

Photoinduced Reactions of PtCl_6^{2-} with Saturated Hydrocarbons and Other C-H Containing Compounds

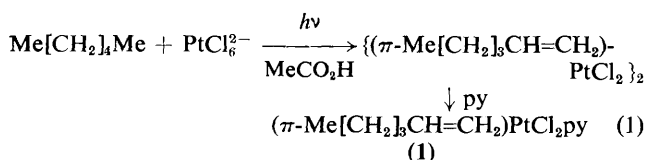
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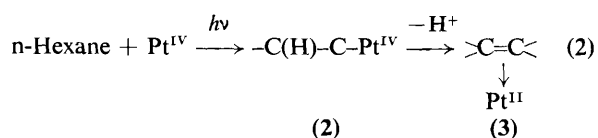
Light irradiation of a solution of PtCl_6^{2-} and an n-alkane (hexane or heptane) in MeCO_2H or $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$ yields the corresponding π -olefin complex of Pt^{II} , the formation of which is assumed to proceed *via* a σ -alkyl complex of Pt^{IV} ; the reaction with acetone, which has no β -hydrogen atoms affords a stable σ -acetyl complex of Pt^{IV} and σ -aryl complexes are formed on irradiation of PtCl_6^{2-} with arenes.

Solutions of Pt^{II} salts activate alkanes to H-D exchange with solvent and also to oxidation by PtCl_6^{2-} .¹ The latter reaction proceeds *via* a fairly stable σ -alkyl complexes of Pt^{IV} . The catalysis by Pt^{II} involves initial alkane interaction with planar Pt^{II} complexes, fully co-ordinated Pt^{IV} complexes being inactive.

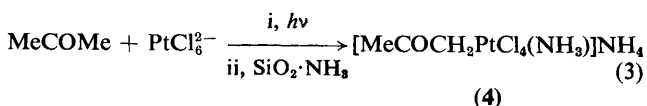
We now report on the photochemical reactions of PtCl_6^{2-} with the C-H bond, which do not appear to involve catalysis by Pt^{II} salts. We have found that when a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.2 g) and n-hexane (1 ml) (purified as described in ref. 2) in MeCO_2H (4.8 ml) is irradiated with light from a 1000 W high pressure mercury lamp for 8 h at 15 °C, a π -hexene complex of Pt^{II} is formed. The complex has been isolated in the form (1) (10% yield) after addition of pyridine (py) and chromatography on silica gel [equation (1)]. Irradiation of a solution of n-heptane and H_2PtCl_6 gives the corresponding π -heptene complex of Pt^{II} .



Complex (1) was previously prepared³ by the thermal reaction of PtCl_6^{2-} with n-hexane, n-hexylacetate, or hex-1-ene and characterized by elemental analysis and ¹H n.m.r. and i.r. spectra. It may be assumed that the first stage of reaction (1) is the formation of the σ -hexyl complex of Pt^{IV} [equation (2)]. Complex (2) is unstable and appears to be converted into the π -hexene complex (3) *via* β -elimination^{3,4} of a proton.



To check this suggestion we have carried out this reaction with acetone, which has no β -hydrogen atoms. Irradiation of a solution of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.55 M) in acetone (30 min, 15 °C) gave a relatively stable σ -complex (4) [equation (3)] which has been isolated by chromatography on silica gel and characterized by elemental analysis (C, H, N) and ¹H n.m.r. and i.r. spectra. {¹H n.m.r. [in $(\text{CD}_3)_2\text{CO}$]: δ 2.16 (Me), 4.38 (CH_2), $J(^1\text{H}-^{195}\text{Pt})$ 87 Hz; i.r.: 1680 cm^{-1} (C=O).}

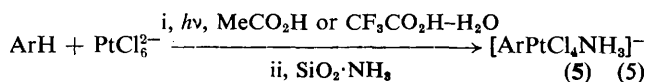


We have also isolated a small amount of complex (1) from the products of the reaction of PtCl_4^{2-} with 1-iodohexane in aqueous solution [equation (4)]. The analogous oxidative

addition with MeI or EtI is known to yield a fairly stable σ -methyl derivative of Pt^{IV} and a much less stable σ -ethyl complex.⁵



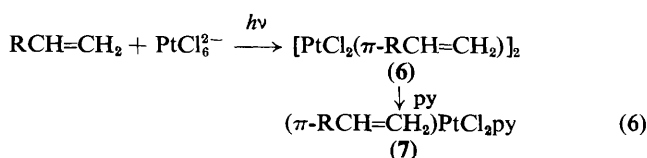
We have also found that arenes (ArH) react with PtCl_6^{2-} on irradiation ($\lambda > 320$ nm) of a solution in MeCO_2H or $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$ at room temperature. After irradiation the arene was extracted with chloroform, the solvent removed under reduced pressure at room temperature, and the residue chromatographed on silica gel containing *ca.* 1% ammonia. The relative yield of the σ -aryl complex decreases with increase of the initial concentration of PtCl_6^{2-} (yield of the anisole complex is 62% at $[\text{PtCl}_6^{2-}]_0 = 0.02$ M and only 10% at



$[\text{PtCl}_6^{2-}]_0 = 0.19$ M). The rate of reaction (5) does not depend on the acidity of the solvent, but decreases if Cl^- or oxidant (SeO_2) is added. In contrast to the thermal reaction⁶ the photoinduced synthesis [equation (5)] gives rise to the *para*-isomer only (ratio *p:m* > 20:1 by n.m.r. spectroscopy) of the Pt^{IV} -substituted toluene or ethylbenzene complex (5) and no *para-meta* isomerisation is observed. The relative rates (given in parentheses) of the photoinduced reaction [equation (5)] for different aromatic compounds were determined using a competitive method: phenol (8), anisole (4), diphenyl ether (1.9), and toluene (1). The logarithms of these values correlate with σ^+ constants ($\rho^+ = -1.5$).

We believe that the photoinduced reaction [equation (5)] is the first example of photoelectrophilic aromatic substitution with photoexcitation of the electrophilic reagent (PtCl_6^{2-}). The photochemical Havinga deuteration of anisole and the Friedel-Crafts acylation of anthracene are thought to occur *via* the excitation of the aromatic compound.⁷

Irradiation of a solution of PtCl_6^{2-} and excess of an olefin (styrene or hex-1-ene) in acetone or MeCO_2H with visible light (100 W halogen tungsten lamp, 1000 W high pressure mercury lamp, or sunlight) at room temperature affords a π -olefin complex of Pt^{II} , which could be isolated by known methods in the dimeric form (6) or as a pyridine derivative (7) [reaction (6)].



The yields of complexes (6) and (7) after irradiation for 15–60 min are 30–100%, thus this method is very convenient for the synthesis of π -olefin complexes of Pt^{II} . Evidently the

reduction of Pt^{IV} in this case proceeds at the expense of some olefin oxidation to form products, the identities of which have not yet been determined.

At present the mechanism of the photochemical reaction of PtCl_6^{2-} with C-H containing compounds is not completely clear. However, it may be that irradiation produces co-ordinatively unsaturated complexes of Pt^{IV} (e.g. PtCl_5^-), which are sufficiently active towards the C-H bond to cause electrophilic substitution of H^+ .

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