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Synthesis of gold-(I) and -(III) complexes with diferrocenylphenylphosphine (PFc_2Ph). Crystal structure of $[Au(PFc_2Ph)_2]ClO_4$

M. Concepción Gimeno [a], Peter G. Jones [b], Antonio Laguna [a,*], Cristina Sarroca [a]

[a] *Departamento de Química Inorgánica, ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain*
[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany*

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Abstract

Diferrocenylphenylphosphine (PFc_2Ph) reacts with gold(I) derivatives to afford neutral, $[AuR(PFc_2Ph)]$ ($R = Cl$, C_6F_5) or cationic complexes, $[Au(PFc_2Ph)(PR_3)]ClO_4$ ($PR_3 = PFc_2Ph$, PPh_3). Reaction with $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2Cl]_2$ gives the gold(III) complexes $[Au(C_6F_5)_3(PFc_2Ph)]$ or $[Au(C_6F_5)_2Cl(PFc_2Ph)]$, respectively. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Gold; Ferrocene; Diferrocenylphenylphosphine

1. Introduction

The chemistry of ferrocene and the design of new ligands containing the ferrocene unit, such as the diphosphine 1,1′-bis(diphenylphosphino)ferrocene, have been widely studied because of the potential applications of such products in fields such as organic synthesis, homogeneous catalysis, material chemistry and the production of fine chemicals [1,2]. However, the monophosphine diferrocenylphenylphosphine (PFc_2Ph) [3] has scarcely been studied. Only a few complexes, such as $[M(CO)_5(PFc_2Ph)]$ ($M = Mo$ or W), $[CoMe\text{-}(DH)_2(PFc_2\text{-}Ph)]$ (DH = dimethylglioximate), $[Ni(acac)_2(PFc_2Ph)]$ [4], $[Ag(TfO)(PFc_2Ph)(PR_3)]$ (TfO = trifluoromethanesulfonate; $PR_3 = PFc_2Ph$, PPh_2Me, PPh_3), $[Ag(PFc_2Ph)_2(dptpm)]TfO$ (dptpm = bis(diph-enylthiophosphoryl)methane), $[Ag(S_2CNEt_2)\ (PFc_2\text{-}Ph)_2]$ [5], or the gold derivatives $[AuCl(PFc_2Ph)]$ [6], or more recently, $[Au(PFc_2Ph)_2]PF_6$ [7], have been reported.

Here we report on the synthesis of mononuclear gold(I) or gold(III) complexes with diferrocenylphenylphosphine as ligand.

2. Results and discussion

Treatment of equimolecular amounts of $[AuR(tht)]$ ($R = Cl$ or C_6F_5, tht = tetrahydrothiophene) with diferrocenylphenylphosphine (PFc_2Ph) in dichloromethane affords the neutral complexes $[AuR(PFc_2Ph)]$ [$R = Cl$ (**1**), C_6F_5 (**2**)] (Scheme 1). Compounds **1** and **2** are moisture- and air-stable yellow solids. They behave as non-conductors in acetone solution. In the IR spectrum, the C_6F_5 group (**2**) gives rise to strong absorptions at 1505, 955 and 790 cm^{-1}; ν(Au–Cl) (**1**) appears at 336 cm^{-1}. In the positive ion liquid secondary ion mass spectra (LSIMS) of both complexes, the most intense peak corresponds to the molecular fragment $[AuR(PFc_2Ph)]^+$ [$m/z = 710$ (**1**) and 842 (**2**)]. For complex **1** the peak assigned to $[Au(PFc_2Ph)]^+$ [$m/z = 675$ (17%)] is also present.

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* Corresponding author. Tel.: +34-976-761-185; fax: +34-976-761-187.
E-mail address: alaguna@posta.unizar.es (A. Laguna)

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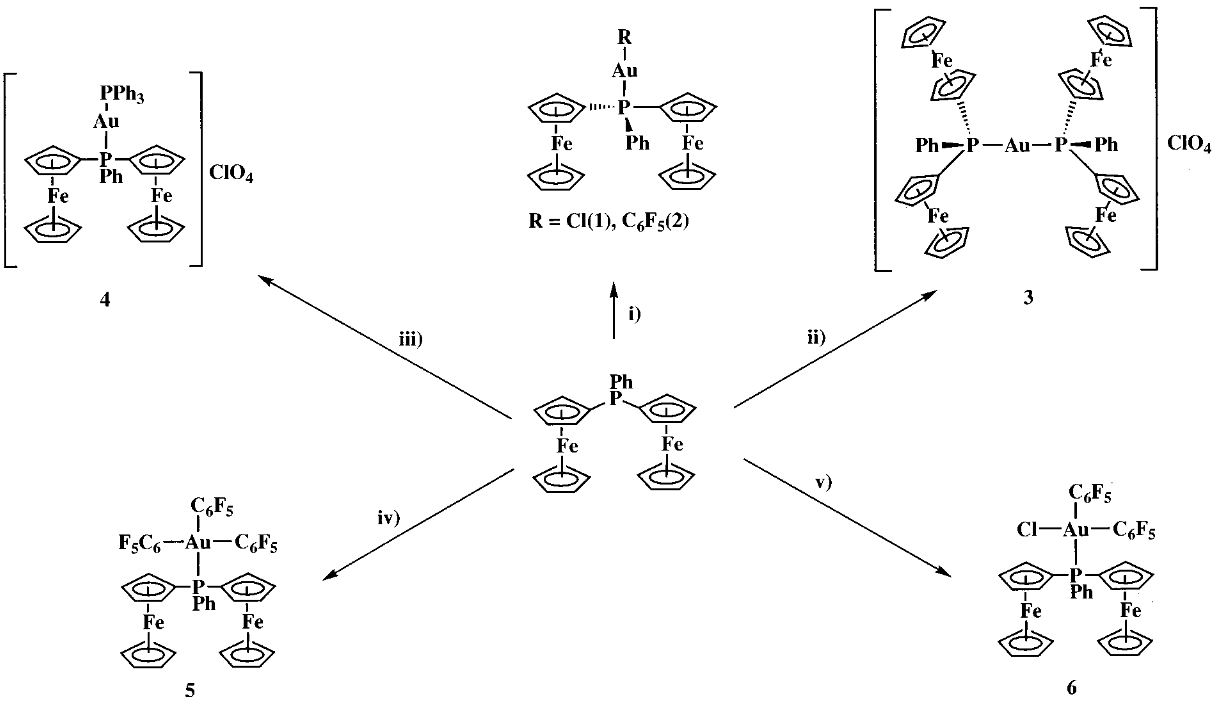

Scheme 1. (i) [AuR(tht)], (ii) 1/2[Au(tht)$_2$]ClO$_4$, (iii) [Au(OClO$_3$)(PPh$_3$)], (iv) [Au(C$_6$F$_5$)$_3$(OEt$_2$)], (v) 1/2 [Au(C$_6$F$_5$)$_2$Cl]$_2$.

The ^{1}H-NMR spectra show the expected four resonances for the four diastereotopic P(C$_5$H$_4$) protons [4.50, 4.48, 4.46 and 4.22 (**1**) and 4.46, 4.43, 4.42 and 4.18 ppm (**2**)] and a singlet for the C$_5$H$_5$ rings [4.18 (**1**) and 4.22 ppm (**2**)]. The ^{31}P{^{1}H}-NMR spectra show a singlet (23.8 ppm) and a multiplet (32.7 ppm), arising from the coupling with the fluorine atoms, for complexes **1** and **2**, respectively. The ^{19}F-NMR spectrum of **2** presents two multiplets at -116.5 and -162.6 ppm and a triplet at -158.9 ppm [J(F–F) = 19.3 Hz], corresponding to the *ortho*-, *meta*- and *para*-F, respectively.

The reaction of [Au(tht)$_2$]ClO$_4$ with the phosphine in a 1:2 molar ratio gives the cationic complex [Au(PFc$_2$Ph)$_2$]ClO$_4$ (**3**). Acetone solutions of complex **3** behave as 1:1 electrolytes. The solid IR spectrum presents bands at 1093 (vs, br) and 623 cm^{-1} (s), arising from ionic ClO$_4^-$. In the LSIMS$^+$ spectrum, the most intense peak corresponds to the fragment [Au(PFc$_2$Ph)$_2$]$^+$ [$m/z = 1153$]. The ^{1}H-NMR spectrum shows the resonances of the P(C$_5$H$_4$) protons at 4.72, 4.68, 4.62 and 4.43 ppm and a singlet for the C$_5$H$_5$ rings at 4.23 ppm. The ^{31}P{^{1}H}-NMR spectrum presents a singlet at 37.2 ppm.

The structure of complex **3** was confirmed by an X-ray diffraction analysis. It crystallises in the space group $P\bar{1}$ as a CHCl$_3$ solvate. The molecule is shown in Fig. 1, with selected bond lengths and angles in Table 1. The bond lengths and angles are very similar to those found for the complex [Au(PFc$_2$Ph)$_2$]PF$_6\cdot$CHCl$_3$ [7], which appears to be isostructural, although the triclinic cell was presented differently.

The geometry around the gold atom is distorted from linearity with an angle P–Au–P of 169.41(6)°. The Au–P distances are 2.293(2) and 2.301(2) Å, which are significantly longer than the corresponding values of 2.234(2) Å in [AuCl(PFc$_2$Ph)] [6] but are similar to those found in other bis(phosphine) gold compounds such as [Au(PR$_3$)$_2$]$^+$ [PR$_3$ = PPh$_2$Me, 2.316(4) Å; PCy$_3$, 2.321(2) Å] [8,9]. This is consistent with the strong mutual *trans* influence of phosphine ligands. There are two shorter intramolecular gold–iron distances of 4.055(1) and 4.073(1) Å associated with the narrower P–Au–P angle.

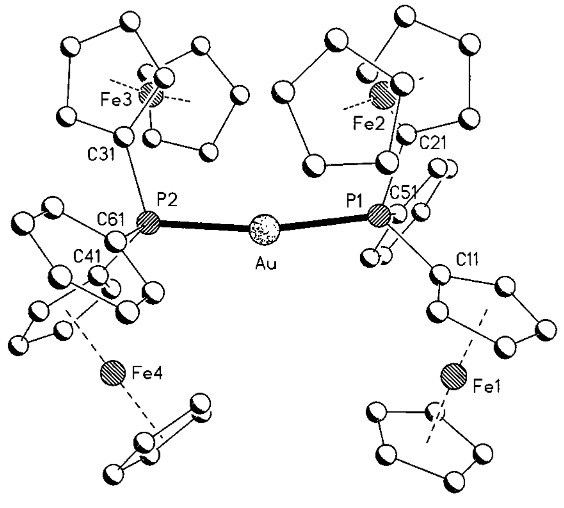

Fig. 1. The cation of complex **3** in the crystal showing the atom numbering scheme. Radii are arbitrary. H atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complex **3**

Bond lengths			
Au–P(1)	2.2929(18)	Au–P(2)	2.3005(17)
P(1)–C(11)	1.765(8)	P(1)–C(21)	1.775(7)
P(1)–C(51)	1.813(8)	P(2)–C(31)	1.801(7)
P(2)–C(41)	1.805(7)	P(2)–C(61)	1.807(7)
Bond angles			
P(1)–Au–P(2)	169.41(6)	C(11)–P(1)–C(21)	103.2(3)
C(11)–P(1)–C(51)	105.3(3)	C(21)–P(1)–C(51)	107.3(3)
C(11)–P(1)–Au	119.6(2)	C(21)–P(1)–Au	109.1(2)
C(51)–P(1)–Au	111.4(2)	C(31)–P(2)–C(41)	106.9(3)
C(31)–P(2)–C(61)	106.5(3)	C(41)–P(2)–C(61)	104.1(3)
C(31)–P(2)–Au	107.7(2)	C(41)–P(2)–Au	119.4(2)
C(61)–P(2)–Au	111.6(2)	C(15)–C(11)–P(1)	126.9(6)
C(12)–C(11)–P(1)	125.6(6)	P(1)–C(11)–Fe(1)	134.1(4)
P(1)–C(21)–Fe(2)	124.8(4)	C(32)–C(31)–P(2)	126.6(5)
C(35)–C(31)–P(2)	124.0(5)	P(2)–C(31)–Fe(3)	123.1(4)
C(45)–C(41)–P(2)	125.1(6)	C(42)–C(41)–P(2)	127.3(5)
P(2)–C(41)–Fe(4)	124.1(3)	C(56)–C(51)–P(1)	119.4(6)
C(52)–C(51)–P(1)	121.5(6)	C(62)–C(61)–P(2)	121.4(5)
C(66)–C(61)–P(2)	119.7(5)		

The cyclopentadienyl rings within each ferrocenyl unit are almost eclipsed, as expressed by the torsion angles C–center–center–C of 13, 10, 5 and 5° for Fe1, Fe2, Fe3 and Fe4, respectively, around the Cp···Cp axis. The C–P–Au angles for the ferrocenyl-C atoms are significantly different from each other, as has been previously observed in the two diferrocenylphenylphosphino-gold complexes reported [6,7]. These angles vary from 109.1(2)° for C(21)–P(1)–Au to 119.6(2)° for C(21)–P(1)–Au and from 107.7(2)° for C(31)–P(2)–Au to 119.4(2)° for C(41)–P(2)–Au. This large angular difference has been associated [7] with the short intramolecular interactions between the ferrocenyl ring carbon atoms and the phenyl ring hydrogen atoms, e.g. C(21)···H(52) 2.69 Å, C(31)···H(62) 2.77 Å.

The reaction of equimolar amounts of $[Au(OClO_3)(PPh_3)]$ and the phosphine leads to the complex $[Au(PFc_2Ph)(PPh_3)]ClO_4$ (**4**). However, in solution, complex **4** is in equilibrium with the homoleptic species $[Au(PFc_2Ph)_2]^+$ (**3**) and $[Au(PPh_3)_2]^+$. Thus, the $^{31}P\{^1H\}$-NMR spectrum presents resonances from the three complexes: a singlet at 37.2 ppm, from complex **3**; a singlet at 45.4 ppm, from $[Au(PPh_3)_2]^+$; and four resonances, corresponding to an AB system [$\delta(PFc_2Ph) = 38.1$, $\delta(PPh_3) = 45.1$ ppm, $J(AB) = 342.3$ Hz] assigned to complex **4**. In the LSIMS$^+$ mass spectrum, the most intense peak corresponds to the cation molecular peak $[Au(PFc_2Ph)(PPh_3)]^+$ [$m/z = 937$]. Additionally, other fragments correspond to $[Au(PFc_2Ph)_2]^+$ (1153, 10%) and $[Au(PPh_3)_2]^+$ (721, 60%).

Diferrocenylphenylphosphine reacts with $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2Cl]_2$, in molar ratio 1:1 or 2:1, respectively, to give the gold(III) complexes $[Au(C_6F_5)_3(PFc_2Ph)]$ (**5**) or $[Au(C_6F_5)_2Cl(PFc_2Ph)]$ (**6**). Complexes **5** and **6** are white solids, moisture- and air-stable. They are non-conductors in acetone solutions. Their IR spectra show bands at 1507(s), 969(s), 820(m) and 792(m) (**5**) and 1513(s), 1506(s), 969(s), 807(m) and 788(m) cm^{-1}, corresponding to the C_6F_5 groups; ν(Au–Cl) appears at 337(m) cm^{-1} (complex **6**). In the LSIMS$^+$ mass spectra of both complexes, the molecular peak $[M]^+$ [$m/z = 1176$ (42) (**1**) and 1044 (42%) (**2**)] is present. The peak assigned to $[Au(C_6F_5)(PFc_2Ph)]^+$ [$m/z = 842$ (7, **5**) (11%, **6**)] is also present.

The complexes **5** and **6** were readily characterised by ^1H-, ^{19}F- and $^{31}P\{^1H\}$-NMR. Their $^{31}P\{^1H\}$-NMR spectra show a singlet at 12.2 (**5**) and 23.2 ppm (**6**). The ^{19}F-NMR spectra show the presence of two different types of pentafluorophenyl groups (with a 2:1 intensity ratio for complex **5**), which confirms the mutually *cis* position in complex **6** (see Section 3).

3. Experimental

IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the LSIMS technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and 85% H_3PO_4 (^{31}P, external). The starting materials PFc_2Ph [3], [AuCl(tht)] [10], $[Au(C_6F_5)(tht)]$ [10], $[Au(tht)_2]ClO_4$ [11] $[Au(C_6F_5)_3(OEt_2)]$ [12] and $[Au(C_6F_5)_2Cl]_2$ [13], were prepared by published procedures. $[Au(OClO_3)(PPh_3)]$ was prepared from $[AuCl(PPh_3)]$ [14] and $AgClO_4$.

3.1. Syntheses

3.1.1. [AuR(PFc$_2$Ph)] [R = Cl (**1**), C$_6$F$_5$ (**2**)]

To a solution of PFc_2Ph (0.048 g, 0.1 mmol) in dichloromethane (20 cm^3), [AuCl(tht)] (0.032 g, 0.1 mmol) or $[Au(C_6F_5)(tht)]$ (0.045 g, 0.1 mmol) were added and the mixture was stirred for 2 h. The solution was concentrated to ca. 5 cm^3 and addition of diethyl ether (15 cm^3) gave complexes **1** or **2** as yellow solids. Complex **1**: Yield 56%, Anal. Calc. for $C_{26}H_{23}AuClFe_2P$: C, 43.95; H, 3.25. Found: C, 43.65, H, 3.2; Λ_M 12 Ω^{-1} cm^2 mol^{-1}. Complex **2**: Yield 66%, Anal. Calc. for $C_{32}H_{23}AuF_5Fe_2P$: C, 45.65; H, 2.75. Found: C, 45.35, H, 2.8; Λ_M 9 Ω^{-1} cm^2 mol^{-1}.

3.1.2. [Au(PFc$_2$Ph)$_2$]ClO$_4$ (**3**)

To a solution of PFc$_2$Ph (0.096 g, 0.2 mmol) in dichloromethane (20 cm^3), [Au(tht)$_2$]ClO$_4$ (0.047 g, 0.1 mmol) was added and the mixture was stirred for 2 h. The solution was concentrated to ca. 5 cm^3 and addition of diethyl ether (15 cm^3) gave complex **3** as a yellow solid. Yield 92%, Anal. Calc. for $C_{52}H_{46}AuClFe_4O_4P_2$: C, 49.95; H, 3.7. Found: C, 50.35, H, 3.7; Λ_M 115 Ω^{-1} cm^2 mol^{-1}.

3.1.3. [Au(PFc$_2$Ph)(PPh$_3$)]ClO$_4$ (**4**)

To a solution of [Au(OClO$_3$)(PPh$_3$)] (0.104 g, 0.1 mmol) in dichloromethane (20 cm^3), PFc$_2$Ph (0.048 g, 0.1 mmol) was added and the mixture was stirred for 15 min. The solution was concentrated to ca. 5 cm^3 and addition of diethyl ether (15 cm^3) gave complex **4** as a yellow solid. Yield 72%, Anal. Calc. for $C_{44}H_{38}AuClFe_2O_4P_2$: C, 50.95; H, 3.7. Found: C, 50.65, H, 3.75; Λ_M 115 Ω^{-1} cm^2 mol^{-1}, ^{1}H-NMR, δ ppm: 7.6 (m, 20H, Ph), 4.57, 4.21 and 4.00 [m, 6H, P(C$_5$H$_4$)] and 4.08 [m, 12H, 2H of P(C$_5$H$_4$) and 10H of C$_5$H$_5$]. There are also present the resonances due to complex **3** and [Au(PPh$_3$)$_2$]ClO$_4$.

3.1.4. [Au(C$_6$F$_5$)$_3$(PFc$_2$Ph)] (**5**) and [Au(C$_6$F$_5$)$_2$Cl(PFc$_2$Ph)] (**6**)

To a dichloromethane solution (20 cm^3) of PFc$_2$Ph (0.048 g, 0.1 mmol), [Au(C$_6$F$_5$)$_3$(OEt$_2$)] (0.077 g, 0.1 mmol) or [Au(C$_6$F$_5$)$_2$Cl]$_2$ (0.042 g, 0.05 mmol) were added. The mixture was stirred for 1 h and then the solution was concentrated under vacuum to ca. 5 cm^3; addition of hexane (15 cm^3) afforded complexes **5** or **6** as a pale orange or orange solid, respectively. Complex **5**: Yield 55%, Anal. Calc. for $C_{44}H_{23}AuF_{15}Fe_2P$: C, 44.95; H, 1.95. Found: C, 44.95, H, 2.0; Λ_M 9 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR, δ ppm: 7.5 (m, 5H, Ph), 4.50, 4.52 and 4.05 [m, 8H, P(C$_6$H$_4$)] and 4.09 (s, 10 H, C$_5$H$_5$). ^{19}F-NMR, δ ppm: -119.3 (m, 4F, F$_o$), -121.6 (m, 2F, F$_o$), -157.8 [t, 1F, F$_p$, J(F–F) 19.3 Hz], -157.9 [t, 2F, F$_p$, J(F–F) 20.67 Hz], -161.3 (m, 4F, F$_m$) and -161.62 (m, 2F, F$_m$). Complex **6**: Yield 60%, Anal. Calc. for $C_{38}H_{23}AuClF_{10}Fe_2P$: C, 43.7; H, 2.2. Found: C, 43.35, H, 2.1; Λ_M 12 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR, δ ppm: 7.5 (m, 5H, Ph), 4.67, 4.62, 4.55 and 4.53 [m, 8H, P(C$_6$H$_4$)] and 4.32 (s, 10 H, C$_5$H$_5$). ^{19}F-NMR, δ ppm: -120.3 (m, 2F, F$_o$), -123.1 (m, 2F, F$_o$), -157.4 [t, 1F, F$_p$, J(F–F) 19.97 Hz], -158.0 [t, 1F, F$_p$, J(F–F) 19.97 Hz], -160.8 (m, 2F, F$_m$) and -161.5 (m, 2F, F$_m$).

3.2. Crystal structure determination of complex 3

3.2.1. Crystal data

3·CH$_2$Cl$_2$, $C_{53}H_{48}AuCl_3Fe_4O_4P_2$, $M_r = 1337.57$, triclinic, space group $P\bar{1}$, $a = 10.367(2)$, $b = 11.422(2)$, $c = 22.724(3)$ Å, $\alpha = 98.548(8)°$, $\beta = 93.759(12)°$, $\gamma = 111.475(10)°$, $V = 2454.9(6)$ Å^3, $Z = 4$, $D_{calc.} = 1.810$ Mg m^{-3}, $\lambda(\text{Mo–K}_\alpha) = 0.71073$ Å, $\mu = 4.41$ mm^{-1}, $F(000) = 1324$, $T = -100$°C.

3.2.2. Data collection and reduction

Single crystals were obtained by slow diffusion of hexane into a chloroform solution of complex **3**. A yellow plate 0.80 × 0.20 × 0.15 mm^3 was used to collect 14 113 intensities to $2\theta_{max}$ 50° (Siemens P4 diffractometer, monochromated Mo–K$_\alpha$ radiation) of which 8545 were independent ($R_{int} = 0.049$). Cell constants were refined from 2θ values of 65 reflections in the range 10.6–25°. An absorption correction was applied on the basis of ψ-scans (transmission factors 0.90–0.98).

3.2.3. Structure solution and refinement

The structure was solved by the heavy atom method and refined on F^2 using the program SHELXL-93 [15]. All non-hydrogen atoms were refined anisotropically. Refinement proceeded to $wR(F^2)$ 0.102 for 8542 reflections, 599 parameters and 534 restraints (to local ring symmetry and light atom displacement factors), with conventional $R(F)$ 0.0429, $S(F^2)$ 1.03, max. $\Delta\rho = 1.57$ e Å^{-3}.

4. Supplementary material

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC-103032. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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