Formation and *X*-Ray Crystal Structure of an Isopropylperoxoplatinum(IV) Complex: A New Test for a Free Radical Mechanism of Oxidative Addition

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Oxidative addition of isopropyl iodide to dimethyl(1,10-phenanthroline)platinum(II) may give an isopropylperoxoplatinum(IV) complex, whose structure has been determined, by incorporation of dioxygen at an intermediate stage; the formation of such products may be used as a criterion for a free radical mechanism of oxidative addition.

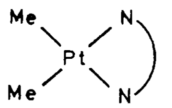
There has been considerable interest in the mechanisms of oxidative addition of alkyl halides to transition metal complexes.[1,2] Three mechanisms have been established (equations 1—3). The first involves S_N2 displacement of the halide by a metal nucleophile, the second involves a free radical chain reaction, and the third involves a free radical non-chain mechanism, perhaps initiated by electron transfer to the alkyl halide.[1-4]

$$L_nM + RX \rightarrow [L_nMR]^+X^- \rightarrow L_nMXR \qquad (1)$$

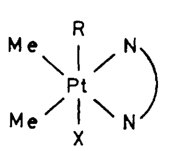
$$L_nM + R\cdot \xrightarrow{RX} [L_nMR]\cdot \xrightarrow{RX} L_nMXR + R\cdot \qquad (2)$$

$$L_nM + RX \rightarrow [L_nM]^{\cdot+}[RX]^{\cdot-} \rightarrow [L_nMX]\cdot + R\cdot \rightarrow L_nMXR \qquad (3)$$

It is now clear that the mechanism adopted depends on the metal substrate, the alkyl halide, and the reaction conditions.[1-4] Furthermore, the tests used to distinguish between mechanisms (1)—(3) are often equivocal, and a combination of tests is usually required.[1-4] The purpose of this article is to report a new and particularly simple test for a free radical mechanism, and the structure of an unexpected product of oxidative addition.

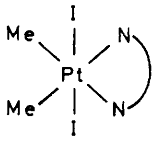


(1)

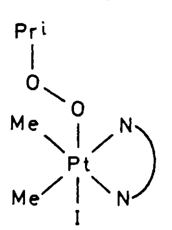


(2)

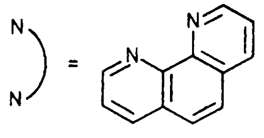
a; R = Me, X = I
b; R = Et, X = I
c; R = Pr^n, X = I
d; R = Pr^i, X = I



(3)



(4)



Reaction of [PtMe$_2$(1,10-phenanthroline)], (**1**), with primary alkyl iodides in acetone solution occurred cleanly to give the adducts (**2a**—**c**), and good second order kinetics were followed [first order in both (**1**) and alkyl halide]. However, a similar reaction of (**1**) with isopropyl iodide generally gave a mixture of (**2d**), (**3**), and (**4**), all of which have been obtained analytically pure and fully characterised by ^{1}H and ^{13}C{^{1}H} n.m.r. spectroscopy.

The formation of the alkylperoxo-complex, (**4**), is apparently unique in oxidative addition reactions of alkyl halides. Indeed alkylperoxo-derivatives of transition metals are rare,[5,6] although they are thought to be intermediates in the transition metal catalysed autoxidation of alkanes and alkenes and in the decomposition of alkyl hydroperoxides,[7] as well as in the autoxidation of some alkyl derivatives of transition metals.[8] For this reason, and because (**4**) was unexpectedly stable and failed to give qualitative tests for peroxides, the structure was determined. The results of the crystal structure analysis†

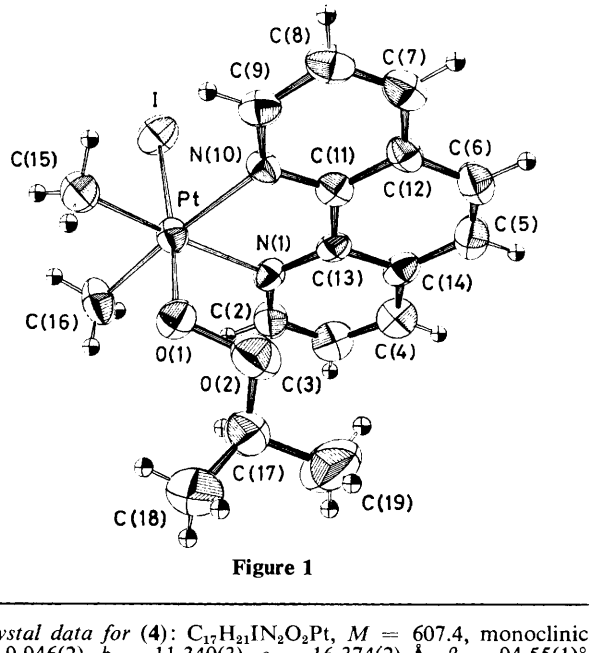


Figure 1

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† *Crystal data for* (**4**): $C_{17}H_{21}IN_2O_2Pt$, $M = 607.4$, monoclinic, $a = 9.946(2)$, $b = 11.340(3)$, $c = 16.374(2)$ Å, $\beta = 94.55(1)°$, $U = 1841.0$ Å^3, $Z = 4$, $D_c = 2.19$ g cm^{-3}, $F(000) = 1136$, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 97.16$ cm^{-1}, space group $P2_1/n$ from systematic absences: $h0l$ if $h + l = 2n + 1$ and $0k0$ if $k = 2n + 1$. Anisotropic refinement of non-hydrogen atoms, with the hydrogen atoms in geometrically idealised positions, converged with $R = 0.0230$ and $R_w = 0.0245$ for 1402 reflections with $I > 3\sigma(I)$, measured on a CAD-4 diffractometer. The data were corrected for absorption. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Products from reactions of (**1**) with Pr^{i}I in acetone.

Concentrations/M			Products/%		
[I]	[Pr^{i}I]	[O$_2$]	(**2d**)	(**4**)	(**3**)
0.0039	0.60	0^a	100	0	0
0.004	0.5	0.011^b	8	89	3
0.015	0.167	0.002^b	44	51	5
0.0077	0.167	0.002^b	34	56	10
0.0024	0.167	0.002^b	0	63	37
0.0115	0.165	0.002^c	13	49	38
0.0088	0.33	0.002^b	17	58	25
0.0088	0.33	0.002^{b,d}	15	75	10

[a] Reaction under N$_2$. [b] Initial [O$_2$]; reaction in sealed flask. [c] Air bubbled through to ensure saturation throughout the reaction. [d] Galvinoxyl present.

establish the structure of (**4**) as shown in Figure 1. The Pt atom has octahedral co-ordination with Pt–O(1) 2.032(6), Pt–Me 2.048(9) and 2.067(8), Pt–N 2.164(7) and 2.175(7), Pt–I 2.624(1), O(1)–O(2) 1.465(9), and O(2)–C(17) 1.455(13) Å, and with Pt–O(1)–O(2) angle 110.2(4)° and Pt–O(1)–O(2)–C(17) torsion angle $-108.2°$.

Complex (**4**) is formed during the oxidative addition of isopropyl iodide to complex (**1**) by incorporation of a molecule of dioxygen. As proof, complex (**4**) is not formed when the reaction is carried out under pure nitrogen and the product ratio (**4**):(**2d**) increases with increasing oxygen concentration (Table 1). In addition, neither (**1**) nor (**2d**) reacts with oxygen showing that (**4**) is not formed by reaction of a dioxygen complex of platinum with isopropyl iodide nor by insertion of dioxygen into the isopropylplatinum bond of (**2d**). The rate of reaction of (**1**) with isopropyl iodide is independent of oxygen concentration showing that oxygen is not involved in a rate determining step. We believe that formation of (**4**) is strong evidence for a free radical mechanism of oxidative addition (equation 2 or 3). It is known that rate constants for the reaction of alkyl radicals with oxygen to give alkylperoxy-radicals are 10^8—10^{10} dm^3 mol^{-1} s^{-1} (*i.e.* close to diffusion control).[7] Complex (**4**) can therefore be formed by the mechanism of equation (2) or (3), with the additional step of equation (4).

$$\mathrm{R\cdot} + \mathrm{O_2} \xrightarrow{\text{fast}} \mathrm{ROO\cdot} \qquad (4)$$

There is no reasonable mechanism by which (**4**) could be formed by the S_N2 mechanism of oxidative addition (equation 1), and thus its formation may be used as a criterion for a free radical mechanism of oxidative addition. This criterion is useful because it can be used quantitatively but it is limited to systems where the metal complexes are inert to oxygen and where the alkylperoxometal derivatives are thermally stable.

In reactions of (**1**) with primary alkyl halides under conditions where [O$_2$] $\sim$ [I] we observe no alkylperoxo-complex and this would appear to disprove the intermediacy of free alkyl radicals in this case. In addition, the reactivity series MeI $\gg$ EtI $>$ Pr^{n}I $\gg$ Pr^{i}I is not consistent with a free radical mechanism for the n-alkyl iodides. Preliminary kinetic studies of the isopropyl iodide oxidative addition show that the reactions are first order in both (**1**) and isopropyl iodide in the early stages (first 40% reaction) and that the reactions are not retarded by the free radical scavenger galvinoxyl, indicating that the non-chain mechanism (equations 3, 4) is dominant. However, in the later stages of reaction the rate increases from that predicted by the initial second-order kinetics, and we tentatively suggest that the chain mechanism (equations 2, 4) becomes more prominent. Further studies to clarify this aspect, as well as to study the great acceleration of the reaction by diffuse daylight, are in progress.

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