Synthesis of (η^5-cyclopentadienyl)-1-(4-benzyloxycarbonyl-3,4-dihydroquinoxalin-2-yl)ethene-1,2-dithiolatocobalt(III) and (η^5-cyclopentadienyl)-1-[2-(*N*,*N*-dimethylaminomethyleneamino)-3-methyl-4-oxopteridin-6-yl]ethene-1,2-dithiolatocobalt(III)

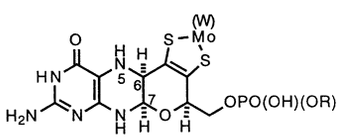
Andrew Dinsmore, Jacqueline H. Birks, C. David Garner and John A. Joule*

Chemistry Department, The University of Manchester, Manchester M13 9PL, UK

Cobalt(III) complexes are reported in which (a) a dihydroquinoxalinylethenedithiolate ligand models the pyrazine ring oxidation level in Moco, and (b) a pteridinylethenedithiolate models the pteridine ligand in Moco.

Introduction

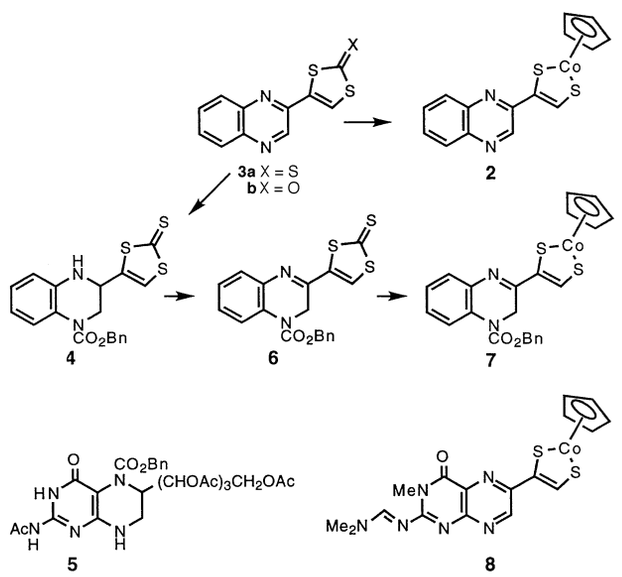
The concept that a small molybdenum-containing unit, now generally known as Moco, might act as a co-factor for the molybdoenzymes was first suggested more than 30 years ago; the ensuing structural work, spectroscopic studies, and studies aimed at the synthesis of model compounds, and Moco itself, have been reviewed recently.[1] Chemical degradations on minute amounts of the unstable co-factor, mainly by Rajagopalan *et al.*[2] produced a structural proposal which was remarkably close to that which emerged from three recent X-ray crystallographic determinations. In the aldehyde oxidase from *Desulfovibrio gigas*,[3] in dimethyl sulfoxide (DMSO) reductase from *Rhodobacter sphaeroides*,[4] and in the hyperthermophilic tungsten enzyme, ferredoxin aldehyde oxidoreductase from *Pyrococcus furiosus*,[5] the molybdenum (tungsten) ligand was shown to have structure **1**. The co-factor has a metal chelating ethene-1,2-



1
(R = H or cytosine)
(other ligands on metal not shown)

dithiolate, attached at C-6 of a pteridine ring, just as originally proposed by Rajagopalan, however, unsuspected from the chemical degradative work, Moco appears also to incorporate a tetrahydropyran ring, which can be viewed formally as the result of a cyclisation of a side-chain hydroxy group at C-7 of a 5,6-dihydropteridine. It is not yet established whether the form found in samples prepared for crystallography represents the catalytically active form; certainly, quite simple proton-catalysed processes would lead from the structure shown in **1** to forms in which the N–C–O unit was cleaved, introducing a double bond into the pyrazine ring and allowing interaction between the molybdenum of the metallocycle and the pteridine unit, and we have speculated on the possible significance of such interactions.[6]

In previous papers in this series we described, in preliminary form, the synthesis and crystal structure of the quinoxalinyl cobalt complex **2**[6] as a model for Moco and showed how both the organic precursor **3a** which we used to make complex **2**, and model pteridines, can be selectively transformed to a tetrahydro oxidation level in the pyrazine ring, giving **4** and *e.g.* **5**, respectively, without reduction of the side-chain functionality.[7,8] In this paper we describe an improved version of an earlier synthesis of **3a** and an efficient synthesis of the oxygen analogue **3b**, give details of the synthesis of **2**, and describe the transformation of **4** into **6**, now at the pyrazine ring oxidation level which it appears Moco itself adopts, and from **6** the formation of cobalt complex, **7**. Finally, we reveal details of the synthesis of the (protected) pteridinyl cobalt complex, **8** as a close model for the co-factor.



Results and discussion

Quinoxalines

We have previously described syntheses of **3a** by oxidation of the corresponding quinoxalinyl dithiolane[9] and, more usefully, using 2-bromoacetylquinoxaline **9a** obtained from 2-acetylquinoxaline **9b**.[10] We give in the Experimental section improved regimes for the preparation of **9b** and for the final step in preparing **3a** by this route. We also disclose a quite different and efficient route for the synthesis of the oxygen analogue **3b**; this 1,3-dithiol-2-one can be employed in the synthesis of complexes by hydrolysis to the corresponding dithiolate ligand in solution as its salt.[10,11] The route to **3b** is based on a recent report that

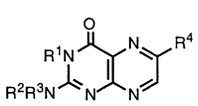
9a R = $C(O)CH_2Br$
b R = COMe
c R = C≡CH
d R = Cl
e R = $C{\equiv}CSiMe_3$

bis(isopropoxythiocarbonyl) disulfide, $[Pr^iOC(S)S]_2$, reacts with terminal alkyl and aryl alkynes, in the presence of radical initiators, to yield 1,3-dithiol-2-ones.[12] Application of this method required 2-ethynylquinoxaline **9c**, which we prepared by palladium/copper mediated coupling of trimethylsilylacetylene with 2-chloroquinoxaline[13] **9d** giving **9e**, then removal of the trimethylsilyl group. Reaction of **9c** and $[Pr^iOC(S)S]_2$ in refluxing toluene in the presence of 1,1′-azo(cyclohexanecarbonitrile) gave **3b** (77%).

The dihydro oxidation state of the pyrazine ring in Moco, suggested by the X-ray crystallographic work and deduced in earlier Rajagopalan studies,[14] prompted us to seek a synthesis of a relevant model cobalt complex, to set alongside those already prepared.[6,15,16] We found that the tetrahydro derivative **4**[7,8] can be oxidised up to the dihydro level using manganese dioxide, producing **6** and that this compound undergoes a comparable reaction with (η^5-cyclopentadienyl)-η^4-cycloocta-1,5-dienecobalt(I) forming **7**.

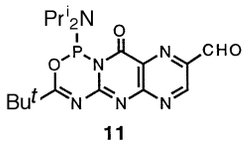
Pteridines

6-Formylpterin **10a**, prepared in 55% yield by the hydrobromic acid–bromine degradation[17] of commercial folic acid, is a convenient source of 6-substituted pteridines. Following Taylor's suggestion[18] for the solubilisation of sparingly soluble pteridines,[19] this highly insoluble compound was *N*-pivaloylated with a mixture of pivalic anhydride and 4-dimethylaminopyridine (DMAP) in refluxing dimethylformamide (DMF) giving the desired 2-pivaloylaminopteridine **10b** (55%) which has an appreciable solubility in organic solvents. A by-product, the 2-*N*,*N*-dimethylaminomethyleneaminopteridine **10c** must have arisen from an interaction of the pteridine, DMF and pivalic anhydride, because the starting material when heated in DMF alone gave none of this compound.



10	R^1	R^2, R^3	R^4
a	H	H, H	CHO
b	H	Bu^tCO, H	CHO
c	H	Me_2NCH=	CHO
d	Me	Me_2NCH=	CHO
e	Me	H, H	CHO
f	Me	Me_2NCH=	CO_2Me
g	$PhCH_2$	Me_2NCH=	CHO
h	CH_2=$CHCH_2$	Me_2NCH=	CHO
i	$MeO(CH_2)_2OCH_2$	Me_2NCH=	CHO
j	Me	Me_2NCH=	OCH_2CH
k	Me	Me_2NCH=	Ac
l	$PhCH_2$	Me_2NCH=	Ac
m	CH_2=$CHCH_2$	Me_2NCH=	Ac
n	$MeO(CH_2)_2OCH_2$	Me_2NCH=	Ac
o	$PhCH_2$	Me_2NCH=	OCH_2CH
p	Me	Me_2NCH=	$C(O)CH_2Br$
q	Me	Me_2NCH=	$C(O)CH_2SC(S)NMe_2$
r	Me	Me_2NCH=	$C(O)CH_2SC(S)SBu^t$
s	Me	Me_2NCH=	$C(O)CH_2SC(S)OPr^i$

Attempts to induce the 6-formyl group of **10b** to react with methyllithium or methylmagnesium bromide in order to form homologous compounds were unsuccessful. Reasoning that our lack of success was probably because of the two acidic *N*-hydrogens, various efforts were made to temporarily mask them. Attempted formation of a glyoxal adduct,[20] gave no characterisable product. Although the pteridine **10b** reacted rapidly with $Pr^i_2NPCl_2$,[21] as judged by precipitation of triethylamine hydrochloride, and a FAB mass spectroscopic analysis showed a strong molecular ion for the required product, **11**; this compound was unstable, could not be fully characterised and did not allow selective reaction at the 6-formyl site with alkyl-



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metal reagents. Attempts to form *N*-silylated derivatives were also unsuccessful.

Although **10c** had poorer solubility in organic solvents than **10b**, it possesses only one acidic *N*-hydrogen and was from this viewpoint judged a more useful starting point. It could be produced efficiently by reaction of **10a** with bis(dimethylamino)-*tert*-butoxymethane (Bredereck's reagent) in DMF at 60 °C. Interestingly, reaction of **10a** with dimethylformamide dimethyl acetal (DMFDMA), gave a mixture of the pteridine **10c** and a product possessing an 'extra' methyl group; higher temperatures favoured the formation of this homologue. Since pterins are known to be methylated at *N*-1 and/or *N*-3 under basic conditions,[22] it seemed very likely that the new product was an *N*-methylated derivative. To distinguish the regio possibilities, valid UV comparison with known compounds was required and so the dimethylaminomethyleneamino group was removed by treatment with aqueous sodium hydroxide. Comparison of the UV spectra of this substance, measured in neutral and acidic solutions, with those of the known 2-amino-1,6-dimethyl- and 2-amino-3,6-dimethyl-pteridin-4-ones[23] left no doubt that the deprotected material, and therefore its precursor, were *N*-3-methylated and thus had structures **10e** and **10d**, respectively. There are previously described instances of *N*-methylation of a guanosine[24] (at *N*-3) and of 2-amino-6-methyl-5-nitropyrimidin-4-one[25] (at *N*-3) under comparable conditions.

A second by-product isolated in low yield from the reaction of the pteridine **10a** with DMFDMA was identified as the ester **10f**, presumably arising by a Cannizzaro-like reaction in which an aldehyde–methoxide adduct donates hydride, perhaps to Me_2N^+=CHOMe, since none of the corresponding pteridin-6-ylmethanol was produced.

Treatment of **10c** with DMFDMA, or with base and methyl iodide or dimethyl sulfate, also yielded **10d**. The choice of base was important since, for example, a suspension of the poorly soluble pteridine **10c** in dichloromethane was not alkylated in the presence of triethylamine. However, addition of 1 equiv. of diazabicycloundecene (DBU) to a suspension of the pteridine **10c** in dichloromethane caused dissolution and formation of a red solution; we surmise that this may be due to the formation of an H-bonded complex, analogous to those believed to be formed between DBU and carboxylic acids.[26] Subsequent addition of dimethyl sulfate to the red solution then produced **10d** efficiently.

Other alkylating agents also brought about *N*-3-alkylation using DBU. Thus the *N*-3-alkylated pteridines **10g–i** were obtained using benzyl bromide, allyl bromide and methoxyethoxymethyl (MEM) chloride, respectively, assignment of the regiochemistry of alkylation resting in each case on UV comparisons with the *N*-3-methylpteridine aldehyde **10d**. We found that the *N*-3-benzylpteridine **10g** could also be formed by treatment of **10c** in dichloromethane with an excess of benzyl alcohol and DMFDMA, presumably *via* dimethylformamide dibenzyl acetal formed *in situ*.

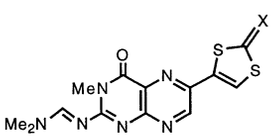
Since in compound **10c** there is still one acidic *N*-hydrogen, attempts were made to form *N*-3-silyl derivatives which would be stable enough for subsequent use. Although a suspension of **10c** in dichloromethane with triethylamine rapidly dissolved on addition of trimethylsilyl chloride with precipitation of triethylamine hydrochloride, if the required derivative was formed, it decomposed to starting material when stored in solution. No reaction with 1,1,2-trimethylpropyl(dimethyl)silyl chloride occurred under similar conditions.

Guanosine nucleotides are known to react with acylating and

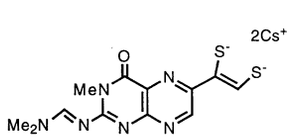
sulfonylating agents at room temperature in the presence of triethylamine and DMAP to yield 4-*O*-acyl and 4-*O*-sulfonyl derivatives with no *N*-hydrogen.[27] Attempts to apply these protecting conditions to **10c** were unsuccessful even after addition of DBU or imidazole. Treatment of a suspension of the pteridine **10c** in dichloromethane with methyl or benzyl chloroformate in the presence of triethylamine gave low yields of the *N*-3-methyl- and *N*-3-benzylpteridines **10d** and **10g**, respectively, and not the expected *O*-acyl derivatives.

Reaction of **10d** with diazomethane at −75 °C gave a mixture of the epoxide **10j** and the ketone **10k** in approximately equal quantities (by ^{1}H NMR) but at higher temperatures there was less epoxide; thus reaction at 25 °C produced the methyl ketone **10k** in 59% yield. The corresponding *N*-benzyl-, *N*-allyl- and *N*-MEM-protected pteridines reacted in similar fashion, to give the ketones, **10l**–**n**, respectively. Traces of the corresponding epoxides were seen in all cases, though only the *N*-benzyl epoxide **10o** was characterised. Clearly, these doubly blocked derivatives have considerable promise for the future synthesis of unsubstituted pteridines, however the remaining chemistry reported in this paper concerns the *N*-3-methyl ketone **10k**.

C-Bromination of the ketone **10k** was achieved in 38% yield employing pyrrolidine hydrotribromide in acetic acid at 60 °C. The resulting α-bromo ketone **10p** was conveniently isolated as its hydrobromide salt which could be filtered off. Treatment of the bromo ketone with sodium dimethyldithiocarbamate gave the pteridine **10q** in excellent yield, but cyclisation in concentrated sulfuric acid following earlier work[10] and treatment of the resulting crude salt with hydrogen sulfide gave only a poor yield of a low quality sample of the desired 1,3-dithiole-3-thione **12a**. Reaction of the bromo ketone with potassium *tert*-butyl trithiocarbonate[28] gave a good yield of **10r**, which was cyclised in sulfuric acid to give **12a** (54%).



12a X = S
b X = O



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A synthesis of the oxygen analogue **12b** resulted from treatment of the bromo ketone with potassium isopropyl xanthate[29] to give a quantitative yield of the pteridine **10s**, cyclisation of which in sulfuric acid gave **12b** (65%).

We produced the target cobalt complex, **8** in two ways. Treatment of **12a** with (η^5-cyclopentadienyl)-η^4-cycloocta-1,5-dienecobalt(I) in refluxing toluene[30] gave the desired cobalt(III) complex **8** in 20% yield following purification by flash chromatography. Alternatively, hydrolysis of **12b** in chloroform–methanol mixtures employing caesium hydroxide gave a solution, assumed to contain the dicaesium dithiolate **13**, which with cyclopentadienyl(carbonyl)cobalt(III) diiodide[31] produced the cobalt complex **8** in 50% yield.

The green microcrystalline complex **8** was completely stable in air and soluble in chlorinated solvents. Its ^{1}H NMR spectrum showed a vinylic signal at δ 9.5, consistent with previously synthesised comparable cobalt complexes.[6,16] All other spectroscopic and microanalytical data were consistent with the proposed structure. A single crystal X-ray analysis[32] confirmed the structure.

Experimental

General

Thin layer chromatography was carried out on Merck silica gel F_{254} 0.255 mm plates, and spots were visualised, where appropriate, by UV fluorescence at 254 or 297 nm or by spraying with phosphomolybdic acid in ethanol. Flash column chromatography was performed using Merck Kieselgel 60 (230–400 mesh) silica. Tetrahydrofuran was dried by distillation from potassium–benzophenone; diethyl ether was pre-dried over calcium chloride before refluxing over sodium–benzophenone; toluene and dichloromethane were dried by distillation from calcium hydride; dimethylformamide was dried over 4 Å molecular sieves. Solutions of lithium diisopropylamide monotetrahydrofuran, butyl- and *tert*-butyl-lithium and methylmagnesium bromide were purchased from the Aldrich chemical company and used without titration. All other chemicals were purified using standard procedures as required. Organic solutions were dried over anhydrous magnesium sulfate. UV spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer, path-length 1 cm and are given in nm with log ε in parentheses and shoulders designated sh. IR spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer and are given in cm^{-1}. ^{1}H NMR spectra were recorded (in $CDCl_3$ unless otherwise specified) on a Varian AC 300E NMR spectrometer operating at 300 MHz or a Varian Gemini 200 spectrometer operating at 200 MHz. All chemical shifts are reported in ppm downfield from tetramethylsilane. Peak multiplicities are denoted by s (singlet), br s (broad singlet), d (doublet), br d (broad doublet), t (triplet), q (quartet) and m (multiplet) or by a combination of these, *e.g.* dd (double doublet), with coupling constants (*J*) given in Hz. ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 75 MHz. Mass spectra were recorded on a Fisons VG Trio 2000 for electron impact (EI) and chemical ionisation (CI) conditions. Fast atom bombardment (FAB) spectra and accurate mass measurements were recorded on a Kratos Concept. Melting points were recorded on a Reichert heated-stage microscope and are uncorrected.

2-Acetylquinoxaline 9b

Saturated aqueous iron(II) sulfate (166.8 g, 600 mmol) and 70% aqueous *tert*-butyl hydroperoxide (125.1 g, 600 mmol) were added dropwise simultaneously, over the course of 20 min to a cooled (5–15 °C) mixture of acetaldehyde (33.5 ml, 26.4 g, 600 mmol), quinoxaline (26.1 g, 201 mmol) and 4 M sulfuric acid (50 ml), with stirring. The mixture was stirred for a further 30 min after which it was diluted with water (200 ml) and cooled in an ice–methanol bath for 1 h. The orange–brown precipitate was filtered off, recrystallisation from aqueous ethanol affording the title compound as orange–brown needles (26.6 g, 78%), mp 75–76 °C (lit.,[10] 76–77 °C).

4-(Quinoxalin-2-yl)-1,3-dithiole-2-thione 3a

Solid 2-(*N*,*N*-dimethylamino)-4-(quinoxalin-2-yl)-1,3-dithiolium hydrogen sulfate[10] (10.0 g, 27.0 mmol) was added to a two-phase mixture of sodium hydrogen sulfide hydrate (30.82 g, 55.0 mmol) in aqueous acetic acid (20%; 1 l) and dichloromethane (2 l) in a 5 l separating funnel. The mixture was shaken vigorously after which the organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 1 l). The combined organic extracts were dried and concentrated *in vacuo*. Chromatography of the resulting residue using dichloromethane as eluent, followed by recrystallisation from dichloromethane–hexane afforded 4-(quinoxalin-2-yl)-1,3-dithiole-2-thione **3a** (6.89 g, 97%) as golden–yellow crystals, mp 252–254 °C (lit.,[10] 253–254 °C).

2-(2-Trimethylsilylethynyl)quinoxaline 9e

2-Chloroquinoxaline **9d**[13] (5.0 g, 0.03 mol) in a mixture of triethylamine and acetonitrile (1:4; 30 ml) was degassed by bubbling argon through it. The solution was then cooled to ice-bath temperature with stirring under nitrogen and palladium(II) acetate (0.43 g, 1.91 mmol), copper iodide (0.36 g, 1.91 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were added to it, followed by trimethylsilylacetylene (5.2 ml, 0.037 mol). The mixture was stirred vigorously under nitrogen for 3 h while being allowed to warm to room temperature. Further trimethylsilylacetylene (1 ml, 7.1 mmol) was then added to it after

30 min. The mixture was concentrated *in vacuo*, partitioned between dichloromethane (30 ml) and water (30 ml) and filtered through Celite. The aqeous phase was separated and extracted twice with dichloromethane (20 ml). The combined organic extracts were filtered through Celite, washed once with brine (20 ml), dried and evaporated *in vacuo* to leave a brown oil which was purified by flash chromatography, eluting with dichloromethane, to give the title compound **9e** as a mobile brown oil (7.5 g, >100%; used without further purification) (Found: M^+, 226.0922. $C_{13}H_{14}N_2Si$ requires *M*, 226.0926); δ_H(200 MHz) 8.99 (1 H, s, 3-H), 8.08 (2 H, m, ArH), 7.77 (2 H, m, ArH) and 0.32 [9 H, s, $Si(CH_3)_3$]; *m*/*z* (CI) 227 (MH^+, 100%).

2-Ethynylquinoxaline 9c

To the quinoxaline **9e** (7.5 g) in methanol (30 ml) was added finely ground potassium carbonate (40 mg, 0.29 mmol). After being stirred for 19 h the mixture was evaporated *in vacuo* and the resultant solid was partitioned between dichloromethane (30 ml) and water (30 ml). The mixture was filtered through Celite to break up an emulsion, after which the aqueous phase was separated and extracted twice with dichloromethane. The combined organic phases were washed once with brine (15 ml), dried and evaporated *in vacuo* to give the title compound **9c** as a dark brown solid (3.99 g, 85% from 2-chloroquinoxaline). An analytical sample had mp 95–96 °C (EtOH) (Found: M^+, 154.0533. $C_{10}H_6N_2$ requires *M*, 154.0531); ν_{max}(KBr)/cm^{-1} 2099, 1637, 1615, 1536 and 1486; δ_H(200 MHz) 8.90 (1 H, s, 3-H), 8.08 (2 H, m, ArH), 7.78 (2 H, m, ArH) and 3.43 (1 H, s, C≡CH); *m*/*z* (CI) 171 (MNH_4^+, 35%) and 155 (MH^+, 100).

4-(Quinoxalin-2-yl)-1,3-dithiol-2-one 3b

A mixture of the quinoxaline **9c** (60 mg, 0.39 mmol), bis(isopropoxythiocarbonyl) disulfide (0.35 ml, 1.55 mmol) and 1,1′-azo(cyclohexanecarbonitrile) (47 mg, 0.19 mmol) was heated at reflux in toluene (5 ml) under nitrogen for 7 h after which it was evaporated *in vacuo*. The resultant oil was purified by flash chromatography, eluting with dichloromethane and then dichloromethane–methanol (98.5:1.5) to give the *title compound* **3b** as a tan solid (74 mg, 77%), mp 144–146 °C (Found: M^+, 245.9916. $C_{11}H_6N_2OS_2$ requires *M*, 245.9922); ν_{max}(KBr)/cm^{-1} 1624, 1545 and 1491; δ_H(200 MHz) 9.18 (1 H, s, 3-H), 8.15 (2 H, m, ArH), 7.83 (2 H, m, ArH) and 7.70 (1 H, s, SCH); *m*/*z* (CI) 246 (MH^+, 100%).

(η^5-Cyclopentadienyl)-1-(quinoxalin-2-yl)ethene-1,2-dithiolatocobalt(III) 2

A solution of the thione **3a** (1.0 g, 3.8 mmol) and (η^5-cyclopentadienyl)-η^4-cycloocta-1,5-dienecobalt(I) (0.9 g, 3.8 mmol) in degassed xylene (150 ml) was refluxed for 24 h under nitrogen. The resulting turquoise–black solution was subjected to chromatography using hexane–dichloromethane (2:1) as eluent, and the product then recrystallised, by Soxhlet extraction, from hexane to afford the title compound **2** as dark blue needles (0.67 g, 51%), mp 203–205 °C (Found: C, 51.5; H, 2.95; N, 8.8%; M^+, 341.9684. $C_{15}H_{11}CoN_2S_2$ requires C, 52.6; H, 3.2; N, 8.2%; *M*, 341.9696); λ_{max}(MeCN)/nm 729, 588, 398, 359, 289, 243 and 221 (2.78, 3.93, 3.98, 3.95, 4.45, 4.23 and 4.30); ν_{max}(KBr)/cm^{-1} 1639, 1620, 1536, 1488, 1438, 1411, 1125, 759, 563 and 407; δ_H(300 MHz) 9.70 (1 H, s, 3-H), 9.64 (1 H, s, SCH), 8.05 (2 H, m, ArH), 7.70 (2 H, m, ArH) and 5.42 (5 H, s, Cp); δ_C($CDCl_3$, 75 MHz) 165.65, 161.24, 150.27, 143.18, 142.92, 141.01, 130.56, 130.30, 130.10, 129.78 and 79.77; *m*/*z* (EI) 342 (M^+, 22%), 282 (100), 200 (30), 191 (20), 188 (32) and 124 (13).

4-(4-Benzyloxycarbonyl-3,4-dihydrohydroquinoxalin-2-yl)-1,3-dithiole-2-thione 6

Portions of manganese(IV) dioxide (0.36 g, 4 mmol) were added to a solution of 4-(4-benzyloxycarbonyl-1,2,3,4-tetrahydroquinoxalin-2-yl)-1,3-dithiole-2-thione **4**[8] (0.82 g, 2 mmol) in dichloromethane (90 ml) under argon at 15 min intervals, over the course of 6 h. The reaction mixture was then stirred for a further 12 h, after which it was filtered through Celite then evaporated *in vacuo* to afford an orange–brown gum. Chromatography of this using dichloromethane as eluent afforded the *title compound* **6** as a yellow solid (0.59 g, 72%), mp 132–134 °C (Found: C, 56.6; H, 3.6; N, 7.0%; M^+, 398.0215. $C_{19}H_{14}N_2O_2S_3$ requires C, 57.26; H, 3.54; N, 7.03%; *M*, 398.0217); λ_{max}(EtOH)/nm 396, 381, 365, 280 and 273 (5.01, 5.09, 4.89, 5.58 and 4.21); ν_{max}(film)/cm^{-1} 1708, 1606, 1498 and 1067; δ_H(300 MHz) 7.63 (1 H, br d, 5-H), 7.47 (1 H, s, SCH), 7.35 (5 H, m, ArH), 7.19 (3 H, m, ArH), 5.26 (2 H, s, CH_2O) and 4.57 (2 H, s, 3-H_2); *m*/*z* (CI) 399 (MH^+, 100%) and 295 (20).

(η^5-Cyclopentadienyl)-1-(4-benzyloxycarbonyl-3,4-dihydrohydroquinoxalin-2-yl)ethene-1,2-dithiolatocobalt(III) 7

A solution of the thione **6** (1.37 g, 3.4 mmol) and (η^5-cyclopentadienyl)-η^4-cycloocta-1,5-dienecobalt(I) (0.95 g, 4.1 mmol) in toluene (60 ml) was refluxed for 4.5 h under an atmosphere of argon. The resulting blue–black solution was concentrated *in vacuo* and then purified by chromatography on neutral alumina using toluene–ethyl acetate (1:1) as eluent. Recrystallisation of the resulting blue–black solid from toluene afforded the title compound **7** as purple–black tabular plates (0.21 g, 13%), mp 155–157 °C (Found: C, 58.2; H, 4.3; N, 5.6; S, 11.2; Co, 11.5%; M^+, 478.0223. $C_{23}H_{19}CoN_2O_2S_2$ requires C, 57.7; H, 4.00; N, 5.8; S, 13.4; Co, 12.3%; *M*, 478.0220); λ_{max}(EtOH)/nm 724, 595, 388, 355, 287 and 234 (2.79, 4.33, 4.42, 4.46, 4.75 and 4.76); ν_{max}(KBr)/cm^{-1} 3500, 1709, 1478, 1324, 1143 and 408; δ_H-[CD_2Cl_2 (base washed), 300 MHz] 9.53 (1 H, s, SCH), 7.63 (1 H, br d, 5-H), 7.42 (5 H, m, ArH), 7.21 (3 H, m, ArH), 5.48 (5 H, s, Cp), 5.27 (2 H, s, CH_2O) and 4.99 (2 H, s, 3-H_2); *m*/*z* (CI) 479 (MH^+, 15%) and 295 (100).

2-Pivaloylamino-6-formylpteridin-4-one 10b and 2-(*N*,*N*-dimethylaminomethyleneamino)-6-formylpteridin-4-one 10c

A mixture of 2-amino-6-formylpteridin-4-one[17] **10a** (1.233 g, 6.45 mmol), pivalic anhydride (3 ml, 19.35 mmol) and 4-dimethylaminopyridine (0.16 g, 1.29 mmol) was heated at reflux in DMF (20 ml) with stirring under nitrogen. After 45 min the suspended solid had dissolved to give a dark-brown solution which was cooled and evaporated *in vacuo* to give a brown oil. This was purified by flash chromatography eluting with dichloromethane–methanol (94:6). First to be eluted was the title compound **10b** (1.004 g, 56%), mp 235–242 °C followed by the *title compound* **10c** as a tan-coloured solid (0.167 g, 10.5%), mp >310 °C (Found: C, 48.8; H, 4.1; N, 34.1%; M^+, 246.0862. $C_{10}H_{10}N_6O_2$ requires C, 48.59; H, 4.10; N, 34.13%; *M*, 246.0865); λ_{max}(MeOH–KOH)/nm 264, 284sh and 368 (4.15, 4.05 and 3.94); λ_{max}(MeOH–HCl)/nm 250, 288 and 316 (3.97, 3.88 and 3.97); ν_{max}(KBr)/cm^{-1} 1697, 1638, 1530, 1383, 1362, 1288 and 1248; δ_H[200 MHz, $(CD_3)_2SO$] 12.25 (1 H, bs, NH), 10.05 (1 H, s, CHO), 9.10 (1 H, s, 7-H), 8.90 (1 H, s, NCHN) and 3.30, 3.18 (2 × 3 H, 2 × s, 2 × NCH_3); *m*/*z* (CI) 264 (MNH_4^+, 43%) and 247 (MH^+, 100). Compound **10c** could be prepared efficiently by the reaction of the pteridinone **10a** (0.284 g, 1.48 mmol) suspended in DMF (3 ml) with bis(dimethylamino)-*tert*-butoxymethane (460 ml, 2.23 mmol) and heated with efficient stirring under nitrogen at 60 °C for 7 min. During this time the suspended solid dissolved to give a dark-red solution which was evaporated *in vacuo* to give a red solid. This was purified by flash chromatography, eluting with dichloromethane–methanol (9:1) to give **10c** as a yellow solid (0.339 g, 93%) identical with the sample characterised above.

2-(*N*,*N*-Dimethylaminomethyleneamino)-6-formyl-3-methylpteridin-4-one 10d

(a) To the pteridinone **10a** (2.048 g, 10.7 mmol) suspended in DMF (20 ml) was added DMFDMA (6.5 ml, 53 mmol) and the mixture was heated at 100 °C for 20 min with efficient stirring and under nitrogen. It was then evaporated *in vacuo* to give a brown oil which was purified by flash chromatography, eluting with dichloromethane–methanol (95:5) to give the *title com-*

pound **10d** as a red solid (1.65 g, 59%). An analytical sample had mp 230–250 °C (DMF) (Found: C, 50.9; H, 4.6; N, 32.1%; M^+, 260.1025. $C_{11}H_{12}N_6O_2$ requires C, 50.76; H, 4.65; N, 32.29%; *M*, 260.1022); λ_{max}(MeOH)/nm 212, 244, 274sh, 312 and 354 (4.05, 4.01, 4.02, 4.37 and 4.02); λ_{max}(MeOH–HCl)/nm 284, 322 and 340 (4.40, 4.17 and 4.04); ν_{max}(KBr)/cm^{-1} 1698, 1637, 1525, 1483, 1445, 1421, 1388, 1324 and 1247; δ_H(200 MHz) 10.22 (1 H, s, CHO), 9.28 (1 H, s, 7-H), 9.02 (1 H, s, NCHN), 3.72, 3.29, 3.24 (3 × 3 H, 3 × s, 3 × NCH_3); δ_C(75 MHz) 191.4, 161.9, 160.0, 159.9, 156.9, 148.6, 142.7, 129.4, 41.9, 35.9 and 30.5; DEPT analysis showed the peaks at 191.4, 159.9 and 148.6 to be CH and the peaks at 41.9, 35.9 and 30.5 to be CH_3; *m*/*z* (CI) 278 (MNH_4^+, 100%) and 261 (MH^+, 97). In addition variable quantities of 2-(N,N-*dimethylaminomethyleneamino*)-6-*methoxycarbonyl*-3-*methylpteridin*-4-*one* **10f** were isolated; an analytical sample had mp 268–275 °C (DMF) (Found: C, 49.7; H, 4.9; N, 28.95%. $C_{12}H_{14}N_6O_3$ requires C, 49.65; H, 4.86; N, 28.95%); λ_{max}(MeOH)/nm 248, 324 and 370 (4.03, 4.47 and 4.34); λ_{max}(MeOH–HCl)/nm 288, 330 and 346 (4.52, 4.41 and 3.24); ν_{max}(KBr)/cm^{-1} 1712, 1695, 1642, 1525 and 1478; δ_H(200 MHz) 9.40 (1 H, s, 7-H), 8.99 (1 H, s, NCHN), 4.03 (3 H, s, OCH_3), 3.70, 3.28 and 3.24 (3 × 3 H, 3 × s, 3 × NCH_3); *m*/*z* (CI) 308 (MNH_4^+, 20%) and 291 (MH^+, 100).

(b) A suspension of the pteridinone **10c** (1.93 g, 7.84 mmol) in dichloromethane (20 ml) was stirred under nitrogen whilst 1,8-diazabicyclo[5.4.0]undec-7-ene (3.25 ml, 23.5 mmol) was added to induce dissolution. The resultant red solution was cooled to −40 °C and treated with dimethyl sulfate (2.23 ml, 23.5 mmol), added dropwise over 7 min. The mixture was allowed to warm to room temperature over 2 h after which it was concentrated *in vacuo* to give a red oil which was purified by flash chromatography, eluting with dichloromethane–methanol (95:5) to give **10d** as a red solid (1.60 g, 78%), identical with material described in (a) above.

In order to establish the regiochemistry of *N*-methylation, **10d** was treated with aqueous NaOH to give 2-amino-6-formyl-3-methylpteridin-4-one **10e**, λ_{max}(MeOH)/nm 284 and 352 (4.19 and 4.08); λ_{max}(MeOH–HCl)/nm 320 (4.1), which were compared with those reported[23] for 2-amino-3,6-dimethylpteridin-4-one: λ_{max}(pH 4.8 buffer)/nm 243, 275 and 359 (4.15, 4.10 and 3.59); λ_{max}(pH 0.6 buffer)/nm 326 (3.87); and for 2-amino-1,6-dimethylpteridin-4-one: λ_{max}(pH 5 buffer)/nm 230, 279 and 336 (4.35, 3.65 and 3.36); λ_{max}(pH 0.3 buffer)/nm 325 (3.9).

3-Benzyl-2-(*N*,*N*-dimethylaminomethyleneamino)-6-formylpteridin-4-one 10g

2-Amino-6-formylpteridin-4-one **10a** (0.798 g, 4.18 mmol), dimethylformamide diethyl acetal (2.15 ml, 12.5 mmol) and benzyl alcohol (1.3 ml, 12.5 mmol) were mixed in DMF (15 ml) and heated at 70 °C with stirring under nitrogen for 1 h during which time the suspended solid dissolved. The mixture was evaporated *in vacuo* and the resultant brown oil purified by flash chromatography, eluting with dichloromethane–methanol (97:3). The collected solid was further purified by recrystallisation to give the title compound **10g** as a yellow solid (184 mg, 13%), mp 219–221 °C (Et_2O) (Found: M^+, 336.1334. $C_{17}H_{16}N_6O_2$ requires *M*, 336.1335); λ_{max}(MeOH)/nm 214, 248, 320 and 366 (4.16, 4.00, 4.30 and 4.19); λ_{max}(MeOH–HCl)/nm 216, 286 and 314 (4.20, 4.44 and 4.21); ν_{max}(KBr)/cm^{-1} 1692, 1636, 1528, 1474 and 1395; δ_H(200 MHz) 10.22 (1 H, s, CHO), 9.30 (1 H, s, 7-H), 9.02 (1 H, s, NCHN), 7.48 (2 H, m, ArH), 7.38 (3 H, m, ArH), 5.60 (2 H, s, $PhCH_2$) and 3.27, 3.23 (2 × 3 H, 2 × s, 2 × NCH_3); *m*/*z* (CI) 354 (MNH_4^+, 50%) and 337 (MH^+, 100).

3-Allyl-2-(*N*,*N*-dimethylaminomethyleneamino)-6-formylpteridin-4-one 10h

To the pteridinone **10c** (0.981 g, 3.98 mmol) suspended in dichloromethane (20 ml) was added DBU (0.90 ml, 6 mmol), causing the solid to dissolve. Allyl bromide (1.0 ml, 12 mmol) was added to the solution which was then left at room temperature for 42 h. Further allyl bromide (1.0 ml, 12 mmol) was added to it after 18 h. The mixture was concentrated *in vacuo* and the resultant brown oil purified by flash chromatography, eluting with dichloromethane–methanol (95:5) to give the *title compound* **10h** as a brown solid (822 mg, 72%), mp 193–196 °C (EtOAc) (Found: C, 54.4; H, 4.8; N, 28.9%; M^+, 286.1179. $C_{13}H_{14}N_6O_2$ requires C, 54.5; H, 4.9; N, 29.35%; *M*, 286.1178); λ_{max}(MeOH)/nm 244, 314 and 352 (4.06, 4.39 and 4.09); λ_{max}(MeOH–HCl)/nm 234, 288 and 324 (3.93, 4.41 and 4.24); ν_{max}(KBr)/cm^{-1} 1696, 1630, 1517, 1480 and 1395; δ_H(200 MHz) 10.13 (1 H, s, CHO), 9.21 (1 H, s, 7-H), 8.96 (1 H, s, NCHN), 5.90 (1 H, m, C=CH), 5.18 (2 H, m, C=CH_2), 4.90 (2 H, m, NCH_2) and 3.25, 3.19 (2 × 3 H, 2 × s, 2 × NCH_3); *m*/*z* (CI) 304 (MNH_4^+, 95%) and 287 (MH^+, 100).

2-(*N*,*N*-Dimethylaminomethyleneamino)-6-formyl-3-(2-methoxyethoxymethyl)pteridin-4-one 10i

The pteridinone **10c** (0.229 g, 0.93 mmol) and DBU (0.153 ml, 1.02 mmol) were dissolved in dichloromethane (5 ml) and the resultant red solution cooled to ice-bath temperature under an atmosphere of nitrogen. Methoxyethoxymethyl chloride (0.211 ml, 1.86 mmol) was added dropwise to the solution over 2 min after which it was stirred for 1 h at ice-bath temperature. The mixture was then evaporated *in vacuo* and the resultant oil purified by flash chromatography, eluting with dichloromethane–methanol (95:5) to give the title compound **10i** as a yellow solid (0.236 g, 76%), mp 147–162 °C (Found: C, 50.3; H, 5.6; N, 25.1%; M^+, 334.1391. $C_{14}H_{18}N_6O_4$ requires C, 50.29; H, 5.43; N, 25.14%; *M*, 334.1389); λ_{max}(MeOH)/nm 240, 316 and 356 (4.04, 4.45 and 4.12); λ_{max}(MeOH–HCl)/nm 288 and 320 (4.43 and 4.23); ν_{max}(KBr)/cm^{-1} 1709, 1638, 1517, 1481 and 1443; δ_H(200 MHz) 10.19 (1 H, s, CHO), 9.28 (1 H, s, 7-H), 9.00 (1 H, s, NCHN), 5.90 (2 H, s, NCH_2O), 3.87–3.53 (4 H, m, CH_2CH_2), 3.32 (3 H, s, OCH_3) and 3.28, 3.22 (2 × 3 H, 2 × s, 2 × NCH_3); *m*/*z* (CI) 335 (MH^+, 100%).

6-Acetyl-2-(*N*,*N*-dimethylaminomethyleneamino)-3-methylpteridin-4-one 10k and 2-(*N*,*N*-dimethylaminomethyleneamino)-3-methyl-6-oxiranylpteridin-4-one 10j

Diazomethane[33] was collected by passing the gas through two cooled receiver flasks containing dichloromethane, connected in series. To a solution prepared in this way from Diazald (5 g) and warmed to 25 °C was added a solution of the pteridinone **10d** (1.07 g, 4.10 mmol) in dichloromethane (40 ml). After 45 min, the remaining diazomethane was quenched by addition of acetic acid (2 ml) and the resultant solution was concentrated *in vacuo* to yield a brown oily solid. Recrystallisation of this from ethanol yielded the title compound **10k** (0.447 g) as a tan solid. The resultant mother-liquors were concentrated *in vacuo* and purified by flash chromatography, eluting with dichloromethane–methanol (95:5) to yield further ketone (0.21 g) (total yield: 0.66 g, 59%). An analytical sample was prepared by recrystallisation, mp 250–255 °C (slow sublimation above 230 °C) (EtOH) (Found: C, 52.2; H, 5.1; N, 30.2%. $C_{12}H_{14}N_6O_2$ requires C, 52.55; H, 5.14; N, 30.64%); λ_{max}(MeOH)/nm 214, 252, 286, 326 and 368 (4.18, 4.00, 4.12, 4.39 and 4.32); λ_{max}(MeOH–HCl)/nm 288, 332 and 378 (4.46, 4.39 and 3.27); ν_{max}(KBr)/cm^{-1} 1720, 1696, 1638, 1531, 1482, 1443, 1397, 1362, 1328 and 1269; δ_H(200 MHz) 9.37 (1 H, s, CHO), 9.00 (1 H, s, NCHN), 3.71, 3.28, 3.24 (3 × 3 H, 3 × s, 3 × NCH_3) and 2.80 (3 H, s, $COCH_3$); *m*/*z* (CI) 292 (MNH_4^+, 50%) and 275 (MH^+, 100). Reaction at 0 °C produced more of a second product and this could be isolated in poor yield by separation from the ketone **10k** by flash chromatography, eluting with dichloromethane–acetone (7:3) to give the *title compound* **10j**, mp 120–130 °C (Found: M^+, 274.1174. $C_{12}H_{14}N_6O_2$ requires *M*, 274.1178); λ_{max}(MeOH)/nm 246, 314 and 360 (4.00, 4.32 and 4.01); λ_{max}(MeOH–HCl)/nm 286 and 330 (4.42 and 4.30); ν_{max}(KBr)/cm^{-1} 1678, 1638 and 1532; δ_H(200 MHz) 8.94 (1 H, br s,

NCHN), 8.62 (1 H, s, 7-H), 4.28 (1 H, dd, *J* 2.5, 4.2, CHO), 3.72, 3.25, 3.21 (3 × 3 H, 3 × s, 3 × NCH_3), 3.27 (1 H, dd, *J* 4.1, 5.24, one of CH_2O) and 3.02 (1 H, dd, *J* 2.5, 5.24, one of CH_2O); *m*/*z* (CI) 292 (MNH_4^+, 15%) and 275 (MH^+, 100).

6-Acetyl-3-benzyl-2-(*N*,*N*-dimethylaminomethyleneamino)-pteridin-4-one 10l and 3-benzyl-2-(*N*,*N*-dimethylamino-methyleneamino)-6-oxiranylpteridin-4-one 10o

The pteridinone **10g** (169 mg, 0.50 mmol) was treated with diazomethane in dichloromethane at ice-bath temperature as described above, after which purification of the crude product by flash chromatography, eluting with dichloromethane–methanol (97:3) gave the *title compound* **10l** (64 mg, 34%), mp 182–188 °C (Found: M^+, 350.1499. $C_{18}H_{18}N_6O_2$ requires *M*, 350.1491); λ_{max}(MeOH)/nm 248, 284, 328 and 364 (3.71, 3.74, 4.01 and 3.97); λ_{max}(MeOH–HCl)/nm 212, 290 and 332 (3.92, 4.11 and 4.04); ν_{max}(KBr)/cm^{-1} 1691, 1636, 1523, 1486 and 1393; δ_H(200 MHz) 9.38 (1 H, s, 7-H), 9.02 (1 H, s, NCHN), 7.48 (2 H, m, ArH), 7.38 (3 H, m, ArH), 5.58 (2 H, s, $PhCH_2$), 3.27, 3.24 (2 × 3 H, 2 × s, 2 × NCH_3) and 2.81 (3 H, s, $COCH_3$); *m*/*z* (CI) 368 (MNH_4^+, 10%), 351 (MH^+, 25) and 102 (100); and then the *title compound* **10o** (21 mg, 11%), mp 108–112 °C (Found: M^+, 350.1495. $C_{18}H_{18}N_6O_2$ requires *M*, 350.1491); ν_{max}(KBr)/cm^{-1} 1692, 1634, 1523 and 1386; λ_{max}-(MeOH)/nm 246, 316 and 360 (4.05, 4.35 and 4.06); λ_{max}-(MeOH–HCl)/nm 290 and 330 (4.38 and 4.20); δ_H(200 MHz) 8.90 (1 H, s, NCHN), 8.59 (1 H, s, 7-H), 7.45 (2 H, m, ArH), 7.23 (3 H, m, ArH), 5.55 (2 H, s, $PhCH_2$), 4.23 (1 H, dd, *J* 4.2 and 2.5, CHO), 3.22 (1 H, m, one of CH_2O), 3.20, 3.16 (2 × 3 H, 2 × s, 2 × NCH_3) and 3.02 (1 H, dd, *J* 2.5 and 5.3, one of CH_2O); *m*/*z* (CI) 368 (MNH_4^+, 12%), 351 (MH^+, 100), 289 (48), 275 (20) and 102 (85).

6-Acetyl-3-allyl-2-(*N*,*N*-dimethylaminomethyleneamino)-pteridin-4-one 10m

Treatment of the pteridinone **10h** (0.28 g, 0.98 mmol) with diazomethane in dichloromethane at room temperature using the procedure described for **10k** above, followed by purification of the crude product by flash chromatography and then recrystallisation gave the *title compound* **10m** as a tan-coloured solid (90 mg, 31%) mp 187–189 °C (EtOAc) (Found: M^+, 300.1337. $C_{14}H_{16}N_6O_2$ requires *M*, 300.1334); λ_{max}(MeOH)/nm 248, 284, 332 and 364 (3.97, 4.04, 4.36 and 4.31); λ_{max}(MeOH–HCl)/nm 238, 290 and 330 (3.94, 4.40 and 4.38); ν_{max}(KBr)/cm^{-1} 1696, 1636, 1522, 1491 and 1422; δ_H(200 MHz) 9.38 (1 H, s, 7-H), 9.03 (1 H, s, NCHN), 5.97 (1 H, m, C=CH), 5.25 (2 H, m, CH_2=C), 4.95 (2 H, m, NCH_2), 3.29, 3.19 (2 × 3 H, 2 × s, 2 × NCH_3) and 2.81 (3 H, s, $COCH_3$); *m*/*z* (CI) 318 (MNH_4^+, 25%) and 301 (MH^+, 100).

6-Acetyl-2-(*N*,*N*-dimethylaminomethyleneamino)-3-methoxy-ethoxymethylpteridin-4-one 10n

Treatment of the pteridinone **10i** (0.776 g, 2.32 mmol) with diazomethane in dichloromethane at room temperature, by the same general procedure as described above for **10k**, and then purification of the crude product by flash chromatography, eluting with dichloromethane–methanol (95:5), gave the *title compound* **10n** as a brown solid (0.246 g, 30%) (Found: M^+, 348.1541. $C_{15}H_{20}N_6O_4$ requires *M*, 348.1546); δ_H(200 MHz) 9.37 (1 H, s, 7-H), 8.99 (1 H, s, NCHN), 5.90 (2 H, s, NCH_2), 3.88–3.53 (4 H, m, CH_2CH_2), 3.34 (3 H, s, OCH_3), 3.30, 3.24 (2 × 3 H, 2 × s, 2 × NCH_3) and 2.79 (3 H, s, $COCH_3$); *m*/*z* (CI) 349 (MH^+, 100%).

6-Bromoacetyl-2-(*N*,*N*-dimethylaminomethyleneamino)-3-methylpteridin-4-one 10p hydrobromide

The pteridinone **10k** (1.345 g, 4.91 mol) and pyrrolidine hydrotribromide (2.44 g, 4.91 mmol) were heated together in acetic acid (15 ml) at 50 °C for 21 h, with efficient stirring under nitrogen. The resultant mixture was maintained at 4 °C for 18 h, filtered and the resultant solid washed with acetic acid and dried *in vacuo* to give the *title compound* **10p** *hydrobromide* (0.806 g, 38%), mp >310 °C; ν_{max}(KBr)/cm^{-1} 1715, 1667, 1595, 1565, 1471, 1431, 1401, 1397, 1297, 1251, 1216, 1141 and 1057; this was converted into the free base by partitioning between saturated aqueous sodium hydrogen carbonate and dichloromethane to produce **10p** as a tan-coloured oil (Found: M^+, 353.0344. $C_{12}H_{14}N_6O_2{}^{79}Br$ requires *M*, 353.0362); λ_{max}(MeOH)/nm 214, 254, 288, 334 and 374 (4.26, 4.05, 4.15, 4.36 and 4.39); λ_{max}(MeOH–HCl)/nm 210, 286, 332 and 382 (4.31, 4.48, 4.39 and 3.36); δ_H(200 MHz) 9.37 (1 H, s, 7-H), 9.03 (1 H, s, NCHN), 4.93 (2 H, s, CH_2Br) and 3.68, 3.32, 3.25 (3 × 3 H, 3 × s, 3 × NCH_3); *m*/*z* (CI) 355 (MH^+, 50%), 275 (100) and 186 (75).

6-{[Dimethylamino(thiocarbonyl)thio]acetyl}-2-(*N*,*N*-dimethyl-aminomethyleneamino)-3-methylpteridin-4-one 10q

The bromo ketone **10p** (65 mg, 0.18 mmol) in methanol–dichloromethane (5:2; 7 ml) was treated with sodium *N*,*N*-dimethyldithiocarbamate dihydrate (50 mg, 0.27 mmol). After 10 min the mixture was evaporated and the residue partitioned between water (10 ml) and dichloromethane (15 ml). The organic layer was washed with brine, dried and evaporated to give the *title compound* **10q** (46 mg, 64%) as a yellow solid, mp 206–216 °C (Found: M^+, 393.1045. $C_{15}H_{19}N_7O_2S_2$ requires *M*, 393.1042); δ_H(200 MHz) 9.34 (1 H, s, 7-H), 8.98 (1 H, s, NCHN), 5.10 (2 H, s, CH_2S) and 3.70, 3.49, 3.45, 3.28, 3.23 (5 × 3 H, 5 × s, 5 × NCH_3); *m*/*z* (FAB) 787 (2M + H^+, 15%), 395 (MH_2^+, 100), 306 (40) and 276 (25).

6-{[*tert*-Butylthio(thiocarbonyl)thio]acetyl}-2-(*N*,*N*-dimethyl-aminomethyleneamino)-3-methylpteridin-4-one 10r

The pteridinone **10p** hydrobromide (0.10 g, 0.23 mmol) was suspended in dichloromethane (5 ml) and pyridine (19 μl, 0.253 mmol) was added to induce dissolution. Potassium *tert*-butyl trithiocarbonate (0.071 g, 0.34 mmol) was then added to the solution and the resulting suspension was stirred for 20 min. It was then diluted with further dichloromethane and washed with saturated aqueous sodium hydrogen carbonate (15 ml). The aqueous phase was separated and extracted with dichloromethane (15 ml) and the combined organic extracts were washed with brine, dried and evaporated *in vacuo* to yield the title compound **10r** as a red solid (0.105 g, 100%), mp 170–182 °C (Found: M^+, 438.0959. $C_{17}H_{22}N_6O_2S_3$ requires *M*, 438.0966); λ_{max}(MeOH)/nm 248, 290sh, 330 and 374 (3.71, 3.89, 4.09 and 4.04); λ_{max}(MeOH–HCl)/nm 292 and 330 (4.14 and 4.12); δ_H(200 MHz) 9.35 (1 H, s, 7-H), 9.01 (1 H, s, NCHN), 5.07 (2 H, s, CH_2S), 3.71, 3.30, 3.24 (3 × 3 H, 3 × s, 3 × NCH_3) and 1.61 [9 H, s, $C(CH_3)_3$]; *m*/*z* (CI) 439 (MH^+, 1%), 292 (15), 275 (100) and 223 (15).

2-(*N*,*N*-Dimethylaminomethyleneamino)-6-{[isopropyloxy-(thiocarbonyl)thio]acetyl}-3-methylpteridin-4-one 10s

The pteridinone **10p** hydrobromide (0.698 g, 1.61 mmol) was suspended in dichloromethane (10 ml) with efficient stirring and pyridine (143 μl, 1.77 mmol) was added to induce dissolution. Potassium isopropyl xanthate (0.464 g, 2.41 mmol) was added to the solution and the resultant suspension stirred for 15 min before being diluted with further dichloromethane and washed with saturated aqueous sodium hydrogen carbonate (10 ml). The aqueous phase was separated and extracted with dichloromethane (15 ml). The combined organic extracts were washed once with brine (15 ml), dried and evaporated *in vacuo* to yield the *title compound* **10s** (0.631 g, 96%) as a pale-red solid, mp 172–190 °C (Pr^iOH) (Found: C, 46.8; H, 4.8; N, 20.4; S, 15.5%; M^+, 408.1043. $C_{16}H_{20}N_6O_3S_2$ requires C, 47.04; H, 4.93; N, 20.57; S, 15.70%; *M*, 408.1038; λ_{max}(MeOH)/nm 214, 282, 334 and 374 (4.36, 4.28, 4.36 and 4.36); λ_{max}(MeOH–HCl)/nm 216, 288, 334 and 384 (4.23, 4.48, 4.40 and 3.36); ν_{max}(KBr)/cm^{-1} 1701, 1689, 1633, 1525, 1481,

1404, 1386, 1331, 1289 and 1242; δ_H(200 MHz) 9.27 (1 H, s, 7-H), 8.94 (1 H, s, NCHN), 5.60 (1 H, m, $OCHMe_2$), 4.83 (2 H, s, CH_2S), 3.63, 3.25, 3.19 (3 × 3 H, 3 × s, 3 × NCH_3) and 1.25 [6 H, d, *J* 6.2, $C(CH_3)_2$]; *m*/*z* (CI) 409 (MH^+, 1%), 349 (1) and 275 (100).

4-[2-(*N*,*N*-Dimethylaminomethyleneamino)-3-methylpteridin-4-on-6-yl]-1,3-dithiole-3-thione 12a

Compound **10r** (103 mg, 0.0235 mmol) was dissolved with swirling in 98% sulfuric acid (2 ml) and the red solution after being kept at room temperature for 1 h was treated with ice (20 ml). The mixture was then neutralised with solid sodium hydrogen carbonate and extracted with dichloromethane (4 × 15 ml). The combined extracts were washed with brine, dried and evaporated *in vacuo* to give a red oily solid which was further purified by flash chromatography, eluting with dichloromethane–methanol (95:5) to give the title compound **12a** as a red solid (47 mg, 54%), mp >310 °C (Found: M^+, 364.0241. $C_{13}H_{12}N_6OS_3$ requires *M*, 364.0235); λ_{max}(MeOH)/nm 248, 290, 332, 364 and 426sh (3.99, 4.07, 4.22, 4.15 and 3.92); λ_{max}(MeOH–HCl)/nm 286, 322 and 394 (4.26, 4.17 and 3.91); δ_H(200 MHz) 8.93 (1 H, s, NCHN), 8.90 (1 H, s, 7-H), 7.76 (1 H, s, SCH) and 3.70, 3.28, 3.22 (3 × 3 H, 3 × s, 3 × NCH_3); *m*/*z* (CI) 365 (MH^+, 20%), 308 (20), 291 (100) and 275 (30).

4-[2-(*N*,*N*-Dimethylaminomethyleneamino)-3-methylpteridin-4-on-6-yl]-1,3-dithiol-3-one 12b

Compound **10s** (0.226 g, 0.55 mmol) was added to concentrated sulfuric acid (5 ml) with swirling at room temperature to give a red solution. After 30 min at room temperature the mixture was poured into iced water (50 ml), basified by the cautious addition of solid sodium hydrogen carbonate and then extracted with dichloromethane (4 × 15 ml). The combined extracts were washed with brine, dried and evaporated *in vacuo* to yield the title compound **12b** as a mustard-coloured solid (0.125 g, 65%), mp >310 °C (Found: M^+, 348.0464. $C_{13}H_{12}N_6O_2S_2$ requires *M*, 348.0463); λ_{max}(MeOH) 280, 340 and 386 (4.15, 4.48 and 4.22); λ_{max}(MeOH–HCl) 278, 322 and 370 (4.27, 4.35 and 4.21); ν_{max}(KBr)/cm^{-1} 1678, 1643, 1519, 1486, 1443, 1421, 1378, 1334 and 1114; δ_H[200 MHz, $(CD_3)_2SO$] 9.52 (1 H, s, 7-H), 8.98 (1 H, s, NCHN), 8.40 (1 H, s, SCH) and 3.69, 3.44, 3.32 (3 × 3 H, 3 × s, 3 × NCH_3); *m*/*z* (CI) 349 (MH^+, 50%) 102 (100) and 85 (70).

(η⁵-Cyclopentadienyl)-1-[2-(*N*,*N*-dimethylaminomethyleneamino)-3-methylpteridin-4-on-6-yl]ethene-1,2-dithiolatocobalt(III) 8

Compound **12b** (0.031 g, 0.089 mmol) was suspended with vigorous stirring in methanol–chloroform (1:1; 5 ml). To this suspension was added caesium hydroxide hydrate (0.032 g, 0.187 mmol), pre-dissolved in 1 ml of the solvent mixture. After being stirred for 20 min, during which time the suspended solid dissolved to give a dark-brown solution, cyclopentadienylcobalt(III) diiodide[31] (0.073 g, 0.18 mmol) was added to the mixture which was then stirred for 15 min. After this it was evaporated *in vacuo*, and the residue was partitioned between dichloromethane (15 ml) and water (15 ml). The aqueous phase was separated and extracted with dichloromethane (10 ml). The combined organic extracts were washed with brine, dried and evaporated *in vacuo* to give a dark oily solid. This was purified by flash chromatography, eluting with dichloromethane–methanol (97:3) to yield the title compound **8** as a microcrystalline green solid (20 mg, 51%), mp >320 °C (Found: M^+, 444.0239. $C_{17}H_{17}N_6OS_2Co$ requires *M*, 444.0237); λ_{max}(MeOH)/nm 240, 288, 328, 414 and 602 (4.14, 4.30, 4.37, 4.09 and 3.85); λ_{max}(MeOH–HCl)/nm 286, 318, 410 and 588 (4.35, 4.40, 3.97 and 3.81); ν_{max}(KBr)/cm^{-1} 1677, 1631, 1525, 1486, 1417, 1374, 1354, 1195 and 1111; δ_H(200 MHz) 9.81 (1 H, s, 7-H), 9.66 (1 H, s, SCH), 8.94 (1 H, s, NCHN), 5.42 (5 H, s, Cp) and 3.70, 3.24, 3.19 (3 × 3 H, 3 × s, 3 × NCH_3); *m*/*z* (CI) 445 (MH^+, 50%), 349 (100), 291 (55) and 275 (70). Crystals of quality suitable for X-ray crystallographic analysis[32] were obtained by vapour diffusion of acetonitrile into a solution of the compound in 1,2-dichloroethane.

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