

## Photoinduced Reactions of $\text{PtCl}_6^{2-}$ with Saturated Hydrocarbons and Other C-H Containing Compounds

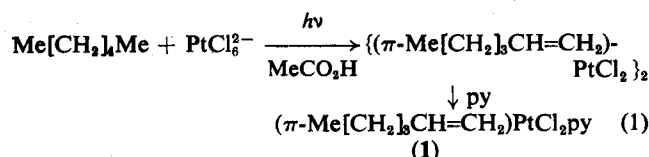
Georgiy B. Shul'pin, Galina V. Nizova, and Alexander E. Shilov\*

Institute of Chemical Physics, USSR Academy of Sciences, 117 977 Moscow, U.S.S.R.

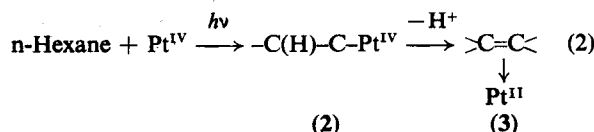
Light irradiation of a solution of  $\text{PtCl}_6^{2-}$  and an n-alkane (hexane or heptane) in  $\text{MeCO}_2\text{H}$  or  $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$  yields the corresponding  $\pi$ -olefin complex of  $\text{Pt}^{\text{II}}$ , the formation of which is assumed to proceed via a  $\sigma$ -alkyl complex of  $\text{Pt}^{\text{IV}}$ ; the reaction with acetone, which has no  $\beta$ -hydrogen atoms affords a stable  $\sigma$ -acetylonyl complex of  $\text{Pt}^{\text{IV}}$  and  $\sigma$ -aryl complexes are formed on irradiation of  $\text{PtCl}_6^{2-}$  with arenes.

Solutions of  $\text{Pt}^{\text{II}}$  salts activate alkanes to H-D exchange with solvent and also to oxidation by  $\text{PtCl}_6^{2-}$ .<sup>1</sup> The latter reaction proceeds via fairly stable  $\sigma$ -alkyl complexes of  $\text{Pt}^{\text{IV}}$ . The catalysis by  $\text{Pt}^{\text{II}}$  involves initial alkane interaction with planar  $\text{Pt}^{\text{II}}$  complexes, fully co-ordinated  $\text{Pt}^{\text{IV}}$  complexes being inactive.

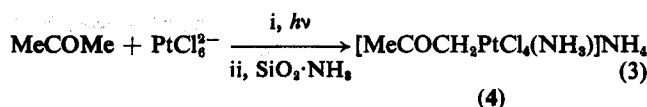
We now report on the photochemical reactions of  $\text{PtCl}_6^{2-}$  with the C-H bond, which do not appear to involve catalysis by  $\text{Pt}^{\text{II}}$  salts. We have found that when a solution of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (0.2 g) and n-hexane (1 ml) (purified as described in ref. 2) in  $\text{MeCO}_2\text{H}$  (4.8 ml) is irradiated with light from a 1000 W high pressure mercury lamp for 8 h at 15 °C, a  $\pi$ -hexene complex of  $\text{Pt}^{\text{II}}$  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  $\text{H}_2\text{PtCl}_6$  gives the corresponding  $\pi$ -heptene complex of  $\text{Pt}^{\text{II}}$ .



Complex (1) was previously prepared<sup>3</sup> by the thermal reaction of  $\text{PtCl}_6^{2-}$  with n-hexane, n-hexylacetate, or hex-1-ene and characterized by elemental analysis and  $^1\text{H}$  n.m.r. and i.r. spectra. It may be assumed that the first stage of reaction (1) is the formation of the  $\sigma$ -hexyl complex of  $\text{Pt}^{\text{IV}}$  [equation (2)]. Complex (2) is unstable and appears to be converted into the  $\pi$ -hexene complex (3) via  $\beta$ -elimination<sup>3,4</sup> of a proton.



To check this suggestion we have carried out this reaction with acetone, which has no  $\beta$ -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  $\sigma$ -complex (4) [equation (3)] which has been isolated by chromatography on silica gel and characterized by elemental analysis (C, H, N) and  $^1\text{H}$  n.m.r. and i.r. spectra. ( $^1\text{H}$  n.m.r. [in  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  2.16 (Me), 4.38 ( $\text{CH}_2$ ),  $J(\text{H}-^{195}\text{Pt})$  87 Hz; i.r.:  $1680\text{ cm}^{-1}$  (C=O).)

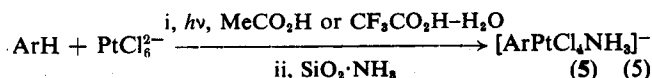


We have also isolated a small amount of complex (1) from the products of the reaction of  $\text{PtCl}_6^{2-}$  with 1-iodohexane in aqueous solution [equation (4)]. The analogous oxidative

addition with MeI or EtI is known to yield a fairly stable  $\sigma$ -methyl derivative of  $\text{Pt}^{\text{IV}}$  and a much less stable  $\sigma$ -ethyl complex.<sup>5</sup>



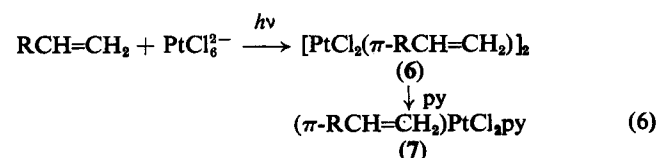
We have also found that arenes (ArH) react with  $\text{PtCl}_6^{2-}$  on irradiation ( $\lambda > 320\text{ nm}$ ) of a solution in  $\text{MeCO}_2\text{H}$  or  $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$  at room temperature. After irradiation the arene was extracted with chloroform, the solvent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



$[\text{PtCl}_6^{2-}]_0 = 0.19\text{ M}$ ). The rate of reaction (5) does not depend on the acidity of the solvent, but decreases if  $\text{Cl}^-$  or oxidant ( $\text{SeO}_2$ ) is added. In contrast to the thermal reaction<sup>6</sup> the photoinduced synthesis [equation (5)] gives rise to the *para*-isomer only (ratio *p*:*m* > 20:1 by n.m.r. spectroscopy) of the  $\text{Pt}^{\text{IV}}$ -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  $\sigma^+$  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 ( $\text{PtCl}_6^{2-}$ ). The photochemical HAVINGA deuteration of anisole and the Friedel-Crafts acylation of anthracene are thought to occur via the excitation of the aromatic compound.<sup>7</sup>

Irradiation of a solution of  $\text{PtCl}_6^{2-}$  and excess of an olefin (styrene or hex-1-ene) in acetone or  $\text{MeCO}_2\text{H}$  with visible light (100 W halogen tungsten lamp, 1000 W high pressure mercury lamp, or sunlight) at room temperature affords a  $\pi$ -olefin complex of  $\text{Pt}^{\text{II}}$ , 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  $\pi$ -olefin complexes of  $\text{Pt}^{\text{II}}$ . 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  $H^+$ .

Received, 10th January 1983; Com. 055

#### References

- 1 A. E. Shilov, *Sov. Sci. Rev., Sect. B*, 1982, **4**, 71.
  - 2 D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, *J. Chem. Soc., Chem. Commun.*, 1982, 1235.
  - 3 G. V. Nizova, J. V. Z. Krevor, A. N. Kitaigorodskii, and G. B. Shul'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2805.
  - 4 S. S. Ling and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1982, 412.
  - 5 V. V. Zamashchikov, E. S. Rudakov, S. A. Mitchenko, and S. L. Litvinenko, *Teor. Eksp. Khim.*, 1982, **18**, 510; V. V. Zamashchikov, E. S. Rudakov, S. A. Mitchenko, S. L. Litvinenko, A. N. Kitaigorodskii, and G. B. Shul'pin, *Dokl. Akad. Nauk Ukr. SSR*, 1983, in the press.
  - 6 G. B. Shul'pin and A. T. Nikitaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1416.
  - 7 J. Cornelisse and E. Havinga, *Chem. Rev.*, 1975, 353; T. Tamaki, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1145.
-