

TERMINAL PENTAFLUOROBENZIMIDOYLPALLADIUM(II) COMPLEXES. X-RAY STRUCTURE OF *trans*-[Pd{C(C₆F₅)=NMe}Cl(CNMe)₂]

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Summary

The preparations of the complexes *trans*-[Pd{C(C₆F₅)=N(R¹)}Cl(CNR²)₂] and [Pd{C(C₆F₅)=N(R¹)}(CNR²)₂]X (R¹ = Me, *p*-Tol; R² = Me, *p*-Tol, Bu^t; X = ClO₄ or BPh₄) from [Pd₂{μ-C(C₆F₅)N(R¹)}₂Cl₂(CNR²)₂] are described. The splitting of the imidoyl bridges is accompanied by an isomerization of the imidoyl group from the *syn* to the *anti* conformation as shown by a single crystal X-ray diffraction study of *trans*-[Pd{C(C₆F₅)=N(Me)}Cl(CNMe)₂]. Attempted preparations of [Pd{C(C₆F₅)=N(R¹)}Cl(PPh₃)₂] from [Pd₂{μ-C(C₆F₅)=N(R¹)}₂Cl₂(PPh₃)₂] led to elimination of CNR and formation of *trans*-[Pd(C₆F₅)Cl(PPh₃)₂]; this is the first example of isonitrile elimination in palladium chemistry.

Introduction

In previous papers [1,2] we have reported the preparation of *cis*-[Pd₂(μ-Cl)₂{μ-C(C₆F₅)=N(R¹)}₂]_n complexes (R¹ = Me, *p*-Tol) and their reactions with monodentate ligands (Pd/L: 1/1) to give dimeric complexes [Pd₂{μ-C(C₆F₅)=N(R¹)}₂Cl₂L₂]; for R¹ = *p*-Tol and L = isonitrile the insolubility of the products suggested a polymeric structure such as [Pd(CNR²)Cl{μ-C(C₆F₅)=N(R¹)}]_n. The crystal structure of the complex [Pd₂{μ-C(C₆F₅)=N(Me)}Cl₂(tht)₂] (tht = tetrahydrothiophen) confirmed the presence of imidoyl bridges and terminal Cl, and showed the imidoyl conformation to be *syn* [1]. Other dimeric palladium(II) complexes containing imidoyl groups had been reported [3–7] but they were assigned terminal imidoyl halo-bridged structures [Pd₂(μ-X)₂{C(R³)=N(R⁴)}₂L₂] (X = Hal) on indirect evidence; some of these [5–7] were reported to react with L (L = CNR⁵ or PR⁶₃) to give mononuclear complexes [Pd{C(R³)=N(R⁴)}XL₂]. It was thus of interest to subject

our complexes to such reactions; similar behaviour might indicate structural analogy. A preliminary account of these results has appeared [8].

Results and discussion

Reactions involving isonitrile ligands

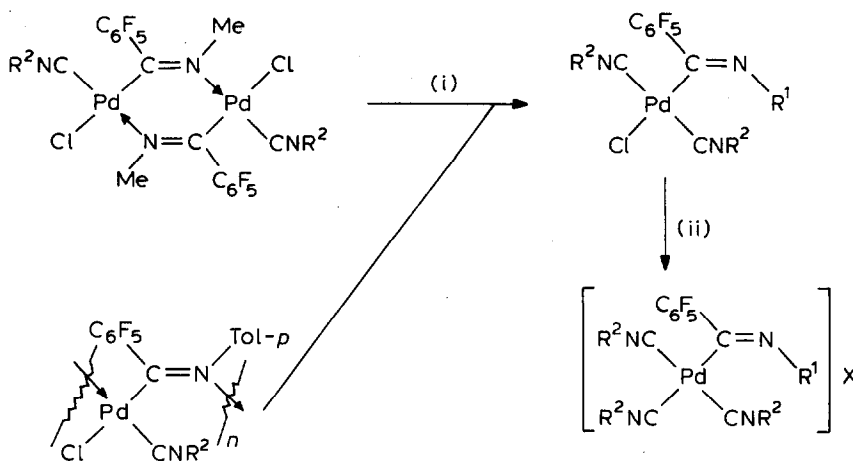
When yellow solutions of $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{R}^1)\}_2\text{Cl}_2(\text{CNR}^2)_2]$ ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Me}$ [1], $p\text{-Tol}$, Bu^t (this paper)) or white suspensions of $[\text{Pd}(\text{CNR}^2)\text{Cl}\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{R}^1)\}_n]$ ($\text{R}^1 = p\text{-Tol}$, $\text{R}^2 = \text{Me}$, $p\text{-Tol}$, Bu^t [2]) in CH_2Cl_2 are treated with CNR^2 (Pd/CNR^2 : 1/1), colourless solutions are formed immediately, from which complexes III–VIII are easily isolated as colourless crystals. Further addition of CNR^2 in the presence of NaClO_4 in acetone or NaBPh_4 in CH_2Cl_2 leads to the cationic complexes IX–XIV (Scheme 1).

The assignment of III–XIV as mononuclear complexes containing a terminal imido ligand in the *anti*-configuration is based on their analytical data (Table 1),

TABLE 1
ANALYTICAL RESULTS, YIELDS AND MOLAR CONDUCTIVITIES

Compound		Analysis(Found (calcd.) (%))			Yield	Λ_M^a
		N	C	H		
$[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{CNTol})_2]$	(I)	5.72 (5.99)	41.05 (41.14)	3.04 (3.15)	60	—
$[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{CNBu}^t)_2]$	(II)	6.23 (6.47)	35.72 (36.06)	3.66 (3.80)	62	—
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}\text{Cl}(\text{CNMe})_2]$	(III)	10.00 (9.73)	33.96 (33.36)	2.34 (2.10)	83	1.2
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}\text{Cl}(\text{CNTol})_2]$	(IV)	7.27 (7.19)	49.80 (49.34)	3.08 (2.93)	43	1.5
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}\text{Cl}(\text{CNBu}^t)_2]$	(V)	7.89 (8.14)	42.36 (41.88)	4.47 (4.10)	78	1.8
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Tol})\}\text{Cl}(\text{CNMe})_2]$	(VI)	8.01 (8.27)	42.47 (42.54)	3.03 (2.58)	88	1.6
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Tol})\}\text{Cl}(\text{CNTol})_2]$	(VII)	6.02 (6.36)	54.30 (54.57)	3.53 (3.21)	80	1.1
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Tol})\}\text{Cl}(\text{CNBu}^t)_2]$	(VIII)	6.85 (7.09)	48.77 (48.67)	4.88 (4.25)	85	1.3
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}(\text{CNMe})_3]\text{BPh}_4$	(IX)	7.21 (7.40)	60.29 (60.30)	3.81 (4.26)	75	95.6
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}(\text{CNTol})_3]\text{ClO}_4$	(X)	6.98 (7.32)	50.30 (50.22)	3.12 (3.16)	83	125
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}(\text{CNBu}^t)_3]\text{ClO}_4$	(XI)	8.22 (8.45)	41.11 (41.65)	4.43 (4.56)	78	132
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Tol})\}(\text{CNMe})_3]\text{BPh}_4$	(XII)	6.56 (6.73)	63.05 (63.44)	4.23 (4.36)	72	88
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Tol})\}(\text{CNTol})_3]\text{ClO}_4$	(XIII)	6.54 (6.66)	54.69 (54.24)	3.31 (3.35)	81	127.3
$[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{Tol})\}(\text{CNBu}^t)_3]\text{ClO}_4$	(XIV)	7.44 (7.58)	46.77 (47.11)	4.64 (4.64)	83	113

^a In $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, in acetone.



SCHEME 1. (i) + CNR^2 , CH_2Cl_2 ; (ii) + $\text{CNR}^2 + \text{NaX}$ ($\text{X} = \text{ClO}_4$ in acetone or BPh_4 in CH_2Cl_2).

IR spectra (Table 2), ^{19}F and ^1H NMR spectra (Table 3) and the X-ray diffraction study of complex III (Fig. 1).

The ^{19}F NMR spectra of complexes III–XIV are typical of $AA'MXX'$ systems, i.e. the two *ortho* fluorines are isochronous (although magnetically inequivalent) and the same applies to the two *meta* fluorine atoms. This spectral pattern is very different from that of the imido-bridged complexes (I, II and complexes in ref. 1) which show chemical inequivalence of the five fluorine atoms arising from the steric restriction to rotation of the C_6F_5 ring around the $\text{C}_6\text{F}_5\text{--C}$ bond in the *syn* conformation.

Thus the molecular structure of complex III shows that the splitting of the bridges is accompanied by an isomerization from the *syn* to the *anti* configuration of the imido group.

TABLE 2
RELEVANT IR ABSORPTION (cm^{-1})

Compound	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{N})$	C_6F_5 absorptions	$\nu(\text{Pd--Cl})$ or X^- group
I	2210,2171	1603,1583	1645 1513,1493, 1128 980,955	303,285
II	2223	1600	1649 1508,1493 1133 980,955	316,283
III	2249,2220	1630	1516,1487 1142 997,983,967	282
IV	2190	1649	1514,1493 1138 1003,980,961	267
V	2213	1630	1512,1485 1143 998,979,966	286
VI	2247	1620	1516,1493 1116 1015,978	272
VII	2236,2211	1642	1517,1488 1115 1015,981	276
VIII	2209	1638	1511,1473 1114 1014,976	269
IX	2251	1655	1523,1498 1148 1003,987	610,605
X	2205	1653	1523,1493 1143 1013,1000,978,966	1100,620
XI	2211	1655	1520,1495 1140 1003,983,963	1100,620
XII	2251	1628(v br)	1518,1491 1120 980	610,605
XIII	2208	1620(v br)	1517,1495 1115 980	1100,620
XIV	2221	1648	1518,1493 1118 978	1100,620

TABLE 3
¹⁹F NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS, AND ¹H NMR CHEMICAL SHIFTS

Complex	¹⁹ F NMR chemical shifts, ref. CFCl ₃				Coupling constants (Hz) ^a				δ(ppm), CDCl ₃ , ref. TMS	
	F ²	F ⁶	F ⁴	F ³	F ⁵	³ J(2-3), ³ J(5-6)	³ J(3-4), ³ J(4-5)	³ J(3-6), ³ J(2-5)	Me(isoc.)	Me(imid)
I	-140.5	-143.8	-153.3	-159.9	-161.0	-24.6	-23.1	-20.7	2.35(3H)	3.39(3H)
II	-139.4	-143.6	-153.7	-159.9	-161.3	-23.6	-23.3	-20.5	1.70(9H)	3.34(3H)
III	-145.1	-157.2	-162.9			-22.4		-20.8	3.44(6H)	3.74(3H)
IV	-144.4	-156.6	-162.4			-22.3		-21.0	2.39(6H)	3.85(3H)
V	-144.0	-157.2	-163.0			-22.9		-20.9	1.47(18H)	3.71(3H)
VI	-144.8	-156.5	-162.5			-22.7		-20.9	3.30(6H)	2.35(3H)
VII	-144.2	-156.5	-162.5			-22.7		-20.8	2.40(6H)	2.37(3H)
VIII	-143.7	-157.0	-162.8			-22.9		-20.8	1.43(18H)	2.37(3H)
IX	-144.4	-155.1	-161.6			-22.7		-21.2	2.15(3H); 2.30(6H)	3.67(3H)
X	-144.0	-155.2	-161.7			-18.9		-20.0	2.37(9H)	3.89(3H)
XI	-143.5	-155.1	-162.0			-22.0		-21.3	1.57(27H)	3.76(3H)
XII	-144.5	-154.5	-161.5			-22.6		-21.0	2.10(3H); 2.36(6H)	2.44(3H)
XIII	-143.7	-154.6	-161.5			^b		^b	2.40(9H)	2.34(3H)
XIV	-143.5	-155.1	-161.9			-22.1		-20.8	1.49(18H); 1.54(9H)	2.40(3H)

^a ⁴J(F²-F⁴), ⁴J(F⁴-F⁶), inappreciable; signs are assigned according to ref. 21 and the fact that the spectra analysis shows ³J(F²-F³) and ³J(F²-F⁵) to be opposite in sign; J(M-N) stands for J(F^M-F^N). ^b Unresolved.

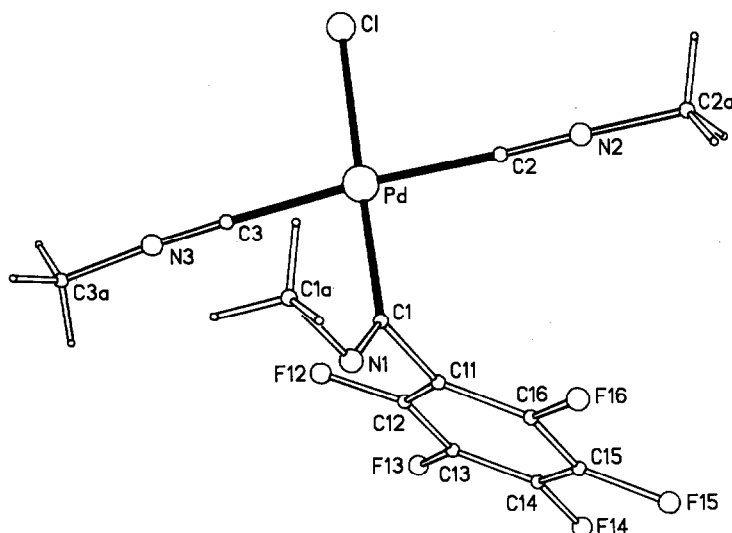


Fig. 1. Perspective view of the molecule of III in the crystal, showing the atom labelling scheme. Radii are arbitrary.



The ^1H NMR spectra of the mononuclear neutral complexes III–VIII reveal chemical equivalence of the two R^2 groups, which indicates a mutually *trans* disposition of the two isonitrile ligands. For the cationic complexes IX–XIV, signals of two different kinds of R^2 groups (2/1 ratio) are to be expected, but in complexes X, XI and XIII the chemical shift differences of the Me groups in these R^2 groups seem to be too small to be resolved; there is no need to invoke exchange between the CNR^2 ligands to explain this apparent equivalence since in the rest of the cationic complexes two distinct but very close signals are observed.

The IR spectra of the complexes show in all cases bands typical of the $\text{C}-\text{C}_6\text{F}_5$ group [1], the two at ca. 1500 cm^{-1} being the most characteristic. Bands appearing near 2200 cm^{-1} reveal the presence of the isonitrile ligand but are not very valuable as a structural probe because the various $\nu(\text{C}\equiv\text{N})$ vibrations [9] often coincide.

The $\nu(\text{C}=\text{N})$ and $\nu(\text{Pd}-\text{Cl})$ vibrations deserve careful consideration since they may indicate which ligands are bridging and which are terminal in the dimeric precursors. Our dimeric imido-bridged complexes $[\text{Pd}_2\{\mu-\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{R}^1)\}_2\text{Cl}_2(\text{CNR}^2)_2]$ generally display two $\nu(\text{C}=\text{N})$ absorptions in the range $1610\text{--}1570\text{ cm}^{-1}$ and also two $\nu(\text{Pd}-\text{Cl})$ vibrations in the range $325\text{--}280\text{ cm}^{-1}$. On the other hand, our terminal imido derivatives $[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{R}^1)\}(\text{CNR}^2)_2\text{Cl}]$ show one $\nu(\text{C}=\text{N})$ absorption in the range $1650\text{--}1620\text{ cm}^{-1}$, whereas $\nu(\text{Pd}-\text{Cl})$ appears at $286\text{--}269\text{ cm}^{-1}$. Thus $\nu(\text{C}=\text{N})$ in the monomers is ca. 30 cm^{-1} higher than

the highest of the two $\nu(\text{C}=\text{N})$ bands of the dimeric precursor, whereas $\nu(\text{Pd}-\text{Cl})$ in the monomers is generally lower than the lowest of the two $\nu(\text{Pd}-\text{Cl})$ of the dimeric precursor. It is instructive to compare this behaviour with related complexes in the literature.

A review of the imidoyl complexes of palladium described previously [3–7,10–15] shows that in complexes of the type $[\text{Pd}(\text{imidoyl})\text{ClL}_2]$ $\nu(\text{C}=\text{N})$ often appears in the range 1630–1600 cm^{-1} whereas complexes formulated as $[\text{Pd}_2(\mu\text{-Cl})_2(\text{imidoyl})_2\text{L}_2]$ usually display $\nu(\text{C}=\text{N})$ bands in the range 1580–1550 cm^{-1} . On the other hand several monomeric (and hence terminal imidoyl) complexes [5,13,15] lie outside this range, showing $\nu(\text{C}=\text{N})$ in the range 1600–1550 cm^{-1} . Moreover, only in one case have related dimeric and monomeric derivatives been described, namely $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{C}(\text{Ph})=\text{N}(\text{Ph})\}_2(\text{PPh}_3)_2]$ and *trans*- $[\text{PdCl}\{\text{C}(\text{Ph})=\text{N}(\text{Ph})\}(\text{PPh}_3)_2]$ [5]; the dimeric derivative displays two $\nu(\text{C}=\text{N})$ bands at 1609 and 1584 cm^{-1} whereas $\nu(\text{Pd}-\text{Cl})$ bands are reported at 276, 266 and 250 cm^{-1} ; the monomeric derivative shows one $\nu(\text{C}=\text{N})$ absorption at 1568 cm^{-1} (i.e. at lower frequency than the dimeric precursor) and $\nu(\text{Pd}-\text{Cl})$ at 275 cm^{-1} . The question arises whether $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{C}(\text{Ph})=\text{N}(\text{Ph})\}_2(\text{PPh}_3)_2]$ is a genuine chloro-bridged dimer or if the different behaviour of the $\nu(\text{C}=\text{N})$ frequencies when the bridges are cleaved has other causes.

The overall picture suggests that, although many complexes fit within the $\nu(\text{C}=\text{N})$ frequency ranges suggested above for terminal or bridging imidoyl groups respectively, this criterion is unreliable; several other factors can influence the $\nu(\text{C}=\text{N})$ frequencies, e.g. the different substituents at the carbon and the nitrogen atoms, the possible *syn-anti* isomerism, and the *trans* influence of the ligand *trans* to the imidoyl group. On the other hand the $\nu(\text{Pd}-\text{Cl})$ frequencies are also of very little value: low $\nu(\text{Pd}-\text{Cl})$ values are observed both in our dimeric complexes (with terminal $\text{Pd}-\text{Cl}$ bonds) and in all the mononuclear complexes (also with terminal $\text{Pd}-\text{Cl}$ bonds), doubtless as a consequence of the high *trans*-influence of the imidoyl ligand; hence the assignment of chloro-bridged structures for the dimeric imidoyl complexes described in the literature, which is based on the observation of low $\nu(\text{Pd}-\text{Cl})$ frequencies, cannot be taken as definitive.

In summary, the IR spectroscopic evidence does not allow reliable conclusions on the chloro-bridged or imidoyl-bridged nature of the dimeric complexes reported previously, but clearly points to the complex $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{C}(\text{Ph})=\text{N}(\text{Ph})\}_2(\text{PPh}_3)_2]$ as the best candidate for a conclusive X-ray diffraction study.

Reactions with PPh₃: elimination of isonitrile

Analogously to reaction (i) in Scheme 1, we attempted to split the imidoyl bridges in $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{PPh}_3)_2]$ [1] by treatment with PPh_3 in benzene. At room temperature the reaction was very slow and most of the starting material was recovered unchanged even after several days of treatment, but some odour of CNMe was detected. On refluxing, the rate of reaction increased, the colour of the solution changed from yellow to reddish and the odour of CNMe became stronger. A similar behaviour was observed on refluxing $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{PPh}_3)_2]$ in benzene in the absence of additional free PPh_3 . The results of several reactions are summarized below (yields of complexes are relative to Pd in the starting complexes; OPPh_3 are relative to the starting additional PPh_3).

(a) $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{PPh}_3)_2]$ refluxed in benzene for 10 h gave: 44% of starting material; 16% of *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$; the rest was isolated as a

mixture which might contain (IR spectroscopy) the two former complexes and $[\text{Pd}_2(\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me}))_2\text{Cl}_2(\text{CNMe})_2]$.

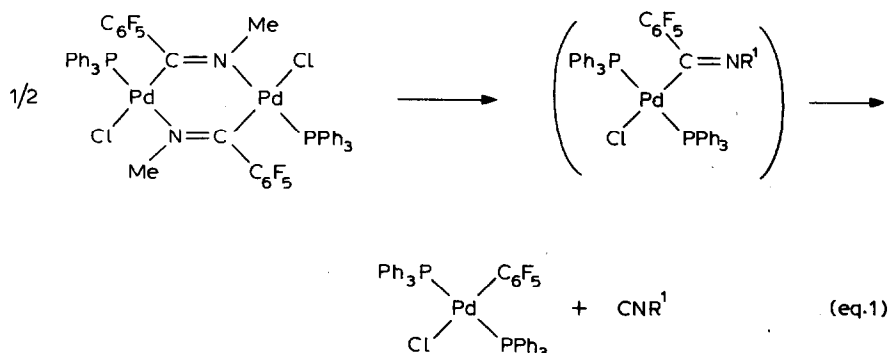
(b) $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{PPh}_3)_2]$ refluxed in benzene for 80 h gave: 10% of *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$; 17% of $[\text{Pd}_2(\mu\text{-Cl})_2(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2]$; the remainder was intractable.

(c) $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{PPh}_3)_2]$ plus PPh_3 ($\text{Pd}/\text{PPh}_3 = 1/1$) refluxed in benzene for 10 h gave: 10% of starting complex; 43% of *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$; 12% of OPPh_3 ; the remaining mixture contained (IR spectroscopy) some starting complex and some *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$, but also unidentified materials.

(d) $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Me})\}_2\text{Cl}_2(\text{PPh}_3)_2]$ plus an excess of PPh_3 ($\text{Pd}/\text{PPh}_3 = 1/3$) refluxed in benzene for 18 h gave: 52% of *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$; 23% of OPPh_3 ; the large content of PPh_3 and OPPh_3 in the residue precluded separation of other identifiable products.

In all reactions an intense odour of CNMe could be detected and traces of black Pd were formed. A treatment of $[\text{Pd}_2\{\mu\text{-C}(\text{C}_6\text{F}_5)=\text{N}(\text{Tol})\}_2\text{Cl}_2(\text{PPh}_3)_2]$ as described in (c) gave 38% of *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$ and an intractable mixture.

These results suggest that the first step in the elimination of isonitrile is the splitting of the imidoyl bridges by PPh_3 to give an unstable mononuclear intermediate, $[\text{Pd}\{\text{C}(\text{C}_6\text{F}_5)=\text{N}(\text{R}^1)\}\text{Cl}(\text{PPh}_3)_2]$ which spontaneously undergoes isonitrile elimination (eq. 1).



In the presence of additional PPh_3 the yield of *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$ increases and the isonitrile liberated possibly polymerizes. When additional PPh_3 is not present it has to be provided by other molecules of the starting material. This lack of PPh_3 is reflected in lower rate and yields of the elimination process, formation of the less PPh_3 -demanding $[\text{Pd}_2(\mu\text{-Cl})_2(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2]$, and detection of complexes containing isonitrile, which has filled the positions left vacant by the liberation of PPh_3 from part of the starting material. The formation of OPPh_3 is not surprising under the conditions used; moreover it is well known [16,17] that palladium(0) species catalyse the oxidation of PPh_3 .

This elimination of an isonitrile is unprecedented in palladium chemistry, in contrast with the related elimination of CO from acyl derivatives of palladium, many examples of which are known [18]. The C_6F_5 group seems to promote the elimination, and this is supported by the observations that many acyl derivatives can be obtained by oxidative addition of acyl chlorides to palladium(0) complexes, although the reaction of $[\text{Pd}(\text{PPh}_3)_4]$ with ClCOC_6F_5 leads to *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}(\text{PPh}_3)_2]$

(instead of the expected *trans*-[Pd(COC₆F₅)Cl(PPh₃)₂], which could not be detected [19]).

Experimental

C, H and N analyses were determined with a Perkin–Elmer 240 microanalyser. Conductivities were measured in approx. 5×10^{-4} M solutions with a Philips PW 9501/01 conductimeter. IR spectra (4000–200 cm⁻¹) were recorded on a Perkin–Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Varian XL-200 spectrometer. The organic isonitriles were prepared by standard methods [20]. Typical methods of preparation of the complexes are described below.

*Preparation of [Pd₂{μ-C(C₆F₅)=N(Me)}₂Cl₂(CNR²)₂]; R² = *p*-Tol (I), Bu^t (II)*

These complexes were prepared as reported earlier for R¹ = Me, method (i) in ref. [1].

Preparation of trans-[Pd{C(C₆F₅)=N(R¹)}Cl(CNR²)₂] (III–VIII)

The stoichiometric amount of isonitrile (Pd/CNR² = 1/1) was added to a solution of [Pd₂{μ-C(C₆F₅)=N(Me)}₂Cl₂(CNR²)₂] or a suspension of [Pd{μ-C(C₆F₅)=N(Tol)}Cl(CNR²)₂]_n (ca. 200 mg) in CH₂Cl₂ (ca. 15 ml), whereupon a colourless solution was formed. On evaporation in vacuo to ca. 1 ml, addition of n-hexane (20 ml) and stirring, a white solid was formed which was filtered, repeatedly washed with n-hexane and air dried.

For complex IV the resulting CH₂Cl₂ solution was yellowish and was purified by filtration through a 5 cm silica gel column. The filtrate was evaporated to dryness and treated with n-hexane to give IV.

All the complexes were stored at –25°C.

Preparation of [Pd{C(C₆F₅)=N(R¹)}(CNR²)₃]X (IX–XIV)

(a) *Compounds IX and XII.* A solution of [Pd{C(C₆F₅)=NR¹}Cl(CNMe)₂] (ca. 100 mg) in CH₂Cl₂ (ca. 20 ml) was stirred with the stoichiometric amount of CNMe and a slight excess of NaBPh₄ for 8 h. The white precipitate was filtered off and the solution was evaporated to dryness; addition of n-hexane to the residue gave complexes IX or XIV.

(b) *Compounds X, XI, XIII and IV.* A solution of [Pd{C(C₆F₅)=NR¹}Cl(CNR²)₂] (ca. 100 mg) in acetone (ca. 20 ml) was stirred with the stoichiometric amount of CNR² and a slight excess of NaClO₄ for 2 h. Evaporation to dryness, extraction with CH₂Cl₂ (ca. 20 ml) and filtration rendered a colourless solution from which the complexes were isolated as white solids by evaporation to dryness, addition of n-hexane and filtration.

X-Ray structure determination of trans-[Pd{C(C₆F₅)=NMe}Cl(CNMe)₂] (III)

Crystal data

Monoclinic, C2/c, *a* 19.123(6), *b* 8.425(3), *c* 20.980(6) Å, β 112.39(2)°, *U* 3125 Å³, *Z* = 8, *D_x* 1.84 g cm⁻³, *F*(000) = 1680, μ(Mo-K_α) 1.4 mm⁻¹.

Colourless plates were obtained by diffusion of cyclohexane into a dichloro-

TABLE 4

ATOM COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR III

Atom	x/a	y/b	z/c	U^a
Pd	3916(1)	3309(1)	263(1)	46(1)
Cl	3191(1)	5034(1)	-667(1)	63(1)
C(1)	4503(2)	1847(4)	1044(2)	50(1)
N(1)	5130(2)	1184(4)	1150(2)	59(1)
C(1a)	5511(2)	1502(6)	685(3)	72(2)
C(2)	3254(2)	1473(5)	-180(2)	51(1)
N(2)	2885(2)	437(4)	-448(2)	55(1)
C(2a)	2419(3)	-903(5)	-778(3)	74(2)
C(3)	4649(2)	4996(5)	753(2)	55(1)
N(3)	5079(2)	5921(4)	1048(2)	60(1)
C(3a)	5641(3)	7031(6)	1454(3)	81(2)
C(11)	4119(2)	1483(5)	1530(2)	53(1)
C(12)	3977(2)	2644(5)	1936(2)	59(1)
C(13)	3610(2)	2344(6)	2370(2)	69(2)
C(14)	3358(3)	837(7)	2402(2)	74(2)
C(15)	3486(2)	-349(5)	2008(2)	69(2)
C(16)	3859(2)	-29(5)	1579(2)	57(1)
F(12)	4226(2)	4138(3)	1928(1)	79(1)
F(13)	3506(2)	3482(4)	2761(2)	104(2)
F(14)	3003(2)	488(5)	2825(2)	114(2)
F(15)	3240(2)	-1833(4)	2047(1)	96(1)
F(16)	3949(2)	-1201(3)	1192(1)	79(1)

^a Equivalent isotropic U calculated from anisotropic U .

methane solution of III containing excess MeNC. Because of slow MeNC loss to the air, crystals were sealed in glass capillaries. A crystal $0.75 \times 0.45 \times 0.08$ mm was used to collect 3686 profile-fitted [22] intensities on a Stoe-Siemens four-circle diffractometer (monochromated Mo- K_α radiation; $2\theta_{\text{max}}$ 55°). After L_p and absorption corrections (ψ -scans) averaging equivalents gave 3588 unique reflections, of which 2863 with $F > 4\sigma(F)$ were used for all calculations. Cell constants were refined from 2θ values of 32 reflections in the range 20 – 23° .

The structure was solved by conventional heavy-atom methods and refined to R 0.037, R_w 0.038 [all non-H atoms anisotropic, H isotropic with rigid methyl groups (C–H 0.96 Å, H–C–H 109.5° , $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$), weighting scheme $w^{-1} = \sigma^2(F) + 0.0003F^2$]. Final atomic coordinates and derived parameters are given in Tables 4 and 5*.

The palladium atom displays the usual square planar coordination, lying < 0.01 Å out of the mean plane of Cl, C(1), C(2), C(3). The Pd–Cl bond is amongst the longest observed in square planar complexes (2.404 Å, cf. the usual range 2.27–2.41 Å [1]), in agreement with the low $\nu(\text{Pd–Cl})$. In contrast, the C=N bond length of 1.264 Å is not, as might have been expected from the high $\nu(\text{C=N})$, particularly short; the same value is observed in one C=N bond of the dimer $[\text{Pd}_2\{\mu-$

* Further crystallographic details (structure factors, H atom coordinates, temperature factors) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, F.R.G. Please quote reference number CSD/51200 and the full literature citation.

TABLE 5
BOND LENGTHS (Å) AND ANGLES (deg.) FOR III

Cl-Pd	2.404(2)	C(1)-Pd	2.016(4)
C(1)-N(1)	1.264(6)	C(1)-C(11)	1.497(8)
C(1a)-N(1)	1.447(9)	C(2)-Pd	1.990(5)
C(2)-N(2)	1.129(6)	C(2a)-N(2)	1.441(6)
C(3)-Pd	1.987(5)	C(3)-N(3)	1.132(6)
C(3a)-N(3)	1.434(7)	C(11)-C(12)	1.391(7)
C(11)-C(16)	1.385(7)	C(12)-C(13)	1.368(9)
C(12)-F(12)	1.348(6)	C(13)-C(14)	1.369(9)
C(13)-F(13)	1.324(7)	C(14)-C(15)	1.377(9)
C(14)-F(14)	1.339(8)	C(15)-C(16)	1.372(8)
C(15)-F(15)	1.349(7)	C(16)-F(16)	1.331(6)
Cl-Pd-C(1)	178.8(2)	Cl-Pd-C(2)	91.4(2)
C(1)-Pd-C(2)	87.9(2)	Cl-Pd-C(3)	93.6(2)
C(1)-Pd-C(3)	87.2(2)	C(2)-Pd-C(3)	174.7(2)
Pd-C(1)-N(1)	127.6(5)	Pd-C(1)-C(11)	114.4(4)
N(1)-C(1)-C(11)	117.9(4)	C(1)-N(1)-C(1a)	119.1(5)
Pd-C(2)-N(2)	177.8(5)	C(2)-N(2)-C(2a)	178.9(5)
Pd-C(3)-N(3)	177.8(4)	C(3)-N(3)-C(3a)	176.7(5)
C(1)-C(11)-C(12)	122.3(5)	C(1)-C(11)-C(16)	121.5(5)
C(12)-C(11)-C(16)	116.2(5)	C(11)-C(12)-C(13)	123.2(5)
C(11)-C(12)-F(12)	119.7(5)	C(13)-C(12)-F(12)	117.1(5)
C(12)-C(13)-C(14)	118.9(6)	C(12)-C(13)-F(13)	120.9(6)
C(14)-C(13)-F(13)	120.2(6)	C(13)-C(14)-C(15)	119.9(6)
C(13)-C(14)-F(14)	120.8(6)	C(15)-C(14)-F(14)	119.3(6)
C(14)-C(15)-C(16)	120.4(6)	C(14)-C(15)-F(15)	119.4(6)
C(16)-C(15)-F(15)	120.2(5)	C(11)-C(16)-C(15)	121.4(5)
C(11)-C(16)-F(16)	120.3(5)	C(15)-C(16)-F(16)	118.3(5)

$C(C_6F_5)=NMe)Cl_2(tht)_2$ [1]. The inherent imprecision of light atom bond lengths tends however to reduce their significance; thus in the latter dimer the other, chemically equivalent, C=N bond length is 1.280 Å.

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References

- 1 R. Usón, J. Forniés, P. Espinet, E. Lalinde, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1982) 2389.
- 2 R. Usón, J. Forniés, P. Espinet and E. Lalinde, *J. Organomet. Chem.*, 254 (1983) 371.
- 3 T. Boschi and B. Crociani, *Inorg. Chim. Acta*, 5 (1971) 477.
- 4 T. Kajimoto, J. Takahashi and J. Tsuji, *J. Organomet. Chem.*, 23 (1970) 275.
- 5 B. Crociani, M. Nicolini and T. Boschi, *J. Organomet. Chem.*, 33 (1971) C81.
- 6 B. Crociani, M. Nicolini and R.L. Richards, *J. Organomet. Chem.*, 104 (1976) 259.
- 7 S. Otsuka, A. Nakamura and T. Yoshida, *J. Am. Chem. Soc.*, 91 (1969) 7198.
- 8 R. Usón, J. Forniés, P. Espinet, E. Lalinde, P.G. Jones and G.M. Sheldrick, *J. Organomet. Chem.*, 253 (1983) C47.

- 9 R. Usón, J. Forniés, P. Espinet and E. Lalinde, *J. Organomet. Chem.*, 220 (1981) 393 and ref. therein.
- 10 Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 13 (1974) 438.
- 11 A. Mantovani and B. Crociani, *J. Organomet. Chem.*, 236 (1982) C37.
- 12 S. Otsuka and K. Ataka, *J. Chem. Soc., Dalton Trans.*, (1976) 327.
- 13 M. Tanaka and M. Alper, *J. Organomet. Chem.*, 168 (1979) 97.
- 14 A. Mantovani and B. Crociani, *J. Organomet. Chem.*, 236 (1982) C37.
- 15 A. Mantovani, L. Calligaro and A. Paschetto, *Inorg. Chim. Acta*, 76 (1983) L145.
- 16 G. Wilke, H. Shott and P. Heimbach, *Angew. Chem. Int. Ed. Engl.*, 6 (1967) 92.
- 17 K. Kikukawa and T. Matsuda, *J. Organomet. Chem.*, 235 (1982) 243.
- 18 A. Wojciki, *Adv. Organomet. Chem.*, 11 (1973) 87.
- 19 A.J. Mukhadkar, M. Green and F.G.A. Stone, *J. Chem. Soc. (A)*, (1969) 3023.
- 20 W.P. Weber, G.W. Gokel and I.K. Ugi, *Angew. Chem. Int. Ed. Engl.*, 11 (1972) 530.
- 21 R.E. Banks and M.G. Barlow, "Fluorocarbon and Related Chemistry", The Chemical Society 1971, Vol. 1, p. 289.
- 22 W. Clegg, *Acta Cryst.*, A37 (1981) 22.