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PENTAFLUOROPHENYL DERIVATIVES OF PALLADIUM(II) AND PLATINUM(II) WITH O-DONOR LIGANDS

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Summary

The preparation of *trans*-$Pt(C_6F_5)_2(dioxan)_2$ by the method previously used for the palladium analogue [1] is described. The compounds, *trans*-$M(C_6F_5)_2(dioxan)_2$ (M = Pd, Pt) have both been employed as starting materials for the preparation of related complexes with pyridine *N*-oxide (pyO), dimethylformamide (DMF), and dimethylsulfoxide (DMSO) ligands.

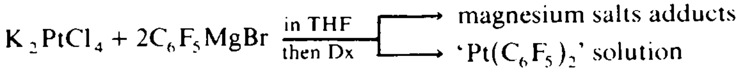
Introduction

Labile transition-metal complexes containing weak donor ligands are being increasingly studied because they are highly reactive and potential catalysts [2].

Solvated pentafluorophenyl complexes of nickel(II) and palladium(II) have been prepared from coordinatively unsaturated species obtained using the 'metal atom-technique' [3,4]. However, THF/dioxan solutions apparently containing $M(C_6F_5)_2$ (M = Co [5], Ni [6] and Pd [1]), prepared via the Grignard reaction, have been employed for the preparation of complexes of the type $M(C_6F_5)_2L_2$, where L can be a weak donor ligand. This paper deals with the isolation of *trans*-$Pt(C_6F_5)_2Dx_2$ (Dx = dioxane) by the THF-Dx method and the use of the solvated complexes *trans*-$M(C_6F_5)_2Dx_2$ (M = Pd, Pt) for the preparation of related complexes containing the ligands pyO, DMF, and DMSO.

Results and discussion

The arylation of K_2PtCl_4 with C_6F_5MgBr in THF and further addition of dioxane to precipitate the magnesium salts as dioxan adducts gives, THF-Dx solutions mainly containing the solvated species $Pt(C_6F_5)_2$:



$$K_2PtCl_4 + 2C_6F_5MgBr \xrightarrow[\text{then Dx}]{\text{in THF}} \begin{cases} \longrightarrow \text{magnesium salts adducts} \\ \longrightarrow \text{'}Pt(C_6F_5)_2\text{' solution} \end{cases}$$

These solutions can be used for the preparation of complexes of the type $Pt(C_6F_5)_2L_2$

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[7], and we have now found that the parent compound *trans*-Pt(C_6F_5)$_2$Dx$_2$ can also be isolated. However, the arylation of $PtCl_4^{2-}$ differs appreciably from that of $PdCl_4^{2-}$ [1] in two respects: (a) the yield of the platinum is lower than of the palladium complex; (b) only the *trans* isomer is obtained for platinum, no matter what C_6F_5/Pt ratio is used (though the best yield is obtained when a 5 : 1 molar ratio is used). However, in the preparation of the Dx compound the *cis* isomer was detected in the THF-Dx solution (by a double band at ca. 800 cm^{-1}; see below).

The compounds *trans*-M(C_6F_5)$_2$Dx$_2$ (M = Pd, Pt) undergo substitution reactions which lead to the formation and isolation of M(C_6F_5)$_2$L$_n$, where L is pyO, DMF or DMSO. Analytical data and melting points of the palladium and platinum compounds are listed in Table 1.

The compounds are white solids, except that for M = Pd and L = pyO, which is pale yellow. They are diamagnetic in the solid and non-electrolytes in ca. 5 × 10^{-4} *M* acetone solutions (Λ_M < 1.6 cm^2 ohm^{-1} mol^{-1}). A study of the thermal behaviour of the Dx compounds [8] has shown that *trans*-Pt(C_6F_5)$_2$Dx$_2$ is more stable in air (up to 140°C) than its Pd analogue (50°C).

The IR spectra show the characteristic bands of the C_6F_5 group [9] at ca. 1630m, 1495vs, 1450vs, 1050s and 950vs cm^{-1}. As in previous cases [1], the number of infrared bands observed for the X-sensitive mode can be correlated with the symmetry of the C–M–C skeleton on the basis that in complexes containing M–C_6F_5 bonds this mode has mainly ν(MC) character. Accordingly, we assign the *cis* configuration to Pd(C_6F_5)$_2$(Opy)$_2$ since its spectrum shows a double band in the range 800–750 cm^{-1} and the *trans* configuration to all other compounds because of a single band in the same spectral region (Table 1).

The presence of the various neutral ligands in the Pd and Pt compounds is

TABLE 1

ANALYTICAL DATA, MELTING POINTS AND SOME IR DATA FOR THE COMPLEXES

Compound	Analysis (Found (calcd. (%))				M.p. (°C)	IR data C_6F_5 (X-sensitive)
	C	H	N	metal		
trans-Pt(C_6F_5)$_2$Dx$_2$ (I)	34.4	2.1		28.3	140 (d)	770vs
	(34.0)	(2.3)		(27.7)		
cis-Pd(C_6F_5)$_2$(Opy)$_2$ (II)	41.2	1.6	4.0	16.2	127 (d)	800s, 785s
	(41.9)	(1.6)	(4.4)	(16.9)		
trans-Pt(C_6F_5)$_2$(Opy)$_2$ (III)	36.5	1.6	3.4	26.3	123–125 (d)	770s
	(36.7)	(1.4)	(3.9	(26.8)		
trans-Pd(C_6F_5)$_2$(DMF)$_x$ ^{a} (IVa)	36.0	1.8	3.6	19.1	^{b}	760vs
(IVb)	34.5	1.1	2.1	20.9		760s
trans-Pd(C_6F_5)$_2$(DMSO)$_x$ ^{a} (V)	32.2	1.7		18.8	^{b}	760s
(Vb)	32.6	0.7		22.0		760s
trans-Pt-(C_6F_5)$_2$(DMF)$_x$ ^{a} (VIa)	30.8	1.6	3.1	30.1	^{b}	770s
(VIb)	29.2	1.0	1.9	32.9		770s
trans-Pt(C_6F_5)$_2$(DMSO)$_x$ ^{a} (VIIa)	28.0	1.3	–	29.9	^{b}	770s
(VIIb)	27.3	0.6		34.0		770s

^{a} Approximate values for *x* can be derived from these analysis (Table 2). ^{b} See Table 2.

demonstrated by their IR spectra which show the more characteristic absorptions of the free ligands. In *trans*-$Pt(C_6F_5)_2Dx_2$ the asymmetric C–O–C stretching vibration, present in the free ligand at 1125 cm^{-1}, appears at 1110 cm^{-1} as a single band, indicating that both oxygen atoms are in the same structural environment [10]. In *cis*-$Pd(C_6F_5)_2(Opy)_2$ the NO stretching band appears at 1200 cm^{-1} and in *trans*-$Pt(C_6F_5)_2(Opy)_2$ it is found at 1220 cm^{-1} (1265 cm^{-1} in the free ligand [11]). The larger frequency shift in the Pd compound can be attributed to a stronger M–O interaction, since in this case the electronegative C_6F_5 group is *trans* to pyO.

With the solvents DMF and DMSO a number of solvated complexes $M(C_6F_5)_2(solvent)_x$ (M = Pd, Pt) can be obtained. Thus, when *trans*-$Pd(C_6F_5)_2Dx_2$ is dissolved in either DMF or DMSO, from the corresponding solution white solids containing a DMF/Pd (or DMSO/Pd) molar ratio of ca. 1.5 are isolated (IVa and Va in Tables 1 and 2). However, thermal analysis shows that at ca. 60°C the DMF compound is converted into an isolable product (IVb) with a DMF/Pd ratio of ca. 0.8, and the DMSO compound into a material (at ca. 70°C) with a DMSO/Pd ratio of ca. 0.5 (Vb).

Similar results are obtained for the platinum complexes with the solvents DMF and DMSO, but the analytical data of the products initially isolated from the respective DMF and DMSO solutions point to a formula containing two molecules of the respective solvent. Nevertheless, on crystallizing from diethyl ether/hexane (DMF compound) or THF/hexane (DMSO compound) the new analytical data fit quite well a solvent/Pt molar ratio of 1.5 (VIa, VIIa).

This kind of behaviour was also observed for the dioxane compounds, *trans*-$M(C_6F_5)_2Dx_2$ (M = Pd, Pt), which lost one dioxane molecule on heating [8]. Complete removal of the solvents DMF, DMSO and Dx was not possible, though the preceding results clearly show that the $M(C_6F_5)_2$ moiety can be partially solvated, behaviour similar to that noted in the toluene/CF_3PdI system [4].

The IR spectra of the DMF compounds show the characteristic absorptions of DMF, the carbonyl stretching vibration being observed at 1655 cm^{-1}, a value somewhat higher than those reported for similar compounds [12]. The presence of

TABLE 2

THERMOGRAVIMETRIC DATA FOR THE DMF AND DMSO COMPOUNDS

Transformation [a]	Temperature interval for weight change T (°C)	Weight loss (Found (calcd.) (%))	Temperature for final decomposition (°C)
IVa (1.5) → IVb (0.8)	60–100	9.3 (9.3)	170
Va (1.5) → Vb (0.5)	70–170	13.8 (14.0)	205
VIa (1.5) → VIb (0.8)	65–130	7.9 (8.0)	185
VIIa (1.5) → VIIb (0.5)	130–200	12.0 (12.1)	235

[a] The elemental analyses of the initial complexes and the product are given in Table 1 and the figures in parentheses are the approximate solvent/metal molar ratios derived from the corresponding analyses.

S-bonded DMSO in the DMSO compounds can be ruled out, since no band assignable to the S=O stretching mode is observed above 1050 cm^{-1} [13,14], but unfortunately the spectral regions where the bands due to *O*-bonded DMSO or free DMSO are to be expected are masked by strong absorptions from C_6F_5. However, ^{1}H NMR spectra of the DMSO compounds show a single peak at δ 2.54 ppm (Pd) or δ 2.55 ppm (Pt) downfield from TMS (free DMSO at 2.53 ppm), respectively (solvent acetone-d_6), which may be indicative of an interaction M–DMSO via the oxygen atom [13] since *S*-bonded DMSO gives a larger downfield shift [14]. On the other hand, only a single band is observed in the IR spectra of these compounds for the X-sensitive mode of C_6F_5, which establishes the linearity of the C–M–C skeleton in the $M(C_6F_5)_2$ moiety.

It should be noted that a plausible explanation for the stoichiometries of the solvated complexes described herein could involve the assumption of the presence of telomeric structures involving C_6F_5 bridges, as proposed by Klabunde et al. for similar compounds [3,4]. A feature of the IR spectra of these compounds is the appearance of two bands in each of the regions where absorptions due to ring and C–F stretching vibrations are found: 1630, 1610, 1045 and 1030 cm^{-1}. Furthermore, the intensities of the bands at 1610 and 1030 cm^{-1} are enhanced as the solvent/$M(C_6F_5)_2$ ratio decreases. Further analysis of the above results would be pointless at this stage, and we must await an X-ray crystal study, all attempts to study *trans*-$Pd(C_6F_5)_2Dx_2$ have been unsuccessful due to the low quality of crystals obtained.

Experimental

trans-$Pd(C_6F_5)_2Dx_2$ was prepared as described in ref. 1 and K_2PtCl_4 was obtained from metallic platinum [15]. All the solvents were dried before use.

Infrared spectra were recorded as KBr pellets and Nujol mulls on a Perkin–Elmer 457 spectrophotometer. Conductivities were measured with a Phillips PW 9501/01 conductimeter. Melting points were determined on a Reichert microscope. Thermal decomposition studies were carried out in nitrogen on a Netzsch STA-429 thermobalance. ^{1}H NMR spectra were obtained in acetone-d_6 solutions with Me_4Si as internal standard on a Varian FT-80A spectrometer.

C, H, N analyses were performed with a Perkin–Elmer 240C microanalyzer. Palladium was determined gravimetrically as dimethylglyoximate [16] and platinum by heating the samples at ca. 550°C and then weighing the residue as metallic platinum [8].

trans-$Pt(C_6F_5)_2Dx_2$ (*I*)

A freshly prepared and filtered solution of C_6F_5MgBr (from 1.50 ml of C_6F_5Br; 12.05 mmol) in THF (20 ml) was added to a suspension of K_2PtCl_4 (1 g; 2.40 mmol) under nitrogen in THF (10 ml). The mixture was then refluxed with stirring for 4 h. After this time, an insoluble reddish solid (the unreacted K_2PtCl_4) and a brown solution were present. Addition of dioxane (20 ml) precipitated most of the magnesium salts as dioxan complexes. The mixture was kept cold overnight, then the solid was filtered off to leave a yellow solution. This solution was concentrated under vacuum at room temperature. Addition of hexane yielded a white solid (I), which was filtered off and washed with hexane (34% yield).

cis-$Pd(C_6F_5)_2(Opy)_2$ *(II)*

0.052 g (0.550 mmol) of pyridine *N*-oxide were added to 0.135 g (0.219 mmol) of *trans*-$Pd(C_6F_5)_2Dx_2$ in dry diethyl ether. The mixture was then stirred at room temperature for 2 h and the excess of Opy was then filtered off. The solution was concentrated under vacuum and hexane was added to give a pale yellow solid (II), which was filtered off and washed with hexane (43% yield).

trans-$Pt(C_6F_5)_2Opy)_2$ *(III)*

0.051 g (0.532 mmol) of pyridine *N*-oxide were added to 0.150 g (0.213 mmol) of *trans*-$Pt(C_6F_5)_2Dx_2$ in dry THF. After stirring for ca. 5 h the excess of ligand was filtered off and the solution was reduced to a small volume under vacuum. Addition of hexane precipitated a white solid (III), which was filtered off and washed with hexane (34% yield).

trans-$Pd(C_6F_5)_2(solvent)_{1.5}$; *(solvent = DMF (IVa), DMSO (Va))*

0.100 g (0.162 mmol) of *trans*-$Pd(C_6F_5)_2Dx_2$ were dissolved in 10 ml of DMF (DMSO). The solution was stirred at room temperature for 2 h then the solvent was evaporated almost to dryness under vacuum. Addition of benzene gave the organocomplex as a white solid which was filtered off and washed with hexane. Yields: 85 and 73% for the DMF and DMSO compounds, respectively. Both complexes were recrystallized from diethyl ether/benzene (IVa, Va).

trans-$Pt(C_6F_5)_2(solvent)_{1.5}$; *(solvent = DMF (VIa), DMSO (VIIa))*

0.100 g (0.142 mmol) of *trans*-$Pt(C_6F_5)_2Dx_2$ were added to 10 ml of DMF (DMSO) and the mixture was stirred for 2 h at room temperature. Removal of solvent under vacuum (at ca. 50°C) gave an oil which was treated with a small amount of THF. Addition of benzene/hexane precipitated the expected organocompounds as white solids, which were filtered off and washed with hexane (52% yield). The products were recrystallized from diethyl ether/hexane (VIa) or THF/hexane (VIIa).

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