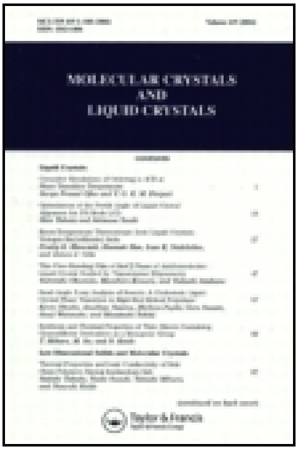

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Electronic Hyperpolarisabilities of Some Mesogenic Stilbazole Complexes of Rh(I) and Ir(I)

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Electronic Hyperpolarisabilities of Some Mesogenic Stilbazole Complexes of Rh(I) and Ir(I)

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The electronic hyperpolarisabilities of a chiral 4-alkoxystilbazole and its complexes with Rh(I) and Ir(I) are reported and discussed in terms of the acceptor properties of the metal fragment.

Keywords: Rhodium, iridium, stilbazole, nonlinear optics

The study of molecular materials for use in non-linear optics is largely motivated by the larger hyperpolarisabilities and higher damage threshholds on offer and to some extent by the way in which the origins of large first hyperpolarisabilities are understood theoretically at the molecular level.[1] A natural development of the study of organic materials for non-linear optics is the design and synthesis of optically non-linear metal complexes,[2] both organometallic and coordination, given the large, polarisable electrons density available from the inclusion of the metal centre.

As part of our work on metal-containing liquid crystals,[3] we had carried out birefringence[4] and linear polarisability[5] measurements on a number of mesogenic metal complexes and found that in many cases, the mean electronic polarisabilities ($\bar{\alpha}$) and birefringence (Δn) were large. For example, the mean electronic polarisability ($\bar{\alpha}$) of the 4-alkoxystilbazole (**I**; Figure 1) was $35 \pm 4 \times 10^{-40}\ J^{-1}\ C^2\ m^2$ while complexation to Ir(I) to give (**II**; Figure 1) increased $\bar{\alpha}$ to $60 \pm 2 \times 10^{-40}\ J^{-1}\ C^2\ m^2$. Similarly, the birefringence (Δn) of the 4-alkoxycyanobiphenyl (**III**; Figure 1) was 0.131 at $T/T_{NI} = 0.985$, while for its Pd(II) complex (**IV**; Figure 1), $\Delta n = 0.161$ at the same reduced temperature; the birefringence of a mixture of complexes of the same general structure as (**IV**) increased to $\Delta n = 0.33$ and 0.4 at T/T_{NI} of 0.84 and 0.73, respectively. These large values were accounted for on the basis that the metal electrons contributed substantially to the observed magnitude of each parameter.

As these materials clearly possessed highly mobile electrons, it was then of

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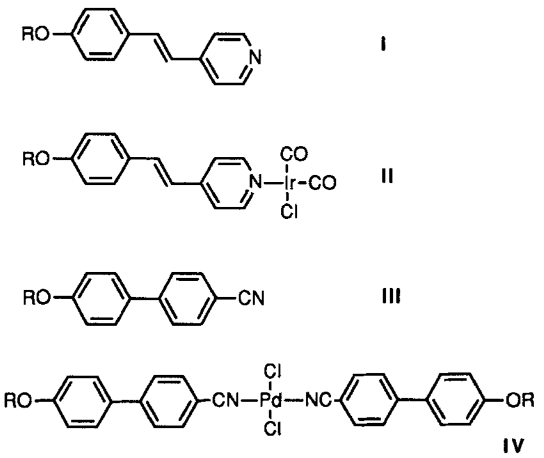
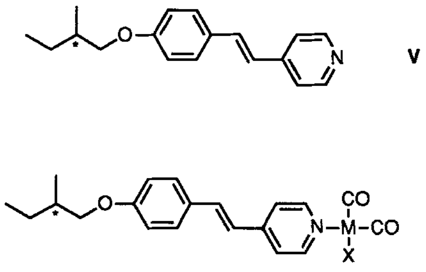


FIGURE 1 Compounds which were the subject of previous studies.



VI M = Ir, X = Cl
VII M = Rh, X = Cl
VIII M = Rh, X = Br

FIGURE 2 Compounds examined in this study.

interest to investigate their hyperpolarisability to see the extent of their quadratic optical nonlinearity. This was done using the EFISH experiment[6] which provides information at the molecular level, as opposed to the Kurtz Powder test which provides macroscopic information and whose results are dominated by crystallographic factors.

Given the molecular centrosymmetry of complexes of type (**IV**), these were not chosen for the present study which concentrated on second order effects (although their third order properties are under investigation) and so the complexes chosen were of the type (**II**). One ligand (**V**; Figure 2) and three complexes (**VI–VIII**; Figure 2) were selected for study; a chiral alkoxy chain was used for the stilbazole in order to try to promote advantageous non-centrosymmetric packing in the solid state to allow the eventual evaluation of solid state second harmonic generation (SHG) efficiencies.

The (*S*)-(+)-2-methylbutoxystilbazole (**V**) was synthesised in two steps. In the first, (*S*)-(+)-2-methylbutyl-*p*-toluenesulphonate (from *p*-toluenesulphonyl chloride and (*S*)-(−)-2-methylbutanol) was reacted with 4-iodophenol under Williamson ether conditions to give (*S*)-(+)-4-(2-methylbutoxy)iodobenzene. This was subsequently reacted with 4-vinylpyridine under Heck conditions[7] to give the corresponding stilbazole. The complexes were formed by reaction of the stilbazole with $[MX(COD)]_2$ (M = Rh, Ir; X = Cl, Br) in dichloromethane under an atmosphere of CO and were obtained as solids by precipitation with hexane, according to Reference 3a.

The hyperpolarisabilities, dipole moments and energies of the lowest energy electronic transition (λ_{max}) for the materials under study were obtained *via* EFISH in chloroform as described elsewhere[8] and using an incident wavelength of 1.907 μm to avoid absorbance of either the fundamental or the frequency-doubled signal; the results are collected in Table I. As expected from its structure, the stilbazole ligand had a reasonable hyperpolarisability which increased appreciably on complexation to the *cis*-$[MCl(CO)_2]$ fragment. Thus, the rather electron-rich, low oxidation state group, *cis*-$[MCl(CO)_2]$, is capable of acting as an electron acceptor. Indeed comparison of the β values of these complexes with that of 4-methoxy-4′-nitrostilbene[7] ($\beta = 28 \times 10^{-30}$ esu) show that the *cis*-$[N\text{-}MCl(CO)_2]$ group has a similar acceptor ability to a C—NO_2 group. The β values found for these new complexes are comparable with those found in various substituted ferrocenes.[9]

That the hyperpolarisability values imply that *cis*-$[N\text{-}MCl(CO)_2]$ is an acceptor of comparable ability to C—NO_2 implies that it is acting as a π-acceptor (as does —NO_2) and it is possible to write a resonance structure (Figure 3) in which π-donation occurs from the pyridine ring into a metal *d*-orbital which subsequently donates that electron density onto the *trans* CO ligand, thus increasing the M—C bond order and decreasing the C—O bond order.

However, comparison of the carbonyl stretching frequencies of compound (**VII**) (ν_{CO} at 2086 and 2012 cm^{-1}) with the related *cis*-$[RhCl(CO)_2(pyridine)]$[10] (ν_{CO} at 2072 and 2015 cm^{-1}) reveals no great difference, whereas if the alkoxystilbazole were acting as an efficient π-donor, one would have expected much lower values for ν_{CO} in this case. The Ir complexes show no difference either. The fact that the stilbazole is probably not properly co-planar with the $IrCl(CO)_2$ unit (by comparison with the structure of $[IrCl(CO)_2(pyridine)]$[11]) is not felt to be significant. Thus we seem forced to conclude that *cis*-$[MX(CO)_2]$ is primarily acting as a σ-acceptor in these materials.

TABLE I

Data from the EFISH Experiment

Compound	λ_{max}/nm	$\mu.10^{18}$/esu	$\beta.10^{30}$/esu
V	335	3.8	15.8
VI	364	6.9	24.4
VII	355	7.4	20.1
VIII	357	7.7	23.9

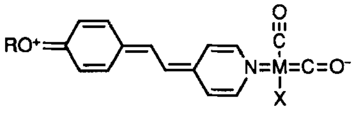


FIGURE 3 Resonance structure of the metal complexes showing the potentially π-acceptor nature of the —M—CO group.

Finally, it has been shown[12] that groups which might be expected to be good electron acceptors (e.g. $[W(CO)_5]$) will only do so in the ground state and are in fact excited-state donors. Given the high electron density and low oxidation state of these Rh and Ir complexes, it is also possible that they too could act as electron donors given a suitable co-ligand and such studies are presently underway.

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