

Preliminary communication

FORMATION OF ORGANOMETALLIC COMPLEXES OF PLATINUM(II) AND PLATINUM(IV) IN REACTIONS OF PtCl_6^{2-} WITH ALKANES, OLEFINS AND AROMATICS INDUCED BY γ -IRRADIATION

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Summary

γ -Irradiation of solutions of the ion PtCl_6^{2-} and n-hexane (or alkene) in MeCO_2H affords a π -olefin complex of platinum(II); σ -aryl complexes of platinum(IV) are formed in analogous reactions with aromatic compounds.

We wish to report the reactions of the ion PtCl_6^{2-} with various organic compounds induced by γ -irradiation. All the reactions were carried out in MeCO_2H solution using irradiation of a ^{60}Co γ -ray source at a nominal dose rate of 6 Mrad h^{-1} .

When a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.3 g) and n-hexane (2 ml) in MeCO_2H (3.7 ml) was γ -irradiated (132 Mrad) at 50°C a π -hex-1-ene complex of platinum(II) was formed. The complex was isolated in the form π -(hex-1-ene)- PtCl_2py (**1**) (yield 16.5% based on Pt) after the addition of pyridine (py) and chromatography. The yields of complex **1** were only 1% for a 10 Mrad dose and 2.7% for 21 Mrad. When a large dose of γ -irradiation (300 Mrad) was used, the conversion of initial PtCl_6^{2-} increased to 100% but the π -complex formed decomposed partially with deposition of platinum metal. Complex **1** has previously been prepared in thermal [1] and photo-induced [2a] reactions. Complex **1** was also prepared by the reaction of PtCl_6^{2-} with hex-1-ene induced by γ -irradiation (20 Mrad, yield 27%). γ -Irradiation of a solution of PtCl_6^{2-} and styrene in MeCO_2H (10 Mrad) afforded the complex π -(styrene) PtCl_2py in 10% yield.

Analogously, γ -irradiation of a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.1 g) and anisole (0.2 ml) in MeCO_2H (1.2 ml) for 4 h (24 Mrad) at 50°C yielded a σ -aryl complex of platinum(IV) which was isolated in the form $[\text{MeOC}_6\text{H}_4\text{PtCl}_4\text{NH}_3]\text{NH}_4$ (**2**) (yield 11%) after chromatography on silica gel containing ammonia. The reaction proceeded selectively and more than 80% of the initial hexachloroplatinic acid could be recovered from the reaction mixture. The yield of complex **2** linearly

increased with increasing dose of γ -irradiation. In the thermally induced interaction at 50°C the yield of **2** after 4 h was less than 1.5%. The NMR spectra indicate that, similar to the photoinduced reaction [2] and in contrast to the thermally induced interaction [3], the *para*-platinated isomer of **2** (>95%) was formed in the reaction induced by γ -irradiation and no *para*—*meta* isomerization occurred in the course of the reaction. The yield of the σ -aryl complex of platinum(IV) in an analogous reaction with phenol (24 Mrad) was 28%. The relative rates of γ -induced platination of phenol and anisole determined using a competitive method (analysis by ^1H NMR), were 2.3 and 1.0, respectively. The reaction of PtCl_6^{2-} with aromatics appears to be the first example of 'electrophilic' substitution in aromatic compounds induced by γ -irradiation.

Light- [2] or γ -irradiation of a solution of $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ and anisole in MeCO_2H at 77 K gave an ESR spectrum with a g -value of ~ 2.4 , which is in good agreement with the g_1 -values for low-spin platinum(III) complex ions produced by photolysis or γ -radiolysis of platinum(IV) and platinum(II) complexes [4]. There were also signals in the region $g \sim 2.0$ due to organic radicals.

One could assume that the first stage of the γ -induced (as well as photoinduced [2]) reactions of organic compounds is electron transfer [5] and formation of the ion radical pair $[\text{RH}]^{+\cdot} [\text{Pt}^{\text{III}}\text{Cl}_5^{2-}]$. If $\text{R} = \text{Ar}$, this ion radical pair then transforms into a Wheland-type complex, which after proton elimination gives a σ -aryl complex of platinum(IV). The non-chain mechanism of formation of σ -aryl complexes of platinum(IV) may be termed as $S_E 2e.t.$ (electrophilic substitution with a crucial associative step and involving an electron transfer step). The reaction with saturated hydrocarbons ($\text{R} = \text{Alk}$) appears to proceed via the formation of a radical $\text{R}^\cdot$ and complex $\text{Pt}^{\text{III}}\text{Cl}_5^{2-}$, which could be produced by the decay of the cation-radical $\text{RH}^{+\cdot} \rightarrow \text{R}^\cdot + \text{H}^+$ (simultaneous oxidation of alkane and extrusion of proton are also probable.) The radical $\text{R}^\cdot$ and $\text{Pt}^{\text{III}}\text{Cl}_5^{2-}$ react in a solvent cage to afford a σ -alkyl complex of platinum(IV) or a carbocation R^+ and a platinum(II) complex. Such a mechanism of substitution at a saturated carbon atom to form a σ -alkyl complex of platinum(IV) may be denoted the $S_E 1e.t.$ mechanism (the crucial dissociative step). Radicals $\text{R}^\cdot$ may also be produced in the reaction of $\text{Cl}^\cdot$ (formed by γ -induced homolysis: $\text{PtCl}_6^{2-} \rightarrow \text{Pt}^{\text{III}}\text{Cl}_5^{2-} + \text{Cl}^\cdot$) with alkanes: $\text{RH} + \text{Cl}^\cdot \rightarrow \text{R}^\cdot + \text{HCl}$. Finally, elimination of the β -hydrogen from the alkyl chain of the σ -alkyl complex of platinum(IV) [2a] or from the carbocation R^+ leads to the formation of the π -olefin complex of platinum(II). Radicals $\text{R}^\cdot$ may also be oxidized with platinum(IV) to produce R^+ and a platinum(III) complex.

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References

- 1 G.V. Nizova, J.V.Z. Krevor, A.N. Kitaigorodskii and G.B. Shul'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 2805.
- 2 (a) G.B. Shul'pin, G.V. Nizova and A.E. Shilov, *J. Chem. Soc., Chem. Commun.*, (1983) 671;
(b) G.B. Shul'pin, G.V. Nizova, A.E. Shilov, A.T. Nikitaev, and M.V. Serdobov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, in press.

- 3 G.B. Shul'pin, A.E. Shilov, A.N. Kitaigorodskii and J.V.Z. Krevor, *J. Organomet. Chem.*, 201 (1980) 319; G.B. Shul'pin, *J. Organomet. Chem.*, 212 (1981) 267; G.B. Shul'pin and A.T. Nikitaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 1416; G.B. Shul'pin, *Zh. Obshch. Khim.*, 51 (1981) 2100.
- 4 I.I. Blinov and G.A. Shagisultanova, *Koord. Khim.*, 8 (1982) 191; T. Krigas and M. Roges, *J. Chem. Phys.*, 55 (1971) 3035; H.M. Khan, W.L. Waltz, J. Lilie and R.J. Woods, *Inorg. Chem.*, 21 (1982) 1489; N.N. Zheligovskaya, N.A. Chernova, R.G. Kileev and V.I. Spitsyn, *Koord. Khim.*, 9 (1983) 666.
- 5 M. Chanan and M.L. Tobe, *Angew. Chem.*, 94 (1982) 27; W. Lau, J.C. Huffman and J.K. Kochi, *J. Am. Chem. Soc.*, 104 (1982) 5515; S. Fukuzumi and J.K. Kochi, *Bull. Chem. Soc. Jpn.*, 56 (1983) 969.

Erratum

Metal clusters in catalysis. The reactivity of alkyne- and vinylidene-substituted homo- and hetero-metallic clusters towards molecular hydrogen in homogeneous conditions; by M. Castiglioni, R. Giordano and E. Sappa (*J. Organomet. Chem.*, 258 (1983) 217–234)

Page 231, line 5 should read:

case for cluster 4. A possible explanation of this behaviour might be that when

Page 233, line 3 of Conclusive remarks should read:

selectivities different from those observed for alkynes bound to bimetallic derivatives.

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