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$K_2[Pd(C_6F_5)_4]$-CATALYZED CYCLOTRIMERIZATION OF MALONONITRILE

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Summary

Potassium tetrachloropalladate(II) can be arylated in tetrahydrofuran/dioxane to give the solvated potassium salts $K_2[Pd(C_6F_5)_4] \cdot 2S$ (S = benzonitrile, acetonitrile, pyridine or aniline), from which the solvent can be removed by heating. With malononitrile (MN) the compound $K_2[Pd(C_6F_5)_4] \cdot 4MN$ is formed, which upon heating is converted into $K_2[Pd(C_6F_5)_4] \cdot$ (MN-trimer). In dry benzene, potassium tetrakis(pentafluorophenyl)palladate(II) acts as an efficient catalyst for the cyclotrimerization of malononitrile, yielding 4,6-diamino-3,5-dicyano-2-cyanomethylpyridine. Structural data for all the compounds are reported.

Of the various methods used for the synthesis of pentafluorophenyl derivatives of palladium(II), that based on the arylation of halocomplexes of palladium(II) either with LiC_6F_5 or C_6F_5MgBr in diethyl ether has been successfully used for introducing four C_6F_5 groups in the coordination sphere of palladium, and $Pd(C_6F_5)_4^{2-}$ has been isolated as the $(NBu_4)^+$ salt [1].

Recent work has shown that pentafluorophenyl complexes of palladium(II) can also be prepared [2,3] by the modification of Smith and Tamborski's method consisting in the arylation with C_6F_5MgBr in tetrahydrofuran as solvent, and addition of more dioxane to precipitate the magnesium halides [4]. We show here that under appropriate conditions the method is also suitable for the tetraarylation of $PdCl_4^{2-}$, and the salt $K_2[Pd(C_6F_5)_4]$ can be isolated. This salt has been found to interact with water in acetone to generate hydroxide ion (behaviour not shown by the tetraarylphosphonium salt) and to be an efficient catalyst for the oligomerization of malononitrile.

Results and discussion

Arylation of K_2PdCl_4 by C_6F_5MgBr in tetrahydrofuran proceeds as shown in eq. 1. The C_6F_5/Pd molar ratio used to produce $[Pd(C_6F_5)_4]^{2-}$ is 6/1. The addition

$$K_2PdCl_4 + 4C_6F_5MgBr \xrightarrow[65^\circ C]{THF} K_2Pd(C_6F_5)_4 + 2MgCl_2 + 2MgBr_2 \qquad (1)$$

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TABLE 1

ANALYSES, DECOMPOSITION TEMPERATURES, AND INFRARED DATA FOR THE PALLADIUM COMPOUNDS

Compound	Analysis (Found (calc) (%))				Temp. (°C) (dec.)	Relevant IR bands (cm^{-1})
	C	H	N	Pd		
$K_2[Pd(C_6F_5)_4]\cdot 2PhCN$	43.0	0.8	2.4	10.0	95	2230 (C≡N stretch)
	(43.1)	(0.9)	(2.6)	(10.1)		
$K_2[Pd(C_6F_5)_4]\cdot 2MeCN$	36.1	0.7	2.9	11.2	90	2260 (C≡N stretch)
	(36.0)	(0.6)	(3.0)	(11.4)		
$K_2[Pd(C_6F_5)_4]\cdot 2py$	40.4	1.1	2.7	10.3	125	610, 410 (ring def.)
	(40.4)	(1.0)	(2.8)	(10.5)		
$K_2[Pd(C_6F_5)_4]\cdot 2PhNH_2$	41.4	1.5	2.7	10.1	115	3440, 3360 (NH_2 stretch)
	(41.6)	(1.3)	(2.7)	(10.2)		1610 (NH_2 def.)
$K_2[Pd(C_6F_4)_4]\cdot 4MN$	38.4	1.0	9.9	9.4	100	2270 (C≡N stretch)
	(38.7)	(0.7)	(10.0)	(9.5)		
$K_2[Pd(C_6F_5)_4]$	33.7			12.5	210	
	(33.8)			(12.5)		

of dioxane to the reaction mixture results in the precipitation of the magnesium halides as dioxane adducts, $MgX_2\cdot 2(\text{dioxane})$ [5]. Work up gives either the benzonitrile- or acetonitrile-solvated potassium salt, $K_2[Pd(C_6F_5)_4]\cdot 2S$ (S = PhCN, MeCN). On heating the solvated salt loses the solvent molecules to give $K_2[Pd(C_6F_5)_4]$ which is a white solid stable up to 210°C. In solvents such as pyridine or aniline it reforms solvates $K_2[Pd(C_6F_5)_4]\cdot 2S$ (S = py or $PhNH_2$). The analytical data, decomposition temperatures and some infrared absorptions of the palladium compounds are listed in Table 1.

The infrared spectra of the compounds display the characteristic absorptions attributed to the C_6F_5 group [6] at ca. 1630, 1600, 1500, 1460, 1050 and 950 cm^{-1}. As noted previously [1], a single band at 755 cm^{-1} for the so-called X-sensitive mode of C_6F_5 is consistent with the D_{4h} symmetry of the $Pd(C_6F_5)_4^{2-}$ species. In all the cases the relevant infrared bands from the solvent molecules indicate that the solvent is loosely bound to the lattice of $K_2[Pd(C_6F_5)_4]$ for example, for the benzonitrile compound the C≡N stretching mode appears at 2230 cm^{-1} (compare with 2230 cm^{-1} in free benzonitrile and 2275 cm^{-1} in *cis*-$Pd(C_6F_5)_2(PhCN)_2$ [7]). In acetone ($c \sim 5 \times 10^{-4}$ M) all the compounds show conductivities corresponding to 2 : 1 electrolytes [8].

The ^{19}F NMR spectrum of an acetone-d_6 solution of $K_2[Pd(C_6F_5)_4]$ consists of the expected three signals at 111.43 (*ortho*-F), 165.44 (*meta*-F) and 166.30 (*para*-F) ppm upfield from $CFCl_3$; it was analyzed as an AA′KXX′ system by methods previously described [9,10]: J_{23} −34.0, J_{25} +6.1, J_{26} −8.4, $J_{35} = J_{24} = 0$ and J_{34} −19.4 Hz (the numbering sequence is clockwise around the benzene ring with palladium at 1 and *ortho*-fluorines at 2 and 6). In contrast to other neutral pentafluorophenyl derivatives of palladium(II) [11], for which the signal from the *para*-fluorine usually appears at a lower δ value than that from the *meta*-fluorine, in the case of $[Pd(C_6F_5)_4]^{2-}$ the signal from the *para*-fluorine occurs at about 1 ppm to high field from that of the *meta*-fluorine, thus indicating that there is a relatively high electron density on the *para*-fluorine atom.

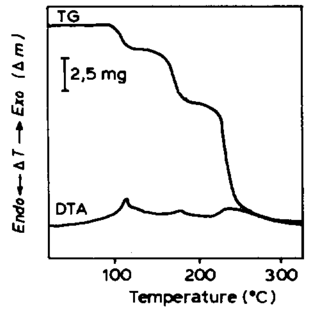


Fig. 1. Simultaneous TG and DTA plots for thermal treatment of $K_2[Pd(C_6F_5)_4]\cdot 4MN$ (15.0 mg) under N_2.

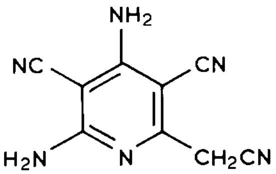
When $K_2[Pd(C_6F_5)_4]$ is treated with malononitrile in diethyl ether the compound $K_2[Pd(C_6F_5)_4]\cdot 4MN$ is formed. This compound shows thermal behaviour completely different from that observed for the other solvates. Thus the thermogravimetric trace for the compound (Fig. 1) shows that between 100–180°C there is a mass loss of 23.2%, which agrees well with the theoretical loss of four malononitrile molecules (23.6%) to give $K_2[Pd(C_6F_5)_4]$. However, an exothermic decomposition process detected in the TG curve at ca. 120°C suggested that something different from the simple release of malononitrile had occurred. This was confirmed when $K_2[Pd(C_6F_5)_4]\cdot 4MN$ was heated at 120°C to constant weight and the infrared spectrum of the resulting solid was studied: new absorptions had appeared in the 2100 (CN stretch) and 3500 (NH_2 stretch) cm^{-1} regions. The solid was $K_2[Pd(C_6F_5)_4]$, together with some product of transformation of malononitrile, the identity of which became apparent from the experiment described below.

When a mixture of $K_2[Pd(C_6F_5)_4]$ and malononitrile (molar ratio = 1/70, respectively) was refluxed in dry benzene, a yellowish white solid separated from the colourless solution. The elemental analysis of the product was identical with that of malononitrile, but its spectral data showed it to be a trimer of malononitrile, namely, 4,6-diamino-3,5-dicyano-2-cyanomethylpyridine; the relevant data are listed in Table 2, and are identical with those previously reported [12] for the so-called Trimer I [13] of malononitrile, the structure of which has been confirmed by synthesis [14] and a crystal-structure study [15]. It should be noted that the existence

TABLE 2

PROPERTIES OF THE PRODUCT FROM TRANSFORMATION OF MALONONITRILE

Elemental analysis (%)	C, 54.1 (54.5); H, 2.9 (3.0); N, 41.9 (42.4)
Mass spectrum, m/z (%)	198(100), 144(18.8), 67(16.2, 66(10.4), 28(9.8), 77(9.0), 171(8.4), 43(7.0)
IR spectrum (cm^{-1})	3400–3200, 1600, 1560, 1500
UV spectrum (nm, in MeOH)	313, 245sh, 237
^1H NMR spectrum (80 MHz, in DMSO-d_6 (δ ppm from TMS))	4.15 (s, 2H), 7.45 (s, 2H), 7.65 (s, 2H)
M.p. (°C)	330

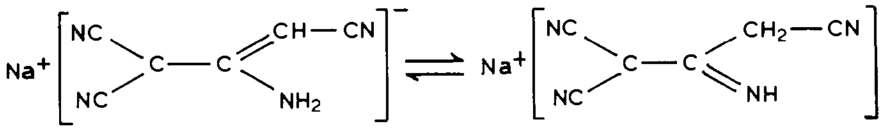


(Trimer I)

of two crystalline modifications of Trimer I has been suggested on the basis of their different infrared spectra, the major differences being the presence of bands at 1252, 1110, 885 and 870 cm^{-1} in the spectrum of one modification [12]. However, we suggest here that these absorptions arise from the presence of dioxane in the crystal lattice of the organic trimer (dioxane being the solvent used for recrystallization) and the preceding bands could be assigned to the ν_{15} (wagging), ν_{17} (ring stretching), ν_{16} (rocking) and ν_{27} (ring stretching) vibrational modes of dioxane [16], respectively.

Malononitrile and its derivatives have become keystones for syntheses of heterocyclic systems [12], and a number of methods for conversion of malononitrile into the Trimer I have been used [12,17]. The α-methylene group in malononitrile is sufficiently acidic to afford a carbanion (eq. 2) in the presence of a basic catalyst;

$$CH_2(CN)_2 \xrightarrow[\text{catalyst}]{\text{basic}} \left\{ NC-\bar{C}H-CN \rightleftarrows NC-CH=C=\bar{N} \right\} \qquad (2)$$



(3)

the carbanion can then react further, to produce a dimer (eq. 3), which can be isolated as the sodium or potassium salt (eq. 3). The reaction of the anionic dimer with a third malononitrile molecule produces the trimer. In our case the basic catalyst must be $K_2[Pd(C_6F_5)_4]$, since no other palladium species other than $[Pd(C_6F_5)_4]^{2-}$ can be detected either during the thermal treatment or the oligomerization in benzene solution. The basic nature of $Pd(C_6F_5)_4{}^{2-}$ can be demonstrated in aqueous medium; thus, when the potassium salt was dissolved in a 1/1 water/acetone mixture ($c \sim 10^{-3}$ M) the measured pH of the resulting solution was about 10.9, indicating that interaction of $Pd(C_6F_5)_4{}^{2-}$ with water had produced hydroxide ion, the identity of the palladium species formed in this interaction is unknown. If $[P(C_6H_5)_3(C_6H_5CH_2)]^+$ is added to the solution the salt $[P(C_6H_5)_3(C_6H_5CH_2)]_2[Pd(C_6F_5)_4]$ precipitates out; this salt was ineffective as a catalyst for the trimerization of malononitrile.

Experimental

Infrared spectra were recorded with Nujol mulls on a Perkin-Elmer 1430 spectrophotometer. The UV spectrum of Trimer I was recorded with a Hitachi U 2300 spectrophotometer. The ^1H and ^{19}F NMR spectra were recorded on a Varian

FT 80A spectrometer. The mass spectrum of Trimer I was obtained at 70 eV by use of Hewlett Packard 5993C instrument. Thermal decomposition studies (TG and DTA) were carried out with a Netzsch STA-429 thermobalance. Conductivities were measured with a Philips PW 9501/01 conductimenter. C, H and N analyses were performed with a Perkin–Elmer 240C microanalyzer. Palladium analyses were carried out by the Department of Analytical Chemistry of the University of Murcia, Spain, using a solvent-extraction method [18]. Potassium was qualitatively detected by use of $Na[BPh_4]$.

Bromopentafluorobenzene was purchased from Aldrich Chemical Co. Potassium tetrachloropalladate(II) was prepared from metallic palladium [19] purchased from Sociedad Española de Metales Preciosos. All the solvents were dried before use by standard methods.

$K_2[Pd(C_6F_5)_4] \cdot 2PhCN$

A solution of C_6F_5MgBr (15 mmol) in tetrahydrofuran (25 cm^3) was added to a suspension of K_2PdCl_4 (1 g, 3.06 mmol) in the same solvent (15 cm^3) under nitrogen. After 4 h stirring at ca. 65°C and subsequent cooling to room temperature, dioxan (20 cm^3) was added with stirring during 0.5 h. The mixture was kept in a refrigerator overnight then the precipitated magnesium halides were filtered off and the filtrate evaporated to dryness under vacuum. The solid was dissolved in benzonitrile (10 cm^3) and the filtered solution was diluted with benzene (20 cm^3). The solution was added to hexane (200 cm^3) with vigorous stirring, which was continued for some time afterwards. The benzonitrile-solvated potassium salt separated as a white solid which was filtered off, washed with hexane, and dried under vacuum (76% yield).

$K_2[Pd(C_6F_5)_4] \cdot 2MeCN$

Work up as above but with acetonitrile (10 cm^3) instead of benzonitrile gave the corresponding acetonitrile-solvate (70% yield).

$K_2[Pd(C_6F_5)_4] \cdot 2S$ ($S = py, PhNH_2$)

When $K_2[Pd(C_6F_5)_4] \cdot 2PhCN$ was heated at 100°C the benzonitrile was released to give $K_2[Pd(C_6F_5)_4]$. When this solvent-free salt (0.1 g, 0.117 mmol) was dissolved in either pyridine (0.3 cm^3) or aniline (3 cm^3) the corresponding title compound was obtained as a precipitate by addition of hexane (85% yield in each case).

$K_2[Pd(C_6F_5)_4] \cdot 4MN$

Malononitrile (0.064 g, 0.973 mmol) was added to a solution of $K_2[Pd(C_6F_5)_4]$ (0.162 mmol) in diethyl ether (4 cm^3) and the solution was stirred at room temperature for 0.5 h. Addition of hexane precipitated the malononitrile compound, which was filtered off, washed with benzene then hexane, and dried in the air (85% yield).

Catalytic conversion of malononitrile into its trimer, 4,6-diamino-3,5-dicyano-2-cyanomethylpyridine.

A solution of $K_2[Pd(C_6F_5)_4]$ (0.113 mmol) and malononitrile (7.6 mmol) in dry benzene (20 cm^3) was refluxed. After ca. 30 min a yellowish brown solid had separated. The mixture was stirred under reflux for a further 10 h until precipitation was complete, and then filtered hot. The solid was washed several times with hexane to remove traces of benzene (65% yield).

The filtrate was concentrated under reduced pressure and hexane was added to precipitate a yellowish white solid, which was filtered off. It was identified as $K_2[Pd(C_6F_5)_4]$ containing some malononitrile trimer ($K_2[Pd(C_6F_5)_4]$/MN trimer molar ratio ~ 1/1).

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