Non-linear Optical Materials containing Molybdenum or Tungsten Mononitrosyl Redox Centres: Diaromatic Azo Derivatives†

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The following compounds have been prepared: $[\mathrm{M(NO)L(X)}_n\{\mathrm{EC_6H_3(R\text{-}3)[N{=}NC_6H_3(R'\text{-}3)(R''\text{-}4)\text{-}4]}\}_{2-n}]$ [L = tris(3,5-dimethylpyrazolyl)hydroborate; R″ = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$, E = O, R = R′ = H, M = Mo, X = Cl or I, *n* = 0 or 1; E = NH, R = R′ = H, *n* = 1, M = Mo or W, X = Cl; E = NH, R = Me, R′ = H, *n* = 1, M = Mo, X = F, Cl, Br, I or OC_6H_{11}; M = W, X = Cl; E = NH, R = R′ = Me, *n* = 1, M = Mo, X = Cl or I; M = W, X = Cl; R″ = NMe_2, E = O, R = R′ = H, M = Mo, X = Cl or I, *n* = 0 or 1; M = W, X = Cl, *n* = 1; E = NH, R = R′ = H, *n* = 1, M = Mo, X = Cl or I; M = W, X = Cl], $[\mathrm{M(NO)L(X)\{OC_{10}H_6[N{=}NC_6H_4(OEt\text{-}4)\text{-}4]\}}]$ (M = Mo, X = Cl or I; M = W, X = Cl) and $[\mathrm{Mo(NO)L(Cl)(NHC_6H_3(Me\text{-}3)\{N{=}NC_6H_3(Me\text{-}3)[N{=}NC_6H_3(Me\text{-}3)(R''\text{-}4)\text{-}4]\}\text{-}4)}]$. Several of the ferrocenyl derivatives have been found to produce frequency doubling of radiation at 1907 nm, whereas the derivatives containing NMe_2 or OEt groups do not. A single-crystal X-ray diffraction study has shown that $[\mathrm{W(NO)LCl\{NHC_6H_3(Me\text{-}3)[N{=}NC_6H_4(R''\text{-}4)]\text{-}4\}}]\cdot\mathrm{CH_2Cl_2}$ crystallises in the space group $P2_1$ and is isostructural with its molybdenum counterpart; in these crystals the molecules appear to be favourably oriented to produce phase matching.

The emergence of optical data transmission and processing technologies is creating a demand for ever more powerful non-linear optical materials. Although a number of purely inorganic materials have been found to exhibit second harmonic generation, as well as other second-order non-linear optical effects,[1-4] molecular organic materials have aroused interest because of the expectation that their non-linear optical properties might be optimised through manipulation of their electronic and structural properties. A wide variety of molecular or polymeric organic non-linear optical materials have now been discovered,[5,6] but materials based on metal–organic compounds have been less extensively studied. Owing to the special properties transition-metal centres may impart to molecular materials, interest in the non-linear optical properties of such compounds is growing.[7-12] The general criteria for obtaining organic molecules with large first hyperpolarisability (β) values are now well established[13] and these are being applied in the search for molecular metal–organic non-linear optical materials. In particular the ferrocenyl group has been successfully used as a donor function in donor–acceptor molecules which exhibit second harmonic generation,[14] and theoretical studies[14] indicate that in *cis*-$[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}CHC_6H_4NO_2\text{-}4)]$ it acts as a π donor primarily through a metal-to-ligand charge transfer (m.l.c.t.)–ligand-to-ligand charge transfer (l.l.c.t.) state. In a further example, recent work has shown that the mixed-oxidation-state homobimetallic ruthenium complexes $[(NC)_5Ru(\mu\text{-}CN)Ru(NH_3)_5]$ and $[(H_3N)_5Ru(\mu\text{-}NC)Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^{3+}$ have very high β values suggesting that such compounds are excellent candidates for producing non-linear optical materials, providing that suitable crystal packing is also obtained.[15]

In our laboratory we have been investigating the use of the 16-electron $\{M(NO)L\}^{2+}$ [L = tris(3,5-dimethylpyrazol-1-yl)hydroborate, $HB(dmpz)_3$; M = Mo or W] moieties as acceptor groups in the production of non-linear optical materials.[12] We have previously obtained materials which produce significant second harmonic generation from 1907 nm by linking the 16-electron $\{Mo(NO)L(X)\}^+$ (X = Cl or I) acceptor group to the ferrocenyl donor group *via* an aryl group.[12a,16] In order to develop more extensive structure–activity relationships for the non-linear optical properties of materials containing the {M(NO)L} group we have sought to use other donor groups and other types of polarisable bridge with which to link these donors to the {M(NO)L} moiety. The azobenzene group has been found to produce high molecular β values in organic compounds[17] and is synthetically accessible. Accordingly our strategy has been to prepare a series of donor–acceptor molecules of the general formula [M(NO)L(X)(ERN=NRZ)] in which E may be O or NH, R is an aromatic group and Z is a donor group selected from OEt, NMe_2 and $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$. The effect of variations in X, R and Z on the ability of these materials to produce second harmonic generation has been evaluated. Structural studies provide a basis for rationalising some of the differences found between compounds containing $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$ and those containing OEt or NMe_2 groups.

Results and Discussion

Synthetic Studies.—The compounds HY, used to prepare complexes of the general formula [M(NO)L(X)Y] (M = Mo, X = halide, alkoxide, or Y; M = W, X = Cl) are illustrated; HY^5–HY^7 were obtained from commercial sources and 4-

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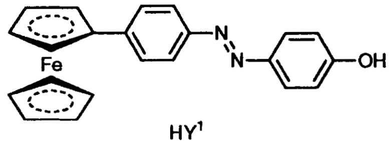
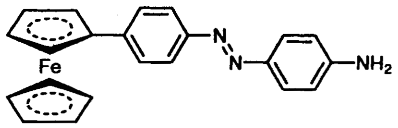
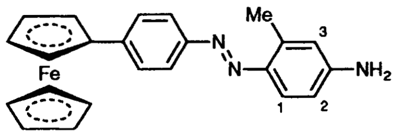
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



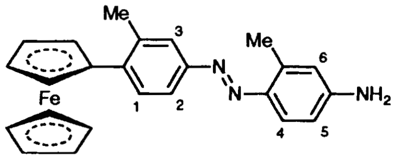
HY^1



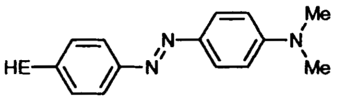
HY^2



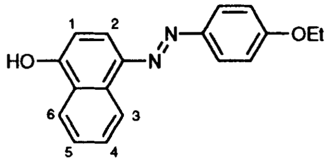
HY^3



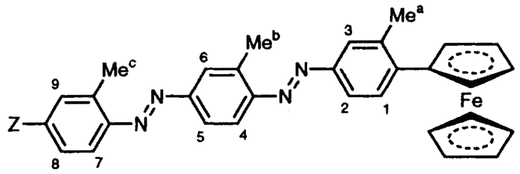
HY^4



HY^5 E = O
HY^6 E = NH



HY^7



Y^8 Z = NO_2
HY^9 Z = NH_2

ferrocenyl-4'-hydroxyazobenzene (HY^1) was prepared in low yield *via* the condensation of 4-ferrocenylaniline and 4-nitrosophenol. The amines HY^2–HY^4 were prepared by reduction of their corresponding nitro derivatives which have been reported previously.[18] The bis(azo) compound HY^9 was prepared *via* a second Mills reaction of 5-nitro-2-nitroso-toluene with HY^4 to give the nitro precursor which was then reduced to the amine using Na_2S.

In an effort to extend the series of complexes to include some sulfur-linked species, a synthesis of the thiophenol 4-ferrocenyl-4'-sulfanylazobenzene was attempted. Thiophenols have been successfully prepared *via* nucleophilic aromatic substitution reactions in which fluoride acts as the leaving group[19] and, since the compounds 4-X-4'-ferrocenylazobenzene (X = Cl, Br or I) are known,[20] 4-ferrocenyl-4'-fluoroazobenzene was selected as a potential precursor to the thiol. 4-Sulfanylazobenzenes have not been prepared in such a way before, but a fluorine *para* to an electron-withdrawing azo group could be expected to be relatively active towards nucleophilic displacement. The new compound 4-ferrocenyl-4'-fluoroazobenzene was synthesised in reasonable yield from the condensation between 4-ferrocenylaniline and the known compound 1-fluoro-4-nitrosobenzene.[21] Although a successful displacement reaction with 4-ferrocenyl-4'-fluoroazobenzene using ethoxide ion in ethanol afforded a high yield of the new compound 4-ethoxy-4'-ferrocenylazobenzene, a large number of attempts to produce the thiol using hydrosulfide or thiourea in a variety of solvents failed to produce the desired product. In all cases where a reaction occurred the regeneration of 4-ferrocenylaniline was observed, implying that, in the presence of sulfur compounds under the conditions needed for substitution to occur, reductive cleavage of the azo linkage takes place before any fluoride displacement can occur.

Monosubstituted derivatives of the form [Mo(NO)L(X)Y] were prepared in a straightforward fashion by reaction of $[Mo(NO)LX_2]$ with a slight excess of the appropriate azobenzene in toluene under reflux. A non-co-ordinating nitrogen base was added to promote reaction; hexamine (hexamethylenetetramine) with phenols and NEt_3 with anilides. The use of NEt_3 with phenols gave good yields of the bis-substituted complexes $[Mo(NO)LY_2]$ (Y = Y^1 **3** or Y^5 **17**).

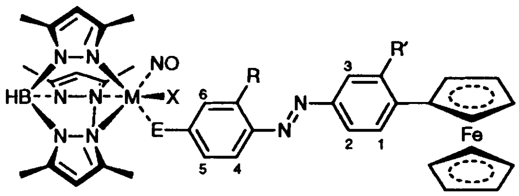
The complete molybdenum halide series F to I was prepared for HY^3 using the previously reported difluoride and dibromide complexes, $[Mo(NO)LF_2]$ and $[Mo(NO)LBr_2]$.[22] The replacement of the second iodide in the complex $[Mo(NO)L(I)Y^3]$ by an alkoxide ligand to give mixed alkoxo–anilido complexes was also investigated. A cyclohexanol derivative is reported here, demonstrating that the $[Mo(NO)L(Y^3)]^+$ group can be further functionalised by the attachment of alkoxide ligands.

The complex $[W(NO)LCl_2]$ is considerably less reactive than $[Mo(NO)LCl_2]$ and so triethylamine was used as the base in the preparation of all of the tungsten derivatives. Even so markedly lower yields were obtained, despite using extended reaction times. Not only were poor yields of azoanilide complexes isolated in the case of tungsten, but cleavage of the azo functionality was also detected giving rise to monoarylanilide complexes. This phenomenon was not observed in the corresponding reactions of $[Mo(NO)LCl_2]$. Longer reaction times were found to give rise to increasing proportions of the monoaryl complexes (up to 50%).

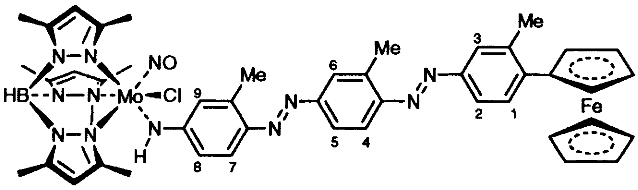
The new complexes were characterised using IR and ^1H NMR spectroscopy, EI mass spectrometry, and elemental analyses (Table 1); UV/VIS absorption spectra were also recorded for selected complexes to determine whether they exhibit any solvatochromism. The complexes generally show satisfactory analyses for C, H and N, but it has been found that some retain between $\frac{1}{4}$ and 1 mol of dichloromethane of crystallisation which may also be detected by ^1H NMR spectroscopy. Further evidence for this tendency to retain solvent is found in X-ray structural studies described below.

All of the new complexes exhibit $\nu_{max}(BH)$ at *ca.* 2550 cm^{-1} as well as $\nu_{max}(NO)$ at frequencies in accord with their formulations.[23] In addition the arylamide derivatives exhibit $\nu_{max}(NH)$ at 3300–3260 cm^{-1}. The fluoride complex **8** shows $\nu_{max}(NO)$ at 1645 cm^{-1}, some 20 cm^{-1} lower than that of its chloride, bromide, and iodide counterparts. This observation goes against expectations based upon halide electronegativity, but is in keeping with the observation that the difluoride precursor has $\nu_{max}(NO)$ at 1685 cm^{-1}, some 15 cm^{-1} lower than for the other dihalide complexes. The most plausible explanation is the strong π-donor ability of fluoride. This renders its co-ordination behaviour more like that of oxygen than of the other halides which are weaker p_π donors. By comparison the mixed alkoxoanilide complex **25** shows $\nu_{max}(NO)$ at 1635 cm^{-1}.

The ^1H NMR spectra of the new complexes contain signals attributable to the L ligand $HB(dmpz)_3$ together with those from the aryl and methyl groups in the arylazo bridges as expected. The complexes which contain the ferrocenyl group show the usual three ^1H NMR signals (ratio 2 : 2 : 5) attributable to that moiety, whilst those containing NMe_2 or OEt donor groups respectively show signals from the methyl or ethyl protons.



		M	X
R = R′ = H; E = O	**1**	Mo	Cl
	2	Mo	I
	3	Mo	Y^1
R = R′ = H; E = NH	**4**	Mo	Cl
	5	W	Cl
R = Me, R′ = H; E = NH	**6**	Mo	Cl
	7	Mo	I
	8	Mo	F
	9	Mo	Br
	25	Mo	OC_6H_{11}
	10	W	Cl
R = R′ = Me; E = NH	**11**	Mo	Cl
	12	Mo	I
	13	W	Cl



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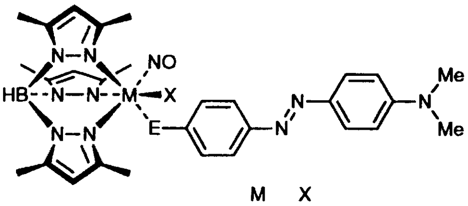
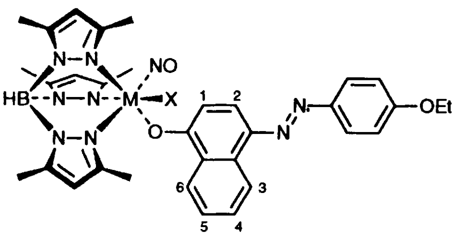


		M	X
E = O	**15**	Mo	Cl
	16	Mo	I
	17	Mo	Y^5
	18	W	Cl
E = NH	**19**	Mo	Cl
	20	Mo	I
	21	W	Cl



	M	X
22	Mo	Cl
23	Mo	I
24	W	Cl

All of the anilide complexes show a sharp singlet attributable to the amide proton. The shift of this signal is highly sensitive to the exact nature of the attached metal centre. In the case of the molybdenum iodide complexes δ(NH) is typically *ca.* 13.0, in the molybdenum chlorides 12.6 and in the tungsten chlorides *ca.* 10.7. The molybdenum fluoride complex shows δ(NH) at a markedly higher shift than for complexes of the other three halides. The total chemical shift difference between the fluoride and iodide complexes is 2.79 ppm, whereas that between the chloride and iodide complexes is only 0.46 ppm. This observation provides further evidence of fluoride p_π donation to the molybdenum centre.

The EI mass spectra of most of the complexes contain molecular-ion envelopes of relatively low intensity along with varying numbers of fragment ions. Owing to the presence of a large number of possible isotope combinations of the elements Mo, W, Fe, B, Cl and I, the ion envelopes have complex forms with the highest peak often not corresponding exactly to the mass calculated from relative atomic mass values. In most cases the highest peak and not the averaged fragment mass is quoted. The only complexes which show no evidence of a molecular ion are the bis(azophenoxide) compound **3**, the fluoroamide **8** and the triarylbis(azo) derivative **14**.

Electrochemical Studies.—The electrochemical properties of the compounds described here were investigated using cyclic voltammetry and the results are summarised in Table 2. Most of the phenoxide and arylamide complexes show reversible or quasi-reversible one-electron molybdenum- or tungsten-based reduction waves. Reversible or quasi-reversible waves for the one-electron oxidation of the ferrocenyl moiety are also present.

The reduction potentials of the molybdenum and tungsten centres are in accord with expectations.[24] In particular the tungsten compounds are reduced at potentials which are some 400–500 mV more cathodic than those of their molybdenum analogues. As expected, substituents attached to aryl rings directly bound to the metal centre are found to exert a large influence on the reduction potential. Thus in going from a ferrocenyl substituent in $[Mo(NO)L(X)\{EC_6H_4[(C_5H_4)Fe(C_5H_5)]\text{-}4\}]$ (E = O or NH, X = Cl or I) to a *p*-azophenyl substituent in **1**, **2** and **4** produces anodic shifts of 140–160 mV for the phenoxide and 250–260 mV for the anilide complexes, reflecting the electron-withdrawing nature of the azo moiety. Addition of a second azoaryl function to give **14** produces a further anodic shift of 70 mV. The addition of *m*-methyl substituents to a ring adjacent to a metal centre produces very slight cathodic shifts of 10–20 mV.

This collection of electrochemical data contains the only complete set of reduction potentials for a series of {Mo(NO)L} halide derivatives from fluoride to iodide and no previous cyclic voltammetry data have been reported for fluoride derivatives. The fluoride complex **8** has a reduction potential of −0.99 V. This is in accord with its low ν_{max}(NO) value and represents a cathodic shift of 410 mV from the reduction potential of the corresponding chloride complex. In contrast a much smaller cathodic shift of only 40 mV is found on going from iodide to chloride in this series. This observation is further evidence for extensive p_π donation from fluoride to molybdenum. Furthermore the reduction potential for **8** is only slightly less cathodic than that of the alkoxoanilide complex **25**.

The oxidation potential of the ferrocenyl moiety in compounds HY^1–HY^4 is only slightly affected by complexation with the $\{M(NO)L(X)\}^+$ moiety, anodic shifts of less than 50 mV being observed on complexation.

Electronic Spectra and Non-linear Optical Properties.—The electronic spectra of several of the ferrocenyl complexes were measured in dichloromethane and in other solvents in order to reveal any solvatochromic behaviour (Tables 3 and 4). Most of the complexes studied have one absorption band in the visible and another in the UV region, the UV bands having the larger

Table 1 Elemental analyses, IR and ^{1}H NMR data used in compound characterisation

Compound, m.p. (°C)	Analysis (%),^{a} m/z^b	IR (cm^{-1})^c	^{1}H NMR^d
HY^1 166–170	69.4 (69.1), 4.9 (4.8), 7.6 (7.3); 382	3400m (OH)	7.89 and 6.95 [2 H, d, J(HH) 8.7; 2 H, d, J(HH) 8.4, $C_6\mathit{H}_4OH$], 7.81 and 7.57 [2 H, d, J(HH) 8.4; 2 H, d, J(HH) 8.4, $C_6\mathit{H}_4C_5H_4$], 5.15 (1 H, br s, OH), 4.76 and 4.42 (2 H, s; 2 H, s, C_5H_4), 4.09 (5 H, s, C_5H_5)
HY^2 180–185	69.3 (69.3), 4.7 (5.0), 11.3 (11.0); 381	3455m (NH_2) 3360m (NH_2)	7.80 and 7.57 [2 H, d, J(HH) 8.6; 2 H, d, J(HH) 8.4, $C_6\mathit{H}_4C_5H_4$], 7.82 and 6.75 [2 H, d, J(HH) 8.6; 2 H, d, J(HH) 8.8, $C_6\mathit{H}_4NH_2$], 4.71 and 4.37 [2 H, t, J(HH) 1.9; 2 H, t, J(HH) 1.9, C_5H_4], 4.05 (5 H, s, C_5H_5), 4.02 (2 H, s, NH_2)
HY^3 143–146	69.7 (69.9), 5.1 (5.4), 10.5 (10.6)	3455m (NH_2) 3360m (NH_2)	7.80 and 7.56 [2 H, d, J(HH) 8.4; 2 H, d, J(HH) 8.6, $C_6\mathit{H}_4C_5H_4$], 7.67 [1 H, d, $J(H^1H^2)$ 8.6, H^1 of C_6H_3], 6.59 [1 H, d, $J(H^2H^3)$ 2.7, H^3 of C_6H_3], 6.56 and 6.53 [$\frac{1}{2}$ H, d, $J(H^2H^3)$ 2.7; $\frac{1}{2}$ H, d, $J(H^2H^3)$ 2.6, $J(H^1H^2)$ 8.5, H^2 of C_6H_3], 4.71 and 4.37 [2 H, t, J(HH) 1.8; 2 H, t, J(HH) 1.8, C_5H_4], 4.06 (5 H, s, C_5H_5), 3.94 (2 H, s, NH_2), 2.67 (3 H, s, CH_3)
HY^4 138–140	70.7 (70.4), 6.0 (5.7), 10.2 (10.3); 409	3455m (NH_2) 3360m (NH_2)	7.77 [1 H, d, J(HH) 8.1, H^1 of C_6H_3], 7.68 and 7.64 (3 H, H$^{2-4}$ of C_6H_3], 6.57 [1 H, d, $J(H^5H^6)$ 2.2, H^6 of C_6H_3], 6.54 and 6.50 [$\frac{1}{2}$ H, d, $J(H^5H^6)$ 2.6; $\frac{1}{2}$ H, d, $J(H^5H^6)$ 2.6, $J(H^4H^5)$ 8.6, H^5 of C_6H_3], 4.56 and 4.33 [2 H, t, J(HH) 1.9; 2 H, t, J(HH) 1.9, C_5H_4], 4.13 (5 H, s, C_5H_5), 3.93 (2 H, s, NH_2), 2.67 and 2.49 (3 H, s; 3 H, s, CH_3)
Y^8 204–208	66.0 (66.0), 4.5 (4.8), 12.3 (12.4);^{e} 557	1530s (NO_2) 1345s (NO_2)	8.24 [1 H, d, $J(H^8H^9)$ 2.0, H^9 of C_6H_3], 8.15 and 8.12 [$\frac{1}{2}$ H, d, $J(H^8H^9)$ 2.8; $\frac{1}{2}$ H, d, $J(H^8H^9)$ 2.6, $J(H^7H^8)$ 8.7, H^8 of C_6H_3], 7.95, 7.89, 7.89, 7.85, 7.83, 7.82, 7.80, 7.78, 7.77, 7.76 (6 H, H$^{2-7}$ of C_6H_3), 7.73 [1 H, d, $J(H^1H^2)$ 9.0, H^1 of C_6H_3], 4.61 and 4.40 [2 H, t, J(HH) 1.8; 2 H, t, J(HH) 1.8, C_5H_4], 4.16 (5 H, s, C_5H_5), 2.84 and 2.83 [3 H, s; 3 H, s, CH_3 (b and c)], 2.55 [3 H, s, CH_3(a)]
HY^9 188–190	69.0 (68.8), 5.4 (5.4), 13.1 (12.9);^{f} 527	3475m (NH_2) 3380m (NH_2)	7.82, 7.82, 7.80, 7.79, 7.76, 7.73, 7.72 and 7.68 (7 H, H$^{1-7}$ of C_6H_3), 6.57 (1 H, s, H^9 of C_6H_3), 6.54 and 6.51 [$\frac{1}{2}$ H, d, $J(H^8H^9)$ 2.4; $\frac{1}{2}$ H, d, $J(H^8H^9)$ 2.6, $J(H^7H^8)$ 8.7, H^8 of C_6H_3], 4.59 and 4.36 [2 H, t, J(HH) 1.8; 2 H, t, J(HH) 1.8, C_5H_4], 4.15 (5 H, s, C_5H_5), 3.99 (2 H, s, NH_2), 2.81 [3 H, s, CH_3(b)], 2.69 [3 H, s, CH_3(c)], 2.53 [3 H, s, CH_3(a)]
4-Ferrocenyl-4′-fluoroazobenzene 193–196	68.6 (68.8), 4.6 (4.5), 7.0 (7.3); 384		7.96 and 7.92 [1 H, d, J(HF) 5.3; 1 H, d, J(HF) 5.1, J(HH) 9.1, C_6H_4F], 7.84 and 7.59 [2 H, d, J(HH) 6.8; 2 H, d, J(HH) 6.8, $C_6\mathit{H}_4C_5H_4$], 7.21 and 7.18 [1 H, d, J(HF) 9.0; 1 H, d, J(HF) 8.4, J(HH) 8.7, C_6H_4F], 4.73 and 4.40 [2 H, t, J(HH) 1.8; 2 H, t, J(HH) 1.8, C_5H_4], 4.06 (5 H, s, C_5H_5)
4-Ethoxy-4′-ferrocenylazobenzene 164–168	70.0 (70.3), 5.4 (5.4), 6.6 (6.8); 410		7.91 and 7.00 [2 H, d, J(HH) 9.2; 2 H, d, J(HH) 9.0, $C_6\mathit{H}_4OEt$], 7.82 and 7.58 [2 H, d, J(HH) 8.6; 2 H, d, J(HH) 8.8, $C_6\mathit{H}_4C_5H_4$], 4.73 and 4.39 [2 H, t, J(HH) 1.9; 2 H, t, J(HH) 1.9, C_5H_4], 4.13 [2 H, q, J(HH) 7.1, $OC\mathit{H}_2CH_3$], 4.06 (5 H, s, C_5H_5), 1.46 [3 H, t, J(HH) 7.0, $OCH_2C\mathit{H}_3$]
1 *ca.* 255	52.9 (52.9), 4.5 (4.7), 14.9 (15.0); 841	1680s (NO)	8.02 and 7.45 [2 H, d, J(HH) 9.0; 2 H, d, J(HH) 9.0, C_6H_4], 7.85 and 7.58 [2 H, d, J(HH) 8.2; 2 H, d, J(HH) 8.4, C_6H_4], 5.94, 5.92 and 5.78 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.77 and 4.42 (2 H, s; 2 H, s, C_5H_4), 4.09 (5 H, s, C_5H_5), 2.59, 2.43, 2.42, 2.40, 2.22 and 2.09 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
2 *ca.* 255	48.0 (47.7), 4.3 (4.2), 13.3 (13.5); 933	1680s (NO)	7.97 and 7.58 [2 H, d, J(HH) 8.6; 2 H, d, J(HH) 8.8, C_6H_4], 7.86 and 7.60 [2 H, d, J(HH) 8.2; 2 H, d, J(HH) 8.4, C_6H_4], 5.92 and 5.86 (1 H, s; 2 H, s, $3Me_2C_3N_2\mathit{H}$), 4.74 and 4.40 (2 H, s; 2 H, s, C_5H_4), 4.07 (5 H, s, C_5H_5), 2.57, 2.46, 2.41, 2.38, 2.32 and 2.01 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
3	59.8 (59.8), 4.9 (4.8), 12.7 (13.0)	1665s (NO)	7.95 and 7.20 [4 H, d, J(HH) 9.2; 4 H, d, J(HH) 8.6, $2C_6H_4$], 7.83 and 7.59 [4 H, d, J(HH) 8.4; 4 H, d, J(HH) 8.2, $2C_6H_4$], 5.90 and 5.75 (2 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.73 and 4.39 (4 H, s; 4 H, s, $2C_5H_4$), 4.07 (10 H, s, $2C_5H_5$), 2.44, 2.28 and 2.07 (9 H, s; 6 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
4 *ca.* 235	53.0 (53.0), 4.9 (4.8), 16.7 (16.7); 839	1660s (NO) 3260m (NH)	12.51 (1 H, s, NH), 8.01 and 7.60 [2 H, d, J(HH) 8.9; 2 H, d, J(HH) 8.4, C_6H_4], 7.86 and 7.60 [2 H, d, J(HH) 8.7; 2 H, d, J(HH) 8.4, C_6H_4], 5.89, 5.88 and 5.81 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.74 and 4.40 [2 H, t, J(HH) 1.7; 2 H, t, J(HH) 1.9, C_5H_4], 4.06 (5 H, s, C_5H_5), 2.70, 2.43, 2.40, 2.38, 2.37 and 2.04 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
5	47.0 (47.0), 5.0 (4.3), 14.8 (14.7);^{g} 926	1630s (NO) 3280m (NH)	10.69 (1 H, s, NH), 8.00 and 7.60 [2 H, d, J(HH) 8.9; 2 H, d, J(HH) 8.7, C_6H_4], 7.85 and 7.51 [2 H, d, J(HH) 8.7; 2 H, d, J(HH) 8.7, C_6H_4], 5.95, 5.89 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.74 and 4.40 [2 H, d, J(HH) 1.7; 2 H, d, J(HH) 1.7, C_5H_4], 4.07 (5 H, s, C_5H_5), 2.74, 2.47, 2.43, 2.38, 2.36 and 2.16 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
6 *ca.* 280	52.6 (52.7), 5.1 (4.9), 16.3 (16.1);^{f} 854	1665s (NO) 3260m (NH)	12.51 (1 H, s, NH), 7.87 and 7.60 [2 H, d, J(HH) 8.4; 2 H, d, J(HH) 8.4, C_6H_4], 7.78 [1 H, d, $J(H^4H^5)$ 8.9, H^4 of C_6H_3], 7.51 (1 H, s, H^6 of C_6H_3), 7.30 [1 H, d, $J(H^4H^5)$ 8.9, H^5 of C_6H_3], 5.89 and 5.81 (2 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.74 and 4.41 [2 H, t, J(HH) 1.7; 2 H, t, J(HH) 1.7, C_5H_4], 4.08 (5 H, s, C_5H_5), 2.80, 2.70, 2.43, 2.41, 2.39, 2.38 and 2.05 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $C_6H_3C\mathit{H}_3$ and $3\mathit{Me}_2C_3N_2H$)
7 *ca.* 280	48.4 (48.3), 4.4 (4.5), 14.5 (14.8); 946	1665s (NO) 3280w (NH)	12.97 (1 H, s, NH), 7.88 and 7.59 [2 H, d, J(HH) 8.7; 2 H, d, J(HH) 8.7, C_6H_4], 7.73 [1 H, d, $J(H^4H^5)$ 8.6, H^4 of C_6H_3], 7.65 (1 H, s, H^6 of C_6H_3), 7.46 [1 H, d, $J(H^4H^5)$ 8.9, H^5 of C_6H_3], 5.95, 5.87 and 5.79 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.75 and 4.41 [2 H, t, J(HH) 1.9; 2 H, t, J(HH) 1.7, C_5H_4], 4.08 (5 H, s, C_5H_5), 2.83, 2.72, 2.51, 2.47, 2.39, 2.38 and 2.01 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $C_6H_3C\mathit{H}_3$ and $3\mathit{Me}_2C_3N_2H$)

Table 1 (*continued*)

Compound, m.p. (°C)	Analysis (%),[a] *m*/*z*[b]	IR (cm^{-1})[c]	^{1}H NMR[d]
8	52.6 (52.6), 5.0 (4.9), 14.9 (15.9)[h]	1645s (NO) 3270w (NH)	10.18 (1 H, s, NH), 7.84 and 7.58 [2 H, d, *J*(HH) 8.4; 2 H, d, *J*(HH) 8.4, C_6H_4], 7.76 [1 H, d, *J*(H^4H^5) 8.7, H^4 of C_6H_3], 7.25 (1 H, s, H^6 of C_6H_3), 7.11 [1 H, d, *J*(H^4H^5) 8.7, H^5 of C_6H_3], 5.87, 5.82 and 5.78 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.72 and 4.38 [2 H, t, *J*(HH) 1.9; 2 H, t, *J*(HH) 1.7, C_5H_4], 4.06 (5 H, s, C_5H_5), 2.75, 2.62, 2.40, 2.39, 2.36, 2.33 and 2.13 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $\mathrm{C_6H_3C}\mathit{H}_3$ and $3\mathit{Me}_2\mathrm{C_3N_2H}$)
9	49.4 (49.2), 4.8 (4.6), 14.9 (14.9);[h] 898	1660s (NO) 3270w (NH)	12.74 (1 H, s, NH), 7.88 and 7.59 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.7, C_6H_4], 7.78 [1 H, d, *J*(H^4H^5) 8.7, H^4 of C_6H_3], 7.57 (1 H, s, H^6 of C_6H_3), 7.37 [1 H, d, *J*(H^4H^5) 8.7, H^5 of C_6H_3], 5.90, 5.87 and 5.80 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.74 and 4.40 (2 H, s; 2 H, s, C_5H_4), 4.07 (5 H, s, C_5H_5), 2.81, 2.71, 2.44, 2.38, 2.37 and 2.03 (3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $\mathrm{C_6H_3C}\mathit{H}_3$ and $3\mathit{Me}_2\mathrm{C_3N_2H}$)
10	48.4 (48.5), 4.2 (4.5), 14.8 (14.9); 940	1630s (NO) 3275m (NH)	10.67 (1 H, s, NH), 7.85 and 7.59 [2 H, d, *J*(HH) 8.4; 2 H, d, *J*(HH) 8.4, C_6H_4], 7.78 [1 H, d, *J*(H^4H^5) 8.6, H^4 of C_6H_3], 7.43 (1 H, s, H^6 of C_6H_3), 7.22 [1 H, d, *J*(H^4H^5) 8.9, H^5 of C_6H_3], 5.95, 5.89 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.73 and 4.39 [2 H, t, *J*(HH) 1.9; 2 H, t, *J*(HH) 1.7, C_5H_4], 4.07 (5 H, s, C_5H_5), 2.78, 2.74, 2.47, 2.42, 2.37, 2.36 and 2.17 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $\mathrm{C_6H_3C}\mathit{H}_3$ and $3\mathit{Me}_2\mathrm{C_3N_2H}$)
11	50.5 (50.5), 5.2 (4.9), 15.3 (14.7);[i] 868	1655s (NO) 3270w (NH)	12.51 (1 H, s, NH), 7.77 and 7.75 [1 H, d, *J*(HH) 8.7; 1 H, d, *J*(HH) 8.2, $H^{1,4}$ of C_6H_3], 7.71 and 7.51 (1 H, s; 1 H, s, $H^{3,6}$ of C_6H_3), 7.31 and 7.17 (1 H, dd; 1 H, dd, $H^{2,5}$ of C_6H_3), 5.88 and 5.81 (2 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.60 and 4.38 (2 H, s; 2 H, s, C_5H_4), 4.16 (5 H, s, C_5H_5), 2.80, 2.70, 2.52, 2.42, 2.40, 2.38, 2.37 and 2.05 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $2\mathrm{C_6H_3C}\mathit{H}_3$ and $3\mathit{Me}_2\mathrm{C_3N_2H}$)
12	49.2 (48.9), 4.8 (4.6), 13.9 (14.6); 960	1655s (NO) 3270w (NH)	12.97 (1 H, s, NH), 7.77 and 7.72 [1 H, d, *J*(HH) 9.1; 1 H, d, *J*(HH) 8.7, $H^{1,4}$ of C_6H_3], 7.73 and 7.65 (1 H, s; 1 H, s, $H^{3,6}$ of C_6H_3), 7.46 and 7.17 (1 H, dd; 1 H, dd, $H^{2,5}$ of C_6H_3), 5.94, 5.87 and 5.79 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.59 and 4.37 (2 H, s; 2 H, s, C_5H_4), 4.15 (5 H, s, C_5H_5), 2.83, 2.72, 2.53, 2.50, 2.47, 2.38, 2.37 and 2.01 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $2\mathrm{C_6H_3C}\mathit{H}_3$ and $3\mathit{Me}_2\mathrm{C_3N_2H}$)
13	48.4 (48.4), 4.8 (4.6), 14.6 (14.4);[f] 954	1630s (NO) 3270w (NH)	10.67 (1 H, s, NH), 7.82, 7.78, 7.75, 7.73 and 7.70 [3 H, $H^{1,3,4}$ of C_6H_3), 7.43 (1 H, s, H^6 of C_6H_3), 7.30–7.10 (2 H, $H^{2,5}$ of C_6H_3), 5.95, 5.89 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.58 and 4.36 (2 H, s; 2 H, s, C_5H_4), 4.15 (5 H, s, C_5H_5), 2.78, 2.74, 2.52, 2.47, 2.43, 2.37, 2.36 and 2.18 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $2\mathrm{C_6H_3C}\mathit{H}_3$) and $3\mathit{Me}_2\mathrm{C_3N_2H}$)
14	55.0 (55.0), 5.1 (5.1), 16.7 (16.6)[g]	1660s (NO) 3270w (NH)	12.48 (1 H, s, NH), 7.91, 7.85, 7.82, 7.82, 7.80, 7.77 and 7.76 (7 H, H^{1-7} of C_6H_3), 7.53 (1 H, s, H^9 of C_6H_3), 7.33 [1 H, d, *J*(H^7H^8) 9.1, H^8 of C_6H_3), 5.89 and 5.82 (2 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.62 and 4.40 (2 H, s; 2 H, s, C_5H_4), 4.17 (5 H, s, C_5H_5), 2.84, 2.83, 2.70, 2.54, 2.43, 2.41, 2.39, 2.38 and 2.05 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathrm{C_6H_3C}\mathit{H}_3$ and $3\mathit{Me}_2\mathrm{C_3N_2H}$)
15	47.9 (47.8), 5.0 (5.0), 18.7 (18.9);[h] 700	1680s (NO)	7.93 and 7.42 [2 H, d, *J*(HH) 9.0; 2 H, d, *J*(HH) 9.0, C_6H_4], 7.88 and 6.77 [2 H, d, *J*(HH) 9.2; 2 H, d, *J*(HH) 9.3, C_6H_4], 5.93, 5.90 and 5.77 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.09 (6 H, s, NMe_2), 2.59, 2.42, 2.41, 2.39, 2.22 and 2.06 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$)
16	43.1 (43.1), 4.4 (4.5), 17.4 (17.2);[g] 792	1685s (NO)	7.89 and 7.55 [2 H, d, *J*(HH) 9.0; 2 H, d, *J*(HH) 9.0, C_6H_4], 7.89 and 6.77 [2 H, d, *J*(HH) 9.0; 2 H, d, *J*(HH) 9.2, C_6H_4], 5.91, 5.85 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.09 (6 H, s, NMe_2), 2.57, 2.45, 2.40, 2.38, 2.32 and 1.99 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$)
17	54.6 (54.5), 5.7 (5.4), 19.1 (18.9);[j] 905	1650s (NO)	7.88 and 7.21 [4 H, d, *J*(HH) 9.0; 4 H, d, *J*(HH) 9.0, $2C_6H_4$], 7.85 and 6.75 [4 H, d, *J*(HH) 9.0; 4 H, d, *J*(HH) 9.2, $2C_6H_4$], 5.86 and 5.74 (2 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.04 (12 H, s, $2NMe_2$), 2.40, 2.25 and 2.09 (9 H, s; 6 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$)
18	43.3 (43.3), 4.8 (4.5), 17.1 (17.2);[g] 786	1640s (NO)	7.92 and 7.55 [2 H, d, *J*(HH) 9.0; 2 H, d, *J*(HH) 9.0, C_6H_4], 7.87 and 6.77 [2 H, d, *J*(HH) 9.2; 2 H, d, *J*(HH) 9.2, C_6H_4], 5.94, 5.91 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.08 (6 H, s, NMe_2), 2.66, 2.40, 2.39, 2.30 and 2.19 (3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$)
19	49.7 (49.9), 5.3 (5.3), 21.8 (22.1); 699	1655s (NO) 3280w (NH)	12.58 (1 H, s, NH), 7.92 and 7.56 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.7, C_6H_4], 7.88 and 6.76 [2 H, d, *J*(HH) 9.1; 2 H, d, *J*(HH) 9.1, C_6H_4], 5.88, 5.87 and 5.80 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.10 (6 H, s, NMe_2), 2.70, 2.42, 2.41, 2.38, 2.37 and 2.02 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$)
20	43.8 (44.1), 4.7 (4.7), 19.8 (19.5); 791	1655s (NO) 3280w (NH)	13.04 (1 H, s, NH), 7.90 and 6.76 [2 H, d, *J*(HH) 9.2; 2 H, d, *J*(HH) 9.2, C_6H_4], 7.87 and 7.70 [2 H, d, *J*(HH) 8.9; 2 H, d, *J*(HH) 8.9, C_6H_4], 5.94, 5.86 and 5.78 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.09 (6 H, s, NMe_2), 2.71, 2.50, 2.47, 2.38, 2.37 and 1.99 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$)
21	43.5 (43.4), 4.8 (4.7), 19.2 (19.0);[g] 785	1625s (NO) 3280w (NH)	10.74 (1 H, s, NH), 7.91 and 7.48 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.9, C_6H_4], 7.86 and 6.75 [2 H, d, *J*(HH) 9.1; 2 H, d, *J*(HH) 9.1, C_6H_4], 5.94, 5.88 and 5.82 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.08 (6 H, s, NMe_2), 2.73, 2.46, 2.42, 2.36, 2.35 and 2.14 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$)

Table 1 (*continued*)

Compound, m.p. (°C)	Analysis (%),[a] m/z[b]	IR (cm^{-1})[c]	^{1}H NMR[d]
22	52.6 (52.9), 5.3 (5.0), 16.9 (16.8); 751	1680s (NO)	8.94 [1 H, d, $J(\mathrm{H^3H^4})$ 8.2, $\mathrm{H^3}$ of $\mathrm{C_{10}H_6}$], 8.04 and 7.05 [2 H, d, J(HH) 9.0; 2 H, d, J(HH) 9.0, $\mathrm{C_6H_4}$], 8.07 [1 H, d, $J(\mathrm{H^5H^6})$ 8.4, $\mathrm{H^6}$ of $\mathrm{C_{10}H_6}$], 7.86 [1 H, d, $J(\mathrm{H^1H^2})$ 8.4, $\mathrm{H^2}$ of $\mathrm{C_{10}H_6}$], 7.67–7.57 (2 H, c m, $\mathrm{H^{1,4}}$ of $\mathrm{C_{10}H_6}$), 7.37 (1 H, t, $\mathrm{H^5}$ of $\mathrm{C_{10}H_6}$), 5.96, 5.83 and 5.78 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.15 [2 H, q, J(HH) 7.0, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 2.61, 2.46, 2.44, 2.16 and 1.77 (3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$), 1.48 [3 H, t, J(HH) 7.0, $\mathrm{OCH_2C}\mathit{H}_3$]
23	45.1 (45.2), 4.8 (4.3), 14.4 (14.1);[k] 843	1680s (NO)	8.94 [1 H, d, $J(\mathrm{H^3H^4})$ 8.4, $\mathrm{H^3}$ of $\mathrm{C_{10}H_6}$], 8.17 [1 H, d, $J(\mathrm{H^5H^6})$ 8.4, $\mathrm{H^6}$ of $\mathrm{C_{10}H_6}$], 8.05 and 7.05 [2 H, d, J(HH) 9.2; 2 H, d, J(HH) 9.2, $\mathrm{C_6H_4}$], 8.01 [1 H, d, $J(\mathrm{H^1H^2})$ 8.4, $\mathrm{H^2}$ of $\mathrm{C_{10}H_6}$], 7.61–7.55 (2 H, c m, $\mathrm{H^{1,4}}$ of $\mathrm{C_{10}H_6}$), 7.38 (1 H, t, $\mathrm{H^5}$ of $\mathrm{C_{10}H_6}$), 5.94, 5.87 and 5.77 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.15 [2 H, q, J(HH) 7.0, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 2.59, 2.51, 2.44, 2.41, 2.25 and 1.71 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$), 1.56 [3 H, t, J(HH) 6.2, $\mathrm{OCH_2C}\mathit{H}_3$]
24	44.7 (44.7), 4.6 (4.3), 13.9 (13.9);[l] 837	1640s (NO)	8.94 [1 H, d, $J(\mathrm{H^3H^4})$ 8.6, $\mathrm{H^3}$ of $\mathrm{C_{10}H_6}$], 8.06 [1 H, d, $J(\mathrm{H^5H^6})$ 8.2, $\mathrm{H^6}$ of $\mathrm{C_{10}H_6}$], 8.03 and 7.04 [2 H, d, J(HH) 9.0; 2 H, d, J(HH) 9.0, $\mathrm{C_6H_4}$], 7.76 [1 H, d, $J(\mathrm{H^1H^2})$ 8.4, $\mathrm{H^2}$ of $\mathrm{C_{10}H_6}$], 7.64–7.55 (2 H, m, $\mathrm{H^{1,4}}$ of $\mathrm{C_{10}H_6}$), 7.34 (1 H, t, $\mathrm{H^5}$ of $\mathrm{C_{10}H_6}$), 5.97, 5.86 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 4.15 [2 H, q, J(HH) 7.0, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 2.69, 2.44, 2.42, 2.25 and 1.89 (3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$), 1.48 [3 H, t, J(HH) 7.0, $\mathrm{OCH_2C}\mathit{H}_3$]
25	58.0 (57.7), 6.1 (5.8), 14.8 (15.3); 918	1635s (NO) 3300w (NH)	9.42 (1 H, s, NH), 7.88 [1 H, d, $J(\mathrm{H^4H^5})$ 8.7, $\mathrm{H^4}$ of $\mathrm{C_6H_3}$], 7.82 and 7.57 [2 H, d, J(HH) 8.7; 2 H, d, J(HH) 8.7, $\mathrm{C_6H_4}$], 7.25 [1 H, d, $J(\mathrm{H^4H^5})$ 8.7, $\mathrm{H^5}$ of $\mathrm{C_6H_3}$], 7.11 (1 H, br s, $\mathrm{H^6}$ of $\mathrm{C_6H_3}$), 5.85, 5.83 and 5.70 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 5.59 [1 H, qnt, OCH], 4.72 and 4.37 [2 H, t, J(HH) 1.7; 2 H, t, J(HH) 1.7, $\mathrm{C_5H_4}$], 4.06 (5 H, s, $\mathrm{C_5H_5}$), 2.71, 2.63, 2.40, 2.33 and 2.12 (3 H, s; 3 H, s; 3 H, s; 9 H, s; 3 H, s, $\mathrm{C_6H_3C}\mathit{H}_3$ and $3\mathit{Me}_2\mathrm{C_3N_2H}$), 1.80–1.20 (10 H, c m, $\mathrm{C_5H_{10}}$)

[a] In the order C, H, N with calculated values in parentheses. [b] Position of the ion of highest m/z in the FAB mass spectrum. These polyisotopic molecules give ion clusters spread over a range of m/z values so the most intense ion in the cluster is quoted. [c] From KBr discs. [d] At 25 °C from solutions in $\mathrm{CDCl_3}$; data cited as δ_H relative to $\mathrm{SiMe_4}$, number of protons, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hz and assignment. [e] Contains 0.1 mol $\mathrm{CH_2Cl_2}$. [f] Contains 0.2 mol $\mathrm{CH_2Cl_2}$. [g] Contains 0.3 mol $\mathrm{CH_2Cl_2}$. [h] Contains 0.5 mol $\mathrm{CH_2Cl_2}$. [i] Contains 1.0 mol $\mathrm{CH_2Cl_2}$. [j] Contains 0.7 mol $\mathrm{CH_2Cl_2}$. [k] Contains 0.6 mol $\mathrm{CH_2Cl_2}$. [l] Contains 0.85 mol $\mathrm{CH_2Cl_2}$.

absorption coefficients. These high absorption coefficients provide evidence of extensive charge-transfer interactions between the ferrocenyl ligands and co-ordinated {M(NO)L} centres. Some shifts in the positions of the absorption bands do occur when the solvent polarity is changed, but differences are generally small. Spectra were recorded from the near IR (1000 nm) into the visible region and absorption 'cut-off wavelengths' above which absorption is less than 1% of that of the visible peak are shown in Table 5. These values are of interest when considering possible second harmonic generation into the visible or near-IR region.

All of the complexes absorb very strongly in the region of 530 nm, making attempts to observe second harmonic generation from a 1064 nm laser fundamental impractical because of extensive absorption of the second harmonic and subsequent thermal damage to the sample. However, doubling of the 1907 nm laser wavelength produces a harmonic at 953 nm, and Table 5 indicates that these complexes show negligible absorption at this wavelength. Some general trends which emerge from the data in Table 5 are that the tungsten complexes show considerably lower wavelength cut-offs than do their molybdenum counterparts. Also, the phenoxide complexes of molybdenum have cut-offs which are substantially higher than those of their anilide analogues. Addition of a methyl substituent has a negligible effect on the cut-off wavelength.

A number of the complexes described were tested for second harmonic generation using modifications of the standard Kurtz powder test on unsized powdered samples. The initial measurements on some of the compounds were carried out at GEC Marconi Laboratories using a single 1907 nm laser pulse and have been reported previously.[11] The same apparatus was used to make measurements on several ferrocenyl derivatives[9,11f,g] synthesised by Green and co-workers so that these earlier results were obtained under similar conditions and are the most directly comparable. More recently measurements on the compounds reported have been made at Durham using a lower-power laser and averaging the intensities of the second harmonic light from 10 laser pulses. This experimental approach gives rather lower values for the second harmonic generation relative to urea. The reasons for this difference are not clear but under these conditions 2-acetamido-1-dimethylamino-4-nitrobenzene exhibits a second harmonic intensity of 30 times that of urea (at 1907 nm) compared to a reported value of 115 (at 1064 nm). These more recent results obtained at Durham are summarised in Table 6 and, although they cannot be directly compared with earlier values, they are internally consistent allowing comparisons between the compounds tested at Durham.

Several of the ferrocenylazobenzene complexes show high relative intensities for second harmonic generation. Although powder second harmonic generation efficiencies can only be used as a semiquantitative guide,[25] the tungsten complexes are found to be significantly less active than are their molybdenum counterparts. Comparison of the values for **4** and **5**, **6** and **10** shows that replacement of Mo by W produces a decrease in second harmonic generation by a factor of between 2 and 6. This is in accord with the electrochemical data which show the tungsten centres to be poorer electron-withdrawing groups than are their molybdenum counterparts as evident in the more cathodic reduction potentials of the tungsten compounds. The observation of only weak second harmonic generation from **11**, and none from either its iodo analogue **12** or its tungsten counterpart **13**, is surprising considering that both of the chemically similar compounds **4** and **5** show high second harmonic generation intensities. In order to determine whether these differences could be attributed to differences in crystal-packing arrangements, some X-ray structural studies were carried out.

Structural Studies.—A single crystal X-ray diffraction study

Table 2 Cyclic voltammetry data for [M(NO)L(X)Y]

Complex	M	X	Y	$E_f(M)^a$/V	ΔE_p/mV	$E_f(Fe)^a$/V	ΔE_p/mV
	Mo	Cl	$OC_6H_4R''^b$	−0.35	125	+0.57	100
	Mo	I	$OC_6H_4R''^b$	−0.31	120	+0.58	100
	Mo	OC_6H_4R''	$OC_6H_4R''^b$	−0.70	120	+0.53	120
	Mo	Cl	$HNC_6H_4R''^b$	−0.82	120	+0.59	100
	Mo	I	$HNC_6H_4R''^b$	−0.78	110	+0.59	100
1	Mo	Cl	Y^1	−0.21	100	+0.61	80
2	Mo	I	Y^1	−0.15	90	+0.60	80
3	Mo	Y^1	Y^1	−0.43	140	+0.60	80
4	Mo	Cl	Y^2	−0.57	110	+0.63	90
5	W	Cl	Y^2	−0.97	105	+0.60	100
8	Mo	F	Y^3	−0.99	180	+0.60	110
6	Mo	Cl	Y^3	−0.58	240	+0.62	80
9	Mo	Br	Y^3	−0.57	100	+0.62	70
7	Mo	I	Y^3	−0.54	80	+0.60	80
10	W	Cl	Y^3	−1.01	110	+0.62	90
25	Mo	OC_6H_{11}	Y^3	−1.09	60	+0.60	55
11	Mo	Cl	Y^4	−0.59	135	+0.61	75
12	Mo	I	Y^4	−0.55	125	+0.61	80
13	W	Cl	Y^4	−1.00	145	+0.60	85
14	Mo	Cl	Y^9	−0.52	630	+0.61	100
15	Mo	Cl	Y^5	−0.26	70	—	—
16	Mo	I	Y^5	−0.21	70	—	—
17	Mo	Y^5	Y^5	−0.52	70	—	—
18	W	Cl	Y^5	−0.78	90	—	—
19	Mo	Cl	Y^6	−0.65	70	—	—
20	Mo	I	Y^6	−0.61	70	—	—
21	W	Cl	Y^6	−1.06	80	—	—
22	Mo	Cl	Y^7	−0.21	95	—	—
23	Mo	I	Y^7	−0.16	75	—	—
24	W	Cl	Y^7	−0.73	100	—	—

[a] All potentials measured relative to the SCE in dry CH_2Cl_2 using a platinum-bead working electrode; 0.2 mol dm^{-3} $[NBu_4][BF_4]$ as supporting electrolyte; scan rate 200 mV s^{-1}; ferrocene used as an internal standard gave E_f = +0.57 V, ΔE_p = 70 mV. [b] Values taken from ref. 16. R″ = $(C_5H_4)Fe(C_5H_5)$.

Table 3 The UV/VIS excitation maxima for selected complexes [M(NO)L(X)Y] *

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1	500 (17 200), 359 (33 600)
2	482 (15 600), 360 (27 900)
3	468 (17 600), 371 (34 700)
8	509 (29 900), 441 (31 300)
6	488 (19 600), 358 (13 500)
7	511 (21 300), 379 (18 600)
10	427 (39 800)
15	572 (13 600), 406 (26 100), 311 (11 200)
19	544 (23 700), 411 (13 900), 280 (8 200)

* All spectra recorded in dichloromethane at ambient temperature, concentration *ca.* 10^{-5} mol dm^{-3}.

Table 4 Solvent dependence of UV/VIS excitation maxima for selected ferrocenyl complexes [M(NO)L(X)Y]

	$\lambda_{max}{}^a$/nm			
Complex	C_6H_{14}	CH_2Cl_2	$HCONMe_2$	$\Delta\lambda^b$/nm
1	508	500	495	13
	354	359	362	8
2	540	482	decomp.	58
	357	360		3
4	480	480	476	4
	351	355	358	7
5	416	422	426	10
8	497	509	528	31
	437	441	445	8
6	496	488	480	16
	350	358	361	11
7	520	511	497	23
	382	379	379	3
10	413	427	432	19

[a] All spectra recorded at ambient temperature, concentrations *ca.* 10^{-5} mol dm^{-3}. [b] Difference between highest and lowest λ_{max} values.

was carried out on the most second harmonic generation-active tungsten complex **10**, which was crystallised by slow evaporation from a mixture of dichloromethane and absolute ethanol. The compound exhibits molecular and crystal-packing arrangements which are isostructural with its molybdenum counterpart **6**.[12b] Fractional atomic coordinates are presented in Table 7 and selected bond distances and angles in Table 8. The complex is chiral, containing an asymmetric tungsten centre and, although grown from a racemate, each of the crystals contains only one enantiomer. The molecular structure, illustrated in Fig. 1, shows no unusual features. As expected, the azobenzene residue has the *trans* configuration, and the two ferrocenyl cyclopentadienyl rings are essentially eclipsed.

The molecular structures of **6** and **10** contain relatively short M–Cl bond lengths of 2.392(7) (Mo, **6**) and 2.382(15) Å (W, **10**) implying some degree of chlorine to metal π donation. The nitrosyl ligands have N–O bond lengths of 1.262(26) (**6**) and 1.241(4) Å (**10**). They are almost linearly co-ordinated with M–N–O angles of 172.0(15) (**6**) and 177(3)° (**10**). The M–NO bond length of 1.729(20) (**6**) and 1.746(26) Å (**10**) are the shortest of all the five M–N bonds in each complex, the average of the three Mo–N (pyrazolyl) bonds being 2.201 and W–N (pyrazolyl) 2.227 Å. The W–N (amido) bond length of 2.041(32) Å is short for a pure single bond indicating the presence of some degree of N p_π–W d_π ligand-to-metal charge donation, and the large W–N(8)–C(16) angle of 133(3)° is consistent with this assertion. The corresponding bond in the molybdenum analogue is significantly shorter at 1.932(14) Å, with a slightly larger Mo–N(1)–C(6) angle of 134.8(10)° in accord with previous structural studies.[26] This may be an indication of an

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increased degree of p_π–d_π donation in the molybdenum complex resulting from the greater electron-acceptor strength of the metal centre. In the only previous case for which both tungsten and molybdenum {M(NO)L} crystal structures have been solved, the bis(2-pyridylamido) complexes [M(NO)L$(NC_5H_4NH\text{-}2)_2$] (M = Mo or W), changing the metal atom has no significant effects on the solid-state structure.[27]

Table 5 Absorption edges for selected ferrocenyl complexes [M(NO)L(X)Y]*

Complex	λ/nm	Complex	λ/nm
1	880	**8**	700
2	800	**6**	770
3	780	**7**	800
4	760	**10**	680
5	680		

* All spectra recorded at ambient temperature in dichloromethane, concentrations *ca.* 10^{-5} mol dm^{-3}.

Table 6 Powder second harmonic generation data for complexes [M(NO)L(X)Y]

Complex	Second harmonic generation*	Complex	Second harmonic generation*
1	vw	**14**	n.d.
2	vw	**15**	n.d.
4	30 ± 5	**16**	n.d.
5	12 ± 4	**17**	n.d.
8	n.d.	**18**	n.d.
6	50 ± 10	**19**	n.d.
9	25 ± 5	**20**	n.d.
7	1 ± 0.5	**21**	n.d.
10	8 ± 2	**22**	n.d.
11	1 ± 0.5	**23**	n.d.
12	n.d.	**24**	n.d.
13	n.d.		

* Relative harmonic intensity measured with a 1907 nm laser wavelength using a urea powder standard; n.d. = no effect detected, vw = very weak signal. Values obtained from 2-acetamido-1-dimethylamino-4-nitrobenzene and *N*-(4-nitrophenyl)-L-pyrrolidine-2-methanol were 35 ± 5 and 150 ± 10.[5b]

Bond lengths and angles for the azobenzene ligand residue are much as would be expected, with a *trans* configuration and an eclipsed ferrocenyl moiety attached. The tilt angle between the C_5H_4 cyclopentadienyl ring and the attached phenyl ring in the tungsten complex is 14.9° which is almost half of the rotation about the C(29)–C(30) bond observed in the ligand precursor 4′-ferrocenyl-2-methyl-4-nitroazobenzene.[28] The C(10)–C(16) bond between the ferrocenyl and aryl groups is slightly, but not significantly, longer in the molybdenum complex [1.48(6) Å] than its tungsten analogue [1.323(33) Å].

The molecules of complexes **6** and **10** pack in the monoclinic non-centrosymmetric space group $P2_1$ with two molecules in the unit cell. A packing diagram for the tungsten complex (Fig. 2) shows how the molecules align in a 'herring-bone' array with one unco-ordinated molecule of dichloromethane included in the lattice. The presence of this solvent is also shown by elemental analyses and ^{1}H NMR spectroscopy. An alternative view of the crystal packing is shown in Fig. 3. The packing of the molybdenum complex is similar.[12b] Since it is known that there are certain optimum angular relations between the molecular dipolar axis and the crystallographic axes to give maximum phase-matched second harmonic generation, some simple calculations have been carried out to assess the effectiveness of the molecular, and hence dipolar, orientation within this packing array. The complicated shape of the polarisation chain between the iron and molybdenum or tungsten centres precludes a totally accurate identification of the true dipolar axis, but estimates can be used with reasonable confidence. The angles between the N(3)–C(16) vectors, which were taken as approximations to the dipolar axes, and the crystallographic *b* axes are 56.88 (Mo, **6**) and 58.7° (W, **10**). Also, the angles between the main M–C(16) vectors, alternative polarisation axes, and the *b* axes are 58.39 (**6**) and 59.5° (**10**). These values are very close to the optimum value of θ_m = 54.74° for phase-matched second harmonic generation in the $P2_1$ space group,[29] so it would seem that the packing of this molecule is close to the ideal for maximum second harmonic generation.

Table 7 Fractional atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for complex **10**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	170(2)	0	575(2)	C(12)	1 637(57)	201(27)	3 248(61)
Fe	−11 126(5)	3 090(3)	−5 654(6)	C(13)	3 051(37)	23(38)	3 767(38)
Cl(1)	−1 397(14)	−255(7)	2 165(14)	C(14)	3 697(43)	−417(21)	3 015(45)
Cl(2)	5 432(23)	1 152(16)	1 815(25)	C(15)	4 835(58)	−782(31)	3 019(62)
Cl(3)	3 610(33)	1 987(15)	733(33)	C(16)	−1 756(29)	265(15)	−1 730(32)
O	−302(36)	1 432(19)	844(37)	C(17)	−2 536(45)	686(24)	−1 095(50)
N(1)	−88(27)	840(13)	707(28)	C(18)	−3 574(42)	1 076(22)	−1 676(45)
N(2)	522(29)	−1 110(15)	515(29)	C(19)	−3 734(43)	1 020(22)	−3 049(45)
N(3)	1 639(30)	−1 316(15)	545(32)	C(20)	−2 893(34)	590(17)	−3 737(36)
N(4)	2 001(24)	49(23)	−600(25)	C(21)	−2 011(42)	212(20)	−3 032(45)
N(5)	2 919(30)	−382(15)	−441(32)	C(22)	−2 935(43)	504(21)	−5 168(42)
N(6)	1 625(26)	−28(34)	2 091(28)	C(23)	−6 123(38)	2 181(19)	−3 882(40)
N(7)	2 766(30)	−451(15)	1 923(33)	C(24)	−7 005(63)	2 603(35)	−3 108(80)
N(8)	−1 025(30)	−136(22)	−1 020(31)	C(25)	−7 850(31)	2 979(17)	−3 697(26)
N(9)	−4 692(33)	1 396(17)	−3 742(35)	C(26)	−8 268(32)	2 940(18)	−5 017(28)
N(10)	−5 145(33)	1 839(17)	−3 122(34)	C(27)	−7 463(60)	2 530(34)	−5 770(44)
B	2 871(75)	−888(38)	715(73)	C(28)	−6 343(47)	2 170(22)	−5 173(48)
C(1)	−1 809(39)	−1 524(22)	111(45)	C(29)	−9 519(44)	3 322(24)	−5 662(49)
C(2)	−285(63)	−1 505(32)	192(65)	C(30)	−9 791(47)	3 301(25)	−6 850(50)
C(3)	221(45)	−2 128(23)	281(46)	C(31)	−10 609(55)	3 701(28)	−7 271(59)
C(4)	1 571(44)	−1 988(24)	463(48)	C(32)	−10 800(37)	4 056(19)	−6 046(38)
C(5)	2 635(5)	−2 404(29)	435(61)	C(33)	−9 922(43)	3 826(22)	−5 082(47)
C(6)	1 309(60)	974(29)	−2 199(62)	C(34)	−12 083(75)	2 722(43)	−3 988(91)
C(7)	2 159(41)	430(21)	−1 621(43)	C(35)	−11 291(80)	2 234(40)	−4 547(88)
C(8)	3 347(47)	188(22)	−2 162(54)	C(36)	−11 666(85)	2 172(44)	−5 839(99)
C(9)	3 623(53)	−247(27)	−1 444(58)	C(37)	−12 745(55)	2 578(28)	−5 918(61)
C(10)	4 988(61)	−710(33)	−1 466(66)	C(38)	−12 881(53)	2 910(28)	−4 961(56)
C(11)	1 031(45)	671(23)	3 798(47)	C(39)	3 993(80)	1 206(41)	1 058(85)

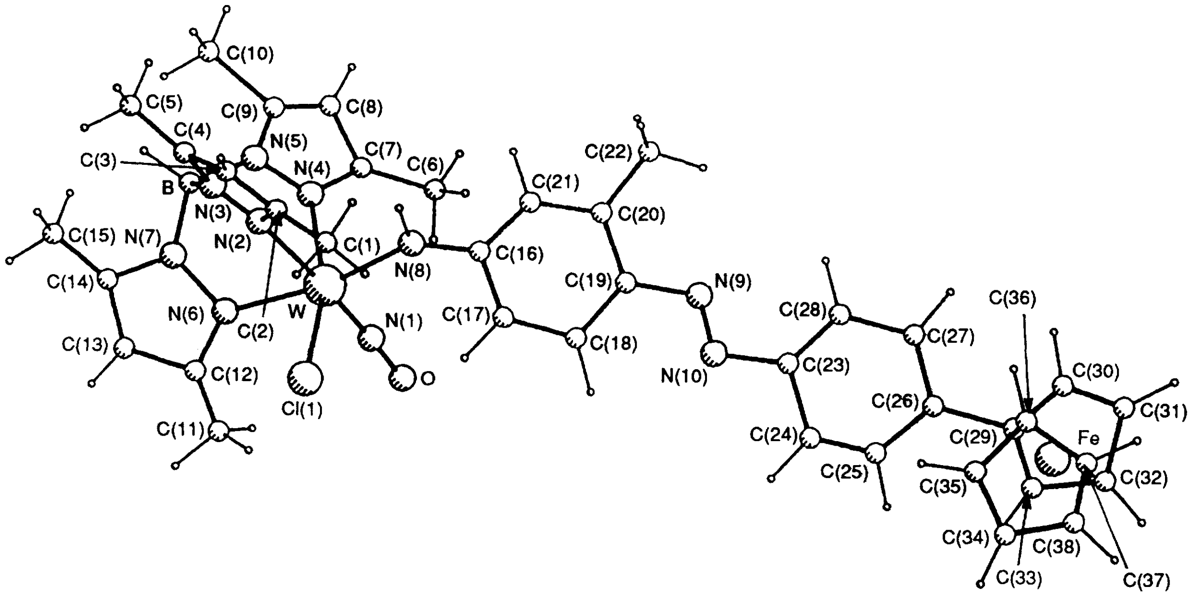

Fig. 1 Crystal structure of complex **10** showing the atom labelling

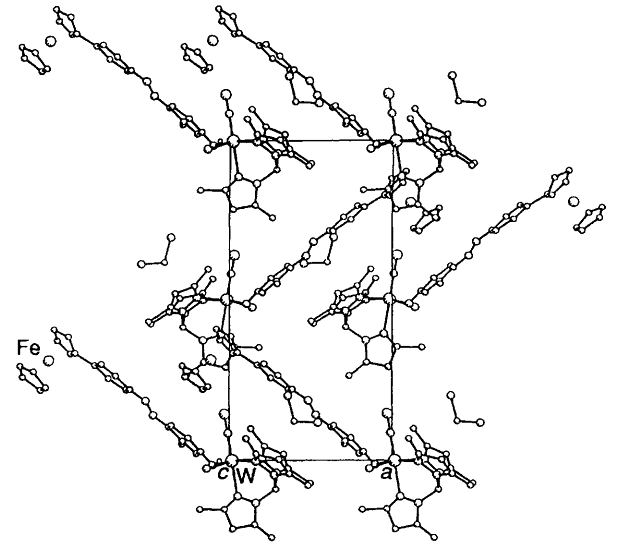

Fig. 2 View along the *b* axis of the molecular packing in complex **10**

A very similar angle of alignment is found in the organic compound *N*-(4-nitrophenyl)pyrrolidine-2-methanol which also crystallises in the $P2_1$ space group,[30] has $\theta = 58.6°$ and exhibits a powder second harmonic generation at 1064 nm of 150 times that of urea. The crystal structure of this organic material is influenced not only by the chirality of the L-pyrrolidinemethanol group, but also by intermolecular hydrogen bonds between the hydroxyl of one molecule and the nitro group of the next. These serve to hold the molecules in the head-to-tail fashion which gives rise to effective dipolar orientation for near-optimum second harmonic generation. By contrast, no hydrogen bonds are present in the crystal structure of the molybdenum complex, and it is the overall shape of the molecule, dominated by the chiral molybdenum centre and the bulky ferrocenyl moiety, which gives rise to the favourable packing arrangement.

Although crystals of several of the other second harmonic generation-active ferrocenyl complexes have been grown, none proved suitable for a single-crystal structure determination. However, the molybdenum bromide complex **9** was found to crystallise in the same space group ($P2_1$)[31] as that of **6** and **10**, described above.

Table 8 Selected bond distances (Å) and angles (°) for complex **10**

W–Cl(1)	2.382(15)	Fe–C(30)	1.91(5)
W–N(1)	1.746(26)	Fe–C(31)	2.17(6)
W–N(2)	2.302(32)	Fe–C(32)	2.05(4)
W–N(4)	2.255(25)	Fe–C(33)	2.02(5)
W–N(6)	2.125(27)	Fe–C(34)	2.14(9)
W–N(8)	2.041(32)	Fe–C(35)	2.11(9)
O–N(1)	1.241(4)	Fe–C(36)	1.97(9)
N(8)–C(16)	1.32(4)	Fe–C(37)	1.96(6)
Fe–C(29)	1.70(5)	Fe–C(38)	1.98(5)
Cl(1)–W–N(1)	93.3(10)	N(2)–W–N(4)	84.1(14)
Cl(1)–W–N(2)	84.9(8)	N(2)–W–N(6)	83.6(20)
Cl(1)–W–N(4)	164.1(9)	N(2)–W–N(8)	86.1(14)
Cl(1)–W–N(6)	86.9(9)	N(4)–W–N(6)	80.5(10)
Cl(1)–W–N(8)	97.9(10)	N(4)–W–N(8)	92.7(11)
N(1)–W–N(2)	177.1(12)	N(6)–W–N(8)	168.2(19)
N(1)–W–N(4)	97.2(15)	W–N(1)–O	177(3)
N(1)–W–N(6)	94.1(21)	W–N(8)–C(16)	133(3)
N(1)–W–N(8)	96.4(15)		

In the absence of any suitable single crystals, powder X-ray diffraction traces were recorded for a number of derivatives in order to gain some further information concerning their solid-state structures. The diffraction patterns for complex **6** and its tungsten analogue **10** were very similar indicating that they adopt the same crystal structure as confirmed by the single-crystal X-ray studies described above. The low second harmonic generation of **7**, the iodo analogue of **6**, is likey to be due to poor sample crystallinity since samples of **7** did not produce any diffraction peaks and appeared to be amorphous.

Comparing the powder X-ray diffraction traces from the other materials examined allows the following conclusions to be drawn. Removal of a methyl group from complex **6** to give **4** does not substantially alter the crystal packing, both materials giving similar diffraction traces. Similarly the addition of a second methyl substituent to **6** to give **11** does not substantially alter the structure. However, **12**, the iodo analogue of **11**, gives a quite different diffraction pattern from **11** and probably has a different crystal structure. Similarly, replacement of the chloride ligand in **6** by fluoride to give **8** produces a different diffraction pattern. Replacing the nitrogen atom in **4** by oxygen to give **1** also gives rise to a different pattern, and **2** has a different pattern

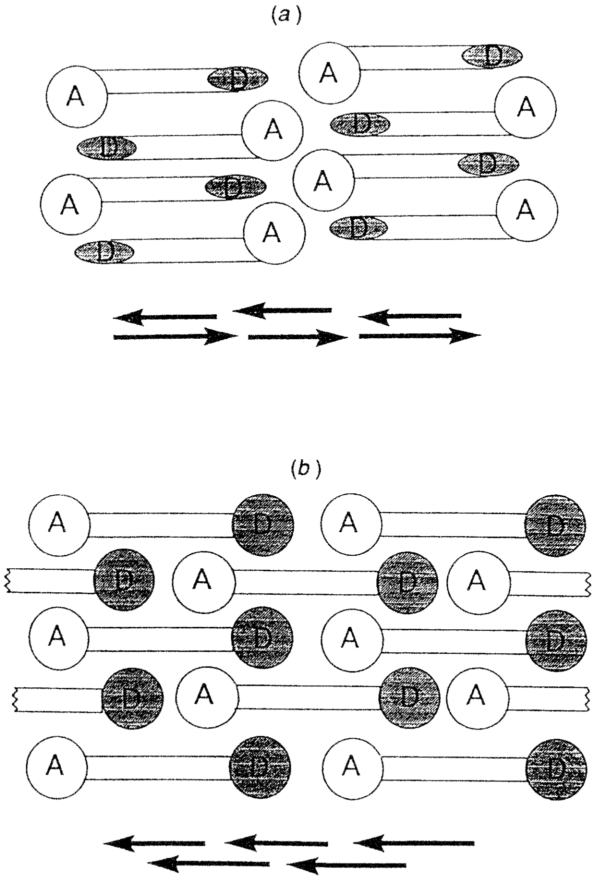

Fig. 3 Possible two-dimensional packing arrangements for a donor (D)–acceptor (A) molecule, D→A, with (*a*) a sterically undemanding donor group D and a sterically bulky terminal group A leading to opposed dipoles, (*b*) sterically bulky terminal groups D and A leading to aligned dipoles

again from that of **1** or **4**. These observations were surprising since we had not expected changes in the donor atom from NH to O or changes in the halide to have major structural consequences. However, the fact that neither of the phenoxide complexes shows any powder second harmonic generation whilst **4** is highly active highlights the sensitivity of this system to the nature of the donor atom bound to the metal. Also it appears that changing the halide co-ligand can alter the solid-state structure and hence the bulk non-linear optical properties of these complexes.

Conclusion

One feature to emerge from this, and an earlier study of the precursors to compounds HY^2–HY^4 which contain nitro groups in place of the amine function,[18] is that only compounds which contain both the {M(NO)L} and the ferrocenyl groups exhibit second harmonic generation. All of these molecules are acentric, dipolar and contain polarisable bridges, so all should have non-zero first hyperpolarisabilities, β. In the cases where the powder test samples produce X-ray diffraction patterns two reasons may be advanced for the failure to detect second harmonic generation. Either the molecules have adopted centric packing arrangements to give non-polar materials,[18,28] or poor phase matching leads to weak second harmonic generation which could not be detected under the experimental conditions used. It is possible to invoke arguments based on molecular shape to explain why molecules which contain both {M(NO)L} and ferrocenyl might tend to pack in an acentric manner while those which contain only one or other of these groups might not. Molecules such as **6** or **10** contain bulky groups at each end of a quite long planar bridging group. In contrast molecules such as **15** and **19** contain a bulky group at only one end. In this latter case the molecular shape predisposes the molecules to pack efficiently with opposed dipoles as illustrated schematically in Fig. 3(*a*) and found in single-crystal X-ray studies.[28,32] In contrast the shape of molecules with two bulky end groups allows an efficient packing with parallel dipoles as shown in Fig. 3(*b*). Although this is only a very crude two-dimensional model it does offer a rationalisation of our findings and indicates how molecular shape might be used to improve the chances of obtaining polar materials from dipolar molecules.

An additional noteworthy aspect of this study is that, through fortuitous and unexpected spontaneous resolution upon crystallisation, we have been able to exploit chirality at octahedral transition-metal centres as an aid in the production of highly non-linear optically active materials. Furthermore, the chiral centre is intimately involved in the polarisable system necessary to produce high β values. This contrasts with the well documented use of chiral tetrahedral carbon auxiliary groups in the preparation of active organic materials such as *N*-(4-nitrophenyl)pyrrolidine-2-methanol.[29]

These structural features, coupled with the inherent 'tunability' of the electronic properties of the acceptor group by subtle isostructural alterations, represent significant advances in the creation of molecular non-linear optical materials.

Experimental

Materials.—The known compounds 4-ferrocenyl-aniline, -4′-nitroazobenzene, -3-methyl-4′-nitroazobenzene and -3,3′-dimethyl-4′-nitroazobenzene were prepared using previously described procedures,[18] as were [$M(NO)LX_2$] [L = $HB(dmpz)_3$].[22,33] Commercial reagents were used as supplied, and all reaction solvents were redistilled from drying agents according to standard methods prior to use. All reactions were performed under an atmosphere of dry nitrogen but the products were handled in air. Silica gel 60 (70–230 mesh) was used for all chromatographic separations which were carried out on a column of dimensions 40 × 2 cm unless otherwise stated. Elemental analyses were carried out by the Microanalytical Laboratory, University of Birmingham.

Physical Measurements.—Infrared spectra were recorded using a Perkin-Elmer 297 spectrometer with samples as KBr discs, 270 MHz ^1H NMR spectra from solutions in $CDCl_3$ using a JEOL GX 270 spectrometer. Cyclic voltammetric measurements were made using a PAR 174A polarograph. Solutions in CH_2Cl_2 were *ca.* 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in [$NBu^n{}_4$][BF_4] as base electrolyte. A platinum-bead test electrode was used with a scan rate of 200 mV s^{-1}. A saturated calomel electrode (SCE) was used as reference with ferrocene as an internal standard (E_f = +0.57 V; ΔE_p = 70 mV). Potentials are quoted relative to the SCE.

The determination of the second harmonic intensity of powder samples (Kurtz powder test)[34] was made relative to that of powdered urea. Samples were contained in small wells of dimensions 2 × 5 mm formed by fixing a metal washer between a microscope slide and a coverslip. The 1064 nm fundamental output of a Nd:YAG laser was passed through a hydrogen cell to produce a Raman-shifted output at 1907 nm. Pulses (width 4 ns, repetition rate 1 Hz) of 2 mJ energy at a wavelength of 1907 nm were weakly focused onto sample cells containing finely ground (ungraded) material and the second harmonic light at 950 nm measured on an S1 response photomultiplier tube. Boxcar gate sampling was used to provide data points averaged over ten pulses and the mean of ten of these points provided the quoted values of relative harmonic intensity for second harmonic generation.

Synthetic Methods.—*4-Ferrocenyl-4′-hydroxyazobenzene* (HY^1). A mixture of 4-nitrosophenol (2.71 g, 22 mmol) and 4-

ferrocenylaniline (5.0 g, 18 mmol) in glacial acetic acids (sp.gr. 1.05, 400 cm^3) was stirred at room temperature for 5 d. Water (1000 cm^3) and dichloromethane (100 cm^3) were added, the mixture shaken and the organic layer separated. The aqueous layer was extracted with dichloromethane (3 × 50 cm^3), and the combined organic extracts were evaporated to dryness. Careful column chromatography using a long (60 × 3.5 cm) column followed by a shorter one (35 × 3.0 cm) with pure dichloromethane as eluent yielded a red fraction which was evaporated to give dark red HY^1 (0.34 g, 5%).

4-*Amino*-4′-*ferrocenylazobenzene* (HY^2). A solution of 4-ferrocenyl-4′-nitroazobenzene (0.5 g, 1.22 mmol) and sodium sulfide hydrate (1.0 g) in ethanol (100 cm^3) was heated at reflux for 1 h during which time the colour changed from purple to red. The solvent was then removed *in vacuo* and the crude product purified by column chromatography in dichloromethane. The major red band afforded upon evaporation a deep burgundy powder which was crystallised from dichloromethane–pentane to give dark red needles of HY^2 (0.44 g, 95%).

4-*Amino*-4′-*ferrocenyl*-2-*methylazobenzene* (HY^3). This compound was prepared in an identical manner to that of HY^2 using 4′-ferrocenyl-2-methyl-4-nitroazobenzene (0.52 g, 1.22 mmol). This yielded deep burgundy HY^3 (0.47 g, 97%).

4-*Amino*-4′-*ferrocenyl*-2,3′-*dimethylazobenzene* (HY^4). This compound was prepared in an identical manner to that of HY^2 using 4′-ferrocenyl-2,3′-dimethyl-4-nitroazobenzene (0.53 g, 1.22 mmol). This yielded deep burgundy HY^4 (0.46 g, 94%).

4′-*Ferrocenyl*-2,3′-*dimethyl*-4-(2-*methyl*-4-*nitrophenylazo*)-*azobenzene* (Y^8). This compound was prepared in an identical manner to that of HY^1 using HY^4 (0.30 g, 0.73 mmol). Quantities of other reagents were also changed to 5-nitro-2-nitrosotoluene (0.25 g, 1.51 mmol), glacial acetic acid (sp.gr. 1.05, 50 cm^3) and water (100 cm^3), and the reaction time was reduced to 24 h. The major dark brown fraction from a single 40 × 2 cm column yielded upon evaporation the dark olive-green microcrystalline Y^8 (0.14 g, 35%).

4-(4-*Amino*-2-*methylphenylazo*)-4′-*ferrocenyl*-2,3′-*dimethylazobenzene* (HY^9). This compound was prepared in an identical manner to that of HY^2 using Y^8 (0.10 g, 0.18 mmol). Quantities of other reagents were also changed to sodium sulfide hydrate (0.5 g) and ethanol (25 cm^3), and the reaction time was reduced to 5 min. Only a short reaction time was allowed because decomposition was expected. Column chromatography gave 7% recovery of starting material and deep red-orange HY^9 (0.041 g, 43%).

4-*Ferrocenyl*-4′-*fluoroazobenzene*. This compound was prepared in an identical manner to that of HY^1 using 1-fluoro-4-nitrosobenzene (2.75 g, 22 mmol). The major red band from chromatography on a 40 × 2 cm column yielded deep red microcrystalline 4-ferrocenyl-4′-fluoroazobenzene (2.77 g, 40%).

4-*Ethoxy*-4′-*ferrocenylazobenzene*. A solution of 4-ferrocenyl-4′-fluoroazobenzene (0.50 g, 1.30 mmol) and sodium hydroxide (0.5 g, 12.5 mmol) in ethanol (20 cm^3) was stirred at reflux for 4 h. The solution was cooled and water (20 cm^3) and dichloromethane (20 cm^3) were added. The organic layer was separated, the aqueous layer extracted with dichloromethane (2 × 10 cm^3), and the combined organic extracts evaporated to give a red solid. This was separated into its components by column chromatography using a 50% dichloromethane–hexane solution as eluent. The first red fraction was unreacted 4-ferrocenyl-4′-fluoroazobenzene (0.40 g, 80% recovery), and the second major red-orange band yielded deep red-brown 4-ethoxy-4′-ferrocenylazobenzene (0.11 g, 20%).

Complex **1**. A solution of [Mo(NO){HB(dmpz)$_3$}Cl$_2$] (0.10 g, 0.20 mmol), HY^1 (0.085 g, 0.22 mmol) and hexamine (0.05 g, 0.36 mmol) was stirred under reflux in toluene (15 cm^3) for 3.5 h. The reaction mixture was then cooled and evaporated to dryness under reduced pressure. The resulting red-purple solid was purified by column chromatography on silica gel using 30% hexane–dichloromethane as the eluent. The major red band was collected affording the deep red-purple product (0.080 g, 48%).

Complex **2**. This compound was prepared in an identical manner using [Mo(NO){HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.20 g, 0.26 mmol) and HY^1 (0.12 g, 0.31 mmol). A deep purple solid was obtained (0.18 g, 75%).

Complex **3**. This compound was prepared from [Mo(NO)-{HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.10 g, 0.13 mmol) and HY^1 (0.10 g, 0.26 mmol) using the procedure described for **1** except that triethylamine (0.2 cm^3, 1.5 mmol) was used in place of hexamine. A dark red-brown solid was obtained (0.046 g, 30%).

Complex **4**. This compound was prepared in a similar manner to that of **1** using HY^2 (0.20 g, 0.52 mmol), [Mo(NO)-{HB(dmpz)$_3$}Cl$_2$] (0.25 g, 0.51 mmol) and triethylamine (0.5 cm^3, 3.7 mmol), with a reaction time of 5 h. This yielded the deep red-purple product (0.31 g, 73%).

Complex **5**. This compound was prepared in a similar manner to **4** using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.10 g, 0.17 mmol) and HY^2 (0.08 g, 0.21 mmol), with a reaction time of 24 h. A dark brown solid was obtained (0.040 g, 25%).

Complex **6**. This compound was prepared in similar manner to **4** using HY^3 (0.25 g, 0.63 mmol) and [Mo(NO){HB-(dmpz)$_3$}Cl$_2$] (0.30 g, 0.61 mmol) to give the deep purple product (0.39 g, 75%).

Complex **7**. This compound was prepared in a similar manner to that of **6** using [Mo(NO){HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.30 g, 0.39 mmol) and HY^3 (0.16 g, 0.41 mmol) to give the deep purple product (0.29 g, 79%).

Complex **8**. This compound was prepared in a similar manner to that of **6** using [Mo(NO){HB(dmpz)$_3$}F$_2$] (0.12 g, 0.26 mmol) and HY^3 (0.12 g, 0.30 mmol). Column chromatography on silica using 1% tetrahydrofuran (thf)–dichloromethane as eluent yielded the deep crimson product (0.065 g, 30%).

Complex **9**. This compound was prepared in a similar manner to that of **6** using [Mo(NO){HB(dmpz)$_3$}Br$_2$] (0.10 g, 0.17 mmol) and HY^3 (0.08 g, 0.20 mmol) to give the deep purple product (0.11 g, 72%).

Complex **10**. This compound was prepared in a similar manner to that of **5** using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.30 g, 0.52 mmol) and HY^3 (0.22 g, 0.56 mmol). A dark red-brown solid was obtained (0.18 g, 37%).

Complex **11**. This compound was prepared in an identical manner to that of **6** using HY^4 (0.26 g, 0.64 mmol) to give the deep pink-purple product (0.39 g, 74%).

Complex **12**. This compound was prepared in an identical manner to that of **7** using HY^4 (0.17 g, 0.42 mmol) to give the deep purple product (0.23 g, 62%).

Complex **13**. This compound was prepared in an identical manner to that of **10** using HY^4 (0.22 g, 0.56 mmol). A dark red-brown solid was obtained (0.10 g, 20%).

Complex **14**. This compound was prepared in similar manner to that of **4** using HY^9 (0.032 g, 0.061 mmol) and [Mo(NO){HB(dmpz)$_3$}Cl$_2$] (0.037 g, 0.075 mmol) in toluene (10 cm^3). Column chromatography on silica gel using dichloromethane as eluent yielded the deep purple product (0.041 g, 69%).

Complex **15**. This compound was prepared in a similar manner to that of **1** using [Mo(NO){HB(dmpz)$_3$}Cl$_2$] (0.037 g, 0.075 mmol), HY^5 (0.17 g, 0.70 mmol) and toluene (20 cm^3) with a reaction time of 3 h. Column chromatography on silica gel using dichloromethane as eluent followed by recrystallisation from dichloromethane–hexane yielded the product as a dark green-black solid (0.34 g, 79%).

Complex **16**. This compound was prepared in an identical manner to that of **15** using [Mo(NO){HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.40 g, 0.52 mmol) and HY^5 (0.15 g, 0.62 mmol). A dark green-black solid was obtained (0.28 g, 67%).

Complex **17**. This compound was prepared from [Mo(NO)-{HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.40 g, 0.52 mmol) and HY^5 (0.30 g, 1.24 mmol) using the procedure described for **15** except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. Column chromatography using 10% thf–dichloromethane as eluent followed by recrystallisation from dichloromethane–hexane afforded a dark brown solid (0.12 g, 26%).

Complex **18**. This compound was prepared in a similar manner to that of **15** using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.40 g, 0.69 mmol), HY^5 (0.18 g, 0.75 mmol), and triethylamine (0.5 cm^3, 3.7 mmol), with a reaction time of 5 h. A dark red-brown solid was obtained (0.38 g, 78%).

Complex **19**. This compound was prepared in a similar manner to that of **15** using HY^6 (0.17 g, 0.70 mmol) in place of HY^5 and triethylamine (0.5 cm^3, 3.7 mmol) to give the product as a deep purple solid (0.29 g, 68%).

Complex **20**. This compound was prepared in an identical manner to that of **19** using [Mo(NO){HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.40 g, 0.52 mmol) and HY^6 (0.15 g, 0.62 mmol) to give a deep blue-purple solid (0.30 g, 74%).

Complex **21**. This compound was prepared in a similar manner to that of **19** using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.40 g, 0.69 mmol) and HY^6 (0.18 g, 0.75 mmol), with a reaction time of 8 h to give a dark red-brown solid (0.065 g, 12%).

Complex **22**. This compound was prepared in a similar manner to that of **15** using HY^7 (0.20 g, 0.68 mmol) to give a deep emerald-green solid (0.067 g, 15%).

Complex **23**. This compound was prepared in an identical manner to that of **16** using HY^7 (0.19 g, 0.65 mmol) to give a dark emerald-green solid (0.23 g, 53%).

Complex **24**. This compound was prepared in a similar manner to that of **18** using HY^7 (0.22 g, 0.75 mmol) to give a dark red-brown solid (0.26 g, 45%).

Complex **25**. A solution of complex **7** (0.10 g, 0.11 mmol), cyclohexanol (0.5 cm^3) and triethylamine (0.5 cm^3) was stirred under reflux in toluene (10 cm^3) for 2 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting deep crimson solid was purified by column chromatography on alumina using 60% hexane–dichloromethane as the eluent. Unreacted **7** was removed as a second purple band, and the first major crimson band was collected and evaporated to afford the deep crimson product (0.064 g, 66%).

Crystallography for Complex **10**.—Crystal data. C$_{38}$H$_{42}$-BClFeNOW·CH$_2$Cl$_2$, M_r = 1025.7, monoclinic, space group $P2_1$, a = 10.151(7), b = 20.470(7), c = 10.367(3) Å, β = 91.72(3)°, U = 2153 Å^3, Z = 2, D_c = 1.582 g cm^{-3}, $F(000)$ = 1024, μ(Mo-Kα) = 3.39 mm^{-1}.

Cell dimensions and intensity data were measured with an Enraf-Nonius CAD-4 diffractionmeter using Mo-Kα radiation, λ = 0.710 69 Å. 3083 Unique reflections were measured in the range θ 2–25° and of these 2338 were considered observed with $F > 5\sigma(F)$ and used in the analysis. Three standard reflections measured every 2 h showed no significant variation in intensity.

The structure was determined by Patterson and Fourier methods and refined by least squares using anisotropic thermal parameters for the Cl and metal atoms. Hydrogen atoms were placed in calculated positions [d(C–H) 1.08 Å] riding on their respective bonded atoms. Weights of the form $w = 1/[\sigma^2(F)]$ were used in the refinement which converged with R and R' 0.083 and 0.104. The inverse structure resulted in R and R' 0.0835 and 0.104. Residual electron density was in the range +2.4 (close to tungsten) to −1.3 e Å^{-3}.

Computations were carried out on the University of Birmingham IBM 3090 computer with the SHELXS 86[35] and SHELX 76[36] programs. The molecular diagrams were drawn using PLUTO.[37] Atomic coordinates and bond lengths and angles are given in Tables 7 and 8 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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