Tris(pentafluorophenyl) Neutral and Anionic Five-co-ordinate Complexes of Rhodium(III). Crystal Structures of $[Rh(C_6F_5)_3(PEt_3)_2]$ and $[Rh(C_6F_5)_3(AsPh_3)_2]$*

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The binuclear compound $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ (**1**) has been prepared by reaction of HCl with $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ (**2**) in methanol. Treatment of (**1**) with thallium(I) acetylacetonate has given the anionic complex $[P(CH_2Ph)Ph_3][Rh(acac)(C_6F_5)_3]$ (acac = acetylacetonate). Addition of neutral ligands L to (**1**) yields anionic derivatives of the type $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3L]$ [L = pyrazole (Hpz), pyridine (py), PPh_3, $AsPh_3$, or CO] (**3**)—(**7**) and the reaction of (**1**) with $AgClO_4$ in the presence of 2 mol of neutral ligands gives rise to neutral compounds $[Rh(C_6F_5)_3L_2]$ [L = $P(OMe)_3$, PPh_3, PEt_3, $AsPh_3$, py, Hpz, 4-methylpyrazole, or 3,5-dimethylpyrazole] (**8**)—(**15**). The crystal structures of the complexes $[Rh(C_6F_5)_3(PEt_3)_2]$ (**10**) and $[Rh(C_6F_5)_3(AsPh_3)_2]$ (**11**) have been determined by *X*-ray diffraction methods. Both structures consist of very flattened square-pyramidal complexes in which two C atoms from C_6F_5 groups and two P from PEt_3 ligands [(**10**)], or two As from $AsPh_3$ ligands [(**11**)], occupy the basal positions, whereas the third C atom from a C_6F_5 ligand lies at the apex.

The chemistry of pentahalogenophenyl complexes of transition metals such as palladium, platinum,[1] and gold[2] has been widely studied and a great variety of compounds have been obtained; among them, much attention has been paid to anionic complexes which, acting as nucleophiles, can be used for the preparation of homo- and hetero-nuclear transition-metal clusters;[3] these pentahalogenophenyl anionic complexes have been prepared by arylating starting compounds which do not contain π-acceptor ligands.[4]

However, rhodium complexes with pentahalogenoaryl ligands are rather scarce and all are neutral compounds of formulae $[RhR(L)(PPh_3)_2]$ (R = C_6F_5 or C_6Cl_5, L = CO or CS) and $[RhCl(C_6F_5)_2(PPh_3)_2]$.[5]

These considerations prompted us to study the arylation of $[RhCl_3(SC_4H_8)_3]$[6] with an excess of $Li(C_6F_5)$ and we have recently reported[7] the synthesis of the first anionic pentafluorophenyl derivatives of rhodium. Due to the great importance of anionic compounds as starting materials or building blocks for the construction of clusters, an area of growing interest,[8] we sought to extend this field by preparing new anionic and neutral pentafluorophenyl complexes of rhodium(III). In this paper we describe the synthesis and properties of new, five-co-ordinated tris(pentafluorophenyl)rhodium(III) complexes and the crystal structures of $[Rh(C_6F_5)_3L_2]$ (L = $AsPh_3$ or PEt_3).

Results and Discussion

The reaction of $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ with aqueous HCl in methanol (1:2 ratio) leads to the cleavage of two of the Rh–C bonds and formation of the binuclear complex $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ (**1**). If the reaction is carried out with a stoicheiometric amount of HCl (1:1) it is not possible to isolate $[P(CH_2Ph)Ph_3]_2[RhCl(C_6F_5)_4]$ or the corresponding binuclear $[P(CH_2Ph)Ph_3]_4[\{Rh(\mu\text{-}Cl)(C_6F_5)_4\}_2]$ because the reaction leads to a mixture which seemingly contains starting product and compound (**1**). This behaviour is similar to that found when $[M(C_6Cl_5)_4]^{2-}$ (M = Pd or Pt)[9] reacts with HCl, but different from that of $[Pt(C_6F_5)_4]^{2-}$ where the HCl can cause selective cleavage of one or two of the Pt–C bonds.[10]

Complex (**1**) is converted into its anionic mononuclear acetylacetonato (acac) derivative on treatment with thallium(I) acetylacetonate; thallium(I) chloride is precipitated and the new complex $[P(CH_2Ph)Ph_3][Rh(acac)(C_6F_5)_3]$ (**2**) can be readily isolated from the solution.

The reaction of (**1**) with neutral ligands (1:2), in dichloromethane solution, gives rise to cleavage of the chloro-bridges and formation of anionic five-co-ordinated mononuclear compounds $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3L]$, according to equation (1). [L = pyrazole (HPz), (**3**); pyridine (py), (**4**); PPh_3, (**5**); $AsPh_3$, (**6**); or CO, (**7**)].

$$[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2] + 2L \longrightarrow 2[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3L] \quad (1)$$

Addition of larger amounts of the neutral ligand L, in acetone or methanol, does not lead to displacement of the chloride and formation of neutral complexes $[Rh(C_6F_5)_3L_2]$. However, a second molecule of neutral ligand can be introduced after displacement of chloride by an appropriated abstractor; so the addition of silver perchlorate to a suspension of complex (**1**) in diethyl ether leads to a solid {mixture of AgCl and $[P(CH_2Ph)Ph_3]ClO_4$} and a yellow solution which probably contains $[Rh(C_6F_5)_3(Et_2O)_x]$ (x = 2 or 3). We have not been able to isolate this compound but it is stable in solution and can be kept, under nitrogen, for a few hours. The addition of neutral ligands to these solutions gives neutral five-co-ordinate compounds of the type $[Rh(C_6F_5)_3L_2]$ [L = $P(OMe)_3$, (**8**); PPh_3, (**9**); PEt_3, (**10**); $AsPh_3$, (**11**); py, (**12**); Hpz, (**13**); 4-methylpyrazole(Hmpz), (**14**), or 3,5-dimethylpyrazole (Hdmpz), (**15**)].

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* Bis(triethylphosphine)- and bis(triphenylarsine)-tris(pentafluorophenyl)rhodium(III).

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Table 1. Analytical and physical data for the new complexes

Compound	Colour	Yield (%)	Analyses (%)[a] C	H	N	$\Lambda_M(C)$[b]	M[a,c]
(1) $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu-Cl)(C_6F_5)_3\}_2]$	Yellow-orange	75	52.35 (52.00)	2.70 (2.20)	—	200.37 (1.06×10^{-4})	—
(2) $[P(CH_2Ph)Ph_3][Rh(C_6F_5)_3(acac)]$	Orange	70	53.75 (54.55)	3.00 (2.75)	—	104.0 (9.85×10^{-5})	—
(3) $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3(Hpz)]$	Orange	97	51.65 (51.55)	2.95 (2.45)	2.60 (2.65)	101.78 (1.62×10^{-4})	—
(4) $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3(py)]$	Yellow-orange	85	53.35 (53.75)	2.85 (2.55)	1.30 (1.30)	107.4 (1.08×10^{-4})	—
(5) $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3(PPh_3)]$	Orange	84	58.00 (58.35)	3.20 (2.95)	—	96.0 (1.56×10^{-4})	—
(6) $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3(AsPh_3)]$	Orange	72	54.95 (56.40)	3.05 (2.85)	—	114.0 (1.05×10^{-4})	—
(7) $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3(CO)]$	White	72	51.80 (51.75)	2.40 (2.15)	—	115.0 (9.53×10^{-5})	—
(8) $[Rh(C_6F_5)_3\{P(OMe)_3\}_2]$	White-yellow	62	33.80 (31.95)	2.15 (2.35)	—	—	851 (852)
(9) $[Rh(C_6F_5)_3(PPh_3)_2]$	Orange	44	56.50 (57.45)	3.20 (2.70)	—	—	950 (1 128)
(10) $[Rh(C_6F_5)_3(PEt_3)_2]$	Yellow	70	40.90 (42.85)	3.40 (3.60)	—	—	920 (840)
(11) $[Rh(C_6F_5)_3(AsPh_3)_2]$	Orange	77	53.15 (53.30)	2.70 (2.50)	—	—	1 300 (1 216)
(12) $[Rh(C_6F_5)_3(py)_2]$	Yellow	78	43.95 (44.10)	2.20 (1.30)	3.00 (3.65)	—	835 (762)
(13) $[Rh(C_6F_5)_3(Hpz)_2]$	Orange	88	38.95 (38.75)	0.80 (0.90)	7.55 (7.60)	—	614 (740)
(14) $[Rh(C_6F_5)_3(Hmpz)_2]$	Yellow	61	41.30 (41.95)	1.85 (1.60)	7.40 (7.55)	—	960 (764)
(15) $[Rh(C_6F_5)_3(Hdmpz)_2]$	Orange	75	43.95 (42.25)	2.30 (2.00)	7.00 (7.05)	—	896 (796)

[a] Calculated values are given in parentheses. [b] $\Lambda_M(\Omega^{-1}\ cm^2\ mol^{-1})$, C (mol dm^{-3}), in acetone. [c] In $CHCl_3$.

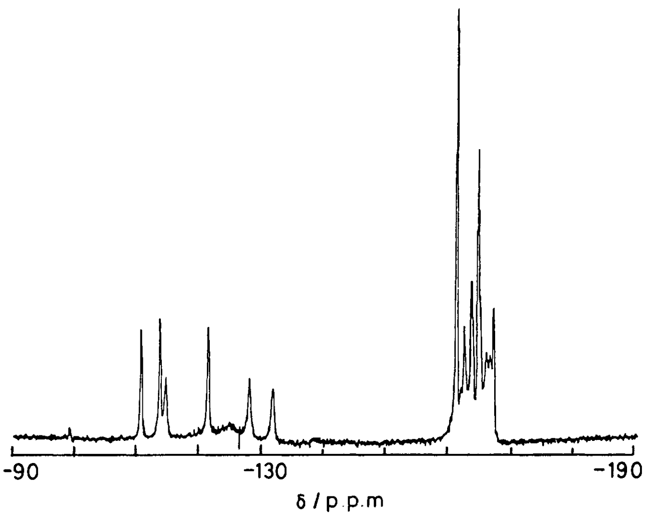

Figure 1. Fluorine-19 n.m.r. spectrum of $[Rh(C_6F_5)_3\{P(OMe)_3\}_2]$, a mixture of isomers (**8a**) and (**8b**) in $CDCl_3$ at -60 °C

These neutral complexes can also be obtained by reaction of the anionic mononuclear complexes $[RhCl(C_6F_5)_3L]^-$ (**3**)—(**7**) with silver perchlorate, filtration of the inorganic salts, and addition of 1 mol of neutral ligand. With this method, we have tried to prepare mixed-ligand neutral complexes such as $[Rh(C_6F_5)_3L(L')]$ by adding a ligand L′ different from that of the anionic compound, L. However, a redistribution reaction seems to occur and an equimolar mixture of the complexes $[Rh(C_6F_5)_3L_2]$ and $[Rh(C_6F_5)_3L'_2]$ is produced; this redistribution reaction has been demonstrated for the compound initially formulated as $[Rh(C_6F_5)_3(Hpz)(PEt_3)]$, resulting in crystals of both non-mixed-ligand complexes.

Reaction yields, analytical results (C, H, and N), colours, and conductivities for the new complexes are listed in Table 1. The conductivities, in acetone solution, are those expected for 2:1 and 1:1 electrolytes or for non-electrolytes.[11] The structural characterization of the new complexes has been made on the bases of their spectra (i.r. and n.m.r.) and the single-crystal *X*-ray diffraction studies for (**10**) and (**11**).

I.r. Spectra.—All the complexes show absorptions at 1 490s, 1 050s, 950s, and 800—765m cm^{-1}, characteristic of the C_6F_5 groups.[12,13] The absorptions around 800 cm^{-1}, assignable to the X-sensitive mode of C_6F_5, had been used for structural elucidation.[10] For our anionic complexes the absorptions in this region cannot be unambiguously assigned since the cation $[P(CH_2Ph)Ph_3]^+$ (used for solubility reasons) absorbs in this zone; the neutral complexes without phosphine ligands show three bands at *ca.* 800 cm^{-1} in agreement with the normal X-sensitive vibration modes expected either for a molecule of C_s ($2A' + A''$) as well as for C_{2v} ($2A_1 + B_2$) symmetry.

Other characteristic bands are as follows: complex (**1**) exhibits an absorption at 265m cm^{-1}, attributable to the 'Rh(μ-Cl)$_2$Rh' moiety. Complex (**2**) shows the absorptions of the acetylacetonate group, acting as a chelate,[14] at 1 515s and 1 575s cm^{-1}. Complexes (**3**)—(**7**) exhibit an absorption at *ca.* 280m cm^{-1} assignable to the ν(Rh–Cl) stretching vibration. The ν(C–O) vibration [complex (**7**)] appears at 2 110s cm^{-1} in dichloromethane solution. Complex (**3**) shows the ν(N–H) vibration as a broad band at *ca.* 3 260 cm^{-1} while complexes (**13**)—(**15**) show theirs as narrow bands at *ca.* 3 460 cm^{-1}.

N.m.r. Spectra.—The ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra of the complexes (Table 2) are in good agreement with the proposed formulae. The signals due to the phosphorus atoms of the PPh_3 [complexes (**5**) and (**9**)] and PEt_3 complex (**10**) appear as doublets of multiplets because of coupling with the rhodium atoms as well as with the fluorine atoms of the C_6F_5 groups. The ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra of complex (**8**) show, at room temperature, a broad singlet and a broad doublet respectively. At -45 °C, both n.m.r. spectra exhibit two groups of signals of relative intensity 2.3:1 which reveal the presence of two isomers in solution, (**8a**) and (**8b**). Isomer (**8a**) shows a virtual triplet ($N = 10.2$ Hz) in the ^1H n.m.r. spectrum and a doublet ($J = 155.4$ Hz) in the ^{31}P n.m.r. spectrum in accord with a square-pyramidal structure with the $P(OMe)_3$ groups located in the basal plane and in mutually *trans*-positions.[15] Isomer (**8b**) shows a multiplet in the ^1H n.m.r spectrum which seems to indicate that the $P(OMe)_3$ groups are in mutually *cis* positions in a similar square–pyramidal environment. The very broad doublet observed in its ^{31}P-$\{^1H\}$ n.m.r. spectrum also suggests that the two P atoms are *trans* to the C_6F_5 groups.[16] All these data are in agreement with the results found in the ^{19}F n.m.r. spectrum (see Table 2 and Figure 1)

Fluorine-19 n.m.r. studies have been useful in determining the structure of the complexes; they show time-averaged signals at around room temperature. Most of these spectra consist of a

Table 2. Fluorine-19, hydrogen-1, and phosphorus-31 n.m.r. data for the five-co-ordinate complexes[a]

(1)	^{19}F([^{2}H$_{6}$]acetone, 20 °C): -123.0 (br, 6 *o*-F), -166.7 (m, 6 *m*-F), -164.6 (m, 3 *p*-F) (-60 °C): -111.3 (dm, 2 *o*-F, $^{3}J_{\mathrm{FF}}$ 30.7), -124.3 (dm, 4 *o*-F, $^{3}J_{\mathrm{FF}}$ 30.1), -163.8, -165.7 (ft, 6 *m*-F), -162.4 (t, $^{3}J_{\mathrm{FF}}$ 20), -167.4 (t, $^{3}J_{\mathrm{FF}}$ 22)
(2)	^{19}F(CDCl$_{3}$, 20 °C): -126.0 (br, 6 *o*-F), -167.6 (ft, 6 *m*-F), -165.8 (ft, 3 *p*-F) (-50 °C): -120.4, -126.6, and -129.6 (m, 2:2:2, *o*-F), -163.7 to -166.7^{b} (*m*- and *p*-F)
(2)	^{1}H(CDCl$_{3}$, 20 °C): 7.8—6.7 (20 H, H aromatic), 5.1 (s, CH, acac^{-}, 1 H), 4.3 (d, CH$_{2}$, benzyl, 2 H, $^{2}J_{\mathrm{PH}}$ 14.2), 1.8 (s, CH$_{3}$, acac^{-}, 6 H)
(3)	^{19}F(CDCl$_{3}$, 20 °C): -123 (br, *o*-F), -166.8 (m, *m*-F), -164.8 (ft, *p*-F)
(3)	^{1}H(CDCl$_{3}$, 20 °C): 7.8—6.8 (22 H, H aromatic, H^{4} and H^{5}, Hpz), 6.3 (ft, 1 H, H^{4}, Hpz), 4.5 (d, CH$_{2}$, benzyl, 2 H, $^{2}J_{\mathrm{PH}}$ 13.7)
(4)	^{19}F(CDCl$_{3}$, 20 °C): -122.6 (br, *o*-F), -166.7 (ft, *m*-F), -164.8 (ft, *p*-F)
(5)	^{19}F(CDCl$_{3}$, 20 °C): -108.9, -110.7, -124.8, -125.5, -126.3 (m, 1:1:1:1:2, *o*-F), -165.1 to -169.2^{b} (*m*- and *p*-F) (-50 °C): 109.6, -111.1, -125.7, -126.3, -126.5, -127.1 (m, 1:1:1:1:1:1, *o*-F), -164.1 to -169.2^{b} (*m*- and *p*-F)
(5)	^{31}P-{^{1}H} (CDCl$_{3}$, 20 °C): 23.1 [s, 1 P, P(CH$_{2}$Ph)Ph$_{3}$], 20.0 (dm, 1 P, $^{1}J_{\mathrm{RhP}}$ 81)
(6)	^{19}F(CDCl$_{3}$, 20 °C): -122.0 (br, *o*-F), -164.4 (m, *m*-F), -162.7 (m, *p*-F) (-50 °C): -110.4, -111.9, -127.9 to -132.1^{b} (m, 1:1:4, *o*-F), -164.2 to -172.1^{b} (*m*- and *p*-F).
(7)	^{19}F(CDCl$_{3}$, 20 °C): -108.8, -110.8 (m, 2:1, *o*-F), -164.0 (ft, *m*-F), -161.8 (ft, *p*-F)
(8)	^{19}F(CDCl$_{3}$, 20 °C): -123.8 (br, 6 *o*-F), -165.5 (m, 6 *m*-F), -161.9 (m, 3 *p*-F) (-60 °C): Isomer (**a**), -110.4, -113.4, -121.2 (m, 2:2:2, *o*-F); (**b**), -114.3, -127.9, -131.8 (m, 2:2:2, *o*-F), -161.2 to -167.4^{b} (*m*- and *p*-F for both isomers)
(8)	^{1}H(CDCl$_{3}$, 20 °C): 3.54 (m) (-60 °C): Isomer (**a**), 3.51 (vt, *N*10.2 Hz); (**b**), 3.71 (m)
(8)	^{31}P-{^{1}H} (CDCl$_{3}$, 20 °C): 105.7 (dm, $^{1}J_{\mathrm{RhP}}$ 170.7) (-44 °C): Isomer (**a**), 106.0 (dm, $^{1}J_{\mathrm{RhP}}$ 155.4); (**b**) 101 (dm, $^{1}J_{\mathrm{RhP}}$ 186)
(9)	^{19}F(CDCl$_{3}$, 20 °C): -120.0 (br, *o*-F), -164.3 (m, *m*-F), -162.9 (m, *p*-F) (-50 °C): -105.8, -124.5, -125.5 (m, 2:2:2, *o*-F), -162.6, -163.5 (m, 4:2, *m*-F), -161.6, -165.8 (m, 1:2, *p*-F)
(9)	^{31}P-{^{1}H} (CDCl$_{3}$, 20 °C): 24.7 (dm, $^{1}J_{\mathrm{RhP}}$ 101.2)
(10)	^{19}F(CDCl$_{3}$, 20 °C): -123.2 (br, *o*-F), -164.0 (m, *m*-F), -161.1 (m, *p*-F) (-50 °C): -112.0, -125.8 (m, 2:4, *o*-F), -159.2 to -167.4^{b} (*m*- and *p*-F)
(10)	^{31}P-{^{1}H} (CDCl$_{3}$, 20 °C): 14.9 (dm, $^{1}J_{\mathrm{RhP}}$ 94.5)
(11)	^{19}F(CDCl$_{3}$, 20 °C): -122.0 (br, *o*-F), -164.4 (m, *m*-F), -162.7 (m, *p*-F) (-60 °C): -106.2, -125.3, -129.2 (m, 2:2:2, *o*-F), -161.5 to -165.5^{b} (*m*- and *p*-F)
(12)	^{19}F(CDCl$_{3}$, 20 °C): -125.3 (m, *o*-F), -161.0 to -166.2^{b} (*m*- and *p*-F) (-60 °C): -120.0, -125.1, -133.4 (br, 2:2:2, *o*-F), -164.5 (m, *m*-F), -161.3 (m, *p*-F)
(12)	^{1}H(CDCl$_{3}$, 20 °C): 8.2 (d, 4 H, *o*-H, $^{3}J_{\mathrm{H_oH_m}}$ 4.8), 7.8 (t, 2 H, *p*-H, $^{3}J_{\mathrm{H}p\mathrm{H}m}$ 7.5), 7.3 (ft, 4 H, *m*-H, $^{3}J_{\mathrm{HH}}$ 6.5)
(13)	^{19}F(CDCl$_{3}$, 20 °C):^{c} -123.1 (br, *o*-F), -164.0 (m, *m*-F), -160.9 (m, *p*-F)
(13)	^{1}H(CDCl$_{3}$, 20 °C): 10.4 (m, 2 H, NH, Hpz), 7.8 (m, 2 H, H^{3} or H^{5}, Hpz), 7.3 (m, 2 H, H^{3} or H^{5}, Hpz), 6.5 (t, 2 H, H^{4}, Hpz, $^{3}J_{\mathrm{HH}}$ 2.2)
(14)	^{19}F(CDCl$_{3}$, 20 °C):^{c} -126.5 (br, *o*-F), -164.3 (m, *m*-F), -161.3 (m, *p*-F)
(14)	^{1}H(CDCl$_{3}$, 20 °C): 9.9 (m, 2 H, NH, Hmpz), 7.1 (s, 2 H, H^{3} or H^{5}, Hmpz), 6.1 (s, 2 H, H^{3} or H^{5}, Hmpz), 2.3 (s, 6 H, CH$_{3}$)
(15)	^{19}F(CDCl$_{3}$, 20 °C): -122.0, -124.3, -134.2 (m, *o*-F), -161.1 to -165.5^{b} (*m*- and *p*-F) (-60 °C): -117.7, -123.1, -124.7, -126.9, -128.3, -138.8 (m, 1:1:1:1:1:1, *o*-F), -160.0 to -165.7^{b} (*m*- and *p*-F)
(15)	^{1}H(CDCl$_{3}$, 20 °C): 9.9 (m, 2 H, NH, Hdmpz), 5.9 (s, 2 H, H^{4}, Hdmpz), 2.3 (s, 6 H, CH$_{3}$), 1.4 (s, 6 H, CH$_{3}$)

[a] Chemical shifts (δ) are given in p.p.m., coupling constants in Hz, br = broad, d = doublet, t = triplet, m = multiplet, dm = doublet of multiplets, ft = false triplet, vt = virtual triplet, *N* = virtual coupling constant. [b] Complicated signal between the values given. [c] Not resolved by cooling.

broad signal for all the *o*-fluorine atoms and two unresolved multiplets for the *m*- and *p*-fluorine atoms. These broad signals can be understood in terms of fluxionality of these complexes which is probably due to rotation of the C_6F_5 group around the Rh–C bond and to the presence of intramolecular ligand exchange, following a Berry pseudorotation process. Both rotations freeze on cooling, in most of the complexes, yielding three signals (2:2:2) for the *o*-fluorine atoms: one, around -110 p.p.m. (2F) and the other two, very close together, and in some cases superimposed, at around -124 p.p.m. In the solid state, complexes (**10**) and (**11**) as well as the $[Rh(C_6F_5)_5]^{2-}$ anion,[7] have square-pyramidal geometry with a C_6F_5 group in axial position and the other four groups (four C_6F_5 or two ligands and two C_6F_5 in mutually *trans* positions) in basal positions. In addition, the molecules of (**10**) and (**11**) (see Figures 2 and 3) have a non-crystallographic C_2 axis which should make equivalent F^1 and F^5, F^{11} and F^6, and F^{15} and F^{10}. So, we can assign the signal at *ca.* -110 p.p.m. to $F^1 + F^5$, the *o*-fluorine atoms of the apical C_6F_5 group, and the signals at *ca.* -124 p.p.m. to $F^{11} + F^6$ and $F^{15} + F^{10}$, the *o*-fluorine atoms of the basal C_6F_5 groups. Complexes (**9**)—(**12**) follow this pattern so they probably have square-pyramidal structures with the neutral ligands in the basal plane and in mutually *trans* positions. Complexes (**1**) and (**2**) also present analogous ^{19}F n.m.r. spectra but their ligands are necessarily in *cis* positions, so they must have a symmetry plane which makes the fluorine atoms equivalent (2:2:2). Complex (**5**) exhibits five signals for the *o*-F atoms (1:1:1:1:2), at room temperature, while at low temperature compounds (**5**), (**6**), and (**15**) give six signals of the same intensity, so in these cases the molecules are probably more distorted or the basal pentafluorophenyl groups are in *cis* positions and consequently the *o*-fluorine atoms do not exhibit the equivalence mentioned before. Complex (**8**) also presents six signals but distributed in two groups of different intensity (Figure 1).

Description of the Crystal Structures of $[Rh(C_6F_5)_3(PEt_3)_2]$ (**10**) *and* $[Rh(C_6F_5)_3(AsPh_3)_2]$ (**11**).—The structures of complexes (**10**) and (**11**) are depicted in Figures 2 and 3 together with the atomic numbering scheme; selected bond distances and angles are given in Table 3. The structures are very similar, two $AsPh_3$ ligands in (**11**) replacing two PEt_3 ligands in (**10**), and consist of discrete five-co-ordinate monomers in which the rhodium atom is in a square-pyramidal arrangement determined by three carbon atoms from C_6F_5 ligands and two phosphorus atoms from PEt_3 ligands in (**10**) or As atoms from $AsPh_3$ ligands in (**11**). Two carbon atoms in a relative *trans* disposition, C(7) and C(13), together with the P[(**10**)] or As [(**11**)] atoms, occupy the basal positions and the third carbon atom, C(1), is at the apex. The square pyramids are rather flattened as the Rh atoms lie 0.151(1) [(**10**)] and 0.226(2) Å [(**11**)] above the basal planes. The co-ordination geometry shows weak distortions (*D*) along the Berry pseudorotation co-ordinate from a square pyramid towards a trigonal bipyramid,[17] 14% for $[Rh(C_6F_5)_3(PEt_3)_2]$ (**10**) and 15% for $[Rh(C_6F_5)_3(AsPh_3)_2]$ (**11**). These values are slightly larger than

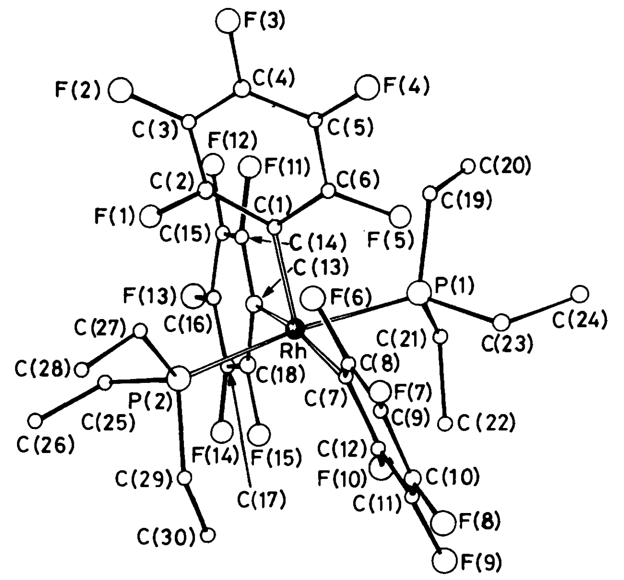

Figure 2. ORTEP drawing of $[Rh(C_6F_5)_3(PEt_3)_2]$ (**10**). Hydrogens have been omitted for clarity

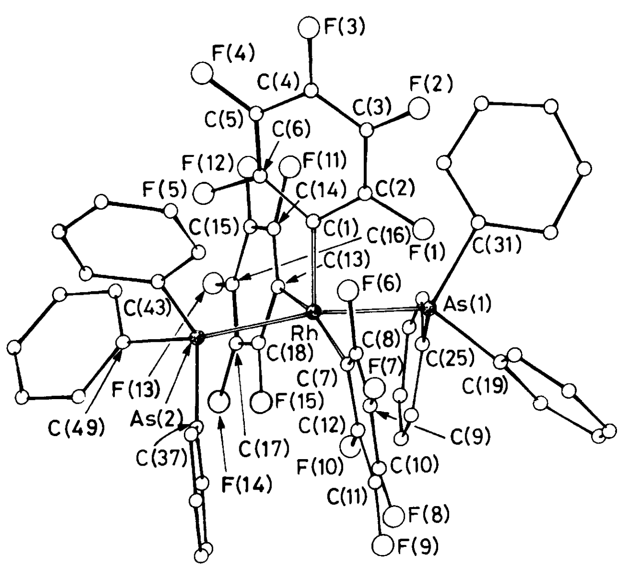

Figure 3. ORTEP drawing of $[Rh(C_6F_5)_3(AsPh_3)_2]$ (**11**). Hydrogens have been omitted for clarity

Table 3. Selected bond distances (Å) and angles (°) in the complexes $[Rh(C_6F_5)_3(PEt_3)_2]$ (**10**) and $[Rh(C_6F_5)_3(AsPh_3)_2]$ (**11**)

(10)		(11)	
Rh–P(1)	2.407(5)	Rh–As(1)	2.477(2)
Rh–P(2)	2.400(5)	Rh–As(2)	2.480(2)
Rh–C(1)	2.014(14)	Rh–C(1)	1.954(15)
Rh–C(7)	2.092(14)	Rh–C(7)	2.096(15)
Rh–C(13)	2.082(14)	Rh–C(13)	2.104(15)
C(1)–Rh–C(7)	97.5(6)	C(1)–Rh–C(7)	98.0(6)
C(1)–Rh–C(13)	94.9(6)	C(1)–Rh–C(13)	97.2(6)
C(1)–Rh–P(1)	95.5(4)	C(1)–Rh–As(1)	96.9(4)
C(1)–Rh–P(2)	91.4(4)	C(1)–Rh–As(2)	93.5(4)
P(1)–Rh–C(7)	92.8(4)	As(1)–Rh–C(7)	92.0(4)
P(1)–Rh–C(13)	86.0(4)	As(1)–Rh–C(13)	86.6(4)
P(2)–Rh–C(7)	91.4(4)	As(2)–Rh–C(7)	86.8(4)
P(2)–Rh–C(13)	94.5(4)	As(2)–Rh–C(13)	91.9(4)
P(1)–Rh–P(2)	173.0(2)	As(1)–Rh–As(2)	169.6(1)
C(7)–Rh–C(13)	167.6(5)	C(7)–Rh–C(13)	164.8(6)

those previously reported for related rhodium(III) complexes $[Rh(Me)I_2(PPh_3)_2]$ (D = 8%) and $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (D = 3%).[18]

As for the parent compound $[Rh(C_6F_5)_5]^{2-}$, the Rh–C bonds involving the apical C_6F_5 ligand are shorter than the corresponding ones in the basal plane [2.014(14) *versus* 2.082(14) and 2.092(14) in (**10**), 1.954(15) *versus* 2.096(15) and 2.104(15) Å in (**11**)]. The main differences in the geometrical features of the two complexes concern the Rh–C apical bond, which is shorter in (**11**) than in (**10**), and the angles involving the *trans* basal ligands, which are slightly larger in (**10**) with respect to those in (**11**). A comparison of the structures of the neutral complexes (**10**) and (**11**) with that of the anionic complex $[Rh(C_6F_5)_5]^{2-}$ reveals that the Rh–C bonds are only insignificantly influenced by the anionic character [1.97(1) Å, for the apical ligand, 2.09(1)—2.13(1) Å for the basal ones].[7]

Within pentafluorophenyl ligands of interest is the distortion of these groups from idealized hexagonal geometry, especially involving the angle α at the C atom bonded to the metal (*ipso* angle), av. 112.0(8)°. This value compares well with those reported for related C_6F_5 transition-metal complexes (range 117.2—109.0°), being lower than the mean value 114.7(2).[19] Also noteworthy is the deviation observed for the binary axes of the basal C_6F_5 ligands [through C(7)–C(10), and C(13)–C(16)] from their respective metal–carbon bonds [Rh–C(7) and Rh–C(13)], 12.3(6) and 15.8(5)° in (**10**) and 13.6(5) and 17.7(5)° in (**11**), while for the apical C_6F_5 ligand this binary axis is completely in line with the Rh–C(1) bond. This distortion, likely due to steric reasons, leads to relatively short interatomic distances between *ortho* fluorines [F(10) and F(15)] and the rhodium atom, 2.862(9) and 2.914(8) Å in (**10**) and 2.759(9) and 2.842(9) Å in (**11**).

Experimental

All reactions were carried out at room temperature. Solvents were dried and distilled under nitrogen immediately prior to use. The starting material $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ was prepared according to the reported method.[7] Fluorine-19, ^1H, and ^{31}P n.m.r. spectra were recorded on a Varian XL-200 spectrometer operating at 188.220, 200.057, and 80.984 MHz respectively; chemical shifts are reported relative to $CDCl_3$, tetramethylsilane and 85% phosphoric acid as external references. I.r. spectra (4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls between polyethylene sheets or in solution in NaCl cells. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Molecular weights were determined with a Knauer osmometer using chloroform solutions.

Preparations.—$[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ (**1**). To a yellow suspension of $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ (200 mg, 0.12 mmol) in methanol (10 cm^3) was added hydrochloric acid (1.13 cm^3, 0.2157 mol dm^{-3} in methanol, 0.24 mmol). The solid dissolved and the solution turned orange; after 15 min of stirring the solvent was pumped off. The residual oil was washed with diethyl ether (1 cm^3) and stirred with propan-2-ol (5 cm^3) to give crystalline (**1**).

$[P(CH_2Ph)Ph_3][Rh(acac)(C_6F_5)_3]$ (**2**). To a solution of complex (**1**) (100 mg, 0.05 mmol) in dichloromethane–acetone (1:1) (20 cm^3) was added thallium(I) acetylacetonate (30.3 mg, 0.1 mmol). After stirring for 30 min the mixture gave an orange solution and a white solid which was filtered off. The solution was evaporated to dryness giving an oily residue which was

Table 4. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of $[Rh(C_6F_5)_3(PEt_3)_2]$ (**10**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	1 370(1)	2 303(1)	2 241(1)
P(1)	1 174(2)	4 079(4)	2 685(4)
P(2)	1 445(2)	490(3)	1 806(4)
F(1)	2 311(3)	1 644(7)	632(8)
F(2)	3 430(4)	1 751(8)	1 099(10)
F(3)	4 030(4)	2 710(9)	3 210(10)
F(4)	3 422(4)	3 558(10)	4 795(10)
F(5)	2 294(4)	3 418(8)	4 388(8)
F(6)	2 319(3)	1 365(8)	5 006(8)
F(7)	2 009(4)	743(10)	7 072(9)
F(8)	906(5)	765(11)	7 303(10)
F(9)	76(4)	1 503(9)	5 385(10)
F(10)	371(3)	2 171(7)	3 293(8)
F(11)	2 022(4)	3 689(8)	74(9)
F(12)	1 532(4)	4 257(10)	−2 205(10)
F(13)	426(4)	3 702(9)	−3 244(8)
F(14)	−195(4)	2 603(7)	−1 862(8)
F(15)	297(3)	2 008(7)	437(8)
C(1)	2 226(6)	2 492(11)	2 452(13)
C(2)	2 552(6)	2 119(13)	1 708(14)
C(3)	3 156(7)	2 169(14)	1 918(15)
C(4)	3 441(7)	2 616(14)	2 973(16)
C(5)	3 147(8)	3 096(14)	3 767(17)
C(6)	2 544(7)	2 967(14)	3 539(17)
C(7)	1 368(6)	1 820(11)	4 046(12)
C(8)	1 747(7)	1 444(12)	5 063(15)
C(9)	1 614(7)	1 110(13)	6 133(17)
C(10)	1 035(7)	1 093(14)	6 236(17)
C(11)	626(7)	1 461(13)	5 270(16)
C(12)	797(6)	1 790(11)	4 219(14)
C(13)	1 180(6)	2 743(12)	387(12)
C(14)	1 466(7)	3 350(13)	−363(15)
C(15)	1 225(7)	3 685(13)	−1 551(16)
C(16)	677(7)	3 395(13)	−2 067(16)
C(17)	367(7)	2 843(13)	−1 394(14)
C(18)	629(6)	2 559(12)	−189(13)
C(19)	1 724(7)	4 997(13)	2 400(17)
C(20)	1 567(9)	5 987(17)	1 850(22)
C(21)	518(6)	4 612(13)	1 701(16)
C(22)	−55(7)	4 082(15)	1 842(18)
C(23)	1 079(7)	4 335(13)	4 270(15)
C(24)	1 029(8)	5 461(15)	4 649(20)
C(25)	1 273(7)	188(12)	165(14)
C(26)	1 240(8)	−932(15)	−170(20)
C(27)	2 141(6)	−119(12)	2 462(15)
C(28)	2 175(8)	−1 257(13)	2 541(18)
C(29)	943(6)	−321(12)	2 419(15)
C(30)	301(6)	−82(14)	1 931(16)

washed twice with hexane (1 cm^3) and stirred in hexane (15 cm^3) for 30 min. The resulting solid was filtered off, washed with hexane, and vacuum dried.

$[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3L]$ (**3**)—(**6**). To a solution of complex (**1**) (50 mg, 0.025 mmol) in dichloromethane (20 cm^3) was added the appropriate ligand (0.05 mmol). The mixture was allowed to react for 15 min and the solvents pumped off. The oily residue was washed with two fractions of hexane (1 cm^3) and stirred in hexane (15 cm^3). The solids were filtered off, washed with hexane, and vacuum dried.

$[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3(CO)]$ (**7**). Carbon monoxide was bubbled though a solution of complex (**1**) (70 mg, 0.035 mmol) in dichloromethane (10 cm^3) for 15 min. The initial yellow solution became colourless. Evaporation of this solution to *ca.* 1 cm^3 and addition of diethyl ether–hexane (1:2) (10 cm^3) gave complex (**7**) which was filtered off, washed with hexane (5 cm^3), and vacuum dried.

$[Rh(C_6F_5)_3L_2]$ (**8**)—(**15**). To a yellow suspension of complex (**1**) (100 mg, 0.05 mmol) in dry diethyl ether (10 cm^3), under a nitrogen atmosphere and with exclusion of light, silver perchlorate (20.8 mg, 0.1 mmol) was added. After 60 min the white solid formed was eliminated by filtration through Kieselguhr. The appropriate neutral ligand (0.2 mmol) was added and allowed to react for 30 min. Evaporation of the solution under vacuum to 1 cm^3 and addition of methanol for (**9**) or hexane for all other compounds rendered the complexes which were separated by filtration, washed with hexane, and vacuum dried.

Crystal Structure Determinations of $[Rh(C_6F_5)_3(PEt_3)_2]$ (**10**) *and* $[Rh(C_6F_5)_3(AsPh_3)_2]$ (**11**).—Crystals of approximate dimensions 0.18 × 0.22 × 0.25 (**10**) and 0.20 × 0.24 × 0.30 mm (**11**) were used for the *X*-ray analyses.

Crystal data. (**10**), $C_{30}H_{30}F_{15}P_2Rh$, $M = 840.40$, monoclinic, space group $P2_1/a$, $a = 23.778(8)$, $b = 12.887(6)$, $c = 11.056(5)$ Å, $\beta = 102.18(2)°$, $U = 3312(2)$ Å^3 (by least-squares refinement from the θ values of 28 accurately measured reflections, $\lambda = 1.54178$ Å), $Z = 4$, $D_c = 1.686$ g cm^{-3}, $F(000) = 1\,680$, μ(Cu-K_α) = 61.86 cm^{-1}.

(**11**), $C_{54}H_{30}As_2F_{15}Rh$, $M = 1\,216.56$, monoclinic, space group $P2_1/n$, $a = 20.626(8)$, $b = 19.908(7)$, $c = 11.477(4)$ Å, $\beta = 91.35(1)°$, $U = 4\,711(3)$ Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections, $\lambda = 0.7093$ Å), $Z = 4$, $D_c = 1.715$ g cm^{-3}, $F(000) = 2\,400$, μ(Mo-K_α) = 18.42 cm^{-1}.

Data collection and processing. A Siemens AED single-crystal diffractometer [θ—2θ scan mode, nickel-filtered Cu-K_α radiation, (**10**), or niobium-filtered Mo-K_α radiation, (**11**)] was employed. All reflections with θ in the ranges 3—65 [(**10**)] and 3—23° [(**11**)] were measured; of 6 209 [(**10**)] and 7 301 [(**11**)] independent reflections, 2 219 and 2 411, having $I > 2\sigma(I)$ were considered observed and used in the analyses. The individual profiles were analysed according to Lehmann and Larsen.[20] A correction for the absorption effects was applied,[21] using the program ABSORB[22] [maximum and minimum transmission factors values 1.362 and 0.710, (**10**); 1.143 and 0.915, (**11**)].

Structure solutions and refinements. Patterson and Fourier methods, full-matrix least-squares refinements with anisotropic thermal parameters in the last cycles for the Rh, P, and F atoms [(**10**)] and for the Rh, As, and F atoms [(**11**)]. All the hydrogen atoms of complexes (**10**) and (**11**) were placed at their calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms. For both structures a weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 0.661$ [(**10**)] and 0.507 [(**11**)] and $g = 0.0138$ [(**10**)] and 0.0011 [(**11**)]. Final *R* and *R'* values were 0.0661 and 0.0857 for (**10**) and 0.0480 and 0.0445 for (**11**) respectively. The SHELX system of computer programs was used.[23] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 24. Final atomic co-ordinates for the non-hydrogen atoms are given in Tables 4 [(**10**)] and 5 [(**11**)] respectively. All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Table 5. Fractional atomic co-ordinates (× 10^4) with (e.s.d.s) in parentheses for the non-hydrogen atoms of $[Rh(C_6F_5)_3(AsPh_3)_2]$ (**11**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	235(1)	2 434(1)	1 365(1)	C(19)	1 713(8)	1 450(8)	398(15)
As(1)	1 338(1)	1 960(1)	1 641(2)	C(20)	2 331(9)	1 584(10)	20(17)
As(2)	−775(1)	3 051(1)	842(2)	C(21)	2 617(11)	1 163(10)	−773(18)
F(1)	319(4)	845(4)	1 818(9)	C(22)	2 287(10)	636(11)	−1 242(19)
F(2)	−318(5)	58(4)	3 246(10)	C(23)	1 673(9)	494(10)	−906(18)
F(3)	−1 172(6)	571(5)	4 762(11)	C(24)	1 391(8)	893(9)	−63(15)
F(4)	−1 384(5)	1 927(5)	4 789(9)	C(25)	1 927(7)	2 711(7)	1 828(13)
F(5)	−787(4)	2 727(4)	3 371(7)	C(26)	2 057(7)	3 123(8)	854(15)
F(6)	−669(4)	968(4)	226(9)	C(27)	2 434(7)	3 694(8)	1 007(14)
F(7)	−783(5)	630(5)	−1 963(10)	C(28)	2 658(8)	3 877(9)	2 081(16)
F(8)	−114(5)	1 289(5)	−3 641(9)	C(29)	2 522(8)	3 505(9)	3 040(17)
F(9)	682(4)	2 316(5)	−2 992(8)	C(30)	2 158(7)	2 912(8)	2 922(15)
F(10)	780(4)	2 696(4)	−758(8)	C(31)	1 599(7)	1 414(8)	2 984(14)
F(11)	408(4)	2 712(4)	4 468(7)	C(32)	2 166(8)	1 048(8)	2 894(16)
F(12)	883(5)	3 790(5)	5 519(8)	C(33)	2 354(8)	658(9)	3 877(15)
F(13)	1 271(6)	4 873(5)	4 269(9)	C(34)	2 002(8)	648(8)	4 855(16)
F(14)	1 148(5)	4 842(5)	1 908(8)	C(35)	1 445(8)	1 008(8)	4 916(16)
F(15)	668(4)	3 750(4)	828(8)	C(36)	1 240(8)	1 398(8)	3 972(14)
C(1)	−197(7)	1 842(7)	2 461(13)	C(37)	−824(7)	3 155(7)	−833(13)
C(2)	−116(8)	1 150(9)	2 514(15)	C(38)	−404(7)	3 600(7)	−1 381(14)
C(3)	−422(8)	725(9)	3 282(16)	C(39)	−404(8)	3 637(9)	−2 580(15)
C(4)	−860(8)	975(9)	4 031(16)	C(40)	−831(8)	3 268(8)	−3 219(17)
C(5)	−980(8)	1 667(9)	4 043(16)	C(41)	−1 247(8)	2 821(8)	−2 709(16)
C(6)	−630(7)	2 060(8)	3 300(14)	C(42)	−1 260(7)	2 778(8)	−1 514(14)
C(7)	66(7)	1 865(8)	−148(13)	C(43)	−1 602(7)	2 660(8)	1 186(14)
C(8)	−313(8)	1 326(8)	−526(15)	C(44)	−1 680(8)	1 980(9)	1 214(14)
C(9)	−384(8)	1 145(8)	−1 692(16)	C(45)	−2 268(8)	1 682(10)	1 490(16)
C(10)	−45(8)	1 472(9)	−2 514(17)	C(46)	−2 774(9)	2 074(10)	1 715(16)
C(11)	363(8)	1 976(9)	−2 181(16)	C(47)	−2 720(9)	2 758(10)	1 685(15)
C(12)	382(7)	2 168(8)	−1 057(15)	C(48)	−2 128(8)	3 074(10)	1 436(15)
C(13)	522(7)	3 178(7)	2 573(13)	C(49)	−891(7)	3 969(7)	1 377(14)
C(14)	581(7)	3 221(8)	3 757(14)	C(50)	−1 115(7)	4 453(8)	616(16)
C(15)	818(8)	3 783(9)	4 338(16)	C(51)	−1 245(7)	5 098(8)	990(14)
C(16)	1 024(8)	4 333(9)	3 726(16)	C(52)	−1 125(7)	5 270(9)	2 125(15)
C(17)	956(8)	4 315(9)	2 537(16)	C(53)	−896(7)	4 799(8)	2 893(15)
C(18)	721(7)	3 746(8)	2 014(15)	C(54)	−772(7)	4 151(8)	2 548(14)

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