Crown-shaped Tetrametallic Imidoyl Complexes of Palladium. *X*-Ray Crystal Structure of [{[Pd_2{μ-C(C_6F_5)=NMe}$_2$](μ-Cl)(μ-$MeCO_2$)}$_2$]*

Rafael Uson, Juan Fornies, Pablo Espinet, Elena Lalinde, and Augustín García
Departamento de Química Inorganica, Universidad de Zaragoza, 50009 Zaragoza, Spain
Peter G. Jones, Karen Meyer-Base, and George M. Sheldrick
Institut fur Anorganische Chemie der Universitat, Tammannstrasse 4, D-3400 Gottingen, Federal Republic of Germany

The complexes [{[Pd_2{μ-C(C_6F_5)=NR^1}$_2$](μ-X^1)(μ-X^2)}$_n$] (R^1 = Me or *p*-tolyl; X^1 = X^2 = Cl) and their derivatives (X^1 = Cl, X^2 = $MeCO_2$ or CF_3CO_2; X^1 = X^2 = $MeCO_2$ or CF_3CO_2), obtained by metathetical reactions with the corresponding silver salts, are shown to be tetrametallic (n = 2) by molecular-weight determinations. Their structures are discussed on the basis of ^1H and ^{19}F n.m.r. data. The crystal structure of the title complex has been solved by *X*-ray diffraction methods [space group $P2_1/n$, a = 14.380(4), b = 19.980(4), c = 15.976(4) Å, β = 103.51(3)°, Z = 4, R' = 0.046 for 5 428 unique observed reflections]. The tetrametallic molecule is crown-shaped. The bond lengths at palladium reflect the strong *trans* influence of the imidoyl-C atom; the Pd–Cl bonds *trans* to C are amongst the longest known.

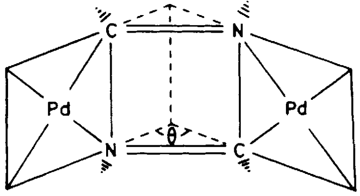
In previous papers[1–3] we have described several types of dimeric imidoyl-bridged complexes that contain the moiety Pd_2{C(C_6F_5)=NR^1}$_2$ (R^1 = Me or *p*-tolyl). The nature of the imidoyl bridges is such that the dipalladacycle displays a boat conformation (I), and the dihedral angle θ between the two square planes around the palladium atoms is *ca.* 70—90°. The precursors of these dimeric complexes have chloro-bridges in addition to the imidoyl double bridge, and we have formulated[1,2] them previously as the polynuclear complexes '[{Pd_2(μ-Cl)$_2$[μ-C(C_6F_5)=NR^1]$_2$}$_n$]' (**1a**, R^1 = Me; **1b**, R^1 = *p*-tolyl).

Chloro-bridges usually lead in palladium chemistry to a planar disposition of the Pd(μ-Cl)$_2$Pd moiety, as observed in the simple chain structure of α-$PdCl_2$[4] and in many dimeric complexes, but a few compounds contain non-planar chloro-bridges, and the dihedral angle φ defined by the two square planes around both palladium atoms, see (II), ranges from 150[5] to 121°.[6] Regardless of the geometry of the chloro-bridges, complexes (**1a**) and (**1b**) could form as polymeric angled ribbons; there is, however, also the possibility of forming a closed, crown-shaped structure.

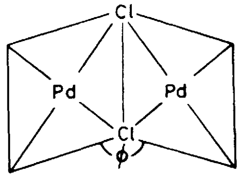
Although the low solubility of the first complex prepared, (**1a**), precluded structural investigations, the preparation of the more soluble complex (**1b**) and other soluble derivatives has enabled us to elucidate the structure of these complexes.

Results and Discussion

Complex (**1a**)[1] was too insoluble to carry out molecular-weight determinations but the more soluble (**1b**)[2] displayed a molecular weight of 1 795 in $CHCl_3$, Table 1, close to the value (1 704.2) calculated for n = 2, indicating that the molecule has a closed structure containing four palladium atoms linked by imidoyl and chloro-bridges. Since the reaction with neutral ligands L[1,2] leads to dimeric complexes [Pd_2{μ-C(C_6F_5)=NR^1}$_2Cl_2L_2$] containing an imidoyl double bridge, it seems reasonable to postulate the closed structure as consisting of two units of (I) linked together by chloro-bridges, discounting structures where two neighbouring palladium atoms are bridged by one imidoyl and one chloro-group. This leads to structures (**III**) and (**IV**) (X^1 = X^2 = X^3 = X^4 = Cl), which are both consistent with the observation of only one type of C_6F_5 and R^1 group in the ^{19}F and ^1H n.m.r. spectra respectively (Tables 2 and 3). We will show later that (**IV**) can be ruled out.



(I)



(II)

At this point it seemed worthwhile to replace the chloro-ligands by other angled bridging groups; $MeCO_2^-$, $CF_3CO_2^-$, PhS^-, and Ph_2P^- were chosen for this study. The replacement of Cl^- by Ph_2P^- led to unexpected products and has been reported elsewhere;[7] the other reactions are discussed below.

We had previously[1] carried out the exchange of Cl^- for $MeCO_2^-$ in complex (**1a**) but we cursorily formulated the resulting complex as a dimer. However, molecular-weight determinations of this and the other carboxylate products described here [(**2a**), (**2b**), (**3a**), and (**3b**)] showed that they too possess a closed structure (**III**) or (**IV**). In the course of the exchange reactions we observed that the red colour of the starting chloro-complex [(**1a**) or (**1b**)] disappeared before all the silver carboxylate had reacted; the reaction could be conducted stepwise to obtain either the half-substituted or the fully-exchanged complex [equation (1)].

$$\underset{(\mathbf{1a}),\,(\mathbf{1b})}{[\{[Pd_2\{\mu\text{-}C(C_6F_5){=}NR^1\}_2](\mu\text{-}Cl)_2\}_2]} \xrightarrow[-2AgCl]{2Ag(O_2CR^2)} \underset{(\mathbf{4a}),\,(\mathbf{4b}),\,(\mathbf{5a}),\,(\mathbf{5b})}{[\{[Pd_2\{\mu\text{-}C(C_6F_5){=}NR^1\}_2](\mu\text{-}Cl)(\mu\text{-}R^2CO_2)\}_2]} \xrightarrow[-2AgCl]{2Ag(O_2CR^2)} \underset{(\mathbf{2a}),\,(\mathbf{2b}),\,(\mathbf{3a}),\,(\mathbf{3b})}{[\{[Pd_2\{\mu\text{-}C(C_6F_5){=}NR^1\}_2](\mu\text{-}R^2CO_2)_2\}_2]} \quad (1)$$

---

* 1,2;3,4-Di-μ-(acetato-*O,O'*)-1,2;3,4-di-μ-chloro-1,4;1,4;2,3;2,3-tetra-μ-(pentafluoro-*N*-methylbenzimidoyl-*C,N*)-tetrapalladium(II).

Additional crystallographic material (complete bond lengths and angles, structure factors, thermal factors, H-atom co-ordinates) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Please quote reference no. CSD/51431 and the names of the authors and the title of the paper.

Table 1. Analytical results, molecular weights, yields, and colours of the complexes

		Analysis[a] (%)					
	Complex	N	C	H	M^b	Yield (%)	Colour
(1a)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2](\mu\text{-}Cl)_2\}_2]$	4.00 (4.00)	27.30 (27.45)	1.05 (0.85)		93	Red
(1b)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=N(C_6H_4Me\text{-}p)\}_2](\mu\text{-}Cl)_2\}_2]$	3.15 (3.30)	39.70 (39.45)	2.00 (1.65)	1 795 (1 704.2)	68	Red
(2a)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2](\mu\text{-}MeCO_2)_2\}_2]$	3.80 (3.75)	32.35 (32.15)	1.55 (1.60)	1 590 (1 494.2)	45	Yellow
(2b)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=N(C_6H_4Me\text{-}p)\}_2](\mu\text{-}MeCO_2)_2\}_2]$	3.10 (3.10)	42.65 (42.80)	2.30 (2.25)	1 849 (1 798.6)	71	Yellow
(3a)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2](\mu\text{-}CF_3CO_2)_2\}_2]$	3.05 (3.25)	28.55 (28.10)	0.80 (0.70)	1 731 (1 710)	45	Yellow
(3b)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=N(C_6H_4Me\text{-}p)\}_2](\mu\text{-}CF_3CO_2)_2\}_2]$	2.85 (2.80)	38.20 (38.15)	1.40 (1.40)	2 089 (2 014.5)	57	Yellow
(4a)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2](\mu\text{-}Cl)(\mu\text{-}MeCO_2)\}_2]$	3.90 (3.85)	29.75 (29.90)	1.20 (1.25)	1 700 (1 447)	73	Yellow
(4b)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=N(C_6H_4Me\text{-}p)\}_2](\mu\text{-}Cl)(\mu\text{-}MeCO_2)\}_2]$	3.45 (3.20)	41.20 (41.15)	2.15 (1.95)	1 822 (1 751)	84	Yellow-orange
(5a)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2](\mu\text{-}Cl)(\mu\text{-}CF_3CO_2)\}_2]$	3.60 (3.60)	27.85 (27.80)	0.80 (0.75)	1 753 (1 554.9)	74	Orange
(5b)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=N(C_6H_4Me\text{-}p)\}_2](\mu\text{-}Cl)(\mu\text{-}CF_3CO_2)\}_2]$	2.95 (3.00)	38.40 (38.75)	1.50 (1.50)	1 872 (1 859.2)	83	Orange
(6a)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2](\mu\text{-}Cl)(\mu\text{-}SPh)\}_n]$	3.50 (3.60)	34.45 (34.15)	1.35 (1.45)	4 688 (1 547)	90	Orange
(6b)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=N(C_6H_4Me\text{-}p)\}_2](\mu\text{-}Cl)(\mu\text{-}SPh)\}_n]$	3.05 (3.00)	43.90 (44.10)	2.45 (2.05)		90	Orange
(7a)	$[\{[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2](\mu\text{-}SPh)_2\}_2]$	3.25 (3.30)	39.10 (39.70)	1.80 (1.90)	∞ (1 694.7)	74	Orange

[a] Calculated values in parentheses. [b] In $CHCl_3$.

Table 2. ^{19}F N.m.r. resonances [δ, reference $CFCl_3$, in $CDCl_3$; **(1a)** in $(CD_3)_2CO$]

Complex	CF_3	F^2	F^6	F^4	F^3	F^5
(1a)	—	−136.2	−141.6	−152.7	−161.0	−161.4
(1b)	—	−133.4	−141.3	−152.4	−160.4	−161.7
(2a)	—	−142.2	−143.6	−155.4	−161.4	−164.2
(2b)	—	−136.1	−142.3	−155.6	−162.6	−165.3
(3a)	−76.2	−142.4	−143.6	−152.2	−160.4	−161.6
(3b)	−76.0	−136.9	−142.5	−152.6	−160.9	−162.5
(4a)	—	−137.0, −139.6	−143.5, −143.9	−153.7, −153.9	−161.2[a]	*a*, −163.5
(4b)	—	−132.3, −136.3	−141.1[b]	−153.4, −154.4	−162.0[a]	*a*, −164.3
(5a)	−76.4	−137.2, −139.5	−143.2, −143.8	−152.2, −152.3	−160.7[b]	−161.0, −162.1
(5b)	−76.2	−132.9, −136.4	−140.7, −141.8	−152.1, −153.0	−161.5[b]	−161.9, −162.4

[a] Overlap of the signals of the two inequivalent F^3 and one of the two F^5 occurs. [b] Overlap of the signals of the two inequivalent F^3 (or F^6) occurs.

Table 3. ^1H N.m.r. resonances [δ, reference $SiMe_4$, in $CDCl_3$; **(1a)** in $(CD_3)_2CO$] and some i.r.* absorptions (cm^{-1})

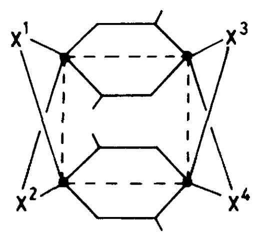
Complex	Me (imid)	C_6H_4	Me (acetate)	ν(C=O) and ν(C=N)
(1a)	3.46 (s)	—	—	1 608, 1 596
(1b)	2.27 (s, 3 H)	7.03 (s, 4 H)	—	1 578, 1 560
(2a)	3.30 (s, 3 H)	—	1.73 (s, 3 H)	1 600, 1 570
(2b)	2.24 (s, 3 H)	6.5—7.7 (m, 4 H)	1.32 (s, 3 H)	1 600, 1 560
(3a)	3.34 (s, 3 H)	—	—	1 700, 1 600
(3b)	2.27 (s, 3 H)	6.8—7.2 (m, 4 H)	—	1 680, 1 560
(4a)	3.44 (s, 3 H), 3.31 (s, 3 H)	—	1.85 (s, 3 H)	1 610, 1 570
(4b)	2.30 (s, 3 H), 2.28 (s, 3 H)	7.05 (s, 8 H)	1.79 (s, 3 H)	1 600, 1 575
(5a)	3.45 (s, 3 H), 3.36 (s, 3 H)	—	—	1 665, 1 605
(5b)	2.30 (s, 3 H), 2.27 (s, 3 H)	7.05 (s, 8 H)	—	1 650, 1 605, 1 580, 1 560

* For all the complexes bands are observed at *ca.* 1 650, 1 515, 1 495, 1 130, 1 020, 990, and 950 cm^{-1}; in addition, for $R^1 = Me$ two bands near 830 and 820 cm^{-1} and for $R^1 = p$-tolyl one band near 890 cm^{-1} are detected.

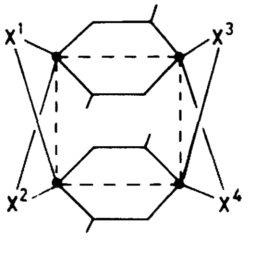
The chloro-carboxylate complexes [**(4a)**, **(4b)**, **(5a)**, and **(5b)**] also have structure **(III)** or **(IV)**, based on their molecular weights. For **(III)** and **(IV)**, three and four stereoisomers respectively [plus three enantiomers for **(III)**] are possible (see Table 4), namely: one containing one chloro double-bridge and one carboxylato double-bridge; and two (three) containing mixed chloro-carboxylato double bridges, with the two identical groups either mutually *cis* or mutually *trans* relative to

Table 4. Number of non-equivalent groups (n.m.r. data) (R^2 = Me or CF_3)

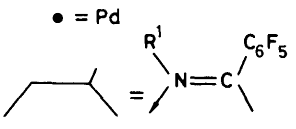
Isomer	Structure (III)	Structure (IV)
$X^1 = X^2 = X^3 = X^4$ = Cl	1 C_6F_5, 1 R^1	1 C_6F_5, 1 R^1
$X^1 = X^2 = X^3 = X^4$ = R^2CO_2	1 C_6F_5, 1 R^1, 1 R^2CO_2	1 C_6F_5, 1 R^1, 2 R^2CO_2
$X^1 = X^2$ = Cl; $X^3 = X^4$ = R^2CO_2 (**A**)	2 C_6F_5, 2 R^1, 1 R^2CO_2	2 C_6F_5, 2 R^1, 2 R^2CO_2
$X^1 = X^4$ = Cl; $X^2 = X^3$ = R^2CO_2 (**B**)	2 C_6F_5, 2 R^1, 1 R^2CO_2	1 C_6F_5, 1 R^1, 1 R^2CO_2
$X^1 = X^3$ = Cl; $X^2 = X^4$ = R^2CO_2 (**C**)	2 C_6F_5, 2 R^1, 1 R^2CO_2	2 C_6F_5, 2 R^1, 2 R^2CO_2
$X^2 = X^3$ = Cl; $X^1 = X^4$ = R^2CO_2 (**D**)		1 C_6F_5, 1 R^1, 1 R^2CO_2



(III)



(IV)



the plane containing the four palladium atoms. There are two different *trans* isomers [(**B**) and (**D**)] of (**IV**). The observation in the ^{19}F spectra of two types of C_6F_5 and R^1 groups and only one type of R^2CO_2 group is consistent (see Table 4) with any of the three isomers for structure (**III**) but with none of the isomers for structure (**IV**). Thus, structure (**IV**) can be ruled out.

Since the three possible isomers of structure (**III**) are indistinguishable by i.r. or n.m.r. means, we tried to distinguish them on the basis of reactivity. Thus, it seems reasonable that, for isomer (A) where $X^1 = X^2$ = Cl, there would be a chance of 'cutting' the molecule across the chloro-bridges in order to obtain a tetrametallic open structure. We attempted this by treating the chloro-carboxylate closed complexes with a neutral ligand (Pd : L = 2 : 1, in order selectively to cleave the chloro-bridges) or with Tl(acac) (acac = acetylacetonate) [Pd : Tl(acac) = 2 : 1, in order to substitute the chloro-bridges by two chelating acac groups] but we obtained in each case mixtures of the corresponding carboxylate tetramer and $[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NR^1\}_2Cl_2L_2]$ (L = pyridine or PPh_3) or, respectively, $[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NR^1\}_2(acac)_2]$, previously reported[1,2] [equations (2) and (3)].

Thus, the attempted selective cleavage of bridges leads to rearrangement, a result which can be easily understood for isomers (**B**) and (**C**) but in no way rules out isomer (**A**). In order to elucidate this point, an *X*-ray diffraction study of complex $[\{[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NMe\}_2](\mu\text{-}Cl)(\mu\text{-}MeCO_2)\}_2]$ (**4a**) was carried out, which revealed that its structure corresponded to that of isomer (**C**).

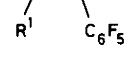
The crown-shaped nature of (**4a**) is shown in the Figure. All the palladium atoms display the usual square-planar geometry [absolute deviations from ligand least-squares planes are 0.03, 0.04, 0.03, 0.04 Å for Pd(1)—Pd(4) respectively]. The angles θ [see (**I**)] between neighbouring ligand planes are Pd(1)–Pd(3) 87, Pd(2)–Pd(3) 92, Pd(1)–Pd(4) 91, and Pd(2)–Pd(4) 88°; *cf.* 77° in $[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NMe\}_2Cl_2(SC_4H_8)_2]$[1] and 69° in $[(Me_2NCH_2CH_2NMe_2)Pd\{\mu\text{-}C(C_6F_5)\text{=}NMe\}_2PdCl_2]$.[3]

There are two types of metal co-ordination: Pd(1) and Pd(2) with acetate-O *trans* to imidoyl-C, imidoyl-N *trans* to Cl; and Pd(3) and Pd(4) with O *trans* to N, C *trans* to Cl. This is reflected in the pattern of bond lengths; Pd(3)–Cl(2) and Pd(4)–Cl(1) are, at 2.423(3), 2.429(3) Å respectively, amongst the longest Pd–Cl bonds known and show the strong *trans* influence of the imidoyl-C atom even more markedly than the other systems we have studied [Pd–Cl 2.376(2);[3] 2.373(2), 2.377(2) Å[1]]. Consistent with this observation are the short Pd(3)–C(37) and Pd(4)–C(47) bonds [1.955(9), 1.953(9); *cf.*

$$2[\{[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NR^1\}_2](\mu\text{-}Cl)(\mu\text{-}R^2CO_2)\}_2] + 4\ L \longrightarrow [\{[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NR^1\}_2](\mu\text{-}R^2CO_2)_2\}_2] + 2[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NR^1\}_2Cl_2L_2] \quad (2)$$

$$2[\{[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NR^1\}_2](\mu\text{-}Cl)(\mu\text{-}R^2CO_2)\}_2] + 4\ Tl(acac) \longrightarrow [\{[Pd_2\{\mu\text{-}C(C_6F_5)\text{=}NR^1\}_2](\mu\text{-}R^2CO_2)_2\}_2]$$

+

2  (3)

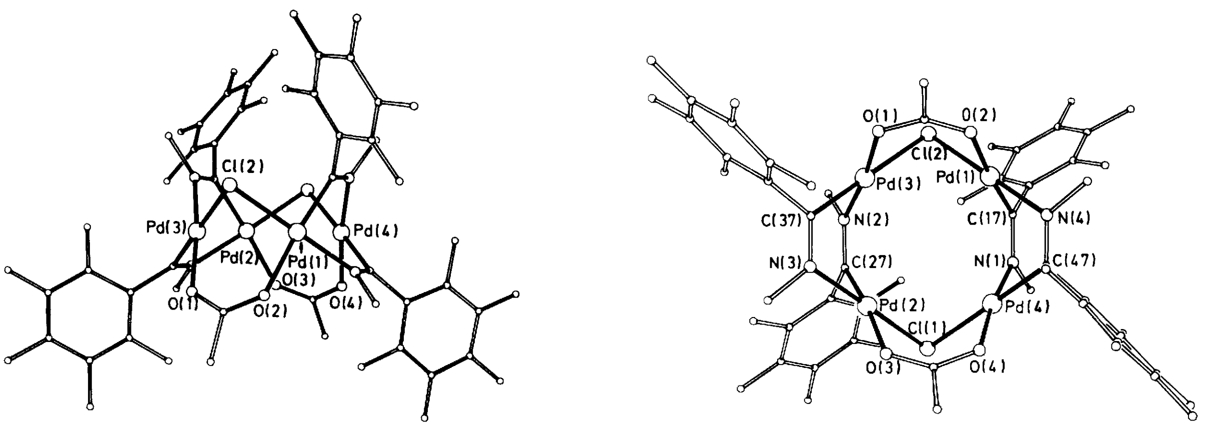


Figure. Two approximately perpendicular views of the molecule of $[\{[Pd_2\{\mu\text{-}C(C_6F_5){=}NMe\}_2](\mu\text{-}Cl)(\mu\text{-}MeCO_2)\}_2]$ (**4a**), showing the atom numbering scheme of the Pd co-ordination spheres (H atoms omitted; radii arbitrary)

Table 5. Atomic co-ordinates (× 10^4) for (**4a**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	2 993(1)	3 088(1)	2 331(1)	C(2)	3 869(7)	1 404(4)	4 129(5)
Pd(2)	−42(1)	3 154(1)	2 740(1)	C(3)	−525(5)	2 002(3)	1 455(5)
Pd(3)	2 128(1)	3 196(1)	3 983(1)	C(4)	−1 092(7)	1 378(4)	1 154(5)
Pd(4)	838(1)	3 028(1)	1 099(1)	C(11)	3 238(5)	4 382(4)	1 527(5)
Cl(1)	−413(1)	3 724(1)	1 433(1)	C(12)	3 216(6)	4 991(4)	1 916(5)
Cl(2)	3 375(1)	3 804(1)	3 516(1)	C(13)	3 921(7)	5 459(4)	1 936(5)
O(1)	2 935(4)	2 352(3)	4 250(3)	C(14)	4 669(6)	5 336(4)	1 573(6)
O(2)	3 503(4)	2 248(3)	3 074(3)	C(15)	4 694(6)	4 724(5)	1 170(6)
O(3)	−630(4)	2 267(2)	2 145(3)	C(16)	4 001(6)	4 258(4)	1 160(5)
O(4)	23(4)	2 195(2)	989(3)	C(17)	2 549(5)	3 830(3)	1 551(4)
N(1)	1 704(4)	3 820(3)	1 074(3)	C(18)	1 340(6)	4 358(4)	442(5)
N(2)	1 276(4)	4 003(3)	3 848(3)	C(21)	−257(5)	4 549(3)	3 217(4)
N(3)	275(4)	2 677(3)	3 894(3)	C(22)	−226(6)	5 054(4)	2 650(5)
N(4)	2 686(5)	2 467(3)	1 304(4)	C(23)	−965(6)	5 489(4)	2 363(5)
F(12)	2 492(4)	5 140(2)	2 270(3)	C(24)	−1 773(6)	5 422(4)	2 667(5)
F(13)	3 862(2)	6 057(3)	2 296(3)	C(25)	−1 828(6)	4 951(4)	3 267(5)
F(14)	5 347(4)	5 787(3)	1 581(4)	C(26)	−1 075(6)	4 514(3)	3 524(5)
F(15)	5 427(4)	4 596(3)	790(4)	C(27)	428(5)	3 973(3)	3 361(4)
F(16)	4 066(4)	3 674(3)	762(4)	C(28)	1 638(6)	4 627(4)	4 318(5)
F(22)	556(4)	5 119(2)	2 330(3)	C(31)	1 414(6)	2 362(4)	5 201(4)
F(23)	−906(4)	5 965(2)	1 798(4)	C(32)	1 702(6)	1 696(4)	5 309(5)
F(24)	−2 524(4)	5 831(3)	2 381(4)	C(33)	2 077(6)	1 423(4)	6 091(5)
F(25)	−2 619(4)	4 887(2)	3 575(4)	C(34)	2 188(6)	1 792(4)	6 814(5)
F(26)	−1 160(3)	4 035(2)	4 102(3)	C(35)	1 923(6)	2 451(4)	6 760(5)
F(32)	1 593(4)	1 310(2)	4 607(3)	C(36)	1 539(6)	2 731(4)	5 967(5)
F(33)	2 354(4)	771(2)	6 157(3)	C(37)	1 121(5)	2 700(3)	4 351(4)
F(34)	2 543(4)	1 526(3)	7 595(3)	C(38)	−521(6)	2 318(4)	4 137(5)
F(35)	2 019(4)	2 822(3)	7 475(3)	C(41)	1 509(6)	1 951(3)	135(4)
F(36)	1 278(4)	3 375(2)	5 918(3)	C(42)	1 168(6)	2 141(4)	−709(5)
F(42)	1 219(4)	2 797(2)	−902(3)	C(43)	790(6)	1 709(5)	−1 373(5)
F(43)	486(4)	1 917(3)	−2 179(3)	C(44)	760(6)	1 043(4)	−1 157(5)
F(44)	397(4)	603(3)	−1 798(4)	C(45)	1 059(7)	814(4)	−337(6)
F(45)	1 006(4)	172(2)	−164(4)	C(46)	1 441(6)	1 272(4)	295(5)
F(46)	1 743(4)	1 048(2)	1 101(3)	C(47)	1 835(6)	2 454(4)	843(4)
C(1)	3 394(5)	2 056(4)	3 782(5)	C(48)	3 455(6)	2 028(4)	1 163(5)

1.960(5), 1.994(6);[3] 1.990(6), 1.982(5) Å[1]]. Similarly, the Pd–O bond lengths at Pd(1) and Pd(2) (*trans* to C) are appreciably longer than those at Pd(3) and Pd(4) (*trans* to N).

Finally, the exchange reactions of Cl^- by PhS^- were disappointing. Although the reactions could be conducted to give orange solids with analyses corresponding well to complexes (**6a**), (**6b**), and (**7a**), neither their molecular-weight data nor their ^{19}F n.m.r. spectra were consistent with structure (**III**). The ^{19}F n.m.r. spectra showed many signals of different intensities in the range of the *p*-fluorine (which is the most easily observable), even more than one could expect considering the new possibility of isomerism introduced in structure (**III**) by the *syn*- or *anti*-conformation of the PhS^- ligand.[8] Moreover, molecular-weight determinations of complexes (**6a**) and (**7a**) gave very high results. These data suggest that the products containing PhS are not homogeneous, at least from a structural point of view, and could correspond to open polymeric species with various degrees of polymerization.

Table 6. Selected bond lengths (Å) and angles (°) for (**4a**)

Cl(1)–Pd(2)	2.329(3)	Cl(1)–Pd(4)	2.429(3)	C(24)–F(24)	1.347(11)	C(24)–C(25)	1.358(13)
Cl(2)–Pd(1)	2.333(3)	Cl(2)–Pd(3)	2.423(3)	C(25)–F(25)	1.347(12)	C(25)–C(26)	1.377(12)
O(1)–Pd(3)	2.034(6)	O(2)–Pd(1)	2.088(6)	C(26)–F(26)	1.356(10)	C(27)–Pd(2)	1.950(8)
O(3)–Pd(2)	2.094(6)	O(4)–Pd(4)	2.021(6)	C(27)–N(2)	1.286(10)	C(28)–N(2)	1.486(10)
N(1)–Pd(4)	2.019(7)	N(2)–Pd(3)	2.006(7)	C(31)–C(32)	1.391(12)	C(31)–C(36)	1.403(11)
N(3)–Pd(2)	2.030(6)	N(4)–Pd(1)	2.023(7)	C(31)–C(37)	1.486(10)	C(32)–F(32)	1.339(10)
C(1)–O(1)	1.256(11)	C(1)–O(2)	1.238(11)	C(32)–C(33)	1.355(12)	C(33)–F(33)	1.358(10)
C(1)–C(2)	1.515(12)	C(3)–O(3)	1.262(10)	C(33)–C(34)	1.347(12)	C(34)–F(34)	1.343(10)
C(3)–O(4)	1.264(11)	C(3)–C(4)	1.506(11)	C(34)–C(35)	1.367(13)	C(35)–F(35)	1.342(10)
C(11)–C(12)	1.371(12)	C(11)–C(16)	1.382(14)	C(35)–C(36)	1.377(11)	C(36)–F(36)	1.338(10)
C(11)–C(17)	1.488(12)	C(12)–F(12)	1.329(12)	C(37)–Pd(3)	1.955(9)	C(37)–N(3)	1.265(10)
C(12)–C(13)	1.374(13)	C(13)–F(13)	1.338(11)	C(38)–N(3)	1.478(11)	C(41)–C(42)	1.377(11)
C(13)–C(14)	1.359(15)	C(14)–F(14)	1.325(11)	C(41)–C(46)	1.388(12)	C(41)–C(47)	1.503(11)
C(14)–C(15)	1.386(14)	C(15)–F(15)	1.359(13)	C(42)–F(42)	1.352(10)	C(42)–C(43)	1.378(12)
C(15)–C(16)	1.360(13)	C(16)–F(16)	1.342(11)	C(43)–F(43)	1.326(10)	C(43)–C(44)	1.378(14)
C(17)–Pd(1)	1.946(8)	C(17)–N(1)	1.276(10)	C(44)–F(44)	1.358(11)	C(44)–C(45)	1.359(13)
C(18)–N(1)	1.484(10)	C(21)–C(22)	1.363(11)	C(45)–F(45)	1.318(11)	C(45)–C(46)	1.378(13)
C(21)–C(26)	1.378(13)	C(21)–C(27)	1.497(11)	C(46)–F(46)	1.335(10)	C(47)–Pd(4)	1.953(9)
C(22)–F(22)	1.347(12)	C(22)–C(23)	1.367(12)	C(47)–N(4)	1.273(10)	C(48)–N(4)	1.470(12)
C(23)–F(23)	1.326(11)	C(23)–C(24)	1.367(15)				

Cl(2)–Pd(1)–O(2)	92.7(2)	Cl(2)–Pd(1)–N(4)	179.0(3)	Pd(4)–N(1)–C(17)	120.5(6)	Pd(4)–N(1)–C(18)	117.4(6)
O(2)–Pd(1)–N(4)	87.0(3)	Cl(2)–Pd(1)–C(17)	91.9(3)	C(17)–N(1)–C(18)	122.0(7)	Pd(3)–N(2)–C(27)	119.8(6)
O(2)–Pd(1)–C(17)	174.8(4)	N(4)–Pd(1)–C(17)	88.4(4)	Pd(3)–N(2)–C(28)	119.2(6)	C(27)–N(2)–C(28)	121.0(7)
Cl(1)–Pd(2)–O(3)	91.3(2)	Cl(1)–Pd(2)–N(3)	178.6(3)	Pd(2)–N(3)–C(37)	119.3(6)	Pd(2)–N(3)–C(38)	116.3(5)
O(3)–Pd(2)–N(3)	89.8(3)	Cl(1)–Pd(2)–C(27)	91.5(3)	C(37)–N(3)–C(38)	124.4(7)	Pd(1)–N(4)–C(47)	118.6(6)
O(3)–Pd(2)–C(27)	174.9(4)	N(3)–Pd(2)–C(27)	87.3(3)	Pd(1)–N(4)–C(48)	117.5(5)	C(47)–N(4)–C(48)	123.8(7)
Cl(2)–Pd(3)–O(1)	93.0(3)	Cl(2)–Pd(3)–N(2)	92.3(3)	O(1)–C(1)–O(2)	126.5(8)	O(1)–C(1)–C(2)	116.2(8)
O(1)–Pd(3)–N(2)	173.1(3)	Cl(2)–Pd(3)–C(37)	179.5(3)	O(2)–C(1)–C(2)	117.3(8)	O(3)–C(3)–O(4)	127.3(7)
O(1)–Pd(3)–C(37)	86.8(4)	N(2)–Pd(3)–C(37)	87.9(4)	O(3)–C(3)–C(4)	117.3(8)	O(4)–C(3)–C(4)	115.4(8)
Cl(1)–Pd(4)–O(4)	92.7(3)	Cl(1)–Pd(4)–N(1)	92.8(3)	Pd(1)–C(17)–C(11)	117.4(6)	Pd(3)–C(37)–C(31)	115.7(6)
O(4)–Pd(4)–N(1)	172.6(3)	Cl(1)–Pd(4)–C(47)	178.8(3)	Pd(1)–C(17)–N(1)	119.6(6)	Pd(3)–C(37)–N(3)	121.6(6)
O(4)–Pd(4)–C(47)	86.3(4)	N(1)–Pd(4)–C(47)	88.3(4)	N(1)–C(17)–C(11)	123.0(7)	N(3)–C(37)–C(31)	122.7(8)
Pd(2)–Cl(1)–Pd(4)	83.7(2)	Pd(1)–Cl(2)–Pd(3)	83.8(2)	Pd(2)–C(27)–C(21)	115.4(6)	Pd(4)–C(47)–C(41)	115.8(6)
Pd(3)–O(1)–C(1)	128.3(6)	Pd(1)–O(2)–C(1)	131.7(6)	Pd(2)–C(27)–N(2)	120.9(6)	Pd(4)–C(47)–N(4)	121.4(6)
Pd(2)–O(3)–C(3)	129.2(6)	Pd(4)–O(4)–C(3)	128.9(6)	N(2)–C(27)–C(21)	123.7(7)	N(4)–C(47)–C(41)	122.5(8)

Experimental

The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyser. I.r. spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates. ^1H N.m.r. and ^{19}F n.m.r. spectra were recorded on a Varian XL-200 instrument (200 MHz for ^1H). Molecular weights were determined in $CHCl_3$ solution on a Perkin-Elmer 115 apparatus. Complexes (**1a**) and (**1b**) were prepared as described earlier.[1,2]

Preparation of Complexes (**2**)—(**5**).—A typical preparation was as follows. To a red solution of (**1a**) (206.3 mg, 0.147 mmol) in acetone (40 cm^3) was added silver acetate (295 mg, 1.768 mmol; Pd : Ag = 1 : 3) and the mixture, protected from the light, was stirred at room temperature for 48 h, evaporated to dryness and the residue extracted with CH_2Cl_2 (40 cm^3) to give a yellow solution and a precipitate of silver salts which was filtered off. The solution was evaporated to 1 cm^3. Upon addition of ethanol (10 cm^3) and cooling in the freezer (**2a**) was obtained as a yellow solid. Complex (**2b**) was obtained similarly from (**1b**).

For (**3a**) and (**3b**) the procedure was the same but a Pd : Ag ratio of 1 : 1 was used; the reaction times were 12 and 7.5 h respectively, and the products were precipitated by adding cyclohexane to the 1-cm^3 solution in CH_2Cl_2.

For (**4a**), (**4b**), (**5a**), and (**5b**) a Pd : Ag ratio of 1 : 0.5 and reaction times of 0.5, 20, 0.5, and 5.5 h respectively were used. Otherwise the procedure was the same as described for (**2a**).

Preparation of Complexes (**6a**) *and* (**7a**).—To a stirred solution of (**1a**) (208.4 mg, 0.149 mmol) in acetone (40 cm^3) was added a solution containing 32.8 mg (0.298 mmol) of PhSH in acetone (2 cm^3), whereupon the solution turned orange. After stirring for 5 min 3.2 cm^3 of a 0.093 mol dm^{-3} solution of KOH in MeOH (16.7 mg, 0.298 mmol of KOH) were added, giving rise to the slow formation of a white precipitate. After stirring at room temperature for 1 h the solvent was evaporated and the residue extracted with CH_2Cl_2 (40 cm^3). The insoluble solid was filtered off and the orange solution dried with $MgSO_4$ and evaporated to a small volume. Addition of ethanol (5 cm^3) and evaporation of the remaining CH_2Cl_2 gave (**6a**).

Complex (**7a**) was obtained similarly but using twice as much PhSH and KOH.

Preparation of Complex (**6b**).—To a stirred suspension of (**1b**) (301.2 mg, 0.177 mmol) in CH_2Cl_2 (60 cm^3) was added a solution containing 38.94 mg (0.353 mmol) of PhSH in CH_2Cl_2 (50 cm^3) and then K_2CO_3 (30 mg, 0.217 mmol). The mixture was stirred for 72 h at room temperature and the insoluble material filtered off. The resulting orange solution was evaporated to 2 cm^3 and n-hexane (20 cm^3) added to give an orange precipitate which was filtered off, washed with n-hexane, and dried. This solid was extracted with CH_2Cl_2 (50 cm^3) at reflux and undissolved material filtered off. The resulting orange solution was evaporated to a small volume and n-hexane added to give (**6b**).

X-*Ray Crystal Structure of Complex* (**4a**).—*Crystal data.* $C_{36}H_{18}Cl_2F_{20}N_4O_4Pd_4$, M = 1 447, monoclinic, space group $P2_1/n$, a = 14.380(4), b = 19.980(4), c = 15.976(4) Å, β = 103.51(3)°, U = 4 463 Å^3 (refined from 2θ values of 40 strong reflections in the range 20—23°), Mo-K_α radiation (λ = 0.710 69 Å), $Z = 4$, $D_c = 2.15$ g cm^{-3}. Yellow, air-stable prisms. Crystal dimensions 0.42 × 0.15 × 0.15 mm, $\mu = 0.18$ mm^{-1}.

Data collection and processing. Stoe-Siemens four-circle diffractometer, monochromated Mo-K_α radiation, 8 508 profile-fitted intensities[9] ($2\theta_{max.}$ 50°), 7 826 unique, 5 428 with $F > 4\sigma(F)$ used for all calculations (program system SHELXTL). Absorption correction based on ψ-scans; transmissions 0.76—0.81. No crystal decay.

Structure solution and refinement. Pd atoms from Patterson function, other non-H atoms from difference synthesis. Least-squares refinement on F to R 0.061, R' 0.046 [non-H atoms anisotropic, rigid methyl groups with C–H 0.96 Å, H–C–H 109.5°, $U(\text{H}) = 1.2\ U_{iso}(\text{C})$; weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,15\ F^2$]. Final atomic co-ordinates and derived parameters are given in Tables 5 and 6.

References

1 R. Uson, J. Fornies, P. Espinet, E. Lalinde, P. G. Jones, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1982, 2389.

2 R. Uson, J. Fornies, P. Espinet, and E. Lalinde, *J. Organomet. Chem.*, 1983, **254**, 371.

3 R. Uson, J. Fornies, P. Espinet, E. Lalinde, P. G. Jones, and G. M. Sheldrick, *J. Organomet. Chem.*, 1983, **253**, C47.

4 A. F. Wells, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1938, **100**, 189.

5 G. R. Davies, R. H. B. Mais, S. O'Brien, and P. G. Owston, *Chem. Commun.*, 1967, 1151.

6 A. G. Constable, W. S. McDonald, L. S. Sawbins, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 1992.

7 R. Uson, J. Fornies, P. Espinet, A. Garcia, M. Tomas, C. Foces-Foces, and F. H. Cano, *J. Organomet. Chem.*, 1985, **282**, C35.

8 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley-Interscience, New York, 1980, p. 178.

9 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

Received *4th March* 1985; *Paper* 5/354