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Towards Photocatalytic Alkane Oxidation: The Insertion of Dioxygen into a Platinum(II)–Methyl Bond**

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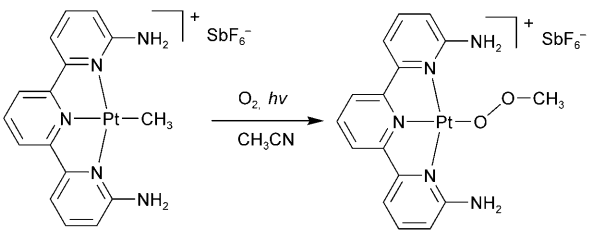
The selective catalytic oxidation of methane and higher alkanes remains one of the great challenges in catalysis research. Considerable progress has been made during the last three decades regarding the C–H activation of alkanes, in particular electrophilic activation reactions with late transition metals.[1–4] Once C–H bond cleavage has occurred at a metal center, a functionalization of the metal–carbon bond is required, followed by release of the product and regeneration of the catalyst. In the case of oxidation reactions, this functionalization of metal–alkyl complexes should be carried out ideally with environmentally benign oxidants such as O_2 or H_2O_2. We previously reported the oxidation of dimethylplatinum(II) complexes with H_2O_2 to generate *cis*-dihydroxoplatinum(IV) complexes.[5] The unusual *cis* isomer was obtained by using amino-substituted bipyridine ligands, which stabilize this isomer through hydrogen bonding. When we extended our work to methylplatinum(II) complexes containing tridentate amino-substituted terpyridine (terpy) ligands, we discovered a remarkable reactivity of the complexes towards O_2.

The reaction of 6,6′-diaminoterpyridine (**1**) with [Pt(SMe$_2$)$_2$MeCl], followed by reaction with AgSbF$_6$, affords the ionic complex [Pt(**1**)Me][SbF$_6$]. A reaction takes place when dioxygen is passed through a solution of [Pt(**1**)Me][SbF$_6$] in a polar solvent such as acetonitrile or acetone at room temperature and in ambient light. The characteristic Pt-Me signal at $\delta = 1.54$ ppm ($J_{\text{Pt-H}} = 72$ Hz, [D$_6$]acetone) in the ^{1}H NMR spectrum disappears over the course of several minutes and a new singlet emerges at $\delta = 3.39$ ppm ([D$_6$]acetone), together with a new set of signals for the 6,6′-diaminoterpyridine ligand (see Figures S1 and S3 in the Supporting Information). This new complex was isolated in quantitative yield and all analytical data suggest that insertion of O_2 into the platinum–methyl bond has occurred to form a methylperoxo complex [Pt(**1**)OOMe][SbF$_6$] [Eq. (1)]. The rate of the O_2 insertion reaction is affected by light: Whereas the reaction proceeds within several minutes at room temperature in ambient light, the reaction is very slow in the absence of light and only 50% conversion is obtained after 13 h at room temperature.



(1)

The solid-state structure of [Pt(**1**)OOMe][SbF$_6$] shows the presence of two crystallographically independent cation/anion pairs, with the two unique cations forming a head-to-tail dimer with a Pt···Pt separation of 3.1999(5) Å (see Figure 1 and the Supporting Information).[6] The formation of such a dimer is quite common for platinum(II)–terpyridine complexes and arises from metal–metal and π–π interactions.[7] It is, for example, also observed in the solid-state structure of [Pt(terpy)Me][BPh$_4$] (mean-plane separation: 3.42 Å).[8]

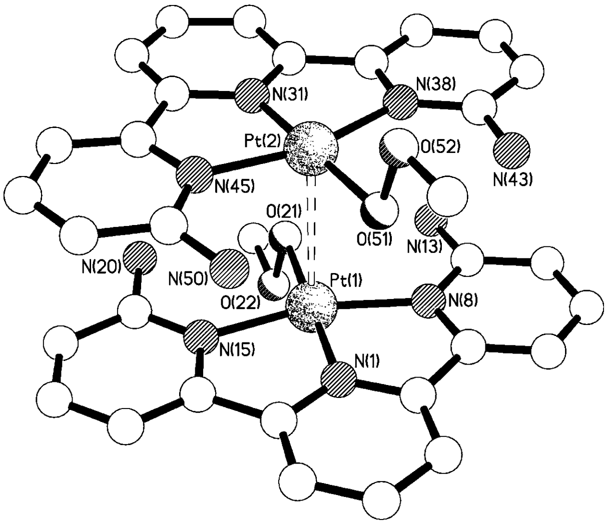


Figure 1. The molecular structure of the cation dimer present in the crystals of [Pt(**1**)OOMe][SbF$_6$].[6]

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In the solid state and in solution, NH···O hydrogen-bonding interactions exist between the amino substituents and the α-O atom (see the Supporting Information). The amino substituents also have a marked effect on the electronic properties, which is illustrated by the UV/Vis spectra of [Pt(**1**)Me][SbF$_6$] and [Pt(terpy)Me][SbF$_6$] (Figure 2). The extinction coefficient (ε) for the absorption in the MLCT region (between 350 and 450 nm) is an order of magnitude greater for the diamino-substituted complex. Preliminary studies have shown that [Pt(**1**)Me][SbF$_6$] shows photoluminescence in CH$_2$Cl$_2$ solution at room temperature, similar to observations with other substituted platinum(II)–terpyridine complexes.[9–11] Excitation of the charge-transfer region at 388 nm results in an emission spectrum with maxima at 580 and 654 nm (see the Supporting Information). It is notable that the diamino-substituted terpyridine ligand itself also shows photoluminescence.[12,13] The luminescent behavior of [Pt(**1**)Me]$^+$ is very different from that of [Pt(terpy)Me]$^+$, which shows no significant photoluminescence at room temperature in CH$_3$CN.[8]

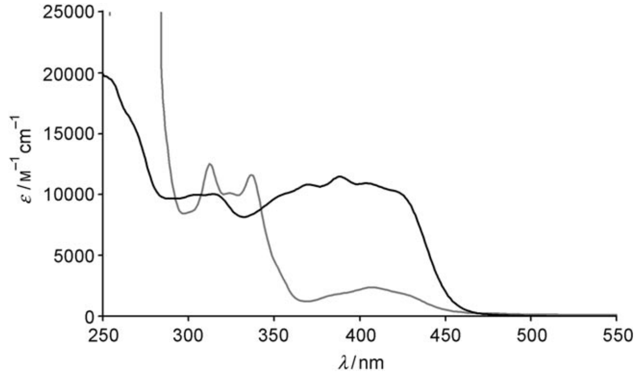


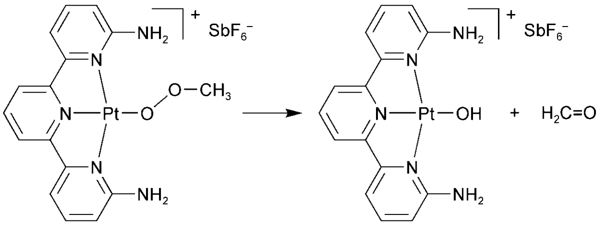
Figure 2. UV/Vis spectra of [Pt(**1**)Me][SbF$_6$] (black) and [Pt(terpy)Me][SbF$_6$] (gray) in CH$_3$CN at 298 K.

The formation of a platinum(II)–methylperoxo complex by insertion of O$_2$ into a Pt^{II}–Me bond, as seen here, appears to be very rare. The only other example is the recently reported complex [(PN)Pt(Me)(OOMe)] (PN = 2-(di-*tert*-butylphosphinomethyl)pyridine) by Grice and Goldberg.[14] In addition, several Pt^{II} and Pt^{IV} complexes containing alkylperoxo ligands other than methylperoxo have been reported, but none of these have been prepared by an O$_2$ insertion reaction.[15–20] The insertion of O$_2$ into the Pt^{II}–Me bond to give complex [(PN)Pt(Me)(OOMe)] is also affected by light, and the authors have proposed a radical mechanism.[14] Similarly, the insertion of O$_2$ into a Pt^{IV}–H bond has been reported to involve a radical pathway,[21] and insertions of O$_2$ into other transition-metal–methyl bonds, such as in Co–Me and Fe–Me complexes, proceed via methyl radicals.[22,23] In contrast, two reports on the direct insertion of O$_2$ into Pd^{II}–H bonds have shown that these insertion reactions are not affected by light.[24,25] Mechanistic investigations suggest that these reactions proceed by a Pd^I/HO$_2$ (triplet) radical-pair intermediate or by a stepwise pathway initiated by reductive elimination of HX to form an O$_2$-reactive Pd^0 intermediate.[26,27]

Dioxygen, in its triplet ground state, is rather unreactive because reactions are spin-forbidden and require a triplet–singlet surface crossing on the reaction coordinate.[28] Many organic O$_2$ sensitizers such as rose bengal or methylene blue are able to convert triplet oxygen (^{3}O$_2$) into singlet oxygen (^{1}O$_2$),[29] but also certain Pt^{II} and Ir^{III} complexes are known to be able to act as O$_2$ sensitizers and generate ^{1}O$_2$.[30–32] In some cases, in situ generated ^{1}O$_2$ can react with organometallic complexes, for example, to generate peroxide complexes.[33,34] Examples of self-sensitization, whereby a metal complex can both generate ^{1}O$_2$ and react with ^{1}O$_2$ are relatively rare, but have been observed for certain platinum(II)–bipyridine dithiolate complexes.[35,36] The electronic spectra and luminescent properties of [Pt(**1**)Me][SbF$_6$] are strong indicators that this complex can act as an O$_2$ sensitizer, and we therefore propose a nonradical mechanism for the insertion of O$_2$ in the case of [Pt(**1**)Me][SbF$_6$], which we believe proceeds through an initial ^{3}O$_2$ sensitization by this complex to generate ^{1}O$_2$, followed by a fast ^{1}O$_2$ insertion into the Pt–Me bond. The difference between the two mechanisms is illustrated by the fact that the O$_2$ insertion reaction reported by Grice and Goldberg provides the methylperoxo complex in 64–79 % yield at 5 atm O$_2$ pressure after 7–11 h,[14] whereas in our case the insertion reaction proceeds quantitatively at 1 atm O$_2$ within minutes. In the case of complex [Pt(**1**)Cl][SbF$_6$], in which O$_2$ cannot be inserted, the formation of ^{1}O$_2$ was confirmed by the oxidation of 2,2,6,6-tetramethylpiperidine (TMP) with O$_2$ in the presence of [Pt(**1**)Cl][SbF$_6$] and light.[31,37,38] The reaction product (TEMPO) is a stable radical, which can be detected by EPR spectroscopy (see the Supporting Information).

Singlet oxygen is similar in character to an electron-deficient alkene, and metal complexes containing a coordinated ^{1}O$_2$ ligand have recently been reported.[39,40] Coordination prior to insertion, akin to alkene insertion into a metal–alkyl bond, to give an intermediate Pt^{II} complex containing an η^2-bound ^{1}O$_2$ ligand cannot be excluded at this stage, although we have not observed any intermediates by NMR spectroscopy at room temperature. In contrast to the reactivity of [Pt(**1**)Me][SbF$_6$] with O$_2$, the reaction of [Pt(terpy)Me][SbF$_6$] with O$_2$ in either acetone or acetonitrile, under identical conditions (ambient light and room temperature), does not result in an insertion reaction. The UV/Vis spectra in Figure 2 show that these two complexes have a distinctly different charge-transfer behavior, and it has been previously reported[8] that [Pt(terpy)Me]$^+$ complexes are non-emissive and, therefore, this complex is not able to act as a photosensitizer and generate ^{1}O$_2$.

The reaction between [Pt(**1**)Me][SbF$_6$] and O$_2$ can be monitored by ^{1}H NMR spectroscopy, and the quantitative formation of complex [Pt(**1**)OOMe][SbF$_6$] typically occurs at room temperature within two to three minutes upon exposure to ambient light. The product can be isolated and is stable for several days at −20 °C in the absence of light. However, prolonged exposure (> 5 min) of the methylperoxo complex [Pt(**1**)OOMe][SbF$_6$] to light at room temperature results in a further reaction. This reaction was monitored by ^{1}H NMR spectroscopy, through the disappearance of [Pt(**1**)OOMe][SbF_6] and the formation of [Pt(**1**)OH][SbF_6] ($\delta = 0.62$ ppm broad, [D_6]acetone) and formaldehyde ($\delta = 9.67$ ppm, [D_6]acetone) [Eq. (2) and Figure S2 in the Supporting Information]. The formation of the platinum(II)–hydroxo complex was confirmed by the independent preparation from [Pt(**1**)Cl]$^+$ and NaOH. This decomposition pathway of a methylperoxo complex has also been observed in the decomposition of FeOOMe complexes.[22,23] We propose that this reaction proceeds via an initial η^2-alkylperoxo intermediate, which after oxidative addition of the O–O bond results in a Pt^{IV}=O(OMe) intermediate. The recently reported Pt^{IV} complex with a terminal oxo ligand by Milstein and co-workers supports the existence of such an intermediate.[41] This rearrangement has precedent in the reaction of the tantalum(III)–methylperoxo complex [$(Cp^*)_2Ta(\eta^2$-OOMe)] ($Cp^* = C_5Me_5$), which can rearrange to [$(Cp^*)_2Ta^{V}$=O(OMe)] as shown by Bercaw and co-workers.[42] In our case, the subsequent hydrogen abstraction results in the formation of [Pt(**1**)OH][SbF_6] and formaldehyde. This process is probably also related to the insertion of O_2 into a chromium(II)–phenyl bond, reported by Theopold and co-workers, which results in the formation of a Cr^{IV}=O(OPh) complex.[43]



(2)

In conclusion, we have shown that a diaminoterpyridine-substituted platinum(II)–methyl complex can insert O_2 to form a methylperoxo complex and that this reaction proceeds via the formation of singlet oxygen. The platinum(II)–methylperoxo complex eliminates formaldehyde and forms a platinum(II)–hydroxo complex. If this complex could be re-converted into a platinum(II)–methyl complex, the exciting prospect arises for a direct low-temperature photocatalytic oxidation of methane to formaldehyde. Recent examples of C–H activation with late-transition-metal–hydroxo complexes suggest that this may not be impossible.[44,45]

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