

Synthesis of Some Heterocyclic Skeletons *via*
Organoiron Complexes. Crystal and Molecular Structure of
(5a,6,7,8,9,9a- η^6 -1,4-Benzoxathiino[3,2-*b*]pyridine)(η^5 -cyclopentadienyl)iron
Hexafluorophosphate

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Received May 16, 1988

Synthesis of the heterocyclic skeletons of some biologically active compounds from (η^6 -*o*-dichlorobenzene)(η^5 -cyclopentadienyl)iron hexafluorophosphate in a two step procedure is described. Cyclopentadienyliron hexafluorophosphate complexes of 1,4-benzodioxino[2,3-*b*]pyridine, 1,4-benzoxathiino[3,2-*b*]pyridine, 10*H*-pyrido[3,2-*b*]benzoxazine, benzo[*b*]naphtho[2,3-*e*][1,4]dioxin, 4-methylbenzo[*b*]benzopyran-2-one[7,6-*e*][1,4]dioxin and benzo[*b*]anthracen-9,10-diono[1,2-*e*][1,4]dioxin were isolated and characterized. Upon pyrolytic sublimation of these complexes the free heterocycles were obtained and characterized. (η^6 -1,4-Benzoxathiino[3,2-*b*]pyridine)(η^5 -cyclopentadienyl)iron hexafluorophosphate crystallizes in the orthorhombic system, space group *Pbca*; the dihedral angle between the planes of outer rings was found to be 176.8 (1).

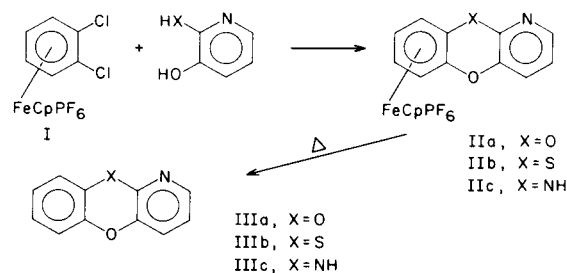
J. Heterocyclic Chem., **25**, 1911 (1988).

Application of organometallic compounds to organic synthesis has attracted considerable attention in recent years and the use of organometallic reagents in the synthesis of heterocycles is published more and more frequently [1]. Recently we have reported on the synthesis of heterocycles related to anthracene with heteroatoms in positions 9 and 10 [2] and the synthesis of cinnolines [3] both employing (η^6 -*o*-dichlorobenzene)(η^5 -cyclopentadienyl)iron hexafluorophosphate as a starting material. The first of these studies concentrated on molecules related to the biologically active phenothiazine system and a general synthetic method involving organoiron complexes has been established. In the present work other heterocyclic systems found in natural products or described as exhibiting biological activity have been targeted and synthesized. Besides the ongoing work on the synthesis and reactivity of (heterocycle)(cyclopentadienyl)iron complexes, we are also interested in assessing the influence of metal complexation on the geometry of the heterocyclic molecule [4,5] and in this work we have examined the geometry of the 1,4-benzoxathiino[3,2-*b*]pyridine molecule in its cyclopentadienyliron complex.

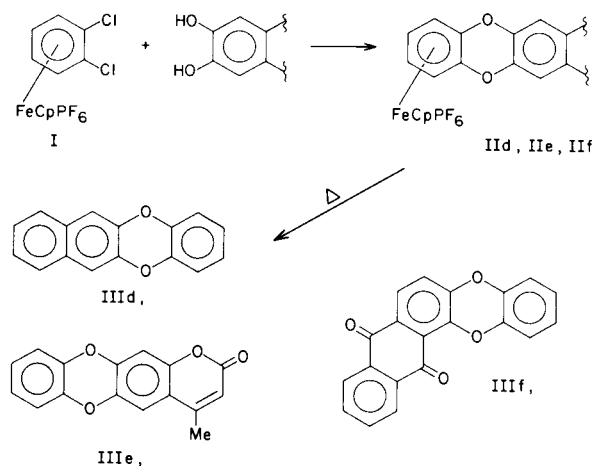
In previous syntheses of 9,10-diheteroanthracenes a double nucleophilic substitution on *o*-dichlorobenzene activated by cyclopentadienyliron with suitable *o*-disubstituted benzene nucleophiles was utilized. Reactions were carried out under very mild conditions in tetrahydrofuran or 9:1 tetrahydrofuran-dimethyl sulfoxide solutions at room temperature. Such conditions are especially valuable in reactions involving arenes possessing thermally unstable or labile groups. In the course of the present

study we found that the conditions described above may be replaced by a gentle reflux which led to shortening of the reaction time to 4-6 hours from 48 hours without reduction in yield. We also noted that high yields of the

Scheme 1



Scheme 2



products were obtained only if both substrates are completely dissolved in the solvent while with suspensions of the substrates much lower yields are observed. Thus in the cases of complexes **IIe** and **IIIf** (Scheme 1 and 2) where the starting phenols are not soluble in tetrahydrofuran, dimethyl sulfoxide was added to the reaction mixture to complete dissolution.

Yields of the cationic products **IIa, b, d, e, f** are high (over 70%) but that of 10*H*-pyrido[3,2-*b*][1,4]benzoxazine complex **IIc** is significantly lower as expected on the basis of a related investigation on the reactivity of the *o*-dichlorobenzene complex in nucleophilic substitution reactions. In that report [6] an explanation was advanced as to why heterocycles possessing one nitrogen atom are formed in lower yields while heterocycles related to dihydrophenazine have not been obtained at all. This study confirms previous findings and the 5,10-dihydropyrido[2,3-*b*]quinoxaline complex was not obtained either by this methodology.

Upon pyrolytic sublimation [2] the complexes liberated the free heterocycles in good yield (over 70%) with the exception of compound **IIc** which undergoes further reac-

tions under these conditions. Currently, we are involved in the search for more efficient methods of demetallation of nitrogen containing heterocycles.

Structures of all new complexes **IIa-f** and of the free heterocycles **IIIa-f** have been established on the basis of the analytical results which are presented both in the experimental part and in Table 1. The data obtained from ¹³C nmr spectroscopy are of particular value for confirmation of the structure showing clearly the difference in the spectra between complexed and free heterocycles (Table 1).

The work reported here complements the previous syntheses of 9,10-diheteroanthracenes and extends the range to the synthesis of compounds with one more nitrogen atom in the molecule and of compounds possessing a dibenzo[*b,e*][1,4]dioxin building block as a part of a larger heterocyclic skeleton. The heterocycles **IIIa-f** either exhibit biological activity or show structural relationships to such active compounds or are found in naturally occurring compounds. To the best of our knowledge three of them, **IIId,e,f** have not been reported before while the others have been the subject of recent studies described below.

Table 1

¹³C NMR Spectra of Complexes **II** and Heterocycles **III** (δ, ppm, TMS = 0)

Compound Number	Cp	Complexed aromatic	Uncomplexed aromatic	The others
IIa a)	79.84	76.72, 77.19, 85.44, 118.99 q, 119.30 q	124.84, 127.79, 136.41 q, 145.52, 147.18 q	
IIIa b)			117.82, 117.93, 123.19, 126.54, 127.81, 131.32, 134.95, 140.82 q, 141.35 q, 141.38 q, 150.04 q	
IIb a)	80.39	79.22, 85.38, 86.55, 86.98, 94.61 q, 123.98 q	125.95, 127.30, 140.17 q, 147.25 q, 148.66	
IIIb b)			118.41, 119.70 q, 123.69, 124.65, 125.91, 127.86, 128.99, 143.79 q, 145.85, 148.61 q, 150.89 q	
IIc a)	78.98	72.82, 76.15, 82.80, 84.52, 108.40 q, 118.19 q	121.58, 125.21, 138.32 q, 142.75 q, 145.46	
IIIc b)			116.74, 116.98, 117.64, 125.23, 126.02, 126.10, 127.29 q, 130.66 q, 143.25 q, 143.59, 145.25 q	
IIId a)	79.22	77.07, 85.01, 118.87 q	115.42, 128.10, 128.72, 132.84 q, 139.43 q	
IIIId c)			112.08, 116.48, 123.70, 125.22, 126.78, 130.82 q, 141.69 q, 141.84 q	
IIe d)	77.83	75.18, 75.32, 83.81, 84.03, 117.01 q, 117.23 q	105.40, 113.83, 116.08 q, 134.89 q, 140.66 q, 150.39 q	17.97 (Me), 113.05 (= C-C=O), 152.35 (C-Me), 159.16 (CO)
IIIe c)			104.82, 113.73, 115.86 q, 116.42, 116.63, 124.23, 124.67, 138.99 q, 140.88 q, 141.46 q, 145.13 q, 150.36 q	18.67 (Me), 110.76 (= C-C=O), 151.51 (C-Me), 160.63 (CO)
IIIf d)	78.52	75.80, 76.05, 84.46, 84.50, 117.01 q, 117.09 q	122.42 q, 122.49, 125.24, 126.64, 126.89, 131.66 q, 132.29 q, 134.35, 134.40 q, 134.73, 138.80 q, 143.69 q	180.81 (CO), 181.28 (CO)
IIIIf c)			116.22, 117.28, 120.88, 124.09, 124.90, 124.94, 126.79, 127.16, 129.95 q, 130.09 q, 132.66 q, 133.63, 134.04, 134.74 q, 141.06 q, 143.03 q, 146.36 q, 147.71 q	181.63 (CO), 181.70 (CO)

Cp-cyclopentadienyl; q-quarternary carbon atoms; a)-nitromethane-d₃; b)-acetone-d₆; c)-chloroform-d; d)-dimethyl sulfoxide-d₆.

Butler has patented a synthesis of 1,4-benzodioxino[2,3-*b*]pyridine by the cyclization of 4-chloro-3-(2-methoxyphenoxy)pyridine in unspecified yield as well as its application to the treatment of senility and the reversal of amnesia [7]. 1,4-Benzoxathiino[3,2-*b*]pyridine was synthesized by Martin *et al.* via the condensation of the disodium salt of 2-mercapto-3-pyridinol with *o*-chloronitrobenzene in 28% yield [8]. Some of its homologues show activity toward CNS [9]. Ito and Hamada obtained 10*H*-pyrido[3,2-*b*][1,4]benzoxazine from 2-chloro-3-nitropyridine and *o*-aminophenol in two steps with an overall yield of 67% [10] and this ring system has been found as a part of some naturally occurring compounds [11]. Compounds related to benzo[*b*]naphtho[2,3-*e*][1,4]dioxin have been synthesized in an unpublished procedure and they appear to show cancerostatic activity [12,13]. The coumarins occur widely in nature [14] and recently have been studied as potential laser dyes [15]. Also many analogues of anthraquinone are found in nature [16] and some of them exhibit antileukemic activity.

Starting from (*o*-dichlorobenzene)(cyclopentadienyl)iron hexafluorophosphate the following heterocycles were obtained (overall yields calculated on starting complex): **IIIa** - 82%; **IIIb** - 80%; **IIIc** - 35%; **IIId** - 80%; **IIIe** - 54% and **IIIf** - 58%, respectively. It may be clearly seen that the yields with the exception that of 10*H*-pyrido[3,2-*b*][1,4]-benzoxazine are good or very good and also the procedure used is relatively simple. Thus once again we have shown that temporary complexation of arenes with a metal moiety is an effective tool in synthesis of heterocyclic systems and that *o*-dichlorobenzene complexed with cyclopentadienyliron is a versatile synthon.

X-Ray Study of (5a,6,7,8,9a- η^6 -1,4-benzoxathiino[3,2-*b*]pyridine)(η^5 -cyclopentadienyl)iron Hexafluorophosphate (**IIb**).

Atomic positional and thermal parameters are listed in Table 2 while bond lengths and angles for selected atoms are listed in Table 3 [18]. A view of **IIb** with the atom labelling scheme is shown in Figure 1. The unit-cell packing diagram (Figure 2) illustrates the alternating layers of cationic complex **IIb** with hexafluorophosphate groups along the *c* axis. The heterocycle in **IIb** is nearly planar and is essentially coplanar with the Cp ring as is generally observed in such sandwich complexes. The PF₆⁻ group is well behaved with the P-F bonds ranging in length from 1.583(3) to 1.597(3) Å. No F-P-F angle deviates from expected octahedral symmetry by more than 1°. The Fe to ring centroid distances are 1.539(2) Å for the heterocycle and the Cp ring, respectively. The Fe to ring C bond lengths are in the normal range observed for these compounds. As is commonly observed, the average Fe to bridgehead C atoms are slightly longer than the average Fe bonds to the other four C atoms of the heterocycle

Table 3

Selected Bond Lengths (Å) and Angles (°) Involving non-H atoms of IIb				
1	2	3	1-2	1-2-3
C5a	Fe		2.106(4)	
C6	Fe		2.071(4)	
C7	Fe		2.082(4)	
C8	Fe		2.074(4)	
C9	Fe		2.076(4)	
C9a	Fe		2.101(4)	
C11	Fe		2.046(5)	
C12	Fe		2.044(4)	
C13	Fe		2.059(5)	
C14	Fe		2.053(5)	
C15	Fe		2.045(5)	
C9a	S10	C10a	1.758(4)	100.0(2)
C10a	S10		1.756(4)	
C4a	O5	C5a	1.389(5)	121.8(3)
C5a	O5		1.364(5)	
C2	N1	C10a	1.344(6)	117.1(3)
C10a	N1		1.338(5)	
C3	C2	N1	1.370(6)	122.9(4)
C4	C3	C2	1.379(6)	119.3(4)
C4a	C4	C3	1.370(6)	118.4(4)
C10a	C4a	O5	1.377(5)	124.8(3)
C10a	C4a	C4		119.2(4)
O5	C4a	C4		116.0(3)
C6	C5a	C9a	1.407(5)	120.0(4)
C6	C5a	O5		114.9(3)
C9a	C5a	O5	1.413(5)	125.0(3)
C7	C6	C5a	1.403(6)	120.7(4)
C8	C7	C6	1.397(6)	119.3(4)
C9	C8	C7	1.404(6)	120.7(4)
C9a	C9	C8	1.414(6)	120.3(4)
S10	C9a	C5a		123.5(3)
S10	C9a	C9		117.7(3)
C5a	C9a	C9		118.9(3)
S10	C10a	N1		112.3(3)
S10	C10a	C4a		124.7(3)
N1	C10a	C4a		123.1(4)
C12	C11	C15	1.396(6)	107.2(4)
C15	C11		1.418(7)	
C13	C12	C11	1.390(7)	108.9(4)
C14	C13	C12	1.385(7)	108.4(4)
C15	C14	C13	1.413(8)	108.2(4)
C11	C15	C14		107.2(4)

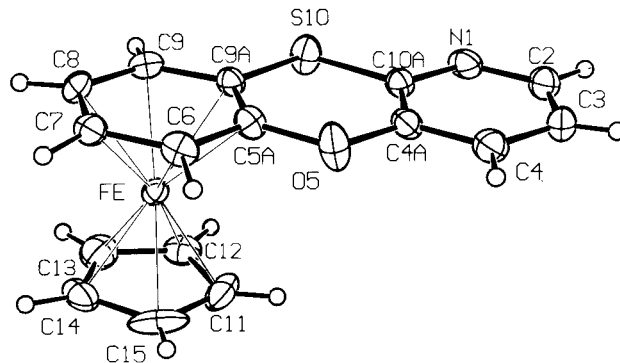


Fig.1. View of the complex (**IIb**) showing atom-labelling scheme.

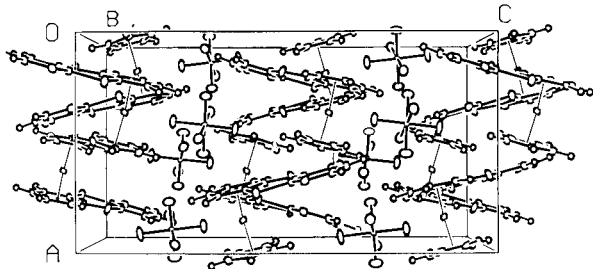
(2.104(3) Å vs. 2.076(2) Å) which may be due to the inductive effects of the electronegative S and O atoms on the bridgehead C atoms. The projection of the Fe atom on the plane defined by atoms C5A through C9A is offset by 0.02 Å from the ring centroid and displaced away from the bridgehead C atoms C5A and C9A. The dihedral angle between outer rings of 1,4-benzoxathiino[3,2-*b*]pyridine in complex **IIb** was found to be 176.8(1)° while it remains unknown for the free heterocycle.

Table 2

Fractional Coordinates and Equivalent Isotropic [a] Thermal Parameters (Å²) for non-H Atoms of **IIb**

Atom	x	y	z	U
Fe	.35734(5)	.14163(3)	.10624(2)	.01745(14)
P	.41526(10)	.36486(6)	.29045(5)	.0220(3)
F1	.3972(3)	.3752(2)	.21174(12)	.0415(9)
F2	.4346(3)	.3546(2)	.36917(12)	.0536(10)
F3	.3505(3)	.45700(15)	.30142(13)	.0421(9)
F4	.4791(3)	.27201(15)	.27880(12)	.0382(8)
F5	.2794(3)	.3192(2)	.29547(14)	.0457(10)
F6	.5522(3)	.4094(2)	.2857(2)	.0540(11)
N1	.1688(3)	-.1292(2)	-.0418(2)	.0277(11)
C2	.1325(4)	-.1280(3)	-.1063(2)	.0340(14)
C3	.1058(4)	-.0531(3)	-.1403(2)	.0314(14)
C4	.1158(4)	.0251(3)	-.1075(2)	.0275(12)
C4a	.1522(4)	.0250(2)	-.0416(2)	.0231(11)
O5	.1594(3)	.1055(2)	-.01090(14)	.0326(10)
C5a	.1845(4)	.1138(2)	.0558(2)	.0211(11)
C6	.1853(4)	.1996(2)	.0796(2)	.0242(12)
C7	.2116(4)	.2174(3)	.1471(2)	.0234(12)
C8	.2411(4)	.1491(3)	.1903(2)	.0256(11)
C9	.2443(4)	.0634(3)	.1669(2)	.0243(12)
C9a	.2162(4)	.0448(2)	.0992(2)	.0201(11)
S10	.22527(12)	-.06374(6)	.07330(5)	.0293(3)
C10a	.1774(4)	-.0528(2)	-.0105(2)	.0217(11)
C11	.4904(5)	.1260(3)	.0318(2)	.0349(15)
C12	.5251(4)	.0770(3)	.0877(2)	.0282(13)
C13	.5426(4)	.1323(3)	.1418(2)	.038(2)
C14	.5182(5)	.2162(3)	.1209(3)	.042(2)
C15	.4854(5)	.2138(3)	.0523(3)	.042(2)

[a] For non-H atoms, the U value is U_{eq} , calculated as $U_{eq} = \frac{1}{3} \sum_i \Sigma_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Fig. 2. Crystal packing diagram for the complex (**IIb**).

EXPERIMENTAL

Preparation of (*o*-dichlorobenzene)(cyclopentadienyl)iron hexafluorophosphate was given previously [17]. All reagents and solvents are commercially available and were used without further purification with the exception of alizarine (97%), which was recrystallized from methanol. Melting points are uncorrected. Infrared spectra (cm⁻¹) were registered in nujol mulls. Mass spectra were obtained using electron impact ionization at 70 eV with exception of **IIIe** where chemical ionization with methane was employed. The ¹H nmr (300.133 MHz) and ¹³C nmr (75.469 MHz) spectra were recorded on Bruker AM 300 instrument; all chemical shifts are given in δ, ppm scale (internal TMS for ¹H; calculated from solvent signals in ¹³C nmr spectra) where $\delta_{TMS} = 0$ ppm.

General Procedure for the Synthesis of Complexes.

Qualitative experiments were carried out at 3 mmoles scale and then repeated at 1 mmole scale and the lower of the two yields is reported. Complex **IIc** was also obtained at the 10 mmoles scale with slightly extended reaction time (6 hours) and the yield of that reaction was higher than that reported here. The general procedure is as follows:

To a solution of 1.24 g (3 mmoles) of (*o*-dichlorobenzene)cyclopentadienyliron hexafluorophosphate and 3.1 mmoles of *o*-difunctional arene in 100 ml of tetrahydrofuran, 0.75 g (5.4 mmoles) of anhydrous potassium carbonate was added. The mixture was then stirred with gently reflux of the solvent for 2-4 hours. After cooling 10 ml of 10% hydrochloric acid was added, followed by 0.5 g (*ca* 3 mmoles) of ammonium hexafluorophosphate. Tetrahydrofuran was evaporated off and the solid product extracted with methylene chloride (or methylene chloride-nitromethane). The combined extracts were washed with water, dried (sodium sulfate) and evaporated to dryness. The crude product was dissolved in acetone; addition of diethyl ether caused small amount of brown semi-solid impurities to appear on the walls; the clear solution was then decanted carefully and upon addition of further amount of diethyl ether the product crystallized overnight at *ca* -17°. The described procedure gave good yields of complexes **IIa-d** but the yields of **IIe** and **IIf** are significantly lower (40% and 21% respectively). The reported yields for **IIe** and **IIf** were obtained when tetrahydrofuran/dimethylsulfoxide 7:3 was used as a solvent (30 ml per 1 mmole) and solution refluxed gently for 6 hours. The mixture after reaction was poured onto 250 ml of water containing 2 ml of concentrated hydrochloric acid (per 1 mmole of substrate); then ammonium hexafluorophosphate was added and product extracted with nitromethane. Slightly lower yields (**IIe** - 42%; **IIf** - 60%) were obtained upon reaction of *o*-dichlorobenzene complex with dipotassium areneoxides of 4-methylesculetine or alizarine in dimethyl sulfoxide (prepared by reaction of the phenols with potassium *t*-butoxide in dimethyl sulfoxide) at 50° for 6 hours.

Pyrolytic sublimation experiments leading to isolation of free heterocycles were carried out as described previously [2].

(5a,6,7,8,9,9a- η^6 -1,4-Benzodioxino[2,3-*b*]pyridine)iron (η^5 -Cyclopentadienyl) Hexafluorophosphate (**IIa**).

This complex was obtained in the yield 89% as a yellow powder; ¹H nmr (acetone-*d*₆): δ 5.36 (s, 5H, cyclopentadienyl), 6.37-6.42 (m, 2H, complexed aromatic), 6.61-6.64 (m, 2H, complexed aromatic), 7.35 (d, J = 8.0 Hz, d, J = 4.9 Hz, 1H, aromatic), 7.65 (d, J = 8.0 Hz, d, J = 1.5 Hz, 1H, aromatic), 8.09 (d, J = 4.9 Hz, d, J = 1.5 Hz, 1H, aromatic).

Anal. Calcd. for C₁₆H₁₂F₆FeNO₂P: C, 42.50; H, 2.67; N, 3.10. Found: C, 42.19; H, 2.96; N, 3.28.

1,4-Benzodioxino[2,3-*b*]pyridine (**IIIa**).

Heterocycle was obtained as a grey-white solid mp 94-95° (lit 95-97° p [7]) in 92% yield; ¹H nmr (chloroform-*d*): δ 7.18 (m, 4H, aromatic), 7.59 (d, J = 7.8 Hz, d, J = 6.2 Hz, 1H, aromatic), 8.02 (d, J = 8.1 Hz, 1H, aromatic), 8.20 (d, J = 6.2 Hz, 1H, aromatic); ms: m/e 185 (M⁺, 100).

(5a,6,7,8,9,9a- η^6 -1,4-Benzoxathiino[3,2-*b*]pyridine)iron (η^5 -Cyclopentadienyl) Hexafluorophosphate (**IIb**).

The complex was obtained as orange microcrystals in 90% yield; ¹H

nmr (acetone- d_6): δ 5.26 (s, 5H, cyclopentadienyl), 6.48-6.53 (m, 2H, complexed aromatic), 6.68-6.72 (m, 2H, complexed aromatic), 7.46 (d, J = 8.2 Hz, d, J = 4.7 Hz, 1H, aromatic), 7.63 (d, J = 8.2 Hz, d, J = 1.4 Hz, 1H, aromatic), 8.39 (d, J = 4.7 Hz, d, J = 1.4 Hz, 1H, aromatic).

Anal. Calcd. for $C_{16}H_{12}F_6FeNOPS$: C, 41.04; H, 2.58; N, 2.99. Found: C, 40.98; H, 2.91; N, 2.96.

1,4-Benzoxathiino[3,2-b]pyridine (IIIb).

Heterocycle was obtained as an orange powder, mp 67-69° (lit 66-68° [8]) with the yield 89%; 1H nmr identical with reported previously [8]; ms: m/e 201 (M^+ , 100).

5a,6,7,8,9,9a- η^5 -10H-Pyrido[3,2-b][1,4]benzoxazine)iron (η^5 -Cyclopentadienyl) Hexafluorophosphate (IIc).

This complex was obtained with 54% yield as brown-orange powder; 1H nmr (acetone- d_6): δ 5.21 (s, 5H, cyclopentadienyl), 6.14-6.22 (m, 3H, complexed aromatic), 6.29-6.53 (m, 1H, complexed aromatic), 6.99 (d, J = 8.0 Hz, d, J = 5.0 Hz, 1H, aromatic), 7.27 (d, J = 8.0 Hz, d, J = 1.2 Hz, 1H, aromatic), 7.89 (d, J = 5.0 Hz, d, J = 1.2 Hz, 1H, aromatic), 8.82 (broad s, 1H, NH).

Anal. Calcd. for $C_{16}H_{13}F_6FeN_2OP$: C, 42.59; H, 2.90; N, 6.21. Found: C, 42.23; H, 3.10; N, 6.21.

10H-Pyrido[3,2-b][1,4]benzoxazine (IIIc).

Heterocycle was obtained in 60% yield as colorless solid, mp 206-207° (lit 209-210° [10]); 1H nmr as reported previously [10]; ms: m/e 184 (M^+ , 3.5), 83 (C_5H_5N , 100).

(1,2,3,4,4a,12a- η^6 -Benzo[b]naphtho[2,3-e][1,4]dioxin)iron (η^5 -Cyclopentadienyl) Hexafluorophosphate (IIId).

This complex was obtained in 88% yield as green-yellow crystals; 1H nmr (acetone- d_6): δ 5.30 (s, 5H, cyclopentadienyl), 6.33-6.37 (m, 2H, complexed aromatic), 6.65-6.69 (m, 2H, complexed aromatic), 7.52-7.56 (m, 2H, aromatic), 7.69 (s, 2H, aromatic), 7.90-7.94 (m, 2H, aromatic).

Anal. Calcd. for $C_{21}H_{13}F_6FeO_2P$: C, 50.32; H, 3.02. Found: C, 50.50; H, 3.06.

Benzo[b]naphtho[2,3-e][1,4]dioxin (IIIId).

Heterocycle was obtained as silver-white microcrystals, mp 202-203° in 91% yield; 1H nmr (chloroform- d): δ 6.93 (s, 4H, aromatic), 7.22 (s, 2H, aromatic), 7.31 (d, J = 6.1 Hz, d, J = 3.3 Hz, 2H, aromatic), 7.62 (d, J = 6.1 Hz, d, J = 3.3 Hz, 2H, aromatic); ms: m/e 234 (M^+ , 100).

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 81.87; H, 4.40.

(6a,7,8,9,10,10a- η^6 -4-Methylbenzo[b]benzopyran-2-on[7,6-e][1,4]dioxin)iron (η^5 -Cyclopentadienyl) Hexafluorophosphate (IIe).

This complex was obtained in 74% yield as yellow-green powder; 1H nmr (1:1 acetone- d_6 -dimethyl sulfoxide- d_6): δ 2.35 (s, 3H, CH_3), 5.22 (s, 5H, cyclopentadienyl), 6.23 (broad s, 2H, complexed aromatic), 6.37 (s, 1H, O=C-CH=), 6.56 (broad s, 2H, complexed aromatic), 7.26 (broad s, 1H, aromatic); 7.54 (broad s, 1H, aromatic).

Anal. Calcd. for $C_{21}H_{13}F_6FeO_4P$: C, 47.30; H, 2.84. Found: C, 46.99; H, 3.14.

4-Methylbenzo[b]benzopyran-2-on[7,6-e][1,4]dioxin (IIIe).

Heterocycle was obtained in 73% yield as brownish-white solid, mp >240° dec; 1H nmr (chloroform- d): δ 2.35 (s, 3H, CH_3), 6.18 (s, 1H, O=C-CH=), 6.83-7.02 (m, 6H, aromatic); ms: (chemical ionization, methane), m/e 266 (M^+ , 100).

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 71.95; H, 3.70.

(1,2,3,4,4a,14a- η^6 -Benzo[b]anthracen-9,10-diono[1,2-e][1,4]dioxin)iron (η^5 -Cyclopentadienyl) Hexafluorophosphate (IIIf).

This complex was obtained in 71% yield as orange-yellow powder; 1H nmr (1:1 acetone- d_6 -dimethyl sulfoxide- d_6): δ 5.36 (s, 5H, cyclopentadienyl), 6.39-6.41 (m, 2H, complexed aromatic), 6.71-6.73 (m, 1H, complexed aromatic), 6.76-6.79 (m, 1H, complexed aromatic), 7.67 (d, J = 8.5 Hz, 1H, aromatic), 7.94-8.02 (m, 2H, aromatic), 8.16 (d, J = 8.5 Hz, 1H,

aromatic), 8.25-8.29 (m, 2H, aromatic).

Anal. Calcd. for $C_{25}H_{15}F_6FeO_4P$: C, 51.66; H, 2.60. Found: C, 51.68; H, 2.80.

Benzo[b]anthracen-9,10-diono[1,2-e][1,4]dioxin (IIIf).

Heterocycle was obtained in 82% yield as orange-yellow solid, mp >250° dec; 1H nmr (chloroform- d): δ 6.86-6.90 (m, 1H, aromatic), 6.94-7.02 (m, 2H, aromatic), 7.09-7.13 (m, 1H, aromatic), 7.17 (d, J = 8.6 Hz, 1H, aromatic), 7.73-7.81 (m, 2H, aromatic), 7.96 (d, J = 8.6 Hz, 1H, aromatic), 8.23-8.28 (m, 2H, aromatic); ms: m/e 314 (M^+ , 100).

Anal. Calcd. for $C_{20}H_{10}O_4$: C, 76.43; H, 3.21. Found: C, 76.40; H, 3.40.

X-Ray.

Crystals grew as yellow-orange plates from acetone-diethyl ether-methylene chloride (255 K). Data crystal had dimensions .14 mm x .35 mm x .35 mm. Data were collected on a Syntex P2₁ diffractometer, with a graphite monochromator, using Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$), and equipped with a Syntex LT-1 low-temperature delivery system (163 K). Lattice parameters were obtained from least-squares refinement of 30 reflections with $21.0 < 2\theta < 28.1^\circ$: a = 10.406(4), b = 15.446(5), c = 19.982(7) \AA , V = 3212(2) \AA^3 . Crystal system is orthorhombic; space group is Pbc₂, Z = 8, $d_x = 1.80 \text{ g-cm}^{-3}$, F(000) = 1872. Space group was determined from the systematic absences. Data collected using the omega scan technique (7288 reflections measured, 3692 unique. $R_{int} = 0.0415$), 2θ range 4.0-55°, $1^\circ \omega$ scan at 6-12°/min. (h = 0 - 13, k = 0 - 20, l = -25 - 25). Four reflections (2,3,0; 0,0,4; 0,-4,0; 3,0,2) were remeasured every 96 reflections to monitor instrument and crystal stability. There was no evidence of crystal decay. Data were corrected for Lp effects and absorption [(based on crystal shape; = 12.31 cm^{-1} [19]; transmission factor range 0.650-0.848)]. Data reduction is described elsewhere [20]. Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (1047 reflections). Structure was solved by the heavy atom method and refined by full-matrix least-squares procedures [21] with anisotropic thermal parameters for the non-H atoms. H atoms from a ΔF map and refined with isotropic thermal parameters. 292 parameters refined. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/(\sigma(F_o))^2$ and $\sigma(F_o) = 0.5kI^{-1/4}[(\sigma(I))^2 + (0.04I)^2]^{1/2}$. Intensity, I, given by $(I_{peak} - I_{background}) \times (\text{scan rate})$, 0.04 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects and absorption. $\sigma(I)$ estimated from counting statistics; $\sigma(I) = [(I_{peak} + I_{background})^{1/2} \times (\text{scan rate})]$. Final R = 0.0488 for 2645 reflections, $wR = 0.0432$ ($R_{all} = 0.0827$, $wR_{all} = 0.0488$) and a goodness of fit = 1.404. Maximum $|\Delta f/\sigma| < 0.1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map where -0.48 and 0.60 $e/\text{\AA}^3$, respectively. Neutral atom scattering factors were used for all atoms [22,23], with anomalous-dispersion corrections for the non-H atoms [24]. The least-squares planes program was supplied by Cordes [25]; other computer programs are listed elsewhere [26].

Acknowledgements.

The financial support given by the Natural Sciences and Engineering Research Council of Canada to RGS, AP and CCL and by the Robert A. Welch Foundation to SHS, VML (Grant F-017) is gratefully acknowledged.

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