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ORGANOMETALLIC FORMATE COMPLEXES OF PLATINUM(II)

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Summary

The compounds *trans*-[Pt(OCHO)R$(PPh_3)_2$] (R = C_6Cl_5; 2,3,4,6-C_6HCl_4; 2,3,4,5-C_6HCl_4; 2,5-$C_6H_3Cl_2$) have been prepared by treatment of [PtIR$(PPh_3)_2$] with $AgClO_4$ followed by reaction with NaOCHO in methanol. The *cis* isomers have been obtained by the direct reaction of HCO_2H with compounds containing Pt–Hg bonds. For these and the analogous compounds containing C_6F_5 ligands, the dependence of $J(^{31}P-^{195}Pt)$ on R has been studied, and the effects of *cis*-R shown to be in the opposite direction from those of *trans*-R ligands.

Introduction

The chemistry of transition metal compounds containing the formate ligand bonded in a monodentate fashion is of considerable interest because of the potential participation of such species as intermediates in the catalysis of both the water-gas shift reaction and the conversion of CO_2 into formic acid [1]. The formate complexes also participate in the decomposition of formic acid to hydrogen and carbon dioxide [2].

The formate complexes are usually prepared by reaction of CO_2 into a transition metal–hydrogen bond, a type of reaction showing some similarity to olefin insertion (eq. 1).

$$MH + CO_2 \rightleftarrows MOCOH \qquad (1)$$

The reverse reaction is of interest because hydrido species can be obtained by CO_2 elimination from formate complexes [3].

Following our previous work on organometallic platinum(II) compounds containing bulky groups such as PPh_3 and polychlorophenyl [4], we report here the preparation of new compounds of this type containing the formate ligand. The preparation involves a new method consisting of treatment of a compound containing a Pt–Hg bond with formic acid.

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Results and discussion

Some platinum formate complexes have been obtained previously by metathesis involving formate ion [5] (eq. 2).

$$\mathrm{PtX} + \mathrm{OCHO}^- \rightarrow \mathrm{PtOCHO} + \mathrm{X}^- \qquad (2)$$

It is well known that organometallic platinum compounds $[\mathrm{PtXRL_2}]$, in which R is a bulky ligand, are difficult to obtain by classical methods such as the use of Grignard or organolithium reagents. The required starting halogeno complexes were prepared by the action of KI in acetone on the compounds $[\mathrm{Pt(CF_3CO_2)R(PPh_3)_2}]$ ($\mathrm{R = C_6Cl_5}$; 2,3,4,6-$\mathrm{C_6HCl_4}$; 2,3,4,5-$\mathrm{C_6HCl_4}$; 2,5-$\mathrm{C_6H_3Cl_2}$), which were obtained by treatment of the compounds $[\mathrm{(PPh_3)_2RPtHgR}]$ with trifluoroacetic acid [4]. The compounds $[\mathrm{PtIR(PPh_3)_2}]$ as well as the $[\mathrm{Pt(CF_3CO_2)R(PPh_3)_2}]$ have a *cis* configuration when R has two chlorine atoms in *ortho* positions ($\mathrm{C_6Cl_5}$; 2,3,4,6-$\mathrm{C_6HCl_4}$), and exist as a mixture of *cis* and *trans* isomers when R has only one chlorine atom in the *ortho* position (2,3,4,5-$\mathrm{C_6HCl_4}$; 2,5-$\mathrm{C_6H_3Cl_2}$) as revealed by the ^{31}P NMR data in Table 2.

Treatment of $[\mathrm{PtIR(PPh_3)_2}]$ with $\mathrm{AgClO_4}$ in methanol followed by reaction with NaOCHO in methanol leads to the formate complexes $[\mathrm{Pt(OCHO)R(PPh_3)_2}]$.

$$[\mathrm{PtIR(PPh_3)_2}] + \mathrm{AgClO_4} \xrightarrow{\mathrm{MeOH}} [\mathrm{Pt(MeOH)R(PPh_3)_2}]\mathrm{ClO_4} \qquad (3)$$

$$[\mathrm{Pt(MeOH)R(PPh_3)_2}]\mathrm{ClO_4} + \mathrm{NaOCHO} \rightarrow \textit{trans}\text{-}[\mathrm{Pt(OCHO)R(PPh_3)_2}] \qquad (4)$$

The configuration is *trans* for all the formate complexes obtained, even though the iodide complexes have a *cis* configuration and so there must be an isomerisation during the reaction. A similar result was reported by Venanzi in the preparation of *trans*-$[\mathrm{Pt(OCHO)(C_6Cl_5)(PEt_3)_2}]$ from *cis*-$[\mathrm{PtCl(C_6Cl_5)(PEt_3)_2}]$ [5].

This general method for the preparation of formate complexes is not very convenient in the case of the complexes we describe because, apart from the difficulty of obtaining the starting complexes $[\mathrm{PtIR(PPh_3)_2}]$, four steps are required starting from the Pt–Hg species, leading to lower overall yields. In addition the method gives only *trans* isomers.

The *cis*-formate complexes were readily obtained in good yield by the reaction of the compounds *cis*-$[\mathrm{(PPh_3)_2RPtHgR}]$ ($\mathrm{R = C_6Cl_5}$; 2,3,4,6-$\mathrm{C_6HCl_4}$; 2,3,4,5-$\mathrm{C_6HCl_4}$; 2,5-$\mathrm{C_6H_3Cl_2}$) with formic acid:

$$\textit{cis}\text{-}[\mathrm{(PPh_3)_2RPtHgR}] + \mathrm{HCO_2H} \rightarrow \textit{cis}\text{-}[\mathrm{Pt(OCHO)R(PPh_3)_2}] + \mathrm{Hg} + \mathrm{RH} \qquad (5)$$

The cleavage of Pt–Hg bonds by trifluoroacetic acid is known but the reaction with formic acid seems not to have been observed previously. The latter offers a direct method for the preparation of formato complexes with *cis* configurations as shown by NMR spectroscopy.

We have observed that isomerization of these *cis*-compounds to the corresponding *trans*-$[\mathrm{Pt(OCHO)R(PPh_3)_2}]$ species takes place in benzene at 50 °C. In contrast, the analogous compounds with $\mathrm{R = C_6F_5}$ show little tendency to isomerize; thus treatment of *cis*-$[\mathrm{PtCl(C_6F_5)(PPh_3)_2}]$ with $\mathrm{AgClO_4}$ and NaOCHO gives exclusively *cis*-$[\mathrm{Pt(OCHO)(C_6F_5)(PPh_3)_2}]$ which does not isomerise when its benzene solution is

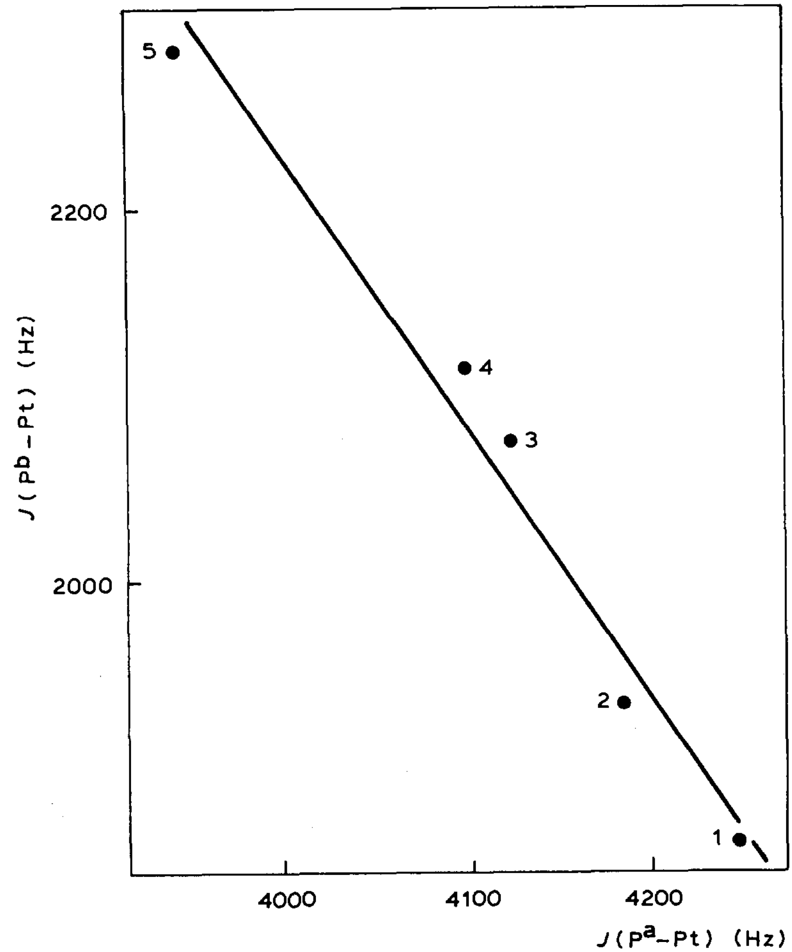

Fig. 1. Plot of $^{1}J(P^{b}\text{-}Pt)$ against $^{1}J(P^{a}\text{-}Pt)$ for *cis*-[Pt(OCHO)R(PPh$_3$)$_2$] complexes ($v = 0.986$). (1) R = 2,5-$C_6H_3Cl_2$; (2) R = 2,3,4,5-C_6HCl_4; (3) R = 2,3,4,6-C_6HCl_4; (4) R = C_6Cl_5; (5) R = C_6F_5.

kept at 50°C. The compound *trans*-[Pt(OCHO)(C_6F_5)(PPh$_3$)$_2$] can only be obtained from *trans*-[PtCl(C_6F_5)(PPh$_3$)$_2$]. This behaviour was not unexpected, since it is known that *cis*-[PtCl(C_6F_5)(PPh$_3$)$_2$] only isomerizes when it is heated in the solid phase [6] and this can be explained by taking account of the smaller size of C_6F_5 than of the polychlorophenyl ligands.

The analytical data and decomposition temperatures for these complexes are given in Table 1. All the compounds are white solids. They are readily soluble in dichloromethane, chloroform, benzene, or acetone, but only sparingly soluble in ethanol and hexane. Their IR spectra show bands from the coordinated ligands which are in accord with published data [7,8]. The IR spectrum in the $\nu(CO)_2$ region is indicative of monodentate coordination of formate to the metal [9]; it involves a strong ν(C=O) band at 1650–1640 cm^{-1} and a somewhat weaker ν(C–O) band at 1270–1260 cm^{-1}. The ^{1}H NMR spectra show the signal from the proton formate only for three of the compounds (see Table 3). For the others, the resonance

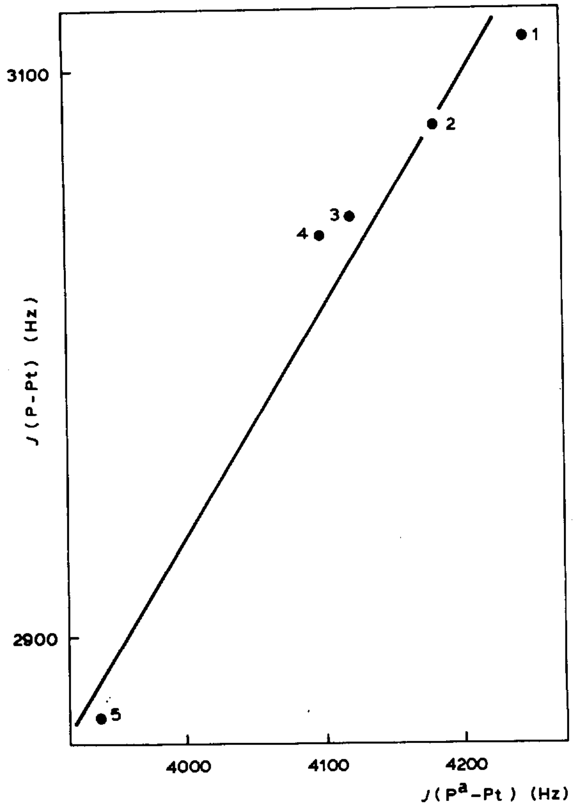

Fig. 2. Plot of ^1J(P–Pt) for *trans*-[Pt(OCHO)R(PPh$_3$)$_2$] against ^1J(P^a–Pt) for *cis*-[Pt(OCHO)R(PPh$_3$)$_2$] ($v = 0.975$). (1) R = 2,5-$C_6H_3Cl_2$; (2) R = 2,3,4,5-C_6HCl_4; (3) R = 2,3,4,6-C_6HCl_4; (4) R = C_6Cl_5; (5) R = C_6F_5.

is obscured by the intense signals of the PPh$_3$ aromatic hydrogen. From the ^{31}P{^{1}H} NMR spectra the *cis* or *trans* configuration can be unambiguously assigned and the spectroscopic parameters given in Table 3 have been derived. For the *trans* compounds the spectra consist of a singlet with ^{195}Pt satellites, and those for the *cis* compounds show two groups of signals arising from the two non-equivalent phosphorus atoms. The assignment of each group of signals is based on the ^1J(P–Pt) values; the larger value corresponds to the phosphorus atom *trans* to the formate group, in accord with the smaller *trans*-influence of this group compared, with those of ligands R. When R is C_6F_5, the assignment can also be based on the fact that the P atom *trans* to C_6F_5 appears as a broad signal due to coupling with F nuclei.

From the J(P–Pt) parameters for the compounds *cis*-[Pt(OCHO)R(PPh$_3$)$_2$] the following sequence of *trans*-influence of R can be derived: $C_6F_5 \ll C_6Cl_5 <$ 2,3,4,6-$C_6HCl_4 \ll$ 2,3,4,5-$C_6HCl_4 <$ 2,5-$C_6H_3Cl_2$. This *trans*-influence series is consistent with the assumption that the major contribution ot J(P–Pt) is the Fermi contact term. Thus, an increase in the electron-withdrawing ability of R increases the ability of the 6*s* orbital of platinum to interact with the *trans*-phosphorus atom and the magnitude of ^1J(P–Pt). The possibility cannot be excluded that steric factors may be

TABLE 1

ANALYTICAL DATA FOR $[Pt(OCHO)R(PPh_3)_2]$ COMPLEXES

cis-R	Decomposition temperature (°C)	Analysis (Found (calcd.) (%))		
		C	H	Cl
C_6Cl_5	130	51.9	3.0	17.0
		(50.92)	(3.06)	(17.49)
2,3,4,6-C_6HCl_4	138	52.7	3.1	14.6
		(52.72)	(3.27)	(14.49)
2,3,4,5-C_6HCl_4	150	52.7	3.0	14.5
		(52.72)	(3.27)	(14.49)
2,5-$C_6H_3Cl_2$	132	56.0	3.7	8.1
		(56.71)	(3.74)	(7.79)
C_6F_5	152	53.3	3.3	–
		(55.42)	(3.35)	
trans-R				
C_6Cl_5	172	50.8	3.0	17.0
		(50.92)	(3.06)	(17.49)
2,3,4,6-C_6HCl_4	180	52.7	3.3	14.4
		(52.72)	(3.27)	(14.49)
2,3,4,5-C_6HCl_4	168	52.0	3.1	15.0
		(52.72)	(3.27)	(14.49)
2,5-$C_6H_3Cl_2$	135	54.9	3.7	7.1
		(56.71)	(3.74)	(7.79)
C_6F_5	170	55.4	3.2	–
		(55.42)	(3.35)	

responsible for the large difference in the ^1J(P–Pt) values for R = C_6F_5 and C_6Cl_5, since their electron-withdrawing abilities are similar. Whereas the *trans* influence has been well established, the *cis* influence is not well understood. In order to compare the *cis* and *trans* influences in the compounds *cis*- and *trans*-$[Pt(OCHO)R(PPh_3)_2]$, we studied the values of J(P–Pt), and noted the following features:

(a) For *cis*-$[Pt(OCHO)R(PPh_3)_2]$ the *cis* influence of R is smaller than its *trans* influence in all cases, and operates in the opposite direction, as can be seen from the inverse linear correlation between $^1J(P^a–Pt)$ and $^1J(P^b–Pt)$ (P^a = P *cis* to R; P^b = P *trans* to R). Similar behaviour is found for the compounds *cis*-$[PtIR(PPh_3)_2]$.

(b) The influences of the R ligands which act in the same direction have similar effects for *cis*- and *trans*-$[Pt(OCHO)R(PPh_3)_2]$, as can be seen from the direct linear

TABLE 2

$^{31}P\{^1H\}$ NMR DATA FOR COMPLEXES $[PtIR(PPh_3)_2]$ [a]

R	$\delta(P^a)$	$^1J(P^a–Pt)$	$\delta(P^b)$	$^1J(P^b–Pt)$	$^2J(P^a–P^b)$	% [b]	δ(P)	^1J(P–Pt)	% [c]
C_6Cl_5	−129.2	3953	−130.7	2101	18	100			
2,3,4,6-C_6HCl_4	−129.1	3971	−130.5	2063	18	100			
2,3,4,5-C_6HCl_4	−126.8	4010	−129.4	1930	17	62	−122.1	2877	38
2,5-$C_6H_3Cl_2$	−126.2	4071	−128.6	1860	18	36	−121.2	2930	64

[a] $^{31}P\{^1H\}$ NMR in $CHCl_3$, reference $P(OMe)_3$, J in Hz; δ in ppm; P^a is *cis* and P^b is *trans* to R. [b] *cis* isomer percentage. [c] *trans* isomer percentage.

TABLE 3

NMR DATA FOR COMPLEXES $[Pt(OCHO)R(PPh_3)_2]$ [a]

cis-R	$\delta(P^a)$	$^1J(P^a-P^b)$	$\delta(P^b)$	$^1J(P^b-Pt)$	$^2J(P^a-P^b)$	$\delta(H)$	$^4J(H-P^a)$	$^4J(H-P^b)$
C_6Cl_5	−133.0	4098	−122.9	2114	18			
2,3,4,6-C_6HCl_4	−133.1	4121	−122.1	2075	18			
2,3,4,5-C_6HCl_4	−131.4	4182	−120.8	1934	16	8.1	13.0	1.0
2,5-$C_6H_3Cl_2$	−130.8	4249	−119.7	1859	16	7.9	11.5	1.0
C_6F_5	−132.2	3936	−120.4	2287	18	7.9	14.0	[b]
trans-R								
C_6Cl_5	−121.0	3043						
2,3,4,6-C_6HCl_4	−121.6	3049						
2,3,4,5-C_6HCl_4	−120.0	3082						
2,5-$C_6H_3Cl_2$	−118.7	3113						
C_6F_5	−120.4	2871						

[a] $^{31}P\{^1H\}$ NMR in $CHCl_3$, reference $P(OMe)_3$; ^1H NMR in $CDCl_3$, reference TMS; J in Hz; δ in ppm; P^a is *cis* and P^b is *trans* to R; δ(H) formate resonance. [b] Not observed.

correlation between the $^1J(P^a-Pt)$ values for *cis* compounds and the $^1J(P-Pt)$ values for *trans* compounds.

Experimental

Elemental analyses were carried out at the "Institut de Química Bio-Orgànica del Centre d'Investigacions i Desenvolupament del Consell Superior d'Investigacions Científiques de Barcelona".

The $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker FT-80-SY spectrometer and the ^1H NMR spectra on a Varian XL-200FT spectrometer. IR spectra were recorded on a Beckman Acculab 4 spectrometer.

Starting materials

The compounds *cis*-$[(PPh_3)_2RPtHgR]$, $[Pt(CF_3CO_2)R(PPh_3)_2]$ and *cis*- and *trans*-$[PtCl(C_6F_5)(PPh_3)_2]$ were prepared by published methods [4,6].

Preparation of $[PtIR(PPh_3)_2]$ ($R = C_6Cl_5$; 2,3,4,6-C_6HCl_4; 2,3,4,5-C_6HCl_4, 2,5-$C_6H_3Cl_2$)

An excess of KI was added to a solution of 1.0 mmol of $[Pt(CF_3CO_2)R(PPh_3)_2]$ in 30 ml of acetone, and the mixture was stirred for 4 h. The solution was then evaporated to dryness and the residue recrystallized from dichloromethane/methanol; yield 80%.

Preparation of trans-$[Pt(OCHO)R(PPh_3)_2]$ ($R = C_6Cl_5$; 2,3,4,6-C_6HCl_4; 2,3,4,5-C_6HCl_4; 2,5-$C_6H_3Cl_2$)

A solution of 1.2 mmol of $AgClO_4$ in 20 ml of methanol was added to a solution of 1.0 mmol of $[PtIR(PPh_3)_2]$ in 20 ml of $CHCl_3$. The mixture was stirred for 24 h, and the AgI was then filtered off and the solution evaporated to dryness, the residue was extracted with $CHCl_3$, and the extract was treated with a solution of 5.5 mmol of NaOCHO in 20 ml of methanol. The mixture was stirred for 6 h than evaporated to dryness, and the residue recrystallized from dichloromethane/methanol; yield 60–70%.

Preparation of cis- and trans-[Pt(OCHO)(C_6F_5)(PPh_3)$_2$]

These were prepared from *cis*- and *trans*-[PtCl(C_6F_5)(PPh_3)$_2$], respectively, by the method described above.

Preparation of cis-[Pt(OCHO)R(PPh_3)$_2$] (R = C_6Cl_5; 2,3,4,6-C_6HCl_4; 2,3,4,5-C_6HCl_4; 2,5-$C_6H_3Cl_2$)

These compounds were prepared by adding HCOOH (4 ml) to a solution of the appropriate [(PPh_3)$_2$RPtHgR] (1.0 mmol) in benzene (25 ml) which caused immediate separation of mercury. The solution was filtered then concentrated to dryness, and the residue washed with hexane then recrystallized from benzene/hexane; yield 70%.

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