*Journal of Organometallic Chemistry*, 275 (1984) 273–282
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION METAL COMPLEXES

## III *. FORMATION OF A $\sigma$-METHYL COMPLEX OF PLATINUM(IV) AND A $\pi$-ETHYLENE COMPLEX OF PLATINUM(II) IN PHOTOCHEMICAL AND THERMAL REACTIONS OF $PtCl_6^{2-}$ WITH METHYL AND ETHYL DERIVATIVES OF TIN OR GERMANIUM. THERMAL OXIDATIVE ADDITION OF $Me_4Sn$ TO $PtCl_4^{2-}$ TO AFFORD THE $\sigma$-METHYL COMPLEX OF PLATINUM(IV)

G.B. SHUL'PIN*, G.V. NIZOVA, A.N. KITAIGORODSKII and M.V. SERDOBOV

*Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Moscow 117977 (U.S.S.R.)*

(Received May 15th, 1984)

## Summary

The photoinduced reaction of $PtCl_6^{2-}$ with alkyl derivatives of tin or germanium in acetic acid or acetone is described. The reaction with $(CH_3)_4Sn$ affords the complex $CH_3PtCl_5^{2-}$ (I) whereas irradiation of $PtCl_6^{2-}$ with $(CH_3)_2Sn(C_2H_5)_2$ leads to the formation of I and $[(CH_2{=}CH_2)PtCl_2]_2$ (III). Complex III is formed in the reaction with $Ge(C_2H_5)_4$. The proposed mechanism of "electrophilic" substitution by the platinum(IV) complex involves electron transfer from the tetraalkylmetal to the platinum(IV) complex and is labelled the $S_E$1e.t. mechanism. The platinum(II)-ethylene complex III appears to be formed from $CH_3CH_2PtCl_5^{2-}$ (II) upon light irradiation via $\beta$-hydrogen elimination. The thermal reaction of $PtCl_6^{2-}$ with $(CH_3)_4Sn$ to afford complex I is catalysed by $PtCl_4^{2-}$. The thermal reaction of $(CH_3)_4Sn$ with $PtCl_4^{2-}$ in acetic acid or aqueous acetone affords the $\sigma$-methyl complex of platinum(IV).

## Introduction

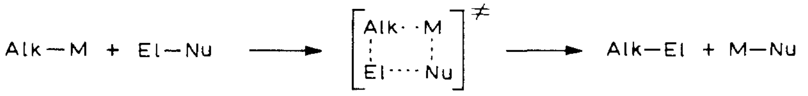
There has been great interest in the electrophilic cleavage of an alkyl–metal bond by metal compounds [1–8] and alkyl transfers in organometals [9–13]. Derivatives of transition metals have been, among other things, used as electrophilic reagents. Either the $S_E2$ ($S_Ei$) mechanism (eq. 1) or the $S_E1$ mechanism (eq. 2 and 3) may

---

* For part II see ref. 18.

0022-328X/84/$03.00

operate in different cases. For example, the $S_E2$ mechanism has been proposed for the reactions 4 to 6.



$$\text{Alk—M} + \text{El—Nu} \longrightarrow \left[\begin{array}{cc}\text{Alk}\cdot & \cdot\text{M}\\ \vdots & \vdots\\ \text{El}\cdots & \text{Nu}\end{array}\right]^{\neq} \longrightarrow \text{Alk—El} + \text{M—Nu} \tag{1}$$

$$\text{Alk–M} \rightleftharpoons \text{Alk}^- + \text{M}^+ \text{ (slow)} \tag{2}$$

$$\text{Alk}^- + \text{El–Nu} \rightarrow \text{Alk–El} + \text{Nu}^- \text{ (fast)} \tag{3}$$

$$\text{Alk}_4\text{Sn} + \text{HgX}_2 \rightarrow \text{Alk}_3\text{SnX} + \text{AlkHgX} \quad [14] \tag{4}$$

$$\text{Alk}_4\text{Sn} + \text{X}_2 \rightarrow \text{AlkX} + \text{Alk}_3\text{SnX} \ (\text{X} = \text{Br, I}) \quad [15] \tag{5}$$

$$\text{Alk}_4\text{Sn} + \text{IBr} \rightarrow \text{AlkI} + \text{Alk}_3\text{SnBr} \quad [16] \tag{6}$$

Recently, we have shown that the $PtCl_6^{2-}$ ion reacts under light irradiation with various organic compounds (acetone [17,18], arenes [17,19,20], olefins [17,21,22] and alkanes [17]) to afford organometallic complexes of platinum(IV) or platinum(II). In the present paper, we wish to report the photochemical reactions of alkyl derivatives of tin and germanium with $PtCl_6^{2-}$. The thermal reactions of $(CH_3)_4Sn$ with $PtCl_6^{2-}$ and/or $PtCl_4^{2-}$ will also be described.

## Results

We have found that light irradiation (light from a 1000 W high-pressure mercury lamp, $\lambda \geqslant 320$ mm) of a solution of $PtCl_6^{2-}$ and $(CH_3)_4Sn$ in $CD_3CO_2D$ or $CD_3COCD_3$ affords a σ-methyl complex of platinum(IV), I, which may also be prepared by oxidative addition of $CH_3I$ to $PtCl_4^{2-}$ [23]. Complex I is rather unstable and was characterized in the present work by its $^1H$ NMR spectra: singlet at $\delta$ 3.22 ppm, $J(^1H-^{195}Pt)$ 80 Hz.

$$(\text{CH}_3)_4\text{Sn} + \text{PtCl}_6^{2-} \xrightarrow{h\nu} \underset{\text{(I)}}{\text{CH}_3\text{PtCl}_5^{2-}} + (\text{CH}_3)_3\text{SnCl} \tag{7}$$

Changes in the $^1H$ NMR spectra of the reaction mixture during irradiation are shown in Fig. 1. The kinetic curves for reaction (7) in two solvents are shown in Figs. 2 and 3. Complex I formed in reaction 7 slowly affords $CH_3Cl$:

$$\text{CH}_3\text{PtCl}_5^{2-} \rightarrow \text{CH}_3\text{Cl} + \text{PtCl}_4^{2-} \tag{8}$$

The kinetics of reactions 7 and 8 were followed by $^1H$ NMR spectroscopy.

The photoinduced reaction of $PtCl_6^{2-}$ with $(CH_3)_2Sn(C_2H_5)_2$ proceeds more rapidly, taking into account the rate of disappearance of the starting compound of tin (Fig. 4). After 2, 4 and 10 min of irradiation, the signals due to complex I and $CH_3Cl$ are observed in the $^1H$ NMR spectra. A new multiplet signal appears in the spectrum in the region of $\delta$ 0.6 ppm after irradiation for 2 min. This signal overlaps the triplet of $(CH_3)_2Sn(C_2H_5)_2$ and the intensity of the signal increases with increasing time of irradiation. This signal may be due to the methyl protons of the σ-ethyl complex of platinum(IV). To check this suggestion, we prepared the complex $CH_3CH_2PtCl_5^{2-}$(II) by oxidative addition of $CH_3CH_2I$ to $PtCl_4^{2-}$ [24] in $CD_3CO_2D/D_2O$. Complex II thus obtained exhibits in its $^1H$ NMR spectrum a triplet at $\delta$ 0.59 ppm accompanied by satellites, $J(^1H-^{195}Pt)$ 21 Hz, due to the methyl protons and a quartet at $\delta$ 4.16 ppm, $J(^1H-^{195}Pt)$ 86 Hz, due to the protons of the $CH_2$ group.

$$CH_3CH_2I + PtCl_4^{2-} \xrightarrow{Cl^-} CH_3CH_2PtCl_5^{2-} \tag{9}$$

Thus, it may be proposed that the photoinduced reaction of $PtCl_6^{2-}$ with $(CH_3)_2Sn(C_2H_5)_2$ affords, initially, $\sigma$-ethyl (II) and $\sigma$-methyl (I) complexes of platinum(IV). Complex II predominates in a mixture, according to the $^1H$ NMR spectrum.

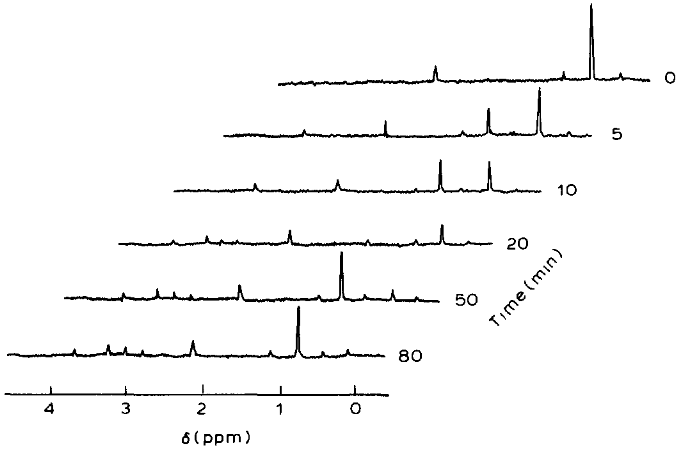


Fig. 1. Changes in the $^1H$ NMR spectra of a solution of $D_2PtCl_6 \cdot 6D_2O$ (0.45 $M$) and $(CH_3)_4Sn$ (0.25 $M$) in $CD_3CO_2D$ during light irradiation.

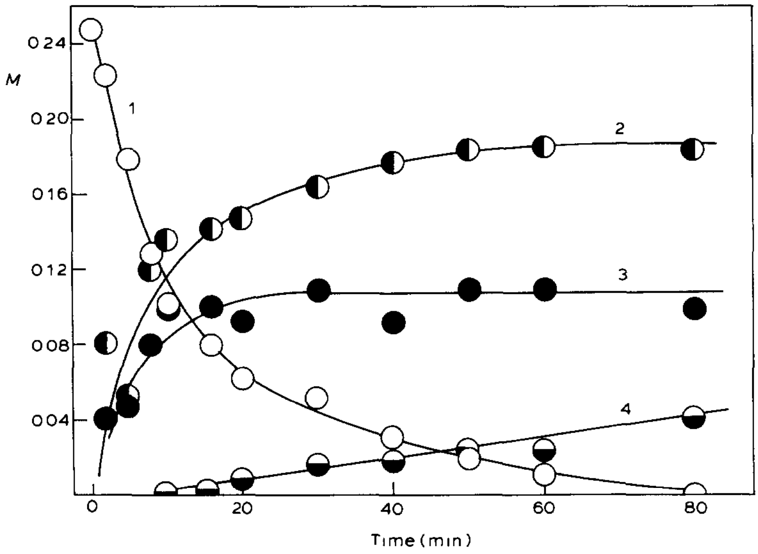


Fig. 2. Plot of the concentrations of reagents and products of reaction (7) (initial concentrations of $D_2PtCl_6 \cdot 6D_2O$ 0.45 $M$ and of $(CH_3)_4Sn$ 0.25 $M$) in $CD_3CO_2D$ versus the time of light irradiation. (1) $(CH_3)_4Sn$, (2) $(CH_3)_3SnCl$, (3) $CH_3PtCl_5^{2-}$, (4) $CH_3Cl$.

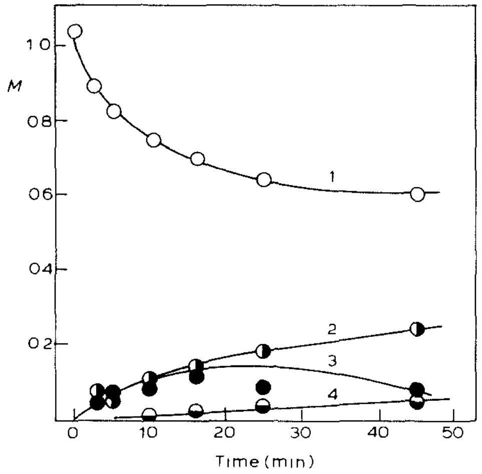


Fig. 3. Plot of the concentrations of reagents and products of reaction (7) at $[D_2PtCl_6 \cdot 6D_2O]_o$ 0.15 *M* and $[(CH_3)_4Sn]_o$ 1.03 *M* in acetone-$d_6$ versus the time of light irradiation. (1) $(CH_3)_4Sn$, (2) $(CH_3)_3SnCl$, (3) $CH_3PtCl_5^{2-}$, (4) $CH_3Cl$.

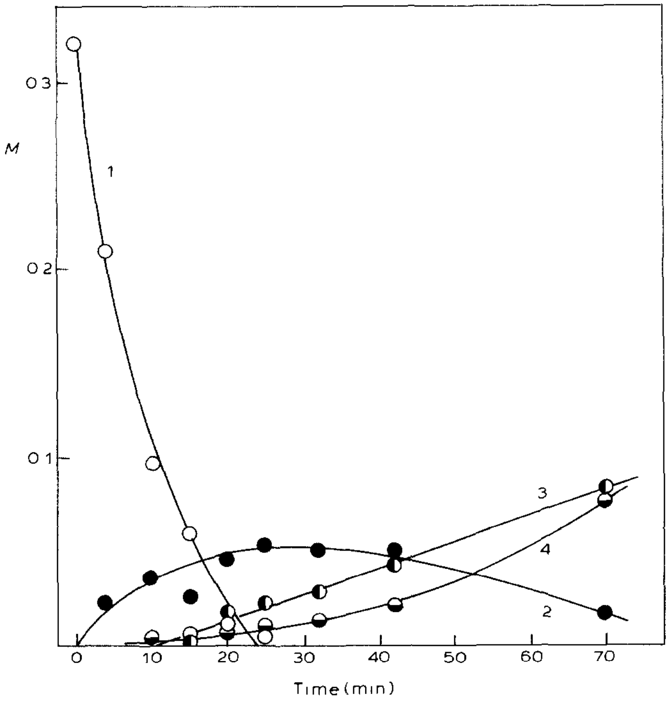


Fig. 4. Plot of the concentrations of reagents and products of the photoinduced reaction of $D_2PtCl_6 \cdot 6D_2O$ (initial concentration 0.092 *M*) with $(CH_3)_2Sn(C_2H_5)_2$ (0.32 *M*) in $CD_3CO_2D$ (reactions 10 and 11) versus the time of light irradiation. (1) $(CH_3)_2Sn(C_2H_5)_2$, (2) $CH_3PtCl_5^{2-}$, (3) $\pi$-$(CH_2{=}CH_2)Pt^{II}$, (4) $CH_3Cl$.

$$(CH_3)_2Sn(CH_2CH_3)_2 + PtCl_6^{2-} \xrightarrow{h\nu} \underset{(I)}{CH_3PtCl_5^{2-}} + \underset{(II)}{CH_3CH_2PtCl_5^{2-}} + CH_3Sn(C_2H_5)_2Cl + (CH_3)_2Sn(C_2H_5)Cl \tag{10}$$

After 15 min of irradiation, a new singlet appears at $\delta$ 6.19 ppm, $J(^1H-^{195}Pt)$ 70 Hz, due to the $\pi$-ethylene complex of platinum(II). The intensity of this signal increases with increasing irradiation time whereas the intensity of the signal at $\delta$ 0.6 ppm decreases.

We have also found that the complex $CH_3CH_2PtCl_5^{2-}$ prepared by reaction 9 affords upon light irradiation under the same conditions the $\pi$-ethylene complex of platinum(II).

$$CH_3CH_2PtCl_5^{2-} \xrightarrow{h\nu} \underset{(III)}{[(CH_2{=}CH_2)PtCl_2]_2} \tag{11}$$

It should be noted that an excess of $CH_3CH_2I$ was present in the reaction mixture and that complex III might be formed by photolysis of ethyl iodide (disproportionation of ethyl radicals may produce ethylene). However, we did not detect the formation of complex III in the photoinduced reaction of $CH_3CH_2I$ with $PtCl_6^{2-}$ in $CD_3CO_2D$.

The rate of the photoinduced reaction of $PtCl_6^{2-}$ with $Ge(C_2H_5)_4$ in $CD_3CO_2D$ is much lower than that of $Sn(CH_3)_4$ and especially that of $(CH_3)_2Sn(C_2H_5)_2$. Complex III was detected in solution in the course of irradiation, and the induction period of the reaction was observed (Fig. 5). The rates of reactions 12 and 11 in this case are approximately equal.

$$Ge(C_2H_5)_4 + PtCl_6^{2-} \xrightarrow{h\nu} CH_3CH_2PtCl_5^{2-} + Ge(C_2H_5)_3Cl \tag{12}$$

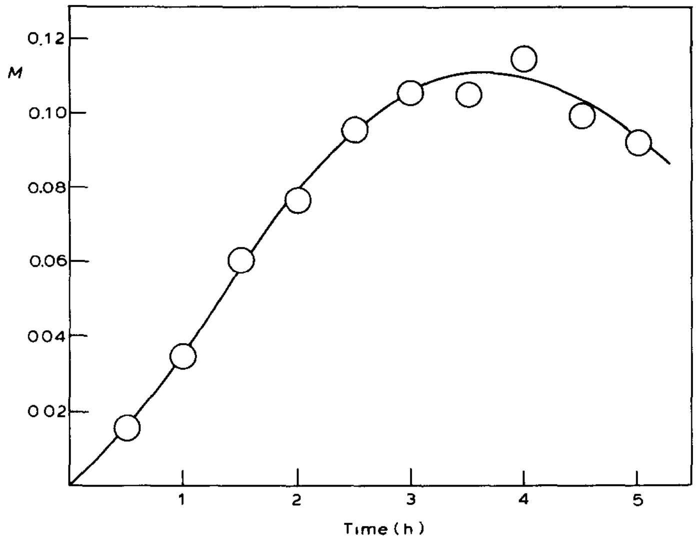


Fig. 5. Plot of the concentration of complex III formed in the reaction of $D_2PtCl_6 \cdot 6D_2O$ (0.18 $M$) with $Ge(C_2H_5)_4$ (0.21 $M$) in $CD_3CO_2D$ (reactions 12 and 11) versus the time of irradiation.

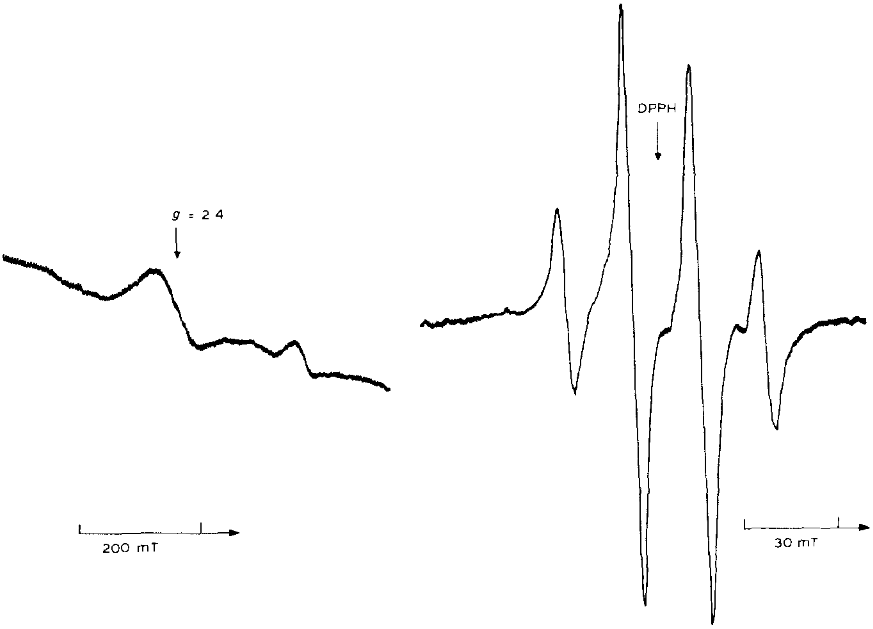


Fig. 6. ESR spectrum of a frozen solution of $H_2PtCl_6$ and $(CH_3)_4Sn$ in $CH_3CO_2H$ irradiated at 77 K.

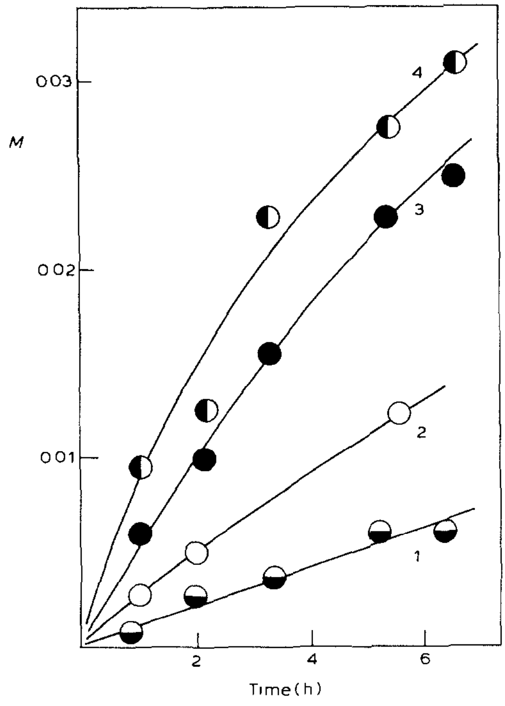


Fig. 7. Plot of the concentration of complex $CH_3PtCl_5^{2-}$ formed in the thermal reaction of $D_2PtCl_6 \cdot 6D_2O$ (0.08 *M*) with $(CH_3)_4Sn$ (0.25 *M*) in $CD_3CO_2D$ versus time, at various concentrations of $Na_2PtCl_4 \cdot 4H_2O$ added: (1) 0; (2) 0.009; (3) 0.018; (4) 0.027 *M*.

The ESR spectrum of a frozen solution of $(CH_3)_4Sn$ and $H_2PtCl_6$ in $CH_3CO_2H$ irradiated at 77 K ($\lambda > 300$ nm) was recorded. The spectrum exhibits a quartet due to the methyl radical ($g \simeq 2.0$) and signals due to a complex of platinum(III) ($g_\perp \simeq 2.4$) (Fig. 6). The spectrum of the platinum(III) complex is similar to those obtained in the photolysis of $PtCl_6^{2-}$ with $CH_3OH$ [25], $CH_3COCH_3$ [18] and anisole [19], and in the radiolysis of $PtCl_4^{2-}$ [26].

We have also found that the $PtCl_6^{2-}$ ion slowly reacts with $(CH_3)_4Sn$ in $CD_3CO_2D$ in darkness. The reaction is catalysed by $PtCl_4^{2-}$ (Fig. 7), the formation of complex I being first order in $PtCl_4^{2-}$ (Fig. 8).

The $PtCl_4^{2-}$ ion also reacts with $(CH_3)_4Sn$ in $CD_3CO_2D/D_2O$ or $CD_3COCD_3/D_2O$ to afford the σ-methyl complex of platinum(IV), which was detected by the $^1H$ NMR spectra.

$$PtCl_4^{2-} + Sn(CH_3)_4 \rightarrow \sigma\text{-}CH_3Pt^{IV} \tag{13}$$

It should be noted that deposition of platinum metal can be observed in the course of this reaction. So one may assume that the reaction proceeds, for example, as follows:

$$2PtCl_4^{2-} + Sn(CH_3)_4 \xrightarrow{H_2O} \sigma\text{-}CH_3PtCl_4(H_2O)^- + Pt + (CH_3)_3SnCl + 3Cl^- \tag{13'}$$

## Discussion

The formation of σ-alkyl complexes of platinum(IV) in the photochemical reactions of alkyltin and alkylgermanium compounds with $PtCl_6^{2-}$ appears to proceed via electron transfer from the organometallic to the platinum(IV) complex. Analogous processes have been proposed for the thermal reactions of $IrCl_6^{2-}$ with alkyllead [27], alkylmercury [28] and alkyltin [29] compounds; for the thermal reaction of the phenanthroline complex of iron(III) with $Sn(CH_3)_4$ [30]; and for the photochemical reactions of $PtCl_6^{2-}$ with organic compounds [18–22]. It is known that the rate of cleavage of the $M-C_2H_5$ bond is much higher than that of the

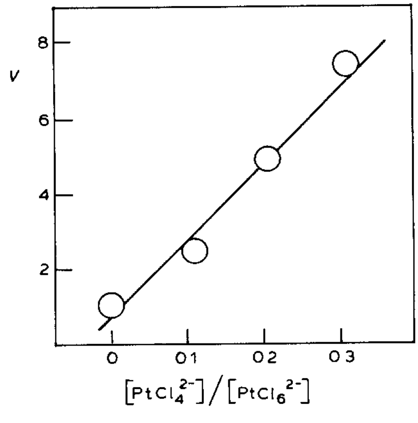


Fig. 8. Plot of the relative rate of the thermal reaction of $PtCl_6^{2-}$ with $(CH_3)_4Sn$ (see Fig. 7) versus the concentration of $PtCl_4^{2-}$ added (relative to $PtCl_6^{2-}$).

M–$CH_3$ bond when electron transfer is involved in contrast to electrophilic substitution [5]. Irradiation of a solution of $(CH_3)_4Sn$ and tetracyanoethylene (TCNE) at 426 nm affords $(CH_3)_3Sn(TCNE)CH_3$ adducts. The reaction is proposed to proceed via electron transfer [5,31].

The first step of reactions 7, 10 and 12 is the photoexcitation of the $PtCl_6^{2-}$ ion [32]:

$$PtCl_6^{2-} \xrightarrow{h\nu} [PtCl_6^{2-}]^{\star} \tag{14}$$

The excited species then reacts with $Alk_4M$.

$$[PtCl_6^{2-}]^{\star} + Alk_4M \rightarrow [Alk_4M]^{+\cdot}[Pt^{III}Cl_5^{2-}] + Cl^- \tag{15}$$

Recently, the cation-radical $SnH_4^{+\cdot}$ was prepared by exposing solutions of $SnH_4$ to γ-rays [33].

The stability of cation-radicals of tetraalkylmetals is low and they rapidly decompose to produce alkyl radicals and $Alk_3M^+$ cations:

$$[Alk_4M]^{+} \rightarrow Alk^{\cdot} + Alk_3M^+ \tag{16}$$

The methyl radical and the complex of platinum(III) were detected in the ESR spectrum of the irradiated solution of $PtCl_6^{2-}$ and $(CH_3)_4Sn$ at 77 K (see above).

The alkyl radicals thus formed and the $Pt^{III}Cl_5^{2-}$ species may then recombine to afford the σ-alkyl complex of platinum(IV):

$$Alk^{\cdot} + Pt^{III}Cl_5^{2-} \rightarrow AlkPt^{IV}Cl_5^{2-} \tag{17}$$

Formally, such a process is electrophilic substitution at the metal atom, the platinum(IV) complex being the electrophilic reagent:

$$Alk–M + Pt–Cl \rightarrow Alk–Pt + M–Cl \tag{18}$$

The mechanism of reaction 18 described above may be denoted as the $S_E$1e.t. mechanism (electrophilic substitution with the crucial dissociative step involving the electron transfer step).

This mechanism may generally be depicted as follows:

$$R–M + El^+ \rightarrow ([R–M]^{+}\ [El]\ )_S \rightarrow (R^{\cdot} + M^+ + El\ )_S \rightarrow R–El + M^+ \tag{19}$$

Here ( $)_S$ denotes a solvent cage.

Alternatively, though in our opinion less probable, the mechanism for the formation of σ-alkyl complexes in the photoinduced reaction is the radical chain process [34] initiated by photoinduced homolysis of the Pt–Cl bond [32]:

$$PtCl_6^{2-} \xrightarrow{h\nu} Pt^{III}Cl_5^{2-} + Cl^{\cdot} \tag{20}$$

$$Cl\ + (CH_3)_4Sn \rightarrow (CH_3)_3SnCl + CH_3^{\cdot} \tag{21}$$

$$CH_3 + PtCl_6^{2-} \rightarrow CH_3PtCl_5^{2-} + Cl^{\cdot} \tag{22}$$

$$CH_3^{\cdot} + PtCl_5^{2-} \rightarrow CH_3PtCl_6^{2-} \tag{23}$$

The process of π-olefin complex formation (eq. 11) was previously assumed by us for the formation of π-olefin complexes of platinum(II) in the photochemical [17] and thermal [35] reactions of alkanes with $PtCl_6^{2-}$. Light irradiation may cause the formation of a coordinatively unsaturated complex by abstraction of $Cl^-$:

$$CH_3CH_2PtCl_5{}^{2-} \overset{(h\nu)}{\rightleftharpoons} CH_3CH_2PtCl_4{}^- + Cl^- \qquad (24)$$

Elimination of the $\beta$-hydrogen from the ethyl group leads to the formation of the $\pi$-ethylene complex of platinum(II).

$$CH_3CH_2PtCl_4{}^- \rightarrow [(CH_2{=}CH_2)Pt(H)Cl_4{}^-] \rightarrow$$
$$\rightarrow \pi\text{-}(CH_2{=}CH_2)PtCl_3{}^- + H^+ + Cl^- \qquad (25)$$

Alternatively, the $\pi$-olefin complex III may be formed via oxidation of $Alk^{\cdot}$ with a platinum(IV) or a platinum(III) complex to $Alk^+$ to afford the alkene after extrusion of $H^+$ (or disproportionation of $Alk^{\cdot}$ to alkene and alkane).

$$CH_3CH_2{}^{\cdot} + Pt^{IV} \rightarrow CH_3CH_2{}^+ + Pt^{III} \qquad (26)$$

$$CH_3CH_2 + Pt^{III} \rightarrow CH_3CH_2{}^+ + Pt^{II} \qquad (27)$$

$$CH_3CH_2{}^+ \rightarrow CH_2{=}CH_2 + H^+ \qquad (28)$$

$$2Pt^{III} \rightarrow Pt^{II} + Pt^{IV} \qquad (29)$$

$$2CH_3CH_2{}^{\cdot} \rightarrow CH_2{=}CH_2 + CH_3CH_3 \qquad (30)$$

$$CH_2{=}CH_2 + Pt^{II} \rightarrow \pi\text{-}(CH_2{=}CH_2)Pt^{II} \qquad (31)$$

However, the kinetics of the reaction are not consistent with such a proposal. We were also unable to detect complex III formation in the photoinduced reaction of $PtCl_6{}^{2-}$, with $CH_3CH_2I$ as a source of ethyl radicals in $CD_3CO_2D$.

The thermal reaction of $PtCl_6{}^{2-}$ with $(CH_3)_4Sn$ is catalysed by $PtCl_4{}^{2-}$, the platinum(II) complex alone reacting with $(CH_3)_4Sn$ to afford the $\sigma$-methyl complex of platinum(IV). It is known that $PtCl_4{}^{2-}$ also catalyses the methyl group transfer from methylcobalamin to $PtCl_6{}^{2-}$ [36–38]. On the other hand, the complex $(CH_3)_2Pt(bipy)$ is known to be capable of oxidative addition of $(CH_3)_3PbCl$, $CH_3HgCl$ or $(CH_3)_4Pb$ to afford $\sigma$-methyl complexes of platinum(IV) [10]. Oxidative addition of alkyl and aryl derivatives of non-transition metals to complexes of platinum(0) followed by extrusion of the non-transition metal is a convenient method of synthesizing organic derivatives of platinum(II) or palladium(II) [39,40]. The thermal reaction of $PtCl_4{}^{2-}$ with $Sn(CH_3)_4$ described in the present paper may be used to prepare the $\sigma$-methyl complex of platinum(IV) which does not contain ligands other than chloride ions.

## Experimental

All the reactions were carried out in NMR glass tubes of 5 mm diameter. Solutions in the NMR tubes were placed in glass vessels cooled with water and were irradiated with light of a 1000 W high-pressure mercury lamp. The kinetics of the reactions were followed by the $^1H$ NMR method. Complex II was detected by the $^1H$ NMR spectrum of a solution of $Na_2PtCl_4$ and $CH_3CH_2I$ in $CD_3CO_2D$-$D_2O$ after 2 h of mixing the reagents. The $^1H$ NMR spectra were recorded on a Bruker SXP-4-100 (90 MHz) spectrometer. The ESR spectra were taken on an EPR-20 (3 cm) instrument.

## References

1 I.P. Beletskaya, Zh. Vses. Khim. Obshch. Im. D.I. Mendeleeva, 12 (1967) 3.

2 O.A. Reutov and I.P. Beletskaya, Reaction Mechanisms of Organometallic Compounds, North-Holland Publishing Company, Amsterdam, 1968.

3 O.A. Reutov, I.P. Beletskaya and V.I. Sokolov, Mekhanizmy Reaktsiy Metalloorganicheskikh Soedineniy, Khimia, Moskva, 1972.

4 O.A. Reutov, I.P. Beletskaya, G.A. Artamkina and A.N. Kashin, Reaktsii Metalloorganicheskikh Soedineniy kak Redoks-protsessy, Nauka, Moskva, 1981.

5 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978.

6 A.N. Kashin and I.P. Beletskaya, Usp. Khim., 51(1982) 881.

7 O.A. Reutov, J. Organomet. Chem., 250 (1983) 145.

8 V.S. Petrosyan, J. Organomet. Chem., 250 (1983) 157.

9 J.K. Kochi, in Organometals and Organometalloids: Occurrence and Fate in the Environment, ACS, Washington, 1978, p. 205.

10 J.K. Jawad and R.J. Puddephatt, Inorg. Chim. Acta, 31 (1978) L 391.

11 R.J. Puddephatt and P.J. Thompson, J. Organomet. Chem., 166 (1979) 251.

12 C. Eaborn, K. Kundu and A. Pidcock, J. Organomet. Chem., 170 (1979) C18.

13 Z. Dawoodi, C. Eaborn and A. Pidcock, J. Organomet. Chem., 170 (1979) 95.

14 M.H. Abraham, J.F.C. Oliver and J.A. Richards, J. Chem. Soc. A, (1970) 203.

15 M. Gielen and J. Nasielski, Rec. Trav. Chim. Pays-Bas, 82 (1963) 228.

16 G. Redl, B. Altner, D. Auker and M. Minot, Inorg. Nucl. Chem. Lett., 5 (1969) 861.

17 G.B. Shul'pin, G.V. Nizova and A.E. Shilov, J. Chem. Soc., Chem. Commun., (1983) 671.

18 G.V. Nizova, M.V. Serdobov, A.T. Nikitaev and G.B. Shul'pin, J. Organomet. Chem., 275 (1984) 139.

19 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.

20 G.B. Shul'pin, G.V. Nizova and A.T. Nikitaev, J. Organomet. Chem., 276 (1984) 115.

21 G.B. Shul'pin and G.V. Nizova, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 669.

22 G.B. Shul'pin, G.V. Nizova and P. Lederer, J. Organomet. Chem., 275 (1984) 285.

23 V.V. Zamashchikov, E.S. Rudakov, S.A. Mitchenko and S.L. Litvinenko, Teor. Eksp. Khim., 18 (1982) 510.

24 V.V. Zamashchikov, E.S. Rudakov, S.A. Mitchenko, A.N. Kitaigorodskii and G.B. Shul'pin, Dokl. Akad. Nauk Ukr. SSR, Ser. B, No. 6, (1983) 33.

25 I.I. Blinov and G.A. Shagisultanova, Koord. Khim., 8 (1982) 191.

26 T. Krigas and M. Roges, J. Chem. Phys., 55 (1971) 3035.

27 H.C. Gardner and J.K. Kochi, J. Am. Chem. Soc., 97 (1975) 1855.

28 J.Y Chen, H.C. Gardner and J.K. Kochi, J. Am. Chem. Soc., 98 (1976) 6150.

29 C.L. Wong and J.K. Kochi, J. Am. Chem. Soc., 101 (1979) 5593.

30 K.L. Rollick and J.K. Kochi, J. Org. Chem., 47 (1982) 435.

31 K. Mochida, J.K. Kochi, K.S. Chen and J.K.S. Wan, J. Am. Chem. Soc., 100 (1978) 2927.

32 M. Julliard and M. Chanon, Chem. Rev., 83 (1983) 425.

33 A. Hasegawa, S. Kaminaka, T. Wakabayashi, M. Hayashi and M.C.R. Symons, J. Chem. Soc., Chem. Commun., (1983) 1199.

34 K.U. Ingold and B.P. Roberts, Free-Radical Substitution Reactions. Wiley-Interscience, New York, 1971.

35 G.V. Nizova, J.V.Z. Krevor, A.N. Kitaigorodskii and G.B. Shul'pin, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2805.

36 Y.-T. Fanchiang, W.P. Ridley and J.M. Wood, J. Am. Chem. Soc., 101 (1979) 1442.

37 Y.-T. Fanchiang, J.J. Pignatello and J.M. Wood, Organometallics, 2 (1983) 1748.

38 Y.-T. Fanchiang, J.J. Pignatello and J.M. Wood, Organometallics, 2 (1983) 1752.

39 V.I. Sokolov and O.A. Reutov, Coord. Chem. Rev., 27 (1978) 89.

40 V.V. Bashilov, V.I. Sokolov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2069.