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Monitoring Light-Driven Oxygen Insertion Reactions into Metal Carbon Bonds by LED-NMR Spectroscopy

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The facile light-driven insertion reaction of oxygen into metal carbon bonds of the BPI (1,3-bis(2-pyridylimino)isoindole) complexes [Pt(BPI)Me] and [Pd(BPI)Me] has been investigated by LED-NMR in CDCl₃. The initial insertion reaction leads to peroxy complexes [Pt(BPI)OOMe] and [Pd(BPI)OOMe], which undergo further reactions over time. Spectra were recorded at 1 minute time intervals, which enabled the tracking of the methyl

substituent, which eventually generates formaldehyde (and methanediol) and methanol in almost equal proportions. Degradation of the solvent CDCl₃ to phosgene and DCl in the presence of oxygen and light leads to several side reactions. DCl reacts with [M(BPI)Me] and [M(BPI)OOMe] to form [M-(BPI)Cl], whereas phosgene reacts with in situ generated methanol to chloro methylformate and dimethyl carbonate.

Introduction

Photochemical and photocatalytic reactions are currently undergoing a resurgence in interest, in particular the application of photoredox catalysis in organic photochemistry and synthesis.^[1] Monitoring photochemical reactions by NMR spectroscopy presents challenges with respect to introducing light into the cavity of the NMR spectrometer in a controlled manner. Initial approaches involved the use of lasers, either directly through holes in the NMR probe, or indirectly via fibre optic cables, for example in the early work by Berliner *et al.*^[2] However, laser light sources are expensive, require special safety precautions and tend to have poor coupling with the optic fiber. An alternative approach is the use of flowNMR, pioneered by Hintermair *et al.*, who used irradiation of a photochemical reaction solution outside the NMR spectrometer in combination with a continuous flow setup.^[3] More recently, the use of light-emitting diodes (LEDs) has been applied in NMR spectroscopy. LEDs are low cost, easy to handle and have a wide range of available wavelengths.^[4] Gschwind and co-workers have made tremendous improvements in the *in-situ* NMR set-up using LED light sources coupled with an optic fiber

and applied this LED-NMR system to study the mechanism of various photochemical reactions.^[5]

Light-driven oxygen insertion reactions of late transition metal alkyl complexes are of interest in the context of developing photocatalytic methods for the oxidation of alkanes with oxygen. The reactivity towards oxygen of Group 10 alkyl complexes featuring terpyridine or 1,3-bis(2-pyridylimino)isoindole (BPI) ligands have been investigated by us and others.^[6] In the case of [M(BPI)Me] complexes, the light-induced oxygen insertion reactions lead initially to the formation of methylperoxy complexes [M(BPI)OOMe], which undergo further reactions to a range of products (Figure 1).^[6d] Here we report our results using LED-NMR spectroscopy to study these light-driven oxygen insertion reactions of Pd and Pt methyl complexes [Pt(BPI)Me] and [Pd(BPI)Me] in CDCl₃ in real time.

Monitoring the reaction progress by LED-NMR has enabled tracking of the oxygen insertion reaction and our particular interest has been to track the fate of the methyl group in [M(BPI)Me], which eventually ends up in several products such as methane, methanol, methyl chloride, formaldehyde and methanediol, as well as in products such as methyl chloroformate and dimethyl carbonate, derived from the photolytic

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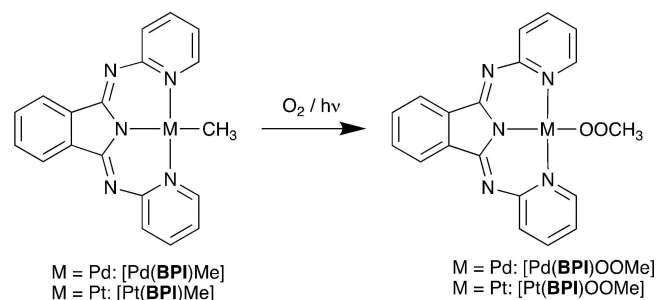


Figure 1. Oxygen insertion reactions of Pd and Pt BPI methyl complexes.

decomposition of the solvent chloroform in the presence of oxygen.

Results and Discussion

A solution of [Pt(BPI)Me] in CDCl_3 was placed in an NMR tube and the solution was saturated with oxygen at room temperature. A coaxial insert containing a fiber optic cable was inserted into the NMR tube and this was lowered into the NMR spectrometer (see Supporting Information for details). The fiber optic cable was coupled to a LED light source (375 nm, 3.2 mW) and the progress of the reaction shown in Figure 1 was monitored from $t=0$ (the time when the light was turned on) by ^1H NMR spectroscopy at room temperature. The amount of light was controlled by the LED driver and the light intensity was determined by actinometry using *o*-nitrobenzaldehyde as the actinometer (see Supporting Information for details). At $t=0$, which is approximately 10–15 minutes after the introduction of oxygen, some starting complex has already reacted due to a slow background reaction in the dark and the inability to

exclude all light during setup and transfer. Spectra were recorded at 1 minute time intervals and the reaction progress was determined by integration of the signals for the individual components in the reaction mixture (see Figure 2 and Figure S8 for the individual spectra). Assignments of the individual reaction components have been reported previously.^[6d]

Upon irradiation, [Pt(BPI)Me] reacts with oxygen to give [Pt(BPI)OOMe] as the initial product. The formation of [Pt(BPI)OOMe] reaches a maximum after approximately 12 minutes under these conditions due to further reactions, either to a mixture of the hydroxo complex [Pt(BPI)OH] and formaldehyde, or to the chloro complex [Pt(BPI)Cl] and methyl hydroperoxide. The formation of the chloro complex is attributed to the formation of DCI (generated from CDCl_3 during irradiation), as shown in our previous report.^[6d] The hydroxo complex [Pt(BPI)OH] converts over time in CDCl_3 to [Pt(BPI)Cl], presumably also due to the *in situ* generated DCI. An additional minor pathway involves the reaction of [Pt(BPI)Me] with DCI to form CH_3D and [Pt(BPI)Cl]. All pathways, as shown in Figure 3, eventually lead to [Pt(BPI)Cl] and the amount of

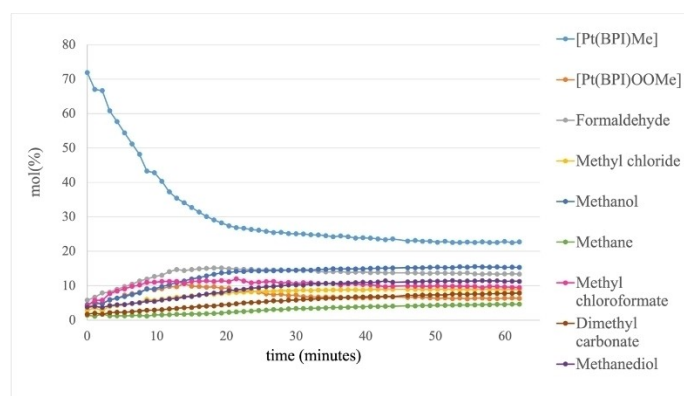


Figure 2. Reaction progress monitored by LED-NMR of the reaction of [Pt(BPI)Me] with oxygen in CDCl_3 during irradiation (375 nm) (100 mol % relates to methyl/methylene containing species only).

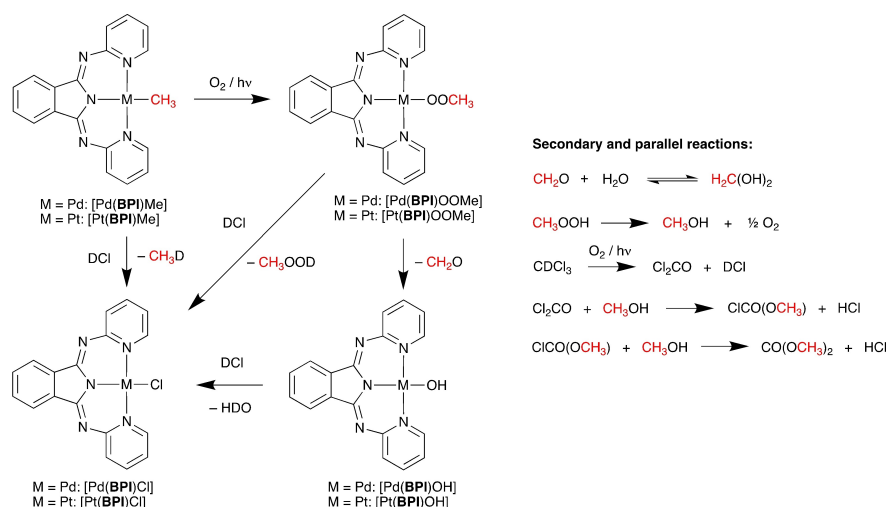


Figure 3. Reaction of methyl BPI complexes with oxygen and light and secondary reactions.

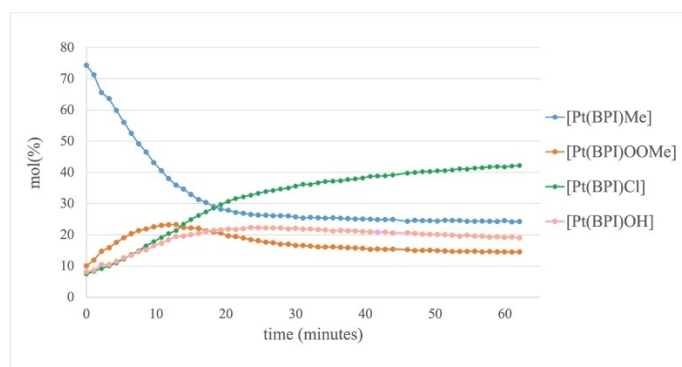


Figure 4. Detailed reaction progress monitored by LED-NMR of the metal complexes formed from reaction of [Pt(BPI)Me] (16 mM) in CDCl_3 at 298 K with oxygen during irradiation (375 nm) (100 mol% refers to all Pt containing species).

[Pt(BPI)Cl] increases over time and becomes the main platinum species in solution at the end of the reaction (see Figure 4).

Full conversion of [Pt(BPI)Me] could not be achieved under these conditions due to the lack of sufficient oxygen in the closed system. As pointed out previously by others,^[4a] one of the main drawbacks of the current LED-NMR setup is the small headspace available in the NMR tube due to the insert diminishing the headspace volume available. Consequently, the amount of oxygen available for the reaction is limited. The solubility of oxygen in chloroform is approximately 10 mM under these conditions,^[7] whereas the concentration of the complex in the NMR tube is typically approximately 20 mM. From Figures 4 and 5, it appears that available oxygen has been depleted after approximately 20 minutes. While this limits the kinetic information that can be obtained from these experiments, the half-life for the reaction of [Pt(BPI)Me] with oxygen as shown in Figure 1 under these conditions can be estimated as approximately 8 minutes. When the complex concentration is lowered to 5 mM, complete conversion of [Pt(BPI)Me] is observed within approximately 1 hour, but the signal-to-noise ratio becomes too low for reliable integration of the signals (see Figure S10).

The methylperoxo complex [Pt(BPI)OOME] generates CH_3OOD over time in CDCl_3 due to in situ generated DCl. CH_3OOD is unstable and decomposes either to methanol and

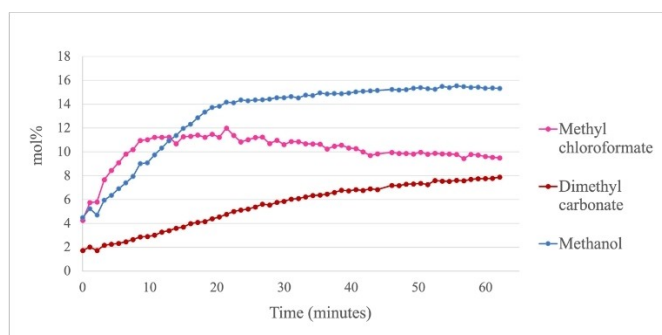


Figure 5. Conversion of in-situ generated methanol and phosgene to methyl chloroformate and dimethyl carbonate by LED-NMR of [Pt(BPI)Me] with oxygen in CDCl_3 during irradiation (375 nm).

oxygen or to formaldehyde and water. Methanol reacts with phosgene, which is generated in situ from the reaction of CDCl_3 with oxygen under irradiation,^[8] to generate initially methyl chloroformate and eventually dimethyl carbonate. The amount of methyl chloroformate increases at the beginning and reaches a maximum after approximately 9 minutes. The amount of dimethyl carbonate gradually increases over time and after 60 minutes a total of 15 mol% methanol, 9 mol% $\text{ClCO}(\text{OMe})$ and 8 mol% $\text{CO}(\text{OMe})_2$ have been generated (see Figure 5).

The amount of formaldehyde increases from the start of the reaction, but reaches a maximum after approximately 12 minutes of irradiation, then decreases and reaches an equilibrium due to reaction with water (or HOD, generated from CH_3OOH decomposition or from [Pt(BPI)OH]) to give methanediol ($\text{CH}_2(\text{OH})_2$, seen at $\delta(\text{CH}_2) = 4.73$ ppm) (see figure S6). After 1 hour of irradiation, a total of 13 mol% formaldehyde and 11 mol% methanediol are generated from the oxygen insertion reaction in CDCl_3 . The fate of the methylperoxo moiety in [Pt(BPI)OOME] can therefore be estimated to end up as approximately 40% formaldehyde (incl. methanediol) and 60% methanol (incl. methyl chloroformate and dimethyl carbonate). It is also interesting to note that the concentration of [Pt(BPI)Me], [Pt(BPI)OH] and [Pt(BPI)OOME] decrease only very slowly once all oxygen has been consumed (see Figure 4), suggesting that the product from the reaction of oxygen with the solvent CDCl_3 , most likely DCl, is responsible for the conversion of these complexes to [Pt(BPI)Cl].

In the case of palladium, the oxygen insertion of [Pd(BPI)Me] was monitored under the same conditions as above using LED-NMR spectroscopy over one hour under irradiation at 375 nm in CDCl_3 at room temperature. The initial reaction of [Pd(BPI)Me] with oxygen is observed with a half-life of approximately 4 minutes under these conditions, and the formation of [Pd(BPI)OOME] reaches a maximum after approximately 6 minutes (Figures 6–7). The faster reaction seen for Pd versus Pt reflects the difference in M–C bond strength (36 kcal/mol for Pt–C versus 28 kcal/mol for Pd–C).^[9] No formation of a [Pd(BPI)OH] complex was observed, which is either not formed or reacts rapidly with HCl to the [Pd(BPI)Cl] complex, which is the main complex observed at the end of the reaction

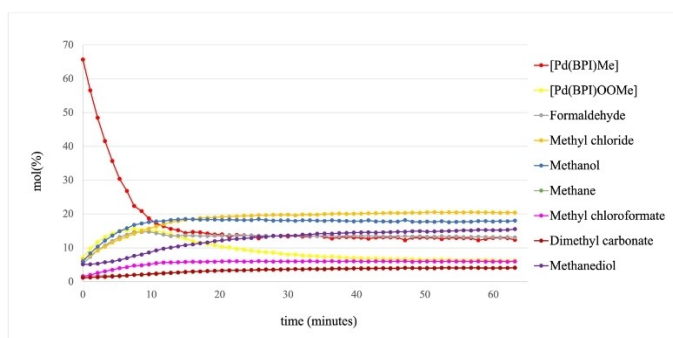


Figure 6. Reaction progress monitored by LED-NMR of the reaction of [Pd(BPI)Me] (24 mM) in CDCl_3 at 298 K with oxygen during irradiation (375 nm) (100 mol% relates to methyl/methylene containing species only).

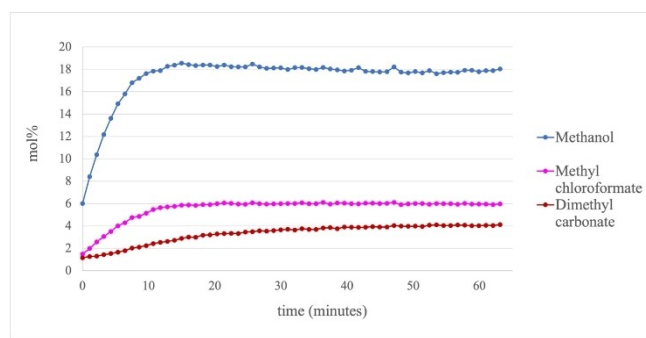


Figure 8. The formation of methanol, methyl chloroformate and dimethyl carbonate formed upon reaction of [Pd(BPI)Me] with oxygen in CDCl_3 during irradiation (375 nm). (100 mol% refers to all methyl/methylene-containing species).

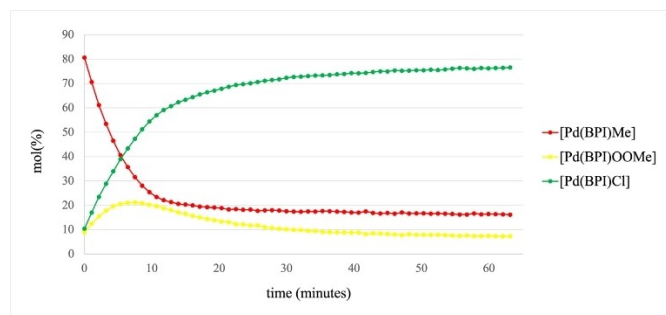


Figure 7. Detailed reaction progress monitored by LED-NMR of the metal complexes formed from reaction of [Pd(BPI)Me] with oxygen in CDCl_3 at 298 K during irradiation (375 nm). (100 mol% refers to all Pd-containing species).

(Figure 7). There is also a greater proportion of methyl chloride in this case, 20 mol% versus 9 mol% in the case of Pt, probably also a reflection of the weaker Pd–C bond compared to Pt–C. As before, full conversion of the starting complex is not observed, due to the lack of sufficient oxygen available in the system and oxygen appears to be depleted after approximately 15 minutes in this case.

In terms of non-metal products, the amount of methyl chloroformate increases initially, then plateaus after approximately 12 minutes, while the amount of dimethyl carbonate slowly increases over time (Figure 8). This behaviour reflects the different rates of methanol formation from the Pd-methyl complex versus phosgene generation from CDCl_3 and oxygen. Once the amount of oxygen in the system has been depleted, no further formation of phosgene takes place and presumably an equilibrium is reached between methanol, methyl chloroformate, dimethyl carbonate and HCl in solution.

The amount of formaldehyde, formed from the decomposition of the methylperoxy moiety, initially increases but the rate of formation slows down after approximately 8 minutes due to a slow conversion to methanediol $\text{H}_2\text{C}(\text{OH})_2$ (see Figure S7). At the end of the reaction, 13 mol% formaldehyde and 15 mol% methanediol are generated from the oxygen insertion. The fate of the methylperoxy moiety in this case can be approximated as 50% to formaldehyde (and methanediol)

and 50% to methanol (and chloroformate and dimethylcarbonate).

Conclusions

To conclude, we have shown that *in-situ* LED-NMR spectroscopy provides an easy and convenient method to monitor the progress of light-driven reactions. The reaction of [Pt(BPI)Me] and [Pd(BPI)Me] with oxygen to give [Pt(BPI)OOMe] and [Pd(BPI)OOMe] respectively, was studied as a function of time, under constant irradiation. According to the NMR data, formaldehyde and methanol are the major final oxidised products, but other products are also observed due to the decomposition of chloroform to phosgene in the presence of light and oxygen. The LED-NMR method is particularly useful to track the fate of individual intermediates and reaction products in a complex reaction mixture. Due to the small headspace available in the reaction setup, problems are encountered when one of the reactants is a gas, as seen here with the use of oxygen. The limited supply of oxygen in this case leads to incomplete conversion of the starting complexes, which hampers the overall kinetic analysis. To overcome these limitations, further developments are underway to generate either a pressurizable LED-NMR setup or enable a constant gas supply.

Supporting Information

Materials and methods, LED-NMR details, additional figures and NMRs. NMR data have been deposited at the Research Data Repository of Imperial College London. Doi: 10.14469/hpc/11676.

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Conflict of Interest

There are no conflicts of interest to declare.

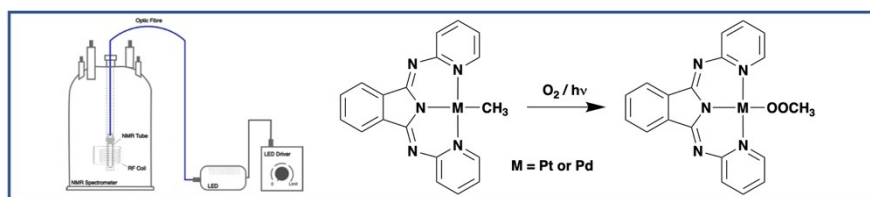
Data Availability Statement

Supporting data (NMR data) are available from DOI:10.14469/hpc/11676.

Keywords: LED-NMR · methylperoxo · oxygen · palladium · platinum

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LED-NMR has been used to monitor the reaction progress of the light-

driven insertion of oxygen into metal methyl bonds.

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**Monitoring Light-Driven Oxygen
Insertion Reactions into Metal
Carbon Bonds by LED-NMR Spec-
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