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# Oxidation of Half-Lantern $Pt_2(II,II)$ Compounds by Halocarbons. Evidence of Dioxygen Insertion into a Pt(III)−$CH_3$ Bond

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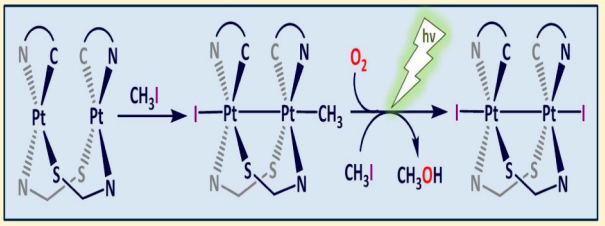
Supporting Information

**ABSTRACT:** The half-lantern compound $[\{Pt(bzq)(\mu\text{-}N\hat{}S)\}_2]$ (**1**) [bzq = benzo[*h*]quinoline, HN^S = 2-mercaptopyrimidine ($C_4H_3N_2HS$)] reacts with $CH_3I$ and haloforms $CHX_3$ (X = Cl, Br, I) to give the corresponding oxidized diplatinum(III) derivatives $[\{Pt(bzq)(\mu\text{-}N\hat{}S)X\}_2]$ (X = Cl **2a**, Br **2b**, I **2c**). These compounds exhibit half-lantern structures with short intermetallic distances (~2.6 Å) due to Pt−Pt bond formation. The halogen abstraction mechanisms from the halocarbon molecules by the $Pt_2(II,II)$ compound **1** were investigated. NMR spectroscopic evidence using labeled reagents support that in the case of $^{13}CH_3I$ the reaction initiates with an oxidative addition through an $S_N2$ mechanism giving rise to the intermediate species $[I(bzq)Pt(\mu\text{-}N\hat{}S)_2Pt(bzq)(^{13}CH_3)\}]$. However, with haloforms the reactions proceed through a radical-like mechanism, thermally ($CHBr_3$, $CHI_3$) or photochemically ($CHCl_3$) activated, giving rise to mixtures of species $[X(bzq)Pt(\mu\text{-}N\hat{}S)_2Pt(bzq)R]$ (**3a−c**) and $[X(bzq)Pt(\mu\text{-}N\hat{}S)_2Pt(bzq)X]$ (**2a−c**). In these cases the presence of $O_2$ favors the formation of species **2** over **3**. Transformation of **3** into **2** was possible upon irradiation with UV light. In the case of $[I(bzq)Pt(\mu\text{-}N\hat{}S)_2Pt(bzq)(^{13}CH_3)\}]$ (**3d**), in the presence of $O_2$ the formation of the unusual methylperoxo derivative $[I(bzq)Pt(\mu\text{-}N\hat{}S)_2Pt(bzq)(O{-}O^{13}CH_3)\}]$ (**4d**) was detected, which in the presence of $^{13}CH_3I$ rendered the final product $[\{Pt(bzq)(\mu\text{-}N\hat{}S)I\}_2]$ (**2c**) and $^{13}CH_3OH$.




## 1. INTRODUCTION

Oxidative-addition (OA) of a molecule AB to unsaturated transition metal complexes has been widely studied as model for many catalytic reactions.[1−3] OA to $d^8$ mononuclear complexes sometimes proceeds through a concerted cis addition,[4] or through a radical-like mechanism.[5,6] However, these reactions very often follow an $S_N2$ pathway,[7−11] with the metal center acting as nucleophile through the filled $d_{z^2}$ orbital. In addition, Puddephatt and Canty have shown that OA to Pt(II) complexes of planar diimines follow a binuclear stepwise mechanism, with two $\pi$−stacked units involved in the initial oxidation step,[12,13] providing evidence of the role of metallophyllic interactions on the chemical reactivity of mononuclear $d^8$ complexes.

In dinuclear complexes the mechanism of OA reactions depends on many factors such as the metal, the ligands, or the nature of the AB molecule. Moreover, the possible actuation of cooperative effects between the two adjacent metals can potentially have lower activation barriers and lead to reaction pathways and products that are unable to be obtained from the mononuclear ones.[14−18] Most usual haloalkanes, such as $CH_3I$ and $CH_2I_2$, are often added to $Ir_2(I,I)$ via a bimetallic $S_N2$ pathway,[19−21] yielding metal−metal bonded Ir(II)−Ir(II) compounds. Sometimes these reactions follow a radical-like[22,23] mechanism or a monometallic $S_N2$ pathway resulting, in the latter case, in mixed valence Ir(I)−Ir(III) compounds.[24,25]

Few examples of OA of chloroalkanes (RCl) to $Ir_2(I,I)$ compounds leading to metal−metal bonded complexes containing Cl−Ir(II)−Ir(II)X (X = R, Cl) frameworks have been reported,[26,27] and in most cases they require visible- or UV-light irradiation. Recently the OA of RCl to $[\{Ir(\mu\text{-}Pz)(CNBut)_2\}_2]$ (R = $CH_2COMe$, $CH_2CO_2Me$, $CH(Me)CO_2Me$)[28] and $[\{Ir(\mu\text{-}NH_2)(cod)_2\}_2]$ (RCl = $CH_2Cl_2$, $CH_3Cl$)[29] in the dark under argon atmosphere, which renders the asymmetric metal−metal bonded $Ir_2(II,II)$ compounds, has been reported. The $Ir_2(II,II)$ systems show relative inertness for further OA of haloalkanes, but when this occurs they render $Ir_2(III,III)$ compounds with no metal−metal bond. Examples are illustrated by the double OA of $CH_3I$ to complexes $[(L)_2Ir(\mu\text{-}Pz)_2Ir(CNBut)_2]$[30] or $ClCH_2R$ (R = Ph, CH=$CH_2$) to $[\{Ir(\mu\text{-}Pz)(CNBut)_2\}_2]$.[28]

In the chemistry of binuclear Pt(II) complexes, OA reactions have been scarcely studied. OA of $CH_3I$ (in excess) to $[Pt_2Me_2(C\hat{}N)_2(\mu\text{-}P\hat{}P)]$ [C^N = 2-phenylpyridyl-H, benzo[*h*]quinoline; P^P = dppf (1,1′-bis(diphenylphosphino)-ferrocene), dppa (1,1′-bis(diphenylphosphino)acetylene)][31−33] or *cis,cis*-$[Me_2Pt(\mu\text{-}NN)(\mu\text{-}dppm)PtMe_2]$ (NN = phthalazine, dppm = bis(diphenylphosphino)methane)[34] takes place in two steps via a monometallic $S_N2$ mechanism to give the diplatinum-

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(IV) derivatives $[Pt_2Me_4I_2(C^N)_2(\mu\text{-}P^P)]$ and $[Me_3Pt(\mu\text{-}I)_2(\mu\text{-dppm})PtMe_3]$. In rigid metal fragments, such as lantern-shaped $Pt_2(II,II)$ compounds with relatively short Pt−Pt separation, the OA of halogens ($X_2$) or $CH_3I$ seem to follow a bimetallic $S_N2$ pathway to give the corresponding metal−metal bonded $Pt_2(III-III)$ complexes.[35−37]

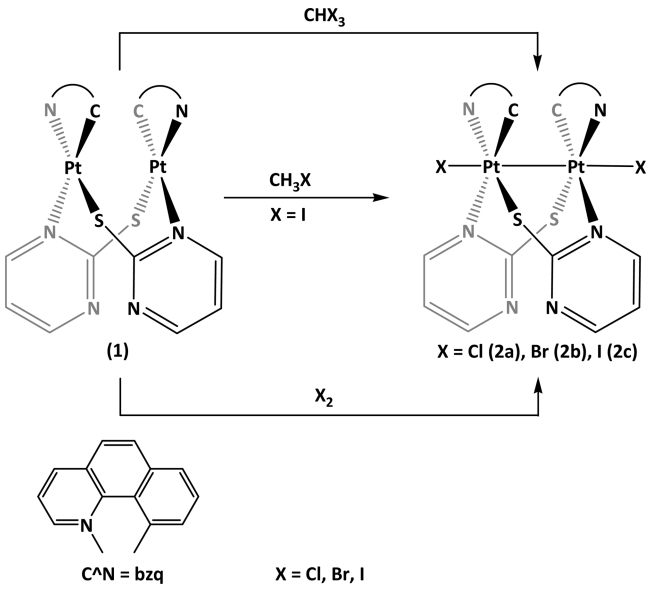
In general, lantern- or half-lantern dihalodiplatinum(III) complexes $Pt_2(III-III)X_2$ (X = Cl, Br, I) seem to be quite stable and available by several ways, as the reaction of the corresponding $Pt_2(II,II)$ derivatives with halogens ($X_2$)[38−40] or with an excess of RX. This behavior is illustrated by complexes $[Pt_2(\kappa^2As,C-C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_2(\mu\text{-}\kappa As,\kappa C-C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_2]$ and $[Pt_2(\mu\text{-}\kappa As,\kappa C-C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4]$, which in $CH_2Cl_2$ solution and more rapidly in $CHCl_3$ or $CCl_4$ render compound $[Pt_2Cl_2(\mu\text{-}\kappa As,\kappa C-C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4]$,[41] and complex $[Pt_2I_2(\mu\text{-}\kappa As,\kappa C-C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4]$, which resulted from the reaction of $[Pt_2(\mu\text{-}\kappa As,\kappa C-C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4]$ with $CH_3I$ in the dark.[41] Other $Pt_2(III,III)X_2$ complexes such as $[Pt_2Cl_2(pyt)_4]$ (Hpyt = pyridine-2-thiol)[42] and $[Pt_2Cl_2(ppy)_2(pyt)_2]$ (Hppy = 2-phenylpyridine)[43] resulted from chloroform solutions of the corresponding $Pt_2(II,II)$ ones and mixtures of $[Pt(pop)_4RI]^4$ and $[Pt(pop)_4I_2]^4$ were obtained from the thermal reaction of $[Pt(pop)_4]^4$ with RI (pop = pyrophosphite, R = Et, $^n$Pr, $^i$Pr, *n*-pentyl).[44] In spite of the surprising behavior of lantern- or half-lantern Pt(II) complexes toward haloalkanes (RX), studies aiming to explain the mechanism by which the $Pt_2(II,II)$ complexes convert into $Pt_2(III-III)X_2$ are scarcely reported.[44]

In the course of our research on half-lantern $Pt_2(II,II)$ complexes and their two-center two-electron [**2c**, **2e**] oxidation products, we prepared the new compound, $[\{Pt(bzq)(\mu\text{-}N^S)\}_2]$ (**1**) [bzq = benzo[*h*]quinoline, HN^S = 2-mercaptopyrimidine ($C_4H_3N_2HS$)], which reacts with excess of haloalkanes ($CHCl_3$, $CHBr_3$, $CHI_3$, and $CH_3I$) to give the dihalocomplexes $[\{Pt(bzq)(\mu\text{-}N^S)X\}_2]$ (X = Cl, Br, I), and the reaction paths were investigated. The $Pt_2(III,III)X_2$ complexes were also available by treatment of **1** with halogens.

## 2. RESULTS AND DISCUSSION

**2.1. Reactivity of a New Half-Lantern $Pt_2(II,II)$ Compound toward Haloforms. Synthesis of New $Pt_2(III,III)X_2$ Compounds (X = Cl, Br, I).** The new half-lantern $Pt_2(II,II)$ complex $[\{Pt(bzq)(\mu\text{-}N^S)\}_2]$ (**1**, Scheme 1) was obtained in good yield (84%) from equimolar amounts of $[Pt(bzq)(NCMe)_2]ClO_4$ and HN^S in the presence of $NEt_3$. The dinuclear nature of **1** was inferred from its mass spectrum and supported by the diffusion coefficient value, which was determined using diffusion-ordered $^1$H-RMN spectroscopy (DOSY) in solution (see Experimental Section in Supporting Information). The $^1$H NMR spectrum of **1** indicates that it exists as a single and symmetric isomer, most probably the anti one, as observed in the related half-lantern compounds $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)\}_2]$ ($C_7H_4NYS$ = 2-mercaptobenzothiazolate (Y = S); 2-mercaptobenzoxazolate (Y = O)).[39,40] As with the aforementioned compounds,[39,40] the electronic absorption spectra of **1** (Figure S1 in Supporting Information) show low-intensity bands centered at 496 nm ($CH_2Cl_2$) or 580 nm (powdered solid), assignable to a metal−metal-to-ligand charge transfer transition, ($^1$MMLCT) $[d\sigma^*(Pt)_2 \rightarrow \pi^*(bzq)]$, which is indicative of the existence of two platinum centers located in close proximity, both in the solid state and in solution. Unlike them, complex **1** is not emissive upon excitation at wavelengths from 350 to 580 nm at either 298 or 77 K.

**Scheme 1. Reactions Leading to $Pt_2(III,III)X_2$ (2a−2c) from $Pt_2(II,II)$ (1)**




Complex **1** readily reacts with an excess of haloforms, $CHX_3$ (X = Cl, Br, I), in the air, to give the corresponding $Pt_2(III,III)X_2$ complexes $[\{Pt(bzq)(\mu\text{-}N^S)X\}_2]$ (X = Cl **2a**, Br **2b**, I **2c**), which were isolated as pure compounds (Scheme 1). The reactions with $CHBr_3$ and $CHI_3$ proceed in the dark to give **2b** and **2c**, respectively, which were isolated in ca. 60% yield after 24 h (see Experimental Section in Supporting Information). However, in $CHCl_3$ solution compound **1** is stable in the dark, but in the sunlight it reacts with $CHCl_3$ to render complex **2a** that was obtained in 88% yield after 6 h (see Experimental Section in Supporting Information).

The same oxidized complexes were also obtained upon treatment of **1** with the corresponding halogen $X_2$ (see Scheme 1 and Experimental Section in Supporting Information). All these $Pt_2(III,III)X_2$ compounds show a half-lantern structure with short Pt−Pt distances (2.6132(2) Å **2a**, 2.6167(4) Å **2b**, 2.6401(2) Å **2c**), in agreement with the existence of a Pt−Pt bond (see Figure 1 for **2c**, Figure S3 in Supporting Information for **2a** and **2b** and Table S3 in Supporting Information). Their structures are similar to those observed for compounds $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)X\}_2]$ (Y = S, O; X = Cl, Br, I).[39,40] In all of them, the Pt(III) centers have distorted octahedral environments with the axial positions occupied by a halogen atom and the other Pt(III) center; the X−Pt-Pt angles are close to 175°. The Pt−Pt distances are similar to those observed in $[Pt_2Cl_2(ppy)_2(pyt)_2]$[43] and shorter than those observed in compounds $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)X\}_2]$ (Y = S, O).[39,40] This fact must be related with the value of the N−C−S bond angle of the bridging ligand, which is smaller in **2a−2c** (∼121°) than in complexes $[\{Pt(bzq)(\mu\text{-}C_7H_4NYS\text{-}\kappa N,S)X\}_2]$ (Y = S, ∼128° or O, ∼ 130°).

In all these $Pt_2(III,III)X_2$ compounds the platinum coordination planes are almost parallel, with interplanar angles close to 10° (7.58(5)° **2a**, 9.31(13)° **2b**, 9.20° **2c**). Angles between the Pt−Pt line and the normal lines to the Pt coordination planes are small too, the biggest one being 5.12(9)° (for compound **2b**). These structures exhibit significant intramolecular $\pi-\pi$ interactions between the bzq groups, with most C−C distances between 3.19 and 3.99 Å (**2a**), 3.26 and 3.98 Å (**2b**), and 3.18 and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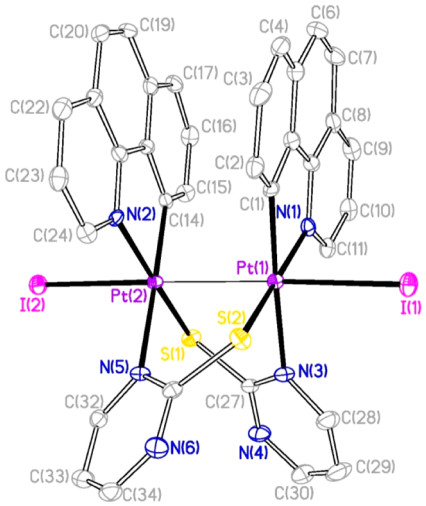



**Figure 1.** Molecular structure of **2c**. Ellipsoids are drawn at their 50% probability level; solvent molecules and hydrogen atoms were omitted for clarity.

3.99 Å (**2c**).[39,40,45−48] Complexes **2a**−**2c** are discrete molecules, and no intermolecular interactions between neighbor molecules were found.

**2.2. Reactivity of 1 toward $CH_3I$. Formation of Compound $Pt_2(III,III)I_2$ (2c).** We observed that complex **1** reacts with an excess of $CH_3I$ (molar ratio 1:3.65) in the dark within 8 min to render the new species [I(bzq)Pt($\mu$-N^S)$_2$Pt-(bzq)($CH_3$)](**3d**), which in the sunlight evolves to **2c** (Scheme 2). Compound **2c** can be directly obtained by reaction of **1** with $CH_3I$ (molar ratio 1:4) in the air and in the sunlight in moderate yield (see Scheme 1 and Experimental Section in Supporting Information). However, in the dark, **3d** has been proven to be stable for at least 22 h.

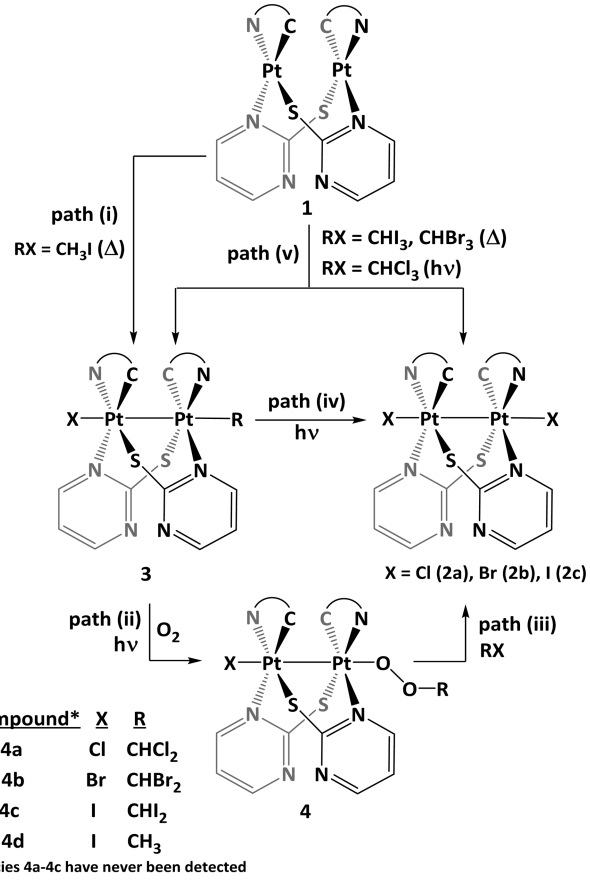
Attempts to isolate **3d** as a pure solid from the reaction crude in different solvents and temperatures were unsuccessful, and mixtures of **3d**, **1**, and free $CH_3I$ were always obtained. These observations suggest that the reaction of **1** with $CH_3I$ is an equilibrium (see eq 1), which would explain that the evaporation of the volatile $CH_3I$ forces the equilibrium to the left, therefore regenerating **1**. This equilibrium happens to be very sensitive to the temperature, in a way that the formation of **1** and $CH_3I$ from **3d** was observed by NMR when the temperature increases over 30 °C. Poor-quality crystals of **3d** were eventually obtained from these reaction mixtures that enabled to establish the connectivity of the atoms, which confirmed the proposed structure for **3d** (Figure S4 in Supporting Information).

$$Pt_2(II,II)\ (\mathbf{1}) + CH_3I \leftrightarrow CH_3 - Pt - Pt - I\ (\mathbf{3d}) \qquad \text{(eq 1)}$$

The reaction mechanisms for the formation of $Pt_2(III,III)X_2$ (X = Cl **2a**, Br **2b**, I **2c**) from **1** and an excess of halocarbons ($CHX_3$, $CH_3I$) were investigated. For a better understanding, the results obtained for the reaction of **1** with $CH_3I$ are described first.

**2.3. Mechanism Insight for the Reaction of 1 with $CH_3I$. Evidence of Dioxygen Insertion into a Pt(III)−$CH_3$ Bond.** The reaction of **1** with $^{13}CH_3I$ (molar ratio 1:3.65) was studied by multinuclear NMR spectroscopy in $CD_2Cl_2$, including two-dimensional techniques ($^1$H COSY and $^1$H, $^{13}$C HSQC). These studies showed that **1** reacts quickly with $^{13}CH_3I$ in the air and in the dark at room temperature to give the new species

**Scheme 2. Mechanism Proposed for the Oxidation of 1 with Halocarbons**




[I(bzq)Pt($\mu$-N^S)$_2$Pt(bzq)($^{13}CH_3$)] (**3d**) (Figure 2 and Scheme 2).

The $^1$H NMR spectrum of **3d** shows a doublet at 1.02 ppm corresponding to the $^{13}CH_3$ fragment with a $^1J_{C-H}$ = 139 Hz. This signal is flanked by two sets of $^{195}$Pt satellites ($^2J_{Pt-H}$ = 55 Hz, $^3J_{Pt-H}$ = 15 Hz) with the $^nJ_{Pt-H}$ values ($n$ = 2, 3) being similar to those reported by H. B. Gray et al. for the full-lantern compound $K_4[Pt_2(pop)_4(CH_3)I]$ ($^2J_{Pt-H}$ = 52.66 Hz, $^3J_{Pt-H}$ = 13.83 Hz).[35] Moreover, the $^{13}$C {$^1$H} NMR spectrum shows a singlet at 3.78 ppm flanked by two sets of $^{195}$Pt satellites ($^1J_{Pt-C}$ = 453 Hz, $^2J_{Pt-C}$ = 160 Hz), also consistent with a dinuclear $Pt_2$(III,III) formulation with the $CH_3$ and I ligands in the axial positions.

Interestingly, when this reaction sample containing [I(bzq)-Pt($\mu$-N^S)$_2$Pt(bzq)($^{13}CH_3$)] (**3d**) and $^{13}CH_3I$ was irradiated with UV light ($\lambda$ = 365 nm) for 1 h, new signals corresponding to three new species emerged (see Figure 3): [I(bzq)Pt($\mu$-N^S)$_2$Pt(bzq)(O−O$^{13}CH_3$)}] (**4d**), **2c**, and $^{13}CH_3OH$ ($\delta$H = 3.40 ppm (d), $^1J_{C-H}$ = 142 Hz; $\delta$C = 50.8 ppm (s)). Species **4d** is a new platinum complex whose $^1$H and $^{13}$C NMR spectra exhibit the signals due to $^{13}CH_3$ with no coupling to $^{195}$Pt ($\delta$H = 2.45 ppm (d), $^1J_{C-H}$ = 140 Hz; $\delta$C = 64.2 ppm (s)). The values of $^1J_{C-H}$ and $\delta$C,[49,50] together with the absence of Pt−$^{13}$C and Pt−H couplings, lead us to propose **4d** to be a methylperoxo[48,51,52] over a methoxo[53−58] species as represented in Scheme 2. The $^1$H NMR signal corresponding to $^{13}CH_3OO$ ($\delta$H = 2.45 ppm) for **4d** appears highfield-shifted with respect to those in the mononuclear Pt(II) methylperoxo ($\delta$H > 3.0 ppm) derivatives previously described.[49,51,52]



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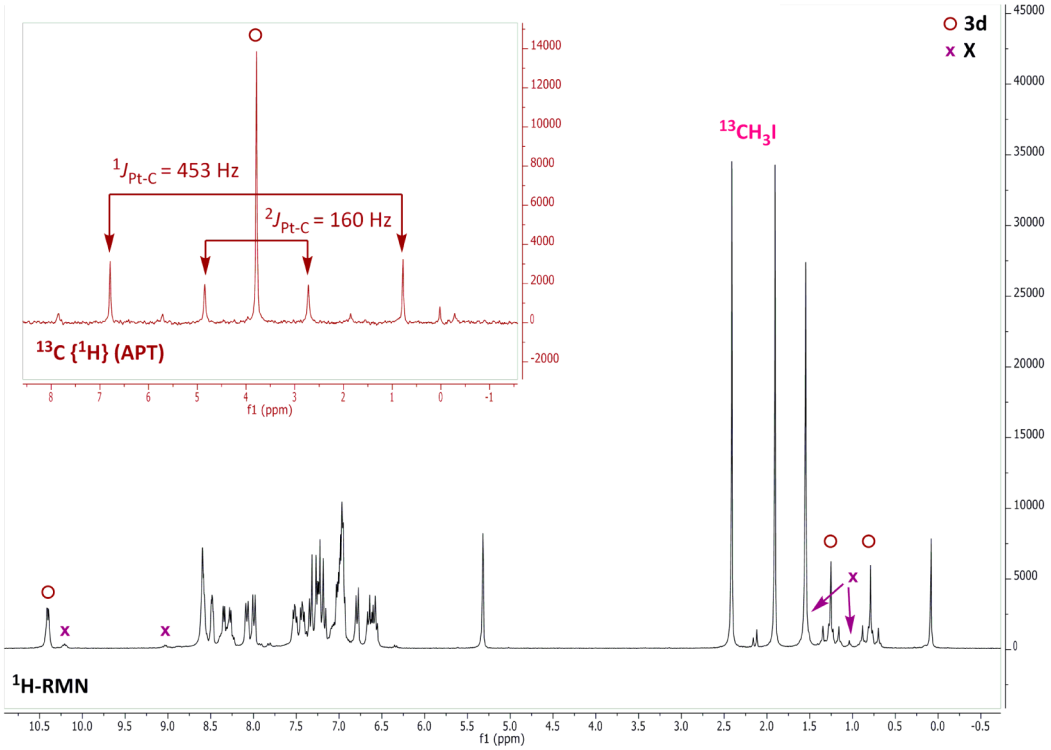


**Figure 2.** $^1$H NMR spectrum of the reaction of **1** with $^{13}CH_3I$ (1:3.65) in $CD_2Cl_2$ in the air and in the dark after 8 min. (inset) Expansion of the Pt−$^{13}CH_3$ signal of **3d** in the $^{13}C\ \{^1H\}$ NMR spectrum (APT).

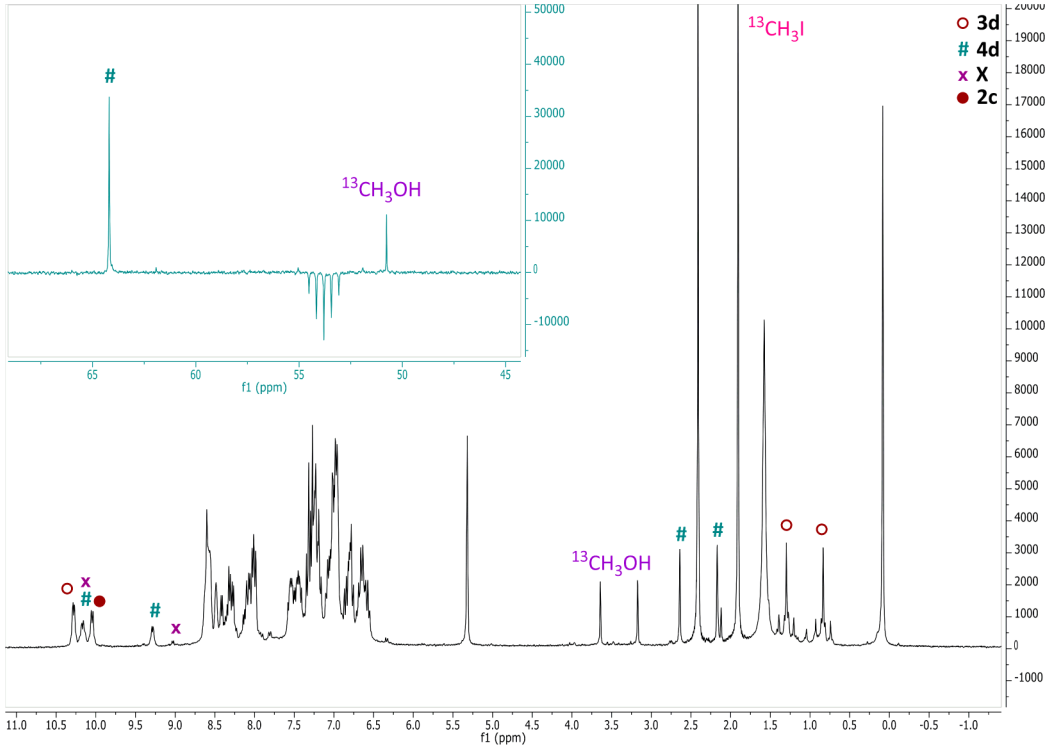


**Figure 3.** $^1$H NMR spectra of the reaction of **1** with $^{13}CH_3I$ (1:3.65) in $CD_2Cl_2$ when exposed for 1 h to UV light ($\lambda$ = 365 nm). (inset) $^{13}C\ \{^1H\}$ (APT) expansion of the new signals observed (**4d** and MeOH).

A comparable shift was observed in the Pt(IV) methoxo complexes, *fac*-$[PtMe_2(OMe)(D_2O)_3]NO_3$ ($\delta$H(OMe) = 2.43 ppm),[58] and $[Pt(OH)(OCH_3)Me_2(bipy)]$,[55] which suggests that the oxidation state of the metal atom could affect the $\delta$H value of the $CH_3OO$ fragment. However, in our case, it is probably due to the anisotropic shielding effect of the aromatic ring current of bzq on these hydrogen atoms lying close to it. When the same sample was irradiated with UV light for 12 additional hours, species **3d** and **4d** were completely transformed into **2c** (path iii, Scheme 2), whereby the amount of $^{13}CH_3OH$ in



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the mixture was increased. The integrals of the $^1$H signals indicate **2c**/$^{13}CH_3OH$ ≈ 1:2, and no other oxygenated organic species, such as formaldehyde, were detected.

Under Ar atmosphere, complex **1** also reacts readily with $CH_3I$ (molar ratio 1:3.65) in the dark at room temperature to give the asymmetric species **3d**. When this sample containing **3d** and excess of $CH_3I$ was exposed to the UV light, only 26% of **3d** appeared quantitatively transformed into **2c** after 3 d, and species **4d** and $CH_3OH$ were not detected during this time, in agreement with the absence of molecular oxygen in the environment. This observation proved that there is an additional "oxygen-free" pathway for the conversion of **3d** into the diiodide complex **2c** (path iv in Scheme 2). Nevertheless, the presence of molecular oxygen provides a faster and more efficient conversion pathway into **2c** (paths ii and iii, Scheme 2).

The above presented data support that the formation of **2c** from **1** and $CH_3I$ follows a stepwise mechanism. The first step consists in the thermal OA of $CH_3I$ to **1** to give **3d** (path (i)). Subsequently the photochemical transformation of **3d** into **2c** may occur through two alternative pathways, with or without oxygen (paths ii and iii or path iv, respectively, in Scheme 2). To get a deeper knowledge of this mechanism, we decided to check whether radicals might be involved in the first (path (i)) and second steps (paths ii and iv, Scheme 2) of the reaction, by testing the effect of a typical radical reagent as galvinoxyl (Gal$^\bullet$). We did not exclude path (i) from this study, keeping in mind that thermal OA can take place not only through an $S_N2$ but also through a radical-like mechanism, as for instance in the reported OA of alkyl iodides to $[Pt_2(pop)_4]^{4-}$[44] and $[PtMe_2(phen)]$ (phen = 1,10-phenanthroline).[59] However, the need for irradiation to reach the transformation of **3d** into **2c** (paths ii and iv) is not an unambiguous sign of a radical-based mechanism, as it occurs in complex $[Pt(CH_3)(N^N^N)](SbF_6)$ (N^N^N = 6,6′-diaminoterpyridine).[49]

Two comparative experiments with and without Gal$^\bullet$ showed that in both cases **1** reacts with $^{13}CH_3I$ readily in the dark to give species **3d**. As no diamagnetic species, arising from coupling of Gal$^\bullet$ with other generated radicals, were observed ($^1$H NMR) in the sample containing Gal$^\bullet$, it could be concluded that path (i) does not follow a radical-like mechanism but rather an $S_N2$ one. To check path ii, one set of two samples containing species **3d** and excess of $^{13}CH_3I$, with and without Gal$^\bullet$, was prepared in the dark and in the air and then exposed to the UV light for 10 min. An identical experiment was performed to check path iv but with the set of samples being prepared under Ar atmosphere.[60] In these experiments we observed that in the samples containing Gal$^\bullet$, the transformation of **3d** into **2c** was faster and that their $^1$H NMR spectra showed the presence of diamagnetic species arising from coupling of Gal$^\bullet$ with other generated radicals.

The observed effect of Gal$^\bullet$ and the invariably required light for the transformation of **3d** into **2c** are consistent with a radical-like mechanism, both in the presence of $O_2$ (path ii, Scheme 2) and in the absence of it (path iv, Scheme 2). In the absence of $O_2$, one possible explanation could come from the photochemical bond homolysis of the Pt−$CH_3$ bond[61] of **3d** upon UV light irradiation; the organometallic radical would abstract I from $CH_3I$ (preferentially than from the $CD_2Cl_2$ used as solvent) to give **2c**. In the presence of $O_2$, an important fraction of this radical-like transformation seems to occur through the methylperoxo intermediate **4d**.

Insertion of $O_2$ into an M−R bond to give an alkylperoxo complex is a rare feature for a late transition metal. Very few examples of stable Pt alkylperoxide complexes have been described, $[Pt(L)OOMe][SF_6]$ (L = 6,6′-diaminoterpyridine),[49,52] [(PN)PtMe(OOMe)] (PN = 2-((di-*tert*-butylphosphino)methyl)pyridine)[51] or $[PtMe_2(NN)(OOR)I]$ (NN = bpy, phen; R = $^i$Pr, $^t$Bu),[59] all of them being mononuclear complexes of Pt(II) and Pt(IV). To the best of our knowledge no dinuclear metal−metal bonded alkylperoxo complexes, like **4d**, have been reported so far. In this context, Goldberg[51] has also proposed a radical mechanism for the thermal reaction of [(PN)$PtMe_2$] (PN = 2-((di-*tert*-butylphosphino)methyl)-pyridine) with $O_2$, in view of the effects of light and the radical inhibitor 4-methyl-2,6-di-*tert*-butylphenol on the reaction rate. The resulting complex [(PN)PtMe(OOMe)] converts to [(PN)PtMe(Cl)] in $CD_2Cl_2$, similarly to the observed transformation of complex **4d** into **2c** in the presence of $CH_3I$ (species **4d** has proven not to be stable in the presence of $^{13}CH_3I$ and to convert into **2c** even in the dark). These results differ from the nonradical mechanism proposed for Britovsek et al. for the light-driven insertion of $O_2$ into the Pt−Me bond in $[Pt(L)Me][SF_6]$ (L = 6,6′-diaminoterpyridine). In this case, the effect of light seemed to be the conversion of the loosely aggregated Pt(II) complexes [Pt(II)···Pt(II)] into a triplet state $^3$[Pt(III)−Pt(III)]*, which can react with $^3O_2$, rather than $^3O_2$ sensitization by the Pt(II) complex, to generate $^1O_2$ before its insertion into the Pt−Me bond.[49] The methylperoxo derivative $[Pt(L)OOMe][SF_6]$ is not stable at room temperature and decomposes in acetone-$d_6$ in the ambient light to give $[Pt(L)OH][SF_6]$ and formaldehyde.

**2.4. Mechanistic Insight for the Oxidation Reaction of the Half-Lantern $Pt_2$(II,II) Complex 1 with Haloforms.** The reactions of **1** with an excess of $CHX_3$ (X = Cl, Br, I) rendered complexes $Pt_2$(III,III)$X_2$ (**2a**−**2c**) in moderate-to-good yield, as we mentioned above. With $CHBr_3$ and $CHI_3$ they proceed in the dark, but the reaction with $CHCl_3$ requires light to go on.

The reaction of **1** with $CHBr_3$ was followed by multinuclear NMR spectroscopy using $^{13}CHBr_3$ (molar ratio 1:3.25) as reagent and $CD_2Cl_2$ as solvent. When the reaction sample was prepared in an NMR tube in the dark and in the air, species $[Br(bzq)Pt(\mu\text{-}N^S)_2Pt(bzq)(^{13}CHBr_2)]$ (**3b**) and **2b** were observed (Scheme 2, path (v)) from the beginning (12 min.) in 2:1 molar ratio, together with the starting compound **1** (see Figure S5 in Supporting Information), and free $^{13}CHBr_3$ ($\delta_H$ = 6.91 ppm; $\delta_C$ = 10.31 ppm; $^1J_{C-H}$ = 206 Hz). The NMR parameters associated with the $^{13}CHBr_2$ fragment in **3b** ($\delta_H$ = 4.49 ppm (d), $^1J_{C-H}$ = 175 Hz, $^{2,3}J_{Pt-H}$ ≈ 11 Hz; $\delta_C$ = 20.85 ppm, $^1J_{Pt-C}$ = 623 Hz; $^2J_{Pt-C}$ = 512 Hz), are similar to those corresponding to the $CHI_2$ unit in $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(CHI_2)I(CO)_4]$ ($\delta_H$ = 4.74 ppm (s), $\delta_C$ = 26.3 ppm),[22] according with the proposed dinuclear $Pt_2$(III,III) formulation for **3b**. Compound **1** was completely transformed into **2b** (33%) and **3b** (66%) in 9.5 h. For comparative purposes, the same reaction was performed in the dark either under Ar or $O_2$ atmospheres (Figure S6 in Supporting Information). Both samples showed, after 2 h, mixtures of the three species (**3b**, **2b**, and **1**) but in different ratios (under Ar: **1** (35%), **2b** (17%), **3b** (48%); in $O_2$: **1** (20%), **2b** (50%), **3b** (30%)). These experimental data proved that $O_2$ is not essential for the formation of **2b** from **1** and $CHBr_3$, but it favors its formation. The direct formation of **2b** from **1** due to small amounts of $Br_2$ (generated by $O_2$) seems unlikely and can be ruled out since it occurred under Ar atmosphere. Then, the simultaneous formation of **2b** and **3b** suggests a radical pathway for the addition reaction.[44] To check this possibility we performed comparative experiments of the reaction of **1** with $^{13}CHBr_3$, both


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with and without Gal•, in the dark. After 2 h (in the air and in Ar atmospheres) the reactions in the presence of Gal• were slower, and the ratio of **2b** in the mixtures was bigger than in the absence of it (Supporting Information, Figure S7). All the experimental results concerning this reaction are in agreement with a radical pathway eq 2−eq 5, in which both $O_2$ and Gal• act as radical (R•) traps, increasing the **2b**:**3b** ratio.[44,62]

$$Pt_2 + RBr \rightarrow Pt_2Br\bullet + R\bullet \quad \text{(eq 2)}$$

$$Pt_2 + R\bullet \rightarrow Pt_2R\bullet \quad \text{(eq 3)}$$

$$Pt_2Br\bullet + RBr \rightarrow Pt_2Br_2 + R\bullet \quad \text{(eq 4)}$$

$$Pt_2R\bullet + RBr\bullet \rightarrow Pt_2RBr + R\bullet \quad \text{(eq 5)}$$

The reaction of **1** with $CHI_3$ (1:2 molar ratio) in $CD_2Cl_2$ at room temperature in the dark was shown to proceed in the same way but faster than that with $CHBr_3$. In the air, compound **2c** was quantitatively formed just upon mixing the reagents, as determined by $^1$H NMR. Under Ar atmosphere a mixture of species [I(bzq)Pt($\mu$-N^S)$_2$Pt(bzq)($CHI_2$)] (**3c**) and **2c** (molar ratio 6:1), with no traces of the starting compound **1**, was detected by $^1$H NMR (Figure S8 in Supporting Information) in just 15 min. So, in this case, $O_2$ acts as an efficient radical (R•) trap facilitating the complete conversion of **1** into **2c** in a few minutes.

Then, we studied the possible transformation of **3b**/**c** into **2b**/**c**. As a result of several experiments, we observed that the reaction mixtures containing species **3** and **2** remained invariable in the dark as much under Ar as in the air. However, irradiation with UV light promotes this transformation, which was revealed to be faster in the air than under Ar atmosphere.

In $CHCl_3$ solution, compound **1** is stable in the dark at room temperature, but in the sunlight it reacts to render complex **2a** in good yield. Most photooxidations of Pt(II) complexes in halocarbons have been described as requiring UV light to occur.[63−66] However, in our case we observed that this reaction takes place simply upon irradiation with green light-emitting diodes (LEDs, $\lambda \approx 500$ nm). Thus, a solvent-initiated radical-like pathway could be excluded. Monitoring by UV−visible spectroscopy the decay of the MMLCT absorption of complex **1** (~495 nm in $CHCl_3$) when it reacts with $CHCl_3$ upon irradiation with green LEDs ($\lambda \approx 500$ nm) (Table S4 and Figures S9 and S10 in Supporting Information) we could observe that the initial reaction rate increases with the concentration of nucleophile **1**. This fact is consistent with an $S_N2$ mechanism[59,60,62] for the OA reaction, but it seems unlikely since complex **1** remained unreacted in refluxing $CHCl_3$ solution in the dark, both in the air and in Ar atmosphere.

For comparative purposes two samples containing **1** and distilled $CDCl_3$ as solvent and reagent were prepared in the dark, one in the air and the other one under Ar atmosphere. Their $^1$H NMR spectra revealed that upon irradiation with green LEDs for 6h the complete oxidation of **1** occurred, with **2a** being the sole species observed in the sample prepared in the air while a mixture of **2a** (15%), **3a** (70%) and unidentified species (15%) was in the other one.[67] In the presence of Gal• the reaction was slower than in the absence of it, and **2a** was the only oxidized species as much in the air as under Ar atmosphere. These observations are in agreement with the free radical (R·) trap role of Gal• and $O_2$ in this reaction.

Then, we studied the possible transformation of **3a** into **2a**. As results of several experiments we observed that the mixtures remained invariable in the dark and that upon irradiation with green LEDs for 17 h **3a** was still present in the mixtures in ≈10%, in the air and under Ar atmospheres. Keeping in mind that irradiation of the sample containing **1** and distilled $CDCl_3$ in the air for 6 h rendered **2a** as the sole oxidized compound, it seems evident that **2a** should be formed directly from **1**, rather than from the slow transformation of **3a**.

Despite similarities, there is an important difference with respect to the reaction of **1** with $CHX_3$ (X = Br, I). While the latter proceeds in the dark, the reaction with $CHCl_3$ needs light to go on, indicating that it is photochemically but not thermally initiated. Given that complex **1** absorbs at 495 nm ($^1$MMLCT band), irradiation with green light would lead to MMLCT excited $Pt_2$(II,II) complexes, whose interaction with $CHCl_3$ will undergo dissociation into $Pt_2Cl$• and $CHCl_2$•, as the first step of a radical reaction pathway.[68]

**2.5. Density Functional Theory Calculations for the Oxidative Addition Reaction Step, through an $S_N2$ Mechanism.** We found that the reactions of **1** with haloforms proceed immediately in the dark for $CH_3I$ and $CHI_3$, slowly with $CHBr_3$, and must be photochemically initiated in the case of $CHCl_3$. This behavior parallels the increasing bond energy of the C−X bond (bond dissociation energies increase in the sequence C−I < C−Br < C−Cl).[69,70] Concerning the OA step of these reactions, the one with $CH_3I$ seems to follow a typical $S_N2$ pathway, whereas a radical-like mechanism seems to be operative for all the three haloforms. To obtain additional pieces of the puzzle, we performed the density functional theory (DFT) modelization of the $S_N2$ mechanism for the OA step, leading to the formation of the asymmetric R−Pt(III)−Pt(III)−X complexes **3**, and compared the results with the experimental data collected. Thus, we studied the gas-phase 1:1 reaction of the haloalkanes with the $Pt_2$(II,II) precursor **1** at the M06/SDD(f)/6-31g* level of theory (see computational details in Supporting Information). Electronic and free energies in the gas phase (Figure 4a) and free energies in $CH_2Cl_2$ solution (Figure 4b) computed by using the PCM model were included in the discussion. In all cases the reference energy values (0.0 kcal/mol) have been assigned to the Pt(II)−Pt(II)···R−X adducts.

In general terms the energy profiles obtained consist of potential energy curves with pre- and post-reaction intermediates separated by a central barrier (Figure 4). Similar profiles were observed in related cases modeled by DFT, as in the bimolecular $S_N2$ reaction $X^- + CH_3Y \rightarrow XCH_3 + Y^-$.[71] Thus, the first step consists of the interaction of the $Pt_2$(II,II) precursor acting as a nucleophile with the haloalkane. The formed adduct results from the stabilizing interaction of the $Pt_2$-centered highest occupied molecular orbital of the dinuclear complex with the electrophillic C atom of the halogenated substrate. The next step consists of the nucleophilic substitution itself, which happens through a transition state showing a hypervalent C atom with two long Pt···C and C···X distances, which subsequently leads to the formation of a cationic Pt(II)−Pt(IV)−R intermediate stabilized by the halide anion. Finally, the migration of the halide to the Pt(II) center of the latter intermediate generates the final R−Pt(III)−Pt(III)−X derivative **3**.

The theoretical results show interesting trends that must be highlighted. From a thermodynamic point of view the formation of the R−Pt(III)−Pt(III)−X derivatives (**3**) through an $S_N2$ mechanism is little exothermic, with $\Delta G_{sol}$ values between −0.7 and −5.2 kcal/mol ($\Delta E_{gas}$ between +1.5 and −2.6 kcal/mol). This indicates that species **3**, directly resulting from the *formal* OA of the RX molecules, are just scarcely favored over the reactants. The nearly reversible character of these processes



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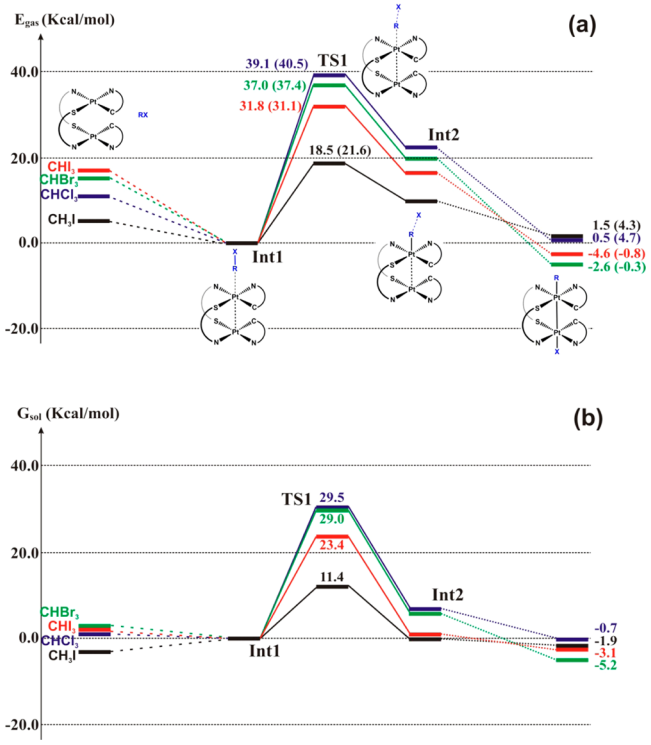


**Figure 4.** DFT-calculated energy profiles for the $S_N2$ reactions of complex **1** with haloalkanes. (a) Electronic energies and free energies (in parentheses), calculated in the gas phase. (b) Free energies, calculated in $CH_2Cl_2$ solution.

justifies the failure to isolate the asymmetric species **3d** as pure compound.

From the kinetic point of view, OA of $CH_3I$ to the $Pt_2(II,II)$ species is rather different than the addition of the $CHX_3$ (X = Cl, Br, I) molecules. The activation energy in the former case is remarkably low ($\Delta G_{sol}$ = +11.4 kcal/mol; $\Delta E_{gas}$ = +18.5 kcal/mol), suggesting that this process shall readily occur through a classical $S_N2$ mechanism with no need of heating or light irradiation. This is in agreement with the easy and fast formation of the $CH_3$−Pt(III)−Pt(III)−I derivative **3d** in solution. In contrast, the activation energies of the OA of the haloforms to the dinuclear precursor are markedly higher, following the order I < Br < Cl. At first sight, the energy barriers calculated in the gas phase may appear very high ($\Delta E_{gas}$ from +31 to +40 kcal/mol); however, correction of the solvent effects by using the polarizable continuum model (PCM) affords a decrease of these energies. Among them, the OA of iodoform shows a $\Delta G_{sol}$ activation barrier of 23.4 kcal/mol, whereas the barriers for bromoform and chloroform are 29.0 and 29.5 kcal/mol. These data suggest that the $S_N2$ mechanism could still be operative, simultaneously with a radical-like mechanism, for the reaction of **1** with $CHI_3$, but it appears unlikely for the reactions of **1** with $CHBr_3$ and $CHCl_3$.

Besides, the experimental data show that the reaction of the $Pt_2(II,II)$ species **1** with RX substrates eventually yields the symmetric X−Pt(III)−Pt(III)−X (**2**) derivatives instead of the asymmetric R−Pt(III)−Pt(III)−X (**3**) species. Thus, the former compounds appear to be thermodynamic sinks in the oxidation processes. Consistent with this, the oxidation of the Pt(II)−Pt(II) precursor with $X_2$ quickly and quantitatively affords the X−Pt(III)−Pt(III)−X species **2** (see Scheme 1). To complete the picture of our DFT studies, the OA of the $Pt_2(II,II)$ species **1** with $X_2$ through an $S_N2$ mechanism was also modeled.

In all three cases (X = Cl, Br, I), the energy profiles obtained in the gas phase are simpler (Figure S11 in Supporting Information), as only one intermediate species between the reactants and products was found. DFT calculations on these oxidation processes predict very favored reactions, in agreement with the high thermodynamic stability of the $Pt_2(III,III)X_2$ derivatives **2**. The formation of the dihalogenated species is increasingly favored in the sequence of I < Br < Cl and present $\Delta G_{sol}$ values between −9 and −31 kcal/mol ($\Delta E_{gas}$ between −11 and −38 kcal/mol). These data are in obvious contrast with the barriers computed for the first series of oxidative addition processes, which are either balanced or slightly exothermic processes.

## 3. CONCLUSIONS

The new half-lantern compound [{Pt(bzq)($\mu$-N^S)}$_2$] (**1**) [bzq = benzo[*h*]quinoline, HN^S = 2-mercaptopyrimidine] has been found to promote C−X bond activation in haloforms $CHX_3$ (X = Cl, Br, I) and $CH_3I$. In excess of RX the reactions lead to the oxidized $Pt_2(III,III)X_2$ (**2a**−**2c**) compounds in reasonable-to-good yields. With $CH_3I$ the reaction consists in the thermal OA of RX to the $Pt_2(II,II)$ complex **1** through an $S_N2$ mechanism, to selectively give [X(bzq)Pt($\mu$-N^S)$_2$Pt(bzq)R] (**3d**). However, with the haloforms, the reactions proceed through a radical-like mechanism, thermally ($CHBr_3$, $CHI_3$) or photochemically ($CHCl_3$) activated, giving rise to mixtures of species [X(bzq)-Pt($\mu$-N^S)$_2$Pt(bzq)R] (**3a**−**c**) and [X(bzq)Pt($\mu$-N^S)$_2$Pt(bzq)-X] (**2a**−**c**) in different ratios. In these cases, $O_2$ acts as radical scavenger ($R^\bullet$), like Galvinoxyl, favoring the formation of species **2** over **3**. Species **3a**−**d** have been proved to be stable in the dark, either under Ar or in the air, but they transform into **2a**−**c** upon irradiation. Spectroscopic evidence supports that in the presence of $O_2$ the transformation of the labeled species [I(bzq)Pt($\mu$-N^S)$_2$Pt(bzq)($^{13}CH_3$)] (**3d**) occurs through the unusual methylperoxo derivative [I(bzq)Pt($\mu$-N^S)$_2$Pt(bzq)(O−O$^{13}CH_3$)] (**4d**), which, in the presence of $^{13}CH_3I$, renders the final products [{Pt(bzq)($\mu$-N^S)I}$_2$] (**2c**) and $^{13}CH_3OH$.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and materials. Numeration scheme for NMR purposes. Synthesis details. Diffusion-ordered $^1$H-RMN spectroscopy (DOSY) in solution. Normalized absorption spectra of **1** at room temperature. X-ray structure determination and crystal data of compounds **2a**−**2c** and **3d**. Computational details including molecular structure of **2a**, **2b**, and **2b′**. Selected bond distances (Å) and angles (deg) of compounds **2a** and **2c**. Molecular structure of **3d**. $^1$H NMR spectra of the reactions of **1** with $^{13}CHBr_3$ (1:3.25) and $CHI_3$ (1:2) in $CD_2Cl_2$ in different conditions. Initial reaction rates of the reaction of **1** with $CHCl_3$. LEDs disposition in the UV−vis spectrophotometer for kinetic measurements. Absorbance−time graphic ($\lambda$ = 490 nm) for the reaction of **1** with $CHCl_3$ under irradiation with green LEDs ($\lambda \approx$ 500 nm) at 25 °C. DFT-calculated energy profiles for the $S_N2$ reactions of $X_2$ and **1**. Electronic energies and free energies (in parentheses) calculated in the gas phase. Free energies calculated in $CH_2Cl_2$ solution. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00846. CCDC Nos. 1056301−1056303 contain the supplementary crystallographic data for compounds **2a**·$CH_2Cl_2$, **2b**·2THF, and **2c**·2$CH_2Cl_2$, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif



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### Notes

The authors declare no competing financial interest.

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## DEDICATION

Dedicated to Dr. Babil Menjón on the occasion of his 55th birthday.

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