Journal of Organometallic Chemistry, 275 (1984) 295–301
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE REACTION OF $PtCl_6^{2-}$ WITH AROMATIC COMPOUNDS TO AFFORD ANIONIC σ-ARYL COMPLEXES OF PLATINUM(IV)

VI *. THE ^{195}Pt AND ^{13}C NMR SPECTRA OF σ-ARYL COMPLEXES

A.N. KITAIGORODSKII, V.M. NEKIPELOV, A.T. NIKITAEV and G.B. SHUL'PIN*
Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Moscow 117977 (U.S.S.R.)

(Received May 15th, 1984)

Summary

^{195}Pt NMR spectra were obtained for solutions of σ-aryl complexes of platinum(IV) bearing various substituents R in the benzene ring, in the *meta*- and *para*-positions with respect to the platinum moiety. With increasing electron-withdrawing ability of R, the ^{195}Pt resonances are shifted towards high field, which is consistent with the changes in the ^{199}Hg, ^{205}Tl and ^{207}Pb NMR spectra of the corresponding aryl derivatives. The ^{13}C NMR spectra of two σ-aryl complexes of platinum(IV) are also reported.

Introduction

Earlier we found a novel reaction of the $PtCl_6^{2-}$ ion with aromatic compounds in organic acids to afford anionic σ-aryl complexes of platinum(IV) [1–4]. The complexes were characterized by ^{1}H [2–4] and ^{19}F [4] NMR spectra and the structures of two complexes were established by X-ray analysis [5]. These complexes can also be prepared by the photoinduced reaction of $PtCl_6^{2-}$ with aromatic compounds [6,7].

In the present paper we report the ^{195}Pt as well as the ^{13}C NMR spectra of several σ-aryl complexes of platinum(IV) prepared as described in refs. [1–4,6,7].

Results and discussion

The ^{195}Pt NMR spectra

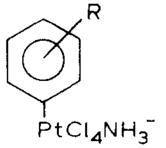
In recent years, there has been a growing interest in the use of ^{195}Pt NMR spectroscopy as a sensitive method to study the structures of platinum-containing inorganic and organometallic compounds [8–19] (for a review see ref. 8).

---

* For part V see ref. 5.

0022-328X/84/$03.00

We studied the ^{195}Pt NMR spectra of the σ-aryl complexes of platinum(IV) in order to establish the details of their structures and to investigate the effect of substituents in the benzene ring on the ^{195}Pt chemical shift. The eight complexes studied are listed below.



(I, R = OH, III, R = CH_3, V, R = Cl, VII, R = $COCH_3$
II, R = OCH_3, IV, R = H, VI, R = COOH, VIII, R = NO_2)

The ^{195}Pt NMR spectra were recorded in acetone solutions at 25 °C, the acetone solution of $Na_2PtCl_6 \cdot 6H_2O$ being used as an internal or external reference (^{195}Pt chemical shift is −227 ppm with respect to H_2PtCl_6 in H_2O). Examples of the spectra (for complexes II and VIII) are presented in Fig. 1. Table 1 lists the experimental data obtained.

The ^{195}Pt NMR spectra of all the complexes studied (except IV) consist of two singlets due to the *para*- and *meta*-isomers of platinated monosubstituted benzenes, the mixture of which is formed in the course of the thermal reaction of $PtCl_6^{2-}$ with the corresponding benzenes [2–4]. Naturally, only one isomer, and hence a single NMR resonance, was observed for complex IV as well as for the platinum(IV) complex of a disubstituted benzene, viz. *meta*-chlorotoluene (δ −924.7 ppm with respect to $Na_2PtCl_6 \cdot 6H_2O$ in acetone). In order to assign the NMR resonances of complexes I–III, we recorded the ^{195}Pt NMR spectrum of the pure *para*-isomer of anisole complex II prepared by the photochemical reaction of $PtCl_6^{2-}$ with anisole at room temperature [6,7]. The spectrum contained a single resonance which

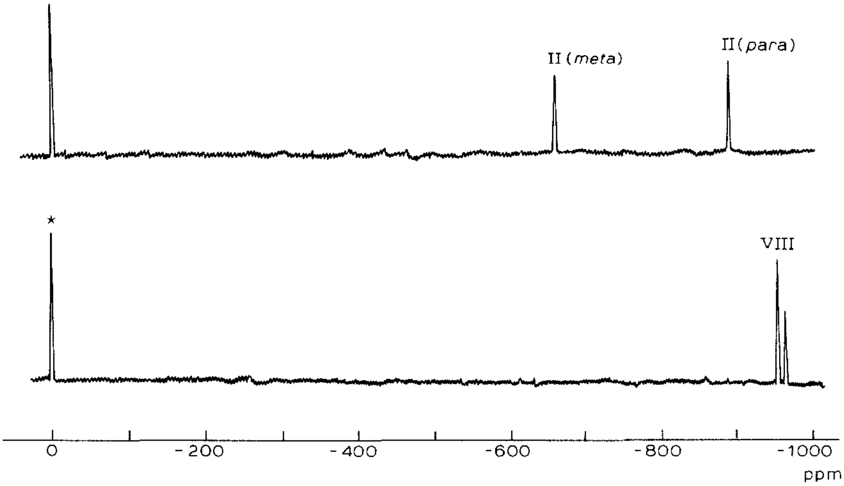


Fig. 1. ^{195}Pt NMR spectra of complexes II and VIII in acetone solutions. * Reference: $Na_2PtCl_6 \cdot 6H_2O$ (δ = 0 ppm).

coincided, within experimental error, with the position of the high-field signal in the spectrum of a mixture of the two isomers. On the basis of this result, the high-field peak in the spectra of complexes bearing electron-releasing substituents can be attributed to the *para*-isomers. In the case of electron-withdrawing substituents (complexes V–VIII), pure isomers could not be isolated, and the assignments in Table 1 are only tentative. This will not, however, affect the following conclusions due to the fact that the chemical shifts of the *para*- and *meta*-isomers of complexes V–VIII differ only slightly.

The data presented in Table 1 show that on going from complex I, which contains a strong electron-releasing substituent (OH), to the σ-phenyl complex IV and further to complex VIII, which contains a strong electron-withdrawing group (NO_2), the resonances of both the *para*- and *meta*-isomers are shifted towards high field. The same trend was observed for aryl derivatives of other heavy metals, the metal (^{199}Hg [20,21], ^{205}Tl [22,23] and ^{207}Pb [24,25]) NMR signals being shifted towards high field with increasing electronegativity of the substituent in the benzene ring.

It is generally accepted that the shielding of heavy metal nuclei like ^{195}Pt is determined by Ramsey's paramagnetic term [26]. A simplified expression for this term is given by the equation [27]:

$$\sigma_p = -\left(2e^2h^2/3m^2c^2\Delta E\right)\left(\langle 1/r^3\rangle_{\mathrm{n}p}P_{\mathrm{n}} + \langle 1/r^3\rangle_{\mathrm{n}d}D_{\mathrm{n}}\right) \qquad (1)$$

where ΔE is the ligand-field splitting energy, $\langle 1/r^3\rangle_{\mathrm{n}p}$ and $\langle 1/r^3\rangle_{\mathrm{n}d}$ are the mean inverse cubes of the valence p and d electron-nuclear distances, and P_{n} and D_{n} reflect the amount of electron imbalance associated with the valence p and d-orbitals of the metal atom.

This expression can serve to account for the observed high-field shifts of the NMR resonances. Although the differences between the ΔE values of the complexes in question cannot be accurately measured from their electronic spectra due to the poor resolutions of the latter, it is reasonable to assume that a substituent in the benzene ring cannot affect ΔE considerably. On the other hand, a more electron-withdrawing substituent will cause an increase of the positive charge at the metal atom and consequently a decrease of the p- and d-electron imbalance factors P_{n} and D_{n} which will result in the high-field shift of the metal NMR resonance.

TABLE 1

CHEMICAL SHIFTS OF THE ^{195}Pt NMR SPECTRA OF THE σ-ARYL COMPLEXES OF PLATINUM(IV) (I–VIII) IN ACETONE (δ,ppm)

Complex	R	δ with respect to Na_2PtCl_6 in acetone		δ with respect to IV		$\Delta = \lvert\delta_{meta} - \delta_{para}\rvert$
		meta	*para*	*meta*	*para*	
I	OH	−646.0	−856.0	263.6	53.6	210.0
II	OCH_3	−667.0	−895.8	242.6	13.8	228.8
III	CH_3	−674.0	−908.2	235.6	1.4	234.2
IV	H	−909.6		0		–
V	Cl	−935.5	−940.9	−25.9	−31.3	5.4
VI	COOH	−932.8	−945.0	−23.2	−35.4	12.2
VII	$COCH_3$	−936.9	−946.9	−27.3	−37.3	10.0
VIII	NO_2	−969.0	−977.7	−59.4	−68.1	8.7

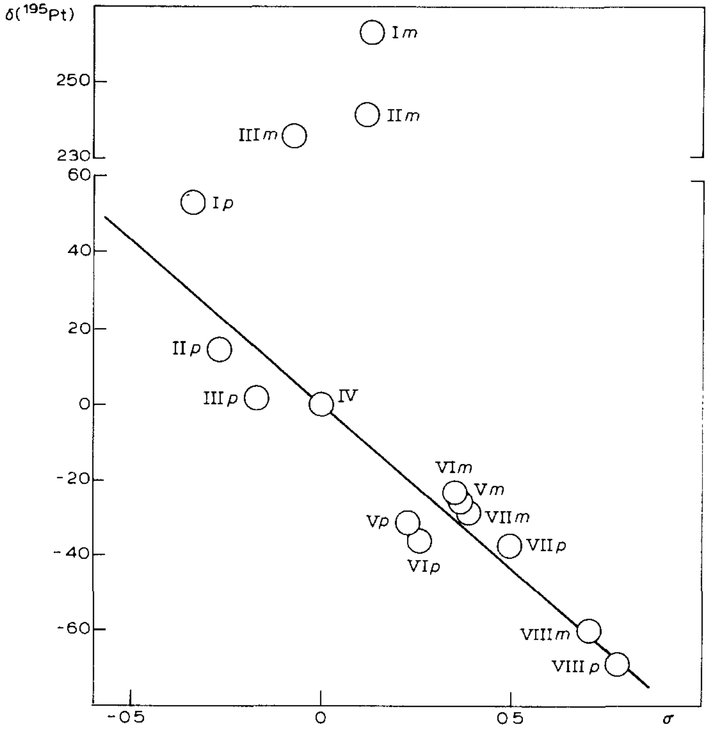


Fig. 2. Plot of the ^{195}Pt chemical shifts δ of complexes I–VIII (with respect to δ of IV) versus Hammett's σ-constants. For numbers of complexes see Table 1.

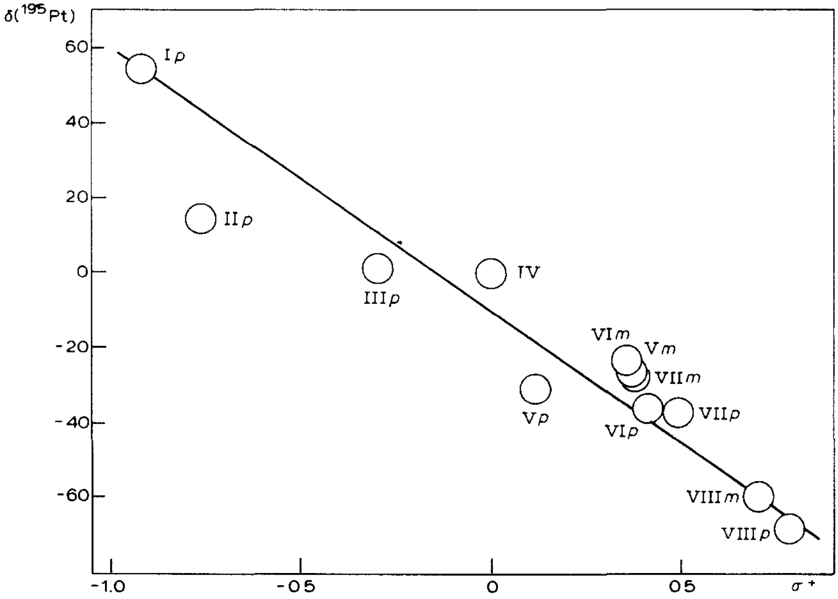


Fig. 3. Plot of the ^{195}Pt chemical shifts δ of complexes I–VIII versus Brown's σ^+-constants.

We have found a good correlation for the ^{195}Pt chemical shifts of the *para*- and *meta*-isomers of the complexes with σ and σ^+-values (Figs. 2 and 3). No correlation was observed between the chemical shifts of the *meta*-isomers of complexes I, II and III containing electron-releasing substituents and the σ_m-constants (Fig. 2). Moreover, there is an abrupt decrease of the chemical shift on going from complex IV to the *meta*-isomers of I, II and III, which possibly suggests a substantial increase in the paramagnetic screening of the platinum nuclei; the nature of this effect is not yet clear.

It is interesting to compare the relative sensitivity of the NMR chemical shifts of various heavy metals to the influence of substituents in σ-aryl ligands. Unfortunately, the data available to data are scarce and refer to σ-complexes of different types and therefore, at present, this comparison can have only a preliminary character. Since the dependence of the metal chemical shifts on the σ-values was found to be linear for mercury(II) [20,21], thallium(III) [23] and platinum(IV), the slopes of the corresponding plots can serve for the measure of their sensitivity to the substituent effect. The values of the tangent of these slopes are 170, 126 and 63 for $(RC_6H_4)_2Hg$, p-$C_6H_4Tl(OOCCF_3)_2$ and $RC_6H_4PtNH_3^-$, respectively. No reliable dependence of δ on σ was obtained for aryl derivatives of lead(IV) [25], which suggests that the sensitivity of ^{207}Pb NMR is much less than that for the other three nuclei.

A direct method of comparison of relative sensitivities is to correlate the chemical shifts of different metal nuclei in complexes with the same substituents in the benzene ring. The corresponding plot is shown in Fig. 4 for the ^{195}Pt NMR shifts in the p-σ-aryl complexes and the chemical shifts of ^{199}Hg resonances in $(p\text{-}RC_6H_4)_2Hg$.The correlation is approximately linear, the range of ^{199}Hg chemical shifts being twice as wide as that for the ^{195}Pt nucleus. However, it should be taken into account that in the mercury compounds, substituents are present in both the benzene rings. If one assumes the effects of the substituents to be additive, it should

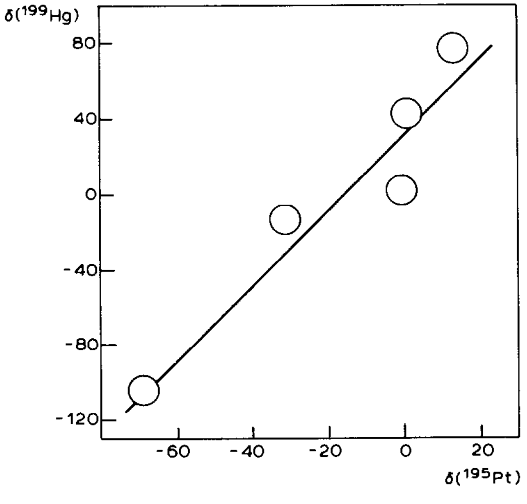


Fig. 4. Plot of the ^{195}Pt chemical shifts δ of the *para*-isomers of complexes II–V and VIII versus the ^{199}Hg chemical shifts of $(p\text{-}RC_6H_4)_2Hg$ (in C_5H_5N, with respect to Ph_2Hg [21], the substituents R correspond to those in the platinum complexes).

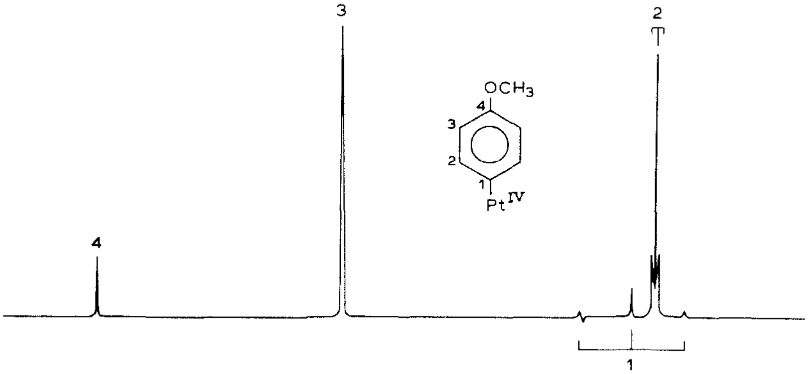


Fig. 5. ^{13}C-$\{^1H\}$ NMR spectrum of complex II(*para*) in acetone solution

follow that the sensitivities of the ^{195}Pt and ^{199}Hg nuclei to *para*-substitution in aryl ligands are approximately equal.

The ^{13}C NMR spectra

In order to obtain additional information concerning the structural and spectroscopic characteristics of the σ-aryl complexes of platinum(IV), we recorded the ^{13}C-$\{^1H\}$ NMR spectrum of pure complex II(*para*) in acetone solution. In this spectrum, there are four signals at 157.8, 137.8, 111.4 and 113.2 ppm (with respect to TMS) which can be assigned to the C(4), C(3), C(2) and C(1) carbon atoms, respectively (Fig. 5). The signals of C(2) and C(1) are accompanied with satellites due to the splitting on the ^{195}Pt nuclei, $J(^{13}C-^{195}Pt)$ 25 and 640 Hz, respectively. The chemical shift of the OCH_3 group is 55.0 ppm. We also obtained the ^{13}C-$\{^1H\}$ NMR spectrum of complex IV in acetone solution. This exhibited singlets at δ 138.3, 125.4 and 119.4 ppm due to C(4), C(3) and C(2), respectively. Unfortunately, the signals of C(1) and satellites were not detected in this case because of the small acquisition time.

Experimental

The ^{195}Pt NMR specta were recorded on Bruker CXP-300 (64.5 MHz) and Bruker SXP-4-100 (19.3 MHz) pulse Fourier spectrometers. The ^{13}C NMR spectra were recorded on a Bruker CXP-300 (75.5 MHz).

References

1 G.B. Shul'pin, R.P. Shibaeva, L.P. Rozenberg and A.E. Shilov, Kinet. Katal. 20(1979) 1570.
2 G.B. Shul'pin, A.E. Shilov, A.N. Kitaigorodskii and J.V.Z. Krevor, J. Organomet. Chem., 201 (1980) 319.
3 G.B. Shul'pin, J. Organomet. Chem. 212 (1981) 267.
4 G.B. Shul'pin and A.N. Kitaigorodskii, J. Organomet. Chem., 212 (1981) 275.
5 R.P. Shibaeva, L.P. Rozenberg, R.M. Lobkovskaya, A.E. Shilov and G.B. Shul'pin, J. Organomet. Chem., 220 (1981) 271.
6 G.B. Shul'pin, G.V. Nizova and A.E. Shilov, J. Chem. Soc., Chem. Commun., (1983) 671
7 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.

8 P.S. Pregosin, Coord. Chem. Rev., 44 (1982) 247.
9 S. Hietkamp, D.J. Stufkens and K. Vrieze, J. Organomet. Chem., 169 (1979) 107.
10 J. Soulié, J.Y. Lallemand and R.C. Rao, Org. Magn. Reson., 12 (1979) 67.
11 J.D. Kennedy, I.J. Colquhoun, W. McFarlane and R.J. Puddephatt, J. Organomet. Chem., 172 (1979) 479.
12 Y. Koie, S. Shinoda and Y. Saito, Inorg. Chem., 20 (1981) 4408.
13 I.M. Ismail, S.J.S. Kerrison and P.J. Sadler, Polyhedron, 1 (1982) 57.
14 G.M. Clore and A.M. Gronenborn, J. Am. Chem. Soc., 104 (1982) 1369.
15 M. Hirayama and Y. Sasaki, Chem. Lett., (1982) 195.
16 M. Chikuma and R.J. Pollock, J. Magn. Reson., 47 (1982) 324.
17 F.E. Wood and A.L. Balch, Inorg. Chim. Acta, 76 (1983) L 63.
18 J.-M. Bret, P. Castan, G. Commenges and J.-P. Laurent, Polyhedron, 2 (1983) 901.
19 C. Carr, P.L. Goggin and R.J. Goodfellow, Inorg. Chim. Acta, 81 (1984) L 25.
20 M. Borzo and G.E. Maciel, J. Magn. Reson., 19 (1975) 279.
21 Yu.K. Grishin, Yu.A. Strelenko, L.A. Margulis, Yu.A. Ustynyuk, L.S. Golovchenko, A.S. Peregudov and D.N. Kravtsov, Dokl. Akad. Nauk SSSR, 249 (1979) 892.
22 J.F. Hinton, K.R. Metz and R.W. Briggs, Annu. Rep. NMR Spectrosc., Vol. 13, London, 1982.
23 J.F. Hinton and R.W. Briggs, J. Magn. Reson., 22 (1976) 447.
24 J.D. Kennedy, W. McFarlane and G.S. Pyne, J. Chem. Soc., Dalton Trans., (1977) 2332.
25 D.C. Van Beelen, H.O. Van der Kooi and J. Walters, J. Organomet. Chem., 179 (1979) 37.
26 N.F. Ramsey, Phys. Rev., 78 (1950) 699.
27 C.J. Jameson and H.S. Gutowski, J. Chem. Phys., 40 (1964) 1714.