catalyzed halogenation reactions.[1] As part of these studies, we examined the oxidation of $Pd^{II}(phpy)_2$ (phpy = 2-phenylpyridine) with electrophilic chlorinating reagents and found that this complex undergoes clean oxidative addition of $PhICl_2$ and *N*-chlorosuccinimide (NCS) to afford the stable Pd^{IV} products **1** and **2**, respectively (Scheme 1).[2,3] On the basis of these results, we anticipated that $Pt^{II}(phpy)_2$ would react with these electrophilic chlorinating reagents to form similar products. This assumption was predicated on literature reports showing that Pt^{II} and Pd^{II} complexes with identical ligand environments typically display similar reactivity toward oxidants.[4]

Scheme 1. Oxidative Addition Reactions of Electrophilic Chlorinating Reagents with $Pd^{II}(phpy)_2$



While the reaction of $Pt^{II}(phpy)_2$ with NCS or $PhICl_2$ has not been previously reported, related transformations with other oxidants have been well documented.[5,6] For example, von Zelewsky and co-workers have demonstrated that $Pt^{II}(phpy)_2$ reacts with diverse electrophiles A-B (A-B = Br_2, I_2, CH_3I, CH_2Cl_2) to afford the Pt^{IV} oxidative addition products $Pt^{IV}(phpy)_2(A)(B)$. Mechanistic studies have shown that these transformations can proceed via thermal or photochemical pathways, depending on the reaction conditions and the oxidant.[5] In addition, Ito and co-workers have carried out studies of the interaction of $Pt^{II}(phpy)_2$ with d^{10} metal salts (M = Cd^{II}, Ag^{I}, Au^{I}). These reactions were shown to result in either the formation of dative M → Pt^{II} bonds[6b,c] or in oxidation to Pt^{III} products,[6a] depending on the nature of M and the reaction conditions.

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[1] For examples of palladium-catalyzed C−H activation/halogenation reactions see: (a) Kalyani, D.; Dick, A. R.; Anani, W. Q.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 11483. (b) Kalyani, D.; Dick, A. R.; Anani, W. Q.; Sanford, M. S. *Org. Lett.* **2006**, *8*, 2523. (c) Wan, X.; Ma, Z.; Li, B.; Zhang, K.; Cao, S.; Zhang, S.; Shi, Z. *J. Am. Chem. Soc.* **2006**, *128*, 7416. (d) Giri, R.; Chen, X.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2005**, *44*, 2112. (e) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300. (f) Kodama, H.; Katsuhira, T.; Nishida, T.; Hino, T.; Tsubata, K. *Chem. Abst.* **2001**, *135*, 344284. (g) Fahey, D. R. *J. Chem. Soc., Chem. Commun.* **1970**, 417. (h) Fahey, D. R. *J. Organomet. Chem.* **1971**, *27*, 283.

[2] Whitfield, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 15142.

[3] Dick, A. R.; Kampf, J. W.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 12790.

[4] For selected examples where direct comparisons have been made between Pd^{II} and Pt^{II} oxidation reactions, see: (a) Canty, A. J.; Rodemann, T.; Skelton, B. W.; White, A. H. *Organometallics* **2006**, *25*, 3996. (b) Canty, A. J.; Patel, J.; Rodemann, T.; Ryan, J. H.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 3466. (c) Canty, A. J.; Denney, M. C.; van Koten, G.; Skelton, B. W.; White, A. H. *Organometallics,* **2004**, *23*, 5432. (d) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.

[5] (a) von Zelewsky, A.; Suckling, A. P.; Stoeckli-Evans, H. *Inorg. Chem.* **1993**, *32*, 4585. (b) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720. (c) Chassot, L.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814. (d) Chassot, L.; von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzini, V. *J. Am. Chem. Soc.* **1986**, *108*, 6084. (e) Chassot, L.; von Zelewsky, A. *Helv. Chim. Acta* **1986**, *69*, 1855. (f) Chassot, L.; Muller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249.

[6] (a) Yamaguchi, T.; Kubota, O.; Ito, T. *Chem. Lett.* **2004**, *33*, 190. (b) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **2001**, *123*, 743. (c) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **1999**, *121*, 7405.

10.1021/om070095e CCC: $40.75

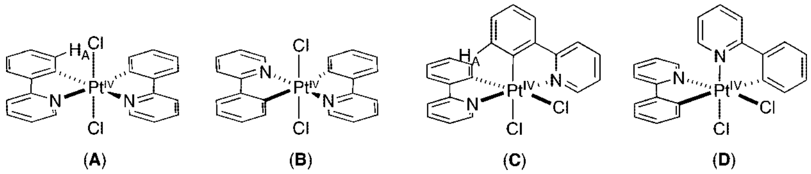
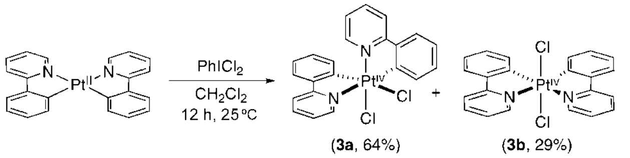


Figure 1. Possible structures for the symmetrical oxidative addition product **3b**.

We report herein that, as predicted, $Pt^{II}(phpy)_2$ reacts with $PhICl_2$ to provide the Pt^{IV} analogue of complex **1**, $Pt^{IV}Cl_2(phpy)_2$, as a mixture of symmetrical and unsymmetrical isomers. However, in contrast, the reaction of $Pt^{II}(phpy)_2$ with NCS proceeds very differently from the analogous palladium system, affording a mixture of the Pt^{III} dimer $[(phpy)_2(Cl)Pt^{III}]_2$ and $Pt^{IV}Cl_2(phpy)_2$, whose ratio varies as a function of reaction time, concentration, and the presence/absence of ambient light. The implications of these results for the mechanisms of the platinum oxidation reactions are discussed.

Results

Reaction of $Pt^{II}(phpy)_2$ with $PhICl_2$. The treatment of $Pt^{II}(phpy)_2$ with $PhICl_2$ under identical conditions to the palladium reaction in Scheme 1 afforded $Pt^{IV}Cl_2(phpy)_2$ as a 1.8:1 mixture of two isomers (**3a** and **3b**). Complexes **3a** and **3b** were readily separated when the reaction time was increased to 12 h, as **3b** precipitated from the CH_2Cl_2 solution. Under these conditions, **3a** and **3b** were isolated as pale yellow solids in 64% and 29% yield, respectively (eq 1). The major isomer (**3a**), which is a direct analogue of **1** from the palladium reaction, is the unsymmetrical product of *cis* oxidative addition. The ^{1}H NMR spectrum of **3a** exhibits 12 sets of peaks due to overlapping signals associated with the 16 inequivalent protons of this complex, while the ^{13}C NMR spectrum shows the expected 22 resonances.

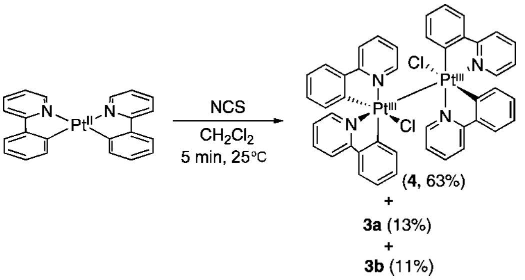


(1)

In contrast, the ^{1}H NMR spectrum of **3b** shows 8 resonances between 7.2 and 9.3 ppm, indicative of a symmetrical oxidative addition product. Notably, no analogous symmetrical product was observed in the Pd reaction. As shown in Figure 1, there are four potential symmetrical isomers of $Pt^{IV}(phpy)_2Cl_2$ (complexes **A**−**D**). Although none of these possibilities can be definitively ruled out, we believe that isomers **B** and **D** are unlikely because they require a trans orientation between the two strongly σ-donating aryl ligands. Additionally, structure **C** can be discounted based on spectroscopic comparison to recently reported *cis*-Pt^{IV}(*p*-F-phpy)$_2$Cl$_2$ (which was confirmed to assume geometry **C** by X-ray crystallography).[7] The ^{1}H NMR spectrum of Pt^{IV}(*p*-F-phpy)$_2$Cl$_2$ exhibits a characteristic upfield resonance at 5.71 ppm for H_A, indicative of shielding due to the proximity of this proton to the ring current of the adjacent aromatic ring.[8] The lack of such an upfield signal in the ^{1}H NMR spectrum of **3b** is inconsistent with geometry **C**; furthermore, an upfield signal for H_A would not be expected in **A**. As such, we propose that isomer **A** is the most likely structure of product **3b**.

Notably, comparable yields and isomer ratios were obtained when the reaction of $Pt^{II}(phpy)_2$ with $PhICl_2$ was conducted in the presence or absence of ambient light (i.e., in clear vials versus amber vials covered in foil). This is indicative of a thermal oxidative addition pathway. In addition, the yield and ratio of **3a**:**3b** was independent of the reaction time (within the range of 0.1–96 h) and reaction concentration (within the range of 1.25–10 mM).

Reaction of $Pt^{II}(phpy)_2$ with *N*-Chlorosuccinimide. We next explored the reaction of $Pt^{II}(phpy)_2$ with *N*-chlorosuccinimide under otherwise identical conditions to the palladium reaction in Scheme 1 (1.1 equiv of NCS, 5 min in CH_2Cl_2). *Intriguingly, this transformation afforded <5% yield of the N−Cl oxidative addition complex $Pt^{IV}(phpy)_2Cl(C_4H_4NO_2)$ (the major product of the analogous palladium reaction).*[9] Instead, ^{1}H NMR analysis of the crude mixture showed that Pt^{III} dimer, $Pt_2Cl_2(phpy)_4$ (**4**), was the major product (63%), along with substantial quantities of Pt^{IV} species **3a** (13%) and **3b** (11%) (eq 2).[10] Notably, dimer **4** has been reported previously by Ito and co-workers from the reaction of $Pt^{II}(phpy)_2$ with Au-Cl(SMe$_2$) in CH_2Cl_2.[6a] As such, we identified and characterized **4** based on data from this prior report.



(2)

To gain further insights into this surprising reaction of $Pt^{II}(phpy)_2$ with NCS, we studied the effect of the reaction conditions on the ratio of oxidized products (Pt^{III} complex **4** relative to Pt^{IV} complexes **3a**/**3b**). We found that this transformation was sensitive to a number of variables, including reaction time, concentration, and the presence/absence of light. Representative data that summarize these observations are shown in Tables 1 and 2, and the trends are discussed below.

In general, increasing the reaction time (from 5 min to 96 h) led to increased yields of Pt^{IV} complexes **3a**/**3b** relative to the Pt^{III} product **4** (Table 1, entries 1–4). Reaction concentration

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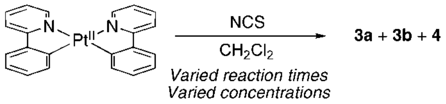
(7) Newman, C. P.; Casey-Green, K.; Clarkson, G. J.; Cave, G. W. V.; Errington, E.; Rourke, J. P. *Dalton Trans.* **2007**, 3170.

(8) Reveco, P.; Medley, J. H.; Garber, A. R.; Bhacca, N. S.; Selbin, J. *Inorg. Chem.* **1985**, *24*, 1096.

(9) The <5% yield of the N−Cl oxidative addition product was determined based on comparison of the crude ^{1}H NMR spectrum of this reaction to the ^{1}H NMR spectrum of **2**. Importantly, structurally analogous Pt^{IV} and Pd^{IV} complexes typically have very similar ^{1}H NMR signals (see refs 2 and 4).

(10) For reactions of $L_2X_2Pt^{II}$ complexes with NCS to afford $L_2X_2Pt^{IV}Cl_2$ and/or $[L_2X_2Pt^{IV}(Cl)(solvent)]^+$, see: (a) Zhang, F.; Broczkowski, M. E.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2005**, *83*, 595. (b) Scollard, J. D.; Day, M.; Labinger, J. A.; Bercaw, J. E. *Helv. Chim. Acta* **2001**, *84*, 3247.

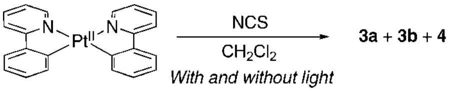
Table 1. Oxidation of $Pt^{II}(phpy)_2$ with NCS as a Function of Time and Concentration[a]



entry	time	concn (mM)	yield of **4** (%)	yield of (**3a** + **3b**) (%)
1	5 min	10	63	24
2	12 h	10	59	31
3	24 h	10	56	35
4	96 h	10	46	41
5	24 h	5	36	43
6	24 h	1.25	11	79

[a] Reactions were carried out in CH_2Cl_2 at 25 °C, evaporated to dryness, and analyzed by ^1H NMR spectroscopy in DMSO-d_6. Yields were determined by integration of the ^1H NMR signals associated with each product relative to an internal standard and represent an average of 2 runs. In cases where the yield does not add up to 100%, small quantities of unidentified minor side products were observed.

Table 2. Oxidation of $Pt^{II}(phpy)_2$ with NCS in the Presence and Absence of Light[a]



entry	concn (mM)	light yield of **4** (%)	light yield of (**3a** + **3b**) (%)	dark yield of **4** (%)	dark yield of (**3a** + **3b**) (%)
1	10	56	35	54	28
2	5	36	43	61	29
3	1.25	11	79	56	35
4[b]	10	65	29	61	24

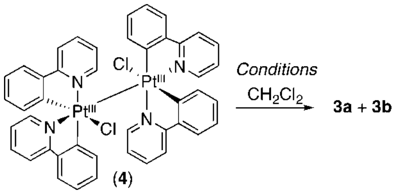
[a] Reactions were carried out in CH_2Cl_2 at 25 °C, evaporated to dryness, and analyzed by ^1H NMR spectroscopy in DMSO-d_6. Yields were determined by integration of the ^1H NMR signals associated with each product relative to an internal standard and represent an average of 2 runs. In cases where the yield does not add up to 100%, small quantities of unidentified minor side products were observed. [b] With 10 equiv of NBu_4Cl.

also had a significant effect on the products obtained from this transformation. Under otherwise identical conditions, higher concentrations led to preferential formation of the Pt^{III} dimer (entry 3), while approximately 10-fold dilution of the reaction mixture resulted in predominance of the Pt^{IV} compounds **3a** and **3b** (entry 6).

We also examined the effect of ambient light on this transformation, since both Pt^{II} and Pt^{III} complexes are well-known to undergo photochemically induced oxidation reactions.[5,11]Interestingly, when the reaction of $Pt^{II}(phpy)_2$ with NCS was carried out under standard conditions (25 °C, 24 h, 10 mM) in the dark (amber vial covered in foil), the yields of Pt^{III} product **4** and of Pt^{IV} products **3a** and **3b** were essentially identical with those observed in ambient light (Table 2, entry 1). However, lowering the reaction concentration had a very different effect on the dark reactions relative to those conducted in the presence of ambient light. In the dark, Pt^{III} complex **4** was the major product at all concentrations examined (1.25–10 mM), while in the light, Pt^{IV} products **3a** and **3b** predominated as the reaction was diluted (Table 2, entries 2 and 3).

Finally, we examined the effect of excess chloride ion on the product distribution of these transformations. These studies revealed that the addition of up to 10 equiv of Cl^- (added as NBu_4Cl) had no discernible effect on the ratio and/or yields of **4** to **3a**/**3b** under both light and dark reaction conditions (Table 2, entry 4).

Table 3. Conversion of 4 to Pt^{IV} Products[a]



entry	time (h)	added oxidant (1.1 equiv)	concn (mM)	amount of **4** remaining (%)	yield of **3a** + **3b** (%)
1	24	NCS	10	80	15
2	24	none	10	83	10
3	96	none	10	66	24
4	24	none	1.25	51	20
5[b]	24	none	1.25	76	12

[a] Reactions were carried out in CH_2Cl_2 at 25 °C, evaporated to dryness, and analyzed by ^1H NMR spectroscopy in DMSO-d_6. Yields were determined by integration of the ^1H NMR signals associated with each product relative to an internal standard and represent an average of two runs. In cases where the yield does not add up to 100%, small quantities of unidentified minor side products were observed. [b] Reaction was conducted in the absence of light.

Oxidation Reactions of Pt^{III} Complex 4. We next sought to investigate whether Pt^{III} complex **4** served as an intermediate to the formation of **3a/3b** in reactions with NCS. Our initial studies showed that isolated samples of **4** do indeed react with NCS in CH_2Cl_2 to form appreciable quantities (15% yield) of **3a/3b** under standard conditions (25 °C, 24 h, 10 mM, Table 3, entry 1). However, interestingly, a comparable yield of $Pt^{IV}(phpy)_2Cl_2$ was obtained when this reaction was conducted in CH_2Cl_2 in the absence of NCS (Table 3, entry 2). In the NCS-free reactions, the yield of Pt^{IV} products increased with reaction time (entry 3) and with lower reaction concentration (entry 4). These trends are analogous to those observed in the reactions between $Pt^{II}(phpy)_2$ and *N*-chlorosuccinimide. However, notably, low conversion of **4** to **3a/b** was observed in the dark, even under dilute conditions (entry 5).

The reactivity of isolated samples of Pt^{III} complex **4** was also examined in the nonhalogenated solvents DMSO and MeOH. Only small quantities (<20%) of the Pt^{IV} dichloride products **3a** or **3b** were observed under the conditions examined (25–100 °C, 12–24 h, 1.25–10 mM). While no appreciable reaction was observed at room temperature, at elevated temperatures, complex **4** underwent isomerization to afford a new product (**5**), which was isolated in 43% yield as a dark yellow solid (eq 3). Complex **5** was assigned as a symmetrical isomer of the Pt^{III} dimer $Pt^{III}{}_2Cl_2(phpy)_4$ based on ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy. The ^1H NMR spectrum of **5** showed 8 resonances between 6.5 and 8.5 ppm and the ^{13}C NMR spectrum exhibited signals associated with 11 distinct aromatic carbons. In addition, ^{195}Pt NMR spectroscopy of **5** showed a resonance at −2293 ppm. This signal is very close to that of Pt^{III} dimer **4** (which appears at −2355 ppm) and differs substantially from that of the Pt^{II} starting material (−3542 ppm) and the Pt^{IV} product **3a** (−1725 ppm). Collectively, these data are consistent with the symmetrical Pt^{III} complex **5**, in which all of the cyclometalated phenylpyridine ligands are in identical environments. HRMS analysis of this product showed $[(Cl)(phpy)_2Pt]^+$ as the major signal, providing further support for the proposed structure of **5**.[12]

Discussion

The reactions of $PhICl_2$ and particularly *N*-chlorosuccinimide with $Pt^{II}(phpy)_2$ afford different products than the analogous transformations at $Pd^{II}(phpy)_2$. These results highlight the

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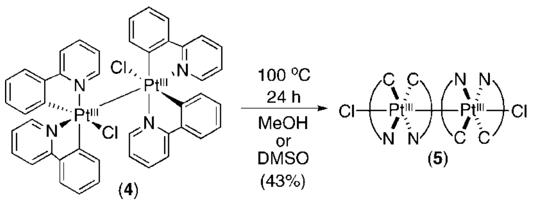
[11] Puddephatt, R. J.; Hill, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 1218.



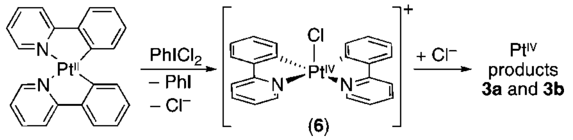
(3)

differences in reactivity between these two group 10 metals, and demonstrate that caution should be used when attempting to draw analogies between their oxidation reactions. In addition, this work provides some preliminary insights into the mechanisms of the Pt^{II} oxidation reactions, which are discussed in more detail below.

Reaction of Pt^{II}(phpy)$_2$ with PhICl$_2$ in CH$_2$Cl$_2$ To Afford 3a/3b. The reaction of Pt^{II}(phpy)$_2$ with PhICl$_2$ afforded two isomers of Pt^{IV}Cl$_2$(phpy)$_2$ (**3a** and **3b**) under all conditions examined. On the basis of extensive literature precedent for closely analogous reactions between Pt^{II} complexes and Cl$_2$[13] or PhICl$_2$,[14] we propose that the current transformation proceeds via PhICl$_2$-promoted two-electron oxidation of Pt^{II}(phpy)$_2$ to form cationic Pt^{IV} intermediate **6** followed by reaction of **6** with Cl$^-$ to yield **3a** and **3b** (Scheme 2). It is unclear why two different isomers are formed here while a single isomer is observed in the analogous Pd reaction; however, several other reports have described differences in cis/trans isomer ratios in oxidative addition as a function of metal (M = Pd versus Pt).[4b–d]

Reaction of Pt^{II}(phpy)$_2$ with NCS in CH$_2$Cl$_2$. The reaction of Pt^{II}(phpy)$_2$ with NCS in CH$_2$Cl$_2$ produced Pt^{III} complex **4** as the major product along with a mixture of **3a** and **3b**. When attempting to assess the mechanism of this transformation, it is important to keep in mind that Pt^{III} product **4** undergoes subsequent reaction with the CH$_2$Cl$_2$ solvent to afford **3a/b** (see below for a full discussion of this process). As such, the observed product distributions reflect contributions from both (1) the ratio of Pt^{III} and Pt^{IV} products produced in the initial reaction between Pt^{II}(phpy)$_2$ and NCS and (2) depletion of the initially formed Pt^{III} product **4** to generate **3a/b**. To gain insights into just the initial reaction between Pt^{II}(phpy)$_2$ and NCS, we examined the product distributions obtained in the absence of light, since there is little background conversion of **4** to **3a/b** under these conditions.

Scheme 2. Proposed Mechanism of Oxidation of Pt^{II}(phpy)$_2$ with PhICl$_2$



A first possible pathway for the formation of Pt^{III} product **4** could be an ionic S$_N$2-type mechanism involving (a) nucleophilic attack of Pt^{II} on NCS to generate a cationic five-coordinate Pt^{IV} intermediate (**6**), (b) reaction of **6** with a second equivalent of Pt^{II}(phpy)$_2$ to generate dimer **A**, followed by (c) attack by free Cl$^-$ in solution to afford **4** (Scheme 3, path i). This mechanism would also account for the generation of Pt^{IV} products **3a** and **3b**, which could be formed by trapping of intermediate **6** with Cl$^-$ prior to the dimerization step (Scheme 3, path ii). Importantly, this type of mechanism has been proposed in the literature for the formation of Pt^{III} products closely related to **4** in reactions of L$_2$X$_2$Pt^{II} with Cl$_2$ and PhICl$_2$.[15–17]

However, we discount the mechanism in Scheme 3 based on several pieces of evidence. First, there is no obvious source of Cl$^-$ (which is required for formation of **3a**, **3b**, and **4** in this cationic mechanism) in this system. While it is possible that the oxidant might be contaminated with traces of chloride salts, this seems unlikely in the context of the other available data. A second result that suggests strongly against an ionic mechanism is that the addition of an excess of free Cl$^-$ to these reactions had a negligible effect on the yield of **4** or on the distribution of Pt^{III} versus Pt^{IV} products. In an ionic, two-electron oxidation, a high concentration of Cl$^-$ would be expected to efficiently compete for the cationic 5-coordinate Pt^{IV} intermediate **6**, resulting in substantially increased yields of Pt^{IV} dichloride products **3a/b** relative to **4**.[15] Third, the same Pt^{III} complex **4** was the major product in reactions with NCS, which can potentially act as either a one- or a two-electron oxidant,[18] and with AuCl(SMe$_2$)[6a] (which should only be capable of acting as a one-electron oxidant). Finally, the reaction of **1** with PhICl$_2$, which is believed to proceed by an ionic mechanism (vide supra, Scheme 2), did not afford any of Pt^{III} complex **4**.[19] If **4** were a kinetically accessible intermediate along this pathway, we would expect to observe it in this transformation as well.[19]

On the basis of the evidence collected above, we hypothesize that the reactions of Pt^{II}(phpy)$_2$ with NCS proceed via a one-electron rather than an ionic pathway. The viability of one-electron oxidation processes of Pt^{II} arylpyridine complexes has been demonstrated previously.[5] For example, Pt^{II}(phpy)$_2$ has been shown to undergo irreversible one-electron electrochemical

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(12) Another possible structure of complex **5** would have each of the four 2-phenylpyridine ligands bridging the two Pt^{III} centers. However, preliminary molecular modeling suggests that this structure would be substantially higher in energy than the unbridged symmetrical structure proposed in eq 3.

(13) For selected examples, see: (a) Westra, A. N.; Bourne, S. A.; Kock, K. R. *Dalton Trans.* **2005**, 2916. (b) Tamasi, G.; Cini, R.; Intini, F. P.; Sivo, M. F.; Natile, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 5081. (c) Ruiz, J.; Lopez, J.; Rodriguez, V.; Perez, J.; Ramirez de Arellano, M. C.; Lopez, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2683. (d) Fornies, J.; Fortuno, C.; Gomez, M. A.; Menjon, B.; Herdtweck, E. *Organometallics* **1993**, *12*, 4368. (e) Chattopadhyay, S.; Sinha, C.; Basu, P.; Chakravorty, A. *J. Organomet. Chem.* **1991**, *414*, 421. (f) Chattopadhyay, S.; Sinha, C.; Basu, P.; Chakravorty, A. *Organometallics* **1991**, *10*, 1135. (g) van Koten, G.; Terheijden, J.; van Beck, J. A. M.; Wehman-Ooyevaar, I. C. M.; Muller, F.; Stam, C. H. *Organometallics* **1990**, *9*, 903. (h) Vicente, J.; Chicote, M-T.; Martin, J. *J. Chem. Soc., Dalton Trans.* **1987**, 881. (i) Drougge, L.; Elding, L. I. *Inorg. Chem.* **1985**, *24*, 2292. (j) Muller, G.; Riede, J.; Beyerle-Pfnur, R.; Lippert, B. *J. Am. Chem. Soc.* **1984**, *106*, 7999. (k) Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882. (l) Uson, R.; Fornies, J.; Espinet, P. *J. Organomet. Chem.* **1976**, *116*, 353. (m) Crociani, B.; Nicolini, M.; Richards, R. L. *Inorg. Chim. Acta* **1975**, *12*, 53. (n) Hodges, K. D.; Rund, J. V. *Inorg. Chem.* **1975**, *14*, 525.

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(15) For L = (*E*)-HN=C(OMe)Me and (*E*)-NH=C(OH)(*t*-Bu), see: (a) Bandoli, G.; Caputo, P. A.; Intini, F. P.; Sivo, M. F.; Natile, G. *J. Am. Chem. Soc.* **1997**, *119*, 10370. (b) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Am. Chem. Soc.* **1991**, *113*, 7805.

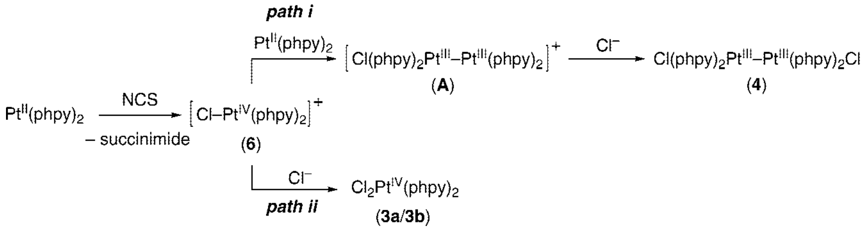
(16) For LX = acetylacetone, see: Prenzler, P. D.; Heath, G. A.; Lee, S. B.; Raptis, R. G. *Chem. Commun.* **1996**, *2271*.

(17) Baxter, L. A. M.; Heath, G. A.; Raptis, R. G.; Willis, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6944.

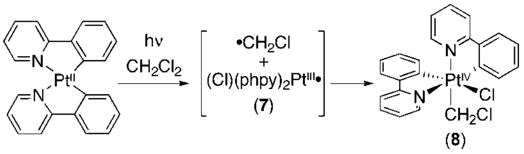
(18) For examples of NCS acting as a two-electron oxidant, see: (a) Zhang, Y.; Shibatomi, K.; Yamamoto, H. *Synlett* **2005**, *18*, 2837. (b) Prakash, G. K. S.; Mathew, T.; Hoole, D.; Esteves, P. M.; Wang, Q.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 15770. (c) Goldberg, Y.; Alper, H. *J. Org. Chem.* **1993**, *58*, 3072. For the existence of chain-carrying radicals in NCS chlorination reactions, see: Walling, C.; El-Taliawi, G. M.; Sopchik, A. *J. Org. Chem.* **1986**, *51*, 736.

(19) Notably, we have independently confirmed that **4** is reasonably stable in the presence of PhICl$_2$; for example, >50% of **4** remained after 24 h at 25 °C in the presence of 2.2 equiv of PhICl$_2$. As such, the inability to observe **4** in these systems does not appear to be due to its instability under the PhICl$_2$ oxidation conditions.

Scheme 3. Ionic Mechanism for Reaction of $Pt^{II}(phpy)_2$ with *N*-Chlorosuccinimide



Scheme 4. Proposed Mechanism for Photochemical Oxidative Addition of CH_2Cl_2 to $Pt^{II}(phpy)_2$[5b]



oxidation in MeCN at +0.26 V versus SCE.[5c,20] In addition, oxidative addition reactions that proceed through Pt^{III} radical intermediates are well-precedented for $Pt^{II}(phpy)_2$ and related heteroarylpyridine complexes.[5b] For example, as summarized in Scheme 4, $Pt^{II}(phpy)_2$ undergoes photochemically induced oxidative addition of CH_2Cl_2 via initial photoexcitation of the Pt^{II} starting material followed by $Cl^\bullet$ abstraction from solvent to form Pt^{III} radical **7** and finally radical cage recombination to afford Pt^{IV} product **8**.[5b]

In light of this precedent, we propose that the current reactions could begin with a dative interaction between the electrophilic oxidant *N*-chlorosuccinimide and the Pt d_{z^2} orbital. Such an interaction could be considered analogous to the $Pt^{II}-I_2$ complexes reported by van Koten,[21] the $Pt^{II}-Ag$ and $Pt^{II}-Cd$ complexes recently described by Yamaguchi and Ito,[6b,c] and the Pt−Au complexes described by Puddephatt.[22] Notably, a similar interaction was proposed by Ito and co-workers in their initial communication on the synthesis of **4** with $AuCl(SMe_2)$.[6a] This coordination would be followed by electron transfer from $Pt^{II}(phpy)_2$ to the oxidant and transfer of a Cl ligand to afford the Pt^{III} radical $(Cl)(phpy)_2Pt^{III\bullet}$ (**7**) (Scheme 5). Importantly, a related one-electron oxidation of $Ni^{II}(PPhMe_2)_2(C_6Cl_5)(Br)$ by *N*-bromosuccinimide has been reported to afford the Ni^{III} product $(PPhMe_2)_2(C_6Cl_5)(Br)_2Ni^{III\bullet}$, which is analogous to the proposed intermediate **7**.[23] In addition, the same Pt^{III}-based radical $(Cl)(phpy)_2Pt^{III\bullet}$ was proposed to be transiently generated in the photochemical oxidative addition reactions shown in Scheme 4.[5b]

The Pt^{III} radical species **7** could potentially then undergo several competing reactions. First, it could react with a chlorine atom source (likely either a second equivalent of NCS or the CH_2Cl_2 solvent) to afford Pt^{IV} products **3a** and **3b** (Scheme 5, path i). Alternatively, it could react with the Pt^{II} starting complex to afford a new dimeric radical that could then react with a chlorine atom source to afford **4** (Scheme 5, path ii). Finally, it could react with a second equivalent of itself to directly generate complex **4**. Notably, the latter reaction is expected to be negligible, due to the very low relative concentrations of **7** in solution at a given time.[24]

Reaction of Pt^{III} Complex 4 To Form 3a/b. The Pt^{III} complex **4** was found to convert to **3a/b** on its own in CH_2Cl_2, in the absence of an oxidant like $PhICl_2$ or NCS. A first possible mechanism for this transformation would involve disproportionation of **4** to Pt^{IV} product **3a/b** and $Pt^{II}(phpy)_2$ (Scheme 6). Other unsupported Pt^{III} dimers, including $Pt^{III}_2Cl_2(acac)_2$, $Pt^{III}_2Cl_6[HN{=}C(OH)C(CH_3)_3]_4$, and $Pt^{III}_2Cl_4[(E)\text{-}HN{=}C(OMe)Me]_2$, have been shown to undergo facile disproportionation reactions of this type.[15–17]

However, several key pieces of data suggest against a disproportionation mechanism for the formation of **3a/b** from **4**. Most importantly, the stoichiometry of this transformation requires the formation of equimolar quantities of $Pt^{II}(phpy)_2$ and Pt^{IV} complex **3a/b**. However, $Pt^{II}(phpy)_2$ was never observed by ^1H NMR spectroscopy in these systems. In addition, negligible conversion of **4** to form **3a/b** was observed in nonhalogenated solvents (e.g., DMSO, MeOH), suggesting that an external source of Cl is required to provide the chlorine atoms important for the generation of **3a/b**.

An alternative mechanism for the formation of **3a/b** from **4** in CH_2Cl_2 would involve initial homolysis of the Pt−Pt bond to afford the monomeric Pt-based radical **7** (Scheme 7). This radical species could then abstract $Cl^\bullet$ from the solvent to afford the observed Pt^{IV} product. Importantly, there is some literature precedent for the photochemically induced homolysis of Pt−Pt bonds.[25] In addition, the Pt^{III} radical **7** has been proposed by von Zelewsky as an intermediate in the photochemical oxidative addition of CH_2Cl_2 to $Pt^{II}(phpy)_2$.[5b] As shown in Scheme 4, this intermediate was proposed to undergo radical cage recombination with $^\bullet CH_2Cl$ to afford the Pt^{IV} oxidative addition product **8**. In the current system, reaction between **7** and the diffusing $^\bullet CH_2Cl$ radical is unlikely due to both the low concentrations of the two radical species (**7** and $^\bullet CH_2Cl$) in solution and the presence of O_2, which can readily quench carbon-based radicals. However, interestingly, when the reaction of **4** in CH_2Cl_2 (10 mM, 100 °C, 24 h, ambient light) was conducted in the absence of air, a trace (∼2% as determined by ^1H NMR analysis of the crude reaction mixture) of oxidative addition product **8** was detected, which is further consistent with the proposed mechanism.

Several additional pieces of data support the mechanism proposed in Scheme 7. Most importantly, the reaction of **4** with CH_2Cl_2 to form **3a/b** is promoted by light (Table 3, entry 4 versus entry 5). In addition, the observed effect of reaction concentration on the reactivity of **4** appears consistent with this mechanism. As the reaction is diluted, the susceptibility of the

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(20) For other examples of electrochemical oxidations to generate Pt^{III} dimers, see: (a) Mason, D. N.; Deacon, G. B.; Yellowlees, L. J.; Bond, A. M. *Dalton Trans.* **2003**, *890.* (b) Bennett, M. A.; Bhargava, S. K.; Boas, J. F.; Boere, R. T.; Bond, A. M.; Edwards, A. J.; Guo, S.-X.; Hammerl, A.; Pilbrow, J. R.; Priver, S. H.; Schwerdtfeger, P. *Inorg. Chem.* **2005**, *44*, 2472.

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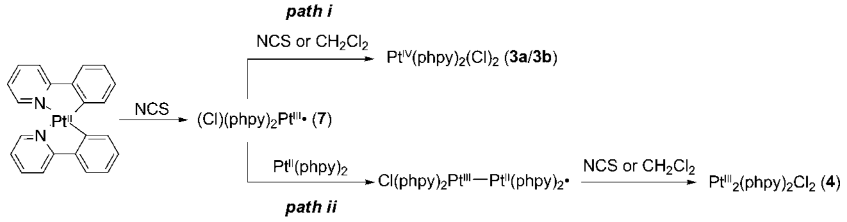
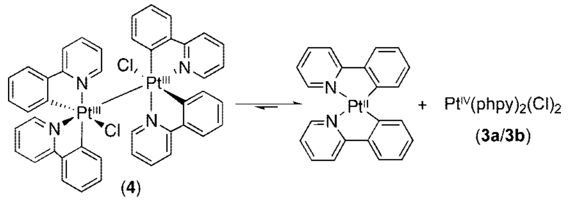
Scheme 5. Proposed Mechanism for Oxidation of $Pt^{II}(phpy)_2$ with NCS



Scheme 6. Possible Disproportionation Mechanism for the Formation of 3a/b from 4



Pt^{III} radicals to diffuse apart and react with solvent (rather than recombine to regenerate **4**) is expected to increase. Finally, the fact that **4** did not undergo extensive oxidation to Pt^{IV} products in solvents that do not possess weak C−Cl bonds (e.g., MeOH, DMSO) offers further evidence in support of this mechanism.

The proposed mechanism suggests that the quantity of Pt^{IV} products formed should be dependent on the relative rate of recombination of the Pt^{III} radicals to produce **4** versus that of $Cl^{\bullet}$ abstraction from solvent. We anticipated that the latter process would be affected by changing the Cl atom source. As such, we compared the product ratio from the reaction of **4** in pure CH_2Cl_2 (C−Cl bond strength of CH_2Cl_2 = 84 kcal/mol) to that from the reaction of **4** in either a 1:3 mixture of $CHCl_3$:CH_2Cl_2 (C−Cl bond of $CHCl_3$ = 81 kcal/mol) or a 1:3 mixture of CCl_4:CH_2Cl_2 (C−Cl bond of CCl_4 = 73 kcal/mol).[26] (Notably, the 75% of remaining CH_2Cl_2 in these reactions was used to maintain an approximately constant dielectric medium as well as to ensure the solubility of **4**.) As summarized in Table 4, these reactions showed a clear trend in which the amount of Pt^{IV} products obtained increased as the homolytic bond strength of the cosolvent decreased, providing further evidence in support of the proposed mechanism.

Conclusions

In conclusion, we have described studies of reactions between $Pt^{II}(phpy)_2$ and two different electrophilic chlorinating reagents—$PhICl_2$ and *N*-chlorosuccinimide. Under a variety of different conditions, $PhICl_2$ reacted to afford isomers of $Pt^{IV}Cl_2(phpy)_2$ as the exclusive products. In contrast, *N*-chlorosucccinimide (NCS) provided mixtures of Pt^{III} and Pt^{IV} oxidation products, whose ratios varied as a function of time, concentration, and the presence/absence of light. The observed results can be rationalized based on a series of competing one- and two-electron oxidation reactions (often involving participation from the solvent) to afford both Pt^{III} and Pt^{IV} products. Importantly, while the reaction of $Pt^{II}(phpy)_2$ with $PhICl_2$ afforded similar products to that of its Pd^{II} analogue, the reaction with NCS proceeded very differently. As such, this work clearly demonstrates that analogies between Pt^{II} and Pd^{II} oxidation reactions should be made with caution, even when considering complexes with identical ligand environments under identical reaction conditions.

Experimental Section

General Considerations. NMR spectra were obtained on a Varian Inova 500 (499.90 MHz for ^1H; 125.70 MHz for ^{13}C) or a Varian Inova 400 (399.96 MHz for ^1H; 100.57 MHz for ^{13}C) spectrometer. ^1H NMR chemical shifts are reported in parts per million (ppm) with the residual solvent peak used as an internal reference. ^{195}Pt NMR spectra were obtained on a Varian Inova 500 (107.25 MHz for ^{195}Pt). ^{195}Pt chemical shifts are reported in parts per million (ppm) and were referenced by using the frequency of the lock signal and the estimated chemical shift of the solvent, DMF-d_7, according to IUPAC recommendations ($\Xi = 21.496784$).[27] Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), triplet of triplets (tt), multiplet (m), and broad resonance (br). IR spectra were obtained on a Perkin-Elmer "Spectrum BX" FT-IR spectrometer. Mass spectral data were obtained on a Micromass magnetic sector mass spectrometer.

Materials and Methods. K_2PtCl_4 was purchased from Pressure Chemical and *N*-chlorosuccinimide from Acros, and both were used as received. $PhICl_2$ was prepared from iodobenzene and Cl_2 according to a literature procedure.[28] $Pt^{II}(phpy)_2$ was synthesized from 2-(*o*-bromophenyl)pyridine[1a] and $PtCl_2(SEt_2)_2$[29] according to a published procedure.[5f] Solvents were obtained from Fisher Scientific and used without further purification. Unless otherwise noted, all reactions were carried out on the benchtop in the presence of ambient air and moisture.

Synthesis and Characterization of Unsymmetrical *cis*-$PtCl_2(phpy)_2$ (3a). $Pt^{II}(phpy)_2$ (100 mg, 0.20 mmol, 1.0 equiv) and $PhICl_2$ (60 mg, 0.22 mmol, 1.1 equiv) were combined in CH_2Cl_2 (10 mL) in a 20 mL vial. The vial was sealed with a Teflon-lined cap, and the reaction was stirred at room temperature for 12 h, during which time a pale yellow solid precipitated from solution. This solid (**3b**) was removed by filtration, the filtrate was concentrated, and hexanes (20 mL) was added to precipitate product **3a**. The pale yellow precipitate was collected by vacuum filtration, washed with hexanes (100 mL), and dried under vacuum to afford **3a** (73 mg, 64%). ^1H NMR (DMSO-d_6): δ 9.61 (d, J = 6 Hz, 1H), 8.50 (d, J = 8 Hz, 1H), 8.36–8.32 (multiple peaks, 2H), 8.07–7.98 (multiple peaks, 4H), 7.88 (m, 1H), 7.56 (d, J = 6 Hz, 1H), 7.48–7.41 (multiple peaks, 2H), 7.22 (m, 1H), 7.09 (m, 1H), 6.92 (m, 1H), 6.19 (d, J = 8 Hz, 1H). ^{13}C NMR (DMSO-d_6): δ 164.10, 160.79, 147.73, 147.06, 143.71, 141.91, 141.72, 141.46, 136.22, 132.03, 131.86, 131.62, 131.29, 131.26, 126.59, 126.47, 126.25, 126.10, 125.70, 125.55, 121.88, 121.77. ^{195}Pt NMR (DMF-d_7): δ −1725.62. FTIR (KBr, cm^{-1}) 3051, 1606, 1582, 1483, 1441, 1023. HRMS-electrospray (*m/z*): $[M - Cl_2]^+$ calcd for $C_{22}H_{16}N_2{}^{194}Pt$ 502.0940, found 502.0920. LRMS-electrospray (*m/z*): $[M]^+$ calcd for $C_{22}H_{16}N_2PtCl_2$ 572.03, found 572.0.

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Scheme 7. Proposed Mechanism for Reaction of 4 To Form Pt^{IV} Products

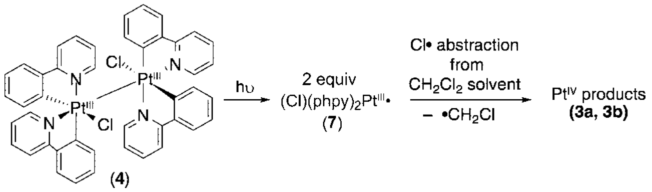

Table 4. Oxidation of 4 with Various Chlorinated Cosolvents[a]

entry	solvent	ratio of **4** to Pt^{IV} products **3a/3b**
1	CH_2Cl_2	2.50
2	1:3 $CHCl_3$:CH_2Cl_2	0.34
3	1:3 CCl_4:CH_2Cl_2	0.17

[a] Reactions were carried out in chlorinated solvents under dilute conditions (1.25 mM, 25 °C, 24 h, light). They were then evaporated to dryness and analyzed by ^1H NMR spectroscopy in DMSO-d_6. Ratios were determined by integration of the ^1H NMR signals associated with each product.

Synthesis and Characterization of Symmetrical $PtCl_2(phpy)_2$(3b). $Pt^{II}(phpy)_2$ (100 mg, 0.20 mmol, 1.0 equiv) and $PhICl_2$ (60 mg, 0.22 mmol, 1.1 equiv) were combined in CH_2Cl_2 (10 mL) in a 20 mL vial. The vial was sealed with a Teflon-lined cap, and the reaction was stirred at room temperature for 12 h during which time a pale yellow solid precipitated from solution. This precipitate was collected by filtration, washed with CH_2Cl_2 (50 mL) and hexanes (100 mL), and dried under vacuum to afford **3b** (33 mg, 29%) as a pale yellow powder. ^1H NMR (DMSO-d_6): δ 9.21 (d, $J = 6$ Hz, 2H), 8.45 (d, $J = 8$ Hz, 2H), 8.23 (m, 2H), 8.00 (d, $J = 6$ Hz, 2H), 7.76 (d, $J = 8$ Hz, 2H), 7.70 (m, 2H), 7.37 (m, 2H), 7.30 (m, 2H). Complex **3b** was not sufficiently soluble to obtain a ^{13}C NMR spectrum. FTIR (KBr, cm^{-1}): 3054, 1605, 1582, 1480, 1313, 1019. HRMS-electrospray (*m*/*z*): $[M - Cl_2]^+$ calcd for $C_{22}H_{16}N_2{}^{194}Pt$ 502.0918, found 502.0940. LRMS-electrospray (*m*/*z*): $[M]^+$ calcd for $C_{22}H_{16}N_2PtCl_2$ 572.03, found 572.0.

Synthesis and Characterization of Unsymmetrical $Pt^{III}{}_2Cl_2(phpy)_4$ (4). $Pt^{II}(phpy)_2$ (100 mg, 0.20 mmol, 1.0 equiv) and *N*-chlorosuccinimide (30 mg, 0.22 mmol, 1.1 equiv) were combined in CH_2Cl_2 (20 mL) in a 50 mL round-bottomed flask. The flask was sealed with a septum, and the reaction was stirred at room temperature for 24 h, during which time a yellow solid precipitated from solution. This precipitate was collected by filtration, washed with CH_2Cl_2 (25 mL) and hexanes (100 mL), and dried under vacuum to afford **4** (59 mg, 55%) as a bright yellow powder. The ^1H, ^{13}C, and ^{195}Pt NMR spectral data for **4** were in agreement with literature values.[6a]

Synthesis and Characterization of Symmetrical $Pt^{III}{}_2Cl_2(phpy)_4$ (5). Complex **4** (30 mg, 0.028 mmol) was dissolved in MeOH (6 mL) in a 20 mL vial. The vial was sealed with a Teflon-lined cap, and the reaction was heated at 100 °C for 24 h. The reaction mixture was concentrated to approximately 1 mL and then diethyl ether (20 mL) was added to precipitate the product. The precipitate was collected by vacuum filtration, washed with hexanes (50 mL), and dried under vacuum to afford **5** (13 mg, 43%) as a dark yellow powder. ^1H NMR (DMSO-d_6): δ 8.52 (d, $J = 8.5$ Hz, 4H), 8.23 (t, $J = 8.5$ Hz, 4H), 8.11 (d, $J = 8$ Hz, 4H), 7.72 (d, $J = 5.5$ Hz, 4H), 7.49 (m, 4H), 7.29 (m, 4H), 7.10 (m, 4H), 6.47 (d, $J = 8$ Hz, $J_{Pt-H} = 22$ Hz, 4H). ^{13}C NMR (DMSO-d_6): δ 162.09, 147.57, 142.46, 142.06, 133.01, 131.77, 127.22, 126.67, 125.24, 122.64, 120.43. ^{195}Pt NMR (DMF-d_7): δ −2293.50. FTIR (KBr, cm^{-1}): 2348, 1658, 1606, 1550, 1529, 1483, 1441. HRMS-electrospray (*m*/*z*): $[(Cl)(phpy)_2Pt]^+$ calcd for $C_{22}H_{16}N_2{}^{194}PtCl$ 538.0649, found 538.0628.

General Procedure for Reactions in Tables 1−4 (light). $Pt^{II}(phpy)_2$ (5 mg, 0.01 mmol, 1.0 equiv) and NCS (1.5 mg, 0.011 mmol, 1.1 equiv) were combined in CH_2Cl_2 (1 mL) in a 4 mL clear vial. The vial was sealed with a Teflon-lined cap, and the reaction was stirred at room temperature. The solvent was removed under vacuum, and the resulting crude solids were redissolved in DMSO-d_6 (1 mL) and analyzed by ^1H NMR spectroscopy. The yields of each product were calculated by integration of characteristic ^1H NMR resonances relative to an internal standard.

General Procedure for Reactions in Tables 1−4 (dark). $Pt^{II}(phpy)_2$ (5 mg, 0.01 mmol, 1.0 equiv) and NCS (1.5 mg, 0.011 mmol, 1.1 equiv) were combined in a 4 mL amber vial, which was subsequently covered with aluminum foil. All lights in the immediate vicinity were turned off and CH_2Cl_2 (1 mL) was added. The vial was rapidly sealed with a Teflon-lined cap, and the reaction was stirred at room temperature. The solvent was removed under vacuum, and the resulting crude solids were redissolved in DMSO-d_6 (1 mL) and analyzed by ^1H NMR spectroscopy. The yields of each product were calculated by integration of characteristic ^1H NMR resonances relative to an internal standard.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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