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Aromatic C–H Activation in the Triplet Excited State of Cyclometalated Platinum(II) Complexes Using Visible Light

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ABSTRACT: The visible-light driven cyclometalation of arene substrates containing an *N*-donor heteroaromatic moiety as directing group by monocyclometalated Pt(II) complexes is reported. Precursors of the type [PtMe(C^N)(N^CH)], where N^CH is 2-phenylpyridine (ppyH) or related compunds with diverse electronic properties and C^N is the corresponding cyclometalated ligand, afford homoleptic *cis*-[Pt(C^N)$_2$] complexes upon irradiation with blue LEDs at room temperature with evolution of methane. Heteroleptic derivatives *cis*-[Pt(ppy)(C'^N')] are obtained analogously from [PtMe(ppy)(N'^C'H)], where N'^C'H represents an extended set of heteroaromatic compounds. Experimental and computational studies demonstrate an unprecedented C–H oxidative addition, which is initiated by a triplet excited state of metal-to-ligand charge-transfer (MLCT) character and leads to a detectable Pt(IV) methyl hydride intermediate.

INTRODUCTION

Photochemical methods often provide access to transformations that are not possible using conventional, thermal synthetic procedures, because the reactivities of electronically excited molecules are usually very different to those in the ground state.[1] Thus, photoexcited species are highly energetic and can follow reaction paths that would require insurmountable activation barriers from the ground state. In addition, they often lead to radical intermediates that are not attainable in thermal reactions without the use very toxic and/or unstable initiators.[2] Visible-light driven reactions add also the key benefit of using a sustainable and harmless source of energy. These advantages have propelled the photochemistry of organic and inorganic compounds for decades.[1] In particular, the photochemistry of transition metal complexes witnessed a tremendous expansion since the realization that their long-lived triplet excited states can participate in bimolecular single electron-transfer (SET) reactions,[3] which opened the way to the development of light-mediated catalytic transformations. This principle is currently being successfully applied in organic photoredox catalysis.[4]

Mechanistic studies on C–H bond activation reactions at metal centers have concentrated extraordinary efforts, associated with the development of economical synthetic strategies for the formation of C–C and C–heteroatom bonds from readily available substrates.[5] Most commonly, the C–H bond cleavage event occurs through electrophilic substitution, sigma-bond metathesis or oxidative addition mechanisms. The latter is typically prevalent in electron-rich complexes of low-valent metal ions, such as Rh(I), Ir(I) or Pt(II), since it requires a two-electron oxidation of the metal. The application of photochemical reaction conditions has been prolific in this field,[6] particularly since the discovery that late transition-metal complexes are capable of activating alkane C–H bonds upon irradiation with ultraviolet light.[7] In these systems, the excited-state reactivity is limited to the dissociation of ancillary ligands from the metal complex to generate a coordinatively unsaturated intermediate, whereas the subsequent coordination and cleavage of the C–H bond occur in the electronic ground state, generally through an oxidative addition mechanism.

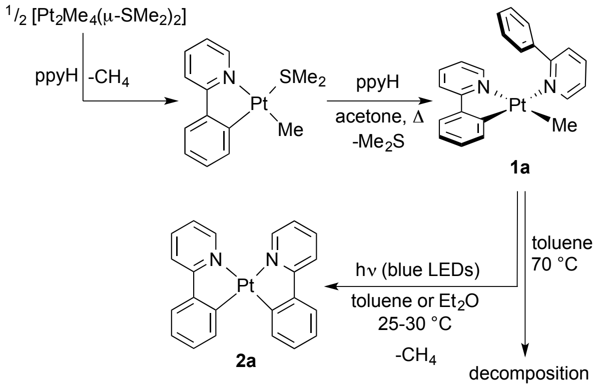
Pt(II) complexes with cyclometalated heteroaromatic ligands, such as 2-arylpyridines and related C^N ligands, continue to attract considerable research efforts because of the wide technological applicability of their luminescence, including the development of electroluminescent devices for lighting and display applications,[8] probes for bioimaging,[9] and chemosensors.[10] Complexes of this class exhibit triplet excited states of mixed ligand-centred/metal-to-ligand charge-transfer character (^{3}LC/MLCT), which are usually capable of producing efficient luminescence thanks to the spin-orbit coupling effects induced by the metal.[11] In addition, photochemical studies have shown that triplet excited states of MLCT character in Pt(II) complexes can engage in electron-transfer reactions to halocarbon compounds, finally resulting in C–halogen bond oxidative additions.[12] However, analogous photoinduced oxidative additions of C–H bonds to Pt(II) complexes have never been reported.

Herein, we present the synthesis of homoleptic *cis*-[Pt(C^N)$_2$] complexes and heteroleptic *cis*-[Pt(ppy)(C'^N')] derivatives (ppy = cyclometalated 2-phenylpyridine) at room temperature *via* visible-light irradiation of precursors of the type [PtMe(C^N)(N^CH)] or [PtMe(ppy)(N'^C'H)], where N^CH or N^'C'H are aromatic compounds containing an *N*-donor heteroaromatic directing group, and C^N or C'^N' are the corresponding cyclometalated forms. The combined experimental and computational data show that the cyclometalation reaction is initiated by a triplet excited state of MLCT character and involves a C–H oxidative addition resulting in the formation of a Pt(IV) methyl hydride intermediate. This process differs fundamentally from the traditional, ground-state oxidative addition of C–H bonds and has no precedent in metal-mediated C–H activations.

RESULTS AND DISCUSSION

Photochemical synthesis of bis-cyclometalated Pt(II) complexes. The most widely employed method for the synthesis of complexes of the type *cis*-[Pt(C^N)$_2$] involves the use *ortho*-lithiated C^N ligands, generated from the corresponding bromo-compounds, typically resulting in low yields.[13] More recently, some authors have reported synthetic procedures based on C–H activation reactions of certain ligands at high temperatures.[14] In search for a more convenient and general procedure, we explored alternative methods starting from the binuclear complex [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$],[15] which readily reacts with 2-phenylpyridine (ppyH) or other N^CH compounds at room temperature to give cyclometalated complexes of the type [PtMe(C^N)(SMe$_2$)] and methane (Scheme 1); the labile Me$_2$S ligand can be easily replaced by a variety of other ligands, allowing further derivatization.[16] We have recently shown that the complex [PtMe(ppy)(ppyH)] (**1a**) can be easily obtained by reacting [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] with excess ppyH[17] (Scheme 1). However, the cyclometalation of the coordinated ppyH ligand did not occur thermally, since **1a** is stable in refluxing acetone, whereas heating at 70 °C in toluene under N$_2$ atmosphere resulted in total decomposition. In contrast, irradiation of toluene-*d*$_8$ solutions of **1a** with a household fluorescent lamp or blue LEDs (wavelength range: 420-500 nm) at room temperature resulted in a clean conversion to *cis*-[Pt(ppy)$_2$] (**2a**) with evolution of methane. This reaction can also be carried out in Et$_2$O, which was chosen for preparative-scale synthesis.

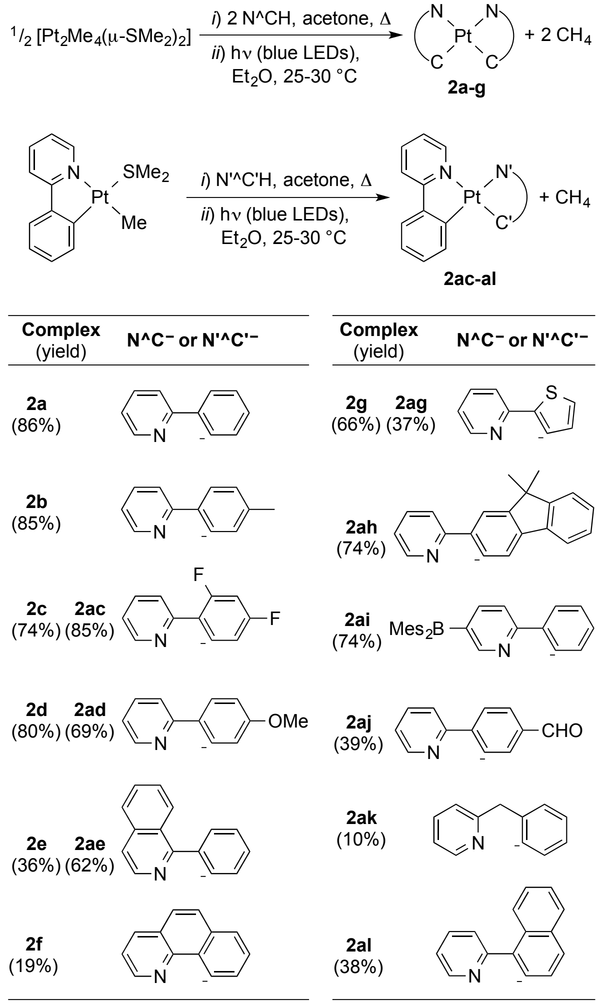
Scheme 1. Exploratory work for the synthesis of bis-cyclometalated Pt(II) complexes from [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$]



$^1/_2$ [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$]
ppyH
-CH$_4$
N
SMe$_2$
Pt
Me
ppyH
acetone, Δ
-Me$_2$S
N
N
Pt
Me
1a
toluene
70 °C
decomposition
hν (blue LEDs)
toluene or Et$_2$O
25-30 °C
-CH$_4$
N
N
Pt
2a

We then optimized a one-pot procedure for the preparation of **2a** from [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] in two steps, *i.e.*, the generation of **1a** in refluxing acetone for 4 h, followed by irradiation with blue LEDs in Et$_2$O at 25-30 °C for 24 h. This methodology was subsequently employed for the preparation of a series of homoleptic bis-cyclometalated complexes with heteroaromatic C^N ligands of different electronic properties (**2a-g**, Scheme 2).

Scheme 2. One-pot photochemical syntheses of homoleptic and heteroleptic bis-cyclometalated Pt(II) complexes and ligand scope[a]



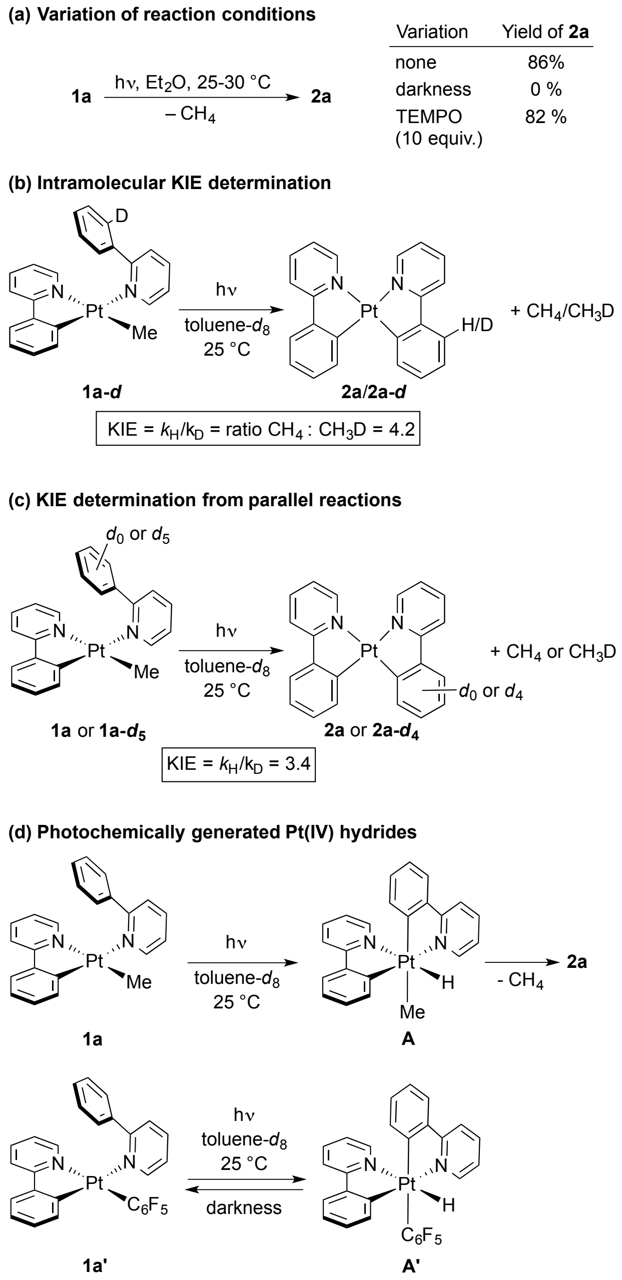
$^1/_2$ [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$]
i) 2 N^CH, acetone, Δ
ii) hν (blue LEDs), Et$_2$O, 25-30 °C
N
N
Pt
C
C
+ 2 CH$_4$
2a-g
N
SMe$_2$
Pt
Me
i) N'^C'H, acetone, Δ
ii) hν (blue LEDs), Et$_2$O, 25-30 °C
N
N'
Pt
C'
+ CH$_4$
2ac-al
Complex (yield)
N^C⁻ or N'^C'⁻
2a (86%)
2b (85%)
2c 2ac (74%) (85%)
F
F
2d 2ad (80%) (69%)
OMe
2e 2ae (36%) (62%)
2f (19%)
Complex (yield)
N^C⁻ or N'^C'⁻
2g 2ag (66%) (37%)
S
2ah (74%)
2ai (74%)
Mes$_2$B
2aj (39%)
CHO
2ak (10%)
2al (38%)
N

[a]Yields refer to the isolated product. Abbreviation: Mes = mesityl or 2,4,6-trimethylphenyl.

To further study the scope of this reaction, we explored the use of complex [PtMe(ppy)(SMe$_2$)][16a] as a platform for the photochemical cyclometalation of an extended set of heteroaromatic compounds. For this purpose, complexes of the type [PtMe(ppy)(N'^C'H)] were generated and irradiated *in situ* using blue LEDs at 25-30 °C. Heteroleptic bis-cyclometalated complexes of the type *cis*-[Pt(ppy)(C'^N')] were thus obtained, generally in moderate to good yields (**2ac-al**, Scheme 2). The metalated moiety in the N'^C'H compounds may be a symple aryl or heteroaryl group, a fused ring system or a benzyl group, and may contain electron-withdrawing or -donating substituents. It is also noteworthy that the photochemical cyclometalation is compatible with sensitive functional groups on the aryl or pyridyl group, such as diarylboranyl or formyl, as demonstrated by the successful synthesis of complexes **2ai** and **2aj**. In the case of the naphthylpyridine ligand, two different C–H bonds of the naphthyl group may in principle be activated, which can lead to 5- or 6-membered cycles, as has been shown by previous works;[18] in our case, the photochemical cyclometalation regioselectively leads to the 5-membered cycle (complex **2al**). The preference for this ring size is common in cyclometalated complexes,[19] and may be in part responsible for the low yield in the photochemical cyclometalation of 2-benzylpyridine (complex **2ak**). The low yield in complex **2f** is caused by the hindered coordination of the benzo[*h*]quinoline (bzqH) ligand under the mentioned one-pot reaction conditions. This was verified by a NMR check of the crude reaction mixture before irradiation, which showed only a 37% conversion to the intermediate complex [PtMe(bzq)(bzqH)] (**1f**). The reaction of [PtMe(ppy)(SMe_2)] with bzqH resulted in ligand scrambling, leading to a mixture of *cis*-[Pt(ppy)(bzq)] (**2af**), **2a** and **2f** in low yield. We note that no ligand scrambling was observed during the preparation of the rest of heteroleptic derivatives. In contrast, complex **2af** was obtained in 62% yield starting from [PtMe(bzq)(SMe_2)] and ppyH (see Supporting Information for further details). We also attempted the photochemical cyclometalation of benzylamine (bzaH). However, in this case the complex [PtMe(ppy)(bzaH)] (**1am**) was obtained in 94% yield after irradiation and no cyclometalation product was detected, suggesting that a π-accepting *N*-donor moiety is required in these photochemical reactions.

Study of the reaction mechanism. A series of experiments were carried out to gain insight into the mechanism of the cyclometalation reactions (Scheme 3). Their photochemical nature was confirmed by the fact that they do not take place in the dark. Reaction quantum yields were determined for the photochemical reaction of **1a** in Et_2O by irradiating at 436 nm and found to decrease with temperature (2.1±0.2% at 25 °C, 1.7±0.2% at 0 °C and 1.2±0.1% at –20 °C), which may indicate the existence of a thermal activation barrier after photoexcitation. Deuterium kinetic isotope effect (KIE) determinations were carried out from two different experiments. An intramolecular H/D competition experiment was performed by irradiating complex [PtMe(ppy)(ppyH-*d*)] [**1a-*d***; ppyH-*d* = 2-(phenyl-2-*d*)pyridine] with blue LEDs in degassed toluene-d_8 (Scheme 3b); the ratio of the evolved CH_4 and CH_3D was measured at different reaction times, yielding a KIE of 4.2 (k_H/k_D; Figure S4). The comparison of the initial rates of the photochemical cyclometalation reactions of **1a** and [PtMe(ppy)(ppyH-d_5)] [**1a-*d*₅**; ppyH-d_5 = 2-(phenyl-d_5)pyridine] carried out in parallel in toluene-d_8 yielded a KIE of 3.4 (Scheme 3c; Figure S5). These large primary KIEs demonstrate that the rate-limiting step involves the cleavage of the C–H bond[20] and also rule out an electrophilic aromatic substitution (S_EAr) mechanism, in which the rate-limiting step would be the formation of an arenium intermediate.[5b] The possibility of a radical mechanism was checked by performing the photoreaction of **1a** in the presence of 10 equivalents of the radical scavenger TEMPO (2,2,6,6-tetramethylpiperinidoxyl); however, the reaction was not affected and **2a** was obtained in 82% yield, which rules out the involvement of free radicals.[21]

Scheme 3. Mechanistic experiments



Variation	Yield of **2a**
none	86%
darkness	0 %
TEMPO (10 equiv.)	82 %

(a) Variation of reaction conditions
1a
hν, Et2O, 25-30 °C
– CH4
2a
(b) Intramolecular KIE determination
D
N
Pt
N
Me
hν
toluene-d8
25 °C
H/D
+ CH4/CH3D
1a-d
2a/2a-d
KIE = kH/kD = ratio CH4 : CH3D = 4.2
(c) KIE determination from parallel reactions
d0 or d5
+ CH4 or CH3D
d0 or d4
1a or 1a-d5
2a or 2a-d4
KIE = kH/kD = 3.4
(d) Photochemically generated Pt(IV) hydrides
H
- CH4
2a
1a
A
C6F5
darkness
1a'
A'

These results, together with the observed photoreactivity of previously reported Pt(II) complexes,[12] led us to hypothesize that an oxidative C–H addition could be operative, which would result in the formation of a Pt(IV) methyl hydride intermediate. To test this hypothesis, a solution of **1a** in toluene-d_8 at room temperature was irradiated with blue LEDs for 5 minutes and its ^1H NMR spectrum was immediately registered. Signals arising from a new complex (**A**) were then observed besides those of **1a** and **2a**. In particular, a singlet at 0.57 ppm (J_{HPt} = 41 Hz) corresponding to a methyl ligand, and another one at –17.44 ppm (J_{HPt} = 1410 Hz) corresponding to a hydride ligand, with intensities in a 3:1 ratio, allowed us to identify complex **A** as the expected Pt(IV) methyl hydride (Figures S6-9). In order to confirm its role as an intermediate in the photochemical synthesis of **2a**, we monitored the changes in the ^1H NMR spectra at room temperature in the dark; under these conditions, its signals gradually disappeared, as those of **2a** increased. Pt(IV) alkyl hydrides have been the subject of numerous studies due to their involvement in C–H activation reactions of alkanes by Pt(II) complexes.[5a,22] These species are highly unstable because they easily undergo C–H reductive elimination of alkanes. In fact, in most cases they have only been detected in solution at low temperatures, while the isolation and structural characterization of some of them has required the use of ancillary ligands that do not dissociate easily.[23] Pt(IV) alkyl hydride intermediates have also been proposed in cyclometalation reactions using electron-rich Pt(II) complexes, although in these cases they have never been detected.[24] To the best of our knowledge, these results represent the first direct detection of a Pt(IV) hydride intermediate in a cyclometalation reaction of a Pt(II) complex. The detection of intermediate **A** demonstrates that the formation of **2a** takes place in two steps, *i.e.*, the photochemical oxidative addition of the C–H bond of the ppyH ligand, and then a thermal (ground-state) reductive elimination of methane.

With the aim of obtaining a stable and isolable Pt(IV) hydride, we attempted the photochemical reaction of the pentafluorophenyl analogue of complex **1a**, [Pt(C_6F_5)(ppy)(ppyH)] (**1a'**), in the expectation that the reductive elimination of pentafluorobenzene would be precluded by a higher activation energy compared to the methyl derivative.[25] To our delight, irradiation of a solution of **1a'** in toluene-d_8 resulted in the gradual consumption of the starting material and formation a new compound (**A'**), whose NMR resonances indicate the presence of two inequivalent cyclometalated ppy ligands, one C_6F_5 and a hydride ligand (Figures S10 and S11). Complex **A'** was observed to slowly revert to **1a'** *via* C–H reductive elimination of the phenyl group at room temperature. In fact, the complete reversion was observed after heating at 50 °C for 1 h. For this reason, complete conversions to **A'** could not be achieved and all attempts to isolate this complex were unsuccessful. A rigorous NMR data analysis allowed the isomer assignment of **A** and **A'** (Supporting Information), which demonstrates that they result from a *cis* oxidative addition of the *ortho* C–H bond of the phenyl group of the ppyH ligand (Scheme 3d).

Lowest-energy excited states in complexes 1. In order to investigate the processes that take place upon light absorption and the role of the non-cyclometalated N^CH ligand, the lowest-energy excited states of two compounds of the type [PtMe(ppy)(N^CH)] [N^CH = ppyH (**1a**), bzaH (**1am**)] were analysed by means of electronic absorption and emission spectroscopy and density functional theory (DFT) and time-dependent DFT (TDDFT) calculations at the B3LYP/(6-31G**+LANL2DZ) level. The absorption spectra of both complexes in Et_2O solution are very similar and display two broad bands in the visible region centered at around 380 and 400 nm and a tail extending to *ca.* 500 nm (Figure 1). These bands exhibit solvatochromic behaviour (Figure S13), which demonstrates their charge-transfer character.[26] They cleary originate from the Pt(ppy) subunit common to both complexes and can be ascribed to singlet LC/MLCT excitations involving π* orbitals of the cyclometalated ppy ligand, which are usually observed for ppy-containing Pt(II) derivatives.[11a] The TDDFT calculations in Et_2O are in good agreement with the experimental data (Tables S3 and S6), predicting two singlet excitations from a combination of metal d orbitals and π orbitals of the ppy ligand to π* orbitals of the same ligand [π(ppy)/d(Pt) → π*(ppy) or LC/MLCT] as the dominant absorptions in the visible region for **1a** and the only ones for **1am**. Two additional singlet excitations of significantly lower intensities are predicted for **1a**, from the same π(ppy)/d(Pt) orbital to π* orbitals of the non-metalated ppyH ligand [π(ppy)/d(Pt)→ π*(ppyH)], but they must be obscured in the experimental absorption spectrum. Therefore, irradiation of complexes **1** with blue LEDs populates states of significant MLCT character involving electronic promotions to π*(ppy) or π*(ppyH) orbitals in **1a**, but only to π*(ppy) orbitals in **1am**.

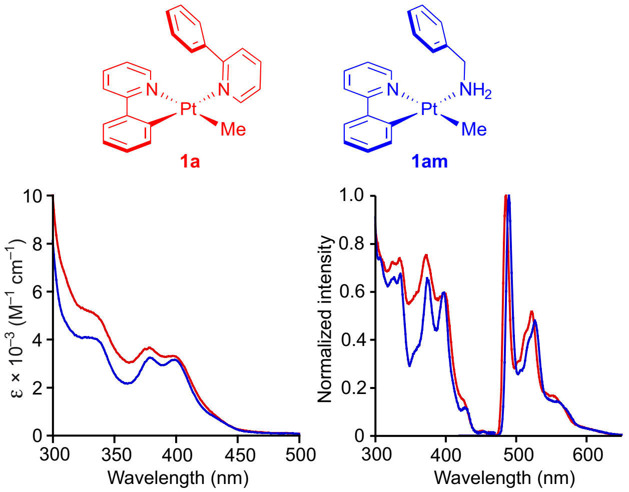


Figure 1. Absorption spectra of **1a** and **1am** in Et_2O at 298 K (left) and excitation/emission spectra in 2-methyltetrahydrofuran at 77 K (right).

Following photoexcitation, very fast intersystem crossing to the triplet manifold must occur, because of the strong spin-orbit coupling induced by the platinum atom.[11c] The observed photoreactivity is thus expected to occur from the lowest triplet excited states, which are usually long lived and can reach thermal equilibrium. The emission spectra of **1a** and **1am** were thus registered to shine light on the nature of their lowest triplet-excited state. In both cases the emissions in deaerated Et_2O solution at 298 K are very weak and the recorded excitation spectra do not match the absorption profiles adequately, suggesting the formation of photoproducts and/or fast non-radiative deactivation. In order to reduce the possible photochemical reactivity and obtain reliable data, the emission spectra were registered in glassy 2-methyltetrahydrofuran at 77 K. Both complexes give rise to very similar, vibrationally structured emissions in this medium (Figure 1), with the highest energy peak at 486 (**1a**) or 490 (**1am**) nm and radiative lifetimes (τ) of 8.0 (**1a**) or 7.3 (**1am**) μs. These emissions are practically identical to those found for other monocyclometalated Pt(II) complexes with ppy,[11a] which have been assigned to a ^{3}LC/MLCT emissive state centered on the Pt(ppy) subunit. The same assignment is thus appropriate for **1a** and **1am**, indicating that the coordinated N^CH ligand is not involved in the lowest triplet excited state.

The calculations correctly predict the nature of the lowest (emissive) triplet excited state in **1a** and **1am**. Thus, the TDDFT results show that the first triplet vertical excitation at the ground-state geometry corresponds to a π(ppy)/d(Pt) → π*(ppy) electronic promotion (^{3}LC/MLCT) in both cases. To model the relaxed, thermally equilibrated state and obtain a more accurate characterization, geometry optimizations were carried out by spin-unrestricted DFT calculations. The optimized geometry of the lowest triplet of **1a** (**1a-T**$_1$) is shown in Figure 2 along with the lowest and highest singly-occupied molecular orbital isosurfaces (LSOMO and HSOMO, respectively), which agree with the topology of the mentioned electronic promotion. The structural variations in the relaxed **1a-T**$_1$ state with respect to the ground state affect only the cyclometalated ppy ligand, consistent with the population of its lowest π* orbital (Table S4). Analogous results were obtained for **1am-T**$_1$.

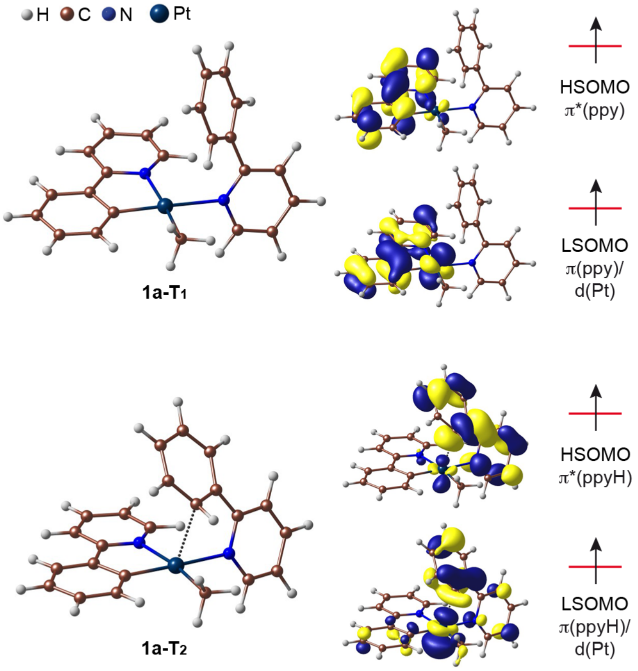


Figure 2. Optimized structures of the two lowest triplet excited states of **1a** and corresponding LSOMO and HSOMO isosurfaces (0.04 e bohr^{-1}).

The second triplet vertical excitation in **1a** corresponds to a π(ppy)/d(Pt) → π*(ppyH) transition and, in contrast to **1a-T**$_1$, the optimization of its geometry led to profound structural changes with respect to the ground state (**1a-T**$_2$, Figure 2). The most striking feature of the relaxed **1a-T**$_2$ structure is an interaction between an *ortho* carbon atom of the phenyl moiety of the ppyH ligand and the metal (Pt–C distance: 2.429 Å), which leads to an intermediate hybridization between sp^2 and sp^3 of this carbon and a partial loss of aromaticity within the phenyl ring. The structural relaxation is accompained by a reorganization of the LSOMO, which becomes essentially a π(ppyH)/d(Pt) orbital, while the HSOMO remains a π*(ppyH) orbital. The relaxed **1a-T**$_2$ state possesses a significant MLCT character, consistent with the calculated natural charge over the ppyH ligand (–0.33), which varies by –0.46 with respect to the ground state (+0.13) as the natural charge on the Pt atom increases by +0.39 (Table S10). As a consequence, the ppyH ligand is partially reduced, acquiring some character of radical anion, while the metal is partially oxidized. The Pt–C interaction can thus be understood as an incipient η^1-coordination of the phenyl moiety of the ppyH ligand to the electron-deficient metal center. The geometry and charge distribution found in **1a-T**$_2$ clearly indicate that it constitutes the starting point of the cyclometalation reaction. It is also a state that can be very easily populated from **1a-T**$_1$ by thermal energy because it lies only slightly higher in energy (3.5 kcal/mol in free energy; Figure 3). It is worth to note that the formation of **1a-T**$_2$ can be formally considered the result of an intramolecular SET to the ppyH ligand under mild conditions and is in sharp contrast with the previously reported aromatic C–H activations initiated by SET events, which generally proceed *via* oxidation of the arene and often require high temperatures.[27]

In contrast to **1a**, the lowest triplet charge-transfer vertical excitation to a π* orbital of the benzylamine ligand in **1am** was found to lie at a significantly higher energy relative to the first triplet excitation and correspond to T$_6$ (Table S7). Although a geometry optimization of this state was not succsessful, a possible reactive state of **1am** (**1am-T**$_\mathbf{R}$) was optimized on the basis of the geometry of **1a-T**$_2$, and found to lie 14.0 kcal/mol higher in free energy relative to **1am-T**$_1$ (Figure 3). The extra energy required to populate **1am-T**$_\mathbf{R}$ may explain why the photochemical cyclometalation of the benzylamine ligand does not proceed under the conditions described for **1a** and is consistent with our assumption that **1a-T**$_2$ is the reactive state in **1a**.

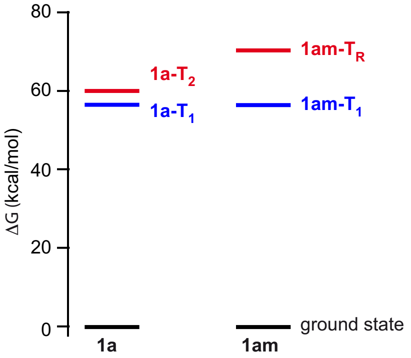
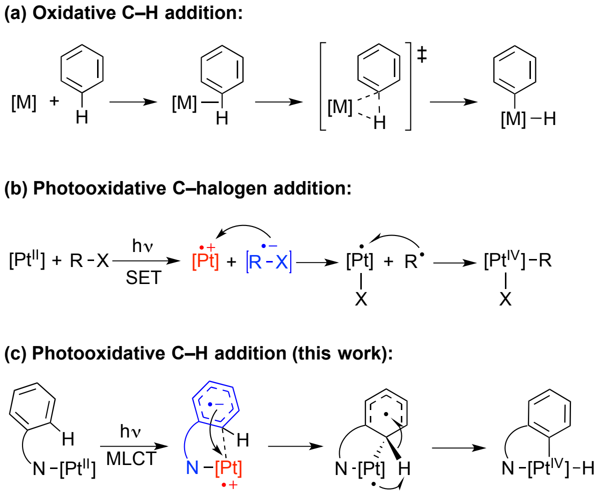


Figure 3. Free energies of the optimized triplet excited states of **1a** and **1am** relative to the respective ground states.

Proposed photooxidative C–H addition mechanism. The established ground-state oxidative addition mechanism in metal mediated C–H activations usually requires the formation of an agostic intermediate (Scheme 4a), after which the oxidative addition occurs in a concerted fashion.[5a] However, the Pt–C interaction and partial oxidation of the metal found in **1a-T**$_2$ clearly indicate a fundamentally different mechanism for the reactions studied in this work. Our proposal is outlined in Scheme 4c. The formation of the hydride intermediate **A** from **1a-T**$_2$ must involve the strengthening of the Pt–C interaction, which may occur through the full donation of an electron pair from the ppyH radical anion. This would lead to the loss of aromaticity on the phenyl ring, as already anticipated by the structure of **1a-T**$_2$. Rearomatization should then occur *via* homolytic C–H bond cleavage and subsequent hydrogen atom transfer to the metal, leading to the hydride intermediate **A**. This mechanism resembles that of the previously reported photooxidative additions of C–halogen bonds to Pt(II) complexes, involving the reduction of the substrate to give a radical anion and its addition to the metal center (Scheme 4b).[12d]

Scheme 4. Mechanisms of ground-state C–H oxidative addition, photooxidative C–halogen addition and proposed photooxidative C–H addition



CONCLUSIONS

The photochemical reaction here presented provides a very general method for the cyclometalation of aromatic compounds containing an *N*-donor heteroaromatic moiety as directing group, starting from a common Pt(II) precursor and using visible light at room temperature. Experimental and computational studies support an unprecedented C–H activation involving a charge transfer to the coordinated aromatic compound, which acquires some character of radical anion and becomes capable of attacking the metal through the *ortho* carbon atom. A Pt(IV) methyl hydride intermediate is then produced, the first detected in a cyclometalation reaction in Pt(II) compounds, which undergoes C–H reductive elimination of methane to afford bis-cyclometalated complexes. Despite being a formal oxidative addition, this photochemical C–H activation is fundamentally different from the traditional ground-state pathway and clearly exemplifies the often disparate behavior of chemical species in the ground and electronically excited states. We expect that further studies on the photochemistry of transition metal complexes will exploit similar methodologies to develop catalytic C–H activation/functionalization reactions using visible light.

EXPERIMENTAL SECTION

General reaction conditions, synthetic procedures for [PtMe(bzq)(SMe$_2$)] and **2af** and characterization data of new compounds are given in the Supporting Information.

Syntheses of [PtMe(ppy)(N'^C'H)] [N'^C'H = 2-(phenyl-2-*d*)pyridine (1a-*d*), 2-(phenyl-*d*$_5$)pyridine (1a-*d*$_5$), or benzylamine (1am)]. To a suspension of [PtMe(ppy)(SMe$_2$)] (148 mg, 0.35 mmol) in acetone (**1a-*d***, **1a-*d*$_5$**) or CH$_2$Cl$_2$ (**1am**) (10 mL) was added the corresponding N'^C'H ligand (0.70 mmol) and the mixture was refluxed (**1a-*d***, **1a-*d*$_5$**) or stirred at room temperature (**1am**) for 4 h. The solvent was removed under reduced pressure and the residue was subjected to three successive dissolution/evaporation cycles using acetone (20 mL) to ensure the removal of Me$_2$S. Treatment with Et$_2$O (10 mL) and *n*-pentane (80 mL) led to the precipitation of a yellow solid, which was filtered off, washed with *n*-pentane (10 mL) and vacuum-dried.

Synthesis of [Pt(C$_6$F$_5$)(ppy)(ppyH)] (1a'). This one-pot procedure is based on previously reported reactions leading to complexes of the type [Pt(C$_6$F$_5$)(C^N)(N^CH)].[28] To a suspension of *cis*-[Pt(C$_6$F$_5$)$_2$(dmso)$_2$)] (409 mg, 0.60 mmol) in toluene (15 mL) was added ppyH (0.30 mL, 2.10 mmol) and the mixture was refluxed for 20 h. The solvent was removed under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$ (10 mL). The addition of *n*-pentane (50 mL) led to the precipitation of pale greenish-yellow solid that was filtered off, washed with *n*-pentane (5 mL) and Et$_2$O (5 mL) and vacuum-dried to give **1a'**.

Photochemical synthesis of homoleptic complexes 2a-g and heteroleptic complexes 2ac-al. To a solution of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (100 mg, 0.17 mmol) (homoleptic complexes) or [PtMe(ppy)(SMe$_2$)] (150 mg, 0.35 mmol) (heteroleptic complexes) in acetone (10 mL) was added the appropriate N^CH (1.04 mmol, homoleptic complexes) or N'^C'H ligand (0.70 mmol, heteroleptic complexes) and the mixture was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was subjected to three successive dissolution/evaporation cycles using acetone (20 mL) to ensure the removal of Me$_2$S, and then washed with *n*-pentane (10 mL). Deoxygenated Et$_2$O (60 mL) was then added under a N$_2$ atmosphere and the resultant suspension was irradiated with blue LEDs for 24 h with vigorous stirring. The solvent was evaporated, the residue dissolved in the minimum amount of CH$_2$Cl$_2$ and the solution passed through silica gel in a short chromatography column, using CH$_2$Cl$_2$ or a 20:1 (v/v) CH$_2$Cl$_2$/AcOEt mixture as the eluent, until the yellow or orange solution was completely collected. The solvent was removed under reduced pressure and the resultant solid was washed with Et$_2$O (5 mL) and vacuum-dried to give the corresponding complex **2**.

Computational methods. DFT calculations were carried out with the Gaussian 09 package,[29] using the hybrid B3LYP functional[30] together with the 6-31G**[31] basis set for the main-group elements and the LANL2DZ[32] basis set and its associated relativistic effective core potential for the platinum atom. The B3LYP functional was chosen for its good accuracy in the prediction of excited-state energies of transition-metal complexes through TDDFT.[33] All geometry optimizations were carried out without symmetry restrictions, using "tight" convergence criteria and "ultrafine" integration grid. Vertical excitation energies were obtained from TDDFT calculations at the ground-state optimized geometries. The solvent effect (Et$_2$O) was accounted for in all cases by using the integral equation formalism variant of the polarizable continuum solvation model (IEFPCM).[34] Triplet-state geometry optimizations were carried out following a two-step strategy.[35] Initially, TDDFT optimizations of the lowest 3 or 4 states were attempted starting from the ground-state geometry. The resulting geometries were then subjected to spin-unrestricted DFT (UB3LYP) optimizations setting a triplet multiplicity. This strategy was successful for the two first triplets (T$_1$ and T$_2$) of **1a** and the first triplet of **1am**, while optimizations of higher-lying states failed because the calculations collapsed to either the T$_1$ or T$_2$ geometries. The optimized structures were confirmed as minima on the potential energy surface by computing the full Hessian (zero negative eigenvalues). Natural atomic charges and spin densities were obtained from natural population analyses using the NBO 5.9 program.[36]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

> General reaction conditions, starting materials, experimental setup for irradiations, spectroscopic and analytical methods, determination of reaction quantum yields, characterization data of new compounds, details on KIE experiments, detection of Pt(IV) hydrides, additional computational data and analysis (PDF).

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Notes

The authors declare no competing financial interest.

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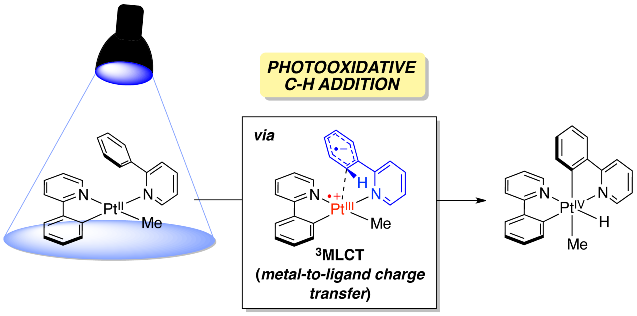
TOC Graphic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