Observation by Electron Spin Resonance Spectroscopy of Free Radicals in Reactions of Dialkylplatinum(II) Complexes with Alkenes

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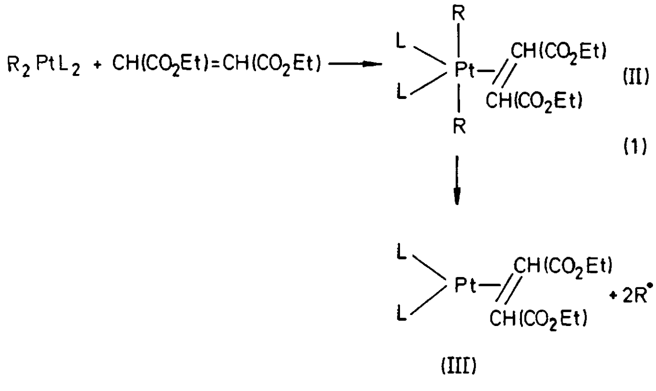
Summary Free radicals are formed under mild conditions, and have been identified by e.s.r. spectroscopy, in reactions of dialkylplatinum(II) complexes with alkenes.

Free-radical intermediates have often been postulated, but have never been observed directly, in the thermal decomposition of transition-metal alkyls[1] or in their oxidative addition[2] or insertion reactions.[3] Only in homolytic substitution (S_H2) reactions of methylplatinum compounds have methyl radicals been observed (either directly or after spin tripping) by e.s.r. spectroscopy.[4] We report that free radicals are generated under exceptionally mild conditions in reactions of alkenes with dialkylplatinum(II) complexes.

Thus, from the reaction of R_2PtL_2 ($R = Me$, CD_3, Et, $L_2 = 2,2'$-bipyridyl; $R = Me$, $L_2 = 1,10$-phenanthroline, cyclo-octa-1,5-diene) with diethyl fumarate (in the dark at room temperature) in the presence of the radical trap $Bu^tN{=}O$,[5] the corresponding free radical $RCH(CO_2Et)CH(CO_2Et)N(Bu^t)O\cdot$ (I) could be detected by e.s.r. spectroscopy after a few minutes. In each case the e.s.r. spectrum consisted of a 1 : 1 : 1 triplet of doublets, with $a_N = 1{\cdot}42$ mT and $a_{H\beta} = 0{\cdot}29$ mT, with further hyperfine splitting from the Bu^t protons, $a_{H\gamma} = 0{\cdot}02$ mT. A radical having an identical e.s.r. spectrum was formed on reaction of dimethyl-(2,2′-bipyridyl)platinum(II) with diethyl maleate in the presence of Bu^{t}NO. However, no radicals could be detected under these conditions unless both the dialkylplatinum complex and the reactive alkene were present, which suggests that the alkene acts as a reagent which causes alkyl radicals to be generated from the alkylplatinum compounds and also as a radical trap.



R_2PtL_2 + CH(CO$_2$Et)=CH(CO$_2$Et) ⟶ (II) ⟶ (III)

(1)

$$R^\bullet + cis\text{- or } trans\text{-CH(CO}_2\text{Et)=CH(CO}_2\text{Et)} \longrightarrow \text{RCH(CO}_2\text{Et)CH(CO}_2\text{Et)}^\bullet \quad (2)$$

$$\downarrow \text{Bu}^t\text{NO}$$

(I)

We believe that the reactions proceed according to equations (1) and (2). This reaction scheme is supported by the following: (i) There is ample precedent for formation of 5-co-ordinate complexes similar to (II),[6] and their formation is especially favourable when L_2 = 2,2′-bipyridyl.[7] (ii) The presence of mutually *trans* alkyl groups on platinum in (II) is expected to lead to considerable weakening of the Pt–R bonds,[8] which are apparently then subject to rapid homolysis. When the reaction of dimethyl-(2,2′-bipyridyl)-platinum(II) with diethyl fumarate is conducted in the absence of a radical trap, some methane is formed (presumably by hydrogen abstraction by methyl radicals) and (III) can be isolated. (iii) We have shown the ethyl radicals, generated from diethylmercury, in the presence of diethyl fumarate and Bu^{t}NO give the radical (I; R = Et) The observation that the e.s.r. spectrum is identical with that obtained in the reaction with the alkylplatinum compounds is strong evidence that the group R in the radical (I), obtained in the latter reaction, is the alkyl group rather than a bulkier platinum containing residue, which would be expected to influence the magnitudes of the spectral parameters.[5]

These observations together with those of Lappert and his co-workers,[4] suggest that many reactions of transition-metal alkyls may need to be reinterpreted in terms of free radical rather than molecular reaction paths.

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