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Priority communication

Synthesis and coordination chemistry of the tethered bis(cyclopentadienyl)-phosphine ligand precursor $PPh(CH_2CH_2C_5H_5)_2$: X-ray structure of *trans*-$PdCl_2[PPh(CH_2CH_2\text{-}\eta^5\text{-}C_5H_4)_2Fe]_2$

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Abstract

The preparation of the tethered bis(cyclopentadienyl)-phosphine compound bis(2-cyclopentadienylethyl)phenylphosphine **1** from phenylphosphine, *n*-butyllithium and spiro[2.4]hepta-4,6-diene is described. The synthesis of the ferrocene complex $PPh(CH_2CH_2\text{-}\eta^5\text{-}C_5H_4)_2Fe$ **2** from **1** and the synthesis of the heterobimetallic Pd–Fe complex *trans*-$PdCl_2[PPh(CH_2CH_2\text{-}\eta^5\text{-}C_5H_4)_2Fe]_2$ **3** from **2**, along with its X-ray structure, is also described.

Keywords: Ferrocene complex; X-ray structure; Phosphine; Palladium

Cyclopentadienyl and phosphine ligands are two of the most important ligands in organometallic chemistry. The major reasons for the successful use of these ligands, particularly in the area of homogeneous catalysis, are their ability to stabilise a range of metal oxidation states and because their steric and electronic properties can be readily altered by changing their substituents. A new class of ligands is being developed in which two or more cyclopentadienyl and heteroatom groups are tethered together such that the ligand is a potential chelate. Apart from an enhanced thermodynamic stability that is imparted through the chelate effect, changes in the coordination bite angle can also be used to alter the frontier orbitals of the metal–ligand fragment and, thus, alter the reactivity [1].

Although there is now a large range of functionalised cyclopentadienyl ligands that are capable of chelation [2], the number of functionalised bis-cyclopentadienyl ligands capable of chelation is still quite small. Ligands prepared to date include pyridyl [3], ether [4], furanyl [5], and arsine [6,7] substituents. The only examples of bis(cyclopentadienyl)-phosphine ligands are $RP(C_5H_4^-)_2$ (R = Cl, alkyl, aryl) [7,8] and $C_6H_{11}P(CHMe\text{-}2\text{-}PPh_2C_5H_3^-)_2$ [9]. This communication reports the synthesis of the bis(cyclopentadienyl)-phosphine ligand precursor, bis(2-cyclopentadienylethyl)phenylphosphine **1**, along with two complexes prepared using this compound.

Treatment of two equivalents of spiro[2.4]hepta-4,6-diene [10] with phenylphosphine and two equivalents of ^nBuLi, followed by aqueous hydrolysis, produces **1** in high yield (Scheme 1) [11]. ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy indicate that there are two major isomers (**A** and **B**), in approximately equal amounts, for the cyclopentadiene rings. No peaks corresponding to the third possible isomer, **C**, have been observed. There are six multiplets in the vinyl proton region (three from ring **A** and three from ring **B**) and two multiplets (2.93 and 2.85 ppm) which are assigned to the cyclopentadiene methylene protons, one from each ring isomer. Combinations of the two ring isomers should give three isomers of compound **1** in about a 1:2:1 ratio. The methylene region is, therefore, expected to be complex — with up to four ABCD patterns that could be observed. Two complex regions due to the methylene protons are observed at 2.40–2.50 ppm and 1.93–2.01 ppm. That there are indeed three isomers for **1** was confirmed by

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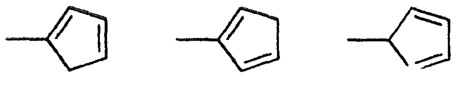
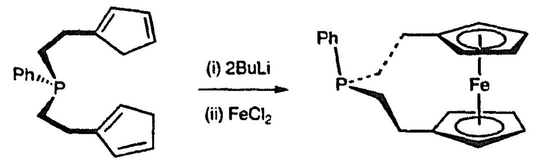


(A) (B) (C)



(1) (2)

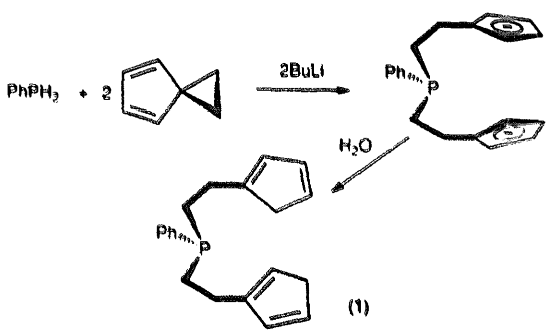
^{31}P{^{1}H}-NMR spectroscopy, which gives three peaks (−22.55, −22.40, and −22.25 ppm) resulting from the **AA**, **AB** and **BB** isomers (though not necessarily in that order). Apparently, the nature of one ring does not significantly affect the ^{1}H and ^{13}C chemical shifts of either the phenyl atoms or the other cyclopentadienylethyl substituent atoms but is able to affect the ^{31}P chemical shift. Paolucci and coworkers, based on ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy, reported that they observed only the mixed **AB** isomer for the related compound 2,6-bis(cyclopentadienylmethyl)pyridine [3]. In the light of our results, their conclusion may need to be modified.

Deprotonation of **1** with two equivalents of ^{n}BuLi followed by treatment with $FeCl_2$ gives the ferrocene complex $PPh(CH_2CH_2\text{-}\eta^5\text{-}C_5H_4)_2Fe$ **2** in moderate yields of 40%–50% [12]. A significant amount of dark brown gelatinous material, which is presumably polymeric, is also produced. We have been unable to isolate any other compounds. The ^{1}H-NMR spectrum is consistent with an average C_s symmetry with the mirror plane through the Ph group and the Fe and P atoms: There is one ABCD pattern for the cyclopentadienyl protons and one ABCD pattern for the methylene protons. The ^{13}C{^{1}H}-NMR spectrum is also consistent with a C_s structure. ^{31}P{^{1}H}-NMR spectroscopy shows one peak at −16.8 ppm. A small upfield shift of 3.6 ppm from the protonated ligand **1** indicates that the P atom is not coordinated to an Fe atom.

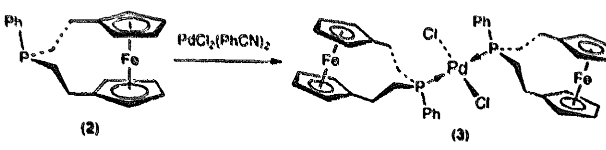
A trinuclear heterobimetallic compound was prepared by treating $PdCl_2(PhCN)_2$ with two equivalents of **2** to give *trans*-$PdCl_2[PPh(CH_2CH_2\text{-}\eta^5\text{-}C_5H_4)_2Fe]_2$ **3** [13]. As with **2**, a single ABCD pattern is observed for the cyclopentadienyl protons in the ^{1}H-NMR spectrum while the methylene protons appear as one ABCD pattern. The ^{31}P chemical shift of 22.1 ppm is 38.9 ppm upfield of that observed for **2** and is consistent with coordination of the phosphine to the palladium centre. A change in the ^{31}P chemical shift of 42.3 ppm upfield is observed for the analogous $PPhMe_2$ system [14].

To assist in the characterisation of **3**, and to investigate the conformation adopted by the ligand, an X-ray crystal structure determination was carried out [15]. The crystal structure shows that one independent molecule of **3** lies with the Pd atom on a crystallographic inversion centre while one independent molecule of THF does not. This gives two molecules of THF for each molecule of **3**. Fig. 1 shows a thermal ellipsoid plot of one molecule of **3** with the adopted numbering scheme.

Molecule **3** consists of a square-planar *trans*-dichlorodiphosphine-Pd centre and, as is usually observed with such complexes [16], the Pd–P bond distances (2.3208(7) Å) are longer than the Pd–Cl bond distances (2.2993(7) Å). Each phosphine has one phenyl substituent and one ferrocenyl substituent ($Fe(C_5H_4\text{-}CH_2CH_2\text{-})_2$) which is linked to the phosphorus atom by two ethylene bridges — one from each cyclopentadienyl group. The tetrahedral geometry of the P atom is distorted such that the angle between the two methylene carbon atoms is reduced to 102.59(13)°. By comparison, the angles between the phenyl and the methylene carbon atoms are 105.24(13)° and 107.11(12)°. Further evidence of ring-strain is provided by the angle between the cyclopentadienyl planes (which are tilted away from the heterocyclic ring) of 6.1° and the angles between each Cp plane and its associated Cp–CH_2 bond vector which are 7.6° (ring C23–C26) and 4.4° (ring C33–C36). Consequently, the angle between the two Cp–CH_2 bond vectors is 19.6° (the C22–C23–C33–C32 dihedral angle of 6.8° contributes only 1.5° to this value). This is in contrast to the apparently ring-strain-free ferrocene complex $Me_2Si(OSiMe_2C_5H_4)_2Fe$ **4** that was reported recently by Manners and coworkers [17]. In **4**, the angle between the cyclopentadienyl rings is less than 1.5(5)° while the average angle between each Cp plane and its *ipso*-Cp–Si bond vector is only 1.6°. It is most likely



Scheme 1. Synthesis of bis(2-cyclopentadienylethyl)phenylphosphine (**1**).



(2) (3)

that any ring-strain in **4** is relieved by the wide angles at the O atoms (average Si–O–Si = 159.7°). By comparison, all of the ring angles at the sp^3 hybridised atoms in **3** are less than 116°. Both **3** and **4** exhibit an eclipsed geometry for the Cp rings (in **3**, the cyclopentadienyl groups are 5.1° from a perfectly eclipsed geometry, whereas, in **4**, the Cp rings are 0.9° from a perfectly eclipsed geometry). The C–Si bonds in **4** are 72.9° from an eclipsed geometry, however, whereas in **3** the Cp–CH_2 bonds are only 5.1° from being eclipsed.

The conformer adopted for the ring backbone of **3** is one that places the $PdCl_2P$ and phenyl groups in approximately equivalent environments and as far away from the ferrocene unit as is possible — allowing for reasonable bond angles and bond distances for the ring atoms. The nature of this conformer can be rationalised by considering the similar steric properties of the phenyl–P and $PdCl_2P_2$ groups which both have flat structures. As a result of this steric similarity, there is a pseudo C_2 axis through the P and Fe centres. The conformer adopted by **4**, however, is dominated by steric interactions between the $SiMe_2$ groups attached to the Cp rings. Fig. 2 illustrates the essential conformational differences between **3** and **4**.

We have described a facile and high-yield synthesis to a new tethered bis(cyclopentadienyl)phosphine ligand and the synthesis and characterisation of two new complexes using this ligand, including a heterobimetallic

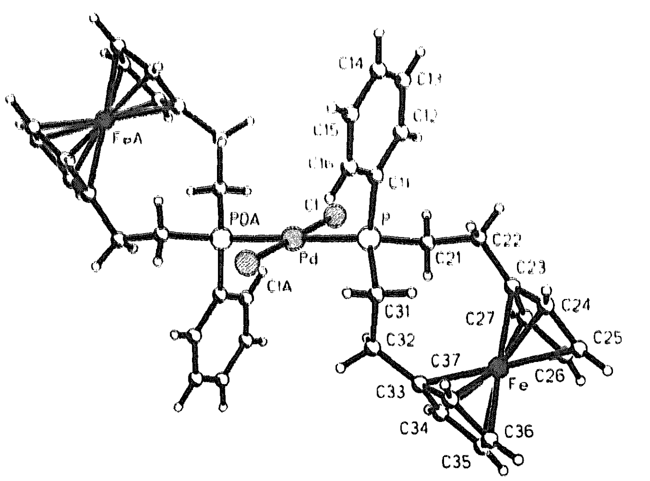


Fig. 1. Plot of **3** showing atom labelling scheme. Selected bond distances (Å), angles (°), and dihedral angles (°): Pd–Cl 2.2993(7), Pd–P 2.3208(7), P–C11 1.819(3), P–C21 1.824(3), P–C31 1.820(3), C21–C22 1.551(4), C22–C23 1.498(4), C31–C32 1.543(4), C32–C33 1.505(4), Fe-(plane C33–C36) 1.657, Fe-(plane C23–C26) 1.662, Cl–Pd–ClA 180.0, P–Pd–PA 180.0, Cl–Pd–P 92.01(3), Cl–Pd–PA 87.99(3), Pd–P–C11 109.70(9), Pd–P–C21 117.53(9), Pd–P–C31 113.82(9), C11–P–C21 105.24(13), C11–P–C31 107.11(12), C21–P–C31 102.59(13), P–C21–C22 114.1(2), C21–C22–C23 115.1(2), P–C31–C32 110.2(2), C31–C32–C33 114.3(2), Fe–C23–C22–C21 48.9, Fe–C33–C32–C31 49.0, C23–C22–C21–P–113.2, C33–C32–C31–P–121.6, C22–C21–P–C31 59.4, C32–C31–P–C21 68.9, Pd–P–C21–C22 174.9, Pd–P–C31–C32 59.2, C11–P–C21–C22 52.5, C11–P–C31–C32–179.4.

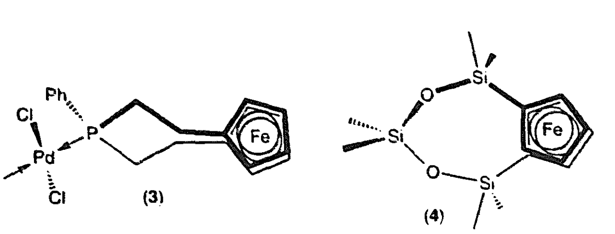


Fig. 2. Drawings of compounds **3** and **4** showing the conformers adopted by the heterocylic ring systems.

Pd_2Fe complex. Syntheses of further transition-metal and non-transition-metal complexes is currently underway.

Acknowledgments

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[11] A solution of phenylphosphine (2.00 g, 18.2 mmol) and spiro[2.4]hepta-4,6-diene (4.15 g, 45.0 mmol) in THF (60 ml) was cooled to −78°C. ^nBuLi (13.0 ml, 1.4 M in hexane, 18.2 mmol) was then added and the solution allowed to warm to room temperature. After stirring for 2 h, the mixture was again cooled to −78°C and ^nBuLi (15.6 ml, 1.4 M in hexane, 21.8 mmol) added. The solution was then allowed to warm to room temperature and stirred overnight. Excess dinitrogen-saturated water was added. The organic layer was collected and the aqueous layer was extracted with 3 ml × 50 ml portions of diethylether which were added to the organic fraction. The

organic solution was dried over Na_2SO_4 and filtered. Removal of the volatiles in vacuo gave an orange oil which, after chromatography down a 5 cm×5 cm SiO_2 column with 1:1 petroleum ether: CH_2Cl_2, produced a colourless oil of **1** (5.05 g, 94% yield). ^{1}H-NMR ($CDCl_3$): δ 7.54 (m, 2H, *ortho*-Ph), 7.36 (m, 2H, *meta*-Ph), 7.34 (m, 1H, *para*-Ph), 6.40 (m, 1H, Cp), 6.39 (m, 2H, Cp), 6.24 (m, 1H, Cp), 6.15 (m, 1H, Cp), 6.01 (m, 1H, Cp), 2.93 (m, 2H, CpH_2), 2.85 (m, 2H, CpH_2), 2.47 (m, 2H, PCH_2CH_2), 2.42 (m, 2H, PCH_2CH_2), 1.99 (m, 2H, PCH_2), 1.95 (m, 2H, PCH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 149.8 (d, $^3J_{PC}$ = 12.2 Hz, *ipso*-Cp), 147.3 (d, $^3J_{PC}$ = 11.0 Hz, *ipso*-Cp), 138.3 (d, $^1J_{PC}$ = 10.0 Hz, *ipso*-Ph), 134.4 (s, Cp), 133.9 (s, Cp), 132.4 (d, $^2J_{PC}$ = 18.3 Hz, *ortho*-Ph), 132.3 (s, Cp), 130.7 (s, Cp), 128.8 (d, $^4J_{PC}$ = 3.0 Hz, *para*-Ph), 128.4 (d, $^3J_{PC}$ = 7.0 Hz, *meta*-Ph), 126.4 (s, Cp), 125.8 (s, Cp), 43.1 (s, CpCH_2), 41.2 (s, CpCH_2), 28.3 (d, $^1J_{PC}$ = 12.4 Hz, PCH_2), 27.3 (d, $^1J_{PC}$ = 11.7 Hz, PCH_2), 27.0 (d, $^2J_{PC}$ = 16.0 Hz, PCH_2CH_2), 26.2 (d, $^2J_{PC}$ = 15.7 Hz, PCH_2CH_2). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −22.25 (s, 4P, **AA** or **BB**), −22.40 (s, 7P, **AB**), −22.55 (s, 3P, **AA** or **BB**). Mass spectrum (EI), *m/z* (rel. intensity): 294 (44) $[M]^+$, 215 (24) $[M-CH_2C_5H_5]^+$, 202 (100) $[PhPH(CH_2CH_2C_5H_5)]^+$, 174 (61) $[Ph(C_5H_5)PH]^+$, 173 (43) $[Ph(C_5H_5)P]^+$, 109 (53) $[PhPH]^+$, 93 (34) $[CH_2CH_2C_5H_5]^+$, 91 (73) $[C_7H_7]^+$, 79 (35) $[CH_2C_5H_5]^+$, 77 (58) $[C_6H_5]^+$. Anal. Calc. for $C_{20}H_{23}P$: C, 81.60; H, 7.88; P, 10.52. Found: C, 81.15; H, 8.23; P, 10.17.

[12] After cooling a solution of **1** (2.40 g, 8.16 mmol) in THF (40 ml) to −78°C, a solution of ^{n}BuLi (11.7 ml, 1.4 M in hexane, 16.3 mmol) was added. The solution was then allowed to warm to room temperature and was stirred for 2 h. A slurry of anhydrous $FeCl_2$ (1.08 g, 8.50 mmol) in THF (250 ml) was added and the solution was then stirred overnight. Filtration through Celite to remove insoluble polymeric material followed by removal of the volatiles in vacuo left an orange oil. Chromatography down a 5 cm×15 cm SiO_2 column with 1:1 petroleum ether: CH_2Cl_2 eluted an orange solid after the solvent was removed in vacuo. Recrystallisation from 10:1 petroleum ether: CH_2Cl_2 yielded orange needle-like crystals (0.97 g, 34% yield), mp 123–125°C. ^{1}H-NMR (DMSO-d_6): δ 7.39 (m, 2H, *ortho*-Ph), 7.29 (m, 2H, *meta*-Ph), 7.21 (m, 1H, *para*-Ph), 4.06 (m, 2H, Cp), 4.02 (m, 2H, Cp), 4.01 (m, 4H, Cp), 2.3–2.5 (m, 4H, CH_2CH_2Cp), 2.20 (m, 2H, CH_2CH_2Cp), 2.05 (m, 2H, CH_2CH_2Cp). $^{13}C\{^1H\}$-NMR (DMSO-d_6): δ 140.7 (d, $^1J_{PC}$ = 16.4 Hz, *ipso*-Ph), 130.6 (d, $^2J_{PC}$ = 15.7 Hz, *ortho*-Ph), 128.0 (d, $^3J_{PC}$ = 5.2 Hz, *meta*-Ph), 127.2 (s, *para*-Ph), 90.4 (d, $^3J_{PC}$ = 2.2 Hz, *ipso*-Cp), 67.9 (d, $^4J_{PC}$ = 3.7 Hz, Cp), 66.8 (s, Cp), 66.5 (s, Cp), 66.1 (s, Cp), 22.9 (d, $^2J_{PC}$ = 10.5 Hz, PCH_2CH_2), 21.4 (d, $^1J_{PC}$ = 18.8 Hz, PCH_2CH_2). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 16.8 (s). Mass spectrum (EI), *m/z* (rel. intensity): 348 (100) $[M]^+$, 347 (62) $[M-H]^+$, 346 (19) $[M-2H]^+$, 320 (42) $[M-C_2H_4]^+$, 270 (15) $[M-CH_2C_5H_4]^+$, 256 (28) $[M-CH_2CH_2C_5H_4]^+$. Anal. Calc. for $C_{20}H_{21}PFe$: C, 68.99; H, 6.08; P, 8.89. Found: C, 68.79; H, 6.17; P, 8.73.

[13] To a solution of bis(benzonitrile)palladium(II) chloride (0.13 g, 0.35 mmol) in THF (25 ml) was added a solution of **2** (0.25 g, 0.72 mmol) in THF (25 ml). After heating to reflux for 12 h the solution was allowed to cool to room temperature, whereupon an orange crystalline product precipitated. The solvent was then filtered off and the solid dried in vacuo to give orange crystals of **3** (0.13 g, 43% yield), mp 199–205°C. ^{1}H-NMR ($CDCl_3$): δ 7.73 (m, 4H, Ph), 7.44 (m, 6H, Ph), 4.12 (m, 4H, Cp), 4.09 (m, 4H, Cp), 4.06 (m, 4H, Cp), 3.97 (m, 4H, Cp), 2.9–2.4 (m, 16H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 131.6 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 5.3 Hz, *meta*-Ph), 131.1 (s, *para*-Ph), 128.7 (t, $|^2J_{PC} + {}^4J_{PC}|$ = 4.2 Hz, *ortho*-Ph), 91.0 (t, $|^3J_{PC} + {}^5J_{PC}|$ = 2.0 Hz, *ipso*-Cp), 67.7 (s, Cp), 67.2 (s, Cp), 67.1 (s, Cp), 67.0 (s, Cp), 22.4 (s, PCH_2CH_2), 17.6 (t, $|^1J_{PC} + {}^3J_{PC}|$ = 13.1 Hz, PCH_2), the *ipso*-Ph carbon was not observed. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 22.06 (s). Mass spectrum (FAB), *m/z* (rel. intensity): 874 (5) $[M]^+$, 837 (4) $[M-Cl]^+$, 802 (2) $[M-2Cl]^+$, 491 (7) $[ClPdP(CH_2CH_2C_5H_4)_2Fe]^+$, 454 (9) $[PdPPh(CH_2CH_2C_5H_4)_2Fe]^+$, 348 (100) $[PPh(CH_2CH_2C_5H_4)_2Fe]^+$. Anal. calc. for $C_{40}H_{42}P_2Cl_2Fe_2Pd.2THF$: C, 56.63; H, 5.75. Found: C, 55.45; H, 5.50. The loss of solvent of crystallisation prevented good microanalysis.

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[15] Single crystals of **3**.2 THF were obtained by cooling a saturated THF solution to −20°C. Crystal data for **3**.2 THF: $C_{48}H_{58}Cl_2Fe_2O_2P_2Pd$, M_r = 1017.88, rectangular plates (0.75 × 0.4 × 0.2 mm^3), monoclinic, space group $P2_1/c$, with a = 16.908(2) Å, b = 7.8432(11) Å, c = 16.686(2) Å, β = 96.303(9)°, V = 2199.4(5) Å^3, Z = 2, $F(000)$ = 1048, d_{calc} = 1.537 g cm^{-1}, absorption coefficient 1.288 mm^{-1}, θ range for data collection 2.42–25.00, index ranges $-19 \le h \le 20$, $-9 \le k \le 0$, $-19 \le l \le 0$, max. and min. transmissions 0.3360 and 0.4225, data/restraints/parameters 3876/0/259, goodness of fit on F^2 was 0.936, final R indices $[I > 2\sigma(I)]$ R_1 = 0.0278, wR_2 = 0.0660, R indices (all data) R_1 = 0.0363, wR_2 = 0.0679, largest difference peak and hole 0.530 and −0.336 eÅ^{-3}. The unit cell parameters were obtained by least-squares refinement of the setting angles of 20 reflections with $4.84° \le 2\theta \le 12.51°$ from a Siemens P4 diffractometer. A unique data set was measured at 158(2) K within $2\theta_{max}$ = 57° limit (ω scans). Of the 3957 reflections obtained, 3876 were unique (R_{int} = 0.0153) and were used in the full-matrix least-squares refinement (G.M. Sheldrick, SHELXL93, *J. Appl. Crystallogr.*, in press) after being corrected for absorption by using the ψ-scan method. The intensities of three standard reflections, measured every 97 reflections throughout the data collection, showed only 4.64% decay. The structure was solved by direct methods (G.M. Sheldrick, *Acta Crystallogr., Sect. A*, *46* (1990) 467.). Hydrogen atoms were fixed in idealised positions. All non-hydrogens atoms were refined with anisotropic displacement parameters. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from J.A. Ibers and W.C. Hamilton (eds.), *International Tables for Crystallography*, Vol. C, Kynoch, Birmingham, 1992. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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