MeNC Insertion into Pd–C_6F_5 Bonds: Bis(μ-imidoyl-*C,N*)palladium Complexes, a Novel Type of Imidoyl Co-ordination in Palladium Chemistry. Single-crystal *X*-Ray Structure of $[Pd_2\{\mu\text{-}C(C_6F_5)=N(Me)\}_2Cl_2(SC_4H_8)_2]$†

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The complex *cis*- or *trans*-$[Pd(C_6F_5)_2(CNMe)_2]$ reacts with $PdCl_2$ or $[PdCl_2(NCPh)_2]$ to give $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNMe)_2]$ which in turn undergoes MeNC insertion to give *cis*-$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)=N(Me)]_2\}_n]$. The latter undergoes cleavage of the chloro-bridges by neutral ligands [L = CNMe, NMe_3, py, 4Me-py, 4Bu^t-py (py = pyridine), PPh_3, and SC_4H_8] affording dimeric complexes $[LClPd\{C(C_6F_5)=N(Me)\}\{(Me)N=C(C_6F_5)\}PdClL]$. {For L = CNMe the complex can also be obtained by heating *trans*-$[Pd(C_6F_5)Cl(CNMe)_2]$.} The polymer also reacts with Tl(acac) (acac = acetylacetonate) or $Ag(O_2CMe)$ affording the corresponding imidoyl-bridged dimers. The ^1H n.m.r. spectra show a mixture of two isomers for L = py, 4Me-py, and 4Bu^t-py; the four ^{19}F n.m.r. spectra recorded reveal restricted rotation for the C_6F_5 group. The bridging location of the imidoyl groups has been ascertained by a single-crystal *X*-ray structure determination of the complex with L = SC_4H_8 (tetrahydrothiophen), which crystallizes in the monoclinic space group $P2_1/c$, with unit-cell dimensions a = 9.304(2), b = 9.563(2), c = 34.979(5) Å, β = 95.76(2)°, and Z = 4. The structure was solved by the heavy-atom method and refined to R = 0.040 for 3 978 observed reflections.

The M–C bonds between transition metals and perfluoroaryl ligands have proved to be remarkably inert towards insertion reactions,[1] particularly when M = Pd or Pt.[2-4] When the present work was already in progress,[5] the insertion of cyclohexyl isocyanide into Ti–C_6F_5 bonds, claimed to be the first example of such a reaction, was reported.[6] However, a few pentafluoro-*N*-methylbenzimidoyliron(II) complexes had been described before,[7] although possibly formed *via* direct attack by $Li(C_6F_5)$ on the co-ordinated isonitrile in the $[Fe(C_5H_5)(CO)(CNMe)_2]PF_6$ precursor.

In the present paper we describe the synthesis of pentafluoro-*N*-methylbenzimidoylpalladium derivatives with the imidoyl groups acting as C,N bridges between two palladium atoms, by MeNC insertion into Pd–C_6F_5 bonds. Since all the imidoylpalladium complexes hitherto reported have been formulated as either mononuclear complexes $[Pd\{C(R)=N(R')\}X(L)L']$ (X = halide) or binuclear halide-bridged complexes $[Pd_2(\mu\text{-}X)_2\{C(R)=N(R')\}_2L_2]$, the compounds described here represent a novel type of co-ordination for the imidoyl group in palladium chemistry.

Results and Discussion

Addition of MeNC to the appropriate precursors affords complexes *cis*-$[Pd(C_6F_5)_2(CNMe)_2]$ (1) and *trans*-$[Pd(C_6F_5)_2(CNMe)_2]$ (2) in virtually quantitative yields, as recently described for similar complexes.[4] Alternatively, complexes (1) and (2) can be prepared by methylating *cis*- and *trans*-$[NBu^n_4]_2[Pd(C_6F_5)_2(CN)_2]$[8] respectively with MeI (*ca.* 65% yield) or Me_3OBF_4 (*ca.* 90% yield), a method which avoids the use of free MeNC and had been applied to the synthesis of some platinum complexes.[9]

Starting from the above derivatives, the syntheses of several types of pentafluoro-*N*-methylbenzimidoyl derivatives were accomplished (Scheme). Complexes (1) and (2) react with $PdCl_2$ or, better and faster, with $[PdCl_2(NCPh)_2]$ in refluxing benzene to give a red solution from which a red product can be isolated; this product analyses as $[\{PdCl(C_6F_5)(CNMe)\}_n]$ and we formulate it as an insertion product (5), in accord with the following observations (Table 2): (*a*) absence of i.r. absorptions in the $\nu(C\equiv N)$ region (*ca.* 2 250 cm^{-1}) and the presence of *two* absorptions ($A + B$ modes) ‡ in the $\nu(C=N)$ region (*ca.* 1 600 cm^{-1}); (*b*) shift and splitting of i.r. absorptions typical of the Pd–C_6F_5 group (*ca.* 1 630, 1 500, 1 060, 950, and 780 cm^{-1})[10] to values characteristic of the C–C_6F_5 group and closely coincident with those observed for pentafluoro-*N*-methylbenzimidoyliron complexes (*ca.* 1 650, 1 515, 1 490, 1 130, 990, 950, and 825 cm^{-1});[7] (*c*) appearance of *two* i.r. absorptions in the ν(Pd–Cl)-bridging region (*ca.* 250 cm^{-1}). The complex is an imidoylpalladium derivative containing chloro-bridges; in order to achieve a co-ordination number of four, the imidoyl group has to be *C,N* bonded; the alternative formulation as a chloro-bridged dimer with an η^2-imidoyl group on each palladium atom has to be discounted as this type of co-ordination leads to higher $\nu(C=N)$ frequencies (*ca.* 1 700—1 650 cm^{-1}).[6,11]

We have previously communicated that the reaction of complexes $[Pd(C_6F_5)_2L_2]$ and $PdCl_2$ leading to dimeric complexes $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2L_2]$ is a fairly general process,[12] so it seems reasonable to think of a dimer of this type as an intertermediate in the formation of the polymeric imidoyl complex

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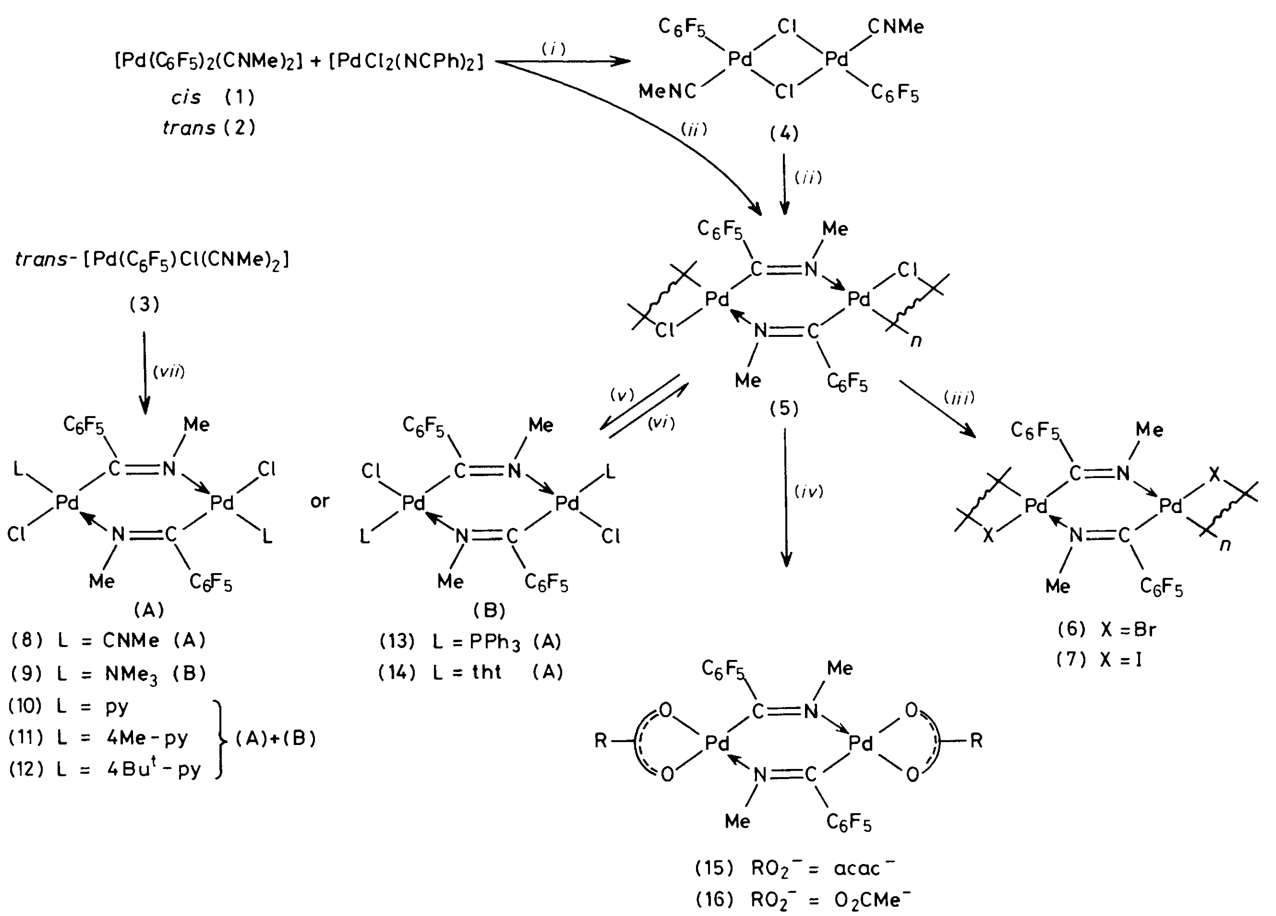
† *trans*-Bis(μ-pentafluoro-*N*-methylbenzimidoyl-*C,N*)-bis[chloro-(tetrahydrothiophen-*S*)palladium(II)].

Supplementary data available (No. SUP 23415, 30 pp): H-atom co-ordinates, thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ Assuming C_2 symmetry for the repeating unit containing two Pd atoms.



Scheme. (*i*) Acetone, room temperature (r.t.), 17 h; (*ii*) benzene, reflux, *ca.* 2 h; (*iii*) LiX or KX in excess; (*iv*) Tl(acac) or Ag(O_2CMe); (*v*) stoicheiometric quantity of L, acetone, r.t.; (*vi*) L = NMe_3, under vacuum; (*vii*) L = CNMe, benzene reflux *ca.* 5 h; tht = tetrahydrothiophen

Table 1. Analytical and molecular-weight data (calculated values in parentheses) and yields

Complex	Analysis (%) N	C	H	*M* (in C_6H_6)	Yield (%)
(1) *cis*-[Pd(C_6F_5)$_2$(CNMe)$_2$]	5.25 (5.35)	36.3 (36.75)	1.25 (1.15)		65
(2) *trans*-[Pd(C_6F_5)$_2$(CNMe)$_2$]	5.50 (5.35)	37.1 (36.75)	1.30 (1.15)		80
(3) *trans*-[Pd(C_6F_5)Cl(CNMe)$_2$]	7.10 (7.15)	31.1 (30.7)	1.75 (1.55)		90
(4) [Pd$_2$(μ-Cl)$_2$(C_6F_5)$_2$(CNMe)$_2$]	4.10 (4.00)	27.7 (27.45)	1.10 (0.85)		54
(5) [{Pd$_2$(μ-Cl)$_2$[μ-C(C_6F_5)=N(Me)]$_2$}$_n$]	4.00 (4.00)	27.3 (27.45)	1.05 (0.85)		93
(6) [{Pd$_2$(μ-Br)$_2$[μ-C(C_6F_5)=N(Me)]$_2$}$_n$]	3.35 (3.55)	24.85 (24.35)	0.95 (0.75)		52
(7) [{Pd$_2$(μ-I)$_2$[μ-C(C_6F_5)=N(Me)]$_2$}$_n$]	3.25 (3.15)	22.1 (21.75)	0.80 (0.70)		58
(8) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$Cl$_2$(CNMe)$_2$]	7.15 (7.15)	31.0 (30.7)	1.75 (1.55)		79
(9) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$Cl$_2$(NMe$_3$)$_2$]	6.85 (6.85)	32.3 (32.3)	2.95 (2.95)		85
(10) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$Cl$_2$(py)$_2$]	6.20 (6.55)	36.0 (36.4)	1.95 (1.90)	883 (858.13)	82
(11) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$Cl$_2$(4Me-py)$_2$]	6.25 (6.30)	38.1 (37.95)	2.45 (2.25)		72
(12) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$Cl$_2$(4Bu^t-py)$_2$]	5.85 (5.75)	42.6 (42.1)	3.55 (3.30)		76
(13) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$Cl$_2$(PPh$_3$)$_2$]	2.00 (2.30)	50.8 (51.0)	3.15 (2.95)		75
(14) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$Cl$_2$(tht)$_2$]	3.30 (3.20)	33.0 (32.9)	2.60 (2.55)	896 (876.27)	90
(15) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$(acac)$_2$]	3.45 (3.40)	38.05 (37.75)	2.55 (2.45)	847 (827.24)	70
(16) [Pd$_2${μ-C(C_6F_5)=N(Me)}$_2$(O$_2$CMe)$_2$]	3.80 (3.75)	32.35 (32.15)	1.55 (1.60)		76

(5). Indeed, by mixing [Pd(C_6F_5)$_2$(CNMe)$_2$] and [PdCl$_2$(NCPh)$_2$] in acetone at room temperature the white complex (4) could be isolated, fully identified, and finally transformed into the red (5) by heating it in benzene at reflux temperature. These facts strongly suggest the intermediacy of (4) in the formation of complex (5).

Complex (5) reacts with LiBr or KI in acetone to give yellow solutions from which the deep red products (6) or (7) separate on evaporation.

More interestingly, treatment of (5) with Tl(acac) (acac = acetylacetonate) or Ag(O_2CMe) leads to the formation of yellow products fairly soluble in organic solvents, and dimeric in nature as revealed by molecular-weight determinations. Their formulation as (15) and (16) follows straightforwardly

Table 2. I.r. absorptions (cm^{-1}) (solid in Nujol, unless otherwise stated)

Complex	ν(C≡N)	ν(C=N)	ν(Pd–Cl)	C_6F_5						Other intense absorptions
(1)	2 240vs,br [a]			1 629m,	1 495vs,		1 055vs,br,	952vs,	785 (sh), 778vs	457s, 430s, 343m
(2)	2 244vs [b]			1 632m,	1 494vs,		1 060vs,br,	962vs, 950 (sh)	770vs	491m, 478vs, 329m
(3)	2 255vs,br		310vs	1 632m,	1 505vs,		1 075 (sh), 1 063vs	957vs, 940s	792vs	473s
(4)	2 272vs,br, 2 235 (sh)		290vs, 280vs	1 633m,	1 503vs,		1 065vs,	958vs,	799vs	445s, 388m
(5)		1 608s, 1 596vs	255 (sh), 250m	1 649s,	1 516vs,	1 494vs,	1 135vs,	989vs, 950s	826vs, 818vs	
(6)		1 605s, 1 593vs		1 649s,	1 516vs,	1 495vs,	1 133vs,	988vs, 952s	824vs, 817vs	
(7)		1 603 (sh), 1 592vs		1 655s,	1 515vs,	1 493vs,	1 132vs,	988vs, 950s	823vs, 816vs	
(8)	2 251vs	1 606s, 1 590vs	295 (sh), 282s	1 648s,	1 515vs,	1 492vs,	1 130vs,	990vs, 952s	825vs	352m, 340m, 327m
(9)		1 587vs	327s	1 648s,	1 515vs,	1 492vs,	1 130vs,	985vs, 950s	823vs	508s, 300m
(10)		1 595vs [c]	331s, 297m	1 645s,	1 510vs,	1 488vs,	1 128vs,	985vs, 952s	826vs, 821m	1 603vs, 761vs, 754 (sh)
(11)		1 593vs [c]	326s, 298m	1 646s,	1 510vs,	1 488vs,	1 127vs,	983vs, 950s	827vs [c]	1 620vs, 1 207s, 813s, 493s
(12)		1 580vs [c]	335 (sh), 322m	1 644s,	1 513vs,	1 489s,	1 130vs,	984vs, 950s	826vs [c]	1 612vs, 834vs, 565m
(13)		1 588s, 1 574vs	300w, 290s, 277m	1 647s	1 515vs,	1 489vs,	1 120vs,	985vs, 940s	823vs, 818s	1 096vs, 766vs, 749s, 740 (sh), 703vs, 687vs, 528vs, 510vs, 495s
(14)		1 596vs	285 (sh), 273m	1 650s,	1 517vs,	1 493vs,	1 128vs,	984vs, 946s	822vs	1 271m, 1 254m, 775s
(15)		*d*		1 650s,	1 510vs,	1 490vs,	1 120vs,	980vs, 950s	828vs	1 585vs,vbr, 934s, 786vs, 776vs, 622s, 449vs
(16)		*d*		1 648s,	1 512vs,	1 495vs,	1 119vs,	985vs, 952s	831vs	1 600vs,br, 681vs, 320s, 301m

[a] 2 246vs and 2 230vs cm^{-1} in $CHCl_3$. [b] 2 243 cm^{-1} in C_6H_6. [c] Intense absorptions due to the pyridine ligands preclude observation of other possible bands in this range. [d] Overlap with ν(C=C) and/or ν(C=O) absorptions by the acac$^-$ or O_2CMe^- groups preclude assignment.

Table 3. Proton n.m.r. data (δ, in $CDCl_3$, unless otherwise stated)

Complex	C=NMe	Ligands other than imidoyl or isonitrile
(9)	3.35 (s, 3 H)	2.65 (s, 9 H, Me)
(10)	3.16 (s, B, 82%) + 3.36 (s, A, 18%) (3 H)	7.44 (m, 2 H, *ortho*), 7.75 (m, 1 H, *para*), 8.99 (m, 2 H, *meta*)
(11)	3.05 (s, B, 80%) + 3.37 (s, A, 20%) (3 H)	2.38 (s, A + B, 3 H, Me), 7.23 (d, A + B, 2 H, *ortho*), 8.80 (d, A + B, 2 H, *meta*) [$J(H_o-H_m)$ 5.8 Hz]
(12)	3.10 (s, B, 75%) + 3.38 (s, A, 25%) (3 H)	1.30 (s, A + B, 9 H, Bu^t), 7.40 (d, A + B, 2 H, *ortho*), 8.85 (d, A + B, 2 H, *meta*) [$J(H_o-H_m)$ 6.6 Hz]
(13)	3.46 [t′, 3 H, ^4J(P–H) ≈ 5, J(P–H) ≈ 3.0 Hz]	7.36—7.83 (m, 15 H)
(14)	3.41 (s, 3 H)	2.19 (m, 4 H), *ca.* 3.5 (br m, 4 H)
(15)	3.29 (s, 3 H)	1.78 (s, 3 H, Me), 1.96 (s, 3 H, Me), 5.66 (s, 1 H, –CH=)
(16)	3.30 (s, 3 H)	1.73 (s, 3 H)

For complexes (1)—(4) and (8), δ(C≡NMe) 3.38(s), 3.32(s), 3.41(s), 3.37(s), and 3.34(s) respectively; for (5) and (8), δ(C=NMe) 3.48(s) (in [$^2H_6$]acetone) and 3.43(s). *t′* = Apparent triplet.

and is consistent with their i.r. and ^{1}H n.m.r. spectra (Tables 2 and 3).

The persistence of the imidoyl double bridges during these reactions suggests a remarkable stability for this structure. On the other hand, all the dimeric imidoylpalladium derivatives so far reported in the literature have been formulated as containing chloro-bridges and terminal imidoyl groups, $[Pd_2(\mu-Cl)_2\{C(R)=N(R')\}_2L_2]$.[13–17] Consequently, it was interesting to test whether treatment of complex (5) with neutral ligands L would cleave the chloro- or the imidoyl bridges.

The Scheme summarizes the stoicheiometric reactions between complex (5) and ligands L at room temperature, (*v*), that lead to cleavage solely of the chloro-bridges. The structures of complexes (8)—(14) are proposed in keeping with their i.r., ^{1}H n.m.r., and (in part) ^{19}F and ^{13}C n.m.r. data (Tables 2—4), and the results of a single-crystal *X*-ray diffraction study of complex (14) (see below). For complexes (8), (13), and (14) the ^{1}H n.m.r. spectra reveal the presence of only one isomer, whereas their i.r. spectra show two ν(Pd–Cl) absorptions below 300 cm^{-1} (corresponding to the two active modes *A* + *B* predicted for C_2 symmetry); consequently we assign to these complexes structure (A), with the Cl atom in the *trans*

Table 4. Fluorine-19 n.m.r. chemical shifts for some of the complexes [a]

Complex	L	Isomer	F^2	F^6	F^4	F^3	F^5	$\delta(F^2) - \delta(F^6)$
(8)	CNMe	(A)	−141.93	−143.94	−153.41	−160.07	−161.14	2.01
(10)	py	(A)	−139.94	−142.89	−153.59	−160.62	−161.86	2.95
	py	(B)	−138.22	−143.61	−154.56	−162.08	−162.35	5.39
(11)	4Me-py	(A)	−139.17	−142.40	−153.31	−160.23	−161.24	3.23
	4Me-py	(B)	−137.48	−142.93	−154.05	−161.38	−161.64	5.45
(14) [b]	tht	(A)	−138.37	−142.26	−153.12	−160.67	−161.21	3.89

[a] In $CDCl_3$, reference $CFCl_3$; for atom labelling, see Figure 1. [b] Full analysis of this spectrum gave: $^3J(F^2-F^3) = 23.1$, $^3J(F^5-F^6) = 24.6$, $^3J(F^3-F^4) \approx {}^3J(F^5-F^4) = 20.8$, $^4J(F^2-F^4) \approx {}^4J(F^6-F^4) = 1.7$, $^4J(F^3-F^5) \approx {}^4J(F^2-F^6) \approx 0$, and $^5J(F^3-F^6) \approx {}^5J(F^2-F^5) \approx 8.5$ Hz.

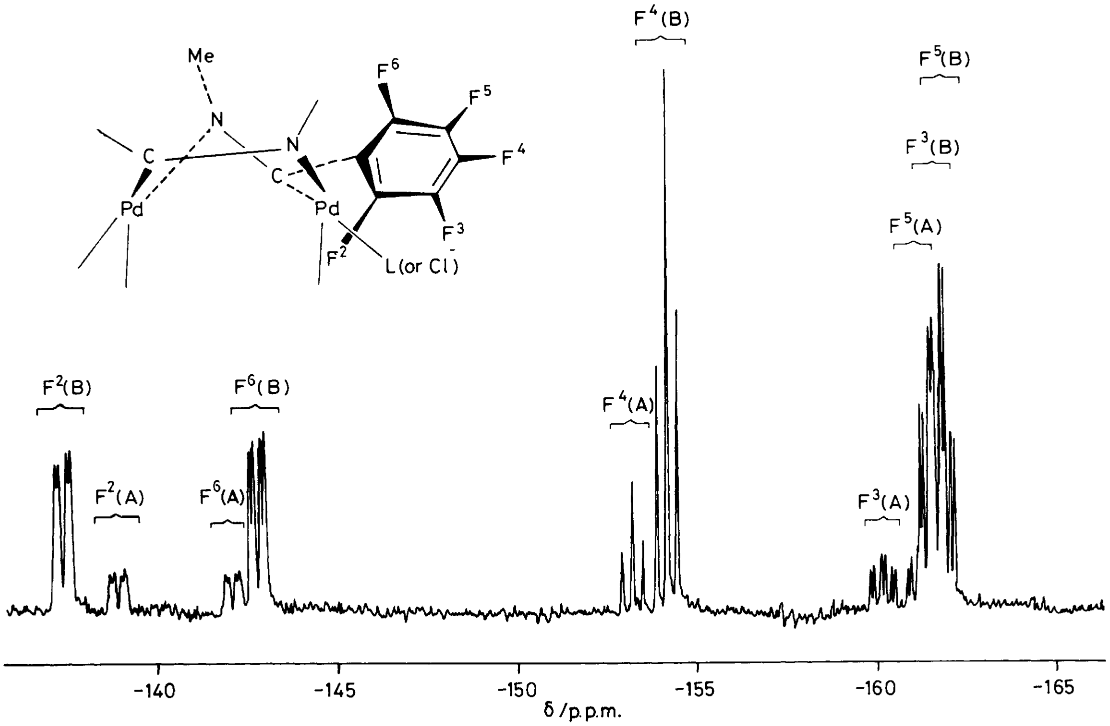


Figure 1. Fluorine-19 n.m.r. spectrum of complex (11) in $CDCl_3$

position to the atom in the bridge with the highest *trans* influence, *i.e.* the carbon atom; this is in fact the structure determined by *X*-ray diffraction for complex (14) (Figure 2), and the long Pd–Cl distances (mean 2.375 Å) reveal a moderately high *trans* influence for the carbon atom in the imidoyl group;[18] hence comparatively low ν(Pd–Cl) frequencies are to be expected for (A) isomers. Complex (8) can also be obtained by heating *trans*-$[Pd(C_6F_5)Cl(CNMe)_2]$ in refluxing benzene.

Complex (9), which slowly loses NMe_3 even in the solid state regenerating (5), exhibits only one isomer according to its ^1H n.m.r. spectrum, but the observation of ν(Pd–Cl) at 327 cm^{-1} suggests structure (B), with the Cl atom in the *trans* position to the ligand with the lowest *trans* influence.

Finally, for the pyridine or 4-substituted pyridine complexes (10)—(12) the ^1H and ^{19}F n.m.r. spectra (Tables 3 and 4 and Figure 1) reveal the presence of two isomers in solution [20—25% (A) + 80—75% (B)] that are also observed in the only ^{13}C n.m.r. spectrum recorded [complex (10) ($CDCl_3$, reference $SiMe_4$): C(imidoyl) δ 191.90 (B), (A) not observed; $C^1 + C^5$(py) 152.98 (A) + 151.48 (B); C^3(py) 138.42 (A + B); $C^2 + C^4$(py) 125.55 (A) + 127.16 (B); C(Me) 47.24 (A) + 46.79 (B)].

These structural assignments are in agreement with the expectations from the antisymbiotic behaviour generally observed for class b metal ions, which show a tendency for the two softer ligands to be in mutually *cis* positions.[19]

An additional interesting feature of the ^{19}F n.m.r. spectra is that they consist of five signals of equal intensity for the complexes exhibiting only one isomer, and five additional ones (slightly shifted from the former and of lower intensity) when two isomers are present in solution (Figure 1 and Table 4). It follows that the five fluorine atoms on each C_6F_5 group are inequivalent and, hence, there is restricted rotation of the C_6F_5 group, as observed before in some six-co-ordinated iridium(III)[20] and platinum(IV)[21] complexes. In our case, scale models show that the Me on the imidoyl group and the L ligand [in the (A) isomers] or the Cl ligand [in the (B) isomers] hinder the C_6F_5 rotation, thus giving rise to inequivalence of the fluorine atoms *exo* (F^6 and F^5) and *endo* (F^2 and F^3) relative to the rigid boat conformation of the dipalladiocycle. The F^4 chemical shifts and the $\delta(F^2) - \delta(F^6)$ values confirm the proposed isomer assignments when compared with the values found for the tetrahydrothiophen (tht) complex; in addition, higher $\delta(F^2) - \delta(F^6)$ values were to be expected

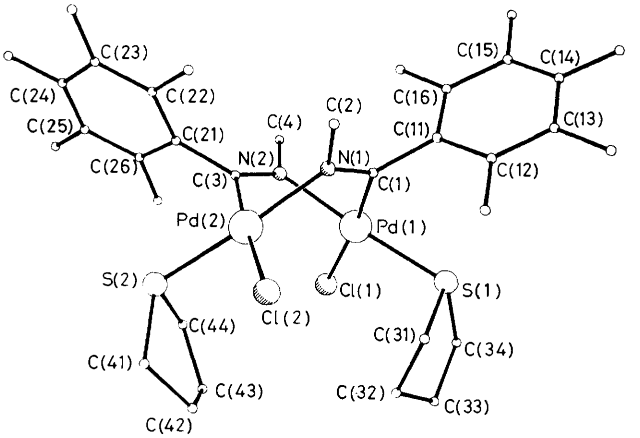


Figure 2. The molecule of (14), showing the atom-numbering scheme. Atom radii are arbitrary, and H atoms have been omitted for clarity

for isomers (B), in which F^2 comes close to Cl instead of L.

The structure found in our dimeric imidoyl derivatives raises the question of whether similar derivatives which had been assigned terminal imidoyl, chloro-bridged structures [13,17] should be reformulated. The present evidence seeems insufficient to draw any conclusion but the data reported for those dimeric complexes would also be consistent with the structure of our (A) isomers.

X-Ray Structural Analysis of [Pd$_2${μ-C(C$_6$F$_5$)=N(Me)}$_2$Cl$_2$(tht)$_2$] (14).—This structure analysis has confirmed that the complex is an imidoyl-bridged dimer (Figure 2). Some interatomic distances and bond angles are given in Table 5.

The co-ordination at both palladium atoms is square planar; root-mean-square (r.m.s.) deviations from the best plane of five atoms are 0.038 and 0.008 Å for Pd(1) and Pd(2) respectively. As mentioned above, the somewhat long Pd–Cl bonds (average 2.375 Å) are to be ascribed to the *trans* influence of the strong Pd–C bonds (average 1.986 Å). For comparison terminal Pd–Cl bonds (with square-planar metal geometry) are found [22] in the range 2.273—2.41 Å, the longer bonds mostly being *trans* to carbon, and Pd–C in the range 1.963—2.15 Å. The Pd–S bond lengths (average 2.309 Å) are typical of palladium thioether complexes.[23]

The nitrogen atoms of the imidoyl ligands do not lie in the planes of their respective C$_6$F$_5$ rings; N(1) and N(2) are 0.80 and 0.85 Å out of the plane respectively. This contrasts with a molybdenum complex of η^2-CH$_3$C=NPh,[11] where the ligand was essentially planar; non-planarity has been associated with σ-imidoyl ligands.[11,24] Similarly, the trend in C=N bond lengths of 1.233 (η^2),[11] 1.266,[11] 1.287 [24] (σ) Å is reversed both in the current structure (average 1.272 Å) and in a dimeric η^2-CH=NBu^t complex of platinum (1.287, 1.267 Å).[25]

Experimental

N.m.r. studies were made with JEOL PFT and P.S. 100 and Varian FT 80A spectrometers. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer. Methyl isocyanide was prepared as described by Ugi and co-workers.[26] Typical preparations of the complexes are given below.

trans-[Pd(C$_6$F$_5$)$_2$(CNMe)$_2$] (2).—*Method* (*i*). As described in ref. 4, 98% yield.

Table 5. Bond lengths (Å) and angles (°)

Pd(1)-S(1)	2.307(2)	Pd(2)-S(2)	2.311(2)
Cl(1)-Pd(1)	2.373(2)	Cl(2)-Pd(2)	2.377(2)
C(31)-S(1)	1.802(7)	C(31)-C(32)	1.479(11)
C(32)-C(33)	1.472(11)	C(33)-C(34)	1.476(10)
C(34)-S(1)	1.826(7)	C(41)-S(2)	1.804(6)
C(41)-C(42)	1.481(10)	C(42)-C(43)	1.472(10)
C(43)-C(44)	1.475(9)	C(44)-S(2)	1.828(7)
C(1)-Pd(1)	1.990(6)	C(1)-N(1)	1.264(8)
C(1)-C(11)	1.506(8)	N(1)-Pd(2)	2.055(5)
C(2)-N(1)	1.476(8)	C(11)-C(12)	1.387(10)
C(11)-C(16)	1.372(11)	C(12)-C(13)	1.367(10)
C(12)-F(12)	1.318(9)	C(13)-C(14)	1.354(13)
C(13)-F(13)	1.329(10)	C(14)-C(15)	1.369(15)
C(14)-F(14)	1.344(12)	C(15)-C(16)	1.419(13)
C(15)-F(15)	1.360(13)	C(16)-F(16)	1.344(10)
C(3)-Pd(2)	1.982(5)	C(3)-N(2)	1.280(7)
N(2)-Pd(1)	2.044(5)	C(4)-N(2)	1.469(7)
C(21)-C(3)	1.493(7)	C(21)-C(22)	1.383(8)
C(21)-C(26)	1.385(8)	C(22)-C(23)	1.374(8)
C(22)-F(22)	1.345(7)	C(23)-C(24)	1.377(8)
C(23)-F(23)	1.345(7)	C(24)-C(25)	1.347(8)
C(24)-F(24)	1.341(7)	C(25)-C(26)	1.382(8)
C(25)-F(25)	1.341(7)	C(26)-F(26)	1.338(7)

Cl(1)-Pd(1)-S(1)	97.3(2)	Cl(1)-Pd(1)-C(1)	173.5(3)
S(1)-Pd(1)-C(1)	87.8(3)	Cl(1)-Pd(1)-N(2)	89.4(2)
S(1)-Pd(1)-N(2)	173.3(2)	C(1)-Pd(1)-N(2)	85.5(3)
Cl(2)-Pd(2)-N(1)	89.9(2)	S(2)-Pd(2)-N(1)	173.6(2)
Cl(2)-Pd(2)-C(3)	175.8(2)	S(2)-Pd(2)-C(3)	87.7(2)
N(1)-Pd(2)-C(3)	86.0(3)	Pd(1)-S(1)-C(31)	103.4(3)
Pd(1)-S(1)-C(34)	111.6(3)	C(31)-S(1)-C(34)	92.5(4)
S(1)-C(31)-C(32)	105.3(5)	C(31)-C(32)-C(33)	109.2(7)
C(32)-C(33)-C(34)	110.7(7)	S(1)-C(34)-C(33)	108.1(5)
Pd(2)-S(2)-C(41)	110.9(3)	Pd(2)-S(2)-C(44)	106.3(3)
C(41)-S(2)-C(44)	91.1(4)	S(2)-C(41)-C(42)	107.1(5)
C(41)-C(42)-C(43)	110.8(6)	C(42)-C(43)-C(44)	112.2(6)
S(2)-C(44)-C(43)	108.9(5)	Pd(1)-C(1)-N(1)	117.7(4)
Pd(1)-C(1)-C(11)	118.8(5)	N(1)-C(1)-C(11)	123.5(5)
Pd(2)-N(1)-C(1)	117.2(4)	Pd(2)-N(1)-C(2)	119.3(4)
C(1)-N(1)-C(2)	123.5(5)	C(1)-C(11)-C(12)	122.0(6)
C(1)-C(11)-C(16)	119.6(7)	C(12)-C(11)-C(16)	118.2(7)
C(11)-C(12)-C(13)	121.5(8)	C(11)-C(12)-F(12)	119.9(6)
C(13)-C(12)-F(12)	118.6(7)	C(12)-C(13)-C(14)	119.9(9)
C(12)-C(13)-F(13)	121.2(8)	C(14)-C(13)-F(13)	118.9(8)
C(13)-C(14)-C(15)	121.5(9)	C(13)-C(14)-F(14)	121.7(9)
C(15)-C(14)-F(14)	116.7(10)	C(14)-C(15)-C(16)	118.3(10)
C(14)-C(15)-F(15)	124.1(10)	C(16)-C(15)-F(15)	117.5(10)
C(11)-C(16)-C(15)	120.6(8)	C(11)-C(16)-F(16)	121.0(7)
C(15)-C(16)-F(16)	118.4(8)	Pd(2)-C(3)-N(2)	117.7(4)
Pd(2)-C(3)-C(21)	120.5(4)	N(2)-C(3)-C(21)	121.7(5)
Pd(1)-N(2)-C(3)	116.8(4)	Pd(1)-N(2)-C(4)	118.6(4)
C(3)-N(2)-C(4)	124.6(5)	C(3)-C(21)-C(22)	121.5(5)
C(3)-C(21)-C(26)	122.0(5)	C(22)-C(21)-C(26)	116.3(5)
C(21)-C(22)-C(23)	122.2(6)	C(21)-C(22)-F(22)	119.0(5)
C(23)-C(22)-F(22)	118.8(5)	C(22)-C(23)-C(24)	119.2(6)
C(22)-C(23)-F(23)	120.0(6)	C(24)-C(23)-F(23)	120.8(6)
C(23)-C(24)-C(25)	120.6(6)	C(23)-C(24)-F(24)	119.0(6)
C(25)-C(24)-F(24)	120.4(6)	C(24)-C(25)-C(26)	119.7(6)
C(24)-C(25)-F(25)	120.2(6)	C(26)-C(25)-F(25)	120.2(6)
C(21)-C(26)-C(25)	122.0(6)	C(21)-C(26)-F(26)	119.9(5)
C(25)-C(26)-F(26)	118.1(5)		

Method (*ii*). The salt [NBu$^n{}_4$]$_2$[*trans*-Pd(C$_6$F$_5$)$_2$(CN)$_2$] (1.318 g, 1.348 mmol) was refluxed in MeI (6 cm^3) for 6 h. Addition of water (3 cm^3) and evaporation of the MeI afforded a white product which was filtered off, washed with ice-cold methanol and dichloromethane, and air dried (65% yield).

Method (*iii*). The salt [NBu$^n{}_4$]$_2$[*trans*-Pd(C$_6$F$_5$)$_2$(CN)$_2$] (2.00 g, 2.046 mmol) in acetone (20 cm^3) was treated with

Table 6. Atom co-ordinates ($\times 10^4$)

Atom	X/a	Y/b	Z/c
Pd(1)	3 009(1)	2 601(1)	1 245(1)
Pd(2)	4 314(1)	5 616(1)	1 321(1)
Cl(1)	2 968(2)	1 563(2)	1 860(1)
Cl(2)	6 657(1)	5 854(2)	1 114(1)
S(1)	4 453(1)	952(1)	991(1)
C(31)	6 232(6)	1 713(6)	1 063(2)
C(32)	6 811(7)	1 296(7)	1 455(2)
C(33)	6 392(7)	−160(7)	1 524(2)
C(34)	4 938(6)	−457(5)	1 332(2)
S(2)	4 922(1)	6 367(1)	1 944(1)
C(41)	6 856(5)	6 409(6)	2 057(2)
C(42)	7 331(6)	4 954(7)	2 142(2)
C(43)	6 209(7)	4 169(6)	2 319(2)
C(44)	4 778(6)	4 838(7)	2 252(1)
C(1)	3 057(5)	3 679(5)	760(1)
N(1)	3 545(4)	4 912(4)	784(1)
C(2)	3 646(7)	5 828(6)	448(1)
C(11)	2 568(7)	2 974(6)	384(1)
C(12)	3 541(8)	2 467(6)	142(2)
C(13)	3 091(9)	1 722(8)	−181(2)
C(14)	1 665(10)	1 475(11)	−273(2)
C(15)	651(11)	1 933(12)	−44(3)
C(16)	1 126(8)	2 713(8)	290(2)
F(12)	4 936(5)	2 683(4)	226(1)
F(13)	4 033(5)	1 191(5)	−404(1)
F(14)	1 181(7)	708(8)	−581(2)
F(15)	−794(7)	1 715(8)	−120(2)
F(16)	130(4)	3 185(6)	512(1)
C(3)	2 305(4)	5 391(5)	1 454(1)
N(2)	1 726(4)	4 180(4)	1 410(1)
C(4)	228(5)	3 854(6)	1 477(2)
C(21)	1 505(4)	6 606(5)	1 597(1)
C(22)	1 220(5)	7 789(5)	1 376(1)
C(23)	562(5)	8 948(5)	1 511(1)
C(24)	193(5)	8 947(6)	1 883(1)
C(25)	461(5)	7 821(6)	2 110(1)
C(26)	1 113(5)	6 657(5)	1 969(1)
F(22)	1 587(3)	7 804(3)	1 013(1)
F(23)	284(4)	10 066(3)	1 282(1)
F(24)	−426(3)	10 090(3)	2 017(1)
F(25)	80(3)	7 822(4)	2 470(1)
F(26)	1 369(3)	5 559(3)	2 203(1)

Me_3OBF_4 (0.605 g, 4.092 mmol). After stirring for 30 min the white precipitate was filtered off, washed with cold acetone, and air dried (90% yield).

$[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNMe)_2]$ (4).—The compound $[Pd(C_6F_5)_2(CNMe)_2]$ (0.200 g, 0.380 mmol) and $[PdCl_2(NCPh)_2]$ (0.148 g, 0.380 mmol) in acetone (40 cm^3) were stirred at room temperature for 17 h. The solution was evaporated *in vacuo* and the residue was extracted with CH_2Cl_2. Evaporation *in vacuo* afforded the desired complex as a white microcrystalline powder.

$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)\text{=}N(Me)]_2\}_n]$ (5).—The compounds $[Pd(C_6F_5)_2(CNMe)_2]$ (0.745 g, 1.430 mmol) and $[PdCl_2(NCPh)_2]$ (0.547 g, 1.430 mmol) were refluxed in benzene (70 cm^3) for 2 h. The hot solution was filtered to remove traces of Pd metal, evaporated to a small volume, and cooled, whereupon a red microcrystalline product appeared. This product contains 0.25 mol of C_6H_6 per Pd atom, which can be eliminated by heating in an oven at 80 °C for 24 h.

$[\{Pd_2(\mu\text{-}Br)_2[\mu\text{-}C(C_6F_5)\text{=}N(Me)]_2\}_n]$ (6).—Complex (5) (0.15 g, 0.214 mmol) was stirred with LiBr (0.075 g, 0.869 mmol) in acetone (40 cm^3), whereupon a yellow solution was formed. On evaporation to a small volume (*ca.* 2 cm^3) a red product precipitated which was filtered off, washed with cold methanol, and air dried.

$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Me)\}_2(acac)_2]$ (15).—Complex (5) (0.15 g, 0.214 mmol) in acetone (40 cm^3) was treated with Tl(acac) (0.130 g, 0.428 mmol). The mixture was stirred at room temperature for 4 h, and the white precipitate (TlCl) was filtered off. Evaporation of the yellow solution to a small volume (*ca.* 3 cm^3) and addition of ethanol afforded (15) as a yellow precipitate.

$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Me)\}_2Cl_2(CNMe)_2]$ (8).—*Method* (*i*). Complex (5) (0.100 g) suspended in CH_2Cl_2 (25 cm^3) was treated with the stoicheiometric amount of a solution of CNMe in CH_2Cl_2 and stirred for 10 min to give a yellow solution. Evaporation to dryness and addition of ethanol (*ca.* 10 cm^3) gave yellow crystals of (8) (55% yield).

Method (*ii*). Complex (3) (0.100 g) was refluxed in C_6H_6 (40 cm^3) for 5 h to give a yellow solution. Evaporation to *ca.* 1 cm^3 and addition of ethanol (*ca.* 10 cm^3) afforded yellow crystals of (8) (79% yield).

$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Me)\}_2Cl_2(NMe_3)_2]$ (9).—Trimethylamine was bubbled through a suspension of complex (5) (0.15 g) in acetone (10 cm^3) until a yellow solution was formed. Addition of hexane (30 cm^3) and cooling of the mixture in a refrigerator afforded yellow crystals of (9) which were filtered off, air dried, and stored in a refrigerator.

$[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Me)\}_2Cl_2(PPh_3)_2]$ (13).—Complex (5) (0.100 g, 0.143 mmol) and PPh_3 (0.075 g, 0.286 mmol) were stirred in CH_2Cl_2 (40 cm^3) for 10 min to give a yellow solution. Evaporation to 5 cm^3 and addition of ethanol afforded yellow crystals of (13).

Crystal Structure Determination of $[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}N(Me)\}_2Cl_2(tht)_2]$ (14).—*Crystal data.* $C_{24}H_{22}Cl_2F_{10}N_2Pd_2S_2$, $M = 876.27$, Monoclinic, space group $P2_1/c$, $a = 9.304(2)$, $b = 9.563(2)$, $c = 34.979(5)$ Å, $\beta = 95.76(2)°$, $U = 3\,097$ Å^3, $Z = 4$, $D_c = 1.88$ g cm^{-3}, $F(000) = 1\,664$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 15$ cm^{-1}.

A crystal in the form of a square plate ($0.25 \times 0.25 \times 0.15$ mm) was used to collect data on a Stoe four-circle diffractometer. 5 949 Reflections were measured in the range $7 < 2\theta < 50°$; after Lorentz polarization and absorption corrections, averaging equivalents gave 5 086 unique reflections, 3 978 of which with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL).

The structure was solved by the heavy-atom method and refined to $R = 0.040$, $R' = 0.035$ (all non-hydrogen atoms anisotropic, fixed C–H 0.96 Å and H–C–H 109.5°). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0001F^2$. Final atomic co-ordinates are given in Table 6. A final difference map showed no peaks >0.55 e Å^{-3}.

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