Hydrogen bonding and self-assembly in the crystal structures of ferrocenylmethanol derivatives having different phosphorus substituents on the ferrocene unit

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Ferrocenylmethanol derivatives bearing a phosphorus substituent in position two of the ferrocene unit, *rac*-2-(diphenylphosphino)ferrocenylmethanol (**3**), *rac*-2-(diphenylphosphinoyl)ferrocenylmethanol (**4**), and *rac*-2-(diphenylthiophosphoryl)ferrocenylmethanol (**5**), have been synthesized and structurally characterized by single-crystal X-ray diffraction. While the overall molecular geometry does not differ significantly in the whole series, showing only differences in the arrangement at the phosphorus atom owing to a replacement of the lone electron pair (**2**, **3**) with oxygen (**4**) and sulfur (**5**), and in the conformation of the hydroxylmethyl group, the compounds form different crystal packing patterns that result from a counterplay of hydrogen bonding of various types and non-polar interactions. Alcohol **3** associates into dimers by double O–H···O hydrogen bridges between disordered hydroxy groups of neighbouring molecules. The distribution of molecules in the crystal of **4** appears identical to that of **3**. However, the structure of **4** comprises intermolecular O–H···O=P hydrogen bridges instead. The packing of phosphine sulfide **5** is different, featuring intramolecular O–H···S bridges. Although the molecular entities are involved in further interactions such as O–H···P and C–H···O hydrogen bonding, and π-π stacking interaction of the phenyl rings, which further propagate the molecular network, the principal force towards self-assembly always results in the formation of entropically favoured, closed cyclic systems. The solid state structure of the common precursor, *rac*-2-(diphenylphosphino)ferrocenylmethyl acetate (**2**) shows only C–H···O intermolecular interactions due to the lack of a better hydrogen bond donor.

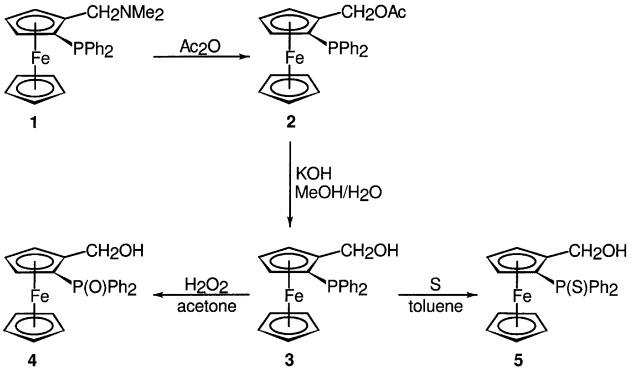
During our studies with ferrocene phosphinocarboxylic ligands[1] and related systems,[2] we have found that introduction or modification of a polar group that can be involved in hydrogen bonding changes significantly the solid-state packing, resulting in some cases in formation of supramolecular assemblies and adducts, and can also dramatically alter crystallization abilities in a pair of compounds that differ only by the presence of the group capable of hydrogen bonding. Considering these observations as well as the fact that the hydrogen bonding in polar ferrocene compounds plays a crucial role in the aggregation of biologically relevant, ferrocene-based molecules[3] and in crystal engineering,[4] we decided to study the factors governing the crystal assembly in a series of ferrocenylmethanol derivatives having different phosphorus substituents in position two of the ferrocene unit.

Compounds derived from ferrocenylmethanol and ferrocenylmethyl acetate represent excellent entries into the synthesis of ferrocene derivatives since they are not only readily available from the corresponding (dimethylaminomethyl)ferrocenes but the hydroxy and acetate groups, respectively, may be easily replaced by many other functional substituents.[5] The numerous chiral compounds obtained by this approach bearing other donor groups on the ferrocene unit in a position adjacent to the methylene tether were tested as ligands in various transition metal mediated organic transformations.[5a,b] Hence, any structural information is of practical relevance as it may allow for a more rational design of new compounds. As a contribution to this field, we report here the solid-state structures of three planarly chiral but racemic ferrocenylmethanol derivatives: 2-(diphenylphosphino)ferrocenylmethanol (**3**), 2-(diphenylphosphinoyl)ferrocenylmethanol (**4**), and 2-(diphenylthiophosphoryl)ferrocenylmethanol (**5**), and their precursor, 2-(diphenylphosphino)ferrocenylmethyl acetate (**2**).

Results and discussion

Syntheses and characterization

Bright yellow, crystalline acetate **2** was obtained in 76% yield from *rac*-*N*,*N*-dimethyl-[2-(diphenylphosphino)ferrocenyl]-methylamine (**1**) using the well-established direct acetylation approach[6] (Scheme 1). A subsequent hydrolysis with potassium hydroxide in refluxing methanol–water mixture afforded



Scheme 1

the yellow-orange phosphinoalcohol **3** (92%), which was converted with hydrogen peroxide to the corresponding phosphine oxide **4** (75% yield after recrystallization) or, with sulfur, to phosphine sulfide **5** (quantitatively). All compounds were characterized by high-resolution mass spectrometry and NMR spectroscopy. The ^{1}H and ^{31}P NMR data for **2** and **3** correspond very well to the data reported for the respective S_p enantiomers.[7] However, we present a different assignment for the ^{13}C NMR signals based on a comparison with NMR spectra of simple $FcCH_2Y$ derivatives (Fc = ferrocenyl, Y = OH, NMe_2, CO_2H), their 2-Ph_2P-, 2-$Ph_2P(O)$- and 2-$Ph_2P(S)$-ferrocenyl analogues, and on a comparison of the observed J_{PC} scalar coupling constants with the values reported for triphenylphosphine and triphenylphosphine oxide.[8]

Solid-state structures

Molecular parameters. The molecular structures of compounds **2**–**5** are shown in Figs. 1–4 and selected geometric parameters are summarized in Table 1. The compounds are all racemic, crystallizing in centrosymmetric space groups. The unit cells accommodate equal numbers of molecules with R_p and S_p configurations related by crystallographic inversion centres. At first glance, the molecular structures of **2**–**5** show no unexpected features. The ferrocene units uniformly exhibit only negligible tilt [max. 1.4(1)° for **5**] but their cyclopentadienyl rings adopt different conformations. While the conformation of **2**, **3**, and **4** are similar with the cyclopentadienyl rings rotated by about 10° from the ideal eclipsed conformation ($\tau = 0°$), the respective τ(C1–Cg1–Cg2–C6) torsion angles being −9.6(2)°, −10.9(2)°, and −12.4 (2)°, the conformation of the phosphine sulfide **5** [$\tau = 23.5(2)°$] also deviates by *ca.* 10° but from the other extreme, the fully staggered conformation with $\tau = 36°$. In all the cases, the Fe–Cg^1 distance is slightly shorter than the Fe–Cg^2 distance (see Table 1 for plane definitions). Although the relative difference amounts to only 1%, it may well reflect the electron-withdrawing nature of the substituents and, hence, a partial electron density transfer in the direction $Cp^2Fe \rightarrow Cp^1$.

The sterically demanding $Ph_2P(E)$ substituent in position two of the ferrocene framework seems to induce no significant torsion at the C1–C2 bond of the cyclopentadienyl ring but, in keeping with the increased bulkiness of the $Ph_2P(E)$ substituent, the maximum deformation was observed for sulfide **5**, where the torsion angle τ(C11–C1–C2–P) amounts to 7.1(3)°. The arrangement of the (pseudo)tetrahedral $Ph_2P(E)$ moiety reflects nicely the different steric requirements of the lone electron pair (**2**, **3**) or the heteroatom (**4**, **5**). Introduction of the heteroatom results in a shortening of the P–C bonds and opening of the C–P–C angles. The P–C distances and C–P–C angles in phosphines **2** and **3** are similar to those in 1′-(diphenylphosphino)ferrocenecarboxylic acid[1a] or [1′-(diphenylphosphino)ferrocenyl]methanol.[2] Similar parameters for phosphine oxide **4** compare well to the data reported for 1′-(diphenylphosphinoyl)ferrocenecarboxylic acid [P=O 1.487(2) Å][1a] or 1,1′-bis(diphenylphosphinoyl)ferrocene [P=O 1.493(2) Å],[9] while the P=S bond length in **5** corresponds to the value reported for triphenylphosphine sulfide [1.9554(7) and 1.9548(7) Å at 180 K].[10]

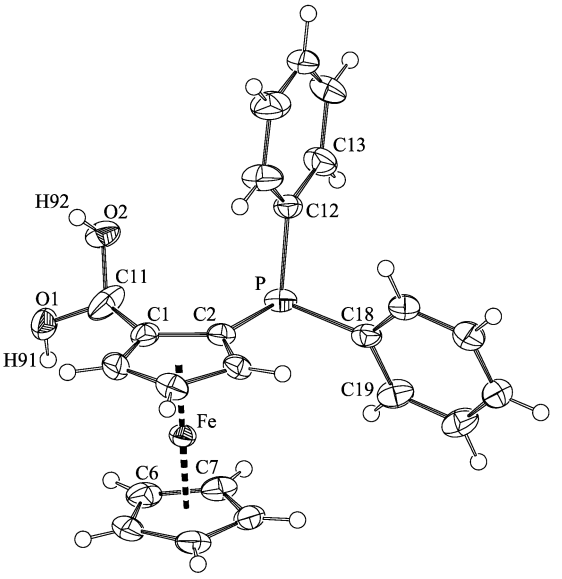


Fig. 2 View of the molecular structure of alcohol **3** with the atom numbering scheme. Both positions of the disordered hydroxy group are shown. The thermal motion ellipsoids are drawn at 50% probability level.

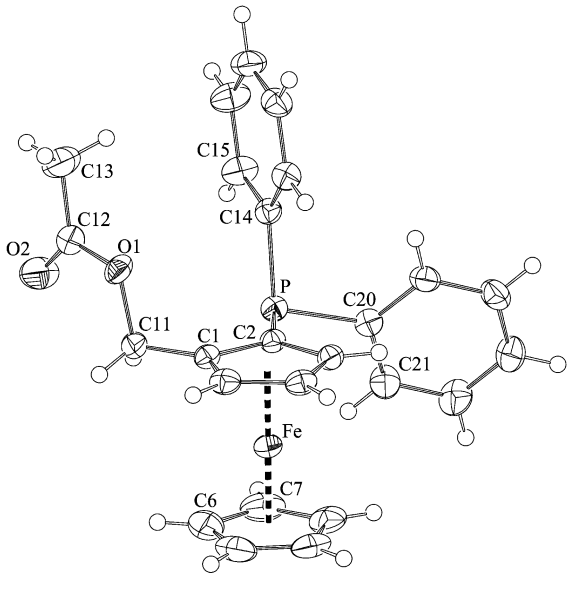


Fig. 1 View of the molecular structure of **2** showing the atom numbering scheme. As the rings are labelled consecutively, only pivotal and their adjacent carbon atoms are labelled. The thermal motion ellipsoids are drawn at 50% probability level.

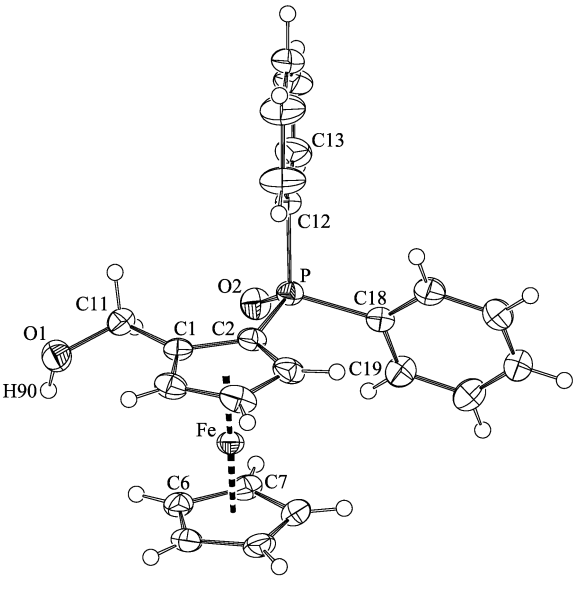


Fig. 3 View of the molecular structure of **4** with the atom numbering scheme. The thermal motion ellipsoids are drawn at 50% probability level.

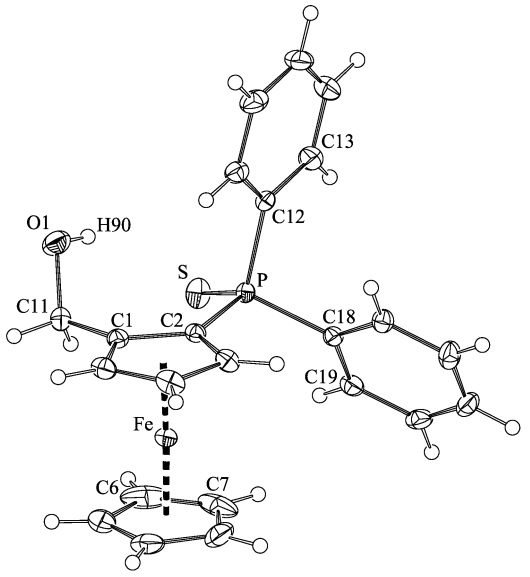


Fig. 4 View of the molecular structure of **5** with the atom numbering scheme. The thermal motion ellipsoids are drawn at 50% probability level.

Albeit the geometry of the hydroxymethyl substituent in **3**, **4**, and **5** is very similar, as judged from the respective bond distances and bond angles that themselves do not deviate in any significant way from those in 1,1′-bis(hydroxymethyl)ferrocene[11] or 1′-(diphenylphosphino)ferrocenylmethanol,[2] for example, the CH_2OH groups have different orientations towards the parent ferrocene unit. The changes in conformation at the C1–C11 bond can be accounted for by differences in crystal packing in which the groups participate. In phosphine **3**, the hydroxymethyl group is statistically disordered, having the oxygen atom distributed equally over two positions, or in other words, with the hydroxymethyl group adopting two different orientations towards the ferrocene unit. The disorder, which likely arises from the crystal packing (see below), renders the C–O bond significantly shorter compared to those in **2**, **4**, and **5** but leaves other parameters intact. The ester part in **2** can be compared to chiral 1-[1′,2-bis(diphenylphosphino)-ferrocenyl]ethyl acetate,[12] which shows a very similar C=O bond length [1.19(2) Å] but slightly shorter C(Cp)–CO [1.49(1) Å] and longer O–C(:O) [1.37(1) Å] and C(Cp)C–O [1.48(1) Å] distances.

Solid-state packing. With the exception of acetate **2**, which lacks a suitable hydrogen bond donor in the structure, the O–H···Y (Y = O or S) hydrogen bonding is the principal force towards intermolecular aggregation in all the studied cases (hydrogen bond parameters are summarized in Table 2). The packing of **2** features only weak intermolecular C–H···O hydrogen bonds between the acyl oxygen atom O2 and two aromatic CH and one methylene groups from three different neighbouring molecules, which link the molecules into a complicated three dimensional net.

As mentioned above, the structure of phosphinoalcohol **3** consists of molecules with two different orientations of the hydroxymethyl substituent in a 1 : 1 ratio. The basic repeating unit in the solid state is a dimer consisting of two neighbouring molecules with *different* configuration of the hydroxymethyl group that are linked by hydrogen bonds at an O···O distance of 2.751(3) Å (see Table 2). However, due to the disorder, a symmetrically related, complementary hydrogen bond system arises within each dimer (Fig. 5, top). Thus, on average, the solid-state packing *emulates* higher symmetry by forming a system of centrosymmetric double hydrogen bridges with 0.50 occupancy for both components. Such an arrangement results very likely from steric properties of the molecule: the bulky, non-polar (diphenylphosphino)ferrocenyl moieties are packed at the normal van der Waals distances so as to fill efficiently the space, leaving enough space for the peripheral hydroxymethyl group so that the latter can adopt two conformations so as not to violate the higher symmetry already imposed by the 2-(diphenylphosphino)ferrocenyl moieties (Fig. 5, bottom). Notably, the O···O hydrogen bonding is not the sole stabilizing interaction in the structure of **3**. The O1–H91 group is further involved in weaker hydrogen bonding to the phosphorus atom of an adjacent molecule, O1–H91···P^v [O1···P^v 3.394 Å; symmetry codes are given in

Table 1 Selected geometric parameters for compounds **2**–**5** (Å, deg)

Parameter[a]	**2**[b]	**3**	**4**	**5**
E	Void	Void	O	S
Fe–Cg^1	1.6446(7)	1.6445(8)	1.6443(9)	1.6375(8)
Fe–Cg^2	1.6572(9)	1.6565(9)	1.6580(9)	1.656(1)
∠Cp,Cp^2	0.5(1)	0.5(1)	0.4(1)	1.4(1)
P=E	–	–	1.488(1)	1.9567(6)
P–C2	1.816(2)	1.810(2)	1.782(2)	1.790(2)
P–C(Ph)[c]	1.840(2), 1.839(2)	1.834(2), 1.838(2)	1.806(2), 1.806(2)	1.818(2), 1.810(2)
∠CPE[d]	–	–	111.11(8)–115.58(8)	111.77(6)–115.72(5)
∠CPC[e]	101.19(7)–103.31(7)	101.66(7)–102.15(7)	105.33(8)–106.84(8)	105.21(7)–106.09(7)
∠Cp^1,Ph^1	89.74(9)	89.7(1)	89.3(1)	82.63(9)
∠Cp^1,Ph^2	76.19(9)	75.11(9)	75.0(1)	62.72(9)
∠Ph^1,Ph^2	73.13(9)	87.84(9)	81.1(1)	77.32(8)
C1–C2–P–E	–	–	39.6(2)	28.2(2)
C11–C1–C2–P	−3.1(2)	−3.8(2)	−0.6(2)	7.1(3)
C1–C11	1.485(2)	1.498(3)	1.500(2)	1.498(2)
C11–O	1.461(2)	1.295(3), 1.291(3)[f]	1.410(2)	1.425(2)
∠C1C11O	106.0(1)	124.0(2), 115.9(2)[f]	113.1(1)	112.7(2)
C2–C1–C11–O	−81.2(2)	153.1(2),−74.7(2)[f]	161.7(2)	67.9(2)

[a] Plane definitions: Cp^1, C(1–5); Cp^2, C(6–10); Cg^1 and Cg^2 are the respective cyclopentadienyl ring centroids. **2**: Ph^1, C(14–19); Ph^2, C(20–25); **3**–**5**: Ph^1, C(12–17); Ph^2, C(18–23). [b] Further data for **2**: C12–O1 1.334(2), C12=O2 1.199(2), C12–C13 1.489(3) Å; O1–C12–O2 123.4(2), ∠Cp^1, Ac 87.4(1)° [Ac = plane of the acetyl group {C12,O1,O2,C13}]. [c] **3**–**5**: P–C(12,18), **2**: P–C(14,20). [d] **2**: C(2,14,20)–P–E; **3**–**5**: C(2,12,18)–P–E. [e] **2**: C(2)–P–C(14,20) and C(14)–P–C(20); **3**–**5**: C(2)–P–C(12,18) and C(12)–P–C(18). [f] Two entries due to the disorder of the hydroxymethyl group (see Experimental). Parameters involving O1 and O2 are given, respectively [O(1)–C(11)–O(2) 104.9(2)°].

Table 2 Hydrogen bond parameters for **2**–**5**[a]

Compd	Type	H-bond D–H···A	D···A [D–H] (Å), D–H···A (°)[b]
2	Inter	C(11)–H(11B)···O(2)^{i}	3.339(2) [0.97], 151
	Inter	C(16)–H(16)···O(2)^{ii}	3.431(2) [0.93], 172
	Inter	C(22)–H(22)···O(2)^{iii}	3.424(2) [0.93], 170
3	Inter[c]	O(2)–H(92)··· O(1)^{iv}	2.751(3) [0.92], 161
	Inter	O(1)–H(91)···P^{v}	3.394(3) [1.09], 157
4	Inter[c]	O(1)–H(90)···O(2)^{vi}	2.687(2) [1.02(3)], 173(2)
	Inter	C(11)–H(11A)···O(1)^{vii}	3.205(2) [0.97], 126
	Intra	C(11)–H(11B)···O(2)	3.297(2) [0.97], 129
	Inter	C(6)–H(6)···O(2)^{vi}	3.361(2) [0.93], 166
	Inter	C(14)–H(14)···O(1)^{viii}	3.376(2) [0.93], 149
5	Intra[c]	O–H(90)···S	3.414(2) [0.82(3)], 147(2)
	Inter	C(16)–H(16)···O^{ix}	3.389(2) [0.93], 158

[a] Symmetry operators: *i* (1 − *x*, 1 − *y*, 1 − *z*), *ii* (−*x*, 1 − *y*, 1 − *z*), *iii* (1 − *x*, 1 − *y*, −*z*), *iv* (1 − *x*, 2 − *y*, −*z*), *v* (−*x*, 2 − *y*, −*z*), *vi* (1 − *x*, 1 − *y*, 1 − *z*), *vii* (2 − *x*, 1 − *y*, 1 − *z*), *viii* (*x*, 1 + *y*, *z*), *ix* (2 − *x*, −*y*, −*z*). [b] Parameters including fixed hydrogen atoms are given without esd. [c] The principal component.

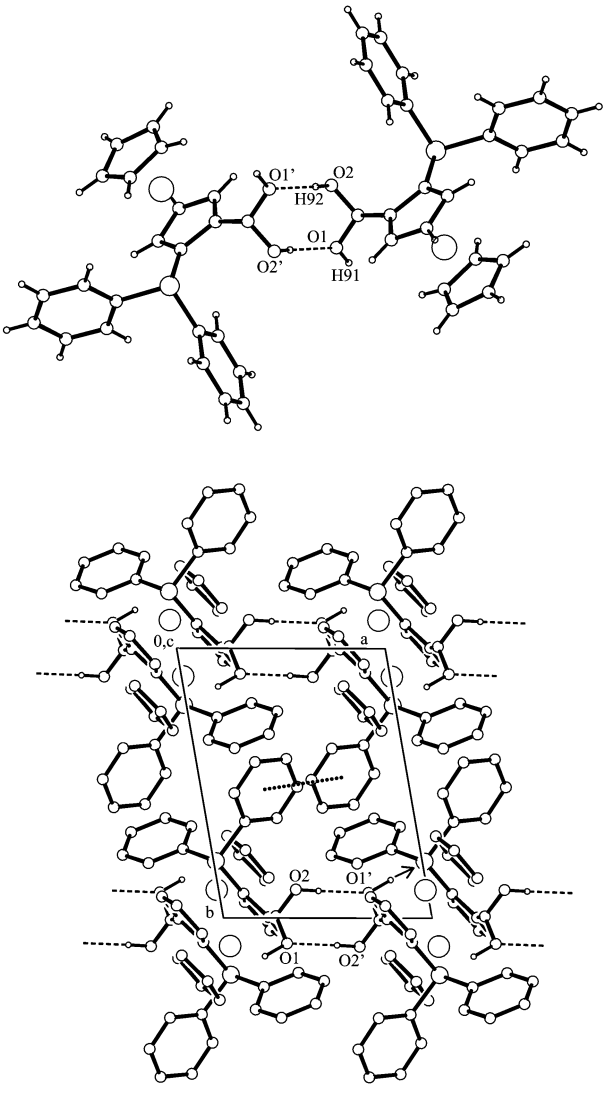


Fig. 5 A perspective view of the dimeric motif in the structure of **3** (top) and a view of the unit cell of **3** along the crystallographic *c* axis (bottom). All the important intermolecular interactions, the O–H···O hydrogen bonds (dashed lines), the π-π stacking interactions (dotted line), and the O–H···P hydrogen bonds (arrow), are shown. For clarity, only hydroxyl hydrogen atoms are displayed in the bottom diagram.

Table 2]. Thus, the alcohol function containing O1 acts as both the hydrogen donor (towards P) and acceptor (towards O2). Furthermore, the molecular entity is connected to its centrosymmetric counterpart by an offset π-π stacking interaction involving two by-symmetry perfectly parallel phenyl rings at a ring centroid distance $Ph^1\cdots Ph^1$&(1 −*x*, 1−*y*, −*z*) of 4.21 Å (Fig. 5, bottom). This distance is about 25% longer than the interlamellar separation in α-graphite (3.35 Å).

According to a search in the Cambridge Structural Database (version 522, release of November 2001), O–H···P hydrogen bonds are not unprecedented but still rather scarce; the known examples are restricted only to hydroxyphosphines. For six entries with H···P distances not exceeding 3.0 Å, the O···P distances in inter- and intramolecular O–H···P bonds span a range of 3.03–3.50 Å.[13] As examples may serve structures of 2-[*tert*-butyl(phenyl)phosphinol]-4-methylphenol [intermolecular, O···P 3.190(1) Å, O–H···P 152° at 143 K],[13a] *rac*-1,1′-bis[diphenylphosphino)-2-[1-(2-hydroxyphenylamino)ethyl]-ferrocene [intermolecular, O···P 3.504 Å, O–H···P 146°],[13b] diphenyl-[2-(2-hydroxyphenyliminomethyl)phenyl]phosphine [intramolecular, O···P 3.483 Å, O–H···P 154°][13c] or 2-[2′-(*tert*-butylphenylphosphino)phenyl]phenol · methanol (1 : 1) solvate which features a combined system of hydrogen bonds very similar to that in **3**, O–H···O(Me)–H···P, with O···P 3.327(2) Å, O–H···P 171°, and O···O 2.703(2) Å, O–H···O 174° (at 143 K).[13d]

Rather surprisingly, the arrangement of molecules in the crystal of phosphine oxide **4** is almost the same as in the parent phosphine **3**. This is best revealed after a transformation of the original unit cell of **4** into a cell similar to **3** and a comparison of the atomic coordinates. Indeed, the structures show an identical distribution and orientation of the molecules in the crystal (Fig. 6), suggesting that even the nature of intermolecular interactions may be similar as well. However, unlike phosphine **3**, the phosphine oxide forms centrosymmetric, hydrogen bonded macrocyclic dimers with O1···O2^{vi} distances of 2.687(2) Å (Fig. 7). The observed O···O distance is similar to that reported for the structure of 1,1′-bis(hydroxymethyl)ferrocene [O···O 2.71 and 2.69 Å][11] and the adduct of 1,1′-bis(diphenylhydoxymethyl)ferrocene · *N*,*N*-dimethylformamide (1 : 1) [fc(CPh_2OH) · Me_2NCHO: CPh_2*O*–H···*O*$CHNMe_2$ 2.721(3) Å (fc = ferrocene-1,1′-diyl)[4e]] but significantly longer than the hydrogen bonds observed in phosphinoyl carboxylic acids, C(=O)*O*–H···*O*=P:1′-(diphenylphosphinoyl)ferrocenecarboxylic acid [*O*···*O* 2.588(3) Å][1a] and (S_p)-2-(diphenylphosphinoyl)ferrocenecarboxylic acid [*O*···*O* 2.556(4) Å].[1h] Besides the strong, double O–H···O hydrogen bond, the packing of **4** is further stabilized by a system of weaker inter- and

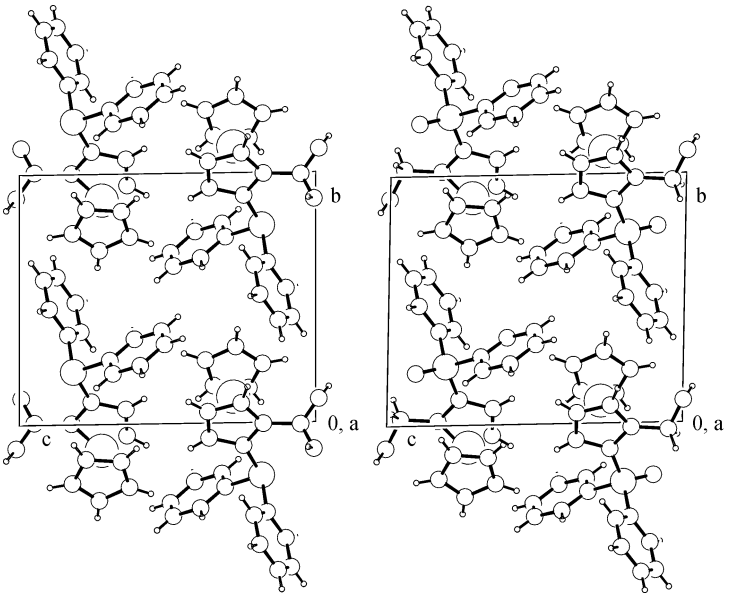


Fig. 6 The unit cell of **3** (left) and the transformed unit cell of **4** (right) as viewed along the crystallographic *a* axis. Hydrogen atoms at C11 in **3** were omitted due to disorder.

intramolecular C–H···O hydrogen bonds (Table 2) and, similarly to **3**, by a face-to-face stacking interaction between the Ph^1 phenyl ring and its symmetry-related counterpart $Ph^1 \cdots Ph^1$&(2−*x*, 2 − *y*, 1 − *z*) with a ring centroid distance of 4.15 Å.

The changes of the intermolecular interactions on going from **3** to **4** can be ascribed to a competition of potential hydrogen bond acceptors for the hydroxymethyl group. While the structure of **3** is dominated by O–H···O interactions between the disordered hydroxymethyl groups with cooperative contribution of weaker O–H···P bonds (a hydroxy group groups wins over the phosphine as a better acceptor), the interaction in the O → P direction but with a better acceptor, O–H···O=P, dominates the structure of **4**. The replacement of the (weak) O–H···P with the (rather strong) O–H···O=P hydrogen bond, which leaves the crystal packing virtually unchanged, indicates that O–H···P hydrogen bonds affect the crystal packing far more than generally acknowledged.

Finally, the hydroxyl group in sulfide **5** participates in intramolecular hydrogen O–H···S bonding to form a cycle of six non-hydrogen atoms with an O···S edge of 3.414(2) Å. Similarly to **3**, the hydroxyl function is further involved in intermolecular C–H···O^{ix} hydrogen bonding as an acceptor. This interaction binds the molecules into cyclic dimers that are packed at the normal van der Waals distances (Fig. 8).

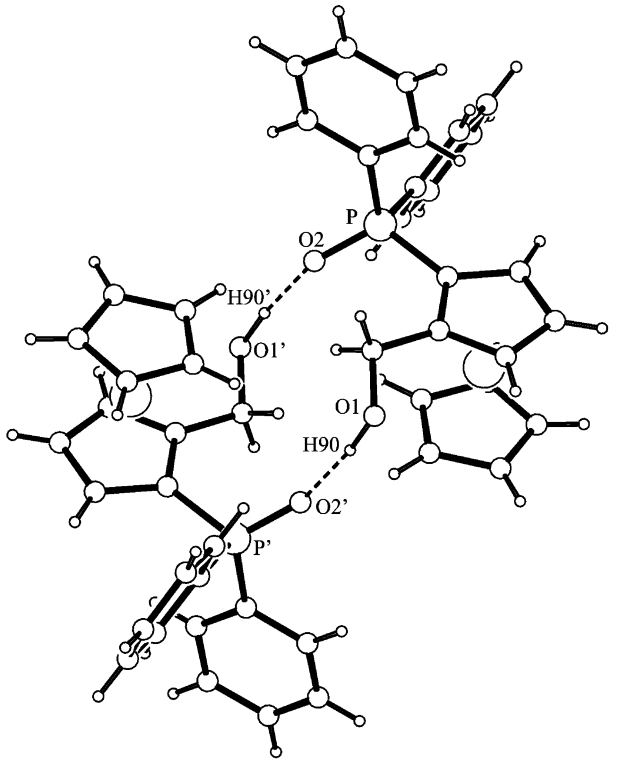


Fig. 7 View of the dimeric, hydrogen-bonded motif in the structure of phosphine oxide **4**.

Conclusions

Ferrocenylmethanol derivatives having (ψ-)tetrahedral $P(E)Ph_2$ (E = void, O, S) substituents on the same or the other[1,2] cyclopentadienyl ring represent well-defined supramolecular building blocks that, in the absence of other molecules capable of hydrogen bond formation, tend to associate primarily through intermolecular O–H···O hydrogen bonds to either neighbouring hydroxy groups or, as shown for **4**, to a better acceptor when available. When another hydroxy group acts as an acceptor, it may become involved in further interactions with other proximal polar groups as the hydrogen bond donor. Furthermore, the variation of the E element allows for different packing patterns due to changed steric demands of the $Ph_2P(E)$ substituent and, more importantly, due to its changed hydrogen bond acceptor power. Further intramolecular interactions influencing the solid-state packing are π-π stacking interactions of the phenyl substituents and also much less predictable C–H···O hydrogen bonds, which represent the only interactions observed for compound **2** where the hydroxy group cannot enter hydrogen bonding as the donor. Regardless of the other interactions accounting for propagation of the molecular network, the principal force towards self-assembly in alcohols **3**–**5** results in the formation of entropically favoured, closed cyclic systems [**3**: 6, **4**: 12, and **5**: 6 (intra) non-hydrogen atoms]. Solid-state packing seems to be in the case of **2**–**5** dictated by the steric requirements of the bulky phosphinylated ferrocene framework (non-polar interactions), which, however, leaves enough space for the attached polar groups and assembles into a crystal so as to force the polar

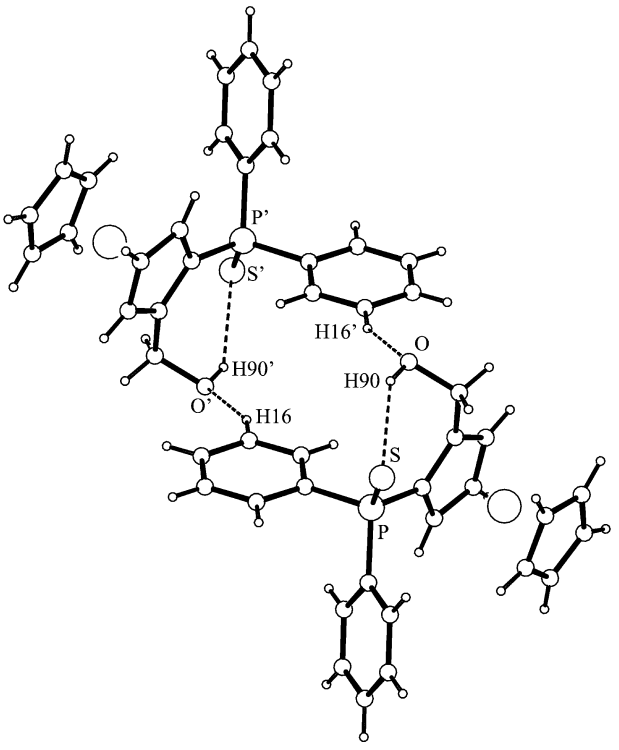


Fig. 8 View of the weakly bonded dimeric arrays in the structure of **5** showing the intramolecular O–H···S and intermolecular C–H···O hydrogen bonds as dashed lines.

groups into mutual proximity. As documented by the virtually isostructural compounds **3** and **4**, any far-reaching conclusions drawn from incomplete structural data for a series of closely related entities with changed peripheral parts or modified only marginally without influencing the overall molecular geometry should be taken with utmost care.

Experimental

General comments

Toluene was dried by storing with potassium and distilled under argon. Acetic anhydride and methanol were distilled under argon. *rac*-*N*,*N*-Dimethyl[2-(diphenylphosphino)ferrocenyl]methylamine (**1**) was synthesized by a literature procedure.[14] All other chemicals were used as received from commercial suppliers.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58; ^{31}P, 161.90 MHz) at 298 K. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). High resolution mass spectra were measured on a VG 7070E spectrometer at 70 eV using perfluorokerosene as an internal mass scale calibrant.

Syntheses

***rac*-[2-(Diphenylphosphino)ferrocenyl]methyl acetate (2).** Amine **1** (0.427 g, 1.0 mmol) and freshly distilled acetic anhydride (1 ml) were charged into a small reaction flask, the flask was flushed with argon and stoppered. The mixture was heated to 100 °C for 2 h with stirring and then allowed to stand at −18 °C overnight. The solidified mixture was transferred to a glass frit, thoroughly washed with methanol and dried in air to yield **2** as a bright yellow crystalline solid (0.334 g, 76%).

^{1}H NMR ($CDCl_3$): δ 1.60 (s, 3 H, Me), 3.77 (m, 1 H, C_5H_3), 4.07 (s, 5 H, C_5H_5), 4.32 (t, $J \approx 2.5$ Hz, 1 H, C_5H_3), 4.53 (dt, $J \approx 2.6$, 1.5 Hz, 1 H, C_5H_3), 4.97 (d, $^2J_{HH} = 12.0$ Hz, 1 H, CH_2), 5.16 (dd, $^2J_{HH} = 12.0$, $^4J_{PH} = 2.4$ Hz, 1 H, CH_2), 7.14–7.56 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.39 (Me), 61.79 (d, $^3J_{PC} = 10$ Hz, CH_2), 69.64 (C_5H_5), 70.02 (CH of C_5H_3), 72.30 (d, $J_{PC} = 4$ Hz, CH of C_5H_3), 73.04 (d, $J_{PC} = 4$ Hz, CH of C_5H_3), 77.70 (d, $^1J_{PC} = 9$ Hz, C–P of C_5H_3), 86.28 (d, $^2J_{PC} = 25$ Hz, C–CH_2 of C_5H_3), 127.82 (CH_p of PPh_2), 127.89 (d, $^3J_{PC} = 6$ Hz, CH_m of PPh_2), 128.18 (d, $^3J_{PC} = 8$ Hz, CH_m of PPh_2), 129.17 (CH_p of PPh_2), 132.49 (d, $^2J_{PC} = 18$ Hz, CH_o of PPh_2), 134.92 (d, $^2J_{PC} = 21$ Hz, CH_o of PPh_2), 136.99 (d, $^1J_{PC} = 8$ Hz, C_{ipso} of PPh_2), 139.65 (d, $^1J_{PC} = 10$ Hz, C_{ipso} of PPh_2), 170.62 (MeCO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.7 (s). HR MS: calcd. for $C_{25}H_{23}FeO_2P$: 442.0785, found 442.0816.

***rac*-2-(Diphenylphosphino)ferrocenylmethanol (3).** A suspension of acetate **2** (0.320 g, 0.72 mmol) in a mixture of methanol (24 ml) and 3 M aqueous potassium hydroxide (12 ml, 36 mmol) was refluxed under argon for 6 h. The reaction mixture was diluted with water (50 ml) and cooled in an ice bath. The separated solid was filtered off, washed well with water, dried in air, and purified by chromatography on silica gel using dichloromethane–methanol (10 : 1, v/v) as the eluent to afford **3** as a yellow-orange solid (0.266 g, 92%).

^{1}H NMR ($CDCl_3$): δ 1.48 (br s, 1 H, OH), 3.75 (m, 1 H, C_5H_3), 4.09 (s, 5 H, C_5H_5), 4.30 (t, $J \approx 2.5$ Hz, 1 H, C_5H_3), 4.42 (d, $^2J_{HH} = 12.4$ Hz, 1 H, CH_2), 4.51–4.57 (m, 2 H, CH_2 and C_5H_3), 7.16–7.58 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 59.88 (d, $^3J_{PC} = 9$ Hz, CH_2), 69.44 (C_5H_5), 69.57 (CH of C_5H_3), 71.52 (d, $J_{PC} = 4$ Hz, CH of C_5H_3), 71.64 (d, $J_{PC} = 4$ Hz, CH of C_5H_3), 76.03 (d, $^1J_{PC} = 7$ Hz, C–P of C_5H_3), 92.59 (d, $^2J_{PC} = 23$ Hz, C–CH_2 of C_5H_3), 128.20 (d, $^3J_{PC} = 7$ Hz, CH_m of PPh_2), 128.22 (CH_p of PPh_2), 128.35 (d, $^3J_{PC} = 6$ Hz, CH_m of PPh_2), 129.19 (CH_p of PPh_2), 132.33 (d, $^2J_{PC} = 18$ Hz, CH_o of PPh_2), 134.75 (d, $^2J_{PC} = 21$ Hz, CH_o of PPh_2), 136.81 (d, $^1J_{PC} = 9$ Hz, C_{ipso} of PPh_2), 139.60 (d, $^1J_{PC} = 11$ Hz, C_{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.6 (s). HR MS: calcd. for $C_{23}H_{21}FeOP$: 400.0679, found 400.0689.

***rac*-2-(Diphenylphosphinoyl)ferrocenylmethanol (4).** In air, a solution of **3** (0.080 g, 0.20 mmol) in acetone (10 ml) was cooled in an ice bath and treated with 30% aqueous hydrogen peroxide (5 drops). A yellow precipitate separated from the mixture. After stirring for 1 h at 0 °C, the mixture was diluted with water (10 ml), the precipitate was filtered off, and dried under vacuum. The crude product was dissolved in a little ethyl acetate and crystallized by hexane diffusion to give **4** as a fine yellow-orange microcrystalline solid (0.062 g, 75%).

^{1}H NMR ($CDCl_3$): δ 3.93 (m, 1 H, C_5H_3), 4.16 (d, $^2J_{HH} = 13.1$ Hz, 1 H, CH_2), 4.26 (s, 5 H, C_5H_5), 4.33 (d, $^2J_{HH} = 13.2$ Hz, 1 H, CH_2), 4.34 (t, $J \approx 2.4$ Hz, C_5H_3), 4.54 (m, 1 H, C_5H_3), 5.46 (very br s, 1 H, OH), 7.36–7.86 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 58.63 (CH_2), *ca.* 69.57 (d, $^1J_{PC} \approx 115$ Hz, C–P of C_5H_3), 69.66 (d, $J_{PC} = 11$ Hz, CH of C_5H_3), 70.17 (C_5H_5), 73.03 (d, $J_{PC} = 15$ Hz, CH of C_5H_3), 74.09 (d, $J_{PC} = 10$ Hz, CH of C_5H_3), 95.48 (d, $^2J_{PC} = 11$ Hz, C–CH_2 of C_5H_3), 128.27, 128.44 (2 × d, $^3J_{PC} = 12$ Hz, CH_m of PPh_2), 131.39, 131.53 (2 × d, $^2J_{PC} = 10$ Hz, CH_o of PPh_2), 131.81, 131.97 (d, $^4J_{PC} = 3$ Hz, CH_p of PPh_2), 132.37 (d, $^1J_{PC} = 108$ Hz, C_{ipso} of PPh_2), 134.23 (d, $^1J_{PC} = 106$ Hz, C_{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 34.1 (s). HR MS: calcd. for $C_{23}H_{21}FeO_2P$: 416.0629, found 416.0673.

***rac*-2-(Diphenylthiophosphoryl)ferrocenylmethanol (5).** Alcohol **3** (0.040 g, 0.10 mmol) and sulfur (6.5 mg, 0.2 mmol) were dissolved in dry toluene (3 ml) under argon and the solution was heated to 100 °C for 1 h. Then, the solvent was removed under reduced pressure and the residue purified by column

Table 3 Crystallographic data, data collection and structure refinement for **2**–**5**

Compound	**2**	**3**	**4**	**5**
Formula	$C_{25}H_{23}FeO_2P$	$C_{23}H_{21}FeOP$	$C_{23}H_{21}FeO_2P$	$C_{23}H_{21}FeOPS$
M/g mol^{-1}	442.25	400.22	416.22	432.28
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)	$P2_1/C$ (No. 14)
a/Å	10.2946(2)	7.8638(1)	7.8574(2)	8.6792(1)
b/Å	10.9414(2)	10.1888(2)	10.1678(2)	17.6265(3)
c/Å	10.9792(2)	12.0270(2)	12.1411(3)	13.2883(2)
α/°	87.570(1)	89.292(1)	90.566(2)	90
β/°	66.034(1)	81.086(1)	100.600(2)	105.749(1)
γ/°	71.624(1)	80.009(1)	97.935(2)	90
U/Å^3	1067.18(3)	937.46(3)	943.68(4)	1956.58(5)
Z	2	2	2	4
μ(Mo Kα)/mm^{-1}	0.800	0.898	0.899	0.969
Unique reflect.	4849	4272	4334	4488
Obsd reflect.[a]	4399	3841	3867	4135
R (obsd reflect)[b] /%	2.90	3.07	3.14	2.94
R (all data)[b] /%	3.30	3.57	3.73	3.28
wR(all data)[b] /%	7.60	8.34	8.19	7.12
R_{int}[c] /%	3.0	2.7	3.0	3.3

[a] Diffractions with $I_o > 2\sigma(I_o)$. [b] $R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR(F^2) = \{\Sigma[w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. [c] $R_{int} = \Sigma|F_o^2-F_{o,mean}^2|/\Sigma F_o^2$.

chromatography (silica gel, dichloromethane–methanol 10 : 1, v/v) to give **5** as an orange solid in quantitative yield (0.043 g).

^{1}H NMR ($CDCl_3$): δ 3.37 (br s, 1 H, OH), 3.78 (m, 1 H, C_5H_3), 4.29–4.33 (m, 1 H, C_5H_3), 4.31 (s, 5 H, C_5H_5), 4.31 (d, $^2J_{HH}$ = 12.8 Hz, 1 H, CH_2), 4.58 (m, 1 H, C_5H_3), 4.68 (d, $^2J_{HH}$ = 12.8 Hz, 1 H, CH_2), 7.34–7.89 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 58.57 (CH_2), 68.96 (d, J_{PC} = 10 Hz, CH of C_5H_3), 70.46 (C_5H_5), 73.87 (d, $^1J_{PC}$ = 95 Hz, C–P of C_5H_3), 74.50 (d, J_{PC} = 12 Hz, CH of C_5H_3), 74.86 (d, J_{PC} = 10 Hz, CH of C_5H_3), 93.48 (d, $^2J_{PC}$ = 12 Hz, C–CH_2 of C_5H_3), 128.12 (d, $^3J_{PC}$ = 13 Hz, CH_m of PPh_2), 128.42 (d, $^3J_{PC}$ = 12 Hz, CH_m of PPh_2), 131.38 (d, $^4J_{PC}$ = 3 Hz, CH_p of PPh_2), 131.57 (d, $^4J_{PC}$ = 4 Hz, CH_p of PPh_2), 131.64, 132.12 (2 × d, $^2J_{PC}$ = 11 Hz, CH_o of PPh_2); 132.72 (d, $^1J_{PC}$ = 87 Hz, C_{ipso} of PPh_2), 134.96 (d, $^1J_{PC}$ = 88 Hz, C_{ipso} of PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ +42.3 (s). HR MS: calcd. for $C_{23}H_{21}FeOPS$: 432.0400, found 432.0386.

X-Ray crystallography

X-ray quality crystals were obtained by recrystallization from methanol (**3**: orange prism, 0.20 × 0.30 × 0.35 mm^3), and ethyl acetate–hexane (**4**: orange prism 0.20 × 0.30 × 0.60 mm^3; **5**: orange prism, 0.25 × 0.43 × 0.45 mm^3), or selected directly from the reaction batch (**2**: orange plate, 0.15 × 0.40 × 0.50 mm^3). Diffraction data (Table 3) for all compounds were collected on a Nonius Kappa CCD diffractometer equipped with Cryostream Cooler (Oxford Crysoystems) at 150 K using graphite monochromated MoKα radiation (λ = 0.71073 Å) and analyzed with the HKL program package.[15] Absorption was neglected.

3: 327 frames were collected (2.0° ω rotation, 40 s counting time), 18 524 integrated diffractions. The cell parameters were determined by least-squares fitting from 10 607 diffractions with 1.0 ⩽ θ ⩽ 27.5°. **4**: 287 frames were collected (2.0° ω rotation, 40 s exposure), 16 395 integrated diffractions. The cell parameters were determined from 11 606 diffractions with 1.0 ⩽ θ ⩽ 27.5°. **5**: 262 frames were collected (2.0° ω rotation, 70 s exposure), 30 351 integrated diffractions. The cell parameters were determined from 17 834 diffractions with 1.0 ⩽ θ ⩽ 27.5°. **2**: 265 frames collected (2.0° ω rotation, 100 s exposure), 17 086 integrated diffractions. The cell parameters were determined from 9409 diffractions with 1.0 ⩽ θ ⩽ 27.5°.

The structures were solved by direct methods (SIR92[16]) and refined by weighted full-matrix least-squares on F^2 (SHELXL97[17]). Final geometric calculations were carried out with a recent version of the Platon program.[18] All non-hydrogen atoms were refined with anisotropic thermal motion parameters. With the exception of the hydroxy hydrogens, the hydrogen atoms were included in calculated positions [C–H bond lengths: 0.93 (aromatic), 0.97 (methylene) and 0.96 (methyl) Å] and assigned U_{iso}(H) = 1.2 U_{eq}(C) (aromatic and methylene) or 1.5 U_{eq}(C) (methyl). Hydroxyl hydrogen atoms in **2**, **4**, and **5** were clearly identified on the electron density maps and isotropically refined. The disordered hydroxylmethyl group in **3** was modelled considering two positions for the oxygen atom with 0.50 occupancies but only one position for the C11 atom as revealed by difference electron density maps. After these non-hydrogen atoms had been refined with anisotropic thermal motion parameters, the two respective hydroxyl hydrogen atoms H91 and H92 could be located on the difference electron density map but they were fixed in the positions identified and assigned U_{iso}(H) = 1.2 U_{eq}(O).

CCDC reference numbers 185007–185010. See http://www.rsc.org/suppdata/nj/b2/b204655p/ for crystallographic data in CIF or other electronic format.

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