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Visible light driven generation and alkyne insertion reactions of stable bis-cyclometalated Pt(IV) hydrides†

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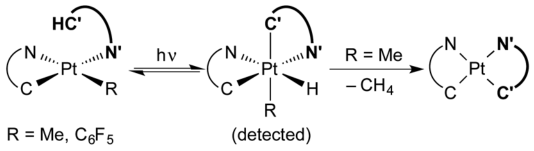
Hydride complexes resulting from the oxidative addition of C–H bonds are intermediates in hydrocarbon activation and functionalization reactions. The discovery of metal systems that enable their direct formation through photoexcitation with visible light could lead to advantageous synthetic methodologies. In this study, easily accessible dimers $[Pt_2(\mu\text{-}Cl)_2(C^\wedge N)_2]$ ($C^\wedge N$ = cyclometalated 2-arylpyridine) are demonstrated as a very convenient source of Pt($C^\wedge N$) subunits, which promote photooxidative C–H addition reactions with different 2-arylpyridines ($N'^\wedge C'H$) upon irradiation with blue light. The resulting $[PtH(Cl)(C^\wedge N)(C'^\wedge N')]$ complexes are the first isolable Pt(IV) hydrides arising from a cyclometalation reaction. A transcyclometalation process involving three photochemical steps is elucidated, which occurs when the $C^\wedge N$ ligand is a monocyclometalated 2,6-diarylpyridine, and a detailed analysis of the photoreactivity associated with the Pt($C^\wedge N$) moiety is provided. Alkyne insertions into the Pt–H bond of a photogenerated Pt(IV) hydride are also reported as a demonstration of the ability of this class of compounds to undergo subsequent organometallic reactions.

Introduction

Transition metal hydride complexes are key intermediates in numerous catalytic transformations and have been the subject of essential studies on their properties, bonding and reactivity that continue to date.[1–10] The focus on Pt(IV) hydrides has been particularly intense, mostly in connection with the development of catalytic hydrocarbon activation and functionalization reactions and their mechanistic investigation.[11–13] The oxidative addition of C–H bonds to Pt(II) species is the crucial step at the core of these processes, but isolation and characterization of the resulting organometallic Pt(IV) hydrides are rare[14,15] and there are no isolated complexes of this kind arising from cyclometalation reactions.[16] In addition, studies on the reactivity of Pt(IV) hydrides are mainly limited to reductive elimination[16] and only in one instance has the insertion of unsaturated molecules into a Pt(IV)–H bond been investigated.[17]

Visible light promoted transformations involving the activation of C–H bonds are being intensively researched because of the inherent benefits of using readily available substrates and a harmless and sustainable energy source, with most of the methodologies making use of photoredox catalysts that engage in bimolecular single-electron transfer (SET).[18–24] Recent research from ours and other laboratories has demonstrated an unprecedented photooxidative C–H addition process that takes place upon visible-light irradiation of Pt(II) complexes of the type *cis-N,N*-$[Pt(R)(C^\wedge N)(N'^\wedge C'H)]$, where $C^\wedge N$ is a cyclometalated ligand of the 2-arylpyridine type, $N'^\wedge C'H$ is an *N*-coordinated, nonmetalated one, and R can be a methyl or pentafluorophenyl ligand, leading to the cyclometalation of the $N'^\wedge C'H$ ligand to give unstable bis-cyclometalated Pt(IV) hydrides $[PtH(R)(C^\wedge N)(C'^\wedge N')]$ (Scheme 1).[25,26] When R = Me, these hydrides undergo the reductive elimination of methane to give bis-cyclometalated Pt(II) complexes $[Pt(C^\wedge N)(C'^\wedge N')]$, whereas pentafluorophenyl derivatives revert to the starting



Scheme 1 Photooxidative C–H addition reactions of methyl and pentafluorophenyl Pt(II) complexes. $C^\wedge N$ = cyclometalated 2-arylpyridine. $N'^\wedge C'H$ = *N*-coordinated 2-arylpyridine.

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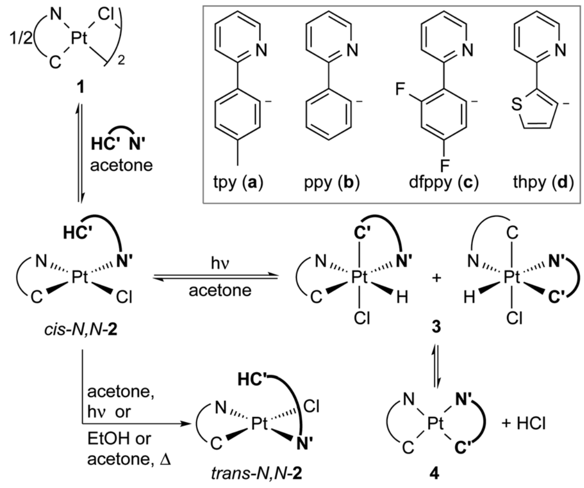
† Electronic supplementary information (ESI) available: Experimental details, characterization data, ^1H and $^{13}C\{^1H\}$ NMR spectra of new compounds, crystallographic information, computational methods and data. CCDC 2018872 (**3aa**·Me_2CO), 2019593 (**5ec**), 2018874 (*trans-N,N*-**6ec**·CH_2Cl_2), 2018873 (**7**), 2018875 (**8a**), 2018876 (**8b**·CH_2Cl_2), 2018877 (**8c**), 2018878 (**9b-BPh$_4$**·$CHCl_3$). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc04879h

Pt(II) complexes in the dark.[25] The C–H addition event in these systems is triggered by a triplet excited state involving a charge transfer from the metal to the coordinated N′^C′H ligand (^{3}ML′CT). This state becomes thermally populated from the lowest triplet excited state, which arises from a photoinduced ligand-centered/metal-to-ligand charge-transfer transition involving the C^N ligand (^{3}LC/MLCT). Therefore, the Pt(C^N) subunit is the key component allowing the formation of a relatively long-lived excited state from which the reactive state can be accessed. A distinctive feature of this process is that a single metal system performs the functions of light harvesting and C–H bond cleavage, the latter occurring through an inner-sphere mechanism.

The exploitation of the photooxidative C–H addition for the development of arene functionalization reactions is highly desirable because it occurs under very mild conditions. However, the synthesis of the Pt(II) precursors employed so far presents some disadvantages, since it requires several steps, the use of organolithium or -magnesium reagents to introduce the methyl or pentafluorophenyl ligands and the handling of unstable intermediates. In addition, the precarious stability of the produced hydrides is an important limitation for further fundamental studies. In this context, it is remarkable that a photooxidative C–H addition has been recently demonstrated as the key step in the borylation of 2-arylpyridines catalyzed by a Rh(I) carbene complex.[27]

In search for alternative and easily accessible Pt-based platforms for the photooxidative C–H addition reaction, we turned our attention to dichlorobridged dimers [$Pt_2(\mu\text{-}Cl)_2(C^\wedge N)_2$] (**1**), which could function as the simplest and most convenient source of the Pt(C^N) subunit. We have recently shown that these dimers establish bridge-splitting equilibria with monomeric complexes *cis-N,N*-[PtCl(C^N)(N′^C′H)] (*cis-N,N*-**2**) upon treatment with different 2-arylpyridines (N′^C′H) in solution at room temperature.[28] In the present study, we explore the photoreactivity of these solutions, which has led to the isolation of bis-cyclometalated Pt(IV) hydrides, the discovery of a photochemical transcyclometalation process and a complete elucidation of the involved photochemical and thermal steps. In addition, the reactivity of a bis-cyclometalated Pt(IV) hydride toward alkynes is reported as an initial assessment of the ability of this class of complexes to take part in subsequent organometallic reactions.



Photooxidative C–H additions:

C^N	HC′^N′	Product (yield)
tpy	tpyH	**3aa** (74%)
ppy	ppyH	**3bb** (71%)
dfppy	dfppyH	**3cc** (n.d.)
ppy	tpyH	**3ba** (22%)
dfppy	tpyH	**3ca** (63%)

Isomerizations:

C^N	HC′^N′	Cond.	Product (yield)
tpy	tpyH	78 °C	*trans-N,N*-**2aa** (74%)
ppy	ppyH	78 °C	*trans-N,N*-**2bb** (94%)
ppy	tpyH	78 °C	*trans-N,N*-**2ba** (63%)
dfppy	tpyH	78 °C	*trans-N,N*-**2ca** (71%)
dfppy	dfppyH	56 °C	*trans-N,N*-**2cc** (84%)
thpy	tpyH	hν	*trans-N,N*-**2da** (65%)

Scheme 2 Photochemical and thermal reactions of *cis-N,N*-**2** complexes.

Results and discussion

Photogeneration of bis-cyclometalated Pt(IV) hydrides

We initially examined the photoreactivity of three complexes *cis-N,N*-**2** bearing the same 2-arylpyridine as the cyclometalated and *N*-coordinated ligand, namely 2-(*p*-tolyl)-, 2-phenyl- or 2-(2,4-difluorophenyl)pyridine (*cis-N,N*-**2aa**, **2bb** or **2cc**, respectively), which were generated *in situ* from the corresponding dimers **1a–c** in acetone (Scheme 2). Irradiation with blue light (λ_{max} = 454 nm) at room temperature for 24 h under rigorous exclusion of oxygen led to very pale yellow solutions that contained the Pt(IV) hydrides [PtH(Cl)(tpy)$_2$] (**3aa**), [PtH(Cl)(ppy)$_2$] (**3bb**) or [PtH(Cl)(dfppy)$_2$] (**3cc**) as the major product. Complexes **3aa** and **3bb** were isolated as colorless solids in 74 or 71% yield, respectively. Their identity was established by ^{1}H NMR, which showed a hydride signal as a singlet at −17.9 ppm with Pt satellites (J_{HPt} = 1323 Hz) and two sets of resonances corresponding to inequivalent cyclometalated ligands. The orthogonal arrangement of these ligands is demonstrated by a distinctive aromatic resonance at 6.48 (**3aa**) or 6.64 (**3bb**) ppm flanked by platinum satellites, arising from the proton *ortho* to the metalated carbon of one of the ligands, which is considerably shielded by the ring current of the aryl group of the other one. The structure of **3aa** was confirmed by single-crystal X-ray diffraction (Fig. 1), which showed the expected ligand arrangement resulting from a *cis* C–H oxidative addition. The Pt–H bond distance of 1.63(2) Å is close to the mean value of 1.554 Å found for Pt(IV) hydride complexes in the Cambridge Structural Database.[29] Derivative **3cc** was identified by NMR in solution, but the attempts to isolate it resulted in the precipitation of the poorly soluble Pt(II) complex [Pt(dfppy)$_2$] (**4cc**) in a large proportion, and therefore it could not be obtained in pure form. This fact indicated the existence of an equilibrium between the Pt(IV) hydrides **3** and the Pt(II) complexes **4** involving reductive elimination/oxidative addition of HCl in solution, which was further supported by ^{1}H NMR monitoring (see below). In accord with this, the bis-cyclometalated Pt(II) complexes **4** were

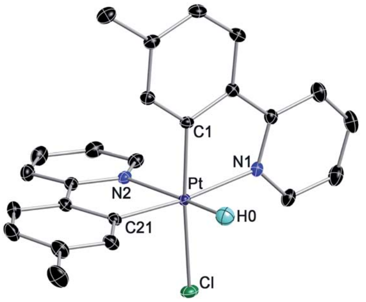


Fig. 1 Crystal structure of **3aa**·Me$_2$CO (thermal ellipsoids at 50% probability). Hydrogen atoms (except for the hydride) and crystallization solvent are omitted.

obtained upon treatment of acetone solutions of the *in situ* generated hydrides with a base (K_2CO_3 or Et_3N) in 71–74% yields with respect to the starting dimers **1**. This method represents the shortest and most convenient way to synthesize this kind of Pt(II) complexes.

To further explore the scope for the photochemical generation of Pt(IV) hydrides, we tested the irradiation of complexes *cis-N,N*-**2** bearing two different 2-arylpyridines. The irradiation of *in situ* generated solutions of *cis-N,N*-[PtCl(C^N)(tpyH)], with C^N = ppy (*cis-N,N*-**2ba**) or dfppy (*cis-N,N*-**2ca**), afforded the corresponding hydrides **3ba** or **3ca**. Even though a single isomer was expected from the cyclometalation of the tpyH ligand, complexes **3ba** and **3ca** were obtained as 1 : 1 mixtures of two structural isomers (Scheme 2), which implies a rapid isomerization process. The ^{1}H NMR spectra show two shielded aromatic resonances with satellites, each one arising from a different cyclometalated ligand; in the case of **3ca**, two hydride resonances are also distinguishable. Isolated yields were appreciably lower than those of **3aa–cc**, particularly for **3ba**, in part because of the difficulties encountered in precipitating them, associated with the higher solubilities of the isomer mixtures. In fact, the corresponding heteroleptic bis-cyclometalated Pt(II) complexes **4ba** and **4ca** were obtained in yields above 60% with respect to the starting dimers **1** upon treatment of the generated hydride mixtures with K_2CO_3.

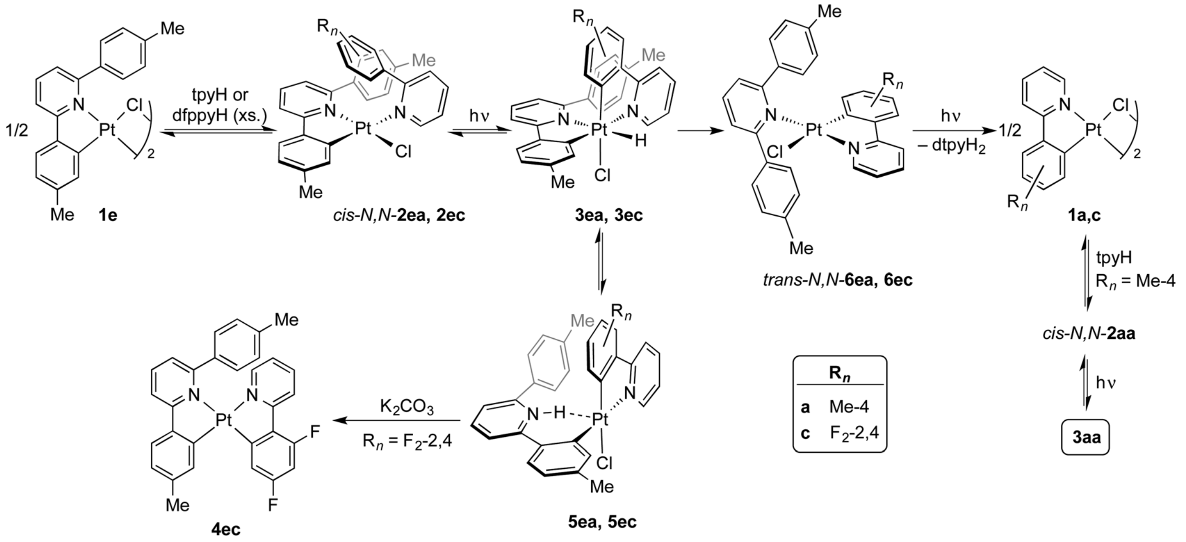
In contrast to the previous *cis-N,N*-**2** complexes, irradiation of an acetone solution of *cis-N,N*-[PtCl(thpy)(tpyH)] [*cis-N,N*-**2da**; thpy = cyclometalated 2-(2-thienyl)pyridine] led to a clean isomerization to *trans-N,N*-**2da** within less than 3 h (Scheme 2 and Fig. S36†). This compound did not undergo any further transformation upon continued photoexcitation. The isomerization of complexes of the type *cis-N,N*-**2** to their *trans-N,N* counterparts has not been directly addressed in the literature. However, the fact that the reported bridge-splitting reactions of dimers **1** with 2-arylpyridines at high temperatures give *trans-N,N*-**2** complexes exclusively indicates that these isomers are thermodynamically more stable.[30,31] Consistent with this, complexes *trans-N,N*-**2aa**, **2bb**, **2cc**, **2ba** and **2ca** were obtained upon heating of the corresponding *cis-N,N* precursors in EtOH or acetone (Scheme 2).

The photochemical generation of **3aa**, **3ba** and **3ca** was monitored by ^{1}H NMR in acetone-d_6 to gain additional understanding of the involved processes (Fig. S37–S39†). The hydrides are already detected after 1 h and the two structural isomers of **3ba** and **3ca** appear simultaneously. Small amounts of *trans-N,N*-**2aa**, **2ba** or **2ca** and the corresponding bis-cyclometalated Pt(II) complex **4** emerge alongside the hydride(s), but remain at low relative proportions (max. 12%). The formation of *trans-N,N*-**2** may indicate that a small fraction of the photoexcited *cis-N,N*-**2** molecules undergo an isomerization process instead of the photooxidative C–H addition. The presence of complexes **4** clearly points to a HCl reductive elimination/oxidative addition equilibrium,[16] which explains the presence of the two structural isomers of **3ba** and **3ca** because the oxidative addition of HCl is not selective. These experiments also showed that the proportion of complexes *trans-N,N*-**2aa** and **2ba** decreased at the end of the monitored time (21 h), suggesting that they could exhibit photochemical reactivity. A separate experiment showed that *trans-N,N*-**2aa** undergoes photodissociation of the coordinated tpyH ligand to give dimer **1a**, finally producing **3aa** *via* *cis-N,N*-**2aa** (see the ESI for details†).

Additionally, the evolution of pure **3aa** was monitored by ^{1}H NMR in CD_2Cl_2 over a period of 24 h at room temperature in the dark, revealing that the complex is fairly stable under an inert atmosphere. It slowly reverts to *cis-N,N*-**2aa**, but it is still the major species after 8 h (Fig. S40†). Complexes *trans-N,N*-**2aa** and **4aa** form in much smaller proportions. Since *cis-N,N*-**2aa** does not isomerize to *trans-N,N*-**2aa** at room temperature in the dark,[28] the formation of the latter may result from a C–H reductive elimination involving the tpy ligand with the N atom *trans* to the hydride, which is supported by the behaviour of the analogous hydride complex bearing 2,6-di(*p*-tolyl)pyridine (see below).

Photochemical transcyclometalation

The photogeneration of Pt(IV) hydrides bearing mono-cyclometalated 2,6-di(*p*-tolyl)pyridine (dtpyH) was also attempted. Irradiation of a solution of *cis-N,N*-[PtCl(dtpyH)(tpyH)] (*cis-N,N*-**2ea**) in acetone, generated *in situ* from the dimer **1e** and excess tpyH, produced complex **3aa** in 79% isolated yield after 24 h, resulting from the cyclometalation of two tpyH ligands with loss of dtpyH$_2$ (Scheme 3). Therefore, this reaction involves a transcyclometalation[32–36] process, leading to the substitution of the dtpyH ligand by tpy. In contrast, the irradiation of an acetone solution of *cis-N,N*-[PtCl(dtpyH)(dfppyH)] (*cis-N,N*-**2ec**) led to the precipitation of the Pt(II) complex [PtCl(dtpyH$_2$-κ*C*)(dfppy)] (**5ec**, 63% yield; Scheme 3). The X-ray diffraction analysis of this compound (Fig. 2) showed the presence of a *C*-bound 2,6-di(*p*-tolyl)pyridinium ligand *trans* to the N atom of a cyclometalated dfppy. There is a N–H···Pt interaction (2.237 Å), for which there are precedents in complexes resulting from the intramolecular deprotonation of Pt(IV) hydrides by metalated aryl ligands bearing an amine functionality.[17,37,38] The NH proton appears as a relatively broad resonance at 17.10 ppm with Pt satellites ($J_{HPt} \sim 76$ Hz) in the ^{1}H NMR spectrum (CD_2Cl_2). Complex **5ec** must originate from [PtH(Cl)(dtpyH)(dfppy)] (**3ec**) *via* decoordination of the pyridine



Scheme 3 Reactions and intermediates leading to photochemical transcyclometalation.

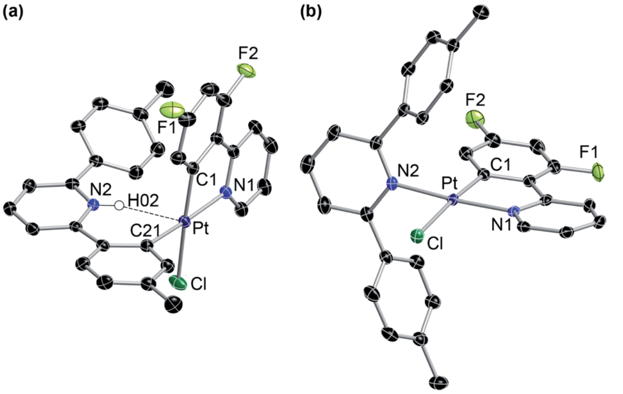


Fig. 2 Crystal structures of complexes **5ec** (a) and *trans-N,N*-**6ec**·CH_2Cl_2 (b). Solvent molecules and hydrogen atoms are omitted, except for the NH moiety in **5ec**.

group of the dtpyH ligand, which can then act as a base toward the hydride. This is probably favoured by the steric repulsion between the nonmetalated *p*-tolyl group and the pyridine ring of the dfppy ligand, as evidenced by the structure of [$PtCl_2$(dtpyH)(tpy)], which shows an elongated Pt–N bond distance.[28] The reaction of **5ec** with K_2CO_3 afforded the biscyclometalated Pt(II) complex **4ec**, *i.e.*, the same reactivity expected from the hydride **3ec**. Monitoring of a CD_2Cl_2 solution of pure **5ec** by ^{1}H NMR in the dark showed the gradual formation of **3ec** (Fig. S42†), giving rise to a singlet resonance at −20.43 ppm with satellites (J_{HPt} = 1426 Hz). Reasonably, these complexes establish an equilibrium in solution which shifts toward **5ec** in acetone because of its low solubility in this solvent. This experiment also showed the formation of small amounts of the new Pt(II) complex *trans-N,N*-[PtCl(dtpyH_2-κ*N*)(dfppy)] (*trans-N,N*-**6ec**), arising from a C–H reductive elimination involving the metalated *p*-tolyl moiety in **3ec**. Complex *trans-N,N*-**6ec** could be isolated in low yield from an *in situ* generated solution of **3ec** *via* irradiation of *cis-N,N*-**2ec** under more diluted conditions and its crystal structure was solved by X-ray diffraction (Fig. 2). Reported metal complexes with *N*-coordinated 2,6-diarylpyridine ligands are extremely rare;[39,40] some of them have been found to form *via* reversible hydrogenolysis of the monocyclometalated ligand, although they have not been isolated.[41]

The identification of complexes **3ec**, **5ec** and *trans-N,N*-**6ec** helped us to find the analogous intermediates in the transcyclometalation reaction leading to **3aa**. Monitoring of the irradiation of an acetone-d_6 solution of *cis-N,N*-**2ea** by ^{1}H NMR (Fig. S43†) demonstrated the formation of the hydride [PtH(Cl)(dtpyH)(tpy)] (**3ea**) as the major product during the initial stages (*ca.* 3 h), which is in equilibrium with small amounts of [PtCl(dtpyH_2-κ*C*)(tpy)] (**5ea**). Upon continued irradiation, complexes **3ea** and **5ea** gradually disappear as *trans-N,N*-**6ea**, *cis-N,N*-**2aa** and **3aa** emerge. The C–H reductive elimination involving the metalated *p*-tolyl group in **3ea** and the substitution of the resulting *N*-coordinated dtpyH_2 ligand in *trans-N,N*-**6ea** for a tpyH ligand are thus key to the transcyclometalation reaction. The latter could take place *via* photodissociation of the dtpyH_2 ligand to give dimer **1a**, as observed for *trans-N,N*-**2aa**, which would then react with tpyH to give *cis-N,N*-**2aa**. Continued photoexcitation would then produce **3aa**. Indirect support for the photodissociation of dtpyH_2 from *trans-N,N*-**6ea** was obtained by irradiating a solution of *trans-N,N*-**6ec** in acetone-d_6, which resulted in the decoordination of the dtpyH_2 ligand and the formation of a precipitate of dimer **1c** (Fig. S44†).

Excited states of complexes *cis-N,N*-2aa and 2da

To get an understanding of their contrasting photochemical reactivity, the lowest-energy excited states of derivatives *cis-N,N*-**2aa** and **2da** were examined by means of electronic absorption spectroscopy and density functional theory (DFT) and time-dependent DFT (TDDFT) calculations at the B3LYP/(6-31G**+LANL2DZ) level considering solvent effects (acetone).

The absorption spectrum of *cis-N*,*N*-**2aa** in acetone solution at 298 K shows two low-intensity, broad bands with maxima at *ca.* 360 and 400 nm, the latter tailing to *ca.* 450 nm, whereas complex *cis-N*,*N*-**2da** gives rise to an additional maximum at 422 nm (Fig. S48 and S52†). These characteristics are compatible with mixed ligand-centered/metal-to-ligand charge-transfer (LC/MLCT) transitions involving the C^N ligand (tpy or thpy), which are typically observed for cyclometalated Pt(II) complexes and are expected to have a lower energy for *cis-N*,*N*-**2da** because of the lower π–π* transition energy of the thpy ligand relative to tpy.[42,43] The TDDFT calculations (Tables S16 and S19†) predict two LC/MLCT transitions involving the C^N ligand as the lowest singlet excitations in both cases. Therefore, irradiation with blue light must mainly populate the lowest ^{1}LC/MLCT state.

The observed photoreactivity is expected to involve the lowest triplet excited states because the strong spin–orbit coupling induced by the Pt atom promotes fast intersystem crossing to the triplet manifold. Vibrational relaxation should then lead to the lowest triplet, from which either deactivation to the ground state or thermal population of higher-lying, reactive excited states can occur. Fig. 3(a) shows an energy diagram of the four lowest vertical triplet excitations from TDDFT calculations (see the ESI for details†). The lowest one (T_1) corresponds to a LC/MLCT transition involving the cyclometalated ligand (tpy or thpy), lying lower in energy for *cis-N*,*N*-**2da**. A similar LC/MLCT transition incorporating some halide-to-ligand charge transfer character [XLCT or p(Cl) → π*(C^N)] is the second triplet excitation (T_2) for *cis-N*,*N*-**2aa** or the third one (T_3) for *cis-N*,*N*-**2da**. There is also a low-lying metal-centered excitation (MC), which is lower in energy for *cis-N*,*N*-**2da** (T_2) than for *cis-N*,*N*-**2aa** (T_3). In both cases, the T_4 excitation is a ML′CT transition involving the coordinated tpyH ligand (L′) with a very similar energy in both complexes.

The geometries of the ^{3}LC/MLCT and ^{3}ML′CT states of both complexes (T_1 and T_4, respectively) and the ^{3}MC state of *cis-N*,*N*-**2da** (T_2) could be successfully optimized. Their free energies relative to the ground state are represented in Fig. 3(b). The spin density distributions (Fig. 4) agree in all cases with the topology of the expected electronic promotions on the basis of the TDDFT assignments. ^{3}LC/MLCT states similar to T_1 in cyclometalated Pt(II) complexes are usually long-lived and non-reactive.[42,44,45] The T_4 state is postulated as the reactive excited state leading to the photooxidative C–H addition in *cis-N*,*N*-**2aa** because it involves a partial reduction of the tpyH ligand by the metal. Its population could take place from the T_1 state, which lies 8.1 kcal mol^{-1} below. Its relaxed structure reveals noticeable changes in the bond distances (Table S21†) and angles within the coordinated tpyH ligand, including a nearly coplanar arrangement of the *p*-tolyl and pyridine rings (Fig. S54†), consistent with an electronic promotion to an extended π* orbital.

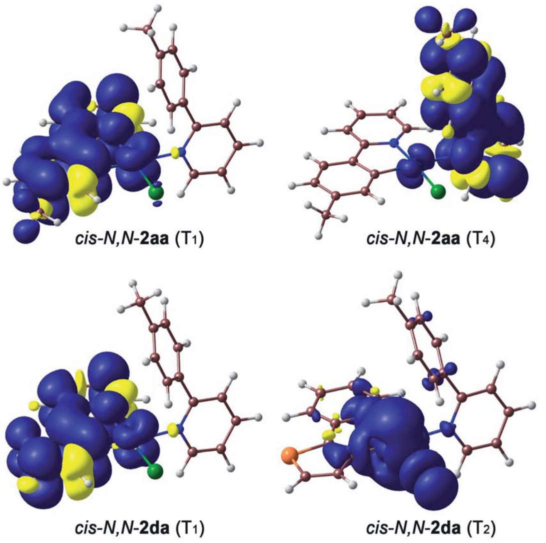


Fig. 4 Spin density distributions (0.001 e bohr^{-3}) for the optimized T_1 and T_4 states of *cis-N*,*N*-**2aa** and T_1 and T_2 of *cis-N*,*N*-**2da**.

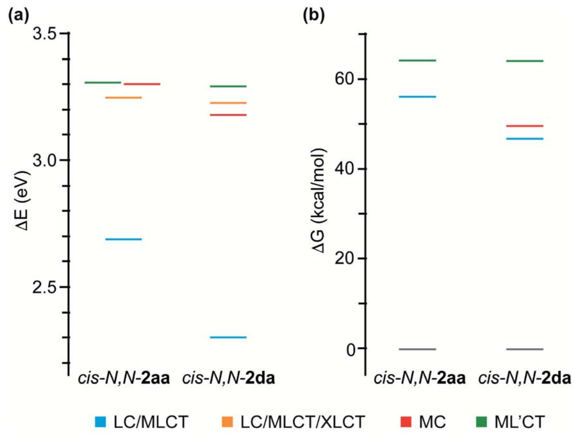


Fig. 3 Energy diagrams showing the lowest vertical triplet excitations at the ground-state geometries of *cis-N*,*N*-**2aa** and **2da** (a) and free energies of the optimized triplet excited states relative to the respective ground states (b).

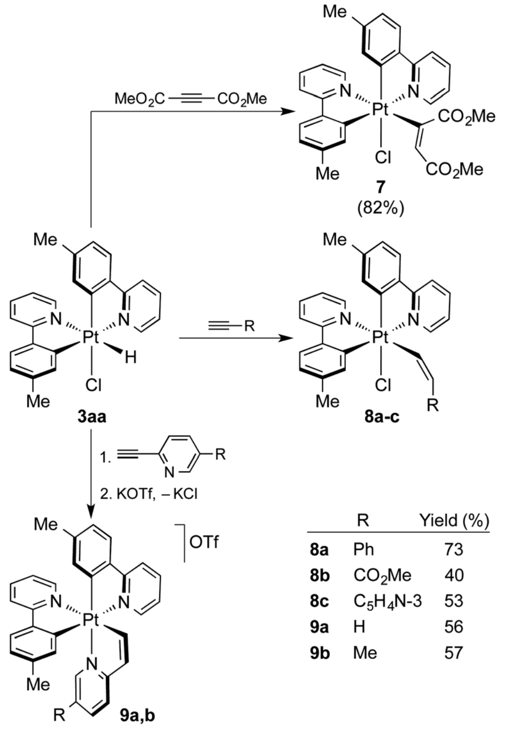
The free energy difference between the T_1 and T_4 states in complex *cis-N*,*N*-**2da** is considerably higher (17.4 kcal mol^{-1}) than in *cis-N*,*N*-**2aa**, meaning that thermal population of T_4 from T_1 should be much more difficult. Instead, it is the T_2 state that apparently gets easily populated. This state involves an electronic promotion to the metal $d_{x^2-y^2}$ orbital, having antibonding character along the Pt–ligand σ-bonds, and its relaxed structure reveals a significant elongation of the N–Pt–Cl axis (Fig. S55 and Table S22†). Hence, its population could be the starting point of the isomerization to *trans-N*,*N*-**2da** *via* σ-bond labilization and ligand dissociation. From this analysis, it is clear that the photooxidative C–H addition requires that the reactive ^{3}ML′CT state be relatively close in energy to the lowest ^{3}LC/MLCT state and therefore should be more favorable when the involved 2-arylpyridine ligands have similar π–π* transition energies. In addition, the population of low-lying dissociative ^{3}MC states may become competitive in this kind of complexes.

Alkyne insertion reactions

To probe the utility of the photogenerated hydrides for subsequent organometallic reactions, the reactivity of **3aa** toward alkynes was investigated. There is only one previous study on the reactions of Pt(IV) hydrides with alkynes,[17] which employed complexes of the type [PtH(X)(C^N)$_2$] [C^N = cyclometalated 1-(dimethylamino)naphthalene; X = Cl$^-$, Br$^-$ or CF$_3$COO$^-$], but only the reaction of the trifluoroacetate derivative with the highly reactive dimethylacetylene dicarboxylate (DMAD) succeeded to give an alkenyl Pt(IV) complex, for which a *Z* stereochemistry was proposed. Treatment of an *in situ* generated solution of **3aa** in acetone with DMAD at room temperature afforded the bis-cyclometalated chloro(alkenyl) complex [PtCl(tpy)$_2$(C(CO$_2$Me)=CHCO$_2$Me)] (**7**; Scheme 4) in high yield, resulting from the hydroplatination (*i.e.*, insertion into the Pt–H bond) of the triple bond. The reaction was completed within less than 2 h. The ^{1}H NMR spectrum in CD$_2$Cl$_2$ showed that only one of the two possible configurations of the alkenyl ligand is obtained. The alkenylic proton gives a relatively broad resonance at 6.17 ppm with Pt satellites, but the J_{HPt} constant of *ca.* 72 Hz is not conclusive enough to assign the stereochemistry. An X-ray diffraction analysis revealed an *E* configuration (Fig. 5) of the alkenyl and also corroborated that the ligand arrangement in **7** is identical to that found for the parent complex **3aa**, except for the replacement of the hydride by an alkenyl ligand. The less reactive internal alkynes diphenylacetylene, 1-phenyl-1-propyne or methyl phenylpropiolate did not react with **3aa** under the same conditions. Relatively fast reactions did take place with terminal alkynes bearing an inductively withdrawing group to give complexes [PtCl(tpy)$_2$(CH=CHR)], with R = Ph (**8a**), COOMe (**8b**) or C$_5$H$_4$N-3 (**8c**) (Scheme 4), whereas *tert*-butylacetylene proved unreactive. The ^{1}H NMR spectra of the crude reaction mixtures showed a single hydroplatination product, which demonstrates that the reactions are regio- and stereoselective. The two alkenylic protons display J_{HH} values of 11–12 Hz, consistent with *cis*-vicinal protons, whereas the J_{HPt} values are very different (*ca.* 30 or 110 Hz), indicating that one of them is geminal with respect to the Pt atom and the other one *trans*-vicinal. Therefore, the Pt atom binds to the terminal carbon of the alkyne and the resulting alkenyl has a *Z* configuration, which was corroborated by X-ray diffraction analyses (Fig. 5, S6 and S7†).

The reactions with 2-ethynylpyridine and 2-ethynyl-5-methylpyridine with **3aa** led to cationic tris-chelate complexes (**9a** or **9b**, respectively), formally resulting from the hydroplatination of the triple bond to give a *Z*-configured alkenyl and subsequent displacement of the chloride ligand by the pyridine moiety. These complexes were isolated as the triflate salts by performing the reactions in the presence of KOTf. To get single crystals suitable for an X-ray diffraction study, the BPh$_4^-$ salt of **9b** (**9b-BPh$_4$**) was also prepared *via* anion metathesis. Its crystal structure revealed a *fac-N*,*N*,*N* configuration around the metal (Fig. 5), suggesting that the relative arrangement of the tpy ligands remains unchanged in the course of the reaction and that the pyridyl moiety occupies the chloride position. The synthesis of tris-cyclometalated Pt(IV) complexes with a *fac* configuration is challenging[46–48] and only in one previous instance has a crystal structure been successfully solved.[49]

The above described results indicate that the insertions of alkynes into the Pt–H bond of **3aa** require the presence of at



	R	Yield (%)
8a	Ph	73
8b	CO$_2$Me	40
8c	C$_5$H$_4$N-3	53
9a	H	56
9b	Me	57

Scheme 4 Alkyne insertion reactions into the Pt–H bond of **3aa**. Yields are given with respect to precursor **1a**.

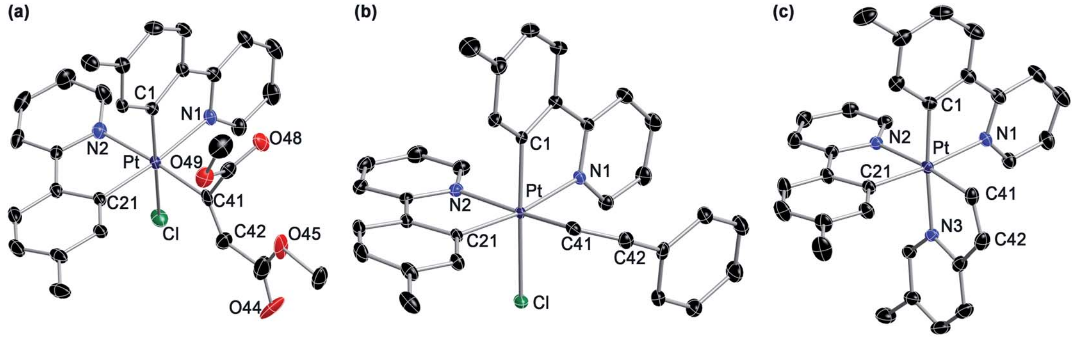


Fig. 5 Crystal structures of complexes **7** (a), **8a**·CH$_2$Cl$_2$ (b) and **9b-BPh$_4$**·CHCl$_3$ (c) (thermal ellipsoids at 50% probability). Hydrogen atoms, crystallization solvent and the anion of **9b-BPh$_4$** are omitted.

least one electron-withdrawing group, implying an electrophilic behaviour of the alkyne. Since most of the tested internal alkynes were found unreactive, it is also clear that the steric requirements of the alkyne substituents have a detrimental effect. In view of the different stereochemistry found for the insertion of DMAD with respect to terminal alkynes, it is possible that different reaction pathways are followed depending on the nature of the alkyne. A migratory insertion mechanism[50–54] seems unlikely because the saturated coordination sphere in **3aa** is expected to hinder the coordination of the alkyne. Moreover, this mechanism would preferentially lead to an *E* stereochemistry, which is inconsistent with the observed outcome of terminal alkyne insertions. The present insertions could involve a H atom or hydride transfer[2,4,55] as the initial step, although conclusive evidence for either of these possibilities could not be gathered. Further investigations to elucidate the behaviour of hydrides **3** are underway.

Conclusions

Dichlorobridged dimers of the type $[Pt_2(\mu\text{-}Cl)_2(C^\wedge N)_2]$ have been demonstrated as a suitable source of Pt(C^N) subunits that can promote the cyclometalation of 2-arylpyridines (N′^C′H) *via* photooxidative C–H addition in intermediates *cis-N*,*N*-[PtCl(C^N)(N′^C′H)] upon excitation with visible light. The resulting [PtH(Cl)(C^N)(C′^N′)] complexes are fairly stable and represent the first isolated Pt(IV) hydrides arising from a cyclometalation reaction. Bis-cyclometalated Pt(II) complexes [Pt(C^N)(C′^N′)] can be obtained in good yields from the photogenerated hydrides upon addition of a base, which represents the shortest and most convenient synthetic method for this kind of derivatives. When the C^N ligand in the dichloro-bridged precursor is a monocyclometalated 2,6-diarylpyridine, a transcyclometalation process takes place, involving three photochemical steps.

The observed photooxidative C–H addition process may compete with photoisomerization depending on the C^N/N′^C′H combination. DFT and TDDFT calculations substantiate that a reactive triplet excited state involving a charge-transfer from the metal to the coordinated N′^C′H ligand (^{3}ML′CT) triggers the C–H addition. This state is thermally accessible from the lowest, C^N-based excited state (^{3}LC/MLCT) when the two states are sufficiently close in energy; otherwise, a low-lying, dissociative metal-centered excited state may become populated, resulting in isomerization.

The present results may provide the basis for the systematic development of novel platforms for the photooxidative C–H addition. In addition, the described alkyne insertion reactions into the Pt–H bond of one of photogenerated Pt(IV) hydrides demonstrate that this kind of complexes are amenable for further organometallic reactions, which might allow their incorporation into catalytic cycles for visible light promoted C–H functionalization.

Conflicts of interest

There are no conflicts to declare.

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