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Functionalization of chlorobenzenes via their $CpFe^+$ salts: a synthesis of substituted diphenyl ethers

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Abstract

In work directed towards the synthesis of functionalized diaryl ethers such as SK+F L-94901 the benzylic carbanion derived from 3-ethoxy-6-methylpyridazine-1-oxide was added *ortho* to an electron-withdrawing chlorine group in (η^5-cyclopentadienyl)(η^6-1,4-dichlorobenzene)iron(1+) hexafluorophosphate(1−) and other η^6-chloroarene cationic complexes to form neutral η^5-cyclohexadienyl ligands. Oxidative aromatization of the adduct occurred with concomitant demetallation. In contrast to the Yanovsky-type reactions of the carbanion, chloride was displaced from (η^6-1,4-dichlorobenzene)$CpFe^+$ by phenoxide anions under mild conditions to give η^6-diphenyl ether cationic complexes.

Introduction

Diaryl and polyaryl ether units occur in a wide variety of naturally occurring compounds which elicit significant biological responses [1]. The hindered diphenyl ether of interest in the present work, SK + F L-94901 (**1**), is a synthetic compound which is a selective thyromimetic and shows hypocholesterolaemic activity [2]. Our strategy for the synthesis of **1** and its analogues was based upon attachment of a nucleophile selectively at either an unsubstituted aromatic carbon or a substituted carbon in cationic (η^5-cyclopentadienyl)(η^6-1,4-dichlorobenzene)iron(1+) complexes. Soft carbanions, such as those generated from diethyl malonate or ethyl acetoacetate, are known [3] to displace chloride from Cp(η^6-chlorobenzene)Fe^+, presumably via a series of reversible addition-elimination reactions resulting ultimately in *ipso* attack, loss of the leaving group, and formation of a new η^6-arene complex. In contrast, hard carbanions such as cyanide [4,5] or those derived from acetone [6,7] or butanone [7] attack a cationic complex *ortho* to an electron-withdrawing arene substituent to give a neutral (η^5-cyclohexadienyl)iron adduct; silyl enol ethers and *C*-silyl esters react similarly [8]. Such transformations are analogous to the Yanovsky reaction [9] in which carbanions derived from ketones

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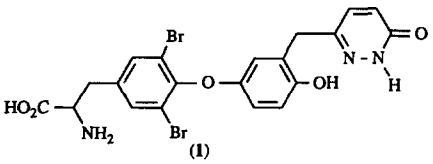

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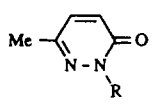
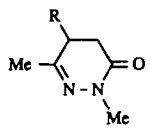
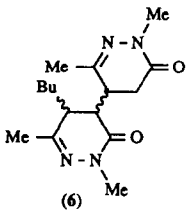


(2 : R = H
3 : R = Me)



(4 : R = Bu
5 : R = ^{t}Bu)

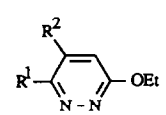


(6)

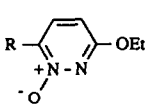
react with polynitroarenes, leading to alkylation *ortho* to a nitro group. In the Yanovsky-type reactions reported previously [5–7] simple and readily available ketones were used in excess together with aqueous (up to 50%) potassium hydroxide. In the present case it was necessary to generate a carbanion from 6-methylpyridazin-3-one (**2**), or from a synthetic equivalent of **2**, under mild conditions and in near-stoichiometric amount.

Results and discussion

In order to protect its NH group, 6-methylpyridazin-3-one (**2**) [10,11] was treated with iodomethane/potassium hydroxide/tetrabutylammonium bromide, or better with dimethyl sulfate/potassium carbonate in acetone, to give the *N*-methyl derivative **3** in yields of 23% and 99%, respectively. However, attempts to deprotonate the *C*-methyl group of **3** with a variety of bases (*e.g.* KOH, KH, LDA, RLi) using a range of solvents and reaction temperatures, followed by attempted trapping with iodomethane as a model electrophile, gave unsatisfactory results. For example, use of BuLi at −78°C resulted in conjugate addition of the base to form the 5-butyl-4,5-dihydropyridazinone **4** (20%) and the pair of diastereoisomeric dimers **6** (5%), while ^{t}BuLi gave the adduct **5** (59%). In an endeavour to avoid not only conjugate addition but also possible competitive deprotonation of the *N*-methyl group in the pyridazinone **3**, it was converted into its *O*-ethyl aromatic

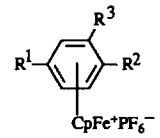


(7 : R^1 = Me, R^2 = H
8 : R^1 = $CH_2C(OH)Ph_2$, R^2 = H
9 : R^1 = Me, R^2 = Bu)
10 : R^1 = $CH_2{}^t$Bu, R^2 = H)

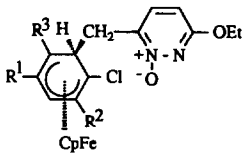


(11 : R = Me
12 : R = Et
13 : R = $CHMe_2$
14 : R = CH_2SiMe_3)

derivative **7** [12]. However, this pyridazine also gave unsatisfactory results, although deprotonation with LDA at −78°C followed by addition of benzophenone [13] did afford the 6-(diphenylhydroxy)ethyl derivative **8** in low yield [7%]. In contrast, deprotonation with BuLi at −100%C and treatment with iodomethane gave only a low yield (10%) of the 5-butylpyridazine (**9**) resulting from nucleophilic substitu-



(15 : $R^1 = R^2 = Cl$, $R^3 = H$
16 : $R^1 = H$, $R^2 = R^3 = Cl$
17 : $R^1 = Me$, $R^2 = R^3 = Cl$
18 : $R^1 = Cl$, $R^2 = R^3 = H$
19 : $R^1 = OMe$, $R^2 = Cl$, $R^3 = H$
20 : $R^1 = R^2 = OMe$, $R^3 = H$)



(21 : $R^1 = Cl$, $R^2 = R^3 = H$
22 : $R^1 = R^3 = H$, $R^2 = Cl$
23 : $R^1 = H$, $R^2 = Cl$, $R^3 = Me$
24 : $R^1 = Me$, $R^2 = Cl$, $R^3 = H$
25 : $R^1 = R^2 = R^3 = H$
26 : $R^1 = p\text{-}MeC_6H_4O$, $R^2 = R^3 = H$
27 : $R^1 = OPh$, $R^2 = R^3 = H$)

tion on the heterocycle [14]. However, regioselective formation [15] of the 1-oxide (**11**) [12] by oxidation of **7** with peroxyacetic acid gave a synthetic equivalent of **2** in which the kinetic acidity of the benzylic methyl protons was enhanced significantly, and from which the desired primary carbanion was generated by brief treatment (3 min) with BuLi (1 molar equiv.) in THF at −100°C. Addition of iodomethane followed by warming to room temperature gave the 6-ethyl homologue **12** (83%). Use of BuLi (1.6 molar equiv.) at −78°C and an excess of iodomethane lowered the yield of **12** to 42% and gave the dialkylated product **13** also (26%).

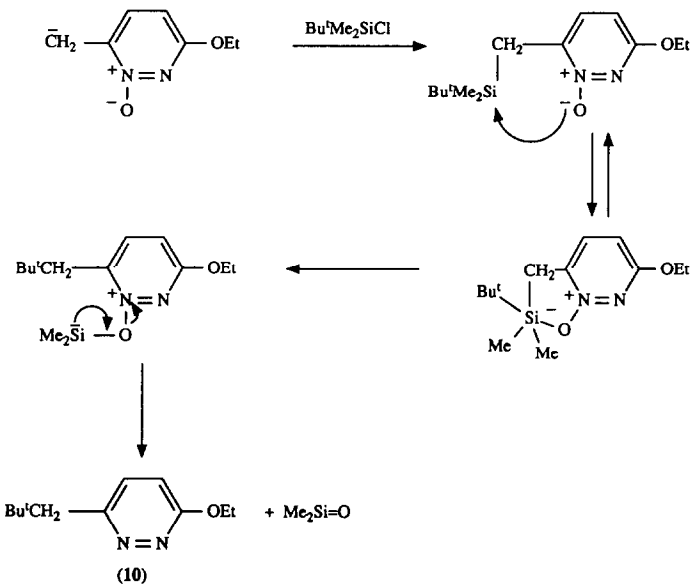
Treatment of the carbanion derived (−100°C, 5 min) from **11** with the cationic complex **15** [8] at −78°C for 30 min afforded the *exo* Yanovsky-type adduct **21** (69%). This (η^5-cyclohexadienyl)iron complex was stable as a solid, but some decomposition occurred in solution (*e.g.* in $CHCl_3$). The structure of **21** was confirmed by its ^1H NMR spectrum in which large upfield shifts [7] were observed for the signals due to the cyclopentadienyl and cyclohexadienyl protons (Table 1) compared with those of the cationic starting complex. The adduct **21** was also prepared, albeit in lower yield (42%), by the simpler practical route of conversion

Table 1

^1H NMR data (ppm, $CDCl_3$) for the complex **21**

Proton	Chemical shift	Multiplicity	Coupling constants (Hz)
1	3.25	dd	$J_{1,6} = 7.0$, $J_{1,3} = 1.8$
3	6.10	dd	$J_{3,4} = 5.2$, $J_{3,1} = 1.8$
4	4.58	dd	$J_{4,3} = 5.2$, $J_{4,6} = 1.6$
6	3.62	dddd [a]	$J_{6,1}$, $J_{6,Ha} = 6.8$, $J_{6,Hb} = 7.1$, $J_{6,4} = 1.6$
H_a [b]	1.79	dd	$J_{Ha,Hb} = 13.2$, $J_{Ha,6} = 6.8$
H_b	2.03	dd	$J_{Hb,Ha} = 13.2$, $J_{Hb,6} = 7.1$
4′	6.48	d	$J_{4',5'} = 8.7$
5′	7.09	d	$J_{5',4'} = 8.7$
CH_2CH_3	1.38	t	$J = 7.1$
CH_2CH_3	4.37	q	$J = 7.1$
C_5H_5	4.41	s	

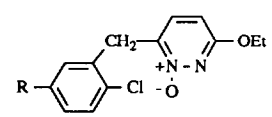
[a] Observed as a quartet of doublets. [b] The diastereotopic methylene proton which lies above the cyclohexadienyl ring.



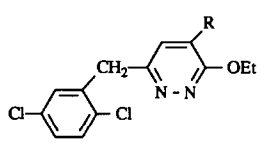
(10)

Scheme 1.

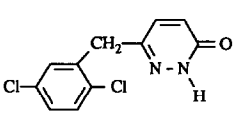
of the pyridazine-1-oxide (**11**) into the benzyl-type trimethylsilane (**14**) [*cf.* 8] followed by fluoride ion promoted exposure of the carbanion in THF at room temperature and reaction with the ion complex **15**. Trapping of the lithio carbanion from the 1-oxide (**11**) with t-butylchlorodimethylsilane unexpectedly gave only the 6-(2,2-dimethylpropyl)pyridazine (**10**) (9%). Expulsion of a silyl species is presumably associated mechanistically with reduction of the 1-oxide during the formation of **10**. Thus, initial capture of the carbanion by the t-butyldimethylsilyl group followed by intramolecular attack at silicon by oxygen to generate a pentavalent silicon anion [16,17], 1,2-migration of the t-butyl group from silicon to carbon, and finally loss of a silanone, leads to **10** (Scheme 1).



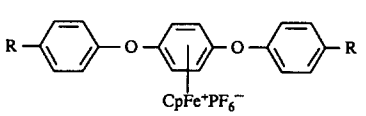
(28 : R = Cl
29 : R = H)



(30 : R = H
31 : R = Cl)



(32)



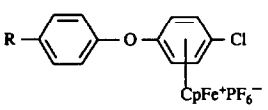
(33 : R = Me
34 : R = H)

In the sequence envisaged for the synthesis of **1**, oxidation of **21** by removal of H(6) is required in order to generate a new substituted cationic η^6-complex which remains activated towards nucleophilic displacement of chloride. In the event, treatment of **21** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [18] in

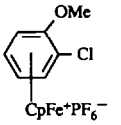
acetonitrile at either room temperature or −23°C gave the decomplexed substituted arene **28** (43%). Attempts to effect aromatization without demetallation by using *N*-bromosuccinimide, or tetrachloro-1,4-benzoquinone, or bis(acetato-*O*)phenyliodine [19] yielded only **28**, while trimethylamine *N*-oxide [20] gave no reaction and thallium(III) trifluoroacetate [21,22] removed the heterocyclic ring instead of hydride and regenerated **15** (59%).

Since hydride removal could not be achieved without demetallation, the original aim of producing a cationic η^6 organoiron complex in which the benzenoid ring carried not only a pyridazine substituent but also two chlorine atoms activated towards nucleophilic displacement could not be realized. In order to provide adducts whose structures more closely reflected that present in the heterocyclic moiety of SK + F L-94901, and also to make available further substrates for π-complexation studies, the arylmethylpyridazine-1-oxide **28** was reduced with phosphorus trichloride to give the pyridazine **30** (63%) and its chloro derivative **31** (10%). Attempted selective reduction of the *N*-oxide in the complex **21** using PCl_3 gave only **11** and **15**. Treatment of **30** with aqueous hydrochloric acid effected hydrolysis of the ethoxypyridazine to give 6-(2,5-dichlorophenyl)-methyl-3(2*H*)-pyridazinone (**32**) (96%). Consideration was then given to η^6-benzenoid re-complexation of either the 1-oxide **28**, or the pyridazine **30**, or the pyridazinone **32**. However, re-complexation to give a $CpFe^+$ salt was not feasible since such complexation of 1,4-dichlorobenzene itself requires catalysis by $AlCl_3$ together with a temperature of *ca.* 140°C, and the dichlorobenzene rings of **28**, **30**, and **32** would be even less reactive due to the additional π-deficient heterocyclic substituent. Since $CpRu^+$ salts of arenes usually can be generated at a lower temperature and in the absence of a Lewis acid catalyst [8], **28**, **30** and **32** were each treated with trisacetonitrile(η^5-cyclopentadienyl)ruthenium(1 +) hexafluorophosphate(1 −) in refluxing 1,2-dichloroethane. Disappointingly, however, no cationic complexes were formed.

In order to investigate further the scope of the Yanovsky-type reaction, the lithio carbanion derived from **11** was treated with some other η^6-arene iron complexes. Thus, Cp(η^6-1,2-dichlorobenzene)Fe^+ (**16**) [8] gave the adduct **22** (37%) while Cp(η^6-1,2-dichloro-4-methylbenzene)Fe^+ (**17**) gave a mixture (2:1) (53%) of the regioisomeric adducts **23** and **24**. The isomers **23** and **24** were identified from the ^1H NMR signals due to their H(3) protons, which normally are the most deshielded of the signals given by the cyclohexadienyl protons. Isomer **23**, which is derived from carbanion attack at C(3) of **16**, would have H(3) *ortho* coupled to H(2), while **24**, which arises from nucleophilic attack at C(6), would have H(3) *meta* coupled to H(1). Although *meta* coupling was not resolved in the ^1H NMR spectrum of the mixture because of further (long range) splitting by the methyl protons, the H(3) signals were observed as a doublet (J 5.0 Hz) due to **23** at 6.01 ppm, and a singlet due to **24** at 6.08 ppm. Under the usual reaction conditions, the less activated Cp(η^6-chlorobenzene)Fe^+ salt (**18**) [8] gave a mixture (1:3) of the unstable adduct **25** and the pyridazine-1-oxide (**11**). Although addition of the pyridazinylmethylene carbanion to **18** was quantitative (^1H NMR) when the reaction time at −78°C was increased from 15 min to 2.5 h, decomposition of isolated **25** into **11** and **18** occurred under nitrogen in the dark at room temperature, and was accelerated greatly by dissolution or by attempted chromatography on either alumina or silica. Oxidative demetallation of crude **25** with DDQ gave



(35 : R = Me
36 : R = H)



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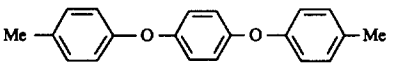

(37)

only a low yield (10%) of the substituted chlorobenzene **29**, the major process involving loss of the heterocyclic substituent rather than loss of hydride.

An alternative approach to the synthesis of **1** involves nucleophilic substitution of one of the chlorine atoms of **15** by a phenoxy group prior to Yanovsky addition of the carbanion; re-complexation of the arene resulting from oxidative demetallation with DDQ might then provide a monochloro diphenyl ether activated towards displacement of the remaining chlorine. Therefore, the reactions of some phenoxide ions with Cp(η^6-1,4-dichlorobenzene)Fe$^+$ (**15**) were examined. Sodium 4-methylphenoxide reacted with **15** in DMF at room temperature to give a mixture (1 : 1) of disubstituted **33** (24%) and monosubstituted **35** (24%) aryl ethers. The slow addition of a solution of the sodium 4-methylphenoxide in THF to a solution of the salt **15** in THF increased the yield of **35** to 65%. Addition of potassium 4-methylphenoxide in HMPA to a suspension of **15** in HMPA gave **33** (26%), **35** (20%), and the decomplexed bis ether **37** (22%). The activating effect of the CpFe$^+$ was significant; 1,4-dichlorobenzene and sodium 4-methylphenoxide in HMPA with or without added copper powder did not yield any diphenyl ether after several hours at temperatures up to 190°C. Monosubstitution could be achieved, albeit in only 32% yield after 20 h, when catalytic amounts of CuCl and the tridentate phase transfer agent TDA-1 [23] were added to a mixture of the reactants in refluxing methoxybenzene. Addition of sodium phenoxide to the complex **15** gave the monoether **36** (58%) and the bis ether **34** (15%). However, neither sodium 2,6-dibromo-4-methylphenoxide in DMF nor the corresponding potassium salt in HMPA displaced chloride from **15** [24]. Since **1** also contains a hydroxy group, sodium methoxide (1 molar equiv.) was used, and gave the monosubstituted product **19** (62%); even under mild conditions, the use of an excess of methoxide [25] afforded the disubstituted complex **20**. Selective monosubstitution of **16** to form the methoxybenzene complex **38** was achieved (83%) by inverse addition of methoxide (1 molar equiv.).

Treatment of the monochloro-substituted complexes **35** and **36** with the lithio carbanion derived from **11** gave the η^5-cyclohexadienyl adducts **26** (35%) and **27** (34%), respectively.

The current work shows that (η^6-chloroarene)CpFe$^+$ complexes can serve a useful role as substrates either for Yanovsky-like attack by functionalized carbanions, leading to functionalized chloroarenes, or for displacement of chloride, leading to functionalized diphenyl ethers.

Experimental

For general experimental details, see ref. 8. Except where otherwise indicated, ^{1}H NMR spectra were recorded at 400.13 MHz and ^{13}C NMR spectra at 100.62 MHz on a Bruker AM400 instrument operating at 9.2 T. Solvent A was CH_2Cl_2/EtOH/Et_3N (100:10:1).

N-Methylation of 6-ethyl-3(2H)-pyridazinone (2)

(a) With dimethyl sulfate in acetone. A vigorously stirred suspension of the pyridazinone (**2**) [26] (1.50 g, 13.62 mmol), K_2CO_3 (2.26 g, 16.35 mmol) and dimethyl sulfate (1.55 mL, 16.35 mmol) in acetone (75 mL) was heated under reflux for 4.5 h. Workup gave an oil which was distilled at 30–35°C/0.1–0.2 mmHg to yield 2,6-dimethyl-3-(2*H*)-pyridazinone (**3**) (1.08 g, 64%) as a white solid, m.p. 49–51°C (lit. [27] m.p. 50–51°C). ν_{max} ($CHCl_3$): 1658 (CO); 1590 (C=N, C=C) cm^{-1}. δ(H) 2.33 (s, CH_3); 3.74 (s, NCH_3); 6.87 (d, $J_{4,5}$ = 9.5 Hz, H(4)); 7.13 (d, $J_{4,5}$ = 9.5 Hz, H(5)) ppm. δ(C) 20.6 (CH_3); 39.9 (NCH_3); 129.4 (C(4)); 133.4 (C(5)); 144.3 (C(6)); 160.0 (C(3)) ppm. *m/z* 124 (100, M), 96 (61, M – CO), 53 (51, 96 – MeN_2), 43 (7, MeN_2). The residue from distillation was triturated with hexanes to afford additional **3** (0.59 g, 35%).

(b) With iodomethane and phase-transfer catalysis. A mixture of tetrabutylammonium bromide (25 mg, 0.08 mmol), powdered KOH (22 mg, 0.39 mmol), the pyridazinone **2** (42 mg, 0.39 mmol) and iodomethane (24 μL, 0.39 mmol) in benzene (15 mL), was agitated in an ultrasonic bath for 15 h. Workup and PLC (solvent A) gave **3** (11 mg, 23%) and **2** (7.5 mg, 18%).

Reaction of the N-methylpyridazinone 3 with butyllithium and chlorotrimethylsilane

Butyllithium (1.7 mol L^{-1} in hexanes, 0.52 mL, 0.89 mmol) was added dropwise to a stirred solution of the *N*-methylpyridazinone **3** (0.10 g, 0.81 mmol) in THF (5 mL) at −78°C under nitrogen. After 1 h, chlorotrimethylsilane (0.20 mL, 1.61 mmol) was added, and after a further 25 min the mixture was warmed to room temperature. After 1 h, MeOH (65 μL, 1.61 mmol) was added and the mixture was worked up and chromatographed (PLC) (solvent A) to yield (i) 5-butyl-4,5-dihydro-2,6-dimethyl-3-(2*H*)-pyridazinone (**4**) (29 mg, 20%) which distilled as a colourless oil, b.p. (Kugelrohr) 52–55°C/0.07 mmHg. Found: M$^{+\cdot}$ 182.1426. $C_{10}H_{18}N_2O$ calc.: M$^{+\cdot}$ 182.1419. ν_{max} (film): 1662 (CO, C=N) cm^{-1}. δ(H) 0.91 (t, J = 6.8 Hz, CH_3); 1.33 (m, 5H, (CH$_a$$H_b$)C$H_2CH_2$Me); 1.79 (m, (C$H_aH_b$)CH$_2$); 2.06 (s, CH_3); 2.29 (m, H(4b, 5)); 2.53 (dd, $J_{4a,5}$ = 6.0, $J_{4a,4b}$ = 16.0 Hz, H(4a)); 3.31 (s, NCH_3) ppm. δ(C) 14.0 (*C*H$_3$); 22.6 (*C*H$_2$Me); 23.5 (CH_3); 28.9 (C(4)); 29.4 ((CH$_a$H$_b$)*C*H$_2$); 31.5 ((*C*H$_a$H$_b$)CH$_2$); 36.1 (C(5*)); 36.2 (NCH_3*); 153.0 (C(6)); 168.3 (C(3)) ppm. *m/z* 182 (13, M), 139 (15, M – C_3H_7), 126 (75, M – C_4H_8), 125 (100, M – C_4H_9), 111 (15, 126 – Me); and (ii) a mixture (1:1) (^{13}C NMR) of the diastereoisomers of 5-butyl-4,5-dihydro-2,6-dimethyl-4-[5-[4,5-dihydro-2,6-dimethyl-3(2*H*)-pyridazinonyl]]-3(2*H*)-pyridazinone (**6**) (13 mg, 5%) as a yellow oil, b.p. (Kugelrohr) 108–112°C/0.085 mmHg. Found: M$^{+\cdot}$ 306.2052. $C_{16}H_{26}N_4O_2$ calc.: M$^{+\cdot}$ 306.2056. ν_{max}($CHCl_3$): 1660 (CO, C=N) cm^{-1}. δ(H) 0.88 (m, CH_3); 1.28 (m, 5H, (CH$_a$$H_b$)C$H_2CH_2$Me); 1.40–1.54 (m, (C$H_aH_b$)CH$_2$); 2.00 (s) and 2.10, 2.11 (2s, CH_3 and CH_3'); 2.28–2.68 (m, 5H, H(4, 4', 5, 5')); 3.32, 3.33 (2s, NCH_3 and NCH_3') ppm. δ(C) 13.8 (*C*H$_3$); 22.3, 22.4 (CH$_2$*C*H$_2$Me); 23.1, 23.9

(2C); 24.9 (CH_3, CH_3'); 28.8, 28.9 (C(4')); 29.8, 29.9 ((CH_aH_b)CH_2); 30.2, 31.2 ((CH_aH_b)); 35.7, 35.90 (C(5)); 35.94, 36.0, 36.6, 37.3 (NCH_3 and NCH_3'); 41.1, 41.9 (C(5')); 42.1, 42.2 (C(4)); 152.0, 152.4, 153.1, 153.9 (C(6,6')); 164.1, 164.3, 166.7, 167.0 (C(3,3')) ppm. *m/z* 306 (5, M), 181 (87, M − $C_6H_9N_2O$), 153 (25, 181 − CO), 125 (100, M − $C_{10}H_{17}N_2O$).

Reaction of the N*-methylpyridazinone 3 with t-butyllithium and chlorotrimethylsilane*

t-Butyllithium (0.99 mol L^{-1} in pentane, 0.49 mL, 0.49 mmol) was added dropwise to a stirred solution of **3** (50 mg, 0.40 mmol) in THF (2 mL) at −78°C under nitrogen. After 10 min, the mixture was warmed to −23°C for 1 h, and again cooled to −78°C. Chlorotrimethylsilane (0.10 mL, 0.79 mmol) was added, the mixture was warmed to room temperature, and MeOH (33 μL, 0.82 mmol) was added after 12 h. Workup and PLC(CH_2Cl_2/EtOH/Et_3N, 100:1.5:1) yielded 5-(t-butyl)-4,5-dihydro-2,6-dimethyl-3(2*H*)-pyridazinone (**5**) (43 mg, 59%), m.p. 45.5–49°C, which was sublimed (Kugelrohr) at 55–60°C/0.07 mmHg to give white crystals. Anal. Found: C, 65.8; H, 10.4; N, 15.4. $C_{10}H_8N_2O$ calc.: C, 65.9; H, 10.0; N, 15.4%. ν_{max} (KBr): 1640 (C=N, CO) cm^{-1}. δ(H) 1.00 (s, $C(CH_3)_3$); 2.06 (s, CH_3); 2.21 (dd, $J_{4a,5} = 5.2$, $J_{4b,5} = 7.9$ Hz, H(5)); 2.47 (dd, $J_{4a,5} = 5.2$, $J_{4a,4b} = 17.6$ Hz, H(4a) cis to H(5)); 2.54 (dd, $J_{4b,5} = 7.9$, $J_{4a,b} = 17.6$ Hz, $H(4_b)$ trans to H(5)); 3.32 (s, NCH_3) ppm. δ(C) 23.1 (CH_3); 28.2 ($C(CH_3)_3$); 28.9 (C(4)); 33.8 (CMe_3); 36.3 (NCH_3); 46.0 (C(5)); 153.2 (C(6)); 166.3 (C(3)) ppm. *m/z* 182 (15, M), 167 (10, M − Me), 137 (46, 167 − 2Me), 126 (72, M − C_4H_8), 125 (100, M − C_4H_9), 57 (72, C_4H_9).

3-Ethoxy-6-methylpyridazine (7)

Silver(I) oxide (4.21 g, 18.16 mmol) and iodoethane (0.87 mL, 10.90 mmol) were added to a solution of the pyridazinone **2** (0.91 g, 8.25 mmol) in MeOH (10 mL) and the suspension was stirred vigorously for 18 h. Workup and chromatography on alumina (CH_2Cl_2) gave 3-ethoxy-6-methyl-pyridazine (0.75 g, 66%) which was distilled to yield a colourless oil, b.p. (Kugelrohr) 50–60°C/0.07 mmHg (lit. [12] b.p. 114–115°C/20 mmHg). ν_{max} (film): 1598, 1450 (C=N, C=C, N=N); 1300, 1028 (C–O) cm^{-1}. δ(H) 1.39 (t, $J = 7.1$ Hz, OCH_2CH_3); 2.56 (s, CH_3); 4.50 (q, $J = 7.1$ Hz, OCH_2Me); 6.82 (d, $J_{4,5} = 9.0$ Hz, H(4)); 7.17 (d, $J_{4,5} = 9.0$ Hz, H(5)) ppm. δ(C) 14.45 (CH_2CH_3); 21.4 (CH_3); 62.8 (OCH_2CH_3); 117.4 (C(4)); 129.7 (C(5)); 154.9 (C(6)); 163.5 (C(3)) ppm. *m/z* 138 (17, M), 123 (32, M − CH_3), 110 (77, M − C_2H_4), 85 (65, M − C_4H_5), 83 (100, 110 − HCN).

Reaction of 3-ethoxy-6-methylpyridazine (7)

(a) With lithium diisopropylamide and benzophenone. Butyllithium (1.6 mol L^{-1} in hexanes, 0.27 mL, 0.43 mmol) was added dropwise to a stirred solution of diisopropylamine (66 μL, 0.47 mmol) in THF (1 mL) at −78°C under nitrogen. The temperature was raised to 0°C after 15 min, and after a further 15 min the solution was cooled to −78°C. A solution of the pyridazine **3** (48 mg, 0.35 mmol) in THF (0.5 mL) was added dropwise, after 5 min the temperature was raised to 0°C, and after a further 1.25 h the solution was cooled to −78°C. A solution of benzophenone (79 mg, 0.43 mmol) in THF (0.5 mL) was added, the mixture was warmed to room temperature, and after 17.5 h treated with a small volume of

water. PLC (CH_2Cl_2) gave (i) diphenylmethanol (17 mg, 22%) as a white solid, m.p. approx. 63°C; and (ii) 3-ethoxy-6-[(2,2-diphenyl-2-hydroxy)ethyl]pyridazine (**8**) (8 mg, 7%) as white crystals, m.p. 163–167°C. Found: $M^{+\cdot}$ 320.1516. $C_{20}H_{20}N_2O_2$ calc.: $M^{+\cdot}$ 320.1525. ν_{max} ($CHCl_3$): 3300 (OH); 1600, 1447 (C=N, C=C, N=N); 1300, 1020 (C–O) cm^{-1}. δ(H) 1.41 (t, $J_{obs} = 7.3$, 7.1 Hz, OCH_2CH_3); 3.79 (s, CH_2); 4.47 (q, $J_{obs} = 7.3$, 7.1, 7.1 Hz, OCH_2CH_3); 6.27 (s, OH); 6.78 (d, $J_{4,5} = 9.0$ Hz, H(4)); 7.01 (d, $J_{4,5} = 9.0$ Hz, H(5)); 7.18 (t, $J_{obs} = 7.4$, 7.2 Hz, 2H(4′)); 7.27 (apparent t, $J = 7.7$, 7.5 Hz, 2H(3′, 5′)); 7.45 (d, $J = 7.2$ Hz, 2(H2′, 6′)) ppm. δ(C) 14.5 (OCH_2CH_3); 45.7 (CH_2); 63.2 (OCH_2Me); 78.1 (COH); 118.1 (C(4)); 126.2 (2C(2′, 6′)); 126.8 (2C(4′)); 128.1 (2C(3′, 5′)); 131.2 (C(5)); 146.5 (2C(1′)); 156.4 (C(6)); 163.7 (C(3)) ppm. *m/z* 320 (3, M), 301 (10, $M - H - H_2O$), 273 (7, $301 - C_2H_4$), 201 (100, $M - C_6H_5C(OH)=CH$), 173 (12, $201 - C_2H_4$), 138 (25, $M - Ph_2CO$), 105 (60, PhCO), 77 (40, Ph).

(b) With butyllithium and iodomethane. Butyllithium (1.48 mol L^{-1} in hexanes, 0.15 mL, 0.22 mmol) was added dropwise to a stirred solution of **3** (28 mg, 0.20 mmol) in THF (0.75 mL) at −100°C under nitrogen, and after 1 min iodomethane (14 μL, 0.22 mmol) was added. Water (0.05 mL) was added after 40 min and the mixture worked up and chromatographed (PLC) (EtOAc) to yield 5-butyl-3-ethoxy-6-methylpyridazine (**9**) (4 mg, 10%) as a colourless oil. Found: $M^{+\cdot}$ 194.1417. $C_{11}H_{18}N_2O$ calc.: $M^{+\cdot}$ 194.1419). *m/z* 194 (18, M), 179 (12, M − Me), 165 (47, $M - C_2H_5$), 151 (14, $M - C_3H_7$), 137 (60, $M - C_4H_9$), 124 (82, $M - C_2H_4 - C_3H_6$), 108 (32, $M - C_2H_5 - C_4H_9$), 43 (100, C_3H_7).

Oxidation of 3-ethoxy-6-methylpyridazine (7)

A solution of the pyridazine **7** (0.80 g, 2.19 mmol) and 30% H_2O_2 (0.75 mL, 6.58 mmol) in acetic acid (2 mL) was heated at 90°C for 7.5 h. Workup and chromatography on alumina (EtOAc/hexanes, 1:1), yielded 3-ethoxy-6-methylpyridazine-1-oxide (**11**) (0.22 g, 66%) as a white solid, m.p. 93–95°C (lit. [12] m.p. 91–92°C). ν_{max} (KBr): 1600, 1565, 1450 (C=N, C=C, N=N); 1277 (N → O) cm^{-1}. δ(H) 1.41 (t, $J = 7.1$ Hz, OCH_2CH_3); 2.46 (s, CH_3); 4.40 (q, $J = 7.0$ Hz, OCH_2CH_3); 6.68 (d, $J_{4,5} = 8.6$ Hz, H(4)); 7.55 (d, $J_{4,5} = 8.6$ Hz, H(5)) ppm. δ(C) 14.3 (OCH_2CH_3); 17.5 (CH_3); 63.9 (OCH_2CH_3); 108.1 (C(4)); 135.8 (C(5)); 136.3 (C(6)); 163.7 (C(3)) ppm. *m/z* (DEI$^+$) 154 (100, M), 137 (18, M − HO), 126 (16, $M - C_2H_4$), 109 (31, $M - HO - C_2H_4$).

The oxide **11** was also obtained (66%) when the reaction was carried out at 80°C for 24 h.

Reaction of 3-ethoxy-6-methylpyridazine-1-oxide (11) with butyllithium and iodomethane

Butyllithium (1.57 mol L^{-1} in hexanes, 0.09 mL, 0.14 mmol) was added dropwise to a stirred solution of the pyridazine-1-oxide (**11**) (20 mg, 0.13 mmol) in THF (0.5 mL) at −78°C under nitrogen. Iodomethane (9 μL, 0.14 mmol) was added after 3 min, and the mixture was warmed to room temperature after 15 min. After 1 h, workup and chromatography (EtOAc/hexanes, 1:1) gave (i) 3-ethoxy-6-ethylpyridazine-1-oxide (**12**) (18 mg, 83%) which was distilled at 55–60°C/0.075 mmHg to give white crystals, m.p. 51–53°C. Anal. Found: C, 57.4; H, 7.5; N, 16.9%; $M^{+\cdot}$ 168.0891. $C_8H_{12}N_2O_2$ calc.: C, 57.1; H, 7.2; N, 16.7%; $M^{+\cdot}$ 168.0899.

ν_{max} (film): 1556, 1452 (C=N, C=C, N=N); 1265 (N → O) cm^{-1}. δ(H) 1.29 (t, $J = 7.5$ Hz, CH_2CH_3); 1.40 (t, $J = 7.1$ Hz, OCH_2CH_3); 2.86 (q, $J_{obs} = 7.5$, 7.7 Hz, CH_2CH_3); 4.41 (q, $J = 7.1$ Hz, OCH_2CH_3); 6.63 (d, $J_{4,5} = 8.7$ Hz, H(4)); 7.44 (d, $J_{4,5} = 8.8$ Hz, H(5)) ppm. δ(C) 10.2 (CH_2CH_3); 14.3 (OCH_2CH_3); 23.7 (CH_2CH_3); 63.9 (OCH_2CH_3); 107.9 (C(4)); 133.7 (C(5)); 140.9 (C(6)); 163.5 (C(3)) ppm. *m/z* 168 (51, M), 151 (39, M − HO), 139 (17, M − C_2H_5), 123 (100, 151 − C_2H_4); and (ii) **11** (3 mg, 15%).

Repetition of the reaction using butyllithium (1.6 molar equiv.), a lithiation period of 15 min, and iodomethane (10 molar equiv.) followed by PLC (EtOAc) yielded (i) 3-ethoxy-6-(1-methylethyl)pyridazine-1-oxide (**13**) (6 mg, 26%) as a colourless oil. Found: $M^{+\cdot}$ 182.1060. $C_9H_{14}N_2O_2$ calc.: $M^{+\cdot}$ 182.1055. δ(H) 1.27 (d, $J = 6.9$ Hz, $CH(CH_3)_2$); 1.40 (t, $J = 7.1$ Hz, OCH_2CH_3); 3.58 (septet, $J_{obs} = 6.7$, 6.9, 6.9, 7.0, 6.7, 6.7 Hz, $CHMe_2$); 4.41 (q, $J_{obs} = 7.0$, 7.1, 7.2 Hz, OCH_2CH_3); 6.63 ($J_{4,5} = 8.8$ Hz, H(4)); 7.42 (d, $J_{4,5} = 8.8$ Hz, H(5)) ppm. *m/z* 182 (43, M), 165 (53, M − HO), 154 (73, M − C_2H_4), 137 (100, M − HO−C_2H_4); and (ii) **12** (9 mg, 42%).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-[6-(3-ethoxy-1-oxido)pyridinylmethyl]-2,4-cyclohexadien-1-yl]iron (21)*

(a) Using a lithio carbanion. Butyllithium (1.7 mol L^{-1} in hexanes, 1.03 mL, 1.75 mmol) was added dropwise to a stirred solution of **11** (0.24 g, 1.56 mmol) in THF (35 mL) at −100°C under nitrogen, and after 5 min the iron complex **15** [8] (0.72 g, 1.74 mmol) was added. After 1 min the mixture was warmed to −78°C, and after 30 min was warmed to room temperature. After 2.5 h, a small volume of water was added and the mixture was worked up and chromatographed on alumina (CH_2Cl_2/hexanes, 2:1) to yield (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-[6-(3-ethoxy-1-oxido)pyridazinylmethyl]-2,4-cyclohexadien-1-yl]iron (0.45 g, 69%) as an orange solid, m.p. 117–121°C. Anal. Found: C, 52.0; H, 4.5; N, 6.5%; $M^{+\cdot}$−O, 404.0118. $C_{18}H_{18}Cl_2FeN_2O_2$ calc.: C, 51.3; H, 4.3; N, 6.7%; $M^{+\cdot}$−O, 404.0146. ν_{max} ($CHCl_3$): 1555, 1438 (C=N, C=C, N=N); 1245 (N → O) cm^{-1}. δ(H) 1.38 (t, $J = 7.1$ Hz, OCH_2CH_3); 1.79 (dd, $J_{Ha,6} = 6.8$, $J_{Ha,Hb} = 13.2$ Hz, H_a); 2.03 (dd, $J_{Hb,6} = 7.1$, $J_{Ha,Hb} = 13.2$ Hz, H_b); 3.25 (dd, $J_{1,3} = 1.8$, $J_{1,6} = 7.0$ Hz, H(1)); 3.62 (apparent dq, $J_{4,6} = 1.6$, $J = 6.9$ Hz, H(6)); 4.37 (q, $J = 7.1$ Hz, OCH_2CH_3); 4.41 (s, C_5H_5); 4.58 (dd, $J_{4,6} = 1.6$, $J_{3,4} = 5.2$ Hz, H(4)); 6.10 (dd, $J_{1,3} = 1.8$, $J_{3,4} = 5.2$ Hz, H(3)); 6.48 (d, $J_{4'5'} = 8.7$ Hz, H(4')); 7.09 (d, $J_{4'5'} = 8.7$ Hz, H(5')) ppm. δ(C) 14.3 (OCH_2CH_3); 35.2 (C(1)); 38.8 (CH_2); 44.3 (C(6)); 62.6 (C(5)); 63.9 (OCH_2CH_3); 74.1 (C(4)); 77.6 (C(3)); 78.3 (C_5H_5); 101.5 (C(2)); 107.3 (C(4)); 135.5 (C(6')); 136.0 (C(5')); 163.7 (C(3')) ppm. *m/z* M not observed, 404 (1, M − O), 403 (1, M − HO), 367 (2, 403 − HCl), 338 (1, 367 − C_2H_5), 267 (100, M − $CH_2C_6H_7N_2O_2$), 121 (35, C_5H_5Fe).

(b) Using a trimethylsilyl-masked carbanion. Tetrabutylammonium fluoride (1 mol L^{-1} in THF, 0.26 mL, 0.26 mmol) was added dropwise to a stirred suspension of the complex **15** (0.11 g, 0.26 mmol) and 3-ethoxy-6-(trimethylsilyl)methylpyridazine-1-oxide **14** (see below) (58 mg, 0.26 mmol) in THF (10 mL) at room temperature under nitrogen. After 20 min, the solvent was removed and the residue triturated with hexanes. Workup and chromatography on alumina (CH_2Cl_2/hexanes, 2:1) yielded the complex **21** (45.5 mg, 42%) and the desilylated pyridazine-1-oxide **11** (12.5 mg, 32%).

3-Ethoxy-6-(trimethylsilyl)methylpyridazine 1-oxide (14)

A cooled (−100°C) and stirred solution of the pyridazine-1-oxide **11** (0.10 g, 0.65 mmol) in THF (2.25 mL) under nitrogen was treated dropwise with butyllithium (1.9 mol L^{-1} in hexanes, 0.38 mL, 0.71 mmol) and after 5 min chlorotrimethylsilane (0.46 mL, 3.62 mmol) was added. After 1 min the mixture was warmed to −78°C, and after 2.5 h was warmed to room temperature. After 15 h, workup and chromatography (EtOAc/hexanes, 2:1) yielded (i) 3-ethoxy-6-(trimethylsilyl)methylpyridazine-1-oxide (54 mg, 37%) as unstable white crystals, m.p. 37–41°C. ν_{max} (film): 1553, 1450 (C=N, C=C, N=N); 1315 (C–O); 1254 ($SiMe_3$), 1230 (N → O), 1025 (C–O), 840 ($SiMe_3$) cm^{-1}. δ(H) 0.05 (s, $Si(CH_3)_3$); 1.35 (t, $J = 7.1$ Hz, OCH_2CH_3); 2.32 (s, CH_2); 4.34 (q, $J = 7.1$ Hz, OCH_2CH_3); 6.51 (d, $J_{4,5} = 8.7$ Hz, H(4)); 7.23 (d, $J_{4,5} = 8.7$ Hz, H(5)) ppm. δ(C) 1.0 ($Si(CH_3)_3$); 14.2 (OCH_2CH_3); 21.7 (CH_2); 63.6 (OCH_2CH_3); 107.6 (C(4)); 134.3 (C(5)); 139.4 (C(6)); 162.5 (C(3)) ppm; and (ii) **11** (22 mg, 21%).

6-(2,2-Dimethylpropyl)-3-ethoxypyridazine (10)

Reaction of **11** (0.65 mmol) with BuLi as above and then with a cooled (−75°C) solution of t-butylchlorodimethylsilane (2.71 mmol) in THF (1 mL) followed by PLC (EtOAc/hexanes, 1:3) gave (i) 6-(2,2-dimethylpropyl)-3-ethoxypyridazine (12 mg, 9%) as a colourless oil, b.p. (Kugelrohr) 60–65°C/0.05 mmHg. Anal. Found: C, 67.8; H, 9.5; N, 14.4. $C_{11}H_{18}N_2O$ calc.: C, 68.0; H, 9.3; N, 14.4%. ν_{max} (film): 1594, 1470, 1440 (C=N, C=C, N=N); 1290, 1023 (C–O) cm^{-1}. δ(H) 0.96 (s, $C(CH_3)_3$); 1.43 (t, $J = 7.1$ Hz, OCH_2CH_3); 2.75 (s, CH_2); 4.55 (q, $J = 7.1$ Hz, OCH_2CH_3); 6.84 (d, $J_{4,5} = 9.0$ Hz, H(4)); 7.17 (d, $J_{4,5} = 9.0$ Hz, H(5)) ppm. δ(C) 14.6 (OCH_2CH_3); 29.4 ($C(CH_3)_3$); 32.0 (CMe_3); 49.0 (CH_2); 62.9 (OCH_2CH_3); 116.6 (C(4)); 130.8 (C(5)); 156.7 (C(6)); 163.6 (C(3)) ppm. m/z 194 (2, M), 179 (14, M − CH_3), 138 (100, M − C_4H_8), 110 (54, 138 − C_2H_4); and (ii) **11** (40 mg, 40%).

Oxidative demetallation of 21

(a) DDQ (11.5 mg, 0.051 mmol) was added to a stirred solution of the complex **21** (21 mg, 0.05 mmol) in acetonitrile (0.5 mL), and after 1.5 h the solid was filtered off and washed with CH_2Cl_2. Solvent was removed from the filtrate and washings and the residue was chromatographed on alumina (CH_2Cl_2/hexanes, 2:1) and re-chromatographed (PLC) to yield 3-ethoxy-6-(2,5-dichlorophenyl)methylpyridazine-1-oxide (**28**) (6 mg, 43%) as a white solid, m.p. 80–83°C. Anal. Found: C, 52.6; H, 4.1; N, 9.0. $C_{13}H_{12}Cl_2N_2O_2$ calc.: C, 52.2; H, 4.0; N, 9.4%. ν_{max} ($CHCl_3$): 1562, 1455 (C=N, C=C, N=N); 1245 (N → O) cm^{-1}. δ(H) 1.41 (t, $J = 7.1$ Hz, OCH_2CH_3); 4.21 (s, CH_2); 4.42 (q, $J = 7.1$ Hz, OCH_2CH_3); 6.57 (d, $J_{4,5} = 8.9$ Hz, H(4)); 7.16 (d, $J_{4,5} = 8.8$ Hz, H(5)); 7.25 (dd, $J_{4',6'} = 2.5$, $J_{3',4'} = 8.5$ Hz, H(4')); 7.34 (d, $J_{3',4'} = 8.5$ Hz, H(3')); 7.40 (d, $J_{4',6'} = 2.4$ Hz, H(6')). δ(C) 14.3 (OCH_2CH_3); 34.4 (CH_2); 64.2 (OCH_2CH_3); 107.8 (C(4)); 129.1 (C(4')); 130.8 (C(3')); 131.9 (C(6')); 132.9 (C(5')); 133.1 (C(2')); 134.7 (C(5)); 135.2 (C(6')); 136.5 (C(1')); 164.0 (C(3)) ppm. m/z M not observed, 281 (4, M − HO), 263 (70, M − Cl), 152 (100, M − $C_6H_4Cl_2$).

(b) Treatment of the complex **21** (20 mg, 0.05 mmol) (12 mg, 0.05 mmol) in acetonitrile (0.5 mL), with 2,3,5,6-tetrachloro-1,4-benzoquinone for 1.5 h and PLC (CH_2Cl_2) gave **28** (5 mg, 33%).

(c) Treatment of the complex **21** (10 mg, 0.02 mmol) in MeOH (2 mL) with NBS (14 mg, 0.08 mmol) under reflux for 6 h and chromatography on alumina (CH_2Cl_2/hexanes, 1:1) gave **28** (2 mg, 34%).

(d) Treatment of the complex **21** (22.5 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL) with bis(acetato-O)phenyliodine (17 mg, 0.05 mmol) for 18 h, followed by concentrated H_2SO_4 (10 μL) and then a solution of ammonium hexafluorophosphate (10 mg, 0.06 mmol) in water (70 μL) and workup gave **28** (2 mg, 13%).

(e) Other oxidants (1,4-benzoquinone, trimethylamine N-oxide, and triphenylmethylithium tetrafluoroborate) either gave no reaction or required heating for some conversion to occur, in which case a mixture was obtained.

Reaction of 3-ethoxy-6-(2,5-dichlorophenyl)methylpyridazine-1-oxide (28) with phosphorus trichloride

A solution of **28** (0.19 mmol) in chloroform was treated with phosphorus trichloride (0.58 mmol) for 3 days. Workup and chromatography gave (i) 4-chloro-3-ethoxy-6-(2,5-dichlorophenyl)methylpyridazine (**31**) (6 mg, 10%) as a colourless oil. Found: M^+·–Cl· 281.0253. $C_{13}H_{11}Cl_3N_2O$ calc.: M^+·–Cl· 281.0248). ν_{max}: 1466, 1431 (C=N, C=C, N=N); 1300, 1015 (C–O) cm^{-1}. δ(H) 1.49 (t, $J = 7.1$ Hz, OCH_2CH_3); 4.31 (s, CH_2); 4.63 (q, $J = 7.1$ Hz, OCH_2CH_3); 7.19 (dd, $J_{4',6'} = 2.5$, $J_{3',4'} = 8.6$ Hz, H(4')); 7.31 (s, H(5)); 7.32 (d, $J_{3',4'} = 8.6$ Hz, H(3')); 7.32 (d, $J_{4',6'} = 2.5$ Hz, H(6')) ppm. δ(C) 14.4 (OCH_2CH_3); 38.6 (CH_2); 64.5 (OCH_2CH_3); 127.8 (C(4)); 128.7 (C(5')*); 128.7 (C(4')*); 130.8 (C(3')); 131.3 (C(6')); 132.2 (C(5')); 133.0 (C(2')); 137.4 (C(1')); 156.2 (C(6)); 160.3 (C(3)) ppm. *m/z* M not observed, 314 (< 1, M – H_2), 281 (100, M – Cl), 253 (70, 281 – C_2H_4), 218 (53, 253 – Cl); and (ii) 3-ethoxy-6-(2,5-dichlorophenyl)methylpyridazine (**30**) (31 mg, 63%) which after PLC on alumina (CH_2Cl_2/hexanes, 1:2) and crystallization at 4°C gave white needles, m.p. 59.5–60.5°C. Anal. Found: C, 55.3; H, 4.4; N, 9.5%; M^+·–Cl· 247.0638. $C_{13}H_{12}Cl_2N_2O$ calc.: C, 55.1; H, 4.3; N, 9.9%; M^+·–Cl· 247.0638. ν_{max} (film): 1467, 1437 (C=N, C=C, N=N); 1295, 1020 (C–O) cm^{-1}. δ(H) 1.42 (t, $J = 7.1$ Hz, OCH_2CH_3); 4.32 (s, CH_2); 4.55 (q, $J = 7.1$ Hz, OCH_2CH_3); 6.86 (d, $J_{4,5} = 9.1$ Hz, H(4)); 7.16 (dd, $J_{4',6'} = 2.5$, $J_{3',4'} = 8.5$ Hz, H(4')); 7.22 (d, $J_{4,5} = 9.1$ Hz, H(5)); 7.30 (d, $J_{3',4'} = 8.7$ Hz, H(3')); 7.31 (d, $J_{4',6'} = 1.6$ Hz, H(6')) ppm. δ(C) 14.5 (OCH_2CH_3): 38.9 (CH_2); 63.2 (OCH_2CH_3); 117.8 (C(4)); 128.3 (C(4')); 129.4 (C(5)); 130.6 (C(3')); 131.3 (C(6')); 132.2 (C(5')); 132.9 (C(2')); 138.1 (C(1')); 155.8 (C(6)); 163.9 (C(3)) ppm. *m/z* M not observed, 281 (< 1, M – H), 267 (1, M – Me), 253 (1, M – C_2H_5), 247 (100, M – Cl), 219 (60, 247 – C_2H_4), 184 (58, 219 – Cl).

Repetition of the reaction with heating under reflux for 5 h gave the same results.

Hydrolysis of 3-ethoxy-6-(2,5-dichlorophenyl)methylpyridazine (30)

A solution of the methylpyridazine **30** (15 mg, 0.05 mmol) in EtOH (0.5 mL) and 10% aqueous HCl (1 mL) was heated under reflux for 24 h. Workup gave 6-(2,5-dichlorophenyl)methyl-3(2*H*)-pyridazinone (**32**) (13 mg, 96%) which crystallized from CH_2Cl_2/hexanes (isopiestic, at 4°C) as off-white crystals, m.p. 178–181°C. Anal. Found: C, 52.1; H, 3.1; N, 11.1. $C_{11}H_8Cl_2N_2O$ calc.: C, 51.8; H, 3.2; N, 11.0%. ν_{max} (KBr): 3075 (NH); 1673 (CO); 1652 (C=N, C=C) cm^{-1}. δ(H) 4.04 (s, CH_2); 6.92 (d, $J_{4,5} = 9.7$ Hz, H(4)); 7.18 (d, $J_{4,5} = 9.3$ Hz, H(5)); 7.20 (dd, $J_{obs} = 1.9$, 2.4, $J_{3',4'} = 8.5$ Hz, H(4')); 7.23 (d, $J_{4',6'} = 2.3$ Hz, H(6')); 7.33 (d, $J_{3',4'} = 8.5$ Hz, H(3')); 11.98 (s, NH) ppm. δ(C) 37.9 (CH_2); 128.7 (C(4')); 130.6 (C(4)); 130.8 (C(3')); 131.0 (C(6')); 132.3 (C(5')), 133.0 (C(2')); 133.9 (C(5)); 136.7 (C(1')); 146.0

(C(6)); 161.5 (C(3)) ppm. *m/z* M not observed, 219 (100, M − Cl), 184 (62, 219 − Cl).

Reaction of (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (16) with 3-ethoxy-6-methylpyridazine-1-oxide (11)

Butyllithium (2.14 mol L^{-1} in hexanes, 0.14 mL, 0.30 mmol) was added dropwise to a stirred solution of **11** (40 mg, 0.26 mmol) in THF (6 mL) at −100°C under nitrogen, and after 5 min the complex **16** (0.12 g, 0.29 mmol) was added. After 1 min the mixture was warmed to −78°C, and after 15 min warmed to room temperature. After 1.5 h, workup and chromatography on alumina (CH_2Cl_2/hexanes/Et_3N, 30:60:1, and CH_2Cl_2/hexanes, 2:1) yielded (η^5-2,4-cyclopentadien-1-yl)-[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-[6-(3-ethoxy-1-oxido)pyridazinylmethyl]-2,4-cyclohexadien-1-yl]iron (**22**) (41 mg, 37%) as an orange solid, m.p. 135.5–137.5°C. Anal. Found: C, 51.0; H, 4.8; N, 6.4. $C_{18}H_{18}Cl_2FeN_2O_2$ calc.: C, 51.3; H, 4.3; N, 6.7%. ν_{max} ($CHCl_3$): 1560, 1452 (C=N, C=C, N=N); 1250 (N → O) cm^{-1}. δ(H) 1.38 (t, J = 7.1 Hz, OCH_2CH_3); 1.77 (dd, $J_{Ha,6}$ = 7.8, $J_{Ha,Hb}$ = 13.3 Hz, H_a); 1.94 (dd, $J_{Hb,6}$ = 5.9, $J_{Ha,Hb}$ = 13.3 Hz, H_b); 2.90 (5 lines, $J_{1,3}$ = 1.1, J_{obs} = 6.7, 6.3 Hz, H(1)); 3.67 (6 lines, $J_{2,6}$ = 0.7, J_{obs} = 6.7, 6.8, 6.9 Hz, H(6)); 4.24 (apparent t, J = 5.5, 5.7 Hz, H(2)); 4.37 (q, J = 7.1 Hz, OCH_2CH_3); 4.38 (s, C_5H_5); 6.20 (dd, $J_{1,3}$ = 1.1, $J_{2,3}$ = 5.0 Hz, H(3)); 6.48 (d, $J_{4',5'}$ = 8.6 Hz, H(4')); 7.08 (d, $J_{4',5'}$ = 8.6 Hz, H(5')) ppm. δ(C) 14.2 (OCH_2CH_3); 34.2 (C(1)); 38.5 (CH_2); 43.8 (C(6)); 62.2 (C(5)); 63.8 (OCH_2,CH_3); 75.1 (C(2)); 78.17 (C_5H_5); 78.21 (C(3)); 100.8 (C(4)); 107.3 (C(4')); 135.7 (C(6')); 136.0 (C(5')); 163.6 (C(3')) ppm. *m/z* M not observed, 404 (1, M − O), 403 (< 1, M − HO), 368 (1, 403 − Cl), 367 (1, 403 − HCl), 338 (2, 367 − C_2H_5), 267 (100, M − $CH_2C_6H_7N_2O_2$), 231 (36, 267 − HCl).

Reaction of (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichloro-4-methylbenzene)iron(1 +) hexafluorophosphate(1 −) (17) with 3-ethoxy-6-methylpyridazine-1-oxide (11)

Reaction of **11** with **17** as above and chromatography of the product on alumina (CH_2Cl_2/hexanes, 2:1) yielded a mixture (2:1) (^{1}H NMR) (53%) of (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-1-methyl-6-*exo*-[6-(3-ethoxy-1-oxido)-pyridazinylmethyl]-2,4-cyclohexadien-1-yl]iron (**23**) and (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-2-methyl-6-*exo*-[6-(3-ethoxy-1-oxido)pyridazinylmethyl]-2,4-cyclohexadien-1-yl]iron (**24**) which was re-chromatographed on alumina to give an orange oil. Anal. Found: C, 51.9; H, 4.7; N, 6.4. $C_{19}H_{20}Cl_2FeN_2O_2$ calc.: C, 52.5; H, 4.6; N, 6.4%. ν_{max} ($CHCl_3$): 1560, 1450 (C=N, C=C, N=N); 1250 (N → O) cm^{-1}. δ(H) (**23**): 1.38 (t, J = 7.1 Hz, OCH_2CH_3); 1.57 (s, CH_3); 1.75 (dd, $J_{Ha,6}$ = 7.7, $J_{Ha,Hb}$ = 13.0 Hz, H_a); 2.16 (dd, $J_{Hb,6}$ = 4.8, $J_{Ha,Hb}$ = 13.1 Hz, H_b); 3.67 (dd, $J_{Hb,6}$ = 4.9, $J_{Ha,6}$ = 7.7 Hz, H(6)); 3.99 (d, $J_{2,3}$ = 4.9 Hz, H(2)); 4.27 (s, C_5H_5); 4.36 (q, J = 7.1 Hz, OCH_2CH_3); 6.01 (d, $J_{2,3}$ = 5.0 Hz, H(3)); 6.48 (d, $J_{4',5'}$ = 8.7 Hz, H(4')); 7.10 (d, $J_{4',5'}$ = 8.7 Hz, H(5')); and (**24**): 1.38 (t, J = 7.1 Hz, OCH_2CH_3); 1.78 (s, CH_3); 1.85 (dd, J_{obs} = 7.2, 7.4, $J_{Ha,Hb}$ = 13.4 Hz, H_a); 1.92 (dd, J_{obs} = 5.8, 5.6, $J_{Ha,Hb}$ = 13.2 Hz, H_b); 2.91 (d, $J_{1,6}$ = 6.6 Hz, H(1)); 3.61 (apparent q, J = 6.5, 6.6, 6.8 Hz, H(6)); 4.29 (s, C_5H_5); 4.36 (q, J = 7.1 Hz, OCH_2CH_3); 6.08 (s, H(3)); 6.48 (d, $J_{4',5'}$ = 8.6 Hz, H(4')); 7.06 (d, $J_{4',5'}$ = 8.7 Hz, H(5')) ppm. δ(C) (**28**): 14.3 (OCH_2CH_3); 23.5 (CH_3); 36.1 (CH_2); 49.5 (C(1)); 49.9 (C(6)); 61.5 (C(5)); 63.8 (OCH_2Me); 75.66 (C(2)); 75.7 (C(3)); 80.0 (C_5H_5); 100.1 (C(4)); 107.2 (C(4')); 136.1 (C(6)); 136.3 (C(5')); and (**24**): 14.3 (OCH_2CH_3); 21.3 (CH_3); 36.4 (C(1));

38.4 (CH_2); 44.9 (C(6)); 62.2 (C(5)); 63.8 (OCH_2CH_3); 78.6 (C(3)); 78.7 (C_5H_5); 90.3 (C(2)); 100.0 (C(4)); 107.2 (C(4')); 135.9 (C(6')); 136.0 (C(5')); 163.2 (C(3')) ppm. *m/z* (DEI^+) 434 (2, M), 417 (1, M − HO), 381 (1 − 417 − HCl), 281 (100, M − $CH_2C_6H_7N_2O_2$).

Reaction of (η⁶-chlorobenzene)(η⁵-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (18) with 3-ethoxy-6-methylpyridazine-1-oxide (11)

Reaction of **11** with **18** as above at −78°C for 2.5 h, and workup after 16 h yielded [(1,2,3,4,5-η)-5-chloro-6-*exo*-[6-(3-ethoxy-1-oxido)pyridazinylmethyl]-2,4-cyclohexadien-1-yl] (η⁵-2,4-cyclopentadien-1-yl)iron (**25**) as an unstable orange oil (100%). δ(H) 1.37 (t, $J = 7.0$ Hz, OCH_2CH_3); 1.80 (dd, $J_{Ha,6} = 6.5$, $J_{Ha,Hb} = 13.3$ Hz, H_a); 1.89 (dd, $J_{Hb,6} = 7.2$, $J_{Ha,Hb} = 13.2$ Hz, H_b); 2.87 (t, $J = 6.5$ Hz, H(1)); 3.53 (apparent q, $J = 6.7$ Hz, H(6)); 4.19 (t, $J = 5.5$ Hz, H(2)); 4.34 (s, C_5H_5); 4.40 (m, OCH_2CH_3); 4.55 (d, $J_{3,4} = 5.0$ Hz, H(4)); 5.85 (t, $J = 5.0$ Hz, H(3)); 6.47 (d, $J_{4',5'} = 8.6$ Hz, H(4')); 7.11 (d, $J_{4',5'} = 8.6$ Hz, H(5')) ppm. δ(C) 14.3 (OCH_2CH_3); 33.8 (C(1)); 38.8 (CH_2); 42.0 (C(6)); 63.8 (OCH_2Me); 63.9 (C(5)); 75.6 (C_5H_5); 76.3 (C(2)); 77.6 (C(4)); 79.1 (C(3)); 107.3 (C(4')); 136.0 (C(5')); 136.2 (C(6')); 163.5 (C(3')) ppm.

Reaction at −100°C for 1 min and then at −78°C for 15 min before warming to room temperature gave a mixture (approx. 1:3) of **25** and **11**.

Reaction of the complex 25 with DDQ

DDQ (29 mg, 0.13 mmol) was added to a stirred solution of a mixture (1:1) (51 mg) of the complex **25** (0.01 mmol) and **11** (0.09 mmol) in CH_2Cl_2 (1 mL). After 1 h workup and chromatography on alumina (CH_2Cl_2/hexanes, 1:2) gave 3-ethoxy-6-(2-chlorophenyl)methylpyridazine-1-oxide (**29**) (2.5 mg, 10%) as a colourless oil. Found: $M^{+\cdot}$ 264.0653. $C_{13}H_{13}ClN_2O_2$ calc.: $M^{+\cdot}$ 264.0666. δ(H) 1.40 (t, $J = 7.1$ Hz, OCH_2CH_3); 4.25 (s, CH_2); 4.41 (q, $J = 7.1$ Hz, OCH_2CH_3); 6.53 (d, $J_{4,5} = 8.8$ Hz, H(4)); 7.06 (d, $J_{4,5} = 8.8$ Hz, H(5)); 7.26–7.30 (m, H(4',6')); 7.36–7.44 (m, H(3',5')) ppm. *m/z* 264 (2, M), 247 (4, M − HO), 229 (100, M − Cl), 201 (58, 229 − C_2H_4), 184 (46, M − $HO^{\cdot}$−$Cl^{\cdot}$−C_2H_4), 153 (11, $CH_2C_6H_7N_2O_2$), 127 (67, C_7H_8Cl).

Reaction of (η⁵-2,4-cyclopentadien-1-yl)(η⁶-1,4-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (15)

(a) With a 4-methylphenoxide. A solution of 4-methylphenol (33 mg, 0.30 mmol) in DMF (1 mL) and NaH (50% dispersion in paraffin, 16 mg, 0.33 mmol, washed with hexanes) under nitrogen was treated with a solution of the complex **15** (0.10 g, 0.24 mmol) in DMF (1 mL). The solution was stirred at room temperature in the dark for 3 h, solvent was removed, and the residue was triturated with CH_2Cl_2. Removal of solvent and then PLC (solvent A) yielded (i) [(1,2,3,4,5,6-η)-1,4-bis(4-methylphenoxy)benzene](η⁵-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (**33**) (33 mg, 24%) which crystallized from Me_2CO/Et_2O (isopiestic, 4°C) as yellow crystals, m.p. 230–232°C (dec). Anal. Found: C, 54.0; H, 4.4. $C_{25}H_{23}F_6FeO_2P$ calc.: C, 54.0; H, 4.2%. ν_{max} (KBr): 1505, 1474 (aryl C=C); 1220 (C–O); 820, 550 (PF) cm^{-1}. δ(H) (CD_3COCD_3): 2.37 (s, $2CH_3$); 5.29 (s, C_5H_5); 6.28 (s, H(2,3,5,6)); 7.20 (d, $J = 7.3$ Hz, 2(H2',6')); 7.36 (d, $J = 7.1$ Hz, 2H(3',5')) ppm. δ(C) (CD_3COCD_3): 20.7 ($2CH_3$); 75.4 (C(2,3,5,6)); 78.8 (C_5H_5);

121.3 (2C(2',6')); 132.0 (2C(3',5')); 132.1 (2C(4')); 137.1 (C(1,4)); 152.2 (2C(1)) ppm.; (ii) [(1,2,3,4,5,6-η)-1-chloro-4-(4-methylphenoxy)benzene](η^5-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (**35**) (28 mg, 24%), yellow crystals from Me_2CO, m.p. 166–168°C. Anal. Found: C, 44.7; H, 3.3. $C_{18}H_{16}ClF_6FeOP$ calc.: C, 44.6; H, 3.3%. ν_{max} (KBr): 1500, 1458 (aryl C=C); 1225 (C–O); 820, 550 (PF) cm^{-1}. δ(H) (CD_3COCD_3): 2.38 (s, CH_3); 5.36 (s, C_5H_5); 6.44 (d, J = 6.6 Hz, H(3,5)); 6.80 (d, J = 6.7 Hz, H(2,6)); 7.24 (d, J = 8.3 Hz, H(2',6')); 7.38 (d, J = 8.3 Hz, H(3',5')) ppm. δ(C) (CD_3COCD_3): 20.8 (CH_3); 76.7 (C(3,5)); 80.3 (C_5H_5); 87.7 (C(2,6)); 104.8 (C(1)); 121.4 (C(2',6')); 132.1 (C(3',5')); 134.2 (C(4')); 137.4 (C(4)); 151.6 (C(1')); and (iii) **15** (13 mg, 13%).

Repetition of the experiment by addition of a solution of 4-methylphenol (26 mg, 0.24 mmol) and NaH (13 mg, 0.27 mmol) in THF (2 mL) to the complex **15** (80 mg, 0.19 mmol) in THF (1 mL) in the dark gave the [bis(4-methylphenoxy)-benzene]iron complex **33** (16 mg, 14%) and the [chloro(4-methylphenoxy)-benzene]iron complex **35** (61 mg, 65%).

Repetition of the reaction using KH in HMPA for 35 min and chromatography of the product gave (i) 1,4-bis(4-methylphenoxy)benzene **38** (6 mg, 22%) as a white solid, m.p. 79–81°C. Found: $M^{+\cdot}$ 290.1295. $C_{20}H_{18}O_2$ calc.: $M^{+\cdot}$ 290.1307. ν_{max} (film): 1492 (aryl C=C); 1247, 1205 (C–O); 732 (aromatic) cm^{-1}. δ(H) 2.33 (s, $2CH_3$); 6.90 (d, J = 8.5 Hz, 2H(2',6')); 6.95 (s, H(2,3,5,6)); 7.13 (d, J = 8.1 Hz, 2H(3',5')) ppm. δ(C) 20.7 ($2CH_3$); 118.4 (2C(2',6')); 119.9 (C(2,3,5,6)); 130.2 (2C(3',5')); 132.6 (2C(4')); 152.9 (C(1,4)); 155.4 (2C(1')) ppm. m/z 290 (100, M), 199 (5, $M - CH_3C_6H_4$), 91 (25, $CH_3C_6H_4$); (ii) **33** (13 mg, 26%); and (iii) **35** (9 mg, 20%).

(b) With phenoxide. A solution of phenol (0.14 g, 1.52 mmol) in THF (10 mL) was added to washed NaH (50% dispersion in paraffin, 79.6 mg, 1.66 mmol) under nitrogen and the phenoxide solution was added over 30 min via a syringe pump to a stirred suspension of the complex **15** (0.50 g, 1.21 mmol) in THF (5 mL) in the dark. After 2.5 h, workup and chromatography on alumina (CH_2Cl_2) yielded (i) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5,6-η)-1,4-diphenoxybenzene]iron(1 +) hexafluorophosphate(1 −) (**34**) (37 mg, 6%) which was precipitated from Me_2CO/Et_2O as yellow crystals, m.p. 213–216°C (dec). Anal. Found: C, 52.4; H, 3.6. $C_{23}H_{19}F_6FeO_2P$ calc.: C, 52.3; H, 3.6%. ν_{max}(KBr): 1470 (aryl C=C); 1210 (C–O); 820, 550 (PF) cm^{-1}. δ(H) (CD_3COCD_3): 5.32 (s, C_5H_5); 6.34 (s, H(2,3,5,6)); 7.32 (d, J = 7.9 Hz, 2H(2',6')); 7.38 (t, J_{obs} = 6.4, 7.2 Hz, 2H(4')); 7.55 (t, J = 7.7 Hz, 2H(3',5')) ppm. δ(C) (CD_3COCD_3): 75.9 (C(2,3,5,6)); 78.9 (C_5H_5); 121.4 (2C(2',6')); 127.3 (2C(4')); 131.6 (2C(3',5')); 131.8 (C(1,4)); 154.6 (2C(1')) ppm; (ii) a mixture (1 : 1) (^{1}H NMR) (0.14 g) of the (diphenoxybenzene)iron complex **34** and the [chloro(phenoxy)benzene]iron complex **36**; and (iii) [(1,2,3,4,5,6-η)-1-chloro-4-phenoxybenzene](η^5-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (**36**) (0.11 g, 18%) which was precipitated from Me_2CO/Et_2O as yellow needles, m.p. 161–163°C. Anal. Found: C, 43.2; H, 3.0. $C_{17}H_{14}ClF_6FeOP$ calc.: C, 43.4; H, 3.0%. ν_{max} (KBr): 1525, 1485, 1455 (aryl C=C); 1230 (C–O); 820, 550 (PF) cm^{-1}. δ(H) (CD_3COCD_3): 5.37 (s, C_5H_5); 6.47 (d, J = 6.9 Hz, H(3,5)); 6.81 (d, J = 6.9 Hz, H(2,6)); 7.35 (d, J = 7.7 Hz, H(2',6')); 7.41 (t, J = 7.4 Hz, H(4')); 7.57 (apparent t, J = 8.4, 7.6 Hz, H(3',5')) ppm. δ(C) (CD_3COCD_3): 77.0 (C(3,5)); 80.4 (C_5H_5); 87.7 (C(2,6)); 104.8 (C(1)); 121.5 (C(2',6')); 127.5 (C(4')); 131.7 (C(3',5')); 133.7 (C(4)); 153.9 (C(1')) ppm. Elution with CH_2Cl_2/EtOH (50 : 1) gave addi-

tional **36** (0.14 g, 26%), and PLC (solvent A) of the mixture (ii) gave **34** (59 mg, 9%) and **36** (61 mg, 11%).

(c) With methoxide. A solution of washed NaH (50% dispersion in paraffin, 35 mg, 0.73 mmol) in MeOH (1 mL) was added dropwise to a stirred ice-cooled solution of the complex **15** (0.10 g, 0.24 mmol) in Me_2CO (0.5 mL) and MeOH (2 mL) in the dark under nitrogen and the mixture was stirred for 1 h. The mixture was warmed to room temperature and after 2.75 h worked up to give (η^5-2,4-cyclopentadien-1-yl)(η^6-1,4-dimethoxybenzene)iron(1 +) hexafluorophosphate-(1 −) (**20**) (74 mg, 76%) which was precipitated from Me_2CO/Et_2O as yellow crystals, m.p. 214–215°C (dec) (lit. [28] m.p. 212–214°C (dec)). ν_{max} (KBr): 1495, 1445 (aryl C=C); 1230 (C–O); 823, 550 (PF) cm^{-1}. δ(H) (CD_3COCD_3): 4.00 (s, $2CH_3O$); 5.15 (s, C_5H_5); 6.26 (s, H(2,3,5,6)) ppm. δ(C) (CD_3COCD_3): 57.6 ($2CH_3O$); 72.6 (C(2,3,5,6)); 77.4 (C_5H_5); 132.7 (C(1,4)) ppm.

Repetition of the reaction, adding methoxide (1 molar equiv.) over 65 min via a syringe pump gave a solid (92 mg) which was chromatographed (PLC) (solvent A) to give (i) a mixture (^{1}H NMR) of the (dimethoxybenzene)iron complex **20** (6.5 mg, 7%) and the [chloro(methoxy)benzene]iron complex **19** (52.5 mg, 53%); and (ii) (η^6-1-chloro-4-methoxybenzene)(η^5-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (**19**) (9 mg, 9%) as a yellow oil. δ(H) (CD_3COCD_3): 4.06 (s, CH_3O); 5.30 (s, C_5H_5); 6.50 (d, J = 6.4 Hz, H(3,5)); 6.75 (d, J = 6.4 Hz, H(2,6)) ppm. δ(C) (CD_3COCD_3): 57.9 (CH_3O); 74.6 (C(3,5)); 79.7 (C_5H_5); 87.6 (C(2,6)); 104.3 (C(1)); 135.2 (C(4)) ppm.

Reaction of (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (15) with methoxide

A solution of washed NaH (50% dispersion in paraffin, 13 mg, 0.27 mmol) in MeOH (10 mL) was added with stirring over 55 min via a syringe pump to an ice-cooled solution of the complex **15** (0.10 g, 0.24 mmol) in Me_2CO (0.5 mL) and MeOH (15 mL) in the dark under nitrogen. The mixture was stirred for 1 h, the solution acidified with 10% hydrochloric acid, and the mixture worked up to give a solid which was precipitated from Me_2CO/Et_2O to yield (η^6-1-chloro-2-methoxybenzene)(η^5-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (**38**) (82 mg, 83%) as yellow crystals, m.p. 121–124°C. ν_{max} (KBr): 1520, 1463 (aryl C=C); 1255 (C–O); 820, 550 (PF) cm^{-1}. δ(H) (CD_3COCD_3): 4.20 (s, CH_3O); 5.21 (s, C_5H_5); 6.27 (t, J = 5.9 Hz, H(5)); 6.35 (apparent t, J = 6.2, 6.0 Hz, H(4)); 6.66 (d, $J_{3,4}$ = 6.5 Hz, H(3)); 6.78 (d, $J_{5,6}$ = 6.1 Hz, H(6)) ppm. δ(C) (CD_3COCD_3): 58.6 (CH_3O); 72.7 (C(3)); 79.4 (C_5H_5); 84.7 (C(5)); 86.3 (C(4)); 88.8 (C(6)); 97.3 (C(1)); 132.8 (C(2)) ppm.

Reaction of [(1,2,3,4,5,6-η)-1-chloro-4-(4-methylphenoxy)benzene](η^5-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (35) with 3-ethoxy-6-methylpyridazine-1-oxide (11)

Butyllithium (2.0 mol L^{-1} in hexanes, 0.06 mL, 0.12 mmol) was added dropwise to a stirred solution of **11** (16 mg, 0.01 mmol) in THF (2 mL) at −100°C under nitrogen, and after 5 min the complex **35** (27 mg, 0.06 mmol) was added. After 1 min the mixture was warmed to −78°C, and after 2.5 h warmed to room temperature. Workup after 16 h and chromatography on alumina (CH_2Cl_2/hexanes, 2:1) gave [(1,2,3,4,5-η)-5-chloro-6-*exo*-[6-(3-ethoxy-1-oxido)pyridazinyl-

methyl]-2-(4-methylphenoxy)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)-iron (**26**) (10 mg, 35%) which crystallized from CH_2Cl_2/hexanes as orange needles, m.p. 137–138.5°C. Anal. Found: C, 61.1; H, 5.1; N, 5.7. $C_{25}H_{25}ClFeN_2O_3$ calc.: C, 60.9; H, 5.1; N, 5.7%. ν_{max} (film): 1554, 1505, 1448 (C=N, C=C, N=N); 1245 (N → O); 1205 (C–O) cm^{-1}. δ(H) 1.37 (t, $J = 7.1$ Hz, OCH_2CH_3); 1.89 (dd, $J_{Ha,6} = 7.8$, $J_{Ha,Hb} = 13.5$ Hz, H_a); 2.05 (dd, $J_{Hb,6} = 6.1$, $J_{Ha,Hb} = 13.5$ Hz, H_b); 2.30 (s, CH_3); 3.17 (dd, $J_{1,3} = 2.2$, $J_{1,6} = 7.1$ Hz, H(1)); 3.56 (6 lines, $J_{4,6} = 1.6$, $J_{obs} = 6.8$, 7.2, 6.8 Hz, H(6)); 4.36 (q, $J = 7.1$ Hz, OCH_2CH_3); 4.40 (s, C_5H_5); 4.56 (dd, $J_{4,6} = 1.7$, $J_{3,4} = 5.4$ Hz, H(4)); 6.00 (dd, $J_{1,3} = 2.2$, $J_{3,4} = 5.4$ Hz, H(3)); 6.41 (d, $J_{4',5'} = 8.7$ Hz, H(4')); 6.81 (d, $J = 8.5$ Hz, H(2'',6'')); 7.06 (d, $J_{4',5'} = 8.7$ Hz, H(3'',5'')); 7.07 (s, $J_{4',5'} = 8.7$ Hz, H(5')) ppm. δ(C) 14.3 (OCH_2CH_3); 20.6 (CH_3); 29.3 (C(1)); 39.1 (CH_2); 43.4 (C(6)); 62.4 (C(5)); 63.8 (OCH_2CH_3); 68.8 (C(3)); 71.7 (C(4)); 76.8 (C_5H_5); 107.2 (C(4')); 118.4 (C(2'',6'')); 127.0 (C(2)); 130.0 (C(3'',5'')); 132.7 (C(4'')); 135.6 (C(5')); 135.8 (C(6')); 155.3 (C(1'')); 163.53 (C(3')) ppm. *m/z* M not observed, 446 (1, M – HO–C_2H_5), 440 (1, M – HO–Cl), 368 (5, M – HO–MeC_6H_4O), 339 (23, M – $CH_2C_6H_7N_2O_2$), 319 (55, 440 – C_5H_5Fe), 304 (6, 339 – Cl), 291 (13, 319 – C_2H_4), 248 (22, 304 – Fe), 218 (100, 339 – C_5H_5Fe), 154 (26, $MeC_6H_7N_2O_2$), 107 (20, MeC_6H_4O), 91 (98, MeC_6H_4), 65 (59, C_5H_5).

Reaction of [(1,2,3,4,5,6-η)-1-chloro-4-phenoxybenzene](η⁵-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (36) with 3-ethoxy-6-methylpyridazine-1-oxide (11)

Reaction of **11** with **36** as above, workup after 2 h and chromatography yielded [(1,2,3,4,5-η)-5-chloro-6-*exo*-[6-(3-ethoxy-1-oxido)pyridazinylmethyl]-2-phenoxy-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)iron (**27**) (34%) which crystallized from CH_2Cl_2/hexanes as pale orange needles, m.p. 151–152.5°C. Anal. Found: C, 60.3; H, 5.5; N, 5.9. $C_{24}H_{23}ClFeN_2O_3$ calc.: C, 60.2; H, 4.8; N, 5.9%. ν_{max} (film): 1590, 1555, 1450 (C=N, C=C, N=N); 1245 (N → O); 1200 (C–O) cm^{-1}. δ(H) 1.36 (t, $J = 7.1$ Hz, OCH_2CH_3); 1.89 (dd, $J_{Ha,6} = 7.9$, $J_{Ha,Hb} = 13.5$ Hz, H_a); 2.08 (dd, $J_{Ha,6} = 5.9$, $J_{Ha,Hb} = 13.5$ Hz, H_b); 3.20 (dd, $J_{1,3} = 2.1$, $J_{1,6} = 7.1$ Hz, H(1)); 3.58 (6 lines, $J_{4,6} = 1.5$, $J_{obs} = 6.8$, 7.2, 6.8 Hz, H(6)); 4.35 (q, $J = 7.1$ Hz, OCH_2CH_3); 4.41 (s, C_5H_5); 4.56 (dd, $J_{4,6} = 1.5$, $J_{3,4} = 5.4$ Hz, H(4)); 6.03 (dd, $J_{1,3} = 2.1$, $J_{3,4} = 5.4$ Hz, H(3)); 6.40 (d, $J_{4',5'} = 8.7$ Hz, H(4')); 6.92 (d, $J = 8.5$ Hz, H(2'',6'')); 7.03 (apparent t, $J = 7.5$, 7.3 Hz, H(4'')); 7.08 (d, $J_{4',5'} = 8.7$ Hz, H(5')); 7.26 (apparent t, $J = 8.1$, 7.7 Hz, H(3'',5'')) ppm. δ(C) 14.3 (OCH_2CH_3); 29.9 (C(1)); 39.2 (CH_2); 43.5 (C(6)); 62.4 (C(5)); 63.8 (OCH_2CH_3); 69.4 (C(3)); 71.8 (C(4)): 76.9 (C_5H_5); 107.3 (C(4')); 118.1 (C(2'',6'')); 123.0 C(4'')); 126.3 (C(2)); 129.5 (C(3'',5'')); 135.6 (C(5')); 135.8 (C(6')); 157.9 (C(1'')); 163.6 (C(3')) ppm. *m/z* M not observed, 426 (1, M – HO–Cl), 325 (37, M – $CH_2C_6H_7N_2O_2$), 305 (62, 426 – C_5H_5Fe), 234 (30, 325 – Cl–Fe), 204 (100, 325 – C_5H_5Fe), 186 (36, 204 – H_2O), 154 (31, $MeC_6H_7N_2O_2$), 141 (60, 204 – Cl–C_2H_4), 77 (68, C_6H_5), 65 (45, C_5H_5).

References

1 D.A. Evans and J.A. Ellman, J. Am. Chem. Soc., 111 (1989) 1063.

2 A.H. Underwood, J.C. Emmett, D. Ellis, S.B. Flynn, P.D. Leeson, G.M. Benson, R. Novelli, N.J. Pearce and V.P. Shal, Nature, 234 (1986) 425.

3 R.M. Moriarty and U.S. Gill, Organometallics, 5 (1986) 253.

4 R.G. Sutherland, R.L. Chowdhury, A. Piorko and C.C. Lee, J. Organomet. Chem., 319 (1987) 379.
5 C.H. Zhang, R.L. Chowdhury, A. Piorko, C.C. Lee and R.G. Sutherland, J. Organomet. Chem., 346 (1988) 67.
6 R.G. Sutherland, R.L. Chowdhury, A. Piorko and C.C. Lee, J. Chem. Soc., Chem. Commun., (1985) 1296.
7 R.G. Sutherland, R.L. Chowdhury, A. Piorko and C.C. Lee, Can. J. Chem., 64 (1986) 2031.
8 R.C. Cambie, S.A. Coulson, S.J. Janssen, P.S. Rutledge and P.D. Woodgate, J. Organomet. Chem., 409 (1991) 385.
9 S.S. Gitis and A.Ya. Kaminskii, Russ. Chem. Rev., 47 (1978) 1061.
10 L. Pitarch, R. Coronas and J. Mallol, Eur. J. Med. Chem., Chim. Ther., 9 (1974) 644.
11 W.G. Overend and L.F. Wiggins, J. Chem. Soc., (1947) 239.
12 M. Kumagai, Nippon Kagaku, Zasshi, 81 (1960) 1148; Chem. Abstr., 56 (1962) 468.
13 A. Ohsawa, T. Uezu and H. Igeta, Chem. Pharm. Bull., 27 (1979) 916.
14 A. Ohsawa, T. Uezu and H. Igeta, Chem. Pharm. Bull., 26 (1978) 2428.
15 T. Nakagome, Chem. Pharm. Bull., 11 (1963) 721.
16 P.G. Spinazze and B.G. Keay, Tetrahedron Lett., 30 (1989) 1765.
17 N. Kirmse and F. Sollenbohmer, J. Chem. Soc., Chem. Commun., (1989) 774.
18 R.G. Sutherland, R.L. Chowdhury, A. Piorko and C.C. Lee, J. Org. Chem., 52 (1987) 4618.
19 L.F. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 1, Wiley, New York, 1967, p. 508.
20 A.J. Pearson, J. Chem. Soc., Perkin Trans. 1, (1979) 1255.
21 G.P. Randall, G.R. Stephenson and E.J.T. Chrystal, J. Organomet. Chem., 353 (1988) C47.
22 G.R. Stephenson, J. Chem. Soc., Perkin Trans. 1, (1982) 2449.
23 G. Soula, J. Org. Chem., 50 (1985) 3717.
24 F. Hossner and M. Voyle, J. Organomet. Chem., 347 (1988) 365.
25 A.N. Nesmeyanov, N.A. Vol'kenau, E.I. Sirotkina and V.V. Deryabin, Dokl. Akad. Nauk SSR, 177 (1967) 1110.
26 R.F. Homer, H. Gregory, W.G. Overend and L.F. Wiggins, J. Chem. Soc., (1948) 2195.
27 R.F. Homer, H. Gregory and L.F. Wiggins, J. Chem. Soc., (1948) 2191.
28 I.U. Khand, P.L. Pauson and W.E. Watts, J. Chem. Soc. (C), (1969) 116.