^{31}P AND ^{1}H NMR STUDY OF REACTION BETWEEN HYDRIDE COMPLEXES OF PLATINUM AND DIVALENT TIN HALIDES

V. I. Bogdashkina, A. B. Permin,
V. S. Petrosyan, V. I. Pol'shakov,
and O. A. Reutov

UDC 543.422.25:542.91:541.49:546.92:546.812'121

Hydride complexes of platinum containing phosphine and halostannyl ligands have been known since 1965 [1]. Despite the important role which these compounds play in homogeneous catalysis reactions [2], no reliable data on their structure in solutions are available in the literature. Compounds obtained by the reaction between trans-[$HPtCl(PPh_3)_2$] and $SnCl_2$ under different conditions, to which the formula of trans-[$PtH(SnCl_3)(PPh_3)_2$] has been ascribed, differed in physical properties [1, 3].

We studied the reaction between trans-[$PtHX(PPh_3)_2$] (I) [X = Cl (Ia), Br (Ib)] and SnX_2 under different conditions. The structure of the products formed was deduced from ^{31}P NMR spectra. Since because of the occurrence of exchange processes at room temperature, the signals in the spectra are broadened [4], all the spectra were recorded at temperatures from −50 to −90°C.

The reaction between (I) and SnX_2 in inert solvents ($CHCl_3$, CH_2Cl_2, toluene), at both room and low temperature, leads to the formation of trans-[$PtH(SnX_3)\cdot(PPh_3)_2$] (II). The spectrum of (IIa) (X = Cl) coincided with that described in [5], and for complex (IIb) (X = Br) in CH_2Cl_2, the following parameters were obtained: P 28.5 ppm $^{1}J_{Pt-P} = 2668$, $^{2}J_{Sn-P} = 200$ Hz.

In acetone and in ethyl acetate, the reaction of complex (I) with SnX_2 proceeds differently: the main product of the reaction at −90 to −80°C is a compound with a cis-structure, according to ^{31}P spectra [Table 1, structures (IIIa) and (IIIb)]. The two doublets from nonequivalent P atoms have satellites from ^{195}Pt and $^{119/117}$Sn isotopes. The value of $^{1}J_{Pt-P_1}$ is typical [6] of the trans-configuration of the hydride and phosphine ligands. The correctness of this assignment is confirmed by the value of $^{2}J_{P_1-H}$, obtained from the ^{31}P spectrum without uncoupling from protons. The structure of the cis-[$PtH(SnX_3)(PPh_3)_2$], products of the reaction between (I) and SnX_2 in acetone and ethyl acetate, is confirmed by the values of $^{2}J_{Sn-P_1}$, characteristic of cis-configuration of the tin-containing and phosphine ligands [7]. The value of $^{2}J_{Sn-P_2}$ is also compatible with this structure. The parameters of the PMR spectra of these complexes in acetone are listed in Table 1.

No cis-isomerization was observed when (II) was dissolved in acetone at −90°C, and also on short-term warming of the solution to ∼25°C; partial splitting off of SnX_2 takes place with the formation of (I).

Heating the acetone solution of (IIIa) from −90°C to ∼+25°C leads to the formation of a mixture of products. The ^{31}P spectrum of this mixture is shown in Fig. 1. Besides the two doublets 3 and 5 related to complex (IIIa) and singlet 1 corresponding to complex (Ia), in the spectrum there is a multiplet of an A_2B type cation [$PtH(PPh_3)_3$]$^+$ (IV). The correctness of this assignment is also confirmed by the presence in the PMR spectrum of this mixture of a doublet of triplets at −5.8 ppm, which agrees with the data in [6] for the [$PtH(PPh_3)_3$]BF_4 salt, and also by the coincidence with the parameters of the ^{31}P spectrum of the [$PtH(PPh_3)_3$]-(NO_3) solution, obtained by an independent method (see experimental part).

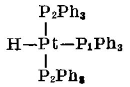
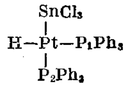
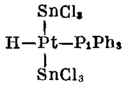
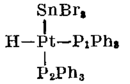
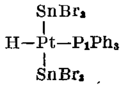
Besides the above signals, in the spectrum there is singlet 4 with satellites from ^{195}Pt and $^{119/117}$Sn. We assigned this singlet preferably to trans-[$PtH(SnCl_3)_2(PPh_3)$] (Va), although because of partial superposition of satellites from $^{119/117}$Sn on other signals, it is impossible to accurately determine the number of tin atoms in the molecule. The proposed structure

---

M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1033-1037, May, 1982. Original article submitted July 1, 1981.

0568-5230/82/3105-0917$07.50

TABLE 1. Parameters of ^{31}P and ^{1}H NMR Spectra of Products of Reaction between trans-[$PtHX(PPh_3)_2$] and SnX_2 in Acetone and Ethyl Acetate (δ, ppm, J, Hz)

Compound	Structure	δP_1	$^1J_{Pt-P_1}$	$^2J_{Sn-P_1}$	δP_2	$^1J_{Pt-P_2}$	$^2J_{Sn-P_2}$	$^2J_{P_1-P_2}$	δH	$^1J_{Pt-H}$	$^2J_{P_1-H}$	$^2J_{Sn-H}$
(IV)	 $H-\overset{\overset{P_2Ph_3}{\vert}}{\underset{\underset{P_2Ph_3}{\vert}}{Pt}}-P_1Ph_3$	20,5	2199	–	22,0	2821	–	18,5	–5,8	805	166 *	–
(IIIa)	 $H-\overset{\overset{SnCl_3}{\vert}}{\underset{\underset{P_2Ph_3}{\vert}}{Pt}}-P_1Ph_3$	5,5	2270	254	13,0	4021	1714	19,0	–13,0	441	150†	66
(Va)	 $H-\overset{\overset{SnCl_3}{\vert}}{\underset{\underset{SnCl_3}{\vert}}{Pt}}-P_1Ph_3$	10,5	2343	294	–	–	–	–	–13,5	387	139	‡
(IIIb)	 $H-\overset{\overset{SnBr_3}{\vert}}{\underset{\underset{P_2Ph_3}{\vert}}{Pt}}-P_1Ph_3$	10,0	2321	269	15,0	4050	1729	16,5	–12,0	441	148†	76
(Vb)	 $H-\overset{\overset{SnBr_3}{\vert}}{\underset{\underset{SnBr_3}{\vert}}{Pt}}-P_1Ph_3$	17,5	2399	**	–	–	–	–	–12,5	344	140	‡

---

* $^2J_{P_2-H}$ = 16.5 Hz.

† $^2J_{P_2-H}$ unresolved.

‡ $^2J_{Sn-H}$ unresolved.

** $^{117/119}Sn$ satellites are overlapped by other signals.

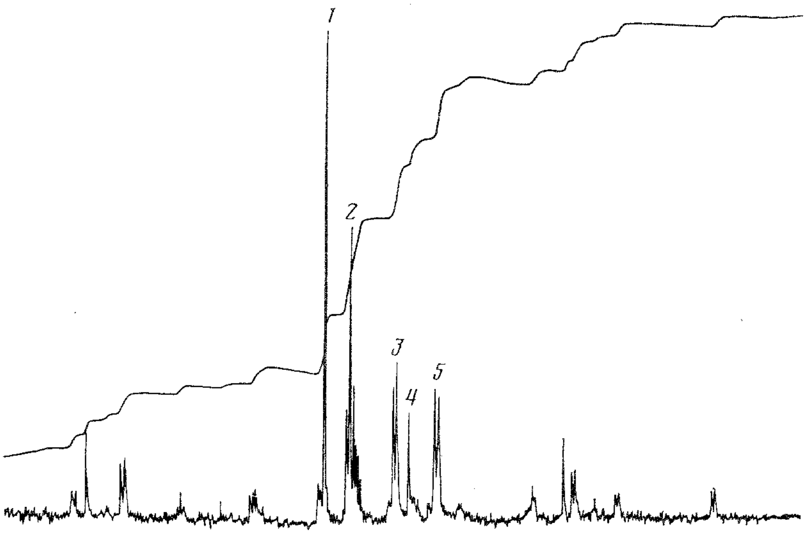


Fig. 1. ^{31}P NMR spectrum of products of reaction between trans-[$PtHCl(PPh_3)_2$] and $SnCl_2$ in acetone.

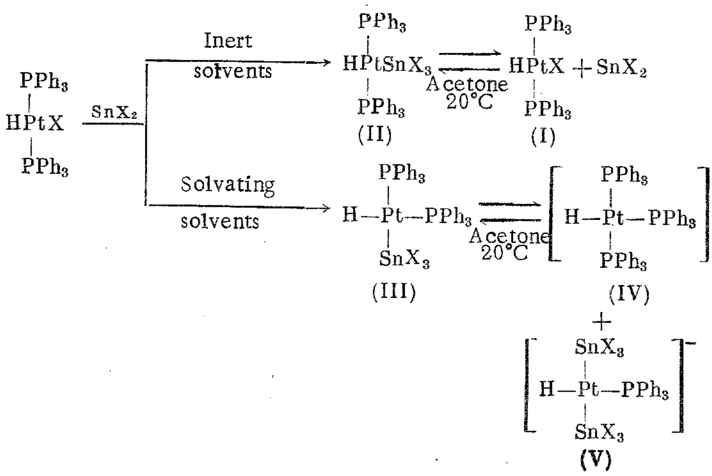
is confirmed by the ^{31}P spectrum with incomplete uncoupling from protons, indicating a trans-configuration of the phosphine and hydride ligands, and by the value of $^2J_{Sn-P_1}$, characteristic of the cis-configuration of the phosphine and tin-containing ligands. The presence of complex (Va) in this mixture probably also determines the presence of a doublet in the PMR spectrum with a center at −13.5 ppm.

The ratio of the signal intensities in the ^{31}P spectrum shows that the content of cation (IV) with three phosphine ligands is 6-7% greater than the content of the monophosphine complex (Va) (accuracy of measurement of integrals ∿2-3%), which is, apparently, due to the presence of a platinum complex in the mixture, which does not contain phosphine ligands.

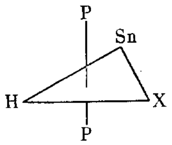
Similar changes take place on heating the acetone solution of (IIIb).

The formation of a mixture of complexes (III), (IV), and (V) was observed also when the reaction between (I) and SnX_2 was carried out in acetone at ∿25°C. In ethyl acetate, the reaction between (I) and SnX_2 at ∿25°C leads to the formation of trans-[$PtH(SnX_3)(PPh_3)_2$] only, i.e., it does not give redistribution products of the phosphine ligands.

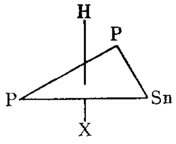
The above experimental data can be represented by the following scheme:



To explain the results obtained, we assume that at the first stage of the reaction, the unsolvated SnX_2 molecules penetrate the Pt—X bonds by a mechanism similar to that proposed in [8], while the SnX_2 molecules solvated by the donor solvents substitute the ligand X at the Pt atom. The change occurring in the geometrical configuration of the complex can be explained by the fact that of the two possible pentacoordinated intermediates (VI) and (VII), the latter is most stable, and splitting off of X from it leads to cis-isomers (IIIa) and (IIIb).



(VI)



(VII)

This supposition agrees with the conclusion made in [9] on the higher stability of the pentacoordinated intermediates, in which the π-bonded ligands lie in the equatorial plane.

The occurrence of the second stage of the reaction, i.e., the redistribution of the phosphine ligands, in the case of the cis-isomer was due to the strong trans-effect of the hydride and SnX$_3$ ligand, which weakens the Pt—P bond. The formation of a thermodynamically more favorable mixture of (IV) and (V) in acetone from the less reactive trans-isomer (II), observed on dissolution in acetone, probably proceeds via the formation of the cis-isomer (III), as a result of a side reaction between the dissociation products of (II) [(I) and SnX$_2$].

The conclusion that the main factor determining the direction of the reaction between (I) and SnX$_2$ is the solvation of tin dihalide is confirmed by experiments with additions (∿0.5%) of a strongly solvating solvent (DMFA) to the inert solvents. Despite the fact that this addition does not appreciably change the polarity of the medium, in the reaction between (I) and SnX$_2$, reaction products of the redistribution of phosphines (IV) and (V) as well as cis-[PtH(SnX$_3$)(PPh$_3$)$_2$] are also formed in the mixture.

EXPERIMENTAL

The ^{31}P and ^{1}H NMR spectra were recorded at temperatures of —50°C to —90°C on a Varian FT-80A spectrometer under pulse regime with a working frequency of 32.196 and 79.5398 MHz, respectively, in ampuls 10 mm in diameter, with internal stabilization on the ^{2}H nuclei. The chemical shifts of ^{31}P and ^{1}H were measured on the δ-scale with reference to external standard 85% H$_3$PO$_4$ (positive values for shifts into a weaker field, ±0.1 ppm) and protons of deuterated solvents (±0.1 ppm), respectively. The δH shifts are given with reference to TMS.

The solvents were purified and dried by standard methods. Anhydrous SnCl$_2$ and SnBr$_2$ were used. trans-[PtHX(PPh$_3$)$_2$] (X = Cl, Br), trans-[PtH(SNX$_3$)(PPh$_3$)$_2$] [3], and trans-[PtH(NO$_3$)(PPh$_3$)$_2$] [10] were obtained by known methods.

Reaction between trans-[PtHX(PPh$_3$)$_2$] and SnX$_2$ in CHCl$_3$, CH$_2$Cl$_2$, or Toluene. An equivalent amount of SnX$_2$ was added to a solution of 0.03-0.05 mmole of the platinum complex. The mixture was stirred to complete dissolution of the materials, and transferred to an ampul for recording the spectra.

Reaction between trans-[PtHX(PPh$_3$)$_2$] and SnX$_2$ in Acetone or Ethyl Acetate. A. Formation of cis-[PtH(SnX$_3$)(PPh3)$_2$]. A 0.05 mmole portion of the platinum complex was added to a cooled (to —90°C) solution of 0.05 mmole of SnCl$_2$ or 0.15 mmole of SnBr$_2$ in 2 ml of a solvent. After 2-3 min of stirring, the NMR spectra were recorded.

B. A 0.05 mmole portion of the platinum complex and 0.05-0.15 mmole of SnX$_2$ were mixed in 2 ml of a solvent at 20°C. After complete dissolution, the NMR spectra were recorded.

C. A solution of 0.03 mmole of cis-[PtH(SnX$_3$)(PPh$_3$)$_2$], obtained as in A, was heated for 1 min to 20°C, and the spectra were recorded.

[PtH(PPh$_3$)$_3$ (NO$_3$). A 0.03 mmole portion of PPh$_3$ was added at 20°C to a solution of 0.03 mmole of trans-[PtH(NO$_3$)(PPh$_3$)$_2$] in 2 ml of acetone. ^{31}P spectrum: δP$_1$ 20.6 ppm, $^1J_{Pt-P_1}$ = 2202 Hz, δP$_2$ 22.0 ppm, $^1J_{Pt-P_2}$ = 2823, $^2J_{P_1-P_2}$ = 18.5 Hz.

CONCLUSIONS

1. In acetone or ethyl acetate, cis-[PtH(SnX$_3$)(PPh$_3$)$_2$] is formed at the first stage of the reaction between [PtHX(PPh$_3$)$_2$] and SnX$_2$; in inert solvent the trans-isomer is the reaction product.

2. With increase in temperature, redistribution of the phosphine ligands in cis-[PtH(SnX$_3$)(PPh$_3$)$_2$] takes place, and [PtH(PPh$_3$)$_3$]$^+$, trans-[PtH(SnX$_3$)$_2$(PPh$_3$)]$^-$, and a platinum complex without phosphine are formed.

LITERATURE CITED

1. J. C. Bailar and H. Itatani, Inorg. Chem., 4, 1618 (1965).
2. G. W. Parshall, Homogeneous Catalysis. The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes, Wiley, N.Y. (1980).
3. P. G. Antonov, Yu. N. Kukushkin, L. P. Mitronina, L. N. Vasil'ev, and V. P. Sass, Zh. Neorg. Khim., 24, 1008 (1979).
4. V. I. Bogdashkina, Yu. E. Zubarev, A. B. Permin, V. S. Petrosyan, and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., 2840 (1980).
5. K. A. Ostoja Starzewski, H. Ruegger, and P. S. Pregosin, Inorg. Chim. Acta, 36, L455 (1979).
6. T. W. Dingler and K. P. Dixon, Inorg. Chem., 13, 846 (1974).
7. P. S. Pregosin and N. Sze, Helv. Chim. Acta, 61, 1848 (1978).
8. E. N. Yurchenko L. V. Fomenko, and A. D. Troitskaya, Koord. Khim., 5, 426 (1979).
9. D. L. Torn and R. Hoffmann, J. Am. Chem. Soc., 100, 2079 (1978).
10. H. C. Clark and H. Kurosawa, J. Organomet. Chem., 36, 399 (1972).

EFFECT OF σ,π CONJUGATION ON ^{199}Hg CHEMICAL SHIFTS

Yu. K. Grishin, Yu. A. Strelenko,
Yu. A. Ustynyuk, A. A. Érdman,
I. V. Shchirina-Éingorn, and I. I. Kritskaya

UDC 543.422.25:457.1'13:546.49

Heteroorganic compounds containing $R_nM{-}C{-}C{=}X$ or $R_nM{-}C{-}Ar$ fragments with readily polarizable C–M bonds in the position alpha to the unsaturated system are characterized by high reactivity, a tendency to undergo reactions involving transfer of the reaction center, and anomalous physical and spectral properties, which are usually interpreted on the basis of σ,π conjugation. This electronic effect was first suggested in 1935 [1] and was extended to organometallic systems by A. N. Nesmayanov [2]. The most detailed information about this effect has been obtained for allyl and benzyl derivatives of mercury and for α-mercurized carbonyl compounds by photoelectron spectroscopy [3, 4], electronic absorption spectroscopy [5], Raman spectroscopy [6, 7] negative-ion mass spectrometry [8], and polarography [6, 7]. Important results have also been obtained by ^{1}H and ^{13}C NMR spectroscopy [7, 9-12], which has revealed marked changes in the $J_{^{199}Hg-^1H}$ and $J_{^{199}Hg-^{13}C}$ values for these compounds.

The wide range of variation of ^{199}Hg chemical shifts (>5000 ppm) and their high sensitivity to intramolecular electronic effects gave us reason to suppose that σ,π conjugation would have a substantial effect on the shielding of the ^{199}Hg nucleus in allylic and benzylic organomercury compounds and mercurized carbonyl compounds. Benzylmercury chloride and its derivatives have been studied by ^{199}Hg NMR in [11, 12], considerable variations in ^{199}Hg chemical shift (δHg) being observed amongst the benzylmercury chlorides in both works. However, an unambiguous interpretation of these variations can be obtained only on the basis of a detailed study of a series of model compounds, since δHg is greatly influenced by various structural factors and by the medium, as has been shown by us [13-15] and by a number of other investigators [16]. In particular, recently performed measurements of the ^{199}Hg NMR spectra of o-substituted diphenylmercury compounds [14] and phenylmercury thiophenolates (results to be published) have shown that steric effects may play a significant role in the shielding of the ^{199}Hg nucleus. The presence of a donor substituent incapable of coordinating with the Hg atom, e.g., an alkyl group, in the ortho position of the phenyl ring in compounds of the type Ar_2Hg and ArHgSAr results in a weak shift in the ^{199}Hg signals, as is also the case when a CH_3 group is introduced into the ortho position of benzylmercury chloride [11]. The difference between the corresponding changes in δHg for these compounds is in accord with their structural characteristics.

On the basis of our ideas concerning the factors which determine the shielding of ^{199}Hg nuclei, the presence of significant σ,π conjugation in a molecule should be accompanied by a strong-field shift in resonance. This being the case, the unsaturated system adjacent to the Hg atom will act as an electron-deficient center and cause substantial delocalization of the electron pair of the C–Hg bond. This delocalization will reduce the population of the corre-

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1038-1042, May, 1982. Original article submitted July 20, 1981.

0568-5230/82/3105-0921\$07.50