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MOLECULAR STRUCTURES OF 1,1′-BIS(DIPHENYLPHOSPHINO)FERROCENE OXIDE AND SULPHIDE AND THEIR THERMAL PROPERTIES

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Abstract—The crystal and molecular structure of anhydrous 1,1′-bis(diphenylphosphino)ferrocene sulphide, $Fe[C_5H_4P(S)Ph_2]_2$ ($dppfS_2$), is reported and compared with the hydrated oxide analogue, $Fe[C_5H_4P(O)Ph_2]_2 \cdot 2H_2O$ ($dppfO_2 \cdot 2H_2O$). It consists of two phosphoryl cyclopentadienyl rings [P—S = 1.938(2) Å] sandwiching an Fe^{II} centre. With four molecules per cell, the molecule is crystallographically required to sit on an inversion centre and hence the two rings are staggered. The thermal properties of $[Fe(C_5H_4PPh_2)_2]$ (dppf), $dppfO_2 \cdot 2H_2O$ and $dppfS_2$ were studied together with $Fe(Cp)_2$ and $Ph_3PO \cdot H_2O$ by TGA and DSC. The thermal stability decreases in the order $dppfO_2 > dppf > dppfS_2$. The hydrogen-bonded hydrate in $dppfO_2 \cdot 2H_2O$ is removed upon heating to 110–160°C.

The chemistry of 1,1′-bis(diphenylphosphino)ferrocene (dppf) has recently been reviewed.[1] This difunctional phosphine has several structural characteristics which distinguish it from other common alkyl-chained diphosphines. The torsional flexibility of the phosphinated cyclopentadienyl (C_5) rings, for example, allows it to display a variety of coordination modes. Like other phosphines, dppf can be oxidized to its oxide $Fe[C_5H_4P(X)Ph_2]_2$ (X = O) ($dppfO_2$)† or sulphide ($dppfS_2$) (X = S). This oxidation usually renders the system ineffective as an organometallic ligand, but transforms it to a flexible oxygen and sulphur difunctional ligand. The ligand chemistry of $dppfO_2$ and $dppfS_2$ is unknown compared to dppf. In this paper, we wish to report the molecular structure and thermal properties of $dppfS_2$ and compare them with those of $dppfO_2$ and dppf. Understanding of these structural and physical properties is a prerequisite for the development of the structural chemistry of their complexes. The thermochemistry of P^{III} compounds has been reviewed recently,[2] but that of phosphine chalcogenides is not well understood. Phosphine sulphides have attracted some

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†$DppfO_2$ has been named 1,1′-bis(diphenylphosphine oxide)ferrocene or 1,1′-bis(oxodiphenylphosphoranyl)ferrocene in the literature. In this paper, we prefer its generic name 1,1′-bis(diphenylphosphino)ferrocene (di)oxide. The sulphide is named accordingly.

attention in recent years as ligands,[3] extractants,[4] photographic sensitizers,[5] and in the manufacture of precious metals and environmental protection. The structure of dppf was reported by Casellato *et al.* in 1988[6] and that of dppfO_2 recently by Pilloni *et al.*[7] and Postel *et al.*,[8] while this manuscript was being prepared. Two different sets of dppfO_2 data on two different crystals were independently refined. There are at least eight reports on the crystal structures of Ph_3PO and different crystal modifications have been found.[9] It was considered to be of interest to see if dppfO_2 could show the same properties.

EXPERIMENTAL

All reactions were performed under pure dry argon by using standard Schlenk techniques. The instruments used were described in our previous reports.[10] All TGA and DSC experiments were recorded under a dynamic flow of nitrogen (75 cm^3 min^{-1}) at a heating rate of 20°C min^{-1}.

Preparation of dppfS_2

A mixture of $Fe_3(\mu_3\text{-}S)(CO)_9$ (0.237 g, 0.49 mmol), dppf (0.320 g, 0.58 mmol) and $Me_3NO \cdot 2H_2O$ (0.054 g, 0.49 mmol) was refluxed in THF (40 cm^3) under argon for 7 h to give a dark red solution. Evaporation of the solvent gave a residue which was extracted by a minimum quantity of CH_2Cl_2 and chromatographed on silica TLC plates. Elution with CH_2Cl_2–hexane (1 : 1) gave $Fe_3(\mu_3\text{-}S)_2(CO)_7(\mu\text{-dppf})$ (0.10 g, 21%)[11] followed by an orange band. Recrystallization of the latter from CH_2Cl_2–hexane mixture gave an analytically pure sample of $Fe[C_5H_4P(S)Ph_2]_2$ (0.061 g, 17%). Found: C, 66.0; H, 4.7; P, 10.2. $C_{34}H_{28}FeP_2S_2$ requires: C, 66.0; H, 4.7; P, 10.2%. δ_H ($CDCl_3$): 7.63–7.59 (m, 10H, Ph), 7.47–7.36 (m, 10H, Ph), 4.64 (dt, 4H, CpH_β), 4.29 (dt, 4H, CpH_α); δ_P ($CDCl_3$): 40.8(s).

Preparation of dppfO_2 was reported by Bishop *et al.*,[12] Riess *et al.*[13] and Hor *et al.*[14] The last procedure was preferred for its convenience. Recrystallization of the sample from hot EtOH gave its dihydrate form.

X-ray crystallography

Orange–red crystals of dppfS_2 were grown at room temperature by slow diffusion of hexane into a concentrated sample solution in CH_2Cl_2. The crystal was mounted in a lithium glass capillary for preliminary characterization and intensity data collection. Cell dimensions were obtained from 25 reflections with 2θ angles in the range of 14.60–33.37°. The structure was solved by a heavy-atom method and refined by a full matrix least-squares method. All hydrogen atoms were fixed with isotropic temperature factor coefficients in the refinement. The iron atom is located on an inversion centre. Only one-half of the molecule is crystallographically independent. The crystallographic data and refinement details are listed in Table 1. Some pertinent bond lengths and angles are listed in Table 2. Some pertinent structural data of dppf, dppf$O_2 \cdot 2H_2O$ and dppfS_2 are listed for comparison in Table 3.

Table 1. Crystallographic data and refinement details for $Fe[(C_5H_4P(S)Ph_2]_2$

Empirical formula	$C_{34}H_{28}FeP_2S_2$
Formula weight	618.51
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	24.378(4)
b (Å)	11.008(1)
c (Å)	12.045(1)
β (°)	113.19(1)
U (Å^3)	2971.1(7)
Z	4
$F(000)$	1279.84
D_c (g cm^{-3})	1.383
λ (Mo-K_α) (Å)	0.70930
μ (mm^{-1})	0.77
Crystal size (mm)	0.41 × 0.25 × 0.41
Diffractometer	Nonius CAD4
Scan mode	θ–2θ
Absorption corrections	Yes
Transmission factors	0.933–0.999
Collection range	$-26 \leqslant h \leqslant 24$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 12$
$2\theta_{max}$ (°)	44.8
No. of unique data measured	1942
No. of obs. data, n	1528 $[|F_0| > 2.0\sigma(|F_0|)]$
Total atoms	34
No. of parameters, p	178
Weights	counting statistics
Weight modifier	0.000100
R_F[a]	0.034
R_w[b]	0.040
GoF[c]	1.93
Max. shift, σ	0.001
Residual extrema in final difference map (e Å^{-3})	+0.180 to −0.220

[a] $R = \Sigma \| F_0| - |F_c\| / \Sigma |F_0|$.
[b] $R_w = [\Sigma w^2(|F_0| - |F_c|)^2 / \Sigma w^2 |F_0|^2]^{1/2}$.
[c] $GoF = [\Sigma w(|F_0| - |F_c|^2)/(n-p)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for $Fe[(C_5H_4P(S)Ph_2]_2$

Fe—C(1)	2.031(3)	Fe—C(2)	2.035(3)
Fe—C(3)	2.043(4)	Fe—C(4)	2.046(4)
Fe—C(5)	2.039(3)	P—S	1.938(2)
P—C(1)	1.796(3)	P—C(6)	1.818(3)
P—C(12)	1.815(4)	C(1)—C(2)	1.417(5)
C(1)—C(5)	1.420(5)	C(2)—C(3)	1.410(6)
C(3)—C(4)	1.398(9)	C(4)—C(5)	1.395(7)
C(1)—Fe—C(1a)	179.9	C(1)—C(2)—C(3)	107.9(4)
C(2)—C(3)—C(4)	108.2(4)	C(3)—C(4)—C(5)	108.6(4)
C(1)—C(5)—C(4)	108.3(4)	C(2)—C(1)—C(5)	107.1(3)
S—P—C(1)	113.4(1)	S—P—C(6)	112.2(1)
S—P—C(12)	114.3(2)	C(1)—P—C(6)	105.3(2)
C(1)—P—C(12)	106.1(2)	C(6)—P—C(12)	104.8(2)

RESULTS AND DISCUSSION

Oxidation of dppf to $dppfO_2$ can be facilitated by H_2O_2 or Me_3NO but, in our hands, the use of H_2O_2 is straightforward and gives a better yield. Oxidation to $dppfS_2$ by elemental sulphur in refluxing 1-butanol has been reported.[12] We have also obtained it as a by-product in the thermal substitution of $Fe_3(\mu_3\text{-}S)_2(CO)_9$ with dppf assisted by Me_3NO in THF,[11] and oxidative sulphurization of $Pt(\eta^2\text{-dppf})_2$ with sulphur at room temperature.[15] Unlike $dppfO_2$, which is almost inevitably isolated as a dihydrate, $dppfS_2$ is easily prepared in its anhydrous form. We have separately obtained two crystallographic data sets on $dppfO_2 \cdot 2H_2O$. In both cases, each phosphoryl oxygen is hydrogen-bonded to a hydrate (Fig. 1). As the data do not differ significantly from those reported by Pilloni *et al.*[7] and Postel *et al.*,[8] only selected data are listed in Table 3 for comparative purposes. All the structural data on $dppfO_2$ refer to its dihydrate form except the one isolated by Pilloni *et al.*, which is anhydrous.

A single-crystal X-ray diffraction study of $dppfS_2$ revealed a sandwiched structure with both phosphine groups sulphurized (Fig. 2). The P—S length

Table 3. A comparison of the key crystallographic data of dppf, $dppfO_2$ and $dppfS_2$

Bond data	dppf	$dppfO_2$[a]	$dppfO_2$[b]	$dppfO_2$[c]	$dppfO_2$[d]	$dppfS_2$
P=X[e]	—	1.493(2)	1.495(1)	1.488(3)	1.488(3)	1.938(2)
$Fe—C_\alpha$[f]	2.033	2.047(3)	2.032(3)	2.029(3)	2.030(4)	2.031(3)
$Fe—C_{\beta/\beta'}$ (mean)[g]	2.030	2.042(4)	2.050(4)	2.043(4)	2.047(5)	2.037(3)
$Fe—C_{\gamma/\gamma'}$ (mean)[h]	2.054	2.057(5)	2.065(5)	2.047(5)	2.054(6)	2.045(4)
$Fe—Cp_{cent}$[i]	1.646	1.653	1.660(3)	1.651(3)	1.653(5)	1.650(2)
$P—C_\alpha$	1.819(5)	1.783(4)	1.780(3)	1.775(4)	1.778(4)	1.796(3)
$C_\alpha—C_{\beta/\beta'}$ (mean)	1.427	1.432	1.427(5)	1.431(6)	1.436(8)	1.419(5)
$C_{\beta/\beta'}—C_{\gamma/\gamma'}$ (mean)	1.417	1.413	1.411(6)	1.400(7)	1.410(8)	1.403(7)
$C_\gamma—C_{\gamma'}$	1.399	1.404	1.423(7)	1.40(1)	1.402(9)	1.398(9)
$X—P—C_{\alpha/Ph/Ph'}$ (mean)[j]	101.4	108.1(2)	112.5(2)	112.3(2)	112.6(2)	113.3(1)

[a] Data from Pilloni *et al.*,[7] triclinic, space group $P1$, $2\theta_{max}$ 56°, $R = 4.8\%$.

[b] Data from Postel *et al.*,[8] monoclinic, space group $P2_1/n$, $2\theta_{max}$ 49.9°, $R = 4.0\%$.

[c] This work (set 1), monoclinic, space group $P2_1/n$, $2\theta_{max}$ 49.8°, $R = 3.9\%$.

[d] This work (set 2), monoclinic, space group $P2/n$ (No. 14), $2\theta_{max}$ 48°, $R = 4.2\%$.

[e] X = O or S.

[f] C_α refers to the carbon of the C_5 ring which is bonded directly to phosphorus.

[g] C_β and $C_{\beta'}$ refer to the neighbouring carbons of C_α of the C_5 ring.

[h] C_γ and $C_{\gamma'}$ refer to the next-nearest neighbouring carbons of C_α of the C_5 ring.

[i] Cp_{cent} refers to the centroid of the C_5 ring.

[j] C_{Ph} and $C_{Ph'}$ refer to the phenyl carbons which are bonded to phosphorus.

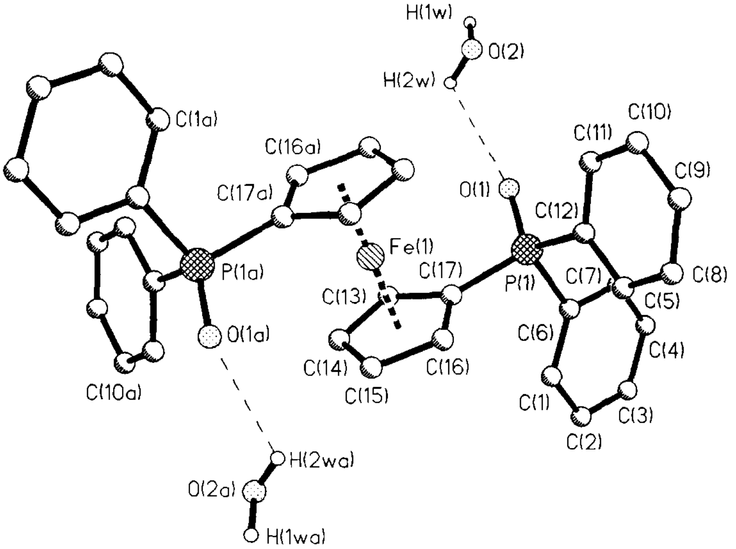

Fig. 1. An ORTEP plot of the molecular structure of $Fe[C_5H_4P(O)Ph_2]_2 \cdot 2H_2O$ ($Fe[C_5H_4P(O)Ph_2]_2$ = $dppfO_2$).

[1.938(2) Å] is indicative of π-bond character, which usually ranges between 1.926 and 1.966 Å[16] (compared to 2.10–2.12 Å for P—S σ-bonds[17]). It is marginally stronger than that in Ph_3PS (1.950 Å).[18] The P═O bond in $dppfO_2$ [1.491(2) Å (mean)*] agrees well with those reported for Ph_3PO (1.483–1.494 Å).[19]

Similar to dppf and $dppfO_2$, $dppfS_2$ is centrosymmetric with the C_5 rings in a staggered orientation. The phosphoryl groups are twisted 180° away from each other and are hence in an exact *anti* conformation. This arrangement, which is sterically favoured, is expected when one or both phosphine (or phosphoryl) groups are uncoordinated or when the end groups on these sites are not linked otherwise, i.e. open bridging.[20] However, there are sufficient exceptions in the literature which show that the prediction of the twist angle is by no means straightforward. The unidentate complex $Mo(CO)_5(\eta^1\text{-dppf})$, for example, shows a twist angle (132.5°) which is significantly less than 180°, even though one phosphine site is dangling and appears to be freely rotating.[21] A similarly small twist is also found in $[M_2(CO)_9]_2(\mu\text{-dppf})$ (M = Mn, Re),[14] although the two end groups, namely $[M_2(CO)_9]$, are bulky and unconnected.

The C_5 rings of $dppfO_2$ and $dppfS_2$ are parallel. Despite this, these rings show a slight but clear tendency to tilt inward such that the phosphinated carbon (C_α or C_{ipso}) is closer to iron [2.035(3) Å (mean) in $dppfO_2$ and 2.031(3) Å in $dppfS_2$] compared to C_γ [2.056(5) Å (mean) and 2.045(4) Å, respectively] and C_β [2.046(4) Å (mean) and 2.037(3) Å, respectively]. Oxidation of dppf to $dppfO_2$ or $dppfS_2$ seemingly weakens the C_5—Fe bonds [Fe···C_5(centroid): 1.646 Å in dppf, 1.654(4) Å (mean) in $dppfO_2$ and 1.650(2) Å for $dppfS_2$]. On the other hand, the P—C_5 link strengthens in the order dppf [1.819(5) Å] < $dppfS_2$ [1.796(3) Å] < $dppfO_2$ [1.779(4) Å (mean)]. The substitutionally induced weakening effect on the carbon–carbon bonds neighbouring the C_α—P bond is observed in all the molecules under examination. As expected, replacement of oxygen by sulphur on phosphorus increases the X—P—C (X = O or S) angles from 111.4(2)° to 113.3(1)°.

The C_5 planes in $dppfS_2$ are planar [max. deviation $\leqslant \pm 0.002(6)$ Å from least-squares plane]. The phosphorus atom is slightly displaced [0.037(7) Å] from the C_5 plane to which it is attached and is away from the iron centre. This direction and degree of displacement are commonly found in unrestrained systems like free dppf and unidentate complexes. This degree of displacement is insignificant compared to some other systems such as $[M_2(CO)_9]_2(\mu\text{-dppf})$ (M = Mn, Re) (0.2–0.3 Å).

The ready hydration of $dppfO_2$ to give $dppfO_2 \cdot 2H_2O$ is in sharp contrast to the anhydrous nature of $dppfS_2$. This prompted us to investigate the possibility of thermal dehydration of the former, and to quantify this process in terms of dehydration enthalpy. It also gives us an opportunity to compare the thermal stability of these two chalcogenides. Both complexes, together with their

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*The mean value refers to the average value obtained from the four structures, as indicated in Table 3.

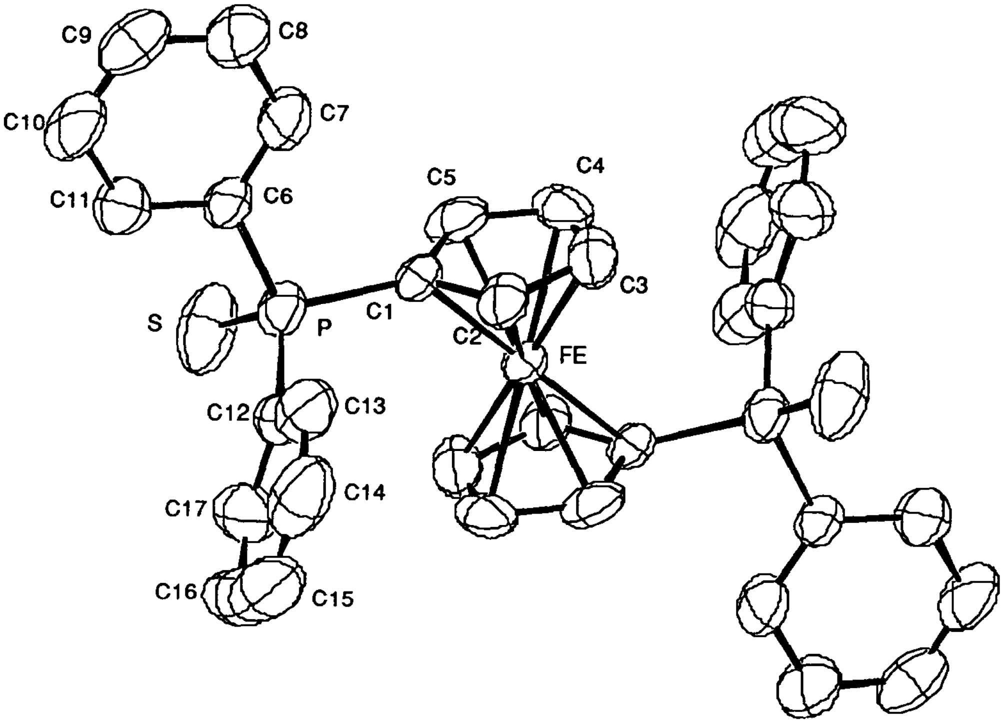

Fig. 2. An ORTEP plot of the molecular structure of $Fe[C_5H_4P(S)Ph_2]_2$ ($dppfS_2$).

parent compounds ferrocene and dppf, were subjected to degradation studies by TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry). We have used similar techniques in the study of some metal complexes.[22] An overlay of TG and DTG profiles of $dppfO_2$, $dppfS_2$ and their parent compounds dppf and $Fe(Cp)_2$ is represented in Fig. 3, and the DSC plots in Fig. 4. With weak van der Waal forces, ferrocene sublimes much easier than it decomposes. A melting point of 178°C ($\Delta H = 20.0$ kJ mol^{-1}) is registered by DSC. Dppf melts cleanly at 186°C ($\Delta H = 44.3$ kJ mol^{-1}). Sulphurization of dppf introduces electrostatic intermolecular interaction and hence raises the m.p. to 247°C ($\Delta H = 38.6$ kJ mol^{-1}). TGA, however, also shows that this sulphurization lowers the thermal resistance of dppf. The similarity in their TGA and DSC profiles suggests that their decomposition pathways are related. $DppfO_2$, however, is thermally the most stable species and undergoes no

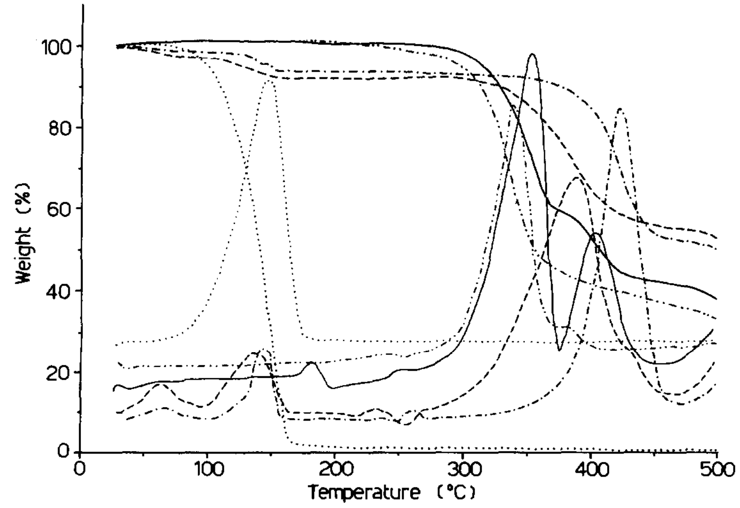

Fig. 3. TGA and DTG plots of ferrocene (· · ·), dppf (———), vacuum untreated (– – –) and treated (– · – · –) $dppfO_2$, and $dppfS_2$ (– · · – · · –).

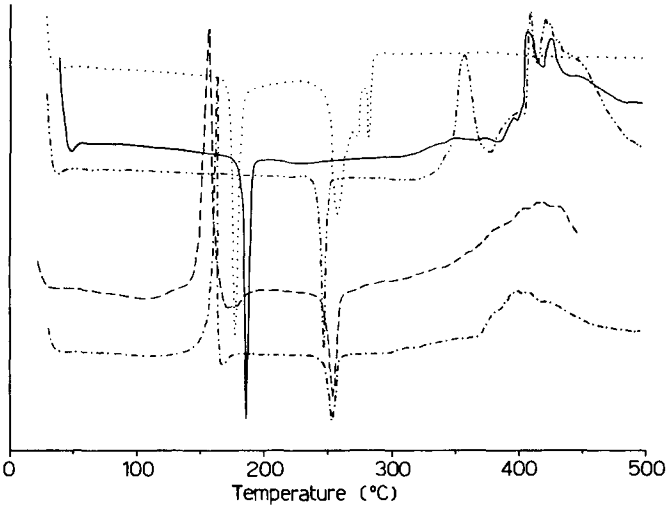

Fig. 4. DSC profiles of ferrocene (· · ·), dppf (———), vacuum untreated (– – –) and treated (– · – · –) dppfO$_2$, and dppfS$_2$ (– · · – · · –).

significant decomposition below 300°C. That this thermally most robust species is found in a molecule with the shortest, and presumably strongest, P—C$_\alpha$(C$_5$) link as found crystallographically could suggest that P—C$_5$ cleavage is a key decompositional step. TGA of dppfO$_2 \cdot 2H_2O$ clearly suggests that, despite the precautions taken, this dihydrate is highly vulnerable to further water adsorption (*ca* 2.6%). This explains why it is difficult to obtain satisfactory microanalytical data of this complex. This surface water can be removed partially (reduced to *ca* 1.1%) under high vacuum (as indicated in Fig. 3 when comparing the TGA curves at temperature <100°C of the vacuum-treated and untreated samples) but cannot be eradicated completely without heating the sample to *ca* 100°C. The hydrogen-bonded hydrate is removed upon heating in the region of 110–160°C. Surprisingly, this dehydration is associated with an exothermic peak of $\Delta H = -137.9$ kJ mol^{-1} at 164°C (vacuum-dried sample). We tentatively attribute this anomaly to a complication by phase change upon dehydration. The dehydrated sample melts at 254°C ($\Delta H = 45.3$) before it decomposes at >300°C. For comparison we have also synthesized $Ph_3PO \cdot H_2O$ similarly. The TGA and DTG plots suggest a liberation of its hydrate (5.2% compared to 6.1% theoretically) at a very similar temperature range of 120–170°C (Fig. 5). However, in contrast to dppfO$_2$, Ph_3PO, upon dehydration, sublimes readily upon heating at tem-

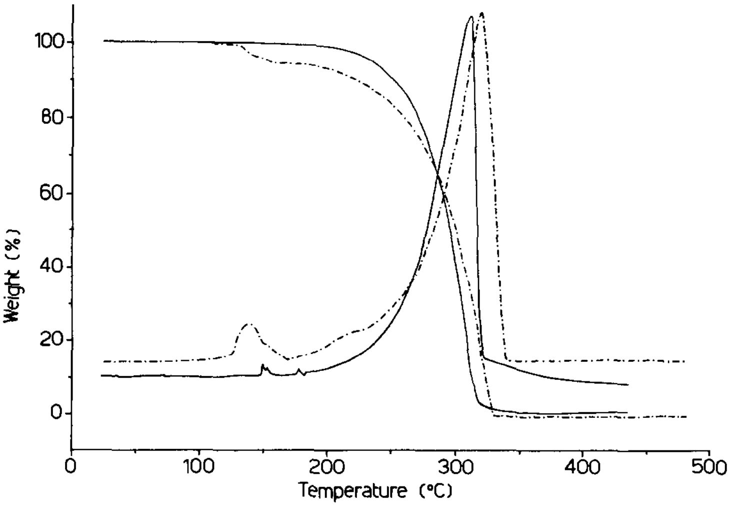

Fig. 5. TGA and DTG plots of the thermally untreated (– · – · –) and treated (———) samples of $Ph_3PO \cdot H_2O$.

peratures >180°C. This complex visually decomposes at 230°C. The DSC profile gives an m.p. of 135°C. Dehydration occurs immediately after melting, and noticeably, and in contrast to that found in dppfO_2, it is an endothermic process. When a sample of $Ph_3PO \cdot H_2O$ is dehydrated by heating to 170°C, cooled to room temperature and the sample re-examined by TGA, it shows a thermal profile which shows no weight loss before 170°C, beyond which it is virtually identical to that of the hydrated sample. This proves that (i) the weight loss before 170°C is indeed a dehydration step without other molecular decompositions; (ii) the dehydration is irreversible upon sample exposure to atmospheric moisture; and (iii) the sublimation (and subsequent degradation) of Ph_3PO is insensitive to its thermal history.

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