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DEMERCURIATION REACTIONS OF THE COMPLEXES $[(PPh_3)_2RPt–HgR']$ CONTAINING PLATINUM–MERCURY BONDS

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Summary

The compounds $[(PPh_3)_2RPt–HgR']$ ($R = CH_3$, $R' = 2,5\text{-}C_6H_3Cl_2$, 2,3,4- and $2,4,6\text{-}C_6H_2Cl_3$, 2,3,4,5-, 2,3,4,6- and $2,3,5,6\text{-}C_6HCl_4$, C_6Cl_5; $R = Et$, $R' = 2,5\text{-}C_6H_3Cl_2$, $2,4,6\text{-}C_6H_2Cl_3$; $R = 2\text{-}C_6H_4Cl$, $R' = 2\text{-}C_6H_4(CH_3)$) have been prepared by the reactions of RHgR′ with $Pt(PPh_3)_3$, in order to study their possible use as intermediates in the preparation of diorganoplatinum complexes with different organic ligands. The dependence of $J(^{31}P–^{195}Pt)$ on slight differences in the electronic character of the ligand R′ in the series of compounds $[(PPh_3)_2(CH_3)Pt–HgR']$ has been studied.

Introduction

We recently described the preparation of the compounds *cis*-$[(PPh_3)_2RPt–HgR]$ (R = a polychlorophenyl group) with platinum–mercury bonds, by the addition of the appropriate HgR_2 compound to a solution of $Pt(PPh_3)_3$ in benzene [1]. When R contains only one *ortho*-chloro substituent, a rapid precipitation of mercury is observed on refluxing the compounds in xylene. This process leads to the synthesis of diorganoplatinum derivatives $[PtR_2(PPh_3)_2]$. However, if the aryl group R does not contain a bulky *ortho* substituent the complexes containing platinum–mercury bonds cannot be isolated because a spontaneous demercuriation reaction occurs giving the $[PtR_2(PPh_3)_2]$ complex directly [2]. In order to check the possible use of this reaction as a method for producing diorgano compounds $[PtRR'(PPh_3)_2]$ with different organic ligands, the action of RHgR′ on $Pt(PPh_3)_3$ has been investigated, and is the subject of this paper.

We have also studied the ^{31}P NMR spectra of the series of compounds $[(PPh_3)_2(CH_3)Pt–HgR']$ in an effort to correlate the ^{31}P chemical shifts, $J(^{31}P–^{195}Pt)$ and $^2J(^{31}P–^{199}Hg)$ with the electronegativity of R′.

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Results and discussion

The complexes *cis*-[$(PPh_3)_2RPt-HgR'$] ($R = CH_3$, $R' = 2,5\text{-}C_6H_3Cl_2$, 2,3,4- or $2,4,6\text{-}C_6H_2Cl_3$, 2,3,4,5-, 2,3,4,6- or $2,3,5,6\text{-}C_6HCl_4$, C_6Cl_5; $R = CH_2CH_3$, $R' = 2,5\text{-}C_6H_3Cl_2$, $2,4,6\text{-}C_6H_2Cl_3$; $R = 2\text{-}C_6H_4Cl$, $R' = 2\text{-}C_6H_4(CH_3)$) were prepared by adding the appropriate $RHgR'$ compound to a solution of $Pt(PPh_3)_3$ in benzene, under nitrogen at room temperature:

$$Pt(PPh_3)_3 + RHgR' \rightarrow cis\text{-}\left[(PPh_3)_2RPt-HgR'\right] + PPh_3$$

That the compound [$(PPh_3)_2(2\text{-}C_6H_4Cl)Pt-Hg(2\text{-}C_6H_4CH_3)$] was obtained has been shown by cleaving the mercury–platinum bond with CF_3COOH, to give the organoplatinum complex [$Pt(2\text{-}C_6H_4Cl)(CF_3COO)(PPh_3)_2$], showing that the ligand which had transferred from mercury to platinum was $2\text{-}C_6H_4Cl$. Furthermore, toluene was detected in the solution by gas chromatography. In the series of complexes [$(PPh_3)_2(CH_3)Pt-HgR'$], the ^1H NMR spectra confirm that the methyl group is attached to platinum (Table 2).

The analytical data and decomposition temperatures of these complexes are given in Table 1. All the compounds are air-stable but gradually darken in solution under sunlight due to a slow deposition of mercury. The compounds are readily soluble in benzene, acetone and dichloromethane, but only sparingly soluble in ethanol and hexane. Their IR spectra show bands of the coordinate ligands which are in accord with published data [3,4]. The ^1H NMR spectra of [$(PPh_3)_2(CH_3)Pt-HgR'$] show only slight changes in the value of the coupling constant $^2J(^1H-^{195}Pt)$ on changing R' (Table 2). The ^{31}P NMR spectra have enabled us to assign a *cis* configuration to all the compounds (see below).

It is not possible to obtain the derivatives [$(PPh_3)_2RPt-HgPh$] by the addition of RHgPh ($R = 2\text{-}C_6H_4CH_3$ and $2,5\text{-}C_6H_3Cl_2$) to a benzene solution of $Pt(PPh_3)_3$, because spontaneous demercuriation takes place immediately. This fact clearly indicates that in both cases the phenyl ligand remains attached to the mercury, R being the transferred group. Thus, the lack of a bulky *ortho* substituent on the aryl group coordinated to mercury precludes isolation of the complex [5]. For example, [$(PPh_3)_2(2,5\text{-}C_6H_3Cl_2)Pt-Hg(2,5\text{-}C_6H_3Cl_2)$] is stable as a solid and in solution,

TABLE 1

ANALYTICAL DATA

[$(PPh_3)_2RPt-HgR'$]		Decomposition temp. (°C)	Analysis (Found(calcd.)(%))	
R	R'		C	H
CH_3	$2,5\text{-}C_6H_3Cl_2$	180	49.5(47.75)	3.3(3.33)
CH_3	$2,3,4\text{-}C_6H_2Cl_3$	160	46.3(46.28)	3.2(3.14)
CH_3	$2,3,4,5\text{-}C_6HCl_4$	200	44.8(44.90)	2.9(2.98)
CH_3	$2,4,6\text{-}C_6H_2Cl_3$	193	47 4(46.28)	3.1(3.14)
CH_3	$2,3,4,6\text{-}C_6HCl_4$	174	45.1(44.90)	3.0(2.98)
CH_3	$2,3,5,6\text{-}C_6HCl_4$	181	45.4(44 90)	3.1(2.98)
CH_3	C_6Cl_5	210	43.6(43.59)	2.8(2.80)
CH_2CH_3	$2.5\text{-}C_6H_3Cl_2$	130	49.1(48.24)	3.5(3 50)
CH_2CH_3	$2,4,6\text{-}C_6H_2Cl_3$	142	45.3(46.77)	3.3(3.28)
$2\text{-}C_6H_4Cl$	$2\text{-}C_6H_4CH_3$	168	53 3(52.41)	3.7(3.68)
[$Pt(4\text{-}C_6H_4OCH_3)_2(PPh_3)_2$]		182	64 2(64.31)	4.7(4.72)

whereas [$(PPh_3)_2$PhPt–HgPh] rapidly loses mercury [2] as does the [$(PPh_3)_2$(4-$C_6H_4OCH_3$)Pt–Hg(4-$C_6H_4OCH_3$)] complex prepared in this work.

The two reactions mentioned above, are difficult to analyse due to the complex mixture of the products. Thus, for R = 2-$C_6H_4(CH_3)$, the ^{31}P NMR spectra in C_6D_6 show, after separation of the mercury, a mixture of three species: the major (~ 60%) is *cis*-[PtPh(2-$C_6H_4CH_3$)$(PPh_3)_2$] which appears as two doublets, δ(P) 19.73 and 17.84 ppm (^2J(P–P) 12 Hz), flanked by satellites of platinum with J(P–^{195}Pt) 1787 and 1697 Hz, respectively. The minor component (~ 18%) show a signal at δ(P) 16.51 ppm (J(P–^{195}Pt) 1725 Hz), which can be assigned to *cis*-[Pt(2-$C_6H_4CH_3)_2(PPh_3)_2$]. Finally, the third compound (~ 22%) is probably *cis*-[Pt$(Ph)_2(PPh_3)_2$] by its δ(P), 19.58 ppm J(P–^{195}Pt) 1734 Hz. When R = 2,5-$C_6H_3Cl_2$, the action of RHgPh on Pt$(PPh_3)_3$ gives four compounds in addition to the mercury: one (~ 45%) gives two doublets at δ(P) 14.71 and 20.14 ppm (^2J(P–P) 11 Hz) with J(P–^{195}Pt) 2000 and 1780 Hz, respectively; this compound is *cis*-[PtPh(2,5-$C_6H_3Cl_2$)$(PPh_3)_2$]; another derivative (~ 20%), with δ(P) 19.65 ppm (J(P–^{195}Pt) 1740 Hz) could be *cis*-[$PtPh_2(PPh_3)_2$]. A third complex (~ 16%) shows a signal at δ(P) 23.60 ppm (J(P–^{195}Pt) 3120 Hz) which corresponds to *trans*-[Pt(2,5-$C_6H_3Cl_2)_2(PPh_3)_2$] [1], and the other compound, which gives a singlet at δ(P) 21.62 ppm (J(P–^{195}Pt) 3080 Hz) is probably *trans*-[PtPh(2,5-$C_6H_3Cl_2$)$(PPh_3)_2$].

Two mechanisms may account for the complicated mixture of products obtained in both reactions. In the first, the formation of a compound containing a platinum–mercury bond is followed by a radical decomposition, giving a mixture of organoplatinum complexes. In the second mechanism, a partial symmetrisation (favoured by free PPh_3) of the unsymmetrical organomercurial RHgR′ gives HgR_2 and HgR'_2, and these could react with Pt$(PPh_3)_3$ to give the different isomers. However, this mechanism is less probable because if the zero-valent platinum complex used is [Pt$(C_2H_4)(PPh_3)_2$], then identical products with similar yields are obtained. Also, a partial symmetrisation of RHgPh (R = 2-$C_6H_4CH_3$ or 2,5-$C_6H_3Cl_2$) must give HgR_2 and these react easily with Pt$(PPh_3)_3$ to give the isolable [$(PPh_3)_2$RPt–HgR] complexes [1] which were not detected in our reactions.

We have also examined the demercuriation reaction in refluxing xylene solutions of the compound [$(PPh_3)_2$(2-C_6H_4Cl)Pt–Hg(2-$C_6H_4CH_3$)] in order to see if these drastic conditions give an improved method for obtaining diorganoplatinum derivatives. The results were similar and four different compounds were detected after the reaction, only one of which has been identified, as *cis*-[Pt(2-$C_6H_4CH_3)_2(PPh_3)_2$] (δ(P) 16.50 ppm; J(P–^{195}Pt) 1726 Hz).

The demercuriation reaction of the compounds [$(PPh_3)_2$RPt–HgR′], where R is methyl or ethyl, occurs simultaneously with other decomposition processes, affording several products that we have not investigated.

In summary, through our studies, we conclude that, (i) the migration of the group from mercury to platinum follows the sequence Cl [6] > alkyl > 2-C_6H_4Cl > 2-$C_6H_4(CH_3)$ > phenyl, and (ii) the suggested method for obtaining diorganoplatinum derivatives, based on the demercuriation reaction of complexes containing platinum–mercury bonds, is not an useful method for compounds with different organic ligands because of the mixture of final products.

$^{31}P\ \{^1H\}$ *NMR spectra*

The ^{1}H decoupled ^{31}P NMR spectra of the new compounds with

(Continued on p. 420)

TABLE 2

NMR DATA FOR THE COMPLEXES *cis*-[$(PPh_3)_2RPt-HgR'$] AND [$Pt(4-C_6H_4OMe)_2(PPh_3)_2$] [a]

cis-[$(PPh_3)_2RPt-HgR'$] R	R′	$\delta(P(a))$	$J(P(a)-Pt)$	$^2J(P(a)-Hg)$	$\delta(P(b))$	$J(P(b)-Pt)$	$^2J(P(b)-Hg)$	$^2J(P(a)-P(b))$	$\delta(H)$	$^2J(H-Pt)$	$^3J(H-P)$
CH_3	C_6Cl_5	21.50	2769	220	46.00	2250	1760	12.6	−0.40	19.8	3.0
CH_3	2,3,5,6-C_6HCl_4	21.70	2740	219	46.57	2258	1750	12.6	−0.34	19.0	3.5
CH_3	2,3,4,6-C_6HCl_4	22.08	2724	216	45.34	2240	1790	12.5	−0.34	19.0	3.4
CH_3	2,4,6-$C_6H_2Cl_3$	22.72	2701	218	44.91	2231	1842	12.2	−0.44	19.2	3.6
CH_3	2,3,4,5-C_6HCl_4	22.44	2540	220	46.04	2145	1860	12.2	−0.39	20.4	3.6
CH_3	2,3,4-$C_6H_2Cl_3$	23.03	2498	220	45.15	2150	1900	12.0	−0.43	20.6	3.6
CH_3	2,5-$C_6H_3Cl_2$	23.11	2465	220	46.38	2146	1920	11.7	−0.51	21.0	3.5
CH_2CH_3	2,4,6-$C_6H_2Cl_3$	23.52	2757	216	44.06	2192	1600	11.5	0.45 [b]	[c]	[c]
									0.80 [b]	[c]	[c]
CH_2CH_3	2,5-$C_6H_3Cl_2$	23.90	2518	210	45.57	2099	1930	10.8	0.40 [b]	[c]	[c]
									0.75 [b]	[c]	[c]
2-C_6H_4Cl	2-$C_6H_4CH_3$	23.24	2430	240	41.50	2250	2080	11.0	–	–	–
[$Pt(4-C_6H_4OCH_3)_2(PPh_3)_2$]		19.63	1742								

[a] $^{31}P-\{^1H\}$ NMR in C_6D_6, reference H_3PO_4 85%, ^1H NMR in $CDCl_3$, reference TMS. *J* in Hz, δ in ppm, P(*a*) is *cis* and P(*b*) is *trans* to the Hg atom; δ(H) Me or Et groups bonded to Pt atom. [b] Multiplet. [c] Unresolved spectrum

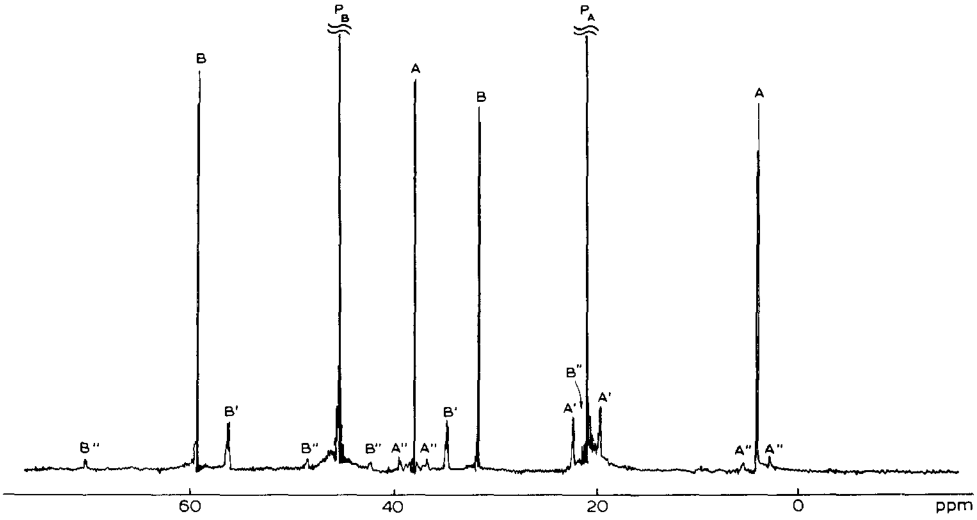

Fig. 1. The ^{31}P {^{1}H} NMR spectrum of {(PPh$_3$)$_2$(CH$_3$)Pt–Hg(C$_6$Cl$_5$)]. Signals due to the four possible isotopomers are: Pt–Hg (55.16%) P_AP_B; Pt*–Hg (28.03%) A, B; Pt–Hg*(11.13%) A′, B′; Pt*–Hg*(5.6%) A″, B″.

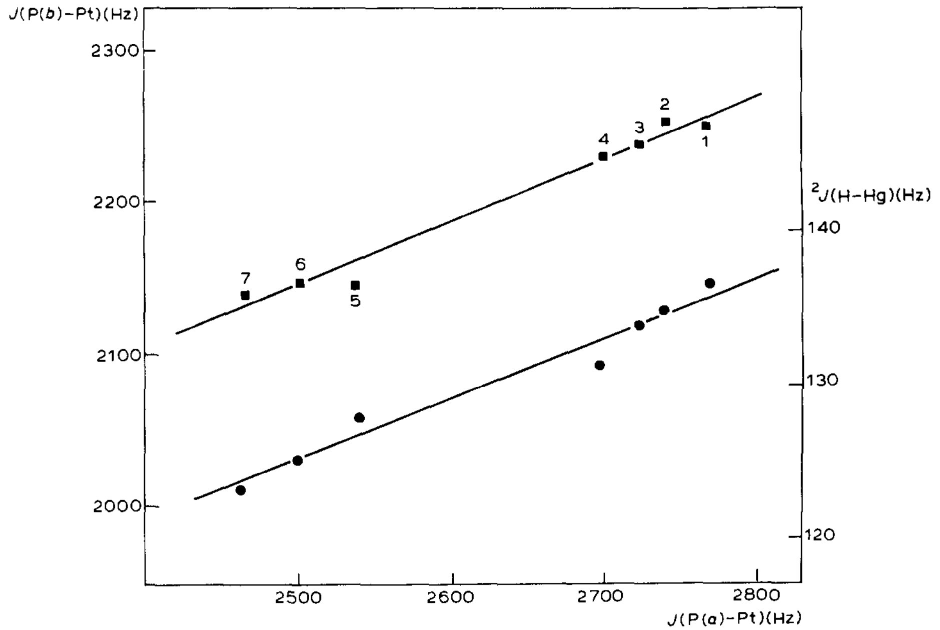

Fig. 2. Plots of J(P(b)–Pt) vs. J(P(a)–Pt) for [(PPh$_3$)$_2$RPt–HgR′] compounds ($r = 0.977$) (■) and J(P(a)–Pt) for [(PPh$_3$)$_2$RPt–HgR′] vs. ^2J(H–Hg) for CH$_3$–HgR′ ($r = 0.975$) (●). (1) R′ C$_6$Cl$_5$, (2) R′ 2,3,5,6-C$_6$HCl$_4$, (3) R′ 2,3,4,6-C$_6$HCl$_4$, (4) R′ 2,4,6-C$_6$H$_2$Cl$_3$, (5) R′ 2,3,4,5-C$_6$HCl$_4$, (6) R′ 2,3,4-C$_6$H$_2$Cl$_3$, (7) R′ 2,5-C$_6$H$_3$Cl$_2$.

platinum–mercury bonds consist of two doublets with chemical shifts of about 22 and 45 ppm, having a mutual coupling constant of about 12 Hz. Each signal is flanked by ^{195}Pt (natural abundance 33.7%) and ^{199}Hg (natural abundance 11.8%) satellites. An example is given in Fig. 1.

The NMR data for all the compounds are listed in Table 2. It is observed that for the compounds $[(PPh_3)_2(CH_3)Pt–HgR']$ a gradual decrease of $J(P(b)–^{195}Pt)$ and $J(P(a)–^{195}Pt)$ (P(b) and P(a) are the phosphorous atoms which *trans* and *cis* relative to HgR′) occurs with decreasing electronegativity of R′. It is widely believed that the Fermi contact term makes the major contribution to the magnitude of Pt–P coupling constants. Therefore, factors which allow the platinum 6*s* orbital to participate more fully in bonding to a phosphorous atom will increase the P–Pt coupling constant. In this case, an increase in the total number of chlorine atoms on the phenyl group decreases the electron donating power of R′, and, consequently, increases the availability of the 6*s* orbital of platinum for interation with the phosphorous atoms. Figure 2 shows an approximately linear correlation when $J(P(a)–^{195}Pt)$ is plotted against the electronegativity of R. As a measure of the electronegativity of R′ we have taken the $^2J(H–Hg)$ values of compounds of the type CH_3HgR [7].

Finally, when $J(P(b)–^{195}Pt)$ is plotted against $J(P(a)–^{195}Pt)$ (Fig. 2), an approximately linear correlation is obtained, suggesting that similar factors influence the magnitude of both coupling constants.

Experimental

Chemical analyses were carried out at the "Institut de Química Bio-Orgànica de Barcelona". The ^{31}P-$\{^1H\}$ NMR spectra were obtained on a Varian XL-200 FT spectrometer. IR spectra were recorded with a Beckman IR 20A spectrophotometer.

Starting materials

The compounds $Pt(PPh_3)_3$ and $[Pt(C_2H_4)(PPh_3)_2]$ were prepared according to literature methods [8,9]. The organomercury compounds RHgR′ were obtained by the action on R′HgCl of ether solutions of RMgBr [7].

Preparation of the complexes $[(PPh_3)_2RPt–HgR']$

All of these complexes were prepared by the following general method. A mixture of $Pt(PPh_3)_3$ (1.0 mmol) and RHgR′ (1.0 mmol) was dissolved in benzene (30 ml) under nitrogen at room temperature and stirred for 2 h. The resulting solution was concentrated to dryness. The residue was washed with hexane and recrystallized from benzene/hexane. Yield 70–80%.

Action of benzene solution of $[Pt(C_2H_4)(PPh_3)_2]$ on RHgPh

A mixture of $[Pt(C_2H_4)(PPh_3)_2]$ or $Pt(PPh_3)_3$ (1.0 mmol) and RHgPh (1.0 mmol) was dissolved in benzene (30 ml) under nitrogen at room temperature and stirred for several h. The resulting solution was filtered and then analyzed by ^{31}P NMR spectroscopy.

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