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$Pt(C_6F_5)_2$ AND ITS ADDUCTS WITH KETONES, ARENES AND WATER

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Summary

A new series of ketone adducts, *trans*-$Pt(C_6F_5)_2L_x$ ($x = 1$, L = Me_2CO, MeEtCO, $(CH_2)_5CO$; or $x = 1.5$, L = $MeBu^iCO$, MePhCO) has been prepared from *trans*-$Pt(C_6F_5)_2(dioxan)_2$. The thermal decomposition of the ketone complexes leads to the formation of $Pt(C_6F_5)_2$; the order of reaction and activation energy for this decomposition have been determined. The new adducts *trans*-$Pt(C_6F_5)_2L$ (L = benzene, toluene and water) have been made from $Pt(C_6F_5)_2$. Infrared data for the new compounds are reported.

Introduction

Recently the compounds *trans*-$M(C_6F_5)_2(dioxan)_2$ (M = Pd, Pt) were shown to be suitable reagents for the preparation of solvated pentafluorophenyl complexes of palladium(II)- and platinum(II)$M(C_6F_5)_2(solvent)_x$, where solvent = dimethylformamide and dimethylsulfoxide [1]. On the other hand, Klabunde et al. [2] showed that in acetone the species $Pd(C_6F_5)Br$ behaves as a trimer containing coordinated acetone. These results prompted us to extend our investigation to $M(C_6F_5)_2$-ketone systems.

In this paper, the isolation and thermal study of compounds $Pt(C_6F_5)_2(ketone)_x$ are reported, where ketone = acetone (Me_2CO), 2-butanone (MeEtCO), 4-methylpentanone ($MeBu^iCO$), cyclohexanone [$(CH_2)_5CO$] and acetophenone (MePhCO). On heating, the ketone compounds yield the perfluoroaryl compound $Pt(C_6F_5)_2$. From this compound the adducts $Pt(C_6F_5)_2L$ (L = benzene, toluene and water) have been made.

Results and discussion

When *trans*-$Pt(C_6F_5)_2(dioxan)_2$ is dissolved in each of the above-mentioned ketones, it is possible to isolate white solids, which can be formulated as *trans*-$Pt(C_6F_5)_2(ketone)_x$ ($x = 1$ or 1.5). Apparently, the ketone ligand replaces dioxan

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according to eq. 1.

$$Pt(C_6F_5)_2(dioxan)_2 + x \text{ ketone} \rightarrow Pt(C_6F_5)_2(ketone)_x + 2 \text{ dioxan} \qquad (1)$$

Since it is known that ethers coordinated to the $M(C_6F_5)_2$ moiety can be oxidized to esters in the presence of traces of water [3], an alternative possibility was that of replacement of a dioxan-derived carbonyl ligand by the ketone. However, the ^1H NMR spectrum of *trans*-$Pt(C_6F_5)_2(dioxan)_2$ in acetone-d_6 solution showed a single resonance at δ3.58 ppm downfield from TMS, a result nearly identical with that obtained for free dioxan (3.56 ppm) indicating that acetone replaces dioxan.

Analytical, thermogravimetric and infrared data are compatible with the proposed formulation. IR spectra show the characteristic absorptions of the C_6F_5 group [4] at ca. 1630m, 1495vs, 1450vs, 1050s and 950 vs cm^{-1}. As in previous cases [1,5], the linearity of the C–M–C skeleton has been assumed on the basis of the presence of a single band at 770s cm^{-1}. The identity of the neutral ligands is also shown by the IR spectra. Table 2 lists the relevant IR bands of acetone in the platinum compound compared with the corresponding ones in free acetone, and the carbonyl stretching mode for every coordinated ketone is given in Table 1. Although there is a general concordance between these data and those observed for other ketone

TABLE 1

ANALYTICAL AND IR DATA FOR THE PLATINUM COMPOUNDS

Compound	Analyses (Found (calcd.) (%))			CO stretching mode (cm^{-1})
	C	H	Pt	
$Pt(C_6F_5)_2 \cdot Me_2CO$ (I)	31.2 (30.7)	1.2 (1.0)	33.0 (33.2)	1697s
$Pt(C_6F_5)_2 \cdot MeEtCO$ (II)	31.2 (31.9)	1.4 (1.3)	32.6 (32.5)	1705s
$Pt(C_6F_5)_2 \cdot (CH_2)_5CO$ (III)	34.9 (34.4)	1.6 (1.6)	31.0 (31.1)	1680s
$Pt(C_6F_5)_2 \cdot 1.5MeBu^iCO$ (IV)	36.8 (37.1)	2.6 (2.6)	28.4 (28.7)	1690, 1680s
$Pt(C_6F_5)_2 \cdot 1.5MePhCO$ (V)	40.1 (40.6)	1.6 (1.7)	27.8 (27.5)	1685, 1677s
$Pt(C_6F_5)_2$ [a] (VI)	27.4 (27.2)	–	37.0 (36.9)	
$Pt(C_6F_5)_2 \cdot C_6H_6$ (VII)	35.6 (35.6)	1.2 (1.0)	32.0 (32.1)	
$Pt(C_6F_5)_2 \cdot C_6H_5CH_3$ (VIII)	36.2 (36.7)	1.6 (1.3)	31.2 (31.4)	
$Pt(C_6F_5)_2 \cdot H_2O$ (IX)	27.9 (26.3)	0.3 (0.4)	35.8 (35.7)	

[a] Average values of samples obtained from the $MeBu^iCO$ and MePhCO compounds (see text).

TABLE 2

INFRARED BANDS OF ACETONE IN *trans*-$Pt(C_6F_5)_2(Me_2CO)$

trans-$Pt(C_6F_5)_2(Me_2CO)$	Liquid Me_2CO [6]	
1697vs	1718vs	CO stretching
1430sh	1425s	CH_3 def. *asym*
1365s	1365vs	CH_3 def. *sym*
1237s	1220s	CC str. *asym*
1095m	1091m	CH_3 rock
537m	527s	CO def.
400w	389m	CCC def.

complexes [6–8], the small shifts of the CO stretching frequencies suggest a rather weak ketone–platinum interaction.

The thermal study of the ketone complexes shows that they decompose in two stages, the first endothermic and the second exothermic in the corresponding DTA curves (Fig. 1). In every case, the first stage decomposition involves the loss of the ketone according to eq. 2.

$$Pt(C_6F_5)_2(\text{ketone})_x \xrightarrow{\Delta} Pt(C_6F_5)_2 + x \text{ ketone} \quad (2)$$

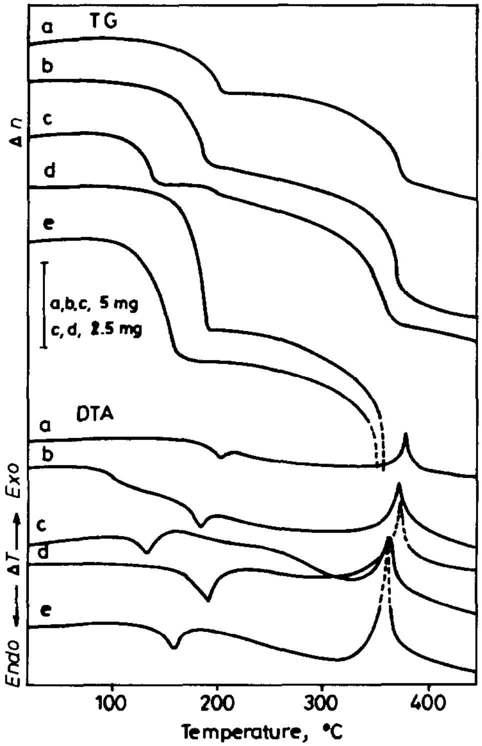

Fig. 1. TG and DTA curves (N_2) for the complexes $Pt(C_6F_5)_2(\text{Ketone})_x$: (a) $Pt(C_6F_5)_2 \cdot (CH_2)_5CO$, 17.6 mg; (b) $Pt(C_6F_5)_2 \cdot 1.5$ MePhCO, 21.4 mg; (c) $Pt(C_6F_5)_2 \cdot 1.5$ $MeBu^iCO$, 22.5 mg; (d) $Pt(C_6F_5)_2 \cdot$ MeEtCO, 35.8 mg; (e) $Pt(C_6F_5)_2 \cdot Me_2CO$, 21.4 mg.

The temperature ranges and weight losses for these thermal decompositions are given in Table 3. In some experiments the infrared spectrum of the residue from the $MeBu^{i}CO$ compound showed the presence of traces of ketone, which disappeared upon prolonged heating at 130°C under N_2. It should be noted, however, that the $MeBu^{i}CO$ compound is the most suitable precursor for the isolation of $Pt(C_6F_5)_2$ because its lower decomposition temperature provides the greatest interval for the existence of $Pt(C_6F_5)_2$. The residue, $Pt(C_6F_5)_2$, can be isolated but if the heating is continued the residue loses weight slowly and progressively, until at ca. 370°C the decomposition becomes explosive in all cases. The thermal behaviour of the $Pt(C_6F_5)_2$ varies slightly with the identity of the initial coordinated ketone.

The apparent orders and activation energies of the corresponding decomposition reactions (eq. 2) have been evaluated for all the complexes. For this purpose, the Coats and Redfern integral method was used. For a reaction in which the order is unknown Coats and Redfern [9] derived the following expression:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT}$$

where α is the fraction of sample decomposed at time t and a is the heating rate. A plot of either

$$\log\left[\frac{1-(1-\alpha)}{T^2(1-n)}\right] \quad \text{versus } 1/T\text{, or where } n = 1,$$

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] \quad \text{versus } 1/T$$

should result in a straight line of slope $-E/2.3R$ for the correct value of n (Fig. 2). The experimental activation energies lie in the 60–100 kJ range (Table 3), the lower values being for those cases that give zero-order reactions. Even taking into account the difficulty in assigning physical meaning to the reaction order for decompositions

TABLE 3

WEIGHT LOSS, TEMPERATURE RANGES AND KINETIC PARAMETERS OF THE DECOMPOSITION REACTIONS $Pt(C_6F_5)_2(ketone)_x \rightarrow Pt(C_6F_5)_2 + x$ ketone

Compound	Weight loss (Found (calcd.) (%))	Temperature ranges for weight loss (°C)	DTA peaks (°C)	Temperature of $Pt(C_6F_5)_2$ decomposition (°C)	Activation energies (kJ mol^{-1})	Orders of reaction
$Pt(C_6F_5)_2 \cdot Me_2CO$	10.1 (9.4)	101–165	160	365	93.49	1/2
$Pt(C_6F_5)_2 \cdot MeEtCO$	12.3 (12.0)	122–194	190	370	93.00	0
$Pt(C_6F_5)_2 \cdot (CH_2)_5CO$	15.2 (15.6)	155–200	200	338–380	102.44	1/2
$Pt(C_6F_5)_2 \cdot 1.5MeBu^{i}CO$	15.7 (15.9)	80–130	125	300–370	63.54	0
$Pt(C_6F_5)_2 \cdot 1.5MePhCO$	24.3 (25.3)	105–195	190	352–383	72.18	0

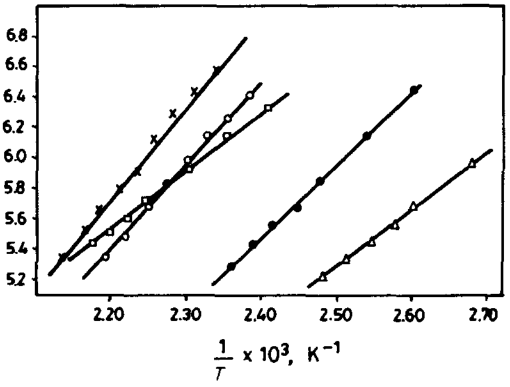

Fig. 2. Coats-Redfern plots for thermal decomposition of $Pt(C_6F_5)_2(Ketone)_x$. Ketone: ●, acetone; ○, 2-butanone; x, cyclohexanone; △, 4-methylpentanone; □, acetophenone. (For *Y* value see text).

of solids, the reaction zero-order may be associated with a chemical desorption process [10].

For the acetone compound, the Šatava method [11] was also used. In this method, the *TG* trace corresponding to a heterogeneous process which proceeds with a constant increase of the temperature is described by the equation:

$$\log \frac{ZE}{qR} = \log g(\alpha) - \log p(x) = B$$

where α is the fraction decomposed, the function $g(\alpha)$ is given by the rate controlling process and the function $p(x)$ depends on the activation energy. Both log $g(\alpha)$ and $\log p(x)$ are approximately linear functions of $1/T$. The method has been shown to be particularly advantageous in deriving kinetic parameters which can be reconciled with results obtained under isothermal methods [12]. Tabulated values of log $g(\alpha)$ as a function of α [13] and $-\log\ p(x)$ of E were used [14]. The best correspondence between log $g(\alpha)$ and $-\log p(x)$ over the full range of values of α was obtained for plots derived from the function R_2, with $E = 22 \pm 0.5$ (Fig. 3), in very good agreement with the result obtained by the Coats and Redfern method. Function R_2 corresponds to $g(\alpha) = 1 - (1 + \alpha)^{1/2} = kt$, which describes a phase boundary reaction with cylindrical symmetry.

Although experimental methods such as the "metal atom technique" [15] or the highly reactive metal slurries [16] have been quite useful for the preparation of some coordinatively unsaturated species of palladium and platinum containing the C_6F_5 radical, as far as we are aware no compound $M(C_6F_5)_2$ has been reported for M = Pd, Pt. By the preparative method described herein, $Pt(C_6F_5)_2$ can be easily prepared (as can $Pd(C_6F_5)_2$, as preliminary investigations have shown). Thus, from the results in ref. 1 and those in this work the overall process is

$$PtCl_4{}^{2-} \xrightarrow[\text{in THF/dioxan}]{C_6F_5MgBr} Pt(C_6F_5)_2(\text{dioxan})_2 \xrightarrow{\text{in ketone}}$$

$$Pt(C_6F_5)_2(\text{ketone})_x \xrightarrow{\Delta} Pt(C_6F_5)_2$$

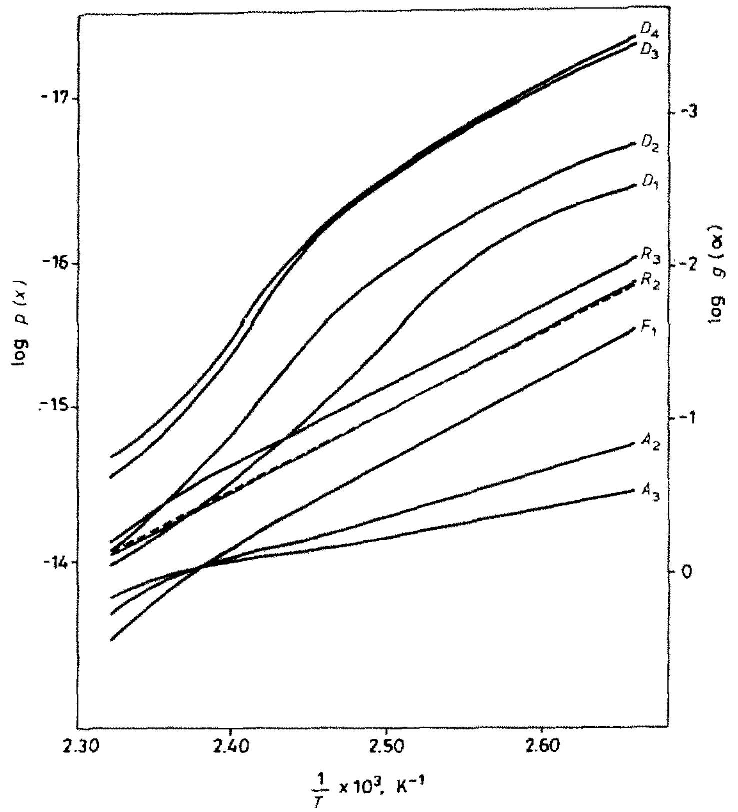

Fig. 3. Dependence of log $g(\alpha)$ on $\frac{1}{T}$ for nine functions $g(\alpha)$, for thermal decomposition of $Pt(C_6F_5)_2 \cdot Me_2CO$. Dashed line corresponds to the plot of log $p(x)$ versus $\frac{1}{T}$ for $E = 22$ kcal (91.96 kJ).

The compound $Pt(C_6F_5)_2$ is a white solid, the amorphous nature of which prevented us of carrying out an X-ray study. It is stable in dry air and very soluble in weak O-donor solvents such as ketones, tetrahydrofuran or methanol, and only slightly soluble in benzene. The IR data (1636s, 1608s, 1525sh, 1500vs, 1450vs(br), 1365m, 1341m, 1319m, 1278s, 1095m, 1083m, 1048vs, 1037sh, 943vs, 940vs, 771vs and 445w cm^{-1}) strongly suggest a polymeric structure, $(MR_2)_n$, in which the π system of the perfluorophenyl ring is involved in the bonding. Thus the absorptions arising from ring and CF vibrational modes are clearly split or appear with shoulders. The interaction must be very weak since the compound $Pt(C_6F_5)_2$ readily takes up weak donor solvents such as acetone, benzene or toluene. Thus, when it is placed in a desiccator containing acetone its conversion into $Pt(C_6F_5)_2(Me_2CO)_x$ is almost immediate, and the IR bands due to CF vibrations are now fully resolved: two doublets at 1050, 1037 and 950, 942 cm^{-1}, respectively. This is a common feature of the IR spectra of all the adducts *trans*-$Pt(C_6F_5)_2(\text{ketone})_x$ ($x = 1$ or 1.5) which was also observed for the dimethylformamide and dimethylsulfoxide adducts [1]. Removal of acetone leads again to the formation of $Pt(C_6F_5)_2$. This behaviour closely resembles that observed for the C_6F_5PdBr/acetone system [2], for which it was assumed that when the acetone is removed the open coordination sites on C_6F_5PdBr are filled in the solid state by bridging through Br and/or the π bonds of C_6F_5. However, the ^{19}F NMR spectrum of an acetone-d_6 solution of $Pt(C_6F_5)_2$ appears to be compatible with the presence (in solution) of monomer units, $Pt(C_6F_5)_2(Me_2CO\text{-}d_6)_2$, since the spectrum exhibits the expected three resonances at 118.98 (*o*-F), $\simeq 169$ (*m*-F) and $\simeq 170$ (*p*-F) ppm upfield from CCl_3F (chemical shifts are shown relative to $CFCl_3$, 163.00 ppm being added to the chemical shifts relative to C_6F_6).

On treating $Pt(C_6F_5)_2$ with PPh_3 in benzene, the phosphine ligand does not go into the coordination sphere of platinum, but instead the benzene adduct, *trans*-$Pt(C_6F_5)_2 \cdot C_6H_6$ is isolated. The infrared spectrum of this compound shows the characteristic bands of benzene at ca. 3090w, 3080w, 3040w, 1605 (partially overlapped), 1480s and a strong doublet at 695 and 685 cm^{-1} for the C–H out-of-plane bending mode. The compound decomposes at 87°C to yield $Pt(C_6F_5)_2$. Similar results are obtained in toluene, where *trans*-$Pt(C_6F_5)_2 \cdot C_6H_5CH_3$ is isolated. This decomposes at 125°C and shows bands at 740 and 700 cm^{-1} for the C–H out-of-plane bending mode. However, when the experiment is carried out in mesitylene unchanged $Pt(C_6F_5)_2$ is recovered.

From solutions of $Pt(C_6F_5)_2$ in methanol, *trans*-$Pt(C_6F_5)_2 \cdot H_2O$ is isolated, in spite of careful drying of the methanol. A similar result has been observed for palladium/methanol systems [17]. The IR spectrum of the aqua complex shows two strong absorptions at 3660 and 3600 cm^{-1} for the *asym* and *sym* OH stretching modes (at 3756 and 3657 cm^{-1} in free H_2O [18]) and a strong band at 1630 cm^{-1} for the HOH bending. The compound is stable up to 195°C, but unlike the ketone adducts it decomposes directly to metallic platinum.

The fact that ketone adducts afford the $M(C_6F_5)_2$ species may be attributed to the lack of β-hydrogen atoms in the $R_2C{=}O \rightarrow M$ fragment. In contrast, the dioxan and tetrahydrofuran adducts decompose to metal upon thermal treatment [19] or undergo nucleophilic attack at the β-carbon [3]. Finally, the rather high thermal stability of some of these compounds should be pointed out; for example, the water, dioxan and acetone adducts are stable up to 195, 140, and 101°C, respectively, in spite of being soft metal-hard ligand systems.

Experimental

trans-$Pt(C_6F_5)_2(dioxan)_2$ was prepared as described in ref. 1. All the solvents were dried before use.

Infrared spectra were recorded as KBr pellets or Nujol mulls on a Perkin–Elmer 457 or Nicolet MX-1 spectrophotometer. Thermal decomposition studies were carried out under nitrogen on a Netzsch STA-429 thermobalance.

C, H analyses were performed with a Perkin–Elmer 240C microanalyzer. Platinum was determined by heating the samples at ca. 550°C, then weighing the residue as metallic platinum [19].

^1H and ^{19}F NMR spectra were recorded on a Varian FT-80A spectrometer.

trans-$Pt(C_6F_5)_2(ketone)_x$ (*x* = 1 or 1.5; see Table 1)

A volume of the respective ketones was added to 50 mg (0.071 mmol) of *trans*-$Pt(C_6F_5)_2(dioxan)_2$. The solution was stirred at room temperature, then the

TABLE 4

EXPERIMENTAL CONDITIONS FOR THE PREPARATION OF *trans*-$\mathrm{Pt(C_6F_5)_2(ketone)}_x$

Ketone	Volume of ketone (ml)	Reaction time (h)	Yield (%)
$\mathrm{Me_2CO}$	10	2	73
MeEtCO	3	2	71
$\mathrm{(CH_2)_5CO}$	2	2	68
$\mathrm{MeBu^iCO}$	3	1/2	70
MePhCO	1.5	2	69

solvent was reduced to a small volume under vacuum. Addition of hexane precipitated the corresponding organocomplexes as white solids, which were filtered off, washed with hexane, and dried in the air. Table 4 lists the reaction conditions.

trans-$Pt(C_6F_5)_2 \cdot H_2O$

A methanol solution (3 ml) of $\mathrm{Pt(C_6F_5)_2}$ (50 mg; 0.095 mmol) was stirred for 0.5 h at room temperature, then concentrated under vacuum to ca. 1 ml. Addition of hexane precipitated the aqua complex as a white solid which was filtered off and washed with hexane, 65% yield.

trans-$Pt(C_6F_5)_2 \cdot C_6H_6$

A suspension of $\mathrm{Pt(C_6F_5)_2}$ (50 mg; 0.095 mmol) in benzene (3 ml) was refluxed for 1.5 h, then cooled to room temperature. The white solid was filtered off and washed with hexane, 60% yield.

trans-$Pt(C_6F_5)_2 \cdot C_6H_5CH_3$

A reaction time of 2 h at 80°C was used, and the work up was similar to that for the benzene complex, 59% yield.

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