

A mixed palladium(0) palladium(II) bis-diphosphaferrocene complex

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Dedicated to Professor Ernest Otto Fischer on the occasion of his 85th birthday

Abstract

Reaction of octa-*n*-propyl-diphosphaferrocene (**1**) with [Pd(COD)Cl₂] affords a dimeric species **2** featuring two *trans*-[PdCl₂] fragments and two diphosphaferrocenes. Reaction of **2** with [Pd(dba)₂] yields a trimetallic complex **3**. An X-ray crystal structure study reveals that **3** features a central palladium atom that does not interact with the two peripheral [PdCl₂] fragments. Complex **3** can also be formed from the reaction of two equivalents of [Pd(COD)Cl₂] with the bis-(octa-*n*-propyl-diphosphaferrocene)Pd(0) complex.

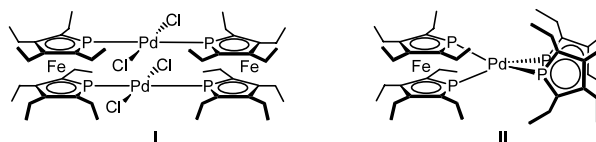
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Keywords: Crystal structures; Diphosphaferrocene; Palladium complexes

1. Introduction

Though diphosphaferrocenes were discovered more than 20 years ago [1], their coordination chemistry remained largely unexplored for a long time [2]. This situation mainly results from the difficulty to control the reactivity of the two phosphorus atom lone pairs towards metallic fragments that possess more than one vacant coordination site. Cowley and coworkers [3] and some of us [4] showed that the introduction of substituents at the α -positions at phosphorus plays a crucial role in preventing the formation of polymeric materials. Thus, octa-*n*-alkyl-substituted diphosphaferrocenes can now be used to build well-defined polymetallic edifices and unusual chelate complexes involving a side-on coordination mode of the ligand. From these studies, it appeared that combination of the ferrocenyl backbone, steric effects provided by the substituents, and the high 3s-character of the phosphorus atom lone pair could be exploited to devise efficient catalytic systems. The two most significant applications were obtained by studying the catalytic potential of palladium complexes

of the octa-*n*-ethyl-diphosphaferrocene. Thus, complex **I** allows the coupling between pinacolborane and iodoarenes (Myaura's coupling process) to yield the corresponding arylboronic esters in very good yields (TON about 3000) [5] and dimer **II** catalyzes the Suzuki cross-coupling reaction between phenylboronic acid and various bromoarenes (TON about 1×10^6) [6].



In pursuing our investigations on the reactivity of these two types of palladium complexes, we recently found that they can be used to build surprising trimetallic edifices incorporating both Pd(II) and Pd(0) centers. Herein we report on these results.

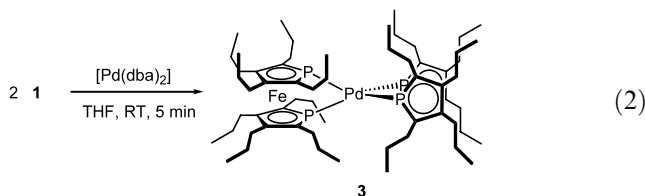
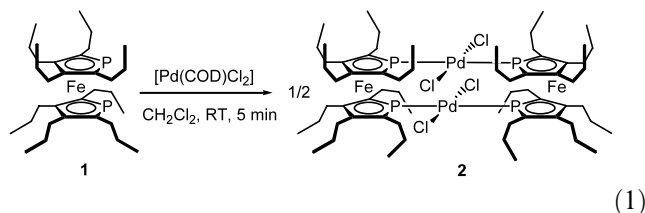
2. Results and discussion

All experiments were carried out with the highly soluble octa-*n*-propyl-diphosphaferrocene (**1**) ligand which is readily available following the zirconium mediated route devised for the synthesis of the octa-*n*-ethyl derivative [7]. Palladium complexes **2** and **3**,

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analogues to **I** and **II**, were thus conventionally prepared by reacting **1** with the appropriate amounts of $[\text{Pd}(\text{COD})\text{Cl}_2]$ and $[\text{Pd}(\text{dba})_2]$ complexes, respectively. Their syntheses are depicted in Eqs. (1) and (2).



Both complexes were successfully characterized by means of NMR spectroscopy and elemental analyses. Their NMR data which are very similar to that of their *n*-ethyl counterparts do not deserve further comments. The reaction of dimer **2** with one equivalent of $[\text{Pd}(\text{dba})_2]$ in THF at room temperature led to a surprising result. Upon addition of the complex, a dark insoluble precipitate formed. The formulation of this complex **4** turned out to be difficult to establish exclusively on the basis of NMR data which show that the structure presents a high symmetry. The most significant structural information was given the ^{31}P -NMR spectrum which shows a strong upfield shift [$\delta(\text{CDCl}_3)$: -9.0 ppm for **2** and $\delta(\text{CDCl}_3)$: -78.0 ppm for **4**]. As previously noted, such a shielding is generally encountered in complexes incorporating a chelated diphosphaferrocene ligand. Fortunately, crystals of **4** could be grown from a slow diffusion of hexanes in a dichloromethane solution of the complex. An ORTEP view of one molecule of **4** is presented in Fig. 1 and the most significant metric data are listed in Table 1.

Consistent with NMR data, the structure of **4** is symmetrical. Contrary to what could be initially envisaged, no disproportionation (leading to a Pd(I) dimer) had taken place and complex **4** is a trimetallic species incorporating two PdCl_2 fragments and a central palladium atom. This edifice results from the insertion of palladium atom in the cavity of dimer **2**. This quite unusual arrangement obviously deserves several comments. A first important point concerns the binding of the two phosphorus atom lone pairs to the two PdCl_2 fragments. As can be seen in Fig. 1, the two ligands are now coordinated in *trans* fashion, the overall geometry around the two palladium atoms remaining square-planar. As previously noted in diphosphaferrocene-

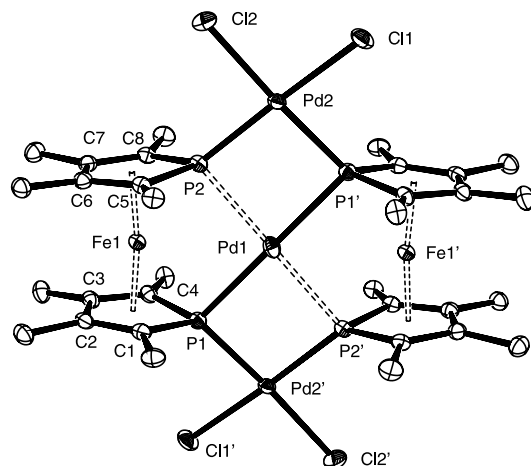


Fig. 1. ORTEP view of one molecule of complex **4**. Ellipsoids are scaled to enclose 50% of the electron density. The ethyl part of each *n*-propyl group has been omitted for clarity. The numbering is arbitrary and different from that used in the assignment of NMR spectra.

based chelate complexes, the deviation from the ideal in-plane coordination of the two phosphorus atom lone pairs is very large ($\theta = 42^\circ$). It must be noted that this non-directional bonding, which results from the pronounced spherical character of the phosphorus atom

Table 1
Crystal data and structural refinement details for the structure of compound **4**

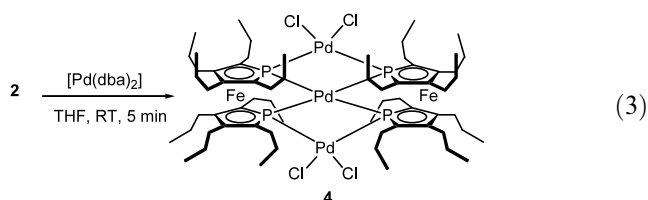
Empirical formula	$\text{C}_{64}\text{H}_{112}\text{Cl}_4\text{Fe}_2\text{P}_4\text{Pd}_3$
Fw	1578.12
Temperature (K)	150.0(10)
Wavelength (\AA)	0.71069
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
<i>a</i> (\AA)	15.058(5)
<i>b</i> (\AA)	15.802(5)
<i>c</i> (\AA)	16.442(5)
α ($^\circ$)	90.000(5)
β ($^\circ$)	116.250(5)
γ ($^\circ$)	90.000(5)
<i>V</i> (\AA^3)	3508.8(19)
<i>Z</i>	2
D_{calcd} (g cm^{-3})	1.494
μ (cm^{-1})	1.437
<i>h, k, l</i> ranges	$-21 \leq h \leq 21, -22 \leq k \leq 17, -23 \leq l \leq 23$
Crystal size (mm^3)	$0.12 \times 0.12 \times 0.12$
Cryst color and habit	deep purple cube
$2\theta_{\text{max}}$ ($^\circ$)	30.03
No. of ref. measured	27 305
No. of ind. refl.	10 257
No. of ref. used	8969
R_1^a [$I > 2\sigma(I)$]	0.0228
wR_2^b [$I > 2\sigma(I)$]	0.0635
GOF on F^2	1.016
Largest diff. peak (e \AA^{-3})	0.677 (0.073), -0.913 (0.073)

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$.

^b $wR_2 = (\sum w ||F_0| - |F_c||^2 / \sum w |F_0|^2)^{1/2}$.

lone pair, has also been observed in other sp^2 -hybridized ligands such as phosphinines [8]. The most striking feature of **4** undoubtedly concerns the central palladium atom which adopts a square-planar geometry. Examining the metric parameters, it is obvious that no bonding occurs between this atom and the two $PdCl_2$ fragments, the intramolecular Pd–Pd distance being too long at 3.336 Å. Additionally, no dative bonding occurs between this palladium atom and the two iron atoms of each ligand (for example, $d Pd(1)–Fe(1) = 3.20(1)$ Å). Indeed, the Pd–Fe bonds in complexes involving such bonding are usually shorter [9]. Surprisingly, it clearly appears that the P–Pd bonds are not strictly equivalent. Thus the $P(2)–Pd(1)$ and $P(2')–Pd(1)$ bond distances (2.5160(7) Å) are slightly longer than $P(1)–Pd(1)$ and $P(1')–Pd(1)$ (2.4304(7) Å) (Table 2). This dissymmetry is not apparent in the other Pd–P and Pd–Cl bond lengths, which are nearly comparable, and it likely results from packing forces in the crystal. It must also be precised that a ^{31}P -NMR study revealed that the overall geometry of **4** remains highly symmetrical in solution, even at -80 °C. At last, we also noted a small out of plane distortion of the two P atoms from the plane defined by the four carbone atoms of the ring ($\theta = 6^\circ$ in **4** vs 1.2° in **1**). Apart from that, all metric parameters in the two diphosphaferrocene moieties are nearly identical with those previously noted in other palladium complexes.

Knowing the structure of **4**, it seemed logical to attempt its synthesis from the reaction of the bis(diphosphaferrocene)Pd(0) (**3**) complex with a source of $[PdCl_2]$ (Eq. (3)). The reaction cleanly proceeded in THF with $[Pd(COD)Cl_2]$ at room temperature to yield **4** as efficiently as obtained using the above-mentioned method (Eq. (4)).



The particular structural arrangement of **4** obviously raises the problem of the electron-counting. If we assume that each diphosphaferrocene ligand simply contributes through its two phosphorus atom lone pairs to bind the $[PdCl_2]$ fragments (16 e), no electron remain to complete the coordination sphere of the central palladium atom. However, as already observed in palladium(II) and Ga(III) complexes, diphosphaferrocenes do not exclusively behave as 4-electron donor ligands. A theoretical study carried out on a chelate

Table 2
Selected bond distances (Å) and angles (°) for complex **4**

Bond distances (Å)	
P(1)–C(1)	1.764(2)
C(1)–C(2)	1.419(2)
C(2)–C(3)	1.442(2)
C(3)–C(4)	1.421(2)
C(4)–P(1)	1.760(2)
P(2)–C(5)	1.765(1)
C(5)–C(6)	1.419(2)
C(6)–C(7)	1.442(2)
C(7)–C(8)	1.423(2)
C(8)–P(2)	1.762(2)
P(1)–Fe(1)	2.2976(6)
P(2)–Fe(1)	2.2873(7)
C(1)–Fe(1)	2.116(2)
C(2)–Fe(1)	2.114(2)
C(3)–Fe(1)	2.111(1)
C(4)–Fe(1)	2.117(1)
C(5)–Fe(1)	2.127(2)
C(6)–Fe(1)	2.110(1)
C(7)–Fe(1)	2.095(2)
C(8)–Fe(1)	2.112(2)
Ct(1)–Fe(1)	1.688
Ct(2)–Fe(2)	1.695
P(1)–Pd(1)	2.4305(7)
P(1)–Pd(2')	2.2271(6)
P(2)–Pd(1)	2.5160(7)
P(2)–Pd(2)	2.2334(7)
P(1')–Pd(1)	2.4304(7)
P(1')–Pd(2)	2.2271(6)
P(2')–Pd(1)	2.5161(7)
Pd(2)–Cl(1)	2.3466(8)
Pd(2)–Cl(2)	2.3548(7)
Pd(1)–Fe(1)	3.020(1)
Pd(1)–Fe(1')	3.0195(8)
Bond angles (°)	
P(1)–C(1)–C(2)	109.4(1)
C(1)–C(2)–C(3)	113.3(1)
C(2)–C(3)–C(4)	113.6(1)
C(3)–C(4)–P(1)	109.3(1)
C(4)–P(1)–C(1)	93.81(7)
Pd(2)–P(2)–Pd(1)	89.05(2)
Pd(2)–P(1')–Pd(1)	91.40(2)
P(1)–Pd(1)–P(2)	96.13(2)
P(1)–Pd(1)–P(1')	180.00(1)
P(1)–Pd(2')–P(2')	95.68(2)
P(2)–Pd(1)–Pd(2')	180.00(1)
P(1)–Pd(1)–P(2')	83.88(2)
P(1)–Pd(2')–Cl(1')	83.15(2)
P(1)–Pd(2')–Cl(2')	175.58(1)
P(2)–Pd(2)–Cl(1)	175.00(1)
P(2)–Pd(2)–Cl(2)	86.92(2)
Cl(1)–Pd(2)–Cl(2)	94.57(2)

complex of the $[GaCl_2]^+$ fragment (isolobal of a PdL_2 fragment) demonstrated that several hybrid orbitals resulting from the combination of 3s, $3p_x$, $3p_z$ orbitals at phosphorus and the $3d_{xz}$ orbital at iron can be involved in the binding to the metal. Furthermore, these calculations also showed that the out of plane distortion of the P atoms (found in **4**: see above in the discussion of the X-ray structure) reflects the participation of the P–

Fe bond in the bonding to the metal. Therefore, we can reasonably propose that in **4**, each diphosphaferrocene contributes with more than two electrons leaving a 14- or 18-electron central palladium atom [10]. Calculations are currently underway in our laboratories to clarify this point.

3. Experimental

3.1. General considerations

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 , CDCl_3 and acetonitrile from P_2O_5 . Dry CD_2Cl_2 was stored, like CDCl_3 , on 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^1H , 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P . Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. The following abbreviations are used: b; broad, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; sext, sextuplet; sept, septuplet; v, virtual. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. $[\text{Pd}(\text{COD})\text{Cl}_2]$ [11] and $[\text{Pd}(\text{dba})_2]$ [12] were prepared according to published procedures.

3.2. Synthesis of the [(*octa-n-propyl-diphosphaferrocene*) PdCl_2]₂ dimer (**2**)

Diphosphaferrocene **1** (100 mg, 0.18 mmol) and $[\text{Pd}(\text{COD})\text{Cl}_2]$ (51 mg, 0.18 mmol) were reacted in dichloromethane (4 ml) at room temperature. After 10 min, ^{31}P -NMR spectroscopy showed the univocal formation of complex **2**. After evaporation of the solvent, the dark residue obtained was washed three times with hexanes (3 × 5 ml) to remove released COD. After drying under vacuum, dimer **2** was isolated as a deep-purple solid. Yield: 128 mg (97%). ^{31}P -NMR (121.5 MHz, CDCl_3): δ -9.0 ppm. ^1H -NMR (300 MHz, CDCl_3): δ 0.81 (t, 24H, $^3J_{\text{HH}} = 7.8$ Hz, CH_3), 1.09 (t, 24H, $^3J_{\text{HH}} = 7.1$ Hz, CH_3), 1.17 (m, 16H, $\Sigma J_{\text{HH}} = 32.1$ Hz, CH_2-CH_3), 1.30 (m, 16H, $\Sigma J_{\text{HH}} = 40.2$ Hz, CH_2-CH_3), 1.72 (t, 16H, $^2J_{\text{HH}} = 12.5$ Hz, $\text{CH}_2-\text{CH}_2\text{CH}_3$), 2.01 (m, 8H, $\Sigma J_{\text{HH}} + \Sigma ^2J_{\text{HP}} = 47.1$ Hz, $\text{CHH}-\text{CH}_2\text{CH}_3$), 2.38 (m, 8H, $\Sigma J_{\text{HH}} = 49.8$ Hz, $\text{CHH}-\text{CH}_2\text{CH}_3$) ppm. ^{13}C -NMR (75.5 MHz, CDCl_3): δ 17.3 (s, CH_3), 17.7 (s, CH_3), 27.9 (s, CH_2-CH_3), 30.8 (s,

CH_2-CH_3), 32.6 (d, $^2J_{\text{CP}} = 3.7$ Hz, $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 32.7 (s, $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 93.1 (s, $\text{P}-\text{C}=\text{C}$), 100.1 (bs, $\Sigma ^1J_{\text{PC}} = 23.6$ Hz, $\text{P}-\text{C}=\text{C}$) ppm; Anal. Calcd for $\text{C}_{64}\text{H}_{112}\text{Cl}_4\text{Fe}_2\text{P}_4\text{Pd}_2$: C, 52.23; H, 7.67. Found: C, 51.75; H, 7.79%.

3.3. Synthesis of the bis-(*octa-n-propyl-diphosphaferrocene*)palladium(0) complex (**3**)

Diphosphaferrocene **1** (111 mg, 0.2 mmol) was reacted with $[\text{Pd}(\text{dba})_2]$ complex (57 mg, 0.1 mmol) in dichloromethane (5 ml) at room temperature. After 20 min, ^{31}P -NMR spectroscopy showed the total conversion of **1** into complex **3**. After evaporation of the solvent, complex **3** was washed with dry acetonitrile (2 × 5 ml) and then dried under vacuum and recovered as a dark green powder. Yield: 120 mg (98%). ^{31}P -NMR (121.5 MHz, CDCl_3): δ -122 ppm. ^1H -NMR (300 MHz, CDCl_3): δ 0.77 (t, 24H, $^3J_{\text{HH}} = 7.1$ Hz, CH_3), 0.99 (t, 24H, $^3J_{\text{HH}} = 7.3$ Hz, CH_3), 1.21 (m, 16H, $\Sigma J_{\text{HH}} = 30.7$ Hz, CH_2-CH_3), 1.38 (m, 16H, $\Sigma J_{\text{HH}} = 55.3$ Hz, CH_2-CH_3), 1.62 (t, 16H, $^2J_{\text{HH}} = 10.5$ Hz, $\text{CH}_2-\text{CH}_2\text{CH}_3$), 1.98 (m, 8H, $\Sigma J_{\text{HH}} + \Sigma ^2J_{\text{HP}} = 52.1$ Hz, $\text{CHH}-\text{CH}_2\text{CH}_3$), 2.40 (m, 8H, $\Sigma J_{\text{HH}} = 47.6$ Hz, $\text{CHH}-\text{CH}_2\text{CH}_3$) ppm. ^{13}C -NMR (75.5 MHz, CDCl_3): δ 15.2 (s, CH_3), 16.0 (s, CH_3), 26.1 (s, CH_2-CH_3), 29.1 (s, CH_2-CH_3), 30.6 (d, $^2J_{\text{CP}} = 5.1$ Hz, $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 31.6 (s, $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 99.3 (s, $\text{P}-\text{C}=\text{C}$), 129.4 (d, $^1J_{\text{PC}} = 43.7$ Hz, $\text{P}-\text{C}=\text{C}$) ppm; Anal. Calcd for $\text{C}_{64}\text{H}_{112}\text{Fe}_2\text{P}_4\text{Pd}$: C, 62.82; H, 9.23. Found: C, 62.55; H, 9.06%.

3.4. Syntheses of complex (**4**)

Complex **4** can be prepared following two different procedures. The first one involves the reaction of dimer **2** (120 mg, 82 μmol) with $[\text{Pd}(\text{dba})_2]$ (47 mg, 82 μmol) in THF at room temperature. After 3 h stirring, a black solid precipitated and the ^{31}P -NMR spectrum of an aliquot of the crude mixture showed no NMR signals indicating the end of the reaction. The solution was then filtrated yielding a black solid. After washings with THF (3 × 5 ml), the black solid obtained was dried under vacuum. Yield: 122 mg (95%). The second procedure involves the reaction of the zerovalent palladium(0) (122 mg, 0.1 mg) complex **3** with two equivalents of $[\text{Pd}(\text{COD})\text{Cl}_2]$ (55.6 mg, 0.2 mmol). The reaction takes place in THF as solvent. After 2 h stirring at room temperature, a black powder precipitated. The solution was then filtrated and the black solid obtained was washed with THF (2 × 5 ml). Like in the former method, complex **4** was isolated as a black solid. Yield: 125 mg (97%). ^{31}P -NMR (121.5 MHz, CD_2Cl_2): δ -78 ppm. ^1H -NMR (300 MHz, CD_2Cl_2): δ 0.82 (t, 24H, $^3J_{\text{HH}} = 7.3$ Hz, CH_3), 0.92 (t, 24H, $^3J_{\text{HH}} = 7.6$ Hz, CH_3), 1.29 (m, 16H, $\Sigma J_{\text{HH}} = 22.8$ Hz, CH_2-CH_3), 1.45 (m,

16H, $\Sigma J_{\text{HH}} = 42.9$ Hz, $\text{CH}_2\text{-CH}_3$), 1.54 (t, 16H, $^2J_{\text{HH}} = 9.2$ Hz, $\text{CH}_2\text{-CH}_2\text{CH}_3$), 1.93 (m, 8H, $\Sigma J_{\text{HH}} + \Sigma ^2J_{\text{HP}} = 41.6$ Hz, $\text{CHH-CH}_2\text{CH}_3$), 2.28 (m, 8H, $\Sigma J_{\text{HH}} = 38.4$ Hz, $\text{CHH-CH}_2\text{CH}_3$) ppm. $^{13}\text{C-NMR}$ (75.5 MHz, CD_2Cl_2): δ 14.6 (s, CH_3), 14.7 (s, CH_3), 24.4 (s, $\text{CH}_2\text{-CH}_3$), 26.9 (s, $\text{CH}_2\text{-CH}_3$), 28.6 (bs, $\text{CH}_2\text{-CH}_2\text{-CH}_3$), 29.9 (s, $\text{CH}_2\text{-CH}_2\text{-CH}_3$), 80.8 (d, $^2J_{\text{PC}} = 10.5$ Hz, P-C=C), 108.3 (d, $^1J_{\text{PC}} = 19$ Hz, P-C=C) ppm; Anal. Calcd for $\text{C}_{64}\text{H}_{112}\text{Fe}_2\text{P}_4\text{Pd}_3$: C, 48.71; H, 7.15. Found: C, 48.39; H, 6.92%.

3.5. X-ray structural determination

Single crystals of compound **4** suitable for X-ray crystallography were obtained at room temperature by diffusing hexane into a dichloromethane solution of the compound in a sealed tube. Data were collected on a Nonius Kappa CCD diffractometer using an Mo-K α ($\lambda = 0.71069$ Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved using SIR-97 [13] and SHELXL-97 [14]. ORTEP drawings were made using ORTEP III for Windows [15].

4. Supplementary material

Crystallographic data for compound **4** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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