Synthesis of ferrocenyl-1,2-diketones and related compounds: crystal and molecular structures of 1,2-diferrocenylethanedione and 1-ferrocenyl-2-(4-biphenylyl)ethanedione

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Received 31 May 1996; revised 6 July 1996

Abstract

Ferrocenyl-1,2-diketones FcCOCOR, **3**, [Fc = $(C_5H_5)Fe(C_5H_4)$] can be prepared by oxidation of acylferrocenes FcCOCH$_2$R or, more efficiently, by oxidation of the isomeric ketones FcCH$_2$COR, **2**. The ketones **2** are in turn readily synthesized from the salt $(FcCH_2PPh_3)^+I^-$ via the acylated salts $[FcCH(COR)PPh_3]^+I^-$. The haloacylferrocenes FcCOCCl$_x$H$_{3-x}$ ($x = 1, 2, 3$, of which the $x = 2$ example is synthetically equivalent to a diketone) are synthesized by Friedel–Crafts acylation of ferrocene using CCl$_x$H$_{3-x}$COCl/AlCl$_3$, but the reaction proceeds via two parallel pathways, one giving the normal acyl derivatives FcCOCCl$_x$H$_{3-x}$ and the other giving the reduced products FcCOCCl$_{x-1}$H$_{4-x}$. Two diketones FcCOCOFc **3b** and FcCOCOC$_6$H$_4$Ph **3c** have been structurally characterised by single-crystal X-ray diffraction.

1. Introduction

Ferrocenyl ketones are potentially valuable intermediates for the synthesis of ferrocenyl-substituted heterocycles. We have recently [1] reported routes to a range of ferrocenyl-1,3-diketones, and we now consider ferrocenyl-1,2-diketones. Oxidation of monoketones of type RCOCH$_2$R' is the simplest route to 1,2-diketones RCOCOR', but the sensitivity of the ferrocene nucleus places restrictions upon the choice of oxidant. Thus the use of selenium dioxide in a wide range of solvents gave extensive decomposition [2]; similarly, potassium permanganate effects oxidative decomposition of the ferrocene fragment. Manganese(IV) oxide is the reagent of choice, but when R and R' are different, there are two isomeric monoketones whose oxidation can yield RCOCOR'. Here we discuss approaches to some ferrocenyl-1,2-diketones FcCOCOR [Fc = $(C_5H_5)Fe(C_5H_4)$] and to dichloroacylferrocenes, which are synthetically equivalent to ferrocenyl-1,2-diketones, and we report the crystal and molecular structures of two examples of ferrocenyl-1,2-diketones.

2. Results and discussion

2.1. Oxidation of acylferrocenes

Oxidation of phenylacetylferrocene, FcCOCH$_2$Ph, with manganese dioxide yields 1-ferrocenyl-2-phenylethanedione, FcCOCOPh: however, regardless of the grade or activity of the MnO$_2$ employed [3], the oxidation is slow and is incomplete even after 24 h reflux in methylcyclohexane. Since FcCOCH$_2$Ph and FcCO-COPh prove to have very similar R_f values, separation of these two components is difficult to achieve: nonetheless, by use of FcCOCOPh only slightly contaminated with monoketone, characterisation was effected by conversion to 2-ferrocenyl-3-phenylquinoxaline using a melt-phase reaction with benzene-1,2-diamine and subsequent chromatographic separation of the quinoxaline from traces of FcCOCH$_2$Ph. The quinoxaline was itself fully characterised by elemental analysis, ^{1}H and ^{13}C NMR, and by single-crystal X-ray diffraction [4]. Similar oxidation of 1,1'-bis(phenylacetyl)ferrocene, Fe(C$_5$H$_4$COCH$_2$Ph)$_2$, gave ferrocene-1,1'-diylbis(phenylethanedione), Fe(C$_5$H$_4$COCOPh)$_2$; however, since acetylferrocene itself proved to be entirely impervious to oxidation by MnO$_2$ during 72 h
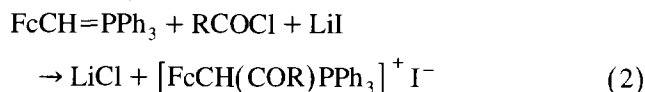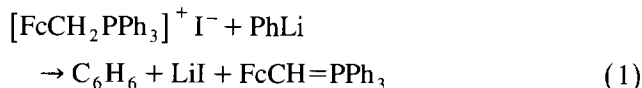
reflux in methylcyclohexane, and more vigorous oxidants caused extensive decomposition of both acetylferrocene and phenylacetylferrocene, we therefore turned to a more reactive class of substrates.

1a R = Ph
1b R = Fc
1c R = C₆H₄-Ph

I⁻

2a R = Ph
2b R = Fc
2c R = C₆H₄-Ph

3a R = Ph
3b R = Fc
3c R = C₆H₄-Ph
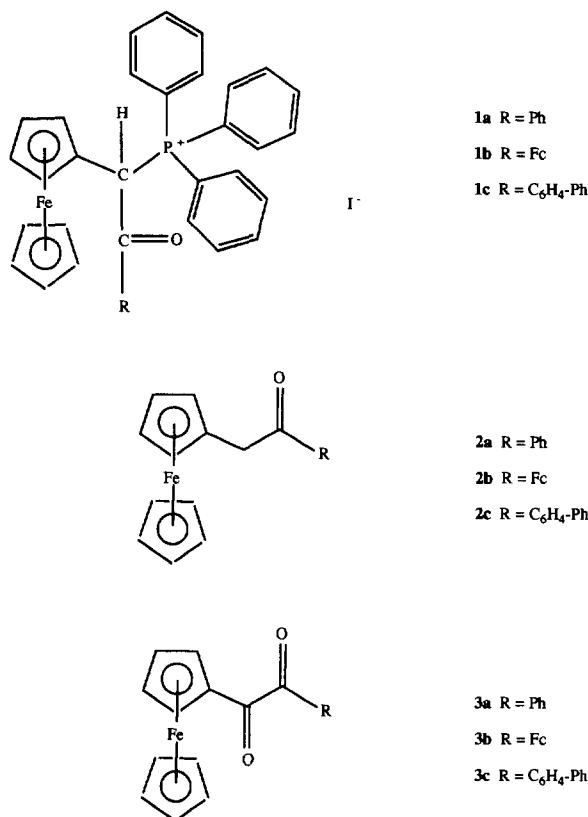
2.2. Oxidation of ferrocenylmethyl ketones

Isomeric with phenylacetylferrocene is phenacylferrocene, $FcCH_2COPh$ **2a**. We have prepared several analogues **2**, exploiting a procedure first explored by Pauson and Watts [5]. Deprotonation of (ferrocenylmethyl)triphenylphosphonium iodide, $[FcCH_2PPh_3]^+I^-$, using phenyl–lithium, followed by reaction with an acyl chloride gives the phosphonium salts **1** in excellent yield [Eqs. (1) and (2)].

$$[FcCH_2PPh_3]^+ I^- + PhLi$$

$$\rightarrow C_6H_6 + LiI + FcCH=PPh_3 \qquad (1)$$

$$FcCH=PPh_3 + RCOCl + LiI$$

$$\rightarrow LiCl + [FcCH(COR)PPh_3]^+ I^- \qquad (2)$$

These red crystalline salts were readily characterised by ^1H and ^{13}C NMR, by elemental analysis (for **1a** and **1c**) and, for **1a**, by single-crystal X-ray diffraction [6]; satisfactory microanalytical data could not be obtained for **1b**, despite the fact that it was successfully con-
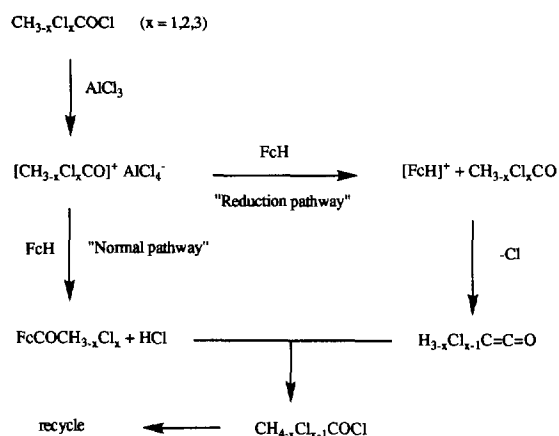
verted to **3b**. The NMR characterisation is simplified by the fact that the stereogenic α-carbon atom in **1** renders magnetically inequivalent all five carbon atoms (and all four hydrogens) in the substituted cyclopentadienyl ring. The elemental analysis and the X-ray study [6] show unambiguously that the salts **1** are iodides, with no chloride substitution whatever. Simple lattice energy considerations rationalise the product distribution described by Eq. (2).

Reduction of the cations in the salts **1**, using zinc dust in refluxing dichloromethane/acetic acid, yields the neutral monoketones **2**. These prove, in general, to be slightly air-sensitive, and indeed **2a** and **2b** proved too labile for satisfactory microanalytical data to be obtained; all however are readily oxidised to the diketones **3** by use of MnO_2. This oxidation is very rapid, and after 2 h in refluxing cyclohexane no **2** can be detected: the sole by-product identified by TLC is ferrocenecarboxaldehyde resulting from cleavage of the $C_\alpha-C_\beta$ bond. The extent of this side-reaction can be diminished by conducting the oxidation of **2** to **3** in dichloromethane at room temperature: in any event, the diketones **3** are readily separated from FcCHO by chromatography on silica. The crystal and molecular structure of **3a** has already been described [7] and those of **3b** and **3c** are reported below.

This route to ferrocenyl-1,2-diketones, involving oxidation of $FcCH_2COR$ rather than of the isomeric $FcCOCH_2R$, has several practical advantages. Firstly, the oxidation, as described above, is rapid and complete; secondly, the route requires acyl chlorides RCOCl rather than the generally less-accessible RCH_2COCl; thirdly, no Friedel–Crafts reactions are involved, allowing access to products containing electron-withdrawing R groups.

2.3. α-Haloacylferrocenes

Synthetically equivalent to the diketones FcCOCOR are the dihaloacyl species $FcCOCX_2R$, while the monohaloacyl species FcCOCHXR are also potentially valuable for the synthesis of heterocycles. When subjected to room temperature Friedel–Crafts acylation using $CHCl_2COCl/AlCl_3$ in CH_2Cl_2, ferrocene yielded two acylated products: the expected $FcCOCHCl_2$ (2%) was accompanied by $FcCOCH_2Cl$ (16%), containing one chlorine atom fewer than expected. A similar reduction has been noted, but not interpreted, by Schlögl and Egger [8]. Neither ^1H nor ^{13}C NMR showed any detectable $CH_2ClCOCl$ contaminant in the $CHCl_2COCl$ employed, so that the reduction of $CHCl_2$– groups to CH_2Cl– groups must have occurred during the reaction. A change of solvent to chlorobenzene did not affect this process, except to give, additionally, traces of the double-reduction product acetylferrocene; this effectively

CH$_{3-x}$Cl$_x$COCl   (x = 1,2,3)

$\downarrow$ AlCl$_3$

[CH$_{3-x}$Cl$_x$CO]$^+$ AlCl$_4^-$ $\xrightarrow{\text{FcH}}$ [FcH]$^+$ + CH$_{3-x}$Cl$_x$CO

"Reduction pathway"

FcH $\downarrow$ "Normal pathway" $\downarrow$ -Cl

FcCOCH$_{3-x}$Cl$_x$ + HCl ———————— H$_{3-x}$Cl$_{x-1}$C=C=O

recycle $\longleftarrow$ CH$_{4-x}$Cl$_{x-1}$COCl

Scheme 1. Normal and reduction pathways for the reaction of ferrocene with CH$_{3-x}$Cl$_x$COCl/AlCl$_3$.

rules out direct solvent participation (e.g. by CH$_2$Cl$_2$) in the reduction reaction. In a similar manner, 2 h room temperature acylations in CH$_2$Cl$_2$ using CCl$_3$COCl gave FcCOCCl$_3$ (1%) and FcCOCHCl$_2$ (17%), while CH$_2$ClCOCl gave FcCOCH$_2$Cl (7%) and FcCOCH$_3$ (3%). Longer reaction times in CH$_2$Cl$_2$ using CHCl$_2$COCl gave increasing yields of FcCOCH$_3$.

The key to understanding these transformations lies in three observations: (i) the yields of the acylated products are rather low, irrespective of whether reduction has occurred or not; (ii) acylation is accompanied by the formation of the oxidised ferricinium cation, usually in high yield; and (iii) with extended reaction times, the double-reduction products can be identified. For the acylation of ferrocene by CH$_{3-x}$Cl$_x$COCl/AlCl$_3$ ($x = 1$, 2 or 3), we envisage two reaction pathways (Scheme 1). In the 'normal pathway' conventional electrophilic substitution occurs, to give FcCOCH$_{3-x}$Cl$_x$ and HCl: the 'reduction pathway' is initiated by an electron transfer from ferrocene to the acylium ion [Eq. (3)], promoted by the high electron affinity of [CH$_{3-x}$Cl$_x$CO]$^+$:

$$\text{FcH} + [\text{CH}_{3-x}\text{Cl}_x\text{CO}]^+ \rightarrow [\text{FcH}]^+ + [\text{CH}_{3-x}\text{Cl}_x\text{CO}]^{\cdot} \quad (3)$$
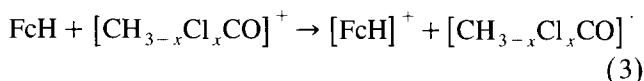
The newly-formed acyl radical can then lose a chlorine atom to form a ketene, which in turn reacts with a molecule of HCl generated in the normal pathway, so converting the initial CH$_{3-x}$Cl$_x$COCl to the reduced CH$_{4-x}$Cl$_{x-1}$COCl. This last in turn then has the choice of the same two reaction channels as CH$_{3-x}$Cl$_x$COCl, so giving rise to the double reduction of CHCl$_2$– groups to CH$_3$– groups. Finally, the chlorine atom lost in the ketene-formation step oxidises a further ferrocene molecule [Eq. (4)].

$$\text{FcH} + \text{Cl} \rightarrow [\text{FcH}]^+ + \text{Cl}^- \quad (4)$$
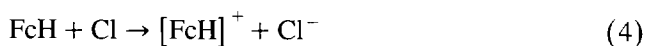
The overall stoichiometry demands oxidation of two

moles of ferrocene per mole of C–Cl transformed to C–H. Despite the modest yields, full analytical and NMR characterisation was achieved for each product of type FcCOCH$_{3-x}$Cl$_x$ ($x = 1$, 2 or 3).

An alternative route to 1,2-diketones has recently been introduced by Floyd et al. [9], in which oxidation of a –COCH$_2$– fragment to –COCO– is effected by a mixture of aqueous HBr and DMSO: this process is postulated to procede via liberation of molecular bromine, which converts the –COCH$_2$– fragment to –COCHBr–, followed by oxygen transfer from DMSO. Consistent with this suggestion, the action of HBr/DMSO on acetylferrocene led to extensive oxidative decomposition. Rather more surprising is the failure of DMSO to effect any oxygen transfer to preformed FcCOCH$_2$Cl: nonetheless, this acylferrocene reacted smoothly with benzene-1,2-diamine to yield 2-ferrocenylquinoxaline, characterised both by analysis and NMR, and by a single-crystal X-ray structure determination [10]. The attempted hydrolysis of FcCOCHCl$_2$ to FcCOCHO (or FcCOCH(OH)$_2$) was unsuccessful; with all reaction conditions employed, the dichloroacylferrocene was either recovered unchanged, or completely decomposed.

2.4. Crystal and molecular structures of compounds 3b and 3c

1,2-Diferrocenylethanedione (3b) and 1-ferrocenyl-2-(4-biphenylyl)ethanedione (3c) both crystallize in the acentric orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit (Figs. 1 and 2). Within the molecules in both structures the acyl fragments are almost coplanar with the substituted cyclopentadienyl rings in 3b and 3c and with the biphenylyl group, itself virtually planar, in 3c; this is typical of the conformations of simple acyl ferrocenes Fc–CO–R [11–13]. In 3b, one of the ferrocene fragments, C11–C20, adopts the eclipsed conformation, with mean torsional angle 1.4(10)°, usually observed in mono-substituted ferrocenes, while the other, C1–C10, adopts a staggered conformation, with mean torsional angle 27.7(10)°.
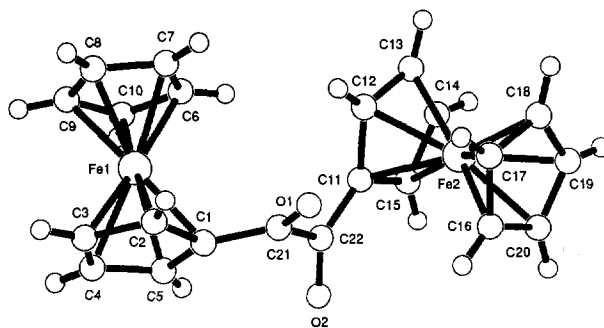

Fig. 1. A view of the molecule of 3b with our atom-numbering scheme.

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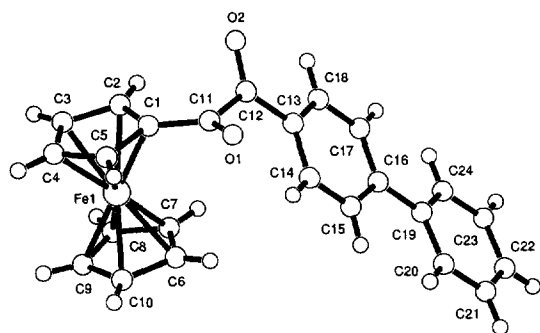
Fig. 2. A view of the molecule of **3c** with our atom-numbering scheme.

The torsional angle O–C–C–O takes the values 126.0(8)° in **3b** and 113.3(9)° in **3c**; the value in **3b** is significantly larger than the values in both FcCOCOPh, 109.1(5)° [7], and benzil PhCOCOPh, 111.6° [14,15]. However, butane-2,3-dione, CH_3–CO–CO–CH_3 [16] and its 1,4-bis-diazo derivative [17] are both centrosymmetric in the solid state ($P2_1/n$, $Z = 2$) and hence adopt the *trans*-planar C_{2h} conformation; similarly, this conformer of butane-2,3-dione was the sole rotamer found in the gas phase even at 525 °C [18]. Despite the observed values for the O–C–C–O torsional angle, rotation about the central C–C bond in these diketones is nonetheless reasonably facile, as demonstrated by the smooth formation of quinoxalines with arylene-1,2-di-amines, a long-established characterisation reaction for both the diamines and the diketones. The conformations found for compounds **3b** and **3c** correspond to molecular point group C_1, so that the molecules are chiral in the solid state, and all have the same handedness in $P2_12_12_1$; in solution, however, the NMR spectra indicate that R/S interconversion is fast at room temperature, so that crystallization in $P2_12_12_1$ represents a case of spontaneous resolution, or 'conglomerate crystallization' [19,20]: although all the molecules in a given crystal are of the same hand, there is no significance in the handedness of the crystal chosen for study, as there will be equal numbers present in the bulk sample of the two enantiomeric forms of $P2_12_12_1$. The intramolecular bond lengths and angles are unexceptional; the central C–C distances, 1.541(10) Å in **3b** and 1.521(10) Å in **3c**, are very similar to the values found in butane-2,3-dione, 1.540(6) Å [16] and in benzil, trigonal high-temperature phase 1.523(6) Å, monoclinic low-temperature phase, range 1.526(13)–1.549(16) Å, mean 1.536 Å [15].

3. Experimental details

(Ferrocenylmethyl)triphenylphosphonium iodide, $[FcCH_2PPh_3]^+I^-$, was prepared as previously described [1]; benzene-1,2-diamine was purified according to the

published method [21]. Samples of activated MnO_2 were either obtained from Aldrich, or were prepared by reduction of aqueous $KMnO_4$ solution with ethanol, followed by air-drying of the precipitate at 110 °C; no difference in activity between these samples was apparent. Ferrocenecarboxylic acid was prepared by reaction of 2-chlorobenzoylferrocene with wet potassium t-butoxide [22], and converted to chlorocarbonylferrocene by reaction with oxalyl chloride in the presence of pyridine. Phenylacetylferrocene, $FcCOCH_2Ph$, was prepared in 84% yield by Friedel–Crafts acylation in CH_2Cl_2 solution, using equimolar quantities of ferrocene and $PhCH_2COCl/AlCl_3$: NMR $\delta(H)$ 4.08(s, 5H, C_5H_5), 4.48(m, 2H) and 4.80(m, 2H) (C_5H_4), 7.30(m, 5H, Ph); $\delta(C)$ 46.9(t, CH_2), 70.0(d), 72.5(d) and 78.0(s) (C_5H_4), 70.1(d, C_5H_5), 127.0(d), 129.0(d), 129.7(d) and 135.1(s) (Ph), 202.0(s, CO).

3.1. Preparation of 1,1'-bis(phenylacetyl)ferrocene

A solution of ferrocene (7.0 g, 0.0376 mol) in CH_2Cl_2 (100 cm³) was added dropwise over 35 min, at room temperature and under N_2, to a stirred solution of phenylacetyl chloride (11.6 g, 0.0752 mol) and $AlCl_3$ (10.0 g, 0.0752 mol) in CH_2Cl_2 (400 cm³). After 24 h, the mixture was poured onto ice, and the whole mixture extracted with CH_2Cl_2 (2 × 50 cm³); the organic extract was washed with water, dried and evaporated to give a dark-red powder. Chromatography on alumina, eluting with light petroleum/CH_2Cl_2, gave 9.9 g (62%) of the product, m.p. 148–149 °C. Anal. Found: C, 73.9; H, 5.1. $C_{26}H_{22}FeO_2$ Calc.: C, 74.0; H, 5.2%. NMR $\delta(H)$ 3.90(s, 4H, CH_2), 4.32(m, 4H) and 4.70(m, 4H) (C_5H_4), 7.37(m, 10H, Ph); $\delta(C)$ 46.9(t, CH_2), 71.1(d), 73.8(d) and 79.8(s) (C_5H_4), 126.9(d), 128.6(d), 129.4(d) and 1354.8(s) (Ph), 201.1(s, CO). The use of more than two equivalents of acylating agent led to acylation of the phenyl rings of the first-formed product.

3.2. Oxidation of acylferrocenes

3.2.1. Phenylacetylferrocene

Phenylacetylferrocene (3.1 g, 0.01 mol) and MnO_2 (9.0 g, 0.1 mol) were heated under reflux in methylcyclohexane (75 cm³) for 24 h. The mixture was cooled and filtered before removal of the solvent. Chromatography on alumina with hexane/acetone (gradient from 99.5:0.5 to 90:10 v/v) gave 1.25 g of 1-ferrocenyl-2-phenylethanedione contaminated with phenylacetylferrocene together with pure 1-ferrocenyl-2-phenylethanedione (50 mg). NMR $\delta(H)$ 4.29(s, 5H, C_5H_5), 4.69(m, 2H) and 4.89(m, 2H) (C_5H_4), 7.5–8.1(m, 5H, Ph); $\delta(C)$ 71.1(d), 74.6(d) and 75.2(s) (C_5H_4), 71.2(d, C_5H_5), 129.5(d), 130.6(d) 133.6(d) and 135.1(s) (C_6H_5), 193.5(s) and 199.6(s) (2 × CO).

3.2.2. 1,1'-Bis(phenylacetyl)ferrocene

Very active manganese(IV) oxide [3] (14.4 g, 165 mmol) was added to a solution of 1,1-bis(phenyl-acetyl)ferrocene (3.15 g, 7.5 mmol) in 1,1,2-trichloro-ethane (125 cm^3). The mixture was stirred vigorously, and heated to 100 °C for 20 h. After cooling, the mixture was filtered and the solid residue washed with CH_2Cl_2 until the washings were colourless. The combined filtrate and washings were evaporated to give a red–black solid, which was recrystallized from CH_2Cl_2/light petroleum (1:1 v/v) to yield the product ferrocene-1,1'-diylbis(phenylethanedione) in 40% yield. Anal. Found: C, 69.4; H, 4.2. $C_{26}H_{18}FeO_4$ Calc.: C, 69.4; H, 4.0%. NMR δ(H) 4.77(m, 4H) and 4.96(m, 4H) (C_5H_4), 7.4–8.0(m, 10H, Ph); δ(C) 72.2(d), 75.5(s) and 75.9(d) (C_5H_4), 128.8(d), 129.0(d), 132.4(s) and 134.6(d) (C_6H_5), 192.0(s) and 197.7(s) (2 × CO).

3.3. Reaction of 1-ferrocenyl-2-phenylethanedione with benzene-1,2-diamine

Crude 1-ferrocenyl-2-phenylethanedione (1.40 g) and benzene-1,2-diamine (0.50 g) were melted together for 10 min at ca. 120 °C. After cooling, the crude mass was chromatographed on alumina with toluene/light petroleum (1:1 v/v) to give 0.45 g (26%) of 2-ferro-cenyl-3-phenylquinoxaline as deep purple plates, m.p. 208–210 °C. Anal. Found: C, 72.9; H, 5.1; N, 6.4. $C_{24}H_{18}FeN_2$ Calc.: C, 73.9; H, 4.7; N, 7.2%. NMR δ(H) 3.96(s, 5H, C_5H_5), 4.30(m, 2H) and 4.55(m, 2H) (C_5H_4), 7.4–7.5(m, 5H, Ph), 7.68(m, 2H) and 8.08(m, 2H) (quinoxalyl); δ(C) 69.9(d, C_5H_5), 70.1(d), 70.9(d) and 72.5(s) (C_5H_4), 128.5(d), 128.8(d), 128.9(d), 129.0(d), 129.2(d), 129.3(d), 129.9(d), 139.8(s), 140.3(s), 141.9(s), 154.1(s) and 154.1(s) (phenyl and quinoxalyl). Identity confirmed and structure established by X-ray analysis [4].

3.4. Preparation of phosphonium salts 1

Typically, (ferrocenylmethyl)triphenylphosphonium iodide (1.6 g, 0.027 mol) was suspended in dry ether (200 cm^3) and phenyl–lithium (0.030 mol, 16.7 cm^3 of a 1.8 mol dm^{-3} solution in cyclohexane/ether) was added under nitrogen, and the mixture was stirred for 3 h. The acyl chloride (0.027 mol) was then added, and the mixture was stirred for a further 2 h, after which the red products 1 were filtered off, and recrystallized from aqueous acetone if necessary.

1a. Anal. Found: C, 62.1; H, 4.5. $C_{36}H_{30}FeIOP$ Calc.: C, 62.4; H, 4.4%. NMR δ(H) 3.78(m, 1H), 4.10(m, 1H), 4.22(m, 1H) and 4.91(m, 1H) (C_5H_4), 3.80(s, 5H, C_5H_5), 7.40(d, 1H, $^2J_{HP}$ = 8.5 Hz, CH), 7.5–7.8(m, 20H, 4 × C_6H_5); δ(C) 46.2(d × d, $^1J_{PC}$ = 43.7 Hz, HCP), 68.8(d), 69.0(d), 69.7(d), 71.9(d) and 73.8(s) (C_5H_4), 69.6(d, C_5H_5), 117.5(s × d, $^1J_{PC}$ =

83.8 Hz), 129.8(d × d, J_{PC} = 12.6 Hz), 134.6(d × d, J_{PC} = 9.6 Hz) and 134.8(d) (C_6H_5P), 129.6(d), 130.8(d), 134.8(d) and 135.9(s) (C_6H_5CO), 192.5(s, CO); δ(P) 24.3.

1b. NMR δ(H) 3.83(s, 5H, C_5H_5), 4.04(s, 5H, C_5H_5), 3.60(m, 1H), 4.01(m, 1H), 4.08(m, 1H), 4.19(m, 1H), 4.51(m, 1H), 4.71(m, 1H), 4.78(m, 1H) and 5.11(m, 1H) (2 × C_5H_4), 76.94(d, 1H, $^2J_{HP}$ = 8.9 Hz, CH), 7.6–8.1(m, 15H, 3 × C_6H_5); δ(C) 45.9(d × d, $^1J_{PC}$ = 47.8 Hz, HCP), 68.2(d), 68.5(d), 68.6(d), 71.5(d), 71.6(d), 72.1(d), 73.3(d), 73.4(d), 80.3(s) and 80.4(s) (2 × C_5H_4), 70.1(d) and 70.5(d) (2 × C_5H_5), 118.8(s × d, $^1J_{PC}$ = 84.1 Hz), 129.7(d × d, J_{PC} = 12.4 Hz), 135.7(d × d, J_{PC} = 9.9 Hz) and 134.5(d) (C_6H_5), 198.9(d, $^2J_{PC}$ = 2.3 Hz, CO).

1c. Anal. Found: C, 65.3; H, 4.9. $C_{42}H_{34}FeIOP$ Calc.: C, 65.6; H, 4.5%. NMR δ(H) 3.82(m, 1H), 4.08(m, 1H), 4.24(m, 1H) and 4.92(m, 1H) (C_5H_4), 3.88(s, 5H, C_5H_5), 7.40(d, 1H, $^2J_{HP}$ = 8.5 Hz, CH), 7.5–7.8(m, 24H, C_6H_4 + 4 × C_6H_5); δ(C) 46.2(d × d, $^1J_{PC}$ = 43.6 Hz, HCP), 68.7(d), 68.8(d), 69.6(d), 71.9(d) and 73.8(s) (C_5H_4), 69.8(d, C_5H_5), 117.5(s × d, $^1J_{PC}$ = 84.0 Hz), 129.7(d × d, J_{PC} = 12.7 Hz), 135.1(d × d, J_{PC} = 9.7 Hz) and 139.0(d) (C_6H_5P), 127.3(d), 127.8(d), 128.5(d), 128.8(d), 131.5(s), 132.2(s), 134.6(d) and 147.3(s) ($C_6H_4C_6H_5$), 191.8(s, CO).

3.5. Preparation of phosphonium salts 2

Typically, the salt 1 (ca. 2 g) was dissolved in dichloromethane (200 cm^3), and zinc dust (20 g) was added. The mixture was heated under reflux, and glacial acetic acid (60 cm^3) was added dropwise during 30 min. After 1 h the mixture was poured into water (100 cm^3): the organic layer was separated, and the aqueous layer was exhaustively extracted with dichloromethane. The combined organic fractions were washed with water (3 × 50 cm^3), dried and evaporated. The residue was chromatographed on alumina; elution with dichloromethane produced the yellow to red products 2.

2a. NMR δ(H) 3.98(s, 2H, CH$_2$), 4.12(s, 5H, C_5H_5), 4.15(m, 2H) and 4.20(m, 2H) (C_5H_4), 7.4–8.0(m, 15H, 3 × C_6H_5); δ(C) 39.4(t, CH$_2$), 67.9(d), 69.1(d) and 81.1(s) (C_5H_4), 68.8(d, C_5H_5), 128.6(d), 128.7(d), 133.1(d) and 136.8(s) (C_6H_5), 197.3(s, CO).

2b. NMR δ(H) 3.67(s, 2H, CH$_2$), 4.16(s, 5H) and 4.18(s, 5H, 2 × C_5H_5), 4.21(m, 2H), 4.25(m, 2H), 4.52(m, 2H) and 4.80(m, 2H) (2 × C_5H_4); δ(C) 41.0(t, CH$_2$), 68.8(d) and 69.9(d) (2 × C_5H_5), 67.8(d), 69.1(d), 69.8(d), 72.3(d), 78.6(s) and 82.1(s) (2 × C_5H_4), 201.5(s, CO).

2c. Anal. Found: C, 75.5; H, 5.4. $C_{24}H_{20}FeO$ Calc.: C, 75.8; H, 5.3%. NMR δ(H) 4.02(s, 2H, CH$_2$), 4.12(m, 2H) and 4.20(m, 2H) (C_5H_4), 4.15(s, 5H, C_5H_5), 7.4–8.1(m, 9H, $C_6H_4C_6H_5$); δ(C) 39.5(t, CH$_2$), 67.9(d), 69.1(d) and 81.2(s) (C_5H_4), 68.8(d, C_5H_5), 127.1(d),

127.3(d), 128.2(d), 129.0(d), 129.2(d), 135.5(s), 139.9(s) and 145.8(s) ($C_6H_4C_6H_5$), 196.9(s, CO).

3.6. Preparation of diketones 3

Typically, the monoketone **2** was stirred overnight at room temperature with at least a 20-fold molar excess of manganese(IV) oxide suspended in dichloromethane. The mixture was then filtered, and the solid residue washed with dichloromethane/light petroleum (1:1 v/v) until the washings were colourless. The combined filtrate and washings were concentrated to small volume and chromatographed on silica, using dichloromethane/methanol (45:1 v/v) as eluent. Typical yields of **3** are 50–65%, accompanied by 20–30% of ferrocenecarboxaldehyde.

3a. Anal. Found: C, 68.3; H, 4.8. $C_{18}H_{14}FeO_2$ Calc.: C, 68.0; H, 4.4%. NMR δ(H) 4.30(s, 5H, C_5H_5), 4.70(m, 2H) and 4.90(m, 2H) (C_5H_4), 7.5–8.1(m, 5H, $3C_6H_5$); δ(C) 70.5(d), 73.9(d) and 74.5(s) (C_5H_4), 70.6(d, C_5H_5), 128.8(d), 129.9(d), 133.0(s) and 134.4(d) (C_6H_5), 192.8(s) and 199.0(s) (2 × CO). Identity confirmed by single-crystal X-ray diffraction [7].

3b. Anal. Found: C, 59.7; H, 4.5. $C_{22}H_{18}Fe_2O_2$ Calc.: C, 62.0; H, 4.3%. NMR δ(H) 4.28(s, 10H, 2 × C_5H_5), 4.68(m, 4H) and 4.95(m, 4H) (2 × C_5H_4); δ(C) 70.6(d, C_5H_5), 70.7(d), 73.6(d) and 74.6(s) (C_5H_4), 197.9(s, CO). Identity confirmed by single-crystal X-ray diffraction.

3c. Anal. Found: C, 72.9; H, 4.8. $C_{24}H_{218}FeO_2$ Calc.: C, 73.1; H, 4.6%. NMR δ(H) 4.30(s, 5H, C_5H_5), 4.72(m, 2H) and 4.92(m, 2H) (C_5H_4), 7.4–8.1(m, 9H,

Table 1
Summary of crystal data, data collection and refinement details

	Compound **3b**	Compound **3c**
(a) Crystal data		
Empirical formula	$C_{22}H_{18}Fe_2O_2$	$C_{24}H_{18}FeO_2$
Molar mass	426.08	394.25
Colour, habit	red, needle	red, plate
Crystal size (mm^3)	0.45 × 0.20 × 0.20	0.50 × 0.40 × 0.05
Crystal system	orthorhombic	orthorhombic
a (Å)	12.022(3)	9.900(3)
b (Å)	13.314(3)	24.423(4)
c (Å)	11.276(4)	7.496(3)
V ($Å^3$)	1804.9(7)	1812.6(9)
Space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
$F(000)$	872	816
d_{calc} ($g\,cm^{-3}$)	1.568	1.445
μ (mm^{-1})	1.619	0.845
(b) Data acquisition [a]		
Temperature (K)	293(1)	293(1)
Unit-cell reflections (2θ range (°))	47.6–50.0	20.00–24.80
Max 2θ (°) for reflections	49.98	50.02
hkl range for reflections	0,14; 0,15; 0,1	0,11; 0,29; −7,8
Decay in three standard reflections (%)	3.8	< 1
Reflections measured	1846	2374
Unique reflections	1846	1876
R_{int}	0.034	
Reflections with $I > n\sigma(I)$, n	1540, 3	1342, 3
Min, max abs. corr. [b]	—	1.000, 0.824
(c) Structure solution and refinement [c]		
Solution method	direct	direct
Final refinement	F	F
No. variables in LS	235	244
R, R_w, GOF	0.033, 0.035, 2.84	0.040, 0.030, 1.93
Range in final Δ map (e $Å^{-3}$)	0.23, −0.48	0.22, −0.21
Final shift/error ratio	0.020	0.01

[a] Data collection on a Rigaku AFC7S diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å).

[b] Absorption correction by means of psi-scans.

[c] All calculations were done on a Silicon Graphics computer system with the TeXsan suite of programs [TeXsan: *Crystal Structure Analysis Package*, Molecular Structure Corporation, The Woodlands, TX 77381 (1985, 1992)].

C_6H_4–C_6H_5); δ(C) 70.6(d), 73.9(d) and 74.6(s) (C_5H_4), 70.7(d, C_5H_5), 127.4(d), 127.5(d), 128.5(d), 129.0(d), 130.5(d), 131.7(s), 139.7(s) and 147.1(s) (C_6H_4–C_6H_5), 192.4(s) and 198.9(s) (2 × CO). Identity confirmed by single-crystal X-ray diffraction.

3.7. Friedel–Crafts reactions of ferrocene with $CH_{3-x}Cl_xCOCl$ / $AlCl_3$

3.7.1. CCl_3COCl / $AlCl_3$

To a stirred solution of ferrocene (5.88 g, 0.03 mol) in dichloromethane (120 cm^3) at 0 °C were added simultaneously CCl_3COCl (5.45 g, 0.03 mol) in CH_2Cl_2 (30 cm^3), added dropwise, and $AlCl_3$ (4.00 g, 0.03 mol), added portionwise during 20 min. The mixture was stirred for 40 min, and then poured into ice-cold water (250 cm^3). The organic layer was separated, and the aqueous layer extracted with dichloromethane (2 × 50 cm^3). The combined organic fractions were washed with water (3 × 150 cm^3), dried, and evaporated to dryness. The residue was chromatographed on alumina; elution with light petroleum gave FcCOCCl$_3$ (0.13 g, 1%): Anal. Found: C, 44.0; H, 2.3. $C_{12}H_9Cl_3FeO$ Calc.: C, 43.5; H, 2.7%. NMR δ(H) 4.30(s, 5H, C_5H_5), 4.70(m, 2H) and 5.10(m, 2H) (C_5H_4); δ(C) 69.5(d), 72.6(d), and 73.2(s) (C_5H_4), 71.0(d, C_5H_5), 96.1(s, CCl$_3$), 187.7(s, CO) and FcCOCHCl$_2$ (1.54 g, 17%):

NMR δ(H) 4.28(s, 5H, C_5H_5), 4.69(m, 2H) and 4.91(m, 2H) (C_5H_4), 6.42(s, 1H, CHCl$_2$); δ(C) 68.0(d, CHCl$_2$), 70.2(d), 72.7(s) and 73.9(d) (C_5H_4), 70.6(d, C_5H_5), 190.7(s, CO).

3.7.2. $CHCl_2COCl$ / $AlCl_3$

In a reaction similar to the foregoing, but using instead $CHCl_2COCl$, the products were FcCOCHCl$_2$ (2%) and FcCOCH$_2$Cl (6%): Anal. Found: C, 54.9; H, 4.2. $C_{12}H_{11}ClFeO$ Calc.: C, 54.9; H, 4.0%. NMR δ(H) 4.26(s, 5H, C_5H_5), 4.43(s, 2H, CH$_2$Cl), 4.60(m, 2H) and 4.85(m, 2H) (C_5H_4); δ(C) 46.0(t, CH$_2$Cl), 69.5(d), 73.1(d) and 75.9(s) (C_5H_4), 70.2(d, C_5H_5), 195.3(s, CO).

3.7.3. $CH_2ClCOCl$ / $AlCl_3$

In a reaction similar to the foregoing, but using instead $CH_2ClCOCl$, the products were FcCOCH$_2$Cl (7%) and FcCOCH$_3$ (3%).

3.8. Reaction of chloroacetylferrocene with benzene-1,2-diamine

FcCOCH$_2$Cl (0.78 g, 3 mmol), benzene-1,2-diamine (0.32 g, 3 mmol), potassium acetate (0.36 g, 3.6 mmol) and potassium iodide (0.03 g, 0.18 mmol) were heated to reflux, in the absence of solvent for 48 h. The mixture

Table 2
Atomic coordinates for compound **3b**

Atom	x	y	z	U_{eq}
Fe(1)	0.75696(7)	0.12150(8)	0.62546(9)	0.0389(3)
Fe(2)	0.29915(7)	0.12539(7)	0.87995(9)	0.0389(3)
O(1)	0.4427(4)	0.1221(5)	0.5869(4)	0.067(2)
O(2)	0.4920(4)	−0.0773(3)	0.7518(5)	0.055(2)
C(1)	0.6184(6)	0.0438(5)	0.5728(6)	0.038(2)
C(2)	0.6620(6)	0.1013(6)	0.4761(6)	0.058(3)
C(3)	0.7719(7)	0.0677(7)	0.4550(7)	0.067(3)
C(4)	0.7962(7)	−0.0081(6)	0.5374(8)	0.058(3)
C(5)	0.7044(6)	−0.0230(5)	0.6096(6)	0.042(2)
C(6)	0.7455(7)	0.1886(8)	0.7892(8)	0.064(3)
C(7)	0.7338(8)	0.2593(6)	0.7023(10)	0.068(3)
C(8)	0.830(1)	0.2589(7)	0.6339(10)	0.098(4)
C(9)	0.8985(7)	0.1886(10)	0.681(1)	0.101(5)
C(10)	0.8451(10)	0.1426(7)	0.7776(10)	0.087(4)
C(11)	0.4565(5)	0.0762(5)	0.8476(6)	0.033(2)
C(12)	0.4519(5)	0.1857(5)	0.8530(7)	0.042(2)
C(13)	0.4141(6)	0.2153(6)	0.9649(7)	0.052(3)
C(14)	0.3943(6)	0.1270(8)	1.0327(6)	0.060(2)
C(15)	0.4181(6)	0.0421(6)	0.9616(7)	0.045(2)
C(16)	0.1993(8)	0.0733(9)	0.748(1)	0.084(4)
C(17)	0.2010(8)	0.1805(9)	0.749(1)	0.087(4)
C(18)	0.1598(7)	0.2118(6)	0.858(1)	0.081(4)
C(19)	0.1342(6)	0.1253(10)	0.9269(8)	0.081(3)
C(20)	0.1588(7)	0.0410(6)	0.858(1)	0.069(3)
C(21)	0.5112(5)	0.0646(5)	0.6285(6)	0.038(2)
C(22)	0.4861(5)	0.0126(5)	0.7477(7)	0.038(2)

Table 3
Atomic coordinates for compound **3c**

Atom	x	y	z	U_{eq}
Fe(1)	1.0076(1)	0.03666(4)	0.3332(1)	0.0449(2)
O(1)	1.1815(7)	0.1501(2)	0.0568(7)	0.101(2)
O(2)	1.4318(5)	0.0993(2)	0.2744(7)	0.084(2)
C(1)	1.1578(6)	0.0585(3)	0.1636(9)	0.046(2)
C(2)	1.2002(6)	0.0144(3)	0.2705(8)	0.047(2)
C(3)	1.1130(6)	−0.0302(3)	0.2404(9)	0.054(2)
C(4)	1.0163(7)	−0.0137(3)	0.1150(9)	0.058(2)
C(5)	1.0407(7)	0.0412(3)	0.0661(8)	0.056(2)
C(6)	0.9211(8)	0.1030(3)	0.449(1)	0.071(3)
C(7)	1.0014(10)	0.0746(3)	0.5750(8)	0.072(2)
C(8)	0.9499(8)	0.0220(3)	0.5875(10)	0.072(3)
C(9)	0.8379(8)	0.0166(3)	0.472(1)	0.066(3)
C(10)	0.8201(8)	0.0670(4)	0.3885(10)	0.068(3)
C(11)	1.2129(7)	0.1139(3)	0.1613(10)	0.060(2)
C(12)	1.3269(8)	0.1256(3)	0.292(1)	0.066(3)
C(13)	1.3122(7)	0.1677(3)	0.4353(10)	0.055(2)
C(14)	1.2029(9)	0.2013(3)	0.446(1)	0.096(3)
C(15)	1.1890(9)	0.2374(3)	0.586(1)	0.098(4)
C(16)	1.2874(7)	0.2428(3)	0.7174(10)	0.059(2)
C(17)	1.3952(7)	0.2078(3)	0.703(1)	0.066(3)
C(18)	1.4096(7)	0.1710(3)	0.565(1)	0.069(3)
C(19)	1.2721(8)	0.2817(3)	0.869(1)	0.060(3)
C(20)	1.1698(7)	0.3192(3)	0.8754(10)	0.067(3)
C(21)	1.1592(8)	0.3561(3)	1.016(1)	0.075(3)
C(22)	1.2484(9)	0.3553(3)	1.152(1)	0.080(3)
C(23)	1.350(1)	0.3185(4)	1.149(1)	0.138(5)
C(24)	1.359(1)	0.2822(4)	1.008(2)	0.140(5)

was cooled, poured into water (50 cm³), and extracted with ether (2 × 50 cm³). The ether solution was washed with water, dried, and evaporated. Chromatography on alumina with toluene as eluent gave 2-ferrocenylquinoxaline as purple needles (23%). Anal. Found: C, 68.8; H, 4.2; N, 8.5. $C_{18}H_{14}FeN_2$ Calc.: C, 68.8; H,

Table 4
Selected geometrical parameters (distances in Å, angles in °)

Compound **3b**			
O1–C21	1.218(7)	O2–C22	1.200(7)
C21–C22	1.541(10)		
O1–C21–C1	123.3(7)	O2–C22–C11	124.4(7)
O1–C21–C22	119.1(6)	O2–C22–C21	118.0(7)
C1–C21–C22	117.(6)	C11–C22–C21	117.6(5)
O1–C21–C22–C11	−53.8(9)	O2–C22–C21–C1	−55.6(9)
O1–C21–C22–O2	126.0(8)		
Compound **3c**			
O1–C11	1.221(8)	O2–C12	1.228(8)
C11–C12	1.521(10)		
O1–C11–C1	125.7(8)	O2–C12–C13	121.1(8)
O1–C11–C12	117.8(7)	O2–C12–C11	117.4(7)
C1–C11–C12	116.4(7)	C11–C12–C13	121.3(7)
O1–C11–C12–C13	66.3(9)	O2–C12–C11–C1	62.1(9)
O1–C11–C12–O2	−113.3(9)		
C15–C16–C19–C20	−8(1)	C17–C16–C19–C24	−4(1)
C15–C16–C19–C24	171(1)	C17–C16–C19–C20	175(1)

4.5; N, 8.9%. NMR δ(H) 4.06(s, 5H, C_5H_5), 4.52(m, 2H) and 5.11(m, 2H) (C_5H_4), 7.65(m, 2H), 8.02(m, 2H) and 8.98(m, 1H) (quinoxalyl $C_8H_5N_2$); δ(C) 67.9(d), 71.1(d) and 80.6(s) (C_5H_4), 69.7(d, C_5H_5), 128.2(d), 128.7(d), 129.1(d), 129.9(d), 140.6(s), 142.5(s), 143.9(d) and 155.1(s) (quinoxalyl $C_8H_5N_2$). Identity confirmed by X-ray analysis [10].

3.9. X-ray crystallography

Crystals of compounds **3b** and **3c** suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol.

Compounds **3b** and **3c** both crystallized in the orthorhombic system; for each, the space group $P2_12_12_1$ was uniquely assigned from the systematic absences. Details of crystal data, and data collection and refinement are given in Table 1. The ORTEP diagrams (Figs. 1 and 2) were prepared using ORTEP-II [23]. Refined atomic coordinates are given in Tables 2 and 3, and selected structural parameters in Table 4.

Acknowledgements

References

[1] C.M. Zakaria, C.A. Morrison, D. McAndrew, W. Bell and C. Glidewell, J. Organomet. Chem., 485 (1995) 201.

[2] M.D. Rausch and A. Siegel, J. Org. Chem., 33 (1968) 4545.

[3] A. Fatiadi, Synthesis, (1976) 65.

[4] G. Ferguson, C. Glidewell and J.P. Scott, Acta Crystallogr., C52 (1996) 770.

[5] P.L. Pauson and W.E. Watts, J. Chem. Soc., (1963) 2990.

[6] S.Z. Ahmed, C. Glidewell and G. Ferguson, Acta Crystallogr., C52 (1996) 1634.

[7] G. Ferguson, C. Glidewell, M. Gottfried and J. Trotter, Acta Crystallogr., C52 (1996) 773.

[8] K. Schlögl and H. Egger, Monatsch. Chem., 94 (1963) 376.

[9] H.B. Floyd, M.T. Diu, P.F. Fabio, L.A. Jacob and B.D. Johnson, J. Org. Chem., 50 (1985) 5022.

[10] G. Ferguson, C. Glidewell and J.P. Scott, Acta Crystallogr., C51 (1995) 1989.

[11] E. Gyepes and F. Hanic, Cryst. Struct. Comm., 4 (1975) 229.

[12] K. Sato, M. Iwai, H. Sano and M. Konno, Bull. Chem. Soc. Jpn., 57 (1984) 634.

[13] J.C. Barnes, W. Bell, C. Glidewell and R.A. Howie, J. Organomet. Chem., 385 (1990) 369.

[14] C.J. Brown and R. Sadanaga, Acta Crystallogr., 18 (1965) 158.

[15] M. More, G. Odou and J. Lefebvre, Acta Crystallogr., B43 (1987) 398.

[16] K. Eriks, T.D. Hayden, S.H. Yang and I.Y. Chan, J. Am. Chem. Soc., 105 (1983) 3940.

[17] H. Hope and K.T. Black, Acta Crystallogr., B28 (1972) 3632.

[18] D.D. Danielson and K. Hedberg, J. Am. Chem. Soc., 101 (1979) 3730.

[19] I. Bernal, Inorg. Chim. Acta, 96 (1985) 99.

[20] I. Bernal, J. Cetrullo, J. Cai and S.S. Massoud, Struct. Chem., 6 (1995) 99.

[21] D.D. Perrin and W.L.F. Amarego, Purification of Laboratory Chemicals, Pergamon, Oxford, 3rd edn., 1988.

[22] P.C. Reeves, Org. Synth., 56 (1977) 28.

[23] C.K. Johnson, ORTEP, A Fortran Thermal Ellipsoid Plot Program, Technical Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.