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SYNTHESIS AND STRUCTURE OF NEUTRAL AND CATIONIC PENTAHALOARYLPALLADIUM(II) ISONITRILE COMPLEXES

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Summary

Complexes of the types (a) *trans-* and *cis-*$[Pd(C_6X_5)_2(CNR)_2]$, (b) *trans-*$[Pd(C_6X_5)Cl(CNR)_2]$ and (c) $[Pd(C_6X_5)(CNR)_3]ClO_4$ (X = F or Cl; R = Bu^t, cyclohexyl or *p*-tolyl) have been made by replacement of the tetrahydrothiophen or Cl groups of appropriate precursors by isonitrile. Their structures have been assigned on the basis of their IR and ^1H NMR spectra.

Introduction

The chemistry of palladium(II) isonitrile complexes containing only isonitrile groups, neutral ligands and halogen atoms coordinated to the palladium has been extensively studied. Complexes such as $[PdX_2(CNR)_2]$ [1—3], $[Pd_2X_4(CNR)_2]$ [3], $[PdX_3(CNR)]^-$ [3] or $[PdX(CNR)L_2]^+$ [4—7] (X = halogen, L = neutral ligand) can be prepared by conventional methods.

Palladium complexes containing isonitrile along with σ-C bonded anionic ligands are much scarcer, because of the ready insertion of the isonitrile group into the Pd—C bonds. The commonest examples are of the type *trans-*$[PdXR'(CNR)_2]$, and can be obtained by oxidative addition of R'X to $[Pd(CNR)_2]$, though even at room temperature spontaneous transformation into the insertion products often takes place [8—12]. The oxidative addition of perfluoro-derivatives containing E=C double bonds (E = C, O or N) to $[Pd(CNR)_2]$ leads to three- or five-membered metallacyclic compounds with two mutually *cis* isonitrile ligands and one or two σ Pd—C bonds [12—14], and in the cases no insertions have been observed. Finally, reactions of isonitriles with $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Cl)_2]$ [15,16] and with norbornenyl (or similar) palladium(II) complexes [17] initially lead to coordination of the isonitrile, though in the presence of an excess of the ligand insertion then occurs.

In previous studies specific methods for the synthesis of perhalophenyl complexes of the types *cis-* and *trans-*$[Pd(C_6X_5)_2L_2]$ [18], *trans-*$[Pd(C_6X_5)X'L_2]$

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[19] and $[Pd(C_6X_5)L_3]ClO_4$ [20] (X = F or Cl; X′ = halide, L = neutral ligands) have been developed. The mildness of the reaction conditions needed and unusual stability of the Pd—C_6X_5 bond prompted us to attempt the synthesis of similar complexes containing isonitrile. We expected the Pd—C_6X_5 bond to be sufficiently inert towards insertion to allow us to obtain new types of organometallic palladium(II) isonitrile complexes.

Results and discussion

a) Preparation of the complexes

The complexes *trans*-$[Pd(C_6X_5)_2(CNR)_2]$ (I-VI) were made according to eq. 1 by displacement of the tht ligand from *trans*-$[Pd(C_6X_5)_2(tht)_2]$ (X = F [21] or Cl [22], tht = tetrahydrothiophen) using a small excess of the isonitrile. The corresponding isomers *cis*-$[Pd(C_6X_5)_2(CNR)_2]$ (VII—XII) were synthesized according to eq. 2 by using $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4](NBu_4)_2$ [21] or $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_4](NBu_4)_2$ [23] as precursors.

$$trans\text{-}[Pd(C_6X_5)_2(tht)_2] + 2\ CNR \xrightarrow{CH_2Cl_2} trans\text{-}[Pd(C_6X_5)_2(CNR)_2] + 2\ tht \qquad (1)$$

$$1/2[Pd_2(\mu - X')_2(C_6X_5)_4](NBu_4)_2 + 2\ CNR \xrightarrow{CH_2Cl_2} cis\text{-}[Pd(C_6X_5)_2(CNR)_2] + (NBu_4)X' \qquad (2)$$

X = F, X′ = Br; X = X′ = Cl; R = Bu^t, Cy (cyclohexyl), *p*-tolyl; tht = tetrahydrothiophen

As with other ligands [18], the reactions take place smoothly at room temperature with retention of configuration, as confirmed by IR spectroscopy. The products are the first isonitrile complexes containing two σ Pd—C bonds which are not involved in the formation of a palladiacycle. They show no tendency to undergo isonitrile insertion at room temperature.

The complexes *trans*-$[Pd(C_6X_5)Cl(CNR)_2]$ (XIII—XVIII) were prepared by treating $[Pd_2(C_6X_5)_2(\mu\text{-}Cl)_2(tht)_2]$ with the relevant isonitrile, according to eq. 3

$$1/2[Pd_2(C_6X_5)_2(\mu - Cl)_2(tht)_2] + 2\ CNR \xrightarrow{CH_2Cl_2} trans\text{-}[Pd(C_6X_5)Cl(CNR)_2] + tht \qquad (3)$$

X = F, Cl ; R = Bu^t, Cy, *p*=tolyl.

For R = Bu^t or Cy the reactions proceed satisfactorily at room temperature, but for R = *p*-tolyl the reaction has to be carried out in an ice-bath since more complex processes occurs at room temperature; these are being studied further.

The cationic complexes $[Pd(C_6X_5)(CNR)_3]ClO_4$ (XIX—XXIV), which to the best of our knowledge are the only reported cationic organopalladium derivatives containing isonitrile, can be obtained according to eq. 4. They do not undergo insertion at room temperature.

$$\textit{trans}\text{-}[Pd(C_6X_5)Cl(CNR)_2] + CNR + NaClO_4 \xrightarrow{\text{acetone}} [Pd(C_6X_5)(CNR)_3]ClO_4 + NaCl \qquad (4)$$

The analytical results and yields for all the complexes are listed in Table 1.

b) Structural study

The structural assignment is based on the IR and (where appropriate) ^{1}H NMR spectra of the complexes.

The absorptions due to ν(C≡N) (at ca. 2200 cm^{-1}) are only of limited structural interest because there is often coincidence of the various ν(C≡N) vibrations with apparent reduction of the number of expected bands [23—24]. The bands due to the C_6F_5 group at approx. 800 cm^{-1} (X-sensitive C_6F_5) are more useful, since their behaviour in terms of symmetry is analogous to that expected for ν(Pd—C) [18]. (A similar feature was noted in the case of C_6Cl_5 derivatives [25] for the absorptions at ca. 830 and 600 cm^{-1}.) Since the 850—800 cm^{-1} region is sometimes complicated by bands due to other ligands, we consider below only the vibrations at ca. 600 cm^{-1}, which have been assigned to ν(Pd—C) modes [26]. The number of IR active bands for these vibrations

TABLE 1

ANALYTICAL DATA AND YIELDS FOR THE COMPLEXES PREPARED

No.	Complex	Analysis: Found (calcd.) (%)			Yield (%)
		N	C	H	
I	*trans*-$[Pd(C_6F_5)_2(CNBu^t)_2]$	4.54(4.62)	43.69(43.55)	3.13(2.99)	97
II	*trans*-$[Pd(C_6Cl_5)_2(CNBu^t)_2]$	3.85(3.64)	34.65(34.26)	2.34(2.36)	55
III	*trans*-$[Pd(C_6F_5)_2(CNCy)_2]$	4.38(4.26)	47.97(47.39)	3.43(3.37)	73
IV	*trans*-$[Pd(C_6Cl_5)_2(CNCy)_2]$	3.48(3.40)	37.61(37.93)	2.80(2.70)	86
V	*trans*-$[Pd(C_6F_5)_2(CNTol)_2]$	4.29(4.16)	49.68(49.83)	2.29(2.10)	94
VI	*trans*-$[Pd(C_6Cl_5)_2(CNTol)_2]$	3.50(3.34)	40.00(40.07)	1.65(1.69)	65
VII	*cis*-$[Pd(C_6F_5)_2(CNBu^t)_2]$	4.47(4.62)	43.84(43.55)	2.86(2.99)	67
VIII	*cis*-$[Pd(C_6Cl_5)_2(CNBu^t)_2]$	3.76(3.64)	34.53(34.26)	2.47(2.38)	63
IX	*cis*-$[Pd(C_6F_5)_2(CNCy)_2]$	4.36(4.26)	47.37(47.39)	3.52(3.37)	50
X	*cis*-$[Pd(C_6Cl_5)_2(CNCy)_2]$	3.55(3.40)	37.75(37.93)	2.64(2.70)	85
XI	*cis*-$[Pd(C_6F_5)_2(CNTol)_2]$	4.27(4.16)	50.00(49.83)	2.42(2.10)	70
XII	*cis*-$[Pd(C_6Cl_5)_2(CNTol)_2]$	3.60(3.34)	40.16(40.07)	1.71(1.69)	72
XIII	*trans*-$[Pd(C_6F_5)Cl(CNBu^t)_2]$	5.87(5.89)	40.55(40.45)	3.82(3.81)	78
XIV	*trans*-$[Pd(C_6Cl_5)Cl(CNBu^t)_2]$	5.12(5.03)	34.63(34.48)	3.09(3.25)	76
XV	*trans*-$[Pd(C_6F_5)Cl(CNCy)_2]$	5.55(5.31)	45.55(45.36)	4.52(4.21)	87
XVI	*trans*-$[Pd(C_6Cl_5)Cl(CNCy)_2]$	4.85(4.65)	39.39(39.41)	3.60(3.63)	52
XVII	*trans*-$[Pd(C_6F_5)Cl(CNTol)_2]$	5.08(5.14)	48.98(48.50)	2.59(2.59)	98
XVIII	*trans*-$[Pd(C_6Cl_5)Cl(CNTol)_2]$	4.54(4.48)	41.59(42.25)	2.36(2.25)	85
XIX	$[Pd(C_6F_5)(CNBu^t)_3]ClO_4$	6.66(6.76)	40.50(40.53)	4.66(4.37)	70
XX	$[Pd(C_6Cl_5)(CNBu^t)_3]ClO_4$	6.19(5.97)	35.73(35.78)	3.67(3.86)	69
XXI	$[Pd(C_6F_5)(CNCy)_3]ClO_4$	6.22(6.00)	46.26(46.30)	5.05(4.75)	70
XXII	$[Pd(C_6Cl_5)(CNCy)_3]ClO_4$	5.41(5.36)	41.89(41.43)	4.75(4.25)	68
XXIII	$[Pd(C_6F_5)(CNTol)_3]ClO_4$	6.05(5.81)	49.18(49.74)	3.22(2.93)	70
XXIV	$[Pd(C_6Cl_5)(CNTol)_3]ClO_4$	5.31(5.21)	44.49(44.67)	2.83(2.63)	72

Bu^t = tert-butyl, Cy = cyclohexyl, Tol = *p*-tolyl.

TABLE 2

POINT GROUPS AND IR ACTIVE STRETCHING MODES FOR THE COMPLEXES

Complex	Point group	$\nu(C{\equiv}N)$	C_6X_5-X-sensitive
trans-$[Pd(C_6X_5)_2(CNR)_2]$	D_{2h}	B_{2u}	B_{2u}
cis-$[Pd(C_6X_5)_2(CNR)_2]$	C_{2v}	$A_1 + B_1$	$A_1 + B_1$
trans-$[Pd(C_6X_5)Cl(CNR)_2]$	C_{2v}	$A_1 + B_1$	A_1
cis-$[Pd(C_6X_5)Cl(CNR)_2]$	C_s	$2A'$	A'
$[Pd(C_6X_5)(CNR)_3]ClO_4$	C_{2v}	$2A_1 + B_1$	A_1

according to group theory are listed in Table 2.

Table 3 lists the absorptions observed for the different complexes (the number of bands derived from group theory is shown in brackets). It will be seen that *trans*- and *cis*-$[Pd(C_6X_5)_2(CNR)_2]$ could be unambiguously identified. In the case of $[Pd(C_6X_5)(CNR)_3]ClO_4$ [the ionic formulation of which is confirmed by the molar conductivity (1 : 1 electrolytes) and the presence of IR absorptions at 1100 and 620 cm^{-1} (characteristic for the perchlorate anion)] only one structure is possible.

Finally, IR spectroscopy does not allow the *cis*- and *trans*-isomers of $[Pd(C_6X_5)Cl(CNR)_2]$ to be distinguished, since the same number of bands are predicted for both. The *trans*-geometry has been assigned because only one type of isonitrile could be observed in their ^1H NMR spectra; the two isonitrile ligands should not be equivalent for the corresponding *cis*-isomer (see Table 4).

The $\nu(C{\equiv}N)$ frequencies are generally appreciably lower for the C_6Cl_5 derivatives than for the analogous C_6F_5 complexes. This suggests that the electronegativity of the C_6Cl_5 group is, as expected, lower than that of the C_6F_5 group. Thus the palladium atom must have a higher electron density in the C_6Cl_5 derivatives and the backdonation to the π^* orbitals of the isonitrile must be more effective, leading to a lowering of $\nu(C{\equiv}N)$. For the same reason, the cationic complexes show an appreciable shift of $\nu(C{\equiv}N)$ towards higher energies compared with the neutral complexes.

Experimental

C, H and N analyses were determined with a Perkin-Elmer 240 microanalyzer. Conductivities were measured in approx. 5×10^{-4} *M* solution with a Philips PW 9501/01 conductimeter. IR spectra were recorded (at 4000—200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. The ^1H NMR spectra were recorded on a Varian FT-80 spectrometer in $CDCl_3$ solutions. The organic isonitriles were prepared by standard methods [27].

Preparation of the complexes

trans-$[Pd(C_6X_5)_2(CNR)_2]$ (I—VI) and trans-$[Pd(C_6X_5)Cl(CNR)_2]$ (XIII—XVIII). The isonitrile was added to a CH_2Cl_2 solution or suspension of the relevant precursor (see eqs. 1 and 3; isonitrile/precursor = 1.1/1 ratio). After stirring for 1 h the solution was concentrated by evaporation of solvent, and where

TABLE 3

RELEVANT INFRARED AND CONDUCTIVITY DATA OF THE COMPLEXES

No.	Complex	$\nu(C\equiv N)$ (cm^{-1})	Prediction [b]	X-sensitive C_6F_5 or $\nu(Pd-C_6Cl_5)$ (cm^{-1})	Prediction [c]	$\nu(Pd-Cl)$ (cm^{-1})	Λ(acetone) ohm^{-1} cm^2 mol^{-1}
I	*trans*-$[Pd(C_6F_5)_2(CNBu^t)_2]$	2220	(1)	760	(1)	—	—
II	*trans*-$Pd(C_6Cl_5)_2(CNBu^t)_2]$	2215	(1)	603	(1)	—	—
III	*trans*-$[Pd(C_6F_5)_2(CNCy)_2]$	2240	(1)	770	(1)	—	—
IV	*trans*-$[Pd(C_6Cl_5)_2(CNCy)_2]$	2220	(1)	605	(1)	—	—
V	*trans*-$[Pd(C_6F_5)_2(CNTol)_2]$	2215	(1)	775	(1)	—	—
VI	*trans*-$[Pd(C_6Cl_5)_2(CNTol)_2]$	2180	(1)	605	(1)	—	—
VII	*cis*-$[Pd(C_6F_5)_2(CNBu^t)_2]$	2235—2220(br)	(2)	790, 783	(2)	—	—
VIII	*cis*-$[Pd(C_6Cl_5)_2(CNBu^t)_2]$	2215, 2205	(2)	615, 607	(2)	—	—
IX	*cis*-$[Pd(C_6F_5)_2(CNCy)_2]$	2235, 2225	(2)	790, 785	(2)	—	—
X	*cis*-$[Pd(C_6Cl_5)_2(CNCy)_2]$	2230, 2215	(2)	612, 606	(2)	—	—
XI	*cis*-$[Pd(C_6F_5)_2(CNTol)_2]$	2210, 2195	(2)	790, 785	(2)	—	—
XII	*cis*-$[Pd(C_6Cl_5)_2(CNTol)_2]$	2205, 2190(br)	(2)	613, 607	(2)	—	—
XIII	*trans*-$[Pd(C_6F_5)Cl(CNBu^t)_2]$	2245, 2225(br)	(2)	790	(1)	315	—
XIV	*trans*-$[Pd(C_6Cl_5)Cl(CNBu^t)_2]$	2243, 2223(br)	(2)	623	(1)	310	—
XV	*trans*-$[Pd(C_6F_5)Cl(CNCy)_2]$	2235(br)	(2)	793	(1)	315	—
XVI	*trans*-$[Pd(C_6Cl_5)Cl(CNCy)_2]$	2225(br)	(2)	626	(1)	315	—
XVII	*trans*-$[Pd(C_6F_5)Cl(CNTol)_2]$	2210(br)	(2)	795	(1)	318	—
XVIII	*trans*-$[Pd(C_6Cl_5)Cl(CNTol)_2]$	2205	(2)	625	(1)	312	—
XIX	$[Pd(C_6F_5)(CNBu^t)_3]ClO_4$	2250(br)	(3)	798	(1)	—	132
XX	$[Pd(C_6Cl_5)(CNBu^t)_3]ClO_4$	2255, 2230(br)	(3)	[a]	(1)	—	110
XXI	$[Pd(C_6F_5)(CNCy)_3]ClO_4$	2250	(3)	795	(1)	—	121
XXII	$[Pd(C_6Cl_5)(CNCy)_3]ClO_4$	2245(br)	(3)	[a]	(1)	—	128
XXIII	$[Pd(C_6F_5)(CNTol)_3]ClO_4$	2230	(3)	795	(1)	—	136
XXIV	$[Pd(C_6Cl_5)(CNTol)_3]ClO_4$	2225(br)	(3)	[a]	(1)	—	127

[a] Absorptions due to the perchlorate group preclude assignment. [b] Number of $\nu(C\equiv N)$ infrared active bands. [c] Number of X-sensitive or $\nu(Pd-C_6Cl_5)$ infrared active bands.

TABLE 4

^{1}H NMR SPECTRA (δ VALUES IN $CDCl_3$; REFERENCE TMS)

XIII	*trans*-[$Pd(C_6F_5)Cl(CNBu^t)_2$]	1.48(s)
XIV	*trans*-[$Pd(C_6Cl_5)Cl(CNBu^t)_2$]	1.38(s)
XV	*trans*-[$Pd(C_6F_5)Cl(CNCy)_2$]	3.92 (brs, 1 H, —CH<); 1.81 (br s, 4 H) 1.50 (br s, 6 H)
XVI	*trans*-[$Pd(C_6Cl_5)Cl(CNCy)_2$]	3.90 (br s, 1 H, —CH<); 1.69 (br s, 4 H) 1.35 (br s, 6 H)
XVII	*trans*-[$Pd(C_6F_5)Cl(CNTol)_2$]	7.25 (s, 4 H, C_6H_4); 2.39 (s, 3 H, CH_3)
XVIII	*trans*-[$Pd(C_6Cl_5)Cl(CNTol)_2$]	7.30 (s, 4 H, C_6H_4); 2.42 (s, 3 H, CH_3)

necessary n-hexane was added to precipitate the product. The oils which sometimes separated were repeatedly stirred with hexane to remove the free tht, which hinders crystallization. The precipitate was finally filtered off and air-dried.

For the preparation of *trans*-[$Pd(C_6X_5)Cl(CNC_6H_4Me$-*p*$)_2$] the reaction and the concentration of the solutions must be carried out in an ice-bath.

cis[Pd(C$_6$X$_5$)$_2$(CNR)$_2$] (VII—XII). The isonitrile was added to a CH_2Cl_2 solution of [$Pd_2(\mu$-$X')_2(C_6X_5)_4$]$(NBu_4)_2$ (see eq. 2; isonitrile/precursor = 1.1/1 ratio). After stirring for 1 h the solution was filtered through a 2 cm silica gel G column and the filtrate was concentrated. Addition of n-hexane caused precipitation of the desired complex, which was filtered off and air-dried.

[Pd(C$_6$X$_5$)(CNR)$_3$]ClO$_4$ (XIX—XXIV). The isonitrile and $NaClO_4$ were added to an acetone solution of [$Pd(C_6X_5)Cl(CNR)_2$] (see eq. 4; isonitrile/$NaClO_4$/precursor = 1.1/1.5/1 ratio). After stirring for 4 h the solution was evaporated to dryness. The residue was extracted with dichloromethane. The resulting solution was filtered and concentrated, and n-hexane was added to precipitate the desired complex.

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