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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 centre, a functionalisation 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 functionalisation of metal alkyl complexes should be carried out ideally with environmentally benign oxidants such as O_2 or H_2O_2. In a previous study, we reported the oxidation of dimethyl Pt^{II} complexes with H_2O_2 to generate *cis*-dihydroxo Pt^{IV} complexes.[5] The unusual *cis* isomer was obtained by using amino-substituted bipyridine ligands, which stabilise this isomer through hydrogen bonding. When we extended our work to Pt^{II} methyl complexes containing tridentate amino-substituted terpyridine ligands, we discovered a remarkable reactivity of the diamino substituted terpy Pt^{II} methyl complex 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$_6$]. 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, a reaction takes place. In the ^{1}H NMR spectrum, the characteristic Pt-Me signal at 1.54 ppm (J_{Pt-H} = 72 Hz, d$_6$-acetone) disappears over the course of several minutes and a new singlet emerges at 3.39 ppm (d$_6$-acetone), together with a new set of signals for the 6,6'-diaminoterpyridine ligand (see Figures S1 and S3). This new complex was isolated in quantitative yield and all analytical data suggest that an insertion of O_2 into the Pt-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, in the absence of light the reaction is very slow and only 50 % conversion is obtained after 13 hours at room temperature.
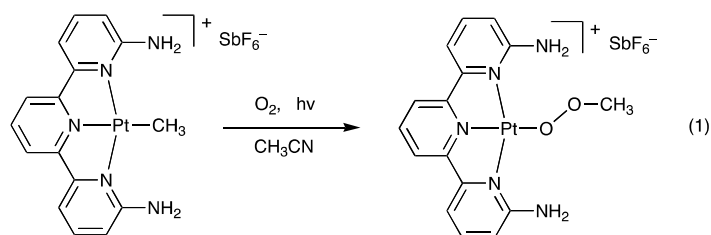
The solid state structure of [Pt(**1**)OOMe][SbF$_6$] shows the presence of two crystallographically independent cation:anion pairs with the two unique cations forming a head-to-tail dimer with a Pt···Pt separation of 3.1999(5) Å (see Figure 1 and the supporting material for further information).[6] This dimer formation is quite common for terpy Pt^{II} 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 of 3.42 Å).[8]
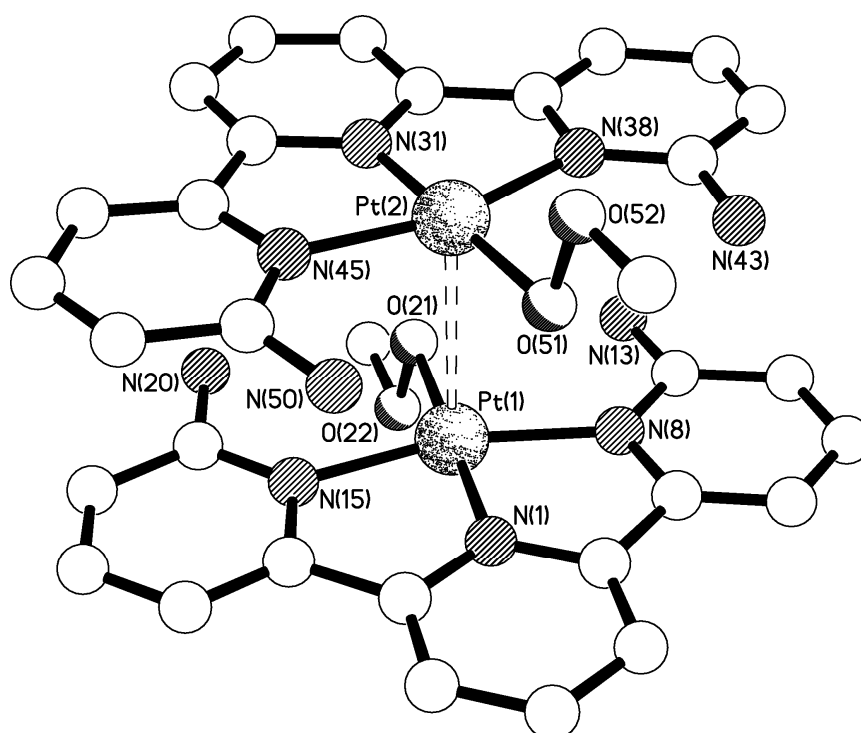
Figure 1. The molecular structure of the cation dimer present in the crystals of [Pt(**1**)OOMe][SbF$_6$].[6]

In the solid state and in solution, NH···O hydrogen bonding interactions exist between the amino substituents and the α-O atom (see Supplementary Material). The amino substituents have also 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$_6$] in 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 complex [Pt(**1**)Me][SbF$_6$] shows photoluminescence in CH$_2$Cl$_2$ solution at room temperature, similar to observations with other substituted terpyridine Pt^{II} 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 Supplementary Information). Noteworthy, the diamino substituted terpyridine ligand itself also shows photoluminescence.[12, 13] The luminescent behaviour of [Pt(**1**)Me]$^+$ is very different from [Pt(terpy)Me]$^+$, which shows no significant photoluminescence at room temperature in CH$_3$CN.[8]
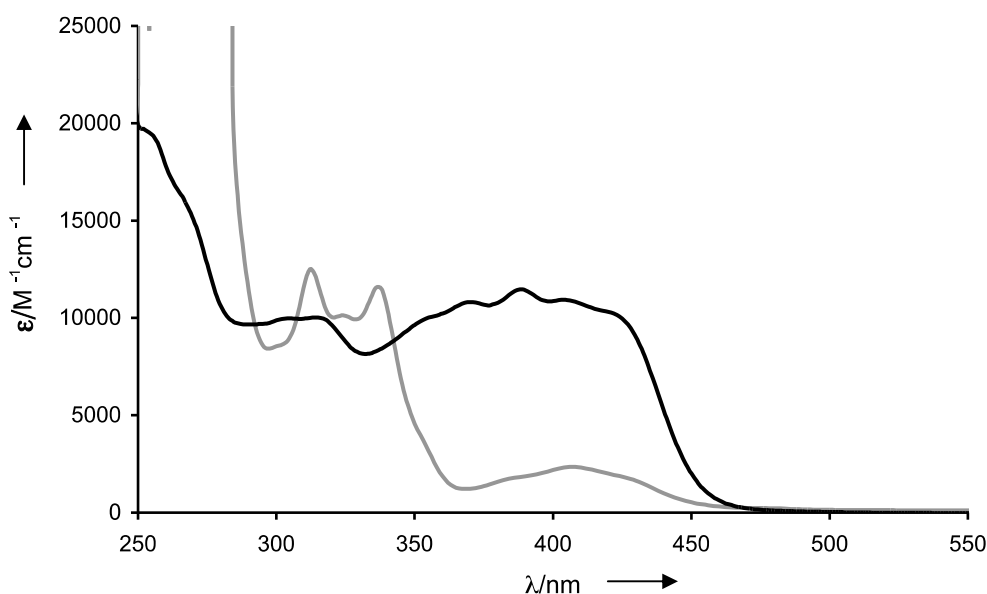

Figure 2. UV-vis spectra for [Pt(**1**)Me][SbF$_6$] (black) and [Pt(terpy)Me][SbF$_6$] (grey) in CH$_3$CN at 298K.

The formation of a methylperoxo Pt^{II} complex *via* insertion of O_2 into a Pt^{II} methyl bond as seen here, appears to be very rare. The only other example is a recently reported complex [(PN)Pt(Me)(OOMe)] by Grice and Goldberg (PN = 2-bis(*tert*-butylphosphinomethyl)pyridine).[14] In addition, several Pt^{II} and Pt^{IV} complexes containing alkylperoxo ligands other than methylperoxo have been reported previously, but none of these have been prepared via an O_2 insertion reaction.[15-20] The O_2 insertion reaction into the Pt^{II}-Me bond in the complex [(PN)Pt(Me)(OOMe)] is also affected by light and the authors have proposed a radical mechanism for their insertion reaction.[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 Co and Fe methyl 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 *via* 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 ($^3O_2$) into singlet oxygen ($^1O_2$),[29] but also certain Pt^{II} and Ir^{III} complexes are known to be able to act as O_2 sensitizers and generate $^1O_2$.[30-32] In some cases, *in situ* generated $^1O_2$ can react with organometallic complexes, for example to generate peroxide complexes.[33, 34] Examples of self-sensitisation, whereby a metal complexes can both generate $^1O_2$ *and* react with $^1O_2$, are relatively rare but have been observed for certain Pt^{II} bipy 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 non-radical mechanism for the insertion of O_2 in the case of complex [Pt(**1**)Me][SbF$_6$], which we believe proceeds via initial $^3O_2$ sensitization by this complex to generate $^1O_2$, followed by a fast $^1O_2$ insertion into the Pt methyl 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 hours,[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$_6$], which cannot insert O_2, the formation of $^1O_2$ 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 (see Supplementary Information).

Singlet oxygen is similar in character to an electron-deficient alkene and metal complexes containing a coordinated $^1O_2$ ligand have recently been reported.[39, 40] Coordination prior to insertion, akin to alkene insertions into a metal alkyl bond, to give an intermediate Pt^{II} complex containing an η^2-bound $^1O_2$ ligand cannot be excluded at this stage, although we have not observed any intermediates by NMR 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 a distinctly different charge transfer behaviour between these two complexes 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 $^1O_2$.

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 2-3 minutes upon exposure to ambient light. The product can be isolated and is stable for days at –20 ˚C in the absence of light. However, prolonged exposure (> 5 min.) of the methyl peroxo complex [Pt(**1**)OOMe][SbF$_6$] to light at room temperature results in a further reaction. This reaction was monitored by ^{1}H NMR and the disappearance of [Pt(**1**)OOMe][SbF$_6$] and the formation of [Pt(**1**)OH][SbF$_6$] (δ = 0.62 ppm broad, d$_6$-acetone) and formaldehyde (δ = 9.67 ppm, d$_6$-acetone) are observed (see eq. 2 and Figure S2 in the Supporting Information). The formation of the hydroxo Pt^{II} 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

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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 methylperoxo Ta^{III} complex [(Cp*)$_2$Ta(η^2-OOMe)], which can rearrange to [(Cp*)$_2$Ta^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 O$_2$ insertion reaction into a Cr^{II} phenyl bond reported by Theopold and co-workers, which results in the formation of a Cr^{IV}=O(OPh) complex.[43]
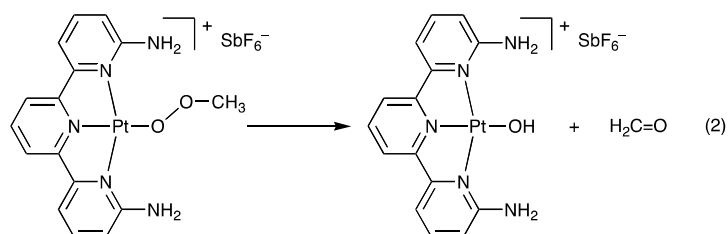
In conclusion, we have shown that a diaminoterpyridine substituted Pt^{II} methyl complex can insert O$_2$ to form a methylperoxo complex and that this reaction proceeds *via* the formation of singlet oxygen. The methylperoxo Pt^{II} complex eliminates formaldehyde and forms a Pt^{II} hydroxo complex. If this Pt^{II} hydroxo complex could be re-converted to a Pt^{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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[6]   *Crystal data for* [Pt(**1**)OOMe][SbF$_6$]: [C$_{16}$H$_{16}$N$_5$O$_2$Pt](SbF$_6$), M = 741.18, triclinic, $P\bar{1}$ (no. 2), a = 11.9822(7), b = 13.1681(13), c = 13.7797(14) Å, α = 76.641(9), β = 80.491(6), γ = 72.974(7)°, V = 2011.5(3) Å^3, Z = 4 [2 independent molecules], ρ_{calcd} = 2.447 g cm^{-3}, μ(Mo$_{K\alpha}$) = 8.369 mm^{-1}, T = 173 K, orange needles, Oxford Diffraction Xcalibur 3 diffractometer; 12981 independent measured reflections, F^2 refinement, R_1 = 0.043, wR_2 = 0.104, 10111 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 65°], 701 parameters. CCDC 699504 contains the supplementary crystallographic data for this paper. 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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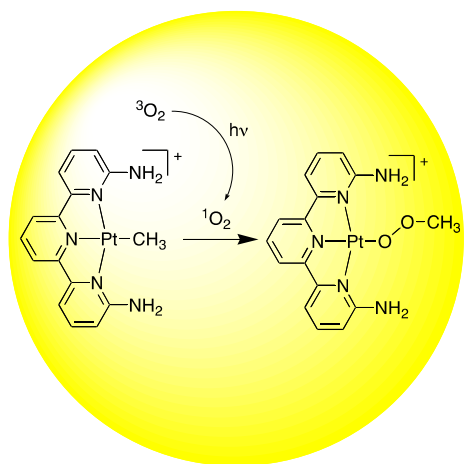
Always look on the bright side: The light-driven insertion of dioxygen into a platinum methyl bond results in a methylperoxo complex which decomposes to formaldehyde and a platinum hydroxo complex.