# Synthesis and Structural Study of Neutral Mononuclear and Anionic Binuclear 2,4,6-Trifluorophenyl Derivatives of Palladium(II). Crystal Structure of $[P(CH_2Ph)Ph_3]_2[(C_6F_3H_2)_2Pd(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(C_6F_3H_2)_2]$ †

**Gregorio López,* Gabriel Garcia, Maria D. Santana, Gregorio Sánchez, and José Ruiz**
*Departamento de Química Inorgánica, Universidad de Murcia, 30071 Murcia, Spain*
**Juan A. Hermoso, Angel Vegas, and Martin Martínez-Ripoll**
*Instituto de Química-Física 'Rocasolano'-CSIC, Serrano 119, 28006 Madrid, Spain*

Arylation of $K_2[PdCl_4]$ with $Mg(C_6F_3H_2)Br$ in tetrahydrofuran–dioxane and subsequent addition of either benzonitrile or dibenzylideneacetone (dba) in diethyl ether leads to the formation of labile complexes $[Pd(C_6F_3H_2)_2(PhCN)_2]$ or $[Pd(C_6F_3H_2)_2(dba)]$ respectively. A number of $[Pd(C_6F_3H_2)_2L_2]$-type complexes [L = $PEt_3$, $AsPh_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, $L_2$ = cycloocta-1,5-diene or *NNN'N'*-tetramethylethylenediamine] have been prepared by addition of the corresponding neutral ligand to chloroform solutions of $[Pd(C_6F_3H_2)_2(PhCN)_2]$. Proton, $^{19}F$, and $^{31}P$ n.m.r. data for all the square-planar palladium(II) complexes have been collected and $^{31}P\text{-}\{^1H\}$ spectra show that they are the *cis* isomers. The complex $[Pd(C_6F_3H_2)_2(PhCN)_2]$ reacts with $NMe_4Cl$ to give $[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}Cl)_2]$ and treatment of this with the appropriate alkali-metal salt (KBr, NaI, or KSCN) leads to $[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}X)_2]$ (X = Br, I, or SCN). The behaviour of the binuclear anions in the solvents acetone and dimethyl sulphoxide has been studied by $^{19}F$ n.m.r. spectroscopy. The crystal structure of $[P(CH_2Ph)Ph_3]_2[(C_6F_3H_2)_2Pd(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(C_6F_3H_2)_2]$ has been solved and refined to *R* = 0.040 based on 3 384 observed reflections, confirming the existence of centrosymmetric binuclear anions where the Pd atoms have square-planar co-ordination [Pd–C 2.02(1) and 1.99(1), Pd–S 2.387(5), and Pd–N 2.07(1) Å].

Polyfluorophenyl derivatives of palladium(II) can be conveniently prepared by metathesis reactions of a labile complex $[PdR_2L_2]$ (L = dioxane,[1,2] tetrahydrofuran,[3] or tetrahydrothiophene[4]). In the course of our research on $Pd(C_6F_5)_2$ derivatives we have shown that the benzonitrile adduct $[Pd(C_6F_5)_2(PhCN)_2]$ is a good precursor for the synthesis of $[Pd(C_6F_5)_2(diolefin)]$,[5] bi-homo- and bi-heterometallic complexes $[(C_6F_5)_2Pd(\mu\text{-}X)_2ML_2]$ (X = halide; M = Ni, Pd, or Pt),[6] or the hydroxo-bridged anion[7] $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$.

On the other hand, 2,4,6-trifluorophenyl ($C_6F_3H_2$) derivatives of palladium(II) are poorly represented in the literature. Some complexes $[Pd(C_6F_3H_2)_2L_2]$ were prepared[8] by addition of L to tetrahydrofuran–dioxane solutions resulting from the arylation of $[PdCl_4]^{2-}$ with $Mg(C_6F_3H_2)Br$. The work described herein shows that $[Pd(C_6F_3H_2)_2(PhCN)_2]$ can be prepared and subsequently used as a precursor to synthesize complexes $[Pd(C_6F_3H_2)_2L_2]$ as well as $[(C_6F_3H_2)_2Pd(\mu\text{-}Cl)_2Pd(C_6F_3H_2)_2]^{2-}$, which in turn leads to $[(C_6F_3H_2)_2Pd(\mu\text{-}X)_2Pd(C_6F_3H_2)_2]^{2-}$ (X = Br, I, or SCN) by corresponding interchange reactions with alkali-metal salts. These are the first binuclear anionic trifluorophenyl derivatives of palladium(II) to be reported, and an *X*-ray diffraction study has confirmed the binuclearity of the thiocyanate complex based on the eight-membered ring Pd(μ-SCN)(μ-NCS)Pd.

The splitting pattern shown by the $^{31}P$ n.m.r. signals of the phosphine complexes, due to coupling to the *o*-fluorine atoms in the $C_6F_3H_2$ group, can be used to elucidate their *cis-trans* configurations. This behaviour contrasts favourably with that of the analogous pentafluorophenyl derivatives, where the $^{31}P$ signals are broadened by further coupling to the *m*-fluorine atoms in the $C_6F_5$ group.[9]

## Results and Discussion

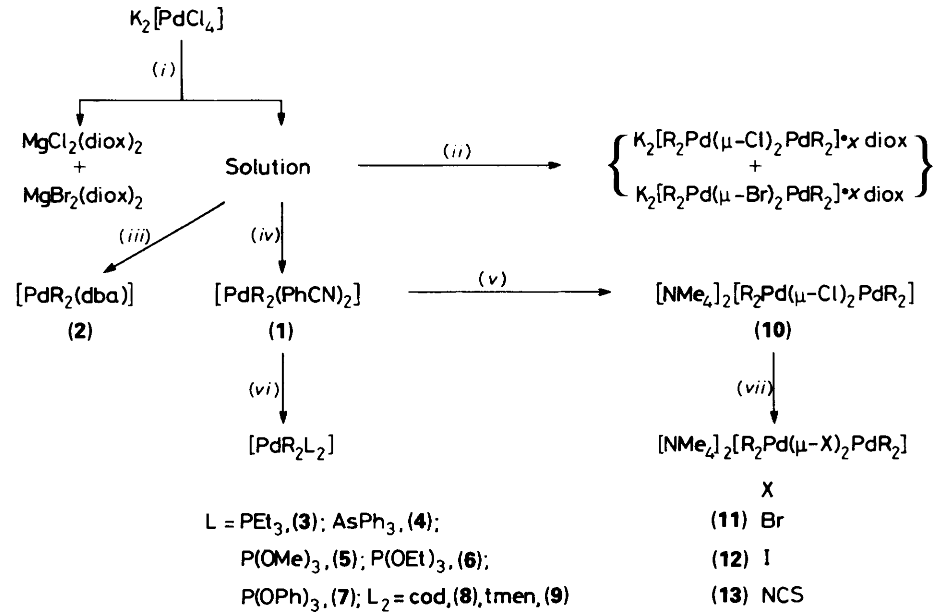
*Mononuclear Complexes.*—The results of our study are shown in the Scheme. In tetrahydrofuran, $K_2[PdCl_4]$ is arylated by $Mg(C_6F_3H_2)Br$ and addition of dioxane results in the precipitation of dioxane-solvated magnesium halides. The potassium salt of $[(C_6F_3H_2)_2Pd(\mu\text{-}X)_2Pd(C_6F_3H_2)_2]^{2-}$ is isolated from the magnesium-free solution, but the elemental analyses, i.r. spectrum [Pd(μ-Cl)$_2$Pd], and qualitative analysis (Cl and Br) indicate that it is a mixture of the chloro- and bromo-bridged compounds. Prolonged treatment of $K_2[PdCl_4]$ with the Grignard reagent reduces the amount of chloro-bridged compound in the mixture, but a pure compound cannot be isolated. This behaviour is similar to that observed in the arylation of $K_2[PdCl_4]$ with $Mg(C_6F_5)Br$ in diethyl ether (1:4 molar ratio, 5 h reflux + 17 h stirring at room temperature),[4] but in this case the pure bromo-bridged compound could be isolated. If, however, the mixture is treated with KBr, pure $K_2[(C_6F_3H_2)_2Pd(\mu\text{-}Br)_2Pd(C_6F_3H_2)_2]$ is obtained. Nevertheless, the binuclear X-bridged compounds are best obtained by the alternative route shown in the Scheme.

On the other hand, when the magnesium-free solution is evaporated to dryness and benzonitrile in diethyl ether is added, the neutral bis(organo) derivative (**1**) is obtained. The insolubility of the alkali-metal halide in the reaction medium should be an important factor in the formation of the benzonitrile adduct according to equation (1) (X = Cl, or Br,

---

† Bis(benzyltriphenylphosphonium) di-μ-thiocyanato-bis[bis(2,4,6-trifluorophenyl)palladate(II)].

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



**Scheme.** (*i*) 2MgRBr in thf, then dioxane (diox); (*ii*) concentration, hexane; (*iii*) dba in $Et_2O$; (*iv*) 2PhCN in $Et_2O$; (*v*) $NMe_4Cl$; (*vi*) 2L in $CHCl_3$; (*vii*) MX (KBr, NaI, or KSCN)

**Table 1.** Analytical data, yields, and physical properties for the new complexes

| | | | | Analysis (%) | | |
|---|---|---|---|---|---|---|
| Complex | Colour | Yield (%) | M.p. (θ/°C) | C | H | N |
| (1) $[Pd(C_6F_3H_2)_2(PhCN)_2]$ | White | 70 | 112 | 54.3<br>(54.3) | 2.7<br>(2.5) | 4.6<br>(4.9) |
| (2) $[Pd(C_6F_3H_2)_2(dba)]$ | Yellow | 63 | 118 | 57.4<br>(57.8) | 3.2<br>(3.0) | |
| (3) $[Pd(C_6F_3H_2)_2(PEt_3)_2]$ | White | 80 | 156 | 47.5<br>(47.7) | 5.8<br>(5.7) | |
| (4) $[Pd(C_6F_3H_2)_2(AsPh_3)_2]$ | White | 40 | 129 | 57.9<br>(58.8) | 3.8<br>(3.5) | |
| (5) $[Pd(C_6F_3H_2)_2\{P(OMe)_3\}_2]$ | White | 82 | 92 | 35.0<br>(35.1) | 3.5<br>(3.6) | |
| (6) $[Pd(C_6F_3H_2)_2\{P(OEt)_3\}_2]$ | White | 75 | 102 | 40.8<br>(41.1) | 4.9<br>(4.9) | |
| (7) $[Pd(C_6F_3H_2)_2\{P(OPh)_3\}_2]$ | White | 60 | 128 | 58.4<br>(58.3) | 3.8<br>(3.5) | |
| (8) $[Pd(C_6F_3H_2)_2(cod)]$ | White | 96 | 129 | 50.1<br>(50.4) | 3.5<br>(3.4) | |
| (9) $[Pd(C_6F_3H_2)_2(tmen)]$ | White | 38 | 222 | 44.8<br>(44.6) | 4.5<br>(4.2) | 5.6<br>(5.8) |
| (10) $[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}Cl)_2]$ | White | 90 | 199 | 39.7<br>(40.2) | 3.6<br>(3.4) | 2.8<br>(2.9) |
| (11) $[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}Br)_2]$ | Pale yellow | 83 | 185 | 36.8<br>(36.7) | 3.3<br>(3.1) | 2.4<br>(2.7) |
| (12) $[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}I)_2]$ | Orange | 73 | 183 | 33.7<br>(33.7) | 2.9<br>(2.8) | 2.7<br>(2.5) |
| (13) $[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}NCS)_2]$ | White | 75 | 188 | 40.8<br>(40.8) | 3.4<br>(3.2) | 5.3<br>(5.6) |

$$K_2[R_2Pd(\mu\text{-}X)_2PdR_2] + 4PhCN \longrightarrow 2KX + 2[PdR_2(PhCN)_2] \quad (1)$$

$R = C_6F_3H_2$) in which the binuclear anion on the left-hand side can be as such or partially dissociated. A similar result is obtained when dibenzylideneacetone (dba) is used instead of benzonitrile, and (**2**) is the reaction product.

Neutral complexes $[Pd(C_6F_3H_2)_2L_2]$ are obtained by treating (**1**) with the corresponding neutral ligand in chloroform, where the substitution reaction occurs smoothly at ambient temperature (Scheme). Compounds (**1**)—(**9**) are air- and moisture-stable solids which gave satisfactory partial elemental analyses (Table 1) and their acetone solutions are non-conducting.

The i.r. spectra of the new compounds show bands attributed to the 2,4,6-$C_6F_3H_2$ group[8,10,11] at *ca.* 1 610m, 1 580s, 1 395s, 1 300m, 1 290m, 1 275m, 1 145m, 1 090s, 990vs, 830s, 730s—m, 590m—w, and 320w $cm^{-1}$. For gold[10] and palladium[8] complexes in which the *cis*-$M(C_6F_3H_2)_2$ fragment is present, the absorption at 830 $cm^{-1}$ was observed as a split

**Table 2.** N.m.r. data (solvent $CDCl_3$) ($J$ in Hz) for the mononuclear palladium complexes

| Complex | $^1H$, δ ($SiMe_4$) | $^{19}F$, δ/p.p.m. ($CFCl_3$) | | $^{31}P$, δ/p.p.m. ($H_3PO_4$) |
|---|---|---|---|---|
| | | $F_o$ | $F_p$ | |
| **(1)** | 7.65—7.41 (10 H, m, Ph)<br>6.32 (4 H, dd, $J_{HF_p}$ 9.4, $J_{HF_o}$ 5.5, $C_6F_3H_2$) | −86.76 | −118.54 | |
| **(2)** | 7.86—7.35 (14 H, m, dba)<br>6.35 (4 H, br d, $C_6F_3H_2$) | −84.16 | −121.86 | |
| **(3)** | 6.25 (4 H, d, $J_{HF_p}$ 9.2, $C_6F_3H_2$)<br>1.61—0.94 (30 H, m, Et) | −84.67 | −119.78 | 9.75 |
| **(4)** | 7.56—7.21 (30 H, m, Ph)<br>6.59 (4 H, dd, $J_{HF_p}$ 9.2, $J_{HF_o}$ 5.7, $C_6F_3H_2$) | −85.14 | −119.85 | |
| **(5)** | 6.29 (4 H, br d, $J_{HF_p}$ 9.0, $C_6F_3H_2$)<br>3.57 (18 H, $CH_3$)* | −85.28 | −118.59 | 126.93 |
| **(6)** | 6.27 (4 H, d, $J_{HF_p}$ 8.8, $C_6F_3H_2$)<br>3.96 (12 H, m, $CH_2$)<br>1.18 (18 H, t, $J_{HH}$ 7.0, $CH_3$) | −85.26 | −119.22 | 122.23 |
| **(7)** | 7.21—6.94 (30 H, m, Ph)<br>6.04 (4 H, d, $J_{HF_p}$ 9.0, $C_6F_3H_2$) | −84.00 | −118.45 | 108.37 |
| **(8)** | 6.32 (4 H, dd, $J_{HF_p}$ 9.3, $J_{HF_o}$ 4.6, $C_6F_3H_2$)<br>2.66 (4 H, br s, CH)<br>2.46 (8 H, br s, $CH_2$) | −87.06 | −117.31 | |
| **(9)** | 6.25 (4 H, d, $J_{HF_p}$ 9.3, $C_6F_3H_2$) | −86.26 | −119.45 | |

* This resonance consists of a doublet at δ 3.57 ($J_{HP}$ 11.9 Hz) and a broad singlet at δ 3.57.

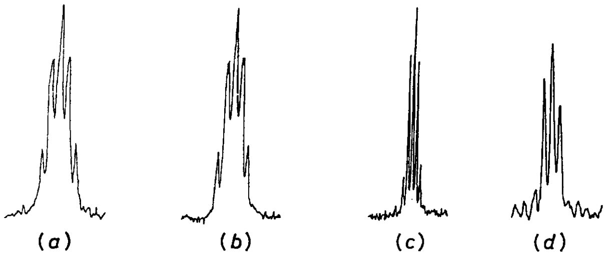


**Figure 1.** Expanded $^{31}P-\{^1H\}$ n.m.r. resonances of the dppe(*a*), $PEt_3$(*b*), $P(OEt)_3$(*c*), and $P(OPh)_3$(*d*) complexes. The apparent quintets and triplet are the AA′ part of a $X_2AA'X'_2$ spin system. (*a*) $J_{PP'} \approx J_{PF} \approx J_{PF'} = 7.7$; (*b*) $J_{PP'} \approx 6.5$, $J_{PF} \approx 8.8$, $J_{PF'} \approx 4.3$; (*c*) $J_{PP'} = 0$, $J_{PF} \approx J_{PF'} = 10.0$; (*d*) $J_{PP'} = J_{PF'} = 0$, $J_{PF} = 9.9$ Hz. The spectrum of (**5**) is similar to (*c*) with $J_{PP'} = 0$ and $J_{PF} \approx J_{PF'} = 9.9$ Hz

band, whereas a single band in this spectral region for some complexes $[Pd(C_6F_3H_2)_2L_2]$ was attributed to the *trans* configuration. This spectral behaviour appears to be similar to that found in square-planar bis(pentafluorophenyl) palladium(II) derivatives[4] for the so-called *X*-sensitive mode of $C_6F_5$.[12] Complexes for which the chelating nature of the neutral ligand [dba, cyclo-octa-1,5-diene (cod), and *NNN′N′*-tetramethylethylenediamine (tmen)] requires the *cis* geometry give a broad band or a band with a shoulder. Compounds (**1**), (**3**), (**5**), and (**6**) show a split band at *ca.* 830 $cm^{-1}$ suggesting they are the *cis* isomers, and the $^{31}P$ n.m.r. data for (**3**), (**5**), and (**6**) are consistent with the above assignments. Compounds (**4**) and (**7**) give a single sharp band in the same i.r. region, but the $^{31}P$ n.m.r. spectrum of (**7**) is incompatible with the *trans* geometry. The 40 $cm^{-1}$ shift to higher wavenumbers observed for ν(C≡N) of complex (**1**) (at 2 230 $cm^{-1}$ for unco-ordinated PhCN) is indicative of an end-on co-ordination, *i.e. via* the lone pair on the nitrogen atom.[13] A similar blue shift was found for *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$.[5]

The $^1H$, $^{19}F$, and $^{31}P$ n.m.r. data for compounds (**1**)—(**9**) are collected in Table 2. The *m*-hydrogen atoms in the $C_6F_3H_2$ rings give a doublet in the range δ 6.40—6.20 due to coupling to the neighbouring $F_p$ atom. Further coupling to the $F_o$ atom gives rise to a doublet of doublets, but this effect is not discernible for the complexes containing P-donor ligands because coupling to the P atoms causes broadening of the doublet. The $^{19}F$ n.m.r. spectra show the expected two resonances for the $F_o$ and $F_p$ atoms (2:1 intensity ratio). Since only a chemical shift is observed for the $^{19}F$ resonances, free rotation of the $C_6F_3H_2$ groups around the Pd–$C_6F_3H_2$ bond is not hindered.

The $^{31}P$ n.m.r. spectra are particularly interesting, for they provide valuable information on the *cis*/*trans* nature of the complexes. The parameters in Table 2 show that the P atoms display positive chemical shifts, but the resonances are broadened due to unresolved coupling to the protons of the substituents on the phosphine as well as to the F and H atoms in the $C_6F_3H_2$ groups. However, the $^{31}P-\{^1H\}$ spectra display resolved coupling to the *o*-fluorine atoms in the trifluorophenyl rings. The expanded resonance signals for compounds (**3**), (**6**), and (**7**) are illustrated in Figure 1, which also shows the spectrum of $[Pd(C_6F_3H_2)_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) for comparative purposes. All the spectra can be satisfactorily interpreted* on the basis of an $[AX_2]_2$ spin system[14] corresponding to the *cis* isomers, which can give an apparent quintet [dppe, $PEt_3$, $P(OMe)_3$, or $P(OEt)_3$ complexes] or triplet [$P(OPh)_3$ complex] according to the relative magnitudes of the coupling constants $J_{PP}$ and $J_{PF}$. Despite the much greater sharpness of the lines of (**5**) and (**6**) compared to the other compounds, the fine structures of these complexes show considerable deviation from the first-order quintet caused by an $AX_4$ spin system, and the *trans* configuration must be rejected.

*Binuclear Complexes.*—Complex (**1**) reacts with $NMe_4Cl$ to give (**10**), which undergoes interchange reactions with alkali-metal salts (Scheme) without formal cleavage of the bridging system to give the corresponding X-bridged compounds (X = Br, I, or SCN). Complexes (**11**)—(**13**) are also air- and moisture-stable solids and their acetone solutions ($c \approx 5 \times 10^{-4}$ mol $dm^{-3}$) exhibited conductance values (150—180 $\Omega^{-1}$ $cm^2$ $mol^{-1}$) corresponding to 2:1 electrolytes.[15] A split band or a broad band (iodo-complex) at 830—820 $cm^{-1}$ is indicative of the *cis*-

---

* We thank a referee for constructive suggestions.

**Table 3.** N.m.r. data ($J$ in Hz) for the binuclear palladium complexes [solvent $(CD_3)_2CO$]

| | | $^{19}F$, $\delta$/p.p.m. ($CFCl_3$) | |
|---|---|---|---|
| Complex | $^1H$, $\delta$ ($SiMe_4$)[a] | $F_o$ | $F_p$ |
| **(10)** | 6.12 (8 H, dd, $J_{HF_p}$ 9.8, $J_{HF_o}$ 4.9, $C_6F_3H_2$) | −81.99 | −120.64 |
| **(11)** | 6.14 (8 H, dd, $J_{HF_p}$ 9.8, $J_{HF_o}$ 5.0, $C_6F_3H_2$) | −81.60 | −120.63 |
| **(12)** | 6.11 (8 H, m, $C_6F_3H_2$) | −80.46<br>−82.01 | −121.02 (36%)[b]<br>−120.64 (64%) |
| **(13)** | 6.19 (8 H, $C_6F_3H_2$)[c] | | |

[a] In all cases a peak from $[NMe_4]^+$ is found at $\delta$ *ca.* 3.7 (24 H, s). [b] See text. [c] Five peaks with relative intensities 1:2:2:2:1 [doublet of doublets from $C_6F_3H_2$ (R) *trans* to S overlapped with another doublet of doublets from $C_6F_3H_2$ (R′) *trans* to N (see text); $J_{HF_p(R)} = J_{HF_p(R')} = 9.8$, $J_{HF_o(R)} = 4.7$, $J_{HF_o(R')} = 5.1$ Hz].

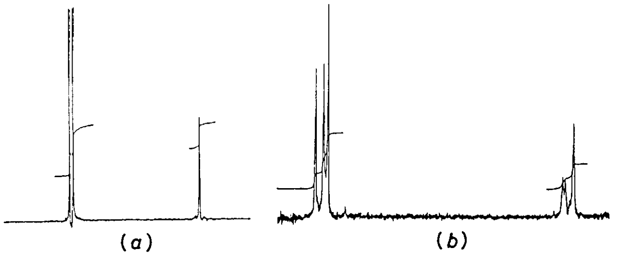

(*a*) (*b*)

**Figure 2.** $^{19}F$ N.m.r. spectra of complex **(13)** in $(CD_3)_2CO$ (*a*) and $(CD_3)_2SO$ (*b*). For interpretation see text

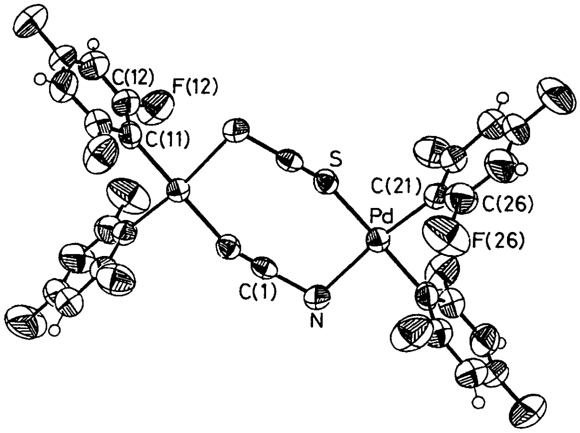


**Figure 3.** ORTEP drawing[17] of the $[(C_6F_3H_2)_2Pd(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(C_6F_3H_2)_2]^{2-}$ anion. Atom C(21) has been labelled in another asymmetric unit. Its symmetry code is that of Table 5

$Pd(C_6F_3H_2)_2$ fragment. Complex **(10)** gives a split band at 250 cm$^{-1}$ attributed to the $Pd(\mu\text{-}Cl)_2Pd$ moiety, but similar absorptions for **(11)** and **(12)** are not detected in the i.r. spectra because they should lie below the lowest limit (200 cm$^{-1}$) of our spectrophotometer. The C≡N stretching mode at 2 120 cm$^{-1}$ is consistent with the presence of SCN bridges[16] in **(13)**.

The $^1H$ and $^{19}F$ n.m.r. data for complexes **(10)**—**(13)** are collected in Table 3. In acetone, **(10)** and **(11)** give two $^{19}F$ resonances for the $F_o$ and $F_p$ atoms (2:1 intensity ratio), but both signals are duplicated in the spectrum of **(13)** [Figure 2(*a*)], which is attributed to a structure containing two $C_6F_3H_2$ groups *trans* to S atoms and two $C_6F_3H_2$ groups *trans* to N atoms, *i.e.* a centrosymetric anion $[(C_6F_3H_2)_2Pd(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(C_6F_3H_2)_2]^{2-}$, which has been confirmed by *X*-ray diffraction. However, when **(13)** is dissolved in the stronger donor solvent [$^2H_6$]dimethyl sulphoxide, the spectrum is that shown in Figure 2(*b*), which is easily interpreted on the assumption that the solvent causes cleavage of one SCN bridge to give $[(C_6F_3H_2)_2(dmso)Pd(\mu\text{-}SCN)Pd(dmso)(C_6F_3H_2)_2]^- + SCN^-$. A similar effect is observed for dimethyl sulphoxide (dmso) solutions of **(10)** and **(11)**, but the $^{19}F$ n.m.r. data indicate that the situation is more complex and a mixture of unidentified species is involved in the dissociation equilibrium. The more labile iodo-complex **(12)** undergoes the same effect even in the solvent acetone and the $^{19}F$ n.m.r. data (Table 3) show that two species coexist, probably $[(C_6F_3H_2)_2Pd(\mu\text{-}I)_2Pd(C_6F_3H_2)_2]^{2-}$ (36%) and $[(C_6F_3H_2)_2(Me_2CO)Pd(\mu\text{-}I)Pd(Me_2CO)(C_6F_3H_2)_2]^-$ (64%).

*X-Ray Crystal Structure of* $[P(CH_2Ph)Ph_3]_2[(C_6F_3H_2)_2Pd(\mu\text{-}SCN)_2Pd(C_6F_3H_2)_2]$.—The structure consists of binuclear centrosymetric $[(C_6F_3H_2)_2Pd(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(C_6F_3H_2)_2]^{2-}$ anions (Figure 3, drawn by ORTEP[17]) and $[P(CH_2Ph)Ph_3]^+$ cations, which are held together by electrostatic interactions. Positional parameters and interatomic distances and angles are collected in Tables 4 and 5 respectively. All of them compare well with those reported for similar compounds.[18]

The Pd atoms and the four atoms co-ordinated to it show slight deviations from the mean plane defined by them. However, these deviations are significant in terms of the attained accuracy ($\chi^2 = 5.99$ at 95% for two degrees of freedom), the most significant being that of S [0.008(2) Å]. The two square planes around the Pd atoms forming the dimer are parallel and are separated from each other by 0.52 Å as a consequence of $sp^3$ hybridization at the S atoms (see torsion angles in Table 5).

The two fluorophenyl rings bonded to Pd are planar and rotated 90.1(3)° from each other. However, most of the F atoms are out of the ring planes with deviations up to 0.0057(5) Å [for F(26)]. Even if they are planar, the rings present severe distortions as indicated by the values of the C–C–C angles which range from 112.3(6) to 126.5(8)°, the highest values corresponding to the central carbons which are bonded to F atoms. Similar distortions have been observed in other fluorophenyl groups.[19] In our case, the angular deformations in both rings match quite well with each other (see Table 5).

In the $PR_4^+$ cation, all the bond lengths and angles are as expected and the four rings are planar.

## Experimental

Carbon, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyser. Conductivities were measured with a Philips PW 9501/01 conductimeter. I.r. spectra were recorded (in the range 4 000—200 cm$^{-1}$) on a Perkin-Elmer 1430 spectrophotometer, and $^1H$, $^{19}F$, and $^{31}P$ n.m.r. spectra on a Varian FT-80A instrument. Melting points were determined on a Reichert microscope.

The salt $K_2[PdCl_4]$ was prepared from metallic Pd,[20] and tetrahydrofuran solutions of $Mg(C_6F_3H_2)Br$ were prepared by treating the corresponding bromo-derivative with Mg, as described elsewhere[1] for $Mg(C_6F_5)Br$. All the solvents were dried by literature methods before use.

*Preparation of Complexes.*—$[Pd(C_6F_3H_2)_2(PhCN)_2]$ **(1)**. A freshly prepared and filtered solution of $Mg(C_6F_3H_2)Br$ [from Mg (0.15 g, 6.17 mmol) and bromo-2,4,6-trifluorobenzene (1.30 g, 6.16 mmol) in tetrahydrofuran (thf) (10 cm$^3$)] was added to $K_2[PdCl_4]$ (0.5 g, 1.532 mmol) in thf (30 cm$^3$). The suspension was boiled under reflux in a nitrogen atmosphere for 4 h. After cooling at room temperature, dioxane (25 cm$^3$) was added and the mixture was stirred for 30 min then set aside in a refrigerator

**Table 4.** Atomic parameters for $[P(CH_2Ph)Ph_3]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}SCN)_2]$

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Pd | 0.331 49(4) | −0.053 14(3) | 0.054 19(3) | C(32) | 0.258 0(6) | 0.137 7(5) | −0.361 1(4) |
| P | 0.310 3(1) | 0.201 5(1) | −0.204 8(1) | C(33) | 0.267 0(7) | 0.082 1(6) | −0.420 9(5) |
| S | 0.658 6(1) | 0.094 2(1) | 0.077 2(1) | C(34) | 0.339 4(7) | 0.015 3(5) | −0.401 1(5) |
| F(12) | 0.256 9(4) | 0.112 9(3) | 0.125 4(3) | C(35) | 0.402 9(7) | 0.004 8(5) | −0.321 9(5) |
| F(14) | 0.277 9(6) | 0.0320 (4) | 0.391 0(3) | C(36) | 0.394 8(6) | 0.061 1(4) | −0.260 8(4) |
| F(16) | 0.364 2(5) | −0.165 5(3) | 0.217 1(3) | C(41) | 0.174 1(5) | 0.209 8(4) | −0.208 7(4) |
| F(22) | 0.303 1(4) | −0.257 7(3) | 0.075 5(4) | C(42) | 0.131 3(6) | 0.151 9(5) | −0.166 8(4) |
| F(24) | −0.063 5(4) | −0.283 9(4) | −0.025 1(4) | C(43) | 0.024 9(7) | 0.157 7(6) | −0.172 0(5) |
| F(26) | 0.094 4(3) | −0.015 4(3) | −0.025 2(3) | C(44) | −0.038 4(7) | 0.218 8(6) | −0.220 3(6) |
| N | 0.461 8(4) | 0.028 1(3) | 0.076 3(3) | C(45) | 0.002 5(6) | 0.275 4(6) | −0.263 0(6) |
| C(1) | 0.541 1(5) | 0.056 2(4) | 0.076 3(3) | C(46) | 0.109 7(6) | 0.271 9(5) | −0.258 1(5) |
| C(11) | 0.309 0(5) | −0.028 3(5) | 0.163 3(4) | C(51) | 0.359 8(5) | 0.302 5(4) | −0.225 8(4) |
| C(12) | 0.279 1(5) | 0.047 8(5) | 0.182 3(4) | C(52) | 0.435 7(6) | 0.302 8(5) | −0.265 8(5) |
| C(13) | 0.267 0(6) | 0.073 0(6) | 0.258 0(6) | C(53) | 0.488 3(8) | 0.378 1(7) | −0.271 4(6) |
| C(14) | 0.288 3(8) | 0.010 6(7) | 0.316 2(5) | C(54) | 0.465 0(8) | 0.452 0(7) | −0.238 0(6) |
| C(15) | 0.320 8(9) | −0.069 5(6) | 0.304 7(5) | C(55) | 0.387 6(7) | 0.452 1(5) | −0.200 9(5) |
| C(16) | 0.330 3(7) | −0.085 2(5) | 0.227 4(5) | C(56) | 0.334 8(6) | 0.377 9(4) | −0.192 8(4) |
| C(21) | 0.205 8(5) | −0.130 8(5) | 0.030 3(4) | C(60) | 0.391 5(5) | 0.168 9(4) | −0.102 6(4) |
| C(22) | 0.208 2(6) | −0.218 4(5) | 0.043 8(5) | C(61) | 0.394 7(5) | 0.238 7(4) | −0.041 1(4) |
| C(23) | 0.120 2(8) | −0.271 5(6) | 0.025 9(6) | C(62) | 0.473 2(6) | 0.300 6(5) | −0.025 6(5) |
| C(24) | 0.024 3(7) | −0.233 3(7) | −0.007 5(6) | C(63) | 0.472 5(6) | 0.368 8(6) | 0.026 9(5) |
| C(25) | 0.013 0(6) | −0.149 2(7) | −0.025 6(5) | C(64) | 0.395 4(8) | 0.374 1(6) | 0.062 4(5) |
| C(26) | 0.105 7(6) | −0.101 2(6) | −0.005 1(5) | C(65) | 0.319 0(7) | 0.312 7(7) | 0.049 4(6) |
| C(31) | 0.322 0(5) | 0.126 0(4) | −0.280 0(4) | C(66) | 0.318 7(6) | 0.243 9(6) | −0.002 6(5) |

**Table 5.** Bond lengths (Å) and angles (°) for $[P(CH_2Ph)Ph_3]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}SCN)_2]$*

| | | | $X = 1$ | $X = 2$ |
|---|---|---|---|---|
| Pd–S$^{\mathrm{I}}$ | 2.387(5) | C(*X*1)–C(*X*2) | 1.32(1) | 1.38(1) |
| Pd–N | 2.07(1) | C(*X*1)–C(*X*6) | 1.37(1) | 1.36(3) |
| Pd–C(11) | 2.02(1) | C(*X*2)–C(*X*3) | 1.41(1) | 1.38(2) |
| Pd–C(21) | 1.99(1) | C(*X*3)–C(*X*4) | 1.36(2) | 1.36(2) |
| S–C(1) | 1.658(7) | C(*X*4)–C(*X*5) | 1.35(1) | 1.34(1) |
| C(1)–N | 1.136(8) | C(*X*5)–C(*X*6) | 1.39(1) | 1.38(2) |
| P–C(31) | 1.788(8) | Mean | 1.37(1) | 1.37(2) |
| P–C(41) | 1.786(8) | | | |
| P–C(51) | 1.783(8) | C(*X*2)–F(*X*2) | 1.37(1) | 1.35(2) |
| P–C(60) | 1.82(4) | C(*X*4)–F(*X*4) | 1.37(1) | 1.36(2) |
| C(60)–C(61) | 1.51(1) | C(*X*6)–F(*X*6) | 1.36(1) | 1.38(1) |

Mean value for the C–C distance in rings of $[P(CH_2Ph)Ph_3]^+$: 1.38(2)

| | | | $X = 1$ | $X = 2$ |
|---|---|---|---|---|
| S$^{\mathrm{I}}$–Pd–N | 92.8(1) | C(*X*6)–C(*X*1)–C(*X*2) | 112.6(7) | 112.3(6) |
| S$^{\mathrm{I}}$–Pd–C(11) | 173.3(2) | C(*X*1)–C(*X*2)–C(*X*3) | 127.0(7) | 125.3(7) |
| S$^{\mathrm{I}}$–Pd–C(21) | 86.0(2) | C(*X*2)–C(*X*3)–C(*X*4) | 115.0(8) | 116.5(8) |
| N–Pd–C(11) | 93.8(2) | C(*X*3)–C(*X*4)–C(*X*5) | 123.6(9) | 123.1(9) |
| N–Pd–C(21) | 178.7(3) | C(*X*4)–C(*X*5)–C(*X*6) | 115.3(8) | 116.2(7) |
| C(11)–Pd–C(21) | 87.3(3) | C(*X*5)–C(*X*6)–C(*X*1) | 126.4(8) | 126.5(8) |
| Pd$^{\mathrm{I}}$–S–C(1) | 102.8(2) | F(*X*2)–C(*X*1)–C(*X*1) | 120.0(7) | 115.0(6) |
| S–C(1)–N | 178.2(6) | F(*X*2)–C(*X*2)–C(*X*3) | 113.0(7) | 115.7(7) |
| Pd–N–C(1) | 161.5(5) | F(*X*4)–C(*X*4)–C(*X*3) | 118.2(9) | 117.6(9) |
| | | F(*X*4)–C(*X*4)–C(*X*5) | 118.2(9) | 119.2(8) |
| | | F(*X*6)–C(*X*6)–C(*X*5) | 114.6(7) | 116.2(7) |
| | | F(*X*6)–C(*X*6)–C(*X*1) | 115.0(7) | 117.2(7) |

| $[P(CH_2Ph)Ph_3]^+$ | | | | Torsion angles | | | |
|---|---|---|---|---|---|---|---|
| C(31)–P–C(41) | 109.4(3) | C(41)–P–C(60) | 110.1(3) | N–C–S–Pd | 175.6(4) | S–Pd–N–C | 33(2) |
| C(31)–P–C(51) | 108.2(3) | C(51)–P–C(60) | 107.2(3) | N–Pd–S–C | 11.9(3) | | |
| C(31)–P–C(60) | 110.8(3) | P–C(60)–C(61) | 110.7(4) | | | | |
| C(41)–P–C(51) | 111.0(3) | | | | | | |

Mean C–C–C angle in phenyl rings: 120(1)

* Symmetry code: I 1 − *x*, −*y*, −*z*.

overnight. The precipitated magnesium halides were removed by filtration (under nitrogen atmosphere) and benzonitrile (0.31 cm$^3$, 3.06 mmol) was added to the resulting yellow-orange solution. After stirring at room temperature for 30 min the solution was evaporated to dryness under reduced pressure and the residue was treated with diethyl ether–dichloromethane

(1:1) (30 $cm^3$), which was filtered to give a pale yellow solution. This was concentrated and addition of n-hexane precipitated a white solid, which was collected by filtration, then washed with n-hexane, and air-dried. The product was recrystallized from chloroform–hexane.

$[Pd(C_6F_3H_2)_2(dba)]$ (**2**). This was prepared as described above but using dibenzylideneacetone (0.358 g, 1.532 mmol) instead of benzonitrile.

$[Pd(C_6F_3H_2)_2L_2]$ [L = $PEt_3$, (**3**); $AsPh_3$, (**4**); $P(OMe)_3$, (**5**); $P(OEt)_3$, (**6**); $P(OPh)_3$, (**7**); $L_2$ = cod, (**8**); or tmen, (**9**)]. In separate experiments, the stoicheiometric amount (0.250 or 0.125 mmol) of the corresponding ligand was added to a solution of $[Pd(C_6F_3H_2)_2(PhCN)_2]$ (0.250 mmol) in chloroform (10 $cm^3$). The solution was stirred at room temperature for 1 h, then concentrated under reduced pressure to half the original volume. Addition of hexane resulted in the precipitation of the expected organo complex as a white or pale yellow solid which was washed with ethanol and n-hexane and dried in the air. The compounds were recrystallized from chloroform–ethanol and the individual yields are collected in Table 1.

$[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}Cl)_2]$ (**10**). A solution of $NMe_4Cl$ (0.038 g, 0.348 mmol) in ethanol (5 $cm^3$) was added to a solution of $[Pd(C_6F_3H_2)_2(PhCN)_2]$ (0.100 g, 0.174 mmol) in acetone (10 $cm^3$). The mixture was stirred at room temperature for 2 h, during which time a white precipitate appeared. Addition of ethanol ($\approx$5 $cm^3$) resulted in the complete precipitation of complex (**10**), which was filtered off, washed with ethanol and n-hexane, and dried under vacuum. The compound was recrystallized from acetone–hexane.

$[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}Br)_2]$ (**11**). An acetone (10 $cm^3$) solution containing complex (**10**) (0.100 g, 0.1046 mmol) and KBr (0.0249 g, 0.2092 mmol) was refluxed for 2 h, then stirred at room temperature for 20 h. The potassium chloride formed during the reaction was removed by filtration under vacuum and the resulting solution was then concentrated under vacuum until a pale yellow solid began to precipitate. The precipitation was completed by addition of n-hexane (5 $cm^3$) and the compound was filtered off under vacuum, washed with n-hexane, and air-dried.

$[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}I)_2]$ (**12**). Sodium iodide (0.0313 g, 0.2092 mmol) was added to an acetone (10 $cm^3$) solution containing complex (**10**), (0.100 g, 0.1046 mmol). The mixture was refluxed for 2 h, then filtered at room temperature to remove the sodium chloride. The resulting solution was concentrated under vacuum to *ca.* 2 $cm^3$. Addition of ethanol–n-hexane precipitated an orange solid which was filtered off, washed with ethanol and n-hexane and air-dried. The compound was recrystallized from acetone–hexane.

$[NMe_4]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}SCN)_2]$ (**13**). Potassium thiocyanate (0.0203 g, 0.2090 mmol) was added to an acetone (10 $cm^3$) solution of complex (**10**) (0.100 g, 0.1046 mmol). Work-up as for the iodo-complex gave white crystals of complex (**13**), which were recrystallized from acetone–hexane. The corresponding salt $[P(CH_2Ph)Ph_3]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}SCN)_2]$ was prepared similarly from phosphonium chloride and crystals suitable for *X*-ray diffraction were obtained by solvent diffusion (acetone–n-hexane) at room temperature.

The individual yields of the binuclear complexes are listed in Table 1.

*Crystal Structure Determination of* $[P(CH_2Ph)Ph_3]_2[Pd_2(C_6F_3H_2)_4(\mu\text{-}SCN)_2]$.—*Crystal data.* $(C_{38}H_{26}F_6NPPdS)_2$, $M$ = 1 560.1, monoclinic, $a$ = 13.227(5), $b$ = 15.557(5), $c$ = 17.167(6) Å, $\beta$ = 108.06(4)°, $U$ = 3 358(2) $Å^3$ (by least-squares refinement on diffractometer angles for 25 centred reflections, $\lambda$ = 0.7107 Å), space group $P2_1/n$ (no. 14), $Z$ = 2, $D_c$ = 1.54 g $cm^{-3}$, colourless prisms, *ca.* 0.3 × 0.25 × 0.12 mm, $\mu(Mo\text{-}K_\alpha)$ = 7.11 $cm^{-1}$, $F(000)$ = 1 568.

*Data collection and processing.* Nonius CAD-4 diffractometer, $\omega$—2$\theta$ scan mode, graphite-monochromated Mo-$K_\alpha$ radiation. 6 548 Reflections measured ($2 < \theta < 27°$), 5 918 unique, with 3 384 having $I > 3\sigma(I)$.

*Structure analysis and refinement.* Heavy-atom method (Pd) followed by normal Fourier synthesis. Full-matrix least-squares refinement. An empirical absorption correction was applied at the end of the isotropic refinement[21] minimum and maximum absorption corrections 0.0887 and 1.150, mean 1.001). Some of the H atoms were located by a difference synthesis, others were fixed at calculated positions (C–H = 1 Å). All of them were held invariant in the last refinements. Thermal motion was considered anisotropic for all non-hydrogen atoms and isotropic for H. Unit weights were applied to each reflection. The final $R$ value was 0.040 for the observed reflections only. Most of the calculations were performed with the *X*-RAY 80 system,[22] and scattering factors for neutral atoms were taken from ref. 23.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

## Acknowledgements

We thank the Direccíon General de Investigacíon Científica y Técnica (project PB87-0690), Spain, for financial support.

## References

1 G. García and G. López, *Inorg. Chim. Acta*, 1981, **52**, 87.
2 G. López, G. García, C. de Haro, G. Sánchez, and M. C. Vallejo, *J. Organomet. Chem.*, 1984, **263**, 247.
3 R. Usón, J. Forniés, M. Tomás, and B. Menjon, *Organometallics*, 1985, **4**, 1912.
4 R. Usón, J. Forniés, F. Martinez, and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1980, 888.
5 C. de Haro, G. García, G. Sánchez, and G. López, *J. Chem. Res.*, 1986, (*S*), 119; (*M*), 1128.
6 G. López, G. García, C. de Haro, G. Sánchez, and J. García, *J. Organomet. Chem.*, 1986, **317**, C23.
7 G. López, G. García, J. Ruiz, G. Sánchez, J. García, and C. Vicente, *J. Chem. Soc., Chem. Commun.*, 1989, 1045.
8 G. López, M. D. Santana, G. García, G. Sánchez, and J. García, *Transition Met. Chem. (Weinheim, Ger.)*, 1987, **12**, 130.
9 R. Usón, J. Forniés, P. Espinet, F. Martínez, and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1981, 463.
10 R. Usón, A. Laguna, J. García, and M. Laguna, *Inorg. Chim. Acta*, 1979, **37**, 201.
11 R. Usón, A. Laguna, E. J. Fernández, A. Mendia, and P. G. Jones, *J. Organomet. Chem.*, 1988, **350**, 129.
12 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, 1968, **24**, 1125.
13 B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, 1977, **23**, 1.
14 D. J. Mowthorpe and A. C. Chapman, *Spectrochim. Acta*, 1967, **23**, 451.
15 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
16 P. P. Singh, *Coord. Chem. Rev.*, 1980, **32**, 33.
17 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
18 R. Usón, J. Forniés, M. A. Usón, J. F. Yagüe, P. G. Jones, and K. Meyer-Bäse, *J. Chem. Soc., Dalton Trans.*, 1986, 947.
19 P. G. Jones, *J. Organomet. Chem.*, 1988, **345**, 405.
20 S. E. Livingstone, *Synth. React. Inorg. Met.-Org. Chem.*, 1971, **1**, 1.
21 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1987, **39**, 158.
22 J. M. Stewart, F. A. Kundell, and J. C. Baldwin, The *X*-RAY 80 system of crystallographic programs, Computer Science Center, University of Maryland, College Park, Maryland, 1976.
23 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

*Received* 29*th July* 1989; *Paper* 9/03215K