DALTON

Synthesis and metallation of ferrocenylimines derived from ligating diaminoheteroarenes

Catherine M. Asselin,[a] Greig C. Fraser,[a] H. K. Hall Jr.,[b] W. Edward Lindsell,[a] Anne B. Padias[b] and Peter N. Preston[a]

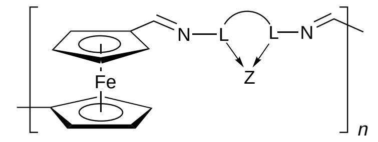
[a] *Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, UK EH14 4AS*
[b] *Department of Chemistry, University of Arizona, Tucson, Arizona, 85721, USA*

A regioisomeric mixture of 1,1′-didodecylferrocenedicarbaldehydes **3** was prepared from the reaction of a regioisomeric mixture of 1,1′-didodecyldilithioferrocenes and dimethylformamide. Three ligating heteroaromatics were synthesized each containing two amino substituents: 5,5′-diamino-2,2′-bipyridine and 5,5″-diamino-2,2′ : 6′,2″-terpyridine were prepared from appropriate dinitro compounds by reduction with palladium on charcoal–hydrazine hydrate. The reaction of 2-cyano-5-nitropyridine and hydrazine hydrate gave an isolable amidine derivative and this was transformed with hydrazine in a separate reaction under more forcing conditions into 3,6-bis(5-amino-2-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine. The latter was converted into the tetrazine by oxidation (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) and then trifluoroacetylated [$(CF_3CO)_2O$] to give the bis(trifluoroacetylamino) derivative. Diels–Alder reaction of the latter with dodec-1-yne afforded 4-*n*-decyl-3,6-bis[5-(trifluoroacetylamino)-2-pyridyl]pyridazine which was deprotected (K_2CO_3) to give the corresponding diamine. Bis(ferrocenyl) Schiff bases were prepared from ferrocenecarbaldehyde and the appropriate diamine in either uncatalysed or acid-catalysed condensations. Tetracarbonylmolybdenum complexes were prepared by treating the appropriate diamines with molybdenum hexacarbonyl. Reaction of one of these complexes with ferrocenecarbaldehyde gave a heterobimetallic complex.

The search for new materials with useful conducting properties has generated interest in the synthesis of mixed-valence homo-[1] and hetero-bimetallic[2] transition organometallic compounds which are suitable for investigating electron-transport phenomena;[1] the latter type are particularly attractive because of the wide preparative scope and the opportunity to evaluate electronic co-operativity through conjugated frameworks. The incorporation of ferrocene into such species[3] is attractive in view of the well characterised redox behaviour and chemical stability of this group. As part of our continuing interest in the synthesis of metallated, highly unsaturated oligomers[4] and polymers,[5] we have embarked on the preparation of novel ferrocene (R)-containing polymers $(R{-}A{-}B)_n$ in which A and B are a conjugated linking group and a diligating heteroaromatic moiety, respectively. Our goal is to prepare polymers (**1a**) in which the linking group (A) is imino, which would furnish a variety of partially or fully metallated species (**1b**); synthesis of the latter can also be approached through polycondensation of 1,1′-diformylferrocene and metallated diaminoheteroarenes. It may be noted that there is current interest in the synthesis of heterobimetallic ferrocene-containing derivatives in which the diligating groups are directly bonded to the metallocene (*e.g.* bipyridinyl,[6] 8-hydroxyquinolinyl,[7] terpyridinyl,[8] and oligopyridinyl[9] substituents).

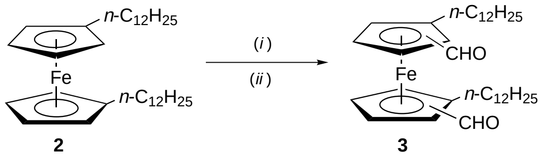
The synthesis of fully conjugated polyimines by condensation of dialdehydes and diamines[10] or through Schiff-base exchange reactions[11] has been pursued for many decades and continues to attract interest.[12] An undesirable feature of many fully aromatic polyimines is their very poor solubility in common organic solvents, but considerable improvement has been achieved using dialdehydes with long flexible side-chains (*e.g.* $CH_2OC_nH_{2n+1}$; *n* up to 12).[13]

Highly insoluble ferrocene-containing polyimines were first prepared[14] more than thirty years ago, but improved solubilities were achieved by Neuse *et al.*[15] by polycondensation of ferrocene-1,1′-dicarbaldehyde and aromatic diamines in dimethylformamide (dmf) or through azomethine exchange reactions. Nevertheless, such polyimines are soluble only in solvents, such as formic acid and *m*-cresol, and molar masses are estimated[15] to be low ($M_w \approx 2000$–3000).



1

	Z
1a	–
1b	ML_n



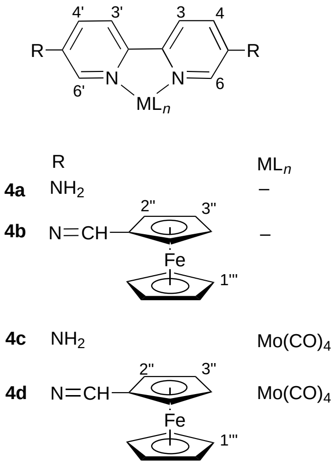
Scheme 1 (i) $LiBu^n$, tmen ($Me_2NCH_2CH_2NMe_2$); (ii) $HCONMe_2$

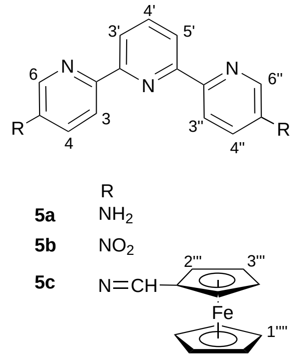
In this paper we describe our preparative work on model compounds relating to polyimines **1a**,**1b** including the following: the synthesis of ferrocene-1,1′-dicarbaldehyde and a ligating diaminoheteroarene, both of which contain long alkyl chains to aid solubilisation; the synthesis of bis(imines) derived from ferrocenecarbaldehyde; and the metallation of such bis(imines) leading to novel heterobimetallic species.

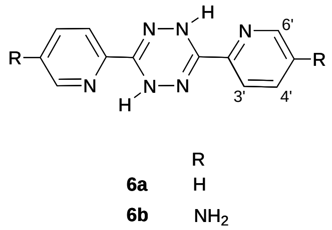
Results and Discussion

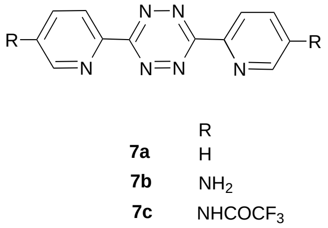
Synthesis of dialdehyde and diamine monomers

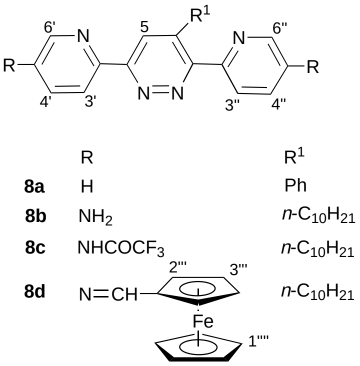
An attempt was made in this work to formylate 1,1′-didodecylferrocene[16] **2** by the Vilsmeier procedure[17] but only a monoaldehyde was formed. The desired dialdehyde, albeit as an inseparable mixture of regioisomers **3**, was prepared[18] through the dilithio tmen species (see Scheme 1). This oily, isomeric mixture **3** is very soluble in common organic solvents (*e.g.* $CHCl_3$, tetrahydrofuran).

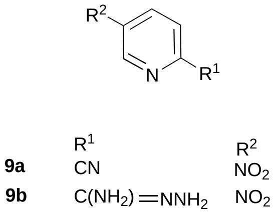












Heterocyclic diamines selected for study were in the bipyridine, terpyridine and bis(2-pyridinyl)pyridazine ring systems. Despite extensive interest in co-ordination complexes derived from bipyridines, there are few references to diamino derivatives. Connor and co-workers[19] prepared the tetracarbonylmolybdenum complex of 4,4′-diamino-2,2′-bipyridine, but there is only an isolated report[20] describing (unco-ordinated) 5,5′-diamino-2,2′-bipyridine **4a**. In the present work, this compound was prepared by reduction of 5,5′-dinitro-2,2′-bipyridine[20] using an improved procedure (Pd–C, N_2H_4), with full details provided in the Experimental section.

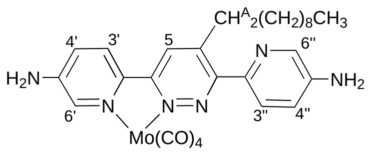
A suitable precursor for synthesis of 5,5″-diamino-2,2′:6′,2″-terpyridine **5a** was the known[21] dinitro derivative **5b**, which was prepared using a modified literature method[21] from 1-methyl-3,5-dinitro-2-pyridone, 2,6-diacetylpyridine and ammonia in methanol. In early, unsuccessful attempts to repeat this procedure we conducted reactions under strictly anhydrous conditions, but later realised that such a regime had an adverse effect on product yield. Reduction of the dinitro derivative **5b** was also conducted with Pd–C/N_2H_4 to give the diamine **5a** in moderate yield.

A diamine **8b** in the 3,6-bis(2-pyridyl)pyridazine series was synthesized through conventional inverse-electron-demand Diels–Alder reaction[22] of a 1,2,4,5-tetrazine derivative (*cf.* **6a** ⟶ **7a** ⟶ **8a**).[23] In contrast to the reaction of 2-cyanopyridine and hydrazine hydrate which gives the dihydrotetrazine derivative **6a** directly,[23] we found that the reaction of 2-cyano-5-nitropyridine **9a** and hydrazine hydrate was very exothermic and led to a complex, inseparable mixture of products. This problem was alleviated by conducting the reaction in ethanol solvent at room temperature to give the amidine derivative **9b**. The latter was then treated with hydrazine hydrate in a separate reaction in which pyridazine ring formation and reduction of the nitro group occurred concomitantly (**9b** ⟶ **6b**); the dihydro compound **6b** was then efficiently oxidised with 2,3-dichloro-5,6-dicyanobenzoquinone to give the tetrazine **7b**. Unsubstituted 3,6-bis(2′-pyridyl)tetrazines **7a** undergo Diels–Alder reactions with a variety of dienophiles,[22–24] but we found that the diamine **7b** did not react with dodec-1-yne in hot toluene or dmf. The undesirable electronic influence of the amino substituent was thus modified by trifluoroacetylation (see **7b** ⟶ **7c**) and a successful Diels–Alder reaction (**7c** ⟶ **8c**) was then accomplished; deprotection (K_2CO_3) of the bis(trifluoroacetyl) derivative **8c** afforded the target pyridazine **8b** in good yield. It may be noted in the context of compound **8b** that bipyridines with strongly hydrophobic substituents have proved of interest for photoinduced redox investigations of ruthenium(II) complexes.[25] The diamines (**4a**, **5a** and **8b**) and intermediates (**6b**, **7b**, **7c**, **9b**) were characterised spectroscopically (IR, ^{1}H and ^{13}C NMR) and also gave satisfactory data from elemental analysis and/or high-resolution mass spectral measurements.

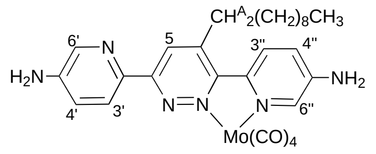
Synthesis of ferrocene-containing imines and tetracarbonylmolybdenum complexes

The bis(ferrocenyl) Schiff bases **4b**, **5c** and **8d** were prepared from ferrocenecarbaldehyde and the appropriate diamine in either uncatalysed (**4b**, **5c**) or acid-catalysed (**8d**) condensations. Their spectral characteristics (IR, NMR) were in accord with the proposed structures.

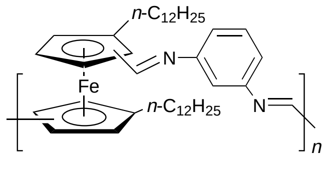
The metallated monomer **4c** was prepared by heating the diamine **4a** with molybdenum hexacarbonyl in toluene;[26] it was isolated as a stable orange solid in quantitative yield, with spectroscopic characteristics (IR, NMR) close to those of the 4,4′-diamino isomer.[19] There is little effect on coupling constants and minor changes in ^{1}H chemical shifts as a result of



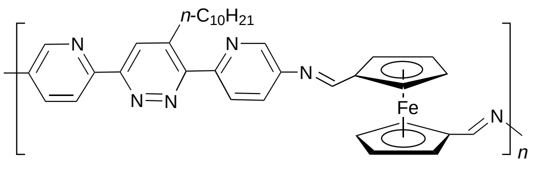
10



11



12



13

metallation. The diamino bis(pyridyl)pyridazine **8b** was also metallated in similar fashion to give the tetracarbonylmolybdenum derivative **10**, which was distinguished from the alternative isomer, **11**, on the basis of ^{1}H NMR spectroscopy. Significant shifts in aromatic ^{1}H resonances occur for the metallated rings, comparable to those found for metal complexes of 3,6-bis(2-pyridyl)pyridazine.[27] In particular, the resonance for H-5 in the pyridazine ring, δ 7.71, is shifted *ca.* 0.6 ppm to low frequency from the resonance in the free ligand, and resonances for H-3′, δ 7.79, and H-6′, δ 8.61, of the metallated pyridyl ring have moved, respectively, to higher and lower frequencies. Analysis of the ^{1}H NMR spectrum of **10** by the nuclear Overhauser enhancement spectroscopy (NOESY) procedure indicates that protons H^A of the *n*-decyl substituent give a positive NOE with H-5 but no interaction with H-3″, as expected for the proposed regiochemistry of metallation and conformation of the unmetallated ring of **10**. Further evidence for structure **10** was adduced through observation of a positive NOE from protons H-3′ and H-5. The preferential formation of isomer **10** may be caused by a combination of electronic and steric effects of the 4-alkyl substituent. For example, a hyperconjugative effect of this group enhancing the electron density of N-1 of the pyridazine ring can be envisaged; also, this substituent could exert a steric effect that might inhibit attainment of the planar conformation required for co-ordination in respect of formation of **11**.

The molybdenum complex **10** proved to be relatively labile in solution (*e.g.* $CHCl_3$) on standing for a few days. Therefore a model condensation reaction in respect of polymer synthesis was conducted with complex **4c** and ferrocenecarbaldehyde in dmf. Although the results of elemental analysis on the resultant red-purple complex **4d** were of low precision (see Experimental section), the spectral characteristics (IR, ^{1}H and ^{13}C NMR) were in accord with the structure shown. The molecular ion (FAB mass spectrum) and fragment ions resulting from loss of carbon monoxide (*e.g.* [$M^+ -$ CO], [$M^+ -$ 4CO]) were too weak in intensity to permit high-resolution mass measurements; nevertheless, the isotopic distribution patterns of such ions were in accord with calculated values.

The monomeric, regioisomeric dialdehyde mixture **3** and the diamine **8b** were selected for polymerisation studies by step-growth reactions with *m*-phenylenediamine and ferreocene-1,1′-dicarbaldehyde, respectively. Condensations were conducted in dmf and acidic dmf, and led to red materials believed to be polymers **12** and **13** respectively. The former is oily and of low molar mass ($M_w = 4650$ from GPC) but encouragingly is soluble in common organic solvents such as chloroform and tetrahydrofuran. The latter **13** is insoluble in common solvents: data from elemental analysis are in accord with the depicted repeat unit and the IR spectrum closely resembles that of the 'model' bis(ferrocenylimine) **8d**. Thermogravimetric analysis of this material indicates an onset of thermal decomposition around 260 °C with 50% loss of mass around 350 °C.

Conclusion

Ligating diamines (**4a**, **5a**, **8b**) and model imines (**4b**, **5c**, **8d**) relating to polyimines **1** have been prepared and characterised. Novel tetracarbonylmolybdenum species **4c** and **10** have also been synthesized for use as monomers for the preparation of such polyimines, but in terms of chemical stability the former (**4c**) should prove to be the most useful. A ferrocenedicarbaldehyde regioisomeric mixture **3** with long-chain alkyl substituents in each ring has proved to be a useful monomer for the synthesis of polyimines with enhanced solubility.

Experimental

Melting points were determined on a Gallenkamp apparatus. Infrared spectra were recorded on Perkin-Elmer 580 and FT-1600 instruments and calibrated against polystyrene, ^{1}H and ^{13}C NMR spectra on Bruker WP 200 and DPX 400 instruments. Chemical shifts are reported with respect to $SiMe_4$ as reference (positive shifts to high frequency/low field). Elemental analyses were performed at Napier University, Edinburgh, UK and at UMIST, Manchester, UK. Sorbsil C60 40/60 H was used for column chromatography and analytical TLC precoated plates were used. Ferrocenecarbaldehyde from Aldrich was purified by vacuum sublimation immediately before use.

Preparations

1,1′-Didodecylferrocenedicarbaldehyde 3. 1.6 M *n*-Butyllithium in *n*-hexane (6.7 cm^3, 4.9 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) (1.6 cm^3, 10.5 mmol) were added to a solution of 1,1′-didodecylferrocene **2**[15] (2.70 g, 4.9 mmol) in diethyl ether (12 cm^3) at −78 °C, and the mixture was stirred at −78 °C for 22 h. Dry dimethylformamide (1.2 cm^3) was added dropwise, the mixture was stirred for 2 h, and finally hydrolysed by addition of water (8 cm^3) at −78 °C. The organic phase was extracted with dichloromethane (3 × 5 cm^3) and the organic extract was dried ($MgSO_4$) and evaporated under reduced pressure to leave a red oil. This oil was purified chromatographically (CH_2Cl_2 eluent) to give the red, oily dicarbaldehyde **3** (1.28 g, 43%), $R_F = 0.12$ (CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 6 H, $J = 6.1$, CH_3), 1.24 (br s, 40 H, CH_2), 2.28 (t, 4 H, $J = 7.6$ Hz, H-6,6′), 4.47 (m, 2 H, ferrocenyl), 4.61 (s, 2 H, ferrocenyl), 4.66 (dd, 2 H, ferrocenyl) and 9.85 (s, 2 H, CHO). ^{13}C NMR ($CDCl_3$): δ 14.0 (primary C), 22.6, 29.2, 30.9, 31.8 (secondary C), 70.6, 71.1, 74.6 (CH, η^5-C_5H_3), 79.4, 96.3 (quaternary C, η^5-C_5H_3) and 193.3 (C=O). High-resolution electron-impact (EI) mass spectrum: *m*/*z* 578.376 66 (100%) ($C_{36}H_{58}FeO_2$, $M^{\cdot +}$ requires 578.378 62), 579.382 30 ($C_{35}{}^{13}CH_{58}FeO_2$ requires 579.381 98).

5,5′-Diamino-2,2′-bipyridine 4a. A slurry of palladium on carbon (10%, 0.20 g) in absolute alcohol (10 cm^3) was added to 5,5′-dinitro-2,2′-bipyridine[20] (1.00 g, 4.06 mmol) in absolute alcohol (95 cm^3) with stirring. The temperature of the mixture was increased to 60 °C and hydrazine hydrate (98%, 4.5 cm^3) was added dropwise under an atmosphere of nitrogen. After 16 h under reflux the suspension was filtered hot through Celite, then the solution was cooled and acidified with concentrated HCl until precipitation was complete. The hydrochloride salt was filtered off, dissolved in the minimum amount of cold water and a small amount of activated charcoal added. After stirring for 15 min the charcoal was filtered off through Celite and the filtrate was basified with 10% aqueous sodium hydroxide. The precipitate was filtered off, washed with deionised water, and dried to give the required colourless *compound* (0.50 g, 66%), m.p. 211–212 °C (lit.,[19] 208 °C); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3308 (asym NH$_2$ str), 3200 (sym NH$_2$ str), 1626 (N–H def), 1596 (C=C str/C=N str), 1563 (C=C str/C=N str), 1473 (C=C str/C=N str), 1426, 1408 and 1285 (C–N str); δ_H[(CD$_3$)$_2$SO] 5.33 (s, 2 H, NH), 5.35 (s, 2 H, NH), 6.96 [dd, 2 H, $J(H^3H^4) = 8.6$, $J(H^4H^6) = 2.6$, H-4], 7.87 [d, 2 H, $J(H^3H^4) = 8.6$, H-3] and 7.92 [d, 2 H, $J(H^4H^6) = 2.6$ Hz, H-6]; *m*/*z* (FAB) 187 (100, $[M + 1]^{\bullet +}$), 186 (48, $[M]^{\bullet +}$) and 185 (4%, $[M - 1]^{\bullet +}$).

5,5″-Dinitro-2,2′:6′,2″-terpyridine 5b. A solution of 1-methyl-3,5-dinitro-2-pyridone (4.97 g, 25 mmol) and 2,6-diacetylpyridine (1.81 g, 11 mmol) in methanol (200 cm^3) and aqueous ammonia (28%, 150 cm^3) was heated at 150 °C for 3 h in an autoclave. The contents were cooled and filtered, and the brown precipitate was washed with cold methanol (50 cm^3). Trituration of this solid with hot ethanol (150 cm^3), followed by washing with cold absolute ethanol (50 cm^3) gave the required *compound* as a tan solid (2.64 g, 74%), m.p. 270–272.5 °C (lit.,[21] 271–273 °C); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3094, 3068 (CH str), 1604, 1574 (C=C and C=N str), 1519 (asym NO$_2$ str), 1445, 1350 (sym NO$_2$ str), 822 and 759; δ_H(CDCl$_3$) 8.09 [t, 1 H, $J(H^{3'}H^{4'}) = J(H^{4'}H^{5'}) = 7.8$, H-4′], 8.64 [dd, 2 H, $J(H^3H^4) = 8.8$, $J(H^4H^6) = 2.6$, H-4 and -4″], 8.66 [d, 2 H, $J(H^{3'}H^{4'}) = J(H^{4'}H^{5'}) = 7.8$, H-3′ and -5′], 8.81 [dd, 2 H, $J(H^3H^4) = 8.8$, $J(H^3H^6) = 0.7$, H-3 and -3″] and 9.52 [dd, 2 H, $J(H^4H^6) = 2.6$, $J(H^3H^6) = 0.7$ Hz, H-6 and -6″]; *m*/*z* (FAB) 324 (2, $[M + 1]^{\bullet +}$), 323 (7, $[M]^{\bullet +}$), 123 (23), 89 (100) and 77 (100%).

5,5″-Diamino-2,2′:6′,2″-terpyridine 5a. A slurry of palladium on carbon (10%, 0.20 g) in butan-1-ol (20 cm^3) was added to 5,5′-dinitro-2,2′:6′,2″-terpyridine[21] **5b** (1.01 g, 3.12 mmol) in butan-1-ol (380 cm^3) and the suspension warmed to 60 °C. Hydrazine hydrate (98%) (5 cm^3) was added and the mixture refluxed for 18 h under an atmosphere of nitrogen. The solution was filtered hot through Celite, the filtrate was cooled and acidified with concentrated HCl until precipitation was complete. The suspension was cooled to 0 °C and the solid filtered off then washed with butan-1-ol (50 cm^3). The yellow hydrochloride salt was dissolved in the minimum amount of cold water and a small amount of activated charcoal was added. The mixture was stirred for 15 min and then filtered through Celite. The filtrate was basified with 10% NaOH to give a crude, tan/brown precipitate of the free base. This product was further purified *via* the hydrochloride, as described above, but using absolute alcohol as solvent in place of butan-1-ol to give the required pure *compound* as a tan solid (0.49 g, 60%), m.p. 235–236 °C; $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3316 (asym NH$_2$ str), 3204 (sym NH$_2$ str), 1625 (N–H def), 1593 (C=C str/C=N str), 1561 (C=C str/C=N str), 1490 (C=C str/C=N str), 1448, 1296 (C–N str) and 1268 (C–N str); δ_H[(CD$_3$)$_2$SO] 5.66 (s, 4 H, NH$_2$), 7.06 [dd, 2 H, $J(H^3H^4) = 8.6$, $J(H^4H^6) = 2.7$, H-4 and H-4″], 7.81 (dd, 1 H, $J = 8.4$, 7.2, H-4′), 8.03 [d, 2 H, $J(H^4H^6) = 2.7$, H-6 and H-6″], 8.05 (d, 2 H, $J = 7.7$, H-3′ and H-5′) and 8.27 [d, 2 H, $J(H^3H^4) = 8.6$ Hz, H-3 and H-3″]; δ_C[(CD$_3$)$_2$SO] 117.3, 120.6, 121.6, 135.9 and 137.8 (aromatic CH), 143.9, 145.9 and 155.7 (quaternary C); *m*/*z* (FAB) 264 (100, $[M + 1]^{\bullet +}$), 171 (5), 100 (22), 89 (17) and 77 (25%) (Found: C, 68.1; H, 5.1; N, 26.4. $C_{15}H_{13}N_5$ requires C, 68.4; H, 5.0; N, 26.6%).

Amidine derivative 9b. 2-Cyano-5-nitropyridine (13.08 g, 87.7 mmol) was dissolved in hot absolute ethanol (250 cm^3) and the solution allowed to cool. Hydrazine hydrate (10 cm^3, 10.4 g, 175 mmol) was added dropwise and the mixture stirred for 12 h under an atmosphere of nitrogen. The precipitate was filtered off, washed with ethanol (100 cm^3), and dried to give an orange solid (11.89 g, 75%). This product was found to contain a small amount of impurity, which for analytical purposes only was removed by vacuum sublimation to give the required pure *compound* as a bright orange solid, m.p. 173–174 °C (decomp.); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3408 (NH$_2$ str), 3380 (NH$_2$ str), 3300 (NH$_2$ str), 1633 (N–H def), 1597 (C=C str/C=N str), 1522 (asym NO$_2$ str), 1479 (C=C str/C=N str), 1345 (sym NO$_2$ str), 1296 (C–NH$_2$ str), 1268 (C–NH$_2$ str) and 829 (C–NO$_2$ str); δ_H[(CD$_3$)$_2$SO] 5.83 (br, 2 H, NH$_2$), 5.91 (br, 2 H, NH$_2$), 8.10 [dd, 1 H, $J(H^3H^4) = 9.0$, $J(H^3H^6) = 0.7$, H-3], 8.45 [dd, 1 H, $J(H^3H^4) = 9.0$, $J(H^4H^6) = 2.7$, H-4] and 9.25 [dd, 1 H, $J(H^4H^6) = 2.7$, $J(H^3H^6) = 0.7$ Hz, H-6); δ_C[(CD$_3$)$_2$SO] 120.3 and 131.9 (aromatic CH), 142.0 and 143.9 (quaternary C), 144.6 (aromatic CH) and 157.2 (quaternary C); *m*/*z* (EI) 181 (100, $[M]^{\bullet +}$), 165 (2), 154 (14), 152 (5), 151 (4), 150 (26) and 135 (4%); *m*/*z* (FAB) 182 (100, $[M + 1]^{\bullet +}$), 181 (30, $[M]^{\bullet +}$), 165 (24), 149 (16) and 136 (20%) (Found: C, 40.0; H, 4.5; N, 38.2. $C_6H_7N_5O_2$ requires C, 39.8; H, 3.9; N, 38.7%).

3,6-Bis(5-amino-2-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine 6b. The amidine derivative **9b** (11.50 g, 63.5 mmol) was added carefully to cooled hydrazine hydrate (98%, 115 cm^3) at 0 °C with vigorous stirring. The suspension was allowed to warm slowly to room temperature then was gradually heated to 110 °C under an atmosphere of nitrogen. After 3 h the solution was cooled and the precipitate filtered off. The solid was finally washed with cold ethanol (50 cm^3) to afford the required *compound* as golden orange needles (3.20 g, 38%), m.p. 227–230 °C; $\tilde{\nu}_{max}$(KBr)/ cm^{-1} 3285 (NH$_2$ str), 1618 (N–H def), 1585 (C=C str/C=N str), 1487 (C=C str/C=N str), 1428, 1385, 1351, 1299 (C–N str) and 1275 (C–N str); δ_H[(CD$_3$)$_2$SO] 5.84 (br, 4 H, NH$_2$), 6.97 [dd, 2 H, $J(H^{3'}H^{4'}) = 8.6$, $J(H^{4'}H^{6'}) = 2.5$, H-4′], 7.61 [d, 2 H, $J(H^{3'}H^{4'}) = 8.6$, H-3′], 7.89 [d, 2 H, $J(H^{4'}H^{6'}) = 2.5$ Hz, H-6′] and 8.40 (s, 2 H, NH); δ_C[(CD$_3$)$_2$SO] 120.8, 122.1 and 134.5 (aromatic CH), 135.0, 146.9 and 147.6 (quaternary C); *m*/*z* (FAB) 269 (79, $[M + 1]^{\bullet +}$), 268 (100, $[M]^{\bullet +}$), 267 (8) and 120 (43); 268.118 78 ($C_{12}H_{12}N_8$, $M^{\bullet +}$ requires 268.118 49) (Found: C, 54.3; H, 5.2. $C_{12}H_{12}N_8$ requires C, 53.7; H, 4.5%).

3,6-Bis(5-amino-2-pyridyl)-1,2,4,5-tetrazine 7b. 3,6-Bis(5-amino-2-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine **6b** (1.96 g, 7.31 mmol) was dissolved in hot tetrahydrofuran (600 cm^3). The volume of solvent was then reduced to approximately 300 cm^3 and the solution was chilled to 0 °C before 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.66 g, 7.31 mmol) in tetrahydrofuran (50 cm^3) was added dropwise with stirring. Although product formed during addition of the oxidant, the mixture was allowed to stir at room temperature for 6 h under an atmosphere of nitrogen. The precipitate was then filtered off, washed with cold tetrahydrofuran (100 cm^3), and finally dried to give pure 3,6-bis(5-amino-2-pyridyl)-1,2,4,5-tetrazine as a crystalline maroon solid (1.57 g, 81%), m.p. 271–273 °C; $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3306 (asym NH$_2$ str), 3194 (sym NH$_2$ str), 1627 (N–H def), 1585 (C=C str/C=N str), 1431, 1399 and 1293 (C–N str); δ_H[(CD$_3$)$_2$SO] 6.37 (br, 4 H, NH$_2$), 7.12 [dd, 2 H, $J(H^{3'}H^{4'}) = 8.6$, $J(H^{4'}H^{6'}) = 2.6$, H-4′], 8.19 [d, 2 H, $J(H^{4'}H^{6'}) = 2.5$, H-6′] and 8.28 [d, 2 H, $J(H^{3'}H^{6'}) = 8.6$ Hz, H-3′]; δ_C[(CD$_3$)$_2$SO] 119.5 and 125.3 (aromatic CH), 137.1 (quaternary C), 137.4 (aromatic CH), 148.0 and 182.7 (quaternary C); *m*/*z* (FAB) 267 (100, $[M + 1]^{\bullet +}$), 266 (25, $[M]^{\bullet +}$), 162 (11), 157 (13), 149 (48), 136 (33), 120 (70) and 119 (18%); 267.109 744 ($C_{12}H_{11}N_8$, $[M + 1]^{\bullet +}$ requires 267.110 668) (Found: C, 53.4; H, 4.5. $C_{12}H_{10}N_8$ requires C, 54.1; H, 3.8%).

3,6-Bis[(5-trifluoroacetylamino)-2-pyridyl]-1,2,4,5-tetrazine 7c. 3,6-Bis(5-amino-2-pyridyl)-1,2,4,5-tetrazine **7b** (1.45 g, 5.45 mmol) and triethylamine (9.16 g, 6.16 cm^3, 44 mmol) were chilled to 0 °C under an atmosphere of nitrogen and trifluoroacetic anhydride (40 cm^3) was added dropwise. The suspension was stirred at room temperature for 2 h and the excess of trifluoroacetic anhydride was then distilled off under reduced pressure. Water (25 cm^3) was added and the mixture was stirred for 15 min. A bright pink solid was filtered off and washed with cold water (25 cm^3). The product was finally dried to give 3,6-bis[5-trifluoroacetylamino)-2-pyridyl]-1,2,4,5-tetrazine (2.37 g, 95%), m.p. 319.5–321 °C (decomp.); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3282 (N–H str), 1713 (amide I), 1592 (C=C str/C=N str), 1546 (amide II), 1410, 1385, 1184 and 1159; δ_H[(CD$_3$)$_2$SO] 8.34 [dd, 2 H, J(H^{3}H^4) = 8.5, J(H^{4}H^6) = 2.5, H-4], 8.54 [d, 2 H, J(H^{3}H^4) = 8.5 Hz, H-3], 8.98 (br s, 2 H, H-6) and 11.83 (br, 2 H, NH); *m*/*z* (FAB) 460 (23, [*M* + 2]$^{\bullet+}$), 459 (13, *M* + 1]$^{\bullet+}$), 289 (16), 216 (45) and 146 (25%); 459.083 244 ($C_{16}H_9F_6N_8O_2$, [*M* + 1]$^{\bullet+}$ requires 459.075 266, 460.085 226 ($C_{16}H_{10}F_6N_8O_2$, [*M* + 2]$^{\bullet+}$ requires 460.083 091 (Found: C, 41.5; H, 1.9. $C_{16}H_8F_6N_8O_2$ requires C, 41.9; H, 1.8%).

4-*n*-Decyl-3,6-bis[5-(trifluoroacetylamino)-2-pyridyl]pyridazine 8c. 3,6-Bis[5-(trifluoroacetylamino)-2-pyridyl]-1,2,4,5-tetrazine **7c** (2.35 g, 5.13 mmol) and dodec-1-yne (1.28 g, 1.65 cm^3, 7.72 mmol) were stirred under an atmosphere of nitrogen at 100 °C for 32 h in degassed dimethylformamide (75 cm^3). After cooling, the solvent was evaporated under reduced pressure, and the solid was purified by column chromatography, having been pre-absorbed on silica gel from acetone. Using an eluent of chloroform gradually enriched to contain 4% methanol gave the required *compound* as a cream solid (2.27 g, 74%), m.p. 223.5–224.5 °C; $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3301 (N–H str), 2924 (asym CH$_2$ str), 2852 (sym CH$_2$ str), 1707 (amide I), 1593 (C=C str/C=N str), 1542 (amide II), 1489 (C=C str/C=N str), 1263, 1186 and 1158; δ_H[(CD$_3$)$_2$SO] 0.82 (br t, 3 H, CH$_3$), 1.17 (br, 14 H, CH$_2$), 1.49 (br qnt, 2 H, CH$_2$), 3.00 (br t, 2 H, CH$_2$), 8.10 (d, 1 H, J = 8.7, H-3′ or H-3″), 8.33 (dd, 1 H, J = 8.7, J = 2.5, H-4′ or H-4″), 8.35 (dd, 1 H, J = 8.7, J = 2.5, H-4′ or H-4″), 8.44 (s, 1 H, H-5), 8.66 (d, 1 H, J = 8.7, H-3′ or H-3″), 9.01 (d, 1 H, J = 2.3, H-6′ or H-6″), 9.04 (d, 1 H, J = 2.3 Hz, H-6′ or H-6″) and 11.75 (br, 2 H, NH); δ_C(CD$_3$COCD$_3$) 14.4 (CH$_3$), 23.4, 29.8, 30.6, 32.7 and 33.1 (CH$_2$), 114.0 and 119.7 (quaternary C), 122.3, 125.7, 126.0, 129.4 and 129.6 (aromatic CH), 134.5 and 135.5 (quaternary C), 141.7 and 142.8 (aromatic CH), 143.4, 151.3, 154.4, 155.9, 156.6, 157.5 and 159.1 (quaternary C); *m*/*z* (EI) 596 (4, [*M*]$^{\bullet+}$), 483 (4) and 149 (3%); 596.233 05 ($C_{28}H_{30}F_6N_6O_2$, *M*$^{\bullet+}$ requires 596.233 44) (Found: C, 56.6; H, 5.2; N, 14.1. $C_{28}H_{30}F_6N_6O_2$ requires C, 56.4; H, 5.1; N, 14.1%).

3,6-Bis(5-amino-2-pyridyl)-4-*n*-decylpyridazine 8b. 4-*n*-Decyl-3,6-bis[5-(trifluoroacetylamino)-2-pyridyl]pyridazine **8c** (1.51 g, 2.53 mmol) and anhydrous potassium carbonate (0.74 g, 5.35 mmol) were heated at reflux in degassed methanol (50 cm^3) under an atmosphere of nitrogen for 40 h. After evaporation of the solvent, the residual solid was extracted with chloroform and the solvent again evaporated. The crude product was purified by column chromatography using an eluent of chloroform gradually enriched with a mixture of methanol (95% by volume) and ammonium hydroxide (5% by volume) until a 95 : 5 ratio of chloroform to methanol–ammonia was achieved. The product from chromatography was vacuum dried to give a foaming yellow film of pure 3,6-bis(5-amino-2-pyridyl)-4-*n*-decylpyridazine (0.86 g, 84%), m.p. 54–57 °C; $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3320 (asym NH$_2$ str), 3198 (sym NH$_2$ str), 2922 (asym, CH$_2$ str), 2851 (sym CH$_2$ str), 1629 (N–H def), 1588 (C=C str/C=N str), 1495 (C=C str/C=N str), 1403, 1283 (C=N str) and 840; δ_H(CDCl$_3$) 0.86 (t, 3 H, CH$_3$), 1.22 (br, 14 H, CH$_2$), 1.57 (qnt, 2 H, CH$_2$), 3.04 (t, 2 H, CH$_2$), 7.11 (dd, 1 H, J = 8.5, 2.8, H-4′ or H-4″), 7.12 (dd, 1 H, J = 8.4, 2.9, H-4′ or H-4″), 7.89 (d, 1 H, J = 8.4, H-3′ or H-3″), 8.15 (d, 1 H, J = 2.7, H-6′ or H-6″), 8.16 (d, 1 H, J = 2.7, H-6′ or H-6″), 8.28 (s, 1 H, H-5) and 8.49 (d, 1 H, J = 8.5 Hz, H-3′ or H-3″); δ_C(CDCl$_3$) 14.0 (CH$_3$), 22.6, 29.2, 29.4, 29.6, 31.8 and 32.4 (CH$_2$), 121.8, 122.1, 124.3, 124.9, 135.6 and 136.4 (aromatic CH), 142.1, 142.6, 143.7, 143.8, 146.3, 156.6 and 158.2 (aromatic quarternary C); *m*/*z* (FAB) 405 (100, [*M* + 1]$^{\bullet+}$), 404 (6, [*M*]$^{\bullet+}$) and 291 (9%) (Found: C, 70.6; H, 8.0; N, 20.8. $C_{24}H_{32}N_6$ requires C, 71.2; H, 8.0; N, 20.8%).

5,5′-Bis(ferrocenylmethylideneamino)-2,2′-bipyridine 4b. 5,5′-Diamino-2,2′-bipyridine **4a** (0.075 g, 0.40 mmol) and ferrocenecarbaldehyde (0.190 g, 0.89 mmol) were stirred in refluxing absolute alcohol (12 cm^3) for 18 h under an atmosphere of nitrogen. After cooling, the solvent was evaporated and the residual solid triturated with chilled absolute alcohol (6 cm^3). The orange suspension was filtered and the solid washed with chilled ethanol (6 cm^3) and finally dried to give the required *compound* (0.072 g, 68%) (decomp. below m.p.); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3078 (C–H str), 1612 (C=N str), 1578 (C=C str/C=N str), 1451 (C–C str), 1370, 1218, 1190 and 836; δ_H(CDCl$_3$) 4.21 (s, 10 H, H-1‴), 4.48 [t, 4 H, J(H$^{2''}$H$^{3''}$) = 1.9, H-3″], 4.77 [t, 4 H, J(H$^{2''}$H$^{3''}$) = 1.9, H-2″], 7.51 [dd, 2 H, J(H^{3}H^4) = 8.4, J(H^{4}H^6) = 2.4, H-4,4′], 8.34 [d, 2 H, J(H^{3}H^4) = 8.4, H-3,3′], 8.37 (s, 2 H, CH=N) and 8.42 [d, 2 H, J(H^{4}H^6) = 2.4 Hz, H-6,6′]; *m*/*z* (FAB) 579 (6, [*M* + 1]$^{\bullet+}$), 578 (6, [*M*]$^{\bullet+}$), 457 (1), 214 (62), 187 (35), 186 (11), 181 (23), 179 (55) and 178 (31%); 578.085 654 ($C_{32}H_{26}Fe_2N_4$, *M*$^{\bullet+}$ requires 578.085 626), 579.092 394 ($C_{32}H_{27}Fe_2N_4$, [*M* + 1]$^{\bullet+}$ requires 579.093 451) (Found: C, 65.3; H, 5.7; N, 10.0. $C_{32}H_{26}Fe_2N_4$ requires C, 66.5; H, 4.5; N, 9.7%).

5,5″-Bis(ferrocenylmethylideneamino)-2,2′ : 6′,2″-terpyridine 5c. 5,5″-Diamino-2,2′ : 6′,2″-terpyridine **5a** (0.032 g, 0.12 mmol) and ferrocenecarbaldehyde (0.060 g,0.28 mmol) were heated under reflux in absolute alcohol (3.5 cm^3) for 12 h under an atmosphere of nitrogen. After cooling, the solvent was evaporated under reduced pressure and the residual solid triturated with chilled ethanol (3 × 1 cm^3). The mixture was filtered and the purple solid finally washed with chilled ethanol (10 cm^3) and then dried to give the required pure *compound* (0.056 g, 70%). $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3079 (C–H str), 1614 (C=N str), 1589 (C=C str/C=N str), 1567 (C=C str/C=N str), 1443 (C–C str), 1372, 1215, 1190, 1105 and 818; δ_H[(CD$_3$)$_2$SO] 4.32 (s, 10 H, H-1⁗), 4.61 [t, 4 H, J(H$^{2'''}$H$^{3'''}$) = 1.7, H-3‴], 4.87 [t, 4 H, J(H$^{2'''}$H$^{3'''}$ = 1.7, H-2‴], 7.82 [dd, 2 H, J(H$^{3''}$H$^{4''}$) = 8.4, J(H$^{4''}$H$^{6''}$) = 2.5, H-4, 4″], 8.08 [t, 1 H, J(H$^{3'}$H$^{4'}$) = J(H$^{4'}$H$^{5'}$) = 7.7, H-4′], 8.40 [d, 2 H, J(H$^{3'}$H$^{4'}$) = J(H$^{4'}$H$^{5'}$) = 7.7, H-3′,5′],8.54 [d, 2 H, J(H$^{4''}$H$^{6''}$) = 2.5, H-6″], 8.62 (s, 2 H, CH=N) and 8.64 [d, 2 H, J(H$^{3''}$H$^{4''}$) = 8.4 Hz, H-3,3″]; *m*/*z* (FAB) 656 (1.5, [*M* + 1]$^{\bullet+}$), 460 (6), 265 (7), 264 (34), 215 (39) and 214 (100%); 655.110 858 ($C_{37}H_{29}Fe_2N_5$, *M*$^{\bullet+}$ requires 655.112 175), 656.120 451 ($C_{37}H_{30}Fe_2N_5$, [*M* + 1]$^{\bullet+}$ requires 656.120 000) (Found: C, 67.0; H, 4.4; N, 11.1. $C_{37}H_{29}Fe_2N_5$ requires C, 67.8; H, 4.5; N, 10.7%).

4-*n*-Decyl-3,6-bis(5-ferrocenylmethylideneamino-2-pyridyl)-pyridazine 8d. 3,6-Bis(5-amino-2-pyridyl)-4-*n*-decylpyridazine **8b** (0.100 g, 0.25 mmol), ferrocenecarbaldehyde (0.108 g, 0.50 mmol), and a catalytic amount of glacial acetic acid were stirred in ethanol (2.5 cm^3) at room temperature for 24 h. The precipitate was washed with chilled ethanol (15 cm^3) and the residual solid finally dried to give the required *compound* as a bright orange solid (0.183 g, 93%), m.p. 172–173 °C (decomp.); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3078 (C–H str), 2918 (asym CH$_2$ str), 2846 (sym CH$_2$ str), 1616 (C=N str), 1574 (C=C str/C=N str), 1463 (C–C str), 1398, 1219 and 1190; δ_H(CDCl$_3$) 0.84 (t, 3 H, CH$_3$), 1.21 (br, 14 H, CH$_2$), 1.62 (br, 2 H, CH$_2$), 3.12 (t, 2 H, CH$_2$), 4.26 (s, 10 H, H-1⁗), 4.54 (m, 4 H, H-3‴), 4.83 (t, 4 H, H-2‴), 7.62 [dd, 2 H, J(H$^{3'}$H$^{4'}$) = J(H$^{3''}$H$^{4''}$) = 8.4, J(H$^{4'}$H$^{6'}$) = J(H$^{4''}$H$^{6''}$) = 2.5, H-4′,4″], 8.15, (d, 1 H, J = 8.4, H-3′ or H-3″), 8.43 (s, 1 H, H-5), 8.45 (s, 2 H, CH=N), 8.50 (d, 1 H, J = 2.5, H-6′ or H-6″) and 8.52 (d, 1 H, J = 2.5 Hz, H-6′ or H-6″); δ_C(CDCl$_3$) 14.1

(CH_3), 22.7, 29.3, 29.5, 29.6, 29.9, 31.9 and 32.6 (CH_2), 69.4, 69.5, 69.7, 71.9 and 72.0 (CH, η^5-C_5H_n), 79.8 and 79.9 (quaternary C, η^5-C_5H_4), 122.1, 125.0, 125.4, 128.2, 128.3, 141.3 and 142.4 (aromatic CH), 142.8, 148.3, 149.4, 150.5, 153.2, 156.9 and 158.6 (aromatic quaternary C), 163.6 (aromatic CH); *m*/*z* (FAB) 798 (17.0, $[M + 2]^{\cdot +}$), 797 (29, $[M + 1]^{\cdot +}$), 796 (20.0, $[M]^{\cdot +}$), 601 (100), 600 (37), 599 (28), 405 (59), 335 (11) and 291 (11%) (Found: C, 69.5; H, 6.1; N, 10.9. $C_{46}H_{48}Fe_2N_6$ requires C, 69.4; H, 6.1; N, 10.5%).

Tetracarbonyl(5,5′-diamino-2,2′-bipyridine)molybdenum 4c. 5,5′-Diamino-2,2′-bipyridine **4a** (0.200 g, 1.07 mmol) and molybdenum hexacarbonyl (0.298 g, 1.13 mmol) were heated under reflux in toluene (35 cm^3) for 1 h. The colourless suspension initially turned yellow then orange before an orange-yellow precipitate formed. After cooling, this solid was filtered off, washed with warm toluene (35 cm^3), and finally dried to give the required *complex* (0.418 g, 99%) (decomp. below m.p.); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3394 (asym NH_2 str), 3235 (sym NH_2 str), 1990, 1898, 1861 and 1805 (CO str), 1618 (N–H def), 1578 (C=C str/C=N str), 1488 (C=C str/C=N str), 1314 (C–N str), 642 and 604; δ_H[$(CD_3)_2SO$], 6.01 (s, 4 H, NH_2), 7.12 [dd, 2 H, $J(H^3H^4) = 8.8$, $J(H^4H^6) = 2.5$, H-4,4′], 7.90 [d, 2 H, $J(H^3H^4) = 8.8$, H-3,3′] and 8.26 [d, 2 H, $J(H^4H^6) = 2.5$, H-6,6′]; δ_C[$(CD_3)_2SO$] 121.8, 122.1 and 137.4 (aromatic CH), 143.7 and 145.5 (aromatic quaternary C), 206.4 and 218.2 (CO); *m*/*z* (FAB) 349 (7), 337 (6), 242 (14) and 187 (5%) (Found: C, 43.1; H, 3.1; N, 14.1. $C_{14}H_{10}MoN_4O_4$ requires C, 42.7; H, 2.6; N, 14.2%).

3,6-Bis(5-amino-2-pyridinyl)-4-*n*-decylpyridazine]tetracarbonylmolybdenum 10. 3,6-Bis(5-amino-2-pyridinyl)-4-*n*-decylpyridazine **8b** (0.100 g, 2.47 mmol) and molybdenum hexacarbonyl (0.066 g, 2.50 mmol) were heated under reflux in toluene (10 cm^3) for 3 h during which time the mixture changed from a pale yellow suspension to a deep red solution. After cooling, the toluene was evaporated under reduced pressure and the residual solid was extracted with chloroform. A dark coloured impurity was removed by filtration of the extract. Solvent was evaporated from the filtrate to afford the required *compound* (0.109 g, 72%) (decomp. below m.p.); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 2924 (asym CH_2 str), 2852 (sym CH_2 str), 2009, 1900, 1872 and 1818 (CO str), 1618 (N–H def), 1592 (C=C str/C=N str) and 1398; δ_H($CDCl_3$) 0.85 (t, 3 H, CH_3), 1.24 (br, 14 H, CH_2), 1.56 (m, 2 H, CH_2), 3.13 (t, 2 H, CH_2), 3.99 (s, 2 H, NH_2), 4.33 (s, 2 H, NH_2), 7.09 [dd, 1 H, $J(H^{3'}H^{4'}) = 8.9$, $J(H^{4'}H^{6'}) = 2.5$, H-4′ or -4″], 7.11 [dd, 1 H, $J(H^{3'}H^{4'}) = 8.9$, $J(H^{4'}H^{6'}) = 2.5$, H-4′ or -4″] 7.71 (s, 1 H, H-5), 7.79 [d, 1 H, $J(H^{3'}H^{4'}) = 8.9$, H-3′], 8.08 [d, 1 H, $J(H^{3''}H^{4''}) = 8.9$, H-3″], 8.11 [d, 1 H, $J(H^{4''}H^{6''}) = 2.5$, H-6″] and 8.61 [d, 1 H, $J(H^{4'}H^{6'}) = 2.5$ Hz, H-6′]; *m*/*z* (FAB, ^{98}Mo) 614 (5, $[M]^{\cdot +}$), 613 (5), 586 (72), 585 (62), 584 (62), 584 (61), 558 (10), 557 (8), 556 (9), 496 (34) and 405 (100%) (Found: C, 54.3; H, 5.4; N, 13.8. $C_{28}H_{32}MoN_6O_4$ requires C, 54.9; H, 5.3; N, 13.7%).

5,5′-Bis(ferrocenylmethylideneamino)-2,2′-bipyridinetetracarbonylmolybdenum 4d. A thoroughly degassed solution of tetracarbonyl(5,5′-diamino-2,2′-bipyridine)molybdenum **4c** (0.104 g, 0.263 mmol) and ferrocenecarbaldehyde (0.113 g, 0.528 mmol) in dimethylformamide (3 cm^3) and glacial acetic acid (0.09 cm^3) was stirred at 60 °C for 19 h. The solvent was evaporated under reduced pressure and chloroform (10 cm^3) was added. The red solution was filtered to remove an insoluble black material. This extraction process was repeated until all the red material had been dissolved. The combined chloroform portions were evaporated and the residual film was triturated with diethyl ether. After filtering, the remaining red-purple solid was washed with hot diethyl ether for 3 h in a Soxhlet apparatus and finally dried to yield the required *compound* (0.128 g, 62%), (decomp. below m.p.); $\tilde{\nu}_{max}$(KBr)/cm^{-1} 2007, 1892, 1868 and 1826 (CO str), 1616 (C=N str), 1585 (C=C str/C=N str), 1481 (C=C str/C=N str), 1456 (C–C str), 1222 and 826; δ_H($CDCl_3$) 4.29 (s, 10 H, H-4″), 4.60 [t, 4 H, $J(H^{2''}H^{3''}) = 1.9$, H-3″], 4.84 [t, 4 H, $J(H^{2''}H^{3''}) = 1.9$, H-2″], 7.64 [dd, 2 H, $J(H^3H^4) = 8.6$, $J(H^4H^6) = 2.4$, H-4,4′], 8.00 [d, 2 H, $J(H^3H^4) = 8.6$, H-3,3′], 8.50 (s, 2 H, CH=N) and 8.89 [d, 2 H, $J(H^4H^6) = 2.4$ Hz, H-6,6′]; δ_C($CDCl_3$) 69.7, 72.5 and 73.2 (CH, η^5-C_5H_n), 79.4 (quaternary C, η^5-C_5H_4), 121.6, 129.1 and 145.0 (aromatic CH), 149.1 and 150.9 (aromatic quaternary C), and 165.1 (aromatic CH); *m*/*z* (FAB, ^{98}Mo) 788 (0.9, $[M]^{\cdot +}$) 760/758 (1.5, $[M - CO]^{\cdot +}$), 674 (0.7, $[M - 4CO]^{\cdot +}$), 564 (2.2), 502 (4.8) and 423 (2.0%) (Found: C, 53.4; H, 4.2; N, 7.1. $C_{36}H_{26}Fe_2MoN_4O_4$ requires C, 55.0; H, 3.3; N, 7.1%).

Polymerisations

1,1′-Didodecylferrocenedicarbaldehyde 3 with *m*-phenylenediamine. A solution of 1,1′-didodecylferrocenedicarbaldehyde (382 mg, 0.66 mmol) and *m*-phenylenediamine (71 mg, 0.66 mmol) in dimethylformamide (7 cm^3) was degassed and stirred under an atmosphere of nitrogen for 24 h at 30 °C, then for 24 h at 60 °C. Water (10 cm^3) was added and the mixture was stirred for 3 h, resulting in the formation of a lower red oily layer (105 mg) (fraction 1) and an upper layer. Centrifugation of the upper layer afforded a second red oily portion (115 mg) (fraction 2). Both polymer fractions were readily soluble in chloroform and tetrahydrofuran, and were almost identical spectroscopically (IR, UV/VIS, ^1H NMR), with evidence (^1H NMR) of the presence of some unchanged starting material (**3**) in fraction 1. Spectral and analytical data: *e.g.* for fraction 2, $\tilde{\nu}_{max}$(film)/cm^{-1} 1621 (C=N str); δ_H($CDCl_3$) 0.9 (m, 6 H, CH_3), 1.3 (m, 40 H, CH_2), 2.3 (br m, 4 H, CH_2), 4.4 (br m, 2 H, ferrocenyl H), 4.7 (br m, 4 H, ferrocenyl H), 7.0 (br m, 4 H, aromatic H) and 8.3 (br m, 2 H, CH=N); λ_{max}(thf)/nm 253, 376 and 469; gel permeation chromatography (thf)/(polystyrene standard) $M_w = 4650$, $M_w/M_n = 2.1$.

3,6-Bis(5-amino-2-pyridyl)-4-*n*-decylpyridazine 8b with ferrocene-1,1′-dicarbaldehyde. A solution of 3,6-bis(5-amino-2-pyridyl)-4-*n*-decylpyridazine **8b** (0.65 g, 0.16 mmol) and ferrocene-1,1′-dicarbaldehyde (39 mg, 0.16 mmol) in degassed dimethylformamide (1 cm^3) containing a catalytic amount of acetic acid was heated for 48 h at 60 °C under an atmosphere of nitrogen. The mixture was cooled, diethyl ether (60 cm^3) was slowly added with stirring and the precipitate filtered off. This solid was washed with diethyl ether (50 cm^3) to give the polymer as a red material (60 mg, 61%) $\tilde{\nu}_{max}$(KBr)/cm^{-1} 2922 (asym CH_2 str), 2851 (sym CH_2 str), 1618 (C=N str), 1577 (C=C/C=N str), 1466 (C–N str), 1400, 1218 and 1191 [Found: C, 70.1; H, 6.4; N, 13.9. $(C_{36}H_{38}FeN_6)_n$ requires C, 70.8; H, 6.3; N, 13.8%]; TGA, onset of decomposition *ca.* 260 °C, 50% mass loss at *ca.* 350 °C.

Acknowledgements

We thank The Carnegie Trust for the Universities of Scotland and The Fulbright Commission for Travel Awards (to P. N. P. and G. C. F., respectively).

References

1 See, for example, M. Sato, T. Hayashi, S. Kumakura, N. Shimizu, M. Katada and S. Kawata, *Organometallics*, 1996, **15**, 721.

2 See, for example, M. J. Begley, P. Mountford, P. J. Stewart, D. Swallow and S. Wan, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 1323.

3 See, for example, C. J. McAdam, N. W. Duffy, B. H. Robinson and J. Simpson, *Organometallics*, 1996, **15**, 3935.

4 W. E. Lindsell, P. J. Tomb and P. N. Preston, *J. Organomet. Chem.*, 1992, **439**, 201.

5 N. M. Agh-Atabay, W. E. Lindsell, P. J. Tomb, P. N. Preston, A. D. Lloyd, R. Rangel-Rojo, G. Spruce and B. S. Wherrett, *J. Mater. Chem.*, 1992, **2**, 1241.

6 I. R. Butler, *Organometallics*, 1992, **11**, 74.

7 I. R. Butler, D. S. Brassington, R. A. Bromley, P. Licence and J. Wrench, *Polyhedron*, 1996, **15**, 4087.

8 E. C. Constable, A. J. Edwards, R. Martinez-Máñez, P. R. Raithby and A. M. W. Cargill-Thompson, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 645.

9 E. C. Constable, A. J. Edwards, R. Martinez-Máñez and P. R. Raithby, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3253.

10 See, for example, R. Adams, R. E. Bullock and W. C. Wilson, *J. Am. Chem. Soc.*, 1923, **45**, 521; C. S. Marvel and P. V. Bonsignore, *J. Am. Chem. Soc.*, 1959, **81**, 2668.

11 See, for example, G. F. D'Alelio, W. F. Strazik, D. M. Feigl and R. K. Schoenig, *J. Macromol. Sci. Chem.*, 1968, **2**, 1457; G. F. D'Alelio, *Encycl. Polym. Sci. Technol.*, 1969, **10**, 659.

12 See, for example, S. Banerjee, P. K. Gutch and C. Saxena, *J. Polym. Sci. A*, 1995, **33**, 1719; C. Mealares and A. Gandini, *Polym. Int.*, 1996, **40**, 33.

13 S. Park, H. Kim, W. Zin and J. C. Jung, *Macromolecules*, 1993, **26**, 1627.

14 K. Sonogashira and N. Hagihari, *Kogyo Kagaku Zasshi*, 1963, **66**, 1090.

15 E. W. Neuse, H. Rosenberg and R. R. Carten, *Macromolecules*, 1968, **1**, 424.

16 M. Vogel, M. Rausch and H. Rosenberg, *J. Org. Chem.*, 1957, **22**, 1016.

17 See G. Tainturier and J. Tirouflet, *Bull. Soc. Chim. Fr.*, 1966, 600.

18 See M. A. Carol, D. A. Widdowson and D. J. Williams, *Synlett*, 1994, 1025.

19 J. A. Connor and C. Overton, *J. Organomet. Chem.*, 1983, **249**, 165; J. A. Connor, C. Overton and N. El. Murr, *J. Organomet. Chem.*, 1984, **277**, 277.

20 F. Calogero, H. S. Freeman, J. F. Esancy, W. M. Whaley and B. J. Dabney, *Dyes Pigm.*, 1987, **8**, 431.

21 Y. Tohda, M. Eiraku, T. Nakagawa, Y. Usami, M. Ariga, T. Kawashima, K. Tani, H. Watanabe and Y. Mori, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2820.

22 D. L. Boger and S. M. Weinreb, *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic Press, London, 1987, ch. 10.

23 J. F. Geldard and F. Lyons, *J. Org. Chem.*, 1965, **30**, 318.

24 See, for example, J. A. Deyrup and H. L. Gingrich, *Tetrahedron Lett.*, 1977, 3115; T. Sasaki, K. Kanematsu and T. Kataoka, *J. Org. Chem.*, 1975, **40**, 1201; A. J. Ashe, D. J. Bellville and H. S. Friedman, *J. Chem. Soc.*, *Chem. Commun.*, 1979, 880.

25 P. J. Delaive, J. T. Lee, H. W. Sprintschnik, H. Albruna, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 7094.

26 See M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.

27 M. Ghedini, M. Longeri and F. Neve, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 2669; M. Ghedini, F. Neve and M. C. Bruno, *Inorg. Chim. Acta*, 1988, **143**, 89.

Received 30*th May* 1997; *Paper* 7/03768F