

THERMAL BEHAVIOUR OF SOME DIOXANE ADDUCTS OF $M(\text{C}_6\text{F}_5)_2$ ($M = \text{Pd}, \text{Pt}$)

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The thermal treatment of the pentafluorophenyl derivatives $M(\text{C}_6\text{F}_5)_2\text{Dx}_n$ [$M = \text{Pd}$ ($n = 2, 3$) or Pt ($n = 2$); $\text{Dx} = \text{dioxane}$] leads to the formation of the new dioxane adducts $M(\text{C}_6\text{F}_5)_2\text{Dx}$ ($M = \text{Pd}, \text{Pt}$) and $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$. Calculations of the order of reaction and the activation energy of some of the decomposition reactions are described. The values were determined by the Coats–Redfern and Freeman–Carroll methods. Structural data on the isolated intermediates were obtained by infrared spectroscopy and magnetic susceptibility measurements.

In a previous paper [1] we described the preparation of tetrahydrofuran-dioxane solutions apparently containing $\text{Pd}(\text{C}_6\text{F}_5)_2$. From these solutions, it was possible to isolate the dioxan adducts $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_n$ ($n = 2, 3$).

Since the same method had been already applied to nickel [2], we extended our investigation to platinum, which we have observed also forms the adduct $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_2$. Moreover, the thermal treatment of the palladium and platinum compounds herein described leads to the formation of new dioxane adducts.

Experimental

Methods

Magnetic susceptibility was determined by the Gouy method at room temperature. IR spectra were recorded in the range $4000-250\text{ cm}^{-1}$ on a Perkin-Elmer 457 spectrophotometer, from Nujol mulls and KBr pellets. Thermal decomposition studies (TG and DTA) were carried out in air or nitrogen on a Netzsch STA-429 thermobalance, working at the following parameters: chart speed, 120 mm/h; flow velocity of gas, 45 ml/min; heating rate, 5 deg/min. $\alpha\text{-Al}_2\text{O}_3$ was used as reference material. Samples and reference material were kept in platinum crucibles.

Microanalyses

C, H analyses were performed with a Perkin-Elmer 240 microanalyzer. Palladium was determined as dimethylglyoximate [3]. Platinum was controlled by heating the samples in air at *ca.* 550° and then weighing the residue as metallic platinum.

Preparation of the complexes

The compounds $\text{trans-Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_n$ ($n = 2, 3$) were prepared as described in ref. [1] and $\text{trans-Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_2$ according to [4].

$\text{trans-Pd}(\text{C}_6\text{F}_5)_2\text{Dx}$, $\text{trans-Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$ and $\text{trans-Pt}(\text{C}_6\text{F}_5)_2\text{Dx}$ were isolated as described below. Their analytical data are collected in Table 1.

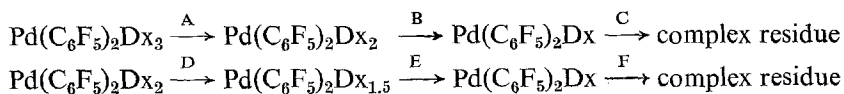
Table 1
Analytical data for the palladium and platinum compounds

Complex	Analyses found (calc.), %			
	C	H	Pd	Pt
$\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}$	36.6 (36.3)	1.2 (1.5)	19.7 (20.1)	—
$\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$	32.53 (32.67)	1.63 (1.81)	—	29.02 (29.51)
$\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}$	31.08 (31.11)	0.97 (1.30)	—	31.43 (31.62)

Results and discussion

The thermal decomposition behaviours of $\text{trans-Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_n$ ($n = 2, 3$) are illustrated in Table 2 and Fig. 1 and may be represented as follows:

in air or nitrogen



Processes *A* and *B* are clearly endothermic in both air and nitrogen, while *D* and *E* are only moderately endothermic. Nevertheless, *C* and *F* are both exothermic, though they are more exothermic in air than in nitrogen, undoubtedly due to the combustion of the decomposition products. On the other hand, it must be noted that the starting compound $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_2$ differs appreciably from the intermediate obtained from $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_3$ (stage *A*) in thermal behaviour, in spite of their same stoichiometries. The former loses one dioxane molecule through two well-discernible stages (*D* and *E*) to give $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}$, while the latter comes directly to the same product, $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}$. The last compound is stable up to 186° and has been characterized as $\text{trans-Pd}(\text{C}_6\text{F}_5)_2(\mu\text{-Dx})$ (see below).

The thermal behaviour of the platinum compound, $\text{trans-Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_2$, depends on the atmosphere used. The results are also shown in Table 2 and Fig. 1. The following stages can be observed:

Table 2
 Temperature ranges and kinetic parameters of some decomposition reactions of the palladium and platinum compounds

Stage*	Decomposition reactions	Temperature ranges, °C		DTA peaks, °C	Activation energies, kJ mole ⁻¹		Orders of reaction	
		TG	DTA		C-R	F-C	C-R	F-C
(A)	$\text{Pd}(\text{C}_6\text{F}_5)_2\text{DX}_3 \xrightarrow{\text{air}} \text{Pd}(\text{C}_6\text{F}_5)_2\text{DX}_2 + \text{DX}$	55-112	43-120	99	76.9	86.9	1	1
(B)	$\text{Pd}(\text{C}_6\text{F}_5)_2\text{DX}_2 \xrightarrow{\text{air}} \text{Pd}(\text{C}_6\text{F}_5)_2\text{DX} + \text{DX}$	112-173	120-186	145	135.4	129.6	1	1
(D)	$\text{Pd}(\text{C}_6\text{F}_5)_2\text{DX}_2 \xrightarrow{\text{air}} \text{Pd}(\text{C}_6\text{F}_5)_2\text{DX}_{1.5} + 0.5 \text{DX}$	50-108	64-110	103	96.1	-	2/3	-
(E)	$\text{Pd}(\text{C}_6\text{F}_5)_2\text{DX}_{1.5} \xrightarrow{\text{air}} \text{Pd}(\text{C}_6\text{F}_5)_2\text{DX} + 0.5 \text{DX}$	108-146	110-152	138	141.3	-	1	-
(G)	$\text{Pt}(\text{C}_6\text{F}_5)_2\text{DX}_2 \xrightarrow{\text{N}_2} \text{Pt}(\text{C}_6\text{F}_5)_2\text{DX}_{1.5} + 0.5 \text{DX}$	120-170	130-178	165	98.2	-	0	-
(H)	$\text{Pt}(\text{C}_6\text{F}_5)_2\text{DX}_{1.5} \xrightarrow{\text{N}_2} \text{Pt}(\text{C}_6\text{F}_5)_2\text{DX} + 0.5 \text{DX}$	200-258	205-265	252	116.2	-	1/2	-
(J)	$\text{Pt}(\text{C}_6\text{F}_5)_2\text{DX}_2 \xrightarrow{\text{air}} \text{Pt}(\text{C}_6\text{F}_5)_2\text{DX}_{1.5} + 0.5 \text{DX}$	140-170	138-178	166	188.9	-	1	-

* See text.

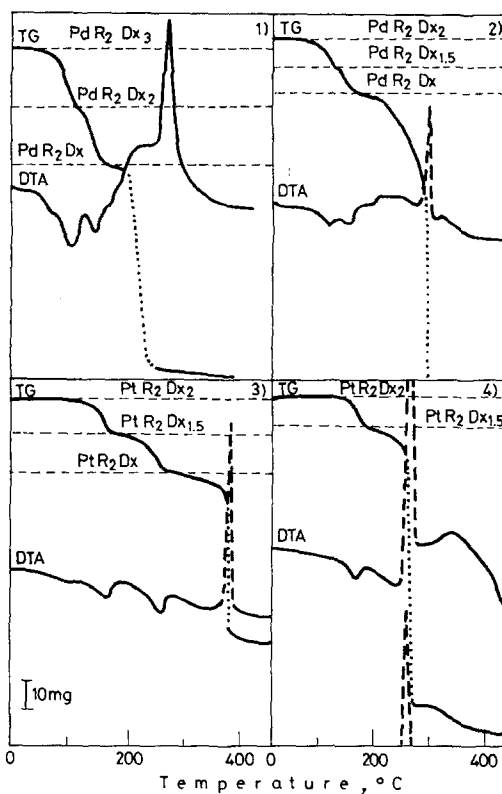
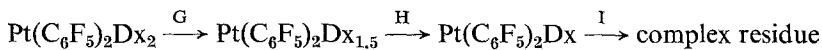
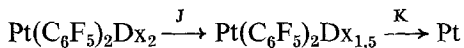


Fig. 1. TG and DTA curves of the complexes $M(\text{C}_6\text{F}_5)_2\text{Dx}_n$. Sample weight: (1) $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_3$ (air), 112 mg; (2) $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_2$ (air), 97 mg; (3) $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_2$ (nitrogen), 50 mg; (4) $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_2$ (air), 55 mg

in nitrogen



in air



Processes *G*, *H* and *J* are moderately endothermic, while *I* and *K* are exothermic, in both air and nitrogen. It is noteworthy that the species $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}$ is formed only in nitrogen, being stable in the range 258–380°. The intermediate $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$ is isolable in both nitrogen and air, but its decomposition in air leads directly to metallic platinum. This result has allowed us to control easily the platinum in the samples. The isolated compounds have been characterized as *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$ and *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-Dx})$, respectively (see below).

Since clear decomposition reactions have been observed of the type $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$, the shapes of the TG curves are functions of the reaction kinetics and can therefore be used to evaluate the kinetic parameters of the reactions. For this purpose, Coats and Redfern's integral method [5] was used. The following apparent reaction orders were tried: $n = 0, 1/2, 2/3$ and 1. The apparent reaction orders ensuring the best linearity of the Coats – Redfern plots are given in Table 2, which

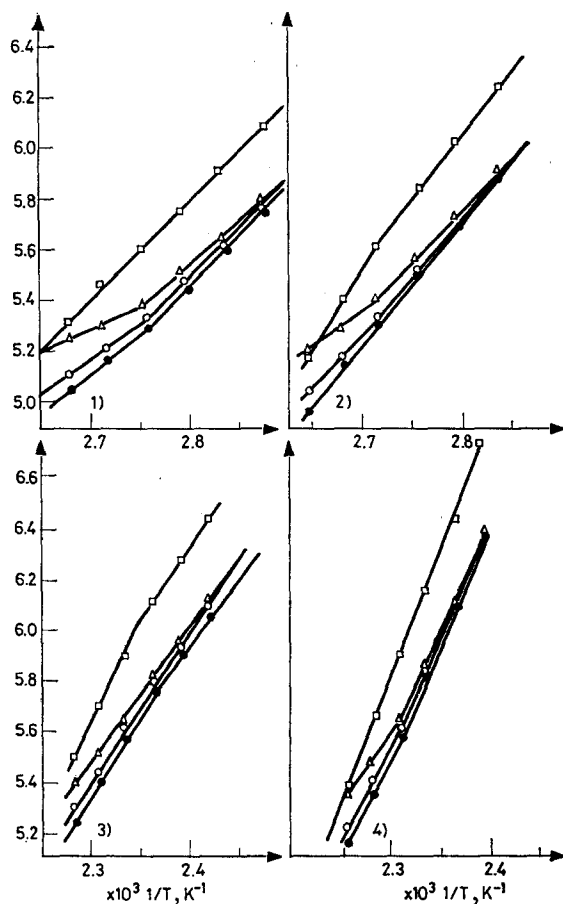


Fig. 2. Coats–Redfern plots of thermal decomposition reactions of some compounds $M(C_6F_5)_2Dx_n$ ($M = Pd, Pt$). 1. Process A; 2. process D; 3. process G; 4. process J (see text)

$$y = -\log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] \quad \text{for } n = 0, 1/2 \text{ and } 2/3;$$

$$\text{and } -\log \left[\frac{-\log(1 - \alpha)}{T^2} \right] \quad \text{for } n = 1.$$

$$(\Delta, n = 0; \circ, n = 1/2; \bullet, n = 2/3; \square, n = 1)$$

also contains the apparent activation energy values derived from the slopes of the straight lines obtained. Figure 2 contains some of the plots obtained by the Coats and Redfern method. One can see from Fig. 3 and Table 2 that if a differential method (Freeman and Carroll [6]) is used (processes *A* and *B*), we obtain the same values of *n* and values of the apparent activation energy which are in good agreement with the above results. It is interesting to point out the analogy between the behaviours of $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_2$ (in nitrogen) and of $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_2$ (in both air and nitrogen) and their respective activation energies, which are sensibly the same in processes *D* and *G* and slightly higher for palladium in stage $M(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5} \rightarrow M(\text{C}_6\text{F}_5)_2\text{Dx}$. This fact would be in agreement with the greater strength of the palladium-oxygen bonds.

The three isolated compounds are diamagnetic in the solid state at room temperature, so that they are square planar species.

The infrared spectra of the compounds show the characteristic absorptions of the C_6F_5 group [7] at *ca.* 1630 (m), 1500 (vs), 1050 (vs), 950 (vs) and 760 (s-vs) cm^{-1} . Moreover, the presence of a single band observed for the X-sensitive mode [7] of mainly $\nu(\text{M}-\text{C})$ character in the range 800–750 cm^{-1} can be correlated [3, 8, 9] with the symmetry of the C-M-C skeleton. The spectra of compounds $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}$, $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$ and $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}$ exhibit a single band at 760, 765 and 765 cm^{-1} , respectively, as expected for the $\nu(\text{M}-\text{C})$ stretching mode of *trans* isomers (D_{2h}): B_{2u} .

The characteristic absorption of the dioxan ligand [10] are also observed in the spectra of the palladium and platinum compounds. They are collected in Table 3, along with the assignment for free dioxane. The asymmetric C–O–C stretching vibration, present in the free ligand at 1125 cm^{-1} , has been used for

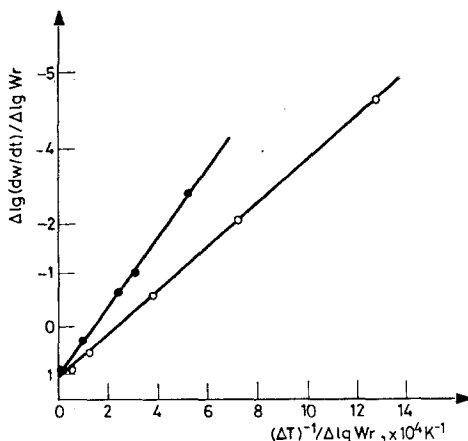


Fig. 3. Freeman-Carroll plots of thermal decomposition of $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_3$ in air

- $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_3 \rightarrow \text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_2 + \text{Dx}$
- $\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}_2 \rightarrow \text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx} + \text{Dx}$

structural elucidation [1, 11]. In the complexes *trans*- $M(\text{C}_6\text{F}_5)_2\text{Dx}$ ($M = \text{Pd}, \text{Pt}$) it appears at 1110 cm^{-1} , which indicates that dioxane acts here as a bidentate ligand: *trans*- $M(\text{C}_6\text{F}_5)_2(\mu\text{-Dx})$. However, in the complex *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$ the above band is split: two peaks are shown, at 1130 and 1110 cm^{-1} (intensity ratio $\approx 1/2$, respectively), which suggests a structure of the type $(\text{C}_6\text{F}_5)_2\text{DxPt}(\mu\text{-Dx})\text{PtDx}(\text{C}_6\text{F}_5)_2$.

Table 3
Dioxan frequencies (cm^{-1}) in compounds $M(\text{C}_6\text{F}_5)_2\text{Dx}_n$

Free dioxane [10]	$\text{Pd}(\text{C}_6\text{F}_5)_2\text{Dx}$	$\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}$	$\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$
1251 ν_{15} (B_u) (wagging)	1260 (s)	1255 (s)	1260 (s) 1250 (m)
1125 ν_{17} (B_u) (ring stretching)	1110 (vs)	1110 (vs)	1130 (m) 1110 (vs)
887 ν_{16} (B_u) (rocking)	890 (s)	887 (s)	885 (s)
874 ν_{27} (A_g) (ring stretching)	870 (vs)	870 (vs)	870 (vs)
610 ν_{18} (ring bending)	610 (m)	610 (m)	610 (m)

vs = very strong; s = strong; m = medium.

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ZUSAMMENFASSUNG — Die thermische Behandlung der Pentafluorphenylderivate $M(\text{C}_6\text{F}_5)_2\text{Dx}_n$ [$M = \text{Pd}$ ($n = 2, 3$) oder Pt ($n = 2$); $\text{Dx} = \text{Dioxan}$] führt zu der Bildung der neuen Dioxanaddukte $M(\text{C}_6\text{F}_5)_2\text{Dx}$ ($M = \text{Pd}, \text{Pt}$) und $\text{Pt}(\text{C}_6\text{F}_5)_2\text{Dx}_{1.5}$. Die Berechnungen der Reaktionsordnung und der Aktivierungsenergie einiger Zersetzungsreaktionen werden beschrieben. Die Werte wurden durch die Methoden von Coats-Redfern und Freeman—Carroll bestimmt. Die Strukturangaben der isolierten Zwischenprodukte wurden durch Infrarotspektroskopie und Messung der magnetischen Suszeptibilität erhalten.

Резюме — Термическая обработка пентафторфенилпроизводных $M(C_6F_5)_2Dx$, где $M = Pd$ и $n = 2, 3$ или Pt и $n = 2$, и Dx -диоксан, приводит к образованию новых аддуктов с диоксаном $M(C_6F_5)_2Dx$ ($M = Pd, Pt$) и $Pt(C_6F_5)_2Dx_{1,5}$. Вычислены порядок реакции и энергии активации некоторых реакций разложения, значения которых определялись по методу Коутса—Рэдферна и Фримен—Кэррола. С помощью ИК спектроскопии и измерений магнитной восприимчивости получены структурные данные выделенных промежуточных продуктов реакции.