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A fusion of metals, cyclophanes and dihydropyrenes

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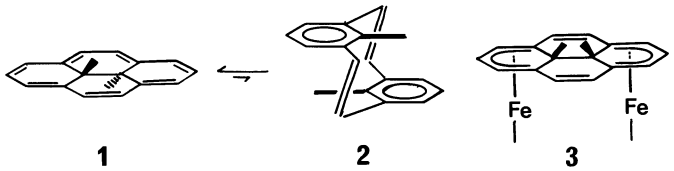
Abstract - The conformational chemistry of 9,18-substituted 2,11-dithia[3,3]metacyclophanes is discussed. When only hydrogen atoms are at the 9,18-positions (7) the molecule is syn, and a syn↔syn conversion is possible and can be studied by ^{77}Se dynamic nuclear magnetic resonance studies. When only one of the 9,18-substituents is hydrogen, the molecule is still syn, but at ambient temperatures is not mobile (except for possible bridge wobbles). When both the 9- and 18-positions are substituted, the anti conformer is preferred, unless one substituent is very much larger than the other. Electron withdrawing groups at other positions on the aryl rings favour the syn conformer. When standard ring contraction reactions are used on all of these [3,3]metacyclophanes, the resulting [2,2]metacyclophanes are usually anti cyclophanes. The parent syn-[2,2]metacyclophanes with either H or Me as substituents at positions 9- or 18- have remained unknown. However use of a chromium(tricarbonyl) group complexed to one or both the aryl rings in the dithiacyclophanes holds the molecule syn during the ring contraction and yet is easily removable, and has allowed synthesis of syn-[2,2]metacyclophane, 5. The latter readily isomerises to the anti conformer at 0°C, $\Delta G^{\neq}_{298}$ for this process being about 21 kcal/mole. Similarly the syn-difluorocyclophane diene 37 has been prepared and converted to the first internal halogen substituted dihydropyrene 38. The complexed cyclophane dienes 32 and 33 are stable to at least 130°C unlike their uncomplexed counterparts, and thus now should allow study of cyclophane diene chemistry.

INTRODUCTION

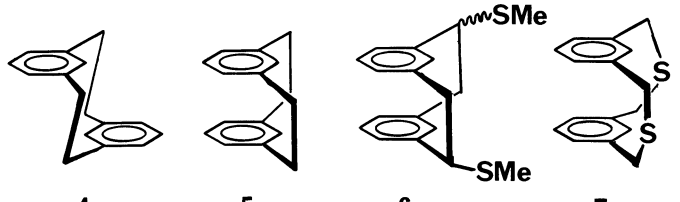
Progress in the chemistry of dihydropyrenes has been closely related to that of metacyclophanes since 1965, when Boekelheide (ref. 1) showed that the trans-dimethyldihydropyrene 1 was in photo-equillibrium with its valence isomer, the anti-cyclophane diene 2.



1 2 3

The facile conversion of 2 to 1 is of considerable importance since,in general,syntheses of 2 are much more readily conceived than are those for 1. The discovery of the thiacyclophane route (ref. 2) to 2 in 1969 for example, made available many examples (ref. 3) of 1 and 2 for study. During the next decade or so,however, it became apparent that whereas anti-[2,2]metacyclophanes and trans-dihydropyrenes were now reasonably accessible, the corresponding syn- and cis-compounds were not. Since we were interested in synthesising compounds of type 3 as potential organic conductors, which require the syn-cyclophanes as precursors, it became clear that a comprehensive investigation into the synthesis and properties of syn-metacyclophanes was required.

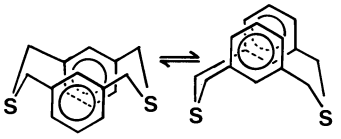
Although anti-[2,2]metacyclophane 4 was probably first prepared by Pellegrin in 1899 (ref. 4), it was rediscovered by Wilson-Baker (ref. 5) in 1950, and was shown by X-ray crystallography (ref. 6) to have the anti stepped like geometry in 1953. This geometry is characterised by the upfield shielding of the internal hydrogen atoms by the opposite aromatic ring to δ 4.17 in its ^{1}H nmr spectrum (ref. 7). No evidence has been found for isomerisation of 4 to 5,however, and until today 5 has remained unknown.



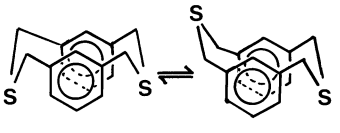
4 5 6 7

RESULTS AND DISCUSSION

In 1969 we thought that we had prepared bridge substituted derivatives of 5, i.e. 6 by Stevens rearrangement of the dithiacyclophane 7 (ref. 2). Attempted desulphurisation of 6 at that time however gave only anti-4. We recently have shown (ref. 8) that 6 was not a syn-isomer but was in fact a mixture of two anti-isomers whose ^{1}H nmr spectrum (100MHz) we mis-interpreted to be that of 6. Separation by HPLC, and 250 MHz spectra have now clarified this point, and thus no syn-[2,2]metacyclophanes with only internal hydrogen substituents are known. At that time the situation was somewhat complicated by the lack of information on the stereochemistry of 7. Indeed it was generally believed (ref. 9) that 7 was probably an anti-cyclophane which was in dynamic equillibrium with the syn-isomer. It was not until 1979 (ref. 10) that we clarified this point and showed that 7 is syn in both the solid state and in solution. It is still not clear however whether 7 is in conformational equilibrium with itself, 7⇌7', or whether the bridges are undergoing a wobble of type A↔B.

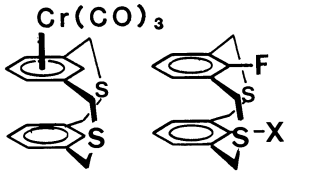


7 7'

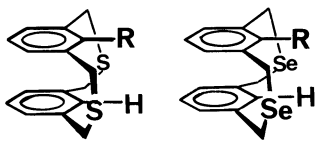


A B

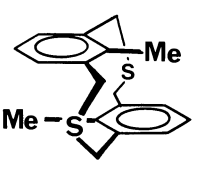
I believe 7↔7' does occur but that the singlet observed for the bridge methylene protons at δ 3.75 is an accidental shift equivalence of the two protons rather than as a result of dynamic exchange between 7 and 7' (which are not actually equivalent because of the locations of the two sulphur atoms). Attachment of a chromium tricarbonyl group as in 8, or substitution of one internal hydrogen by fluorine as in 9, or by other alkyl groups such as R=Me, t-Bu, Ø in 11, leaves one set of bridge methylenes (the internal-H side) a singlet. These are cases where conformational inversion does not occur at room temperature. In fact for 8 the bridge protons appear as two singlets at 90MHz, one set only revealing itself as a closely spaced AB quartet at 250MHz. We have determined that the F/H and F/F phanes 9 and 10 are both syn in solution and the solid state. In both cases the 7⇌7' interconversion does not occur at room temperature, since the clear AB patterns for the bridge methylene protons on the fluorine side of the phane do not collapse to a singlet until above 160°C. The bridge protons on the hydrogen side of the phane in 9 are, as for 7, a singlet, which broadens somewhat at 160°C. Given the similar size of fluorine and hydrogen, it might seem somewhat surprising that 7 is mobile, while 9 and 10 are not, especially since cooling 7, 9 or 10 to -100°C produces almost no change in all signals in the proton spectrum. However, ^{77}Se nmr spectra provide some answers. For 12(R=H), the Se singlet collapses at low temperatures and reappears as two singlets, consistent with freezing out 7 and 7' at low temperature. In the case of 12(R=Me or F) where 7↔7' does not occur, only one Se singlet is found between ambient and -100°C, consistent with no conformational interconversion. For 12(R=H), T_c=-70°C and Δν=2553Hz, and therefore $\Delta G_c^{\neq}$=8.2 kcal/mole, considerably smaller than that found (ref. 9) for 9 or 10 where $\Delta G_c^{\neq}$ = 21 kcal/mole. Whether the bridge wobble occurs in these compounds is not known. When the internal substituent is sufficiently large, i.e. 11(R=t-Bu), the AB for the bridge methylene protons collapses on cooling (T_c=-55°C), and reappears as a new AB at lower temperatures. This may be the first evidence for the bridge wobble A↔B. This is different than for 11(R=Me) where the AB for one set of the bridge methylene protons actually becomes a singlet on cooling to -90°C, probably because of a slight change of



8 9 X=H 10 X=F



11 12



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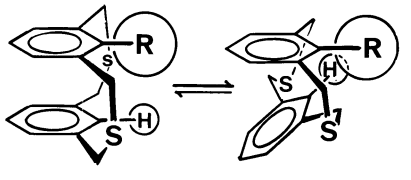
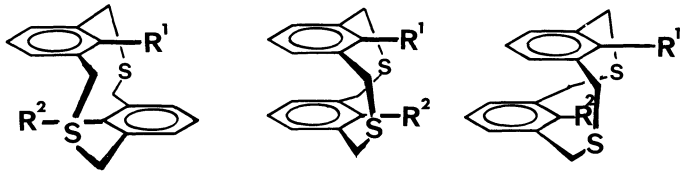


C D

chemical shifts. This is probably caused by a small geometry change of type C↔D, also found (ref. 11) for 11(R=Ø). Care must be exercised,however,that a singlet for the bridge methylene protons in such compounds is not interpreted as evidence for a 7↔7' equilibrium; the bridge protons in anti-13 are also a singlet, a case where conformational ring inversion is certainly not occurring!

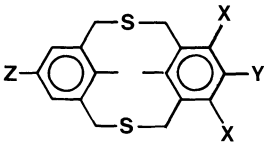
Because of the above work, it is now clear that when only one internal substituent R is present in 12, the syn-cyclophane is the preferred conformer. It is interesting that in all of these cases an internal substituent other than hydrogen breaks the chemical shift degeneracy of the bridge methylene protons. When two similar alkyl or aryl substituents are present, the anti-cyclophane is normally formed in greatest yield. Thus the ratio observed in the preparation of 14 and 15 is 7:1 for R^1=R^2=Me, 10:1 for R^1=R^2=Ø, and >10:1 for R^1=R^2=t-Bu. If different groups are present the ratio does not appear to be as predictable; when R^1=Me and R^2=Ø it is 4:1 (anti:syn) whereas for R^1=Me and R^2=t-Bu it is 1:2. The X-ray data we have obtained so far suggest that the rings can slide over each



14 **15** **E**

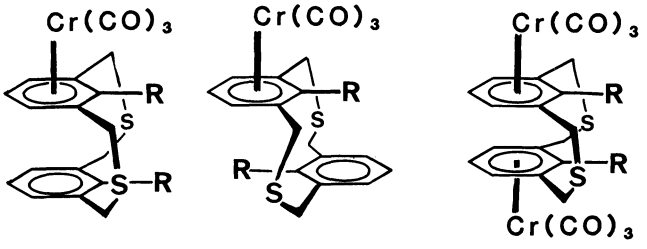
other in the latter case, as in E, to reduce the interaction between the two substituents, making it more favourable relative to the anti-isomer in which the t-butyl group must be severely compressed into the opposite benzene ring. In all of the above cases, the chemical shift of the R substituent in 14 is shielded relative to that in 15 and thus assignment of stereochemistry is unambiguous (ref. 12,13).

Whilst the dithiacyclophanes discussed above can all be ring contracted to [2,2]meta-cyclophanes using Wittig or Steven type rearrangements, nearly always isomerisation of syn-cyclophane occurs, such that mostly anti-product is formed. In those cases, e.g. 15(R=Me) where contraction does lead to syn-[2,2]phane, thus far all attempts at removal of the bridge substituents, have led entirely to anti-phane as product (see for example ref. 2). Thus even substituted syn-analogues of 2 and hence 1 have proved extremely inaccessible. One route that looked promising was based on observations made by Boekelheide (ref. 14), Vogtle (ref. 15) and ourselves (ref. 16) that when 14/15 bear electron withdrawing groups on one of the rings, the syn/anti ratio is increased:



X	Y	Z	SYN/ANTI RATIO
H	H	H	1:7
H	NO_2	H	1:1
Br	Me	H	1.3:1
Cl,H	Cl	H	1.8:1
Br	Me	OMe	2.5:1
CN	Me	OMe	10:1

Unfortunately removal of these substituents later in the synthetic sequence to give the parent cyclophanes or dihydropyrenes proceeded only poorly (ref. 14,16), and so the advantage gained from the increased syn/anti ratio was lost. We thus decided to investigate whether a chromium tricarbonyl group attached to the arene ring would in the stabilise the syn-cyclophane preferentially to the anti-phane, and yet be easily removed at the end of the sequence. We anticipated that the electron removal from the aryl ring by the chromium would be better accommodated in the syn-phane, since some charge transfer could occur 16, clearly not possible in the anti-phane 17. An alternative interpretation leading to the same result is that electron density between the two rings of 16 is reduced by the chromium, reducing the repulsion between the rings, and hence increasing the stability of 16 relative to 17.



16 **17** **18**

No arene-chromium(tricarbonyl) derivatives of simple dithiacyclophanes were known at the start of this work; Fortunately, our first experiment was tried on the unsubstituted dithiacyclophane 7. This readily reacts with 1.2 equivalents of $Cr(CO)_6$ in refluxing n-butyl ether for 4 hours and gives a 70% yield of mono-adduct 16(R=H) together with unchanged starting material. It is easier to stop the reaction at this point, than to separate the mono from the bis-adduct, which is formed with longer reaction times. Indeed reaction of 7 with 6 equivalents of $Cr(CO)_6$ yielded 60-70% of 18(R=H). Surprisingly similar reaction of the anti-methyl substituted phane 14(R=Me) fails, whereas the syn-phane 15(R=Me) proceeds readily to give 70% of 16(R=Me)! At first sight this might seem to support our hypothesis that the syn-complexed phanes should be stabilised better than the anti-ones, however, anti-[2,2]metacyclophane itself is readily complexed by $Cr(CO)_6$ (ref. 17). anti-14 could be complexed in 20% yield however using the more reactive $Cr(CO)_3(CH_3CN)_3$. The ^1H nmr spectra of these compounds are shown in Figures 1 and 2. The comparison of 16(R=Me) with 17(R=Me) is instructive: In the syn-phane 16 the aryl protons of the un-coordinated deck are shielded (δ 6.88-7.01) with respect to those of the anti-phane 17, δ 7.01-7.40, as are those of the complexed deck, δ 4.82 relative to δ 5.52. In the un-complexed phanes, the internal methyl protons of anti-14 occur at δ 1.30 while those of syn-15 are at δ 2.54. Complexation has very little effect on the syn-phane 16 (δ 2.50, 2.60), but a very large effect on the anti-phane 17 (δ 1.10, 1.80). Clearly the shielding of the methyl group on the uncomplexed ring is only about 50% of the other one, indicating the dramatic reduction of ring current in the complexed ring (see also ref. 18). As might be expected, addition of the second chromium(tricarbonyl) moiety to 16(R=H or Me) to give 18(R=H or Me) reduces the mutual shielding of each aryl ring. In the absence of an anti- cyclophane for comparison, the internal hydrogen chemical shifts for 16(R=H) of δ 7.23 and 4.83 might be hard to assign unambiguously, and therefore we confirmed the syn nature of this by an X-ray structure determination.

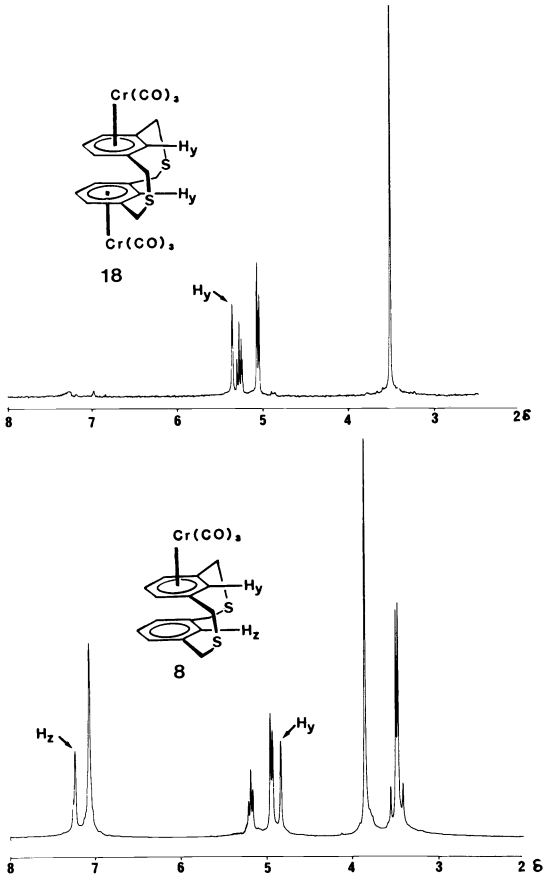


Figure 1: ^1H nmr spectra (250MHz) of 8 and 18(R=H)

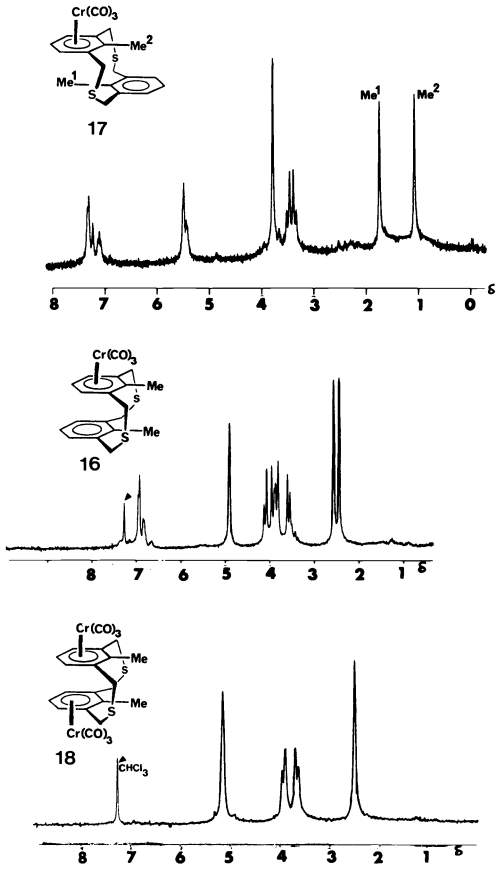
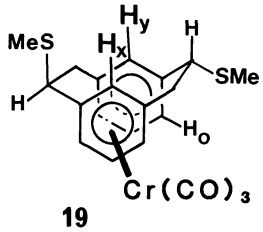


Figure 2: ^1H nmr spectra (250MHz) of 16, 17 and 18 (R=Me).

Conversion of 7 to 6 cannot be achieved using any of the tried (ref. 3) ring contraction methods, **entirely** anti-[2,2]cyclophane being produced. Methylation of 16(R=H) with $(CH_3O)_2CHBF_4$ followed by Stevens rearrangement (ref. 2) gave 70% of 19 as an exclusive isomer, mp 120-121°C. This compound is thus the first authentic syn-[2,2]metacyclophane with internal hydrogen atoms. Its structure was also confirmed by an X-ray structure determination.

The ^{1}H nmr spectrum of 19 and 20 are shown in Figure 3. Note the aryl protons occur below δ 7 (un-complexed deck) and below δ 5 (complexed deck). In the corresponding anti-phane which is formed completely when 19 is heated at 80°C for 1 hour, the two sets of protons are above δ 7 and δ 5 respectively. The internal hydrogens of syn-19 are at δ 6.93 and 5.51 while those of the anti-20 are shielded at δ 5.91 and 3.43 for the uncomplexed and complexed decks respectively. The -SMe groups of 19 are uniquely assigned as axial (complexed ring) and equatorial (un-complexed ring) by the deshielding of the ortho-aryl proton of the latter. As well, H_x is deshielded to δ 5.51 from about δ 5 by the axial-SMe while H_y is normal. In 20 both -SMe groups are axial, and thus in isomerisation of 19→20 only the uncomplexed ring flips. Decomplexation of 20 gives the known 21 which can be reconverted to 20 with $Cr(CO)_6$.



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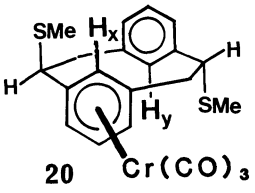

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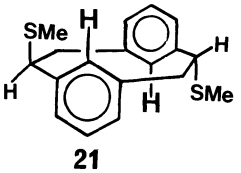

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Careful decomplexation of 19 with Ce^{IV} in CH_3CN at -35°C, followed by isolation and chromatography of the product also at low temperature, yielded 22 . This cleanly isomerised to the anti-phane 23 when allowed to warm above 0°C. In this case the other

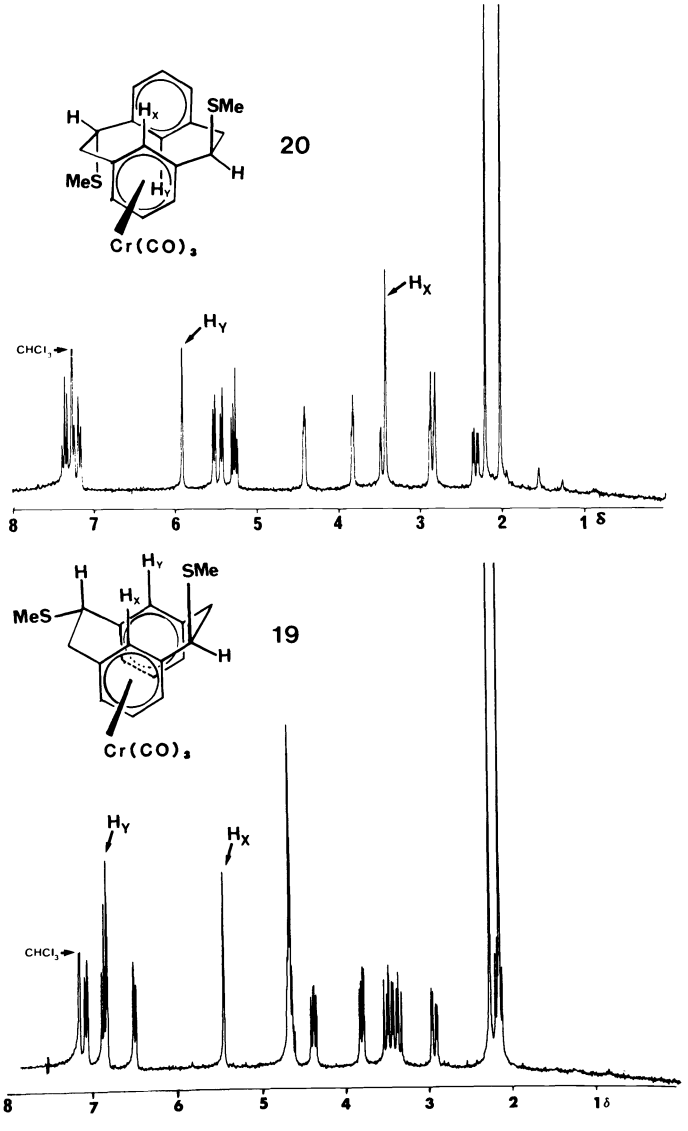
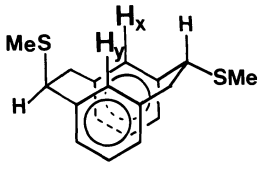


Figure 3: ^{1}H nmr spectra (250MHz) of 19 and 20.

ring flipped (i.e. the one on the axial-SMe side) such that the product 23 was the di-equatorial isomer. The ^{1}H nmr spectra of 22 and 23 are shown in Figure 4. (A small amount of 23 can be seen in the spectrum of 22). Of note are the internal hydrogens of syn-22 at δ 6.75 and 7.04(deshielded by axial -SMe), and the shielded co-facial ring protons at δ 6.37-7.04, whereas in the anti-phane 23 these are shielded at δ 4.31 and not shielded at δ 7.17-7.64 respectively.



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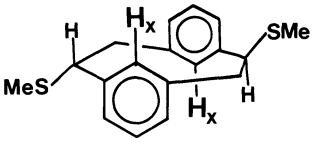

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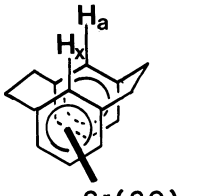
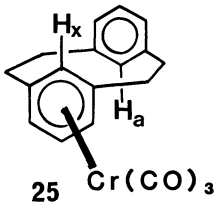


24

Removal of the -SMe groups from 19 or 22 did not yield any 5 or 24, rather 4 or 25 was obtained, even when using Li/NH_3 at -40°C. Isomerisation of 5 to 4 (or at least of an intermediate in the reduction) was evidently rather easy!

In order to inhibit this isomerisation, we next decided to investigate the bis-complex 18, which would not be expected to ring flip at all easily, since the two chromium(tricarbonyl) groups would have to be sandwiched inside the phane. Thus Stevens rearrangement of methylated 18 as above gave 40% of the syn-bis-complexed product 26. Direct reduction of this with Li/NH_3 at -40°C gave a mixture of the two syn-cyclophanes 24 and 27. Heating 24 above room temperature isomerises it cleanly to the known anti-cyclophane 25, providing a convenient proof of structure. The ^{1}H nmr spectra of 24 and 25 are shown in Figure 5.



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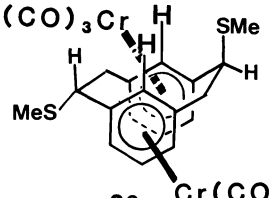

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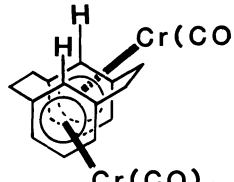

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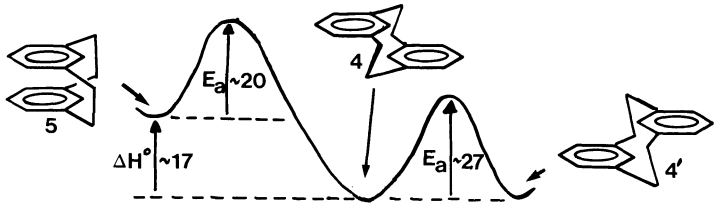
The difference between the syn and anti phanes is quite dramatic: the complexed deck protons of syn-24 are below δ 5 while those of anti-25 are above δ 5, similarly for the uncomplexed deck below δ 7 and above δ 7 respectively. The internal hydrogens of syn-24 at δ 4.8(H_x) and 6.9(H_a) are very much less shielded than those of anti-25, δ 2.4(H_x) and 5.5(H_a). The bis-complexed syn-27 shows internal hydrogens at δ 5.09 and external complexed deck protons at δ 5.10 and 4.75.

Removal of the chromium(tricarbonyl) moiety from 24 or 27 with m-chloroperbenzoic acid or Ce^{IV} at -45°C in CH_3CN yielded the parent syn-[2,2]metacyclophane 5. Careful low temperature isolation and chromatography of 5 was required since at temperatures above 0°C isomerisation to 4 was rapid. The ^{1}H nmr spectrum of syn-5 at -40°C is shown together with that for anti-4 in Figure 6. The internal hydrogens appear at δ 6.6, together with the b type external hydrogens, while the a type are at δ 6.36. The latter are identical to those of [2,2]paracyclophane, δ 6.37 (ref. 19), and are shielded from those of anti-4 by the co-facial ring.

We have studied the rates of isomerisation of the syn-phanes to the anti-phanes using nmr. The results were obtained by integrating selected peaks in the spectra at various times for runs conducted at different temperatures:

	COMPOUND	$\Delta H^{\neq}$ [kcal/mole]	$\Delta S^{\neq}$ [cal/K/mole]	$\Delta G^{\neq}_{298}$ [kcal/mole]	E_a [kcal/mole]
	19	22.3	-6	24.1	21.7
	22	19.5	-6	21.3	18.9
Ref. 20:	4	27.5	-10	30.5	27.5

Clearly isomerisation of syn-[2,2]metacyclophane is a considerably easier process than the anti→anti change 4⇌4'. This is drawn schematically below:



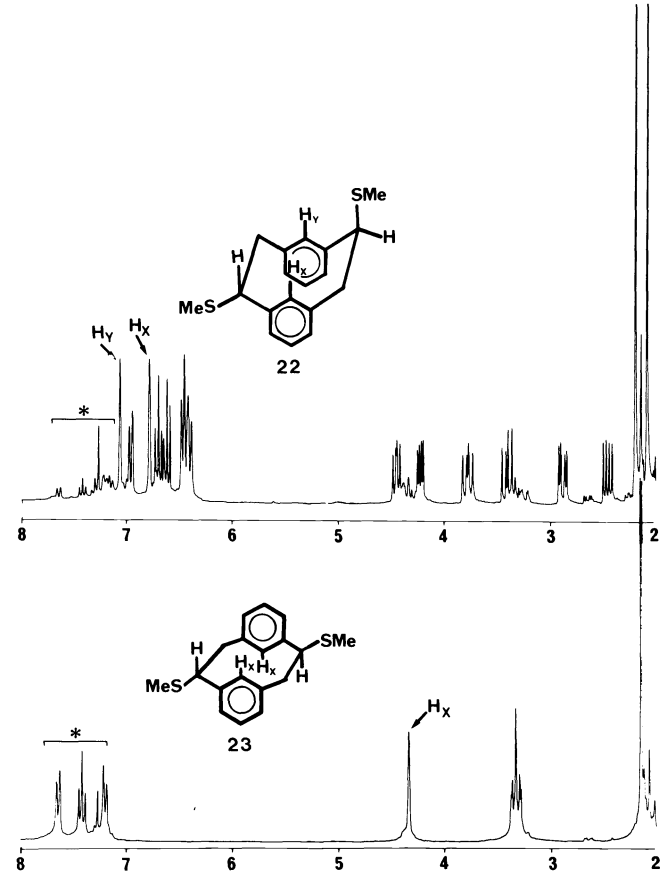


Figure 4: ^{1}H nmr spectra (250MHz) of 22 and 23.

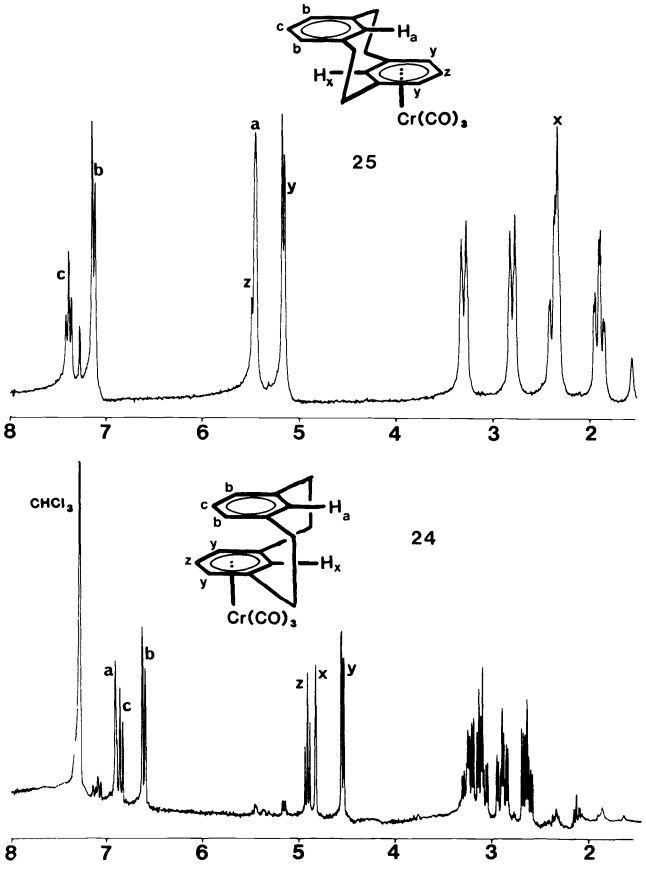


Figure 5: ^{1}H nmr spectra (250MHz) of 24 and 25.

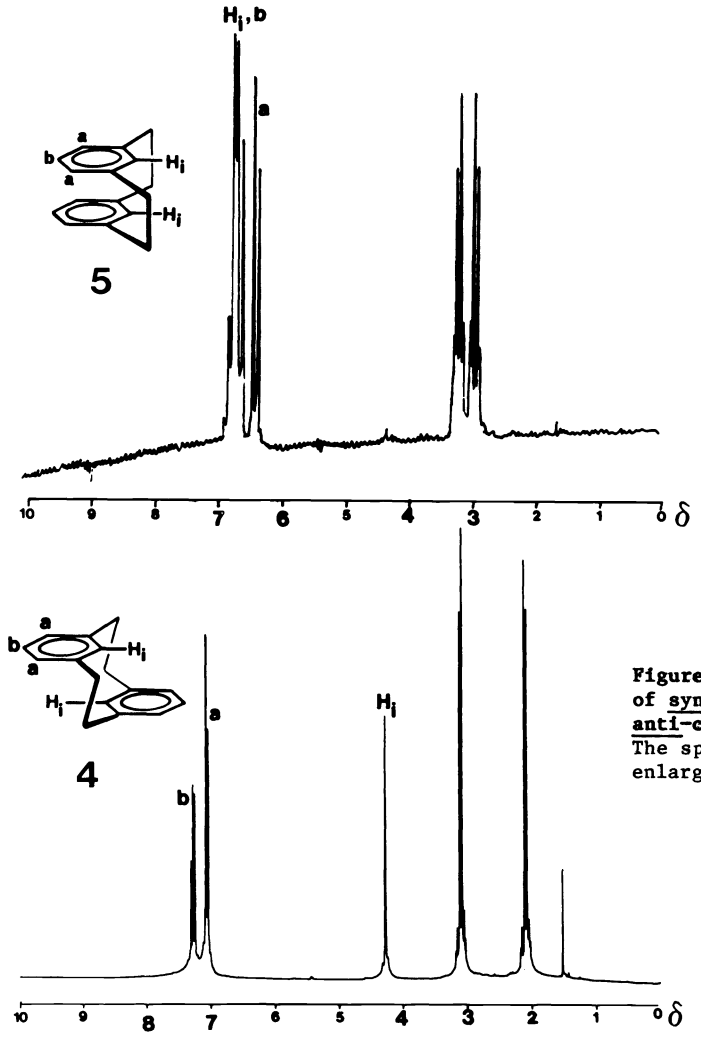


Figure 6: ^{1}H nmr spectra (250 MHz) of syn-cyclophane 5 at -40°C and anti-cyclophane 4 at 25°C. The spectrum for 5 has been hand enlarged to the same scale as 4.

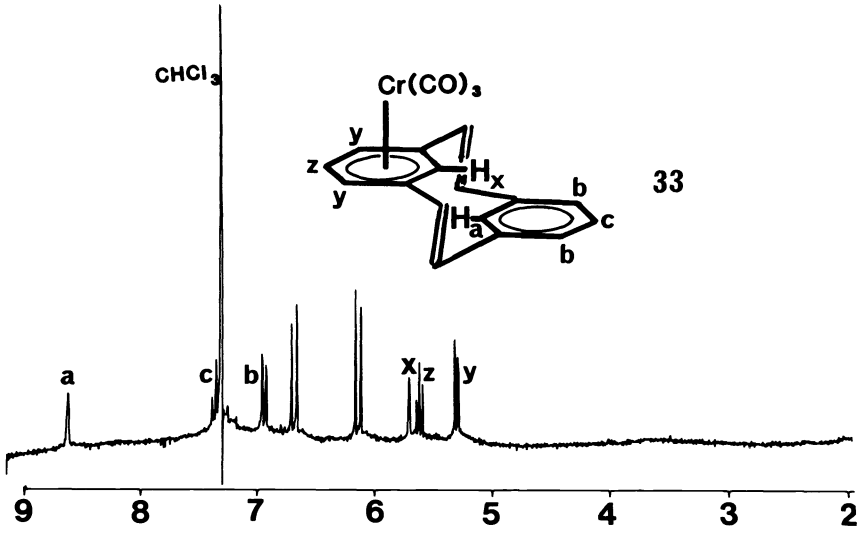
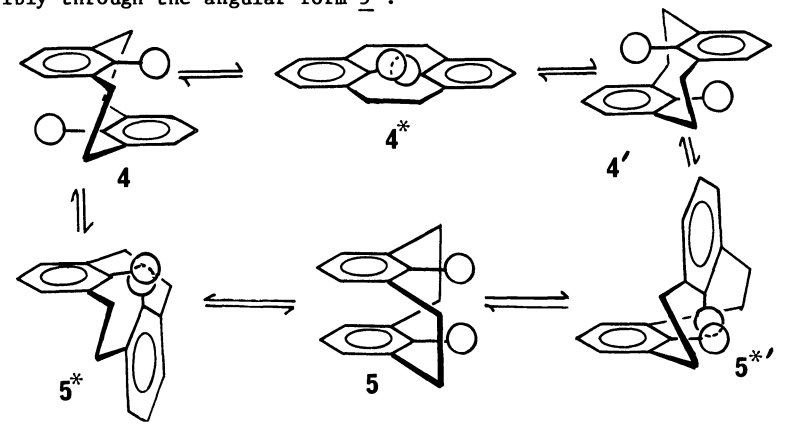


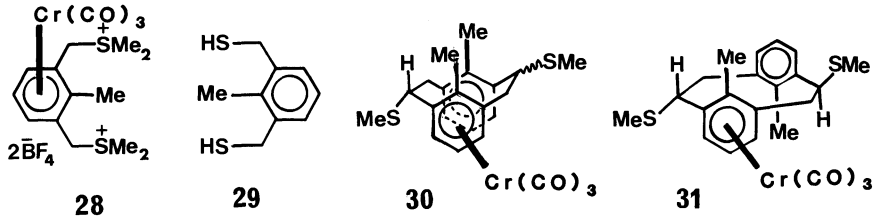
Figure 7: ^{1}H nmr spectrum (250 MHz) of cyclophane diene 33.

The estimate for $\Delta H°$ for 5→4 is made by approximating this to the difference between 4 and [2,2]paracyclophane (ref. 21). This suggests that the two processes probably are different: for 4→4' either the molecule must pass through a planar conformation (4*) or through the syn-conformer 5, which given the probable value of $\Delta H°$ shown above seems somewhat unlikely. syn-5 appears to be able to get to anti-4 with a lower activation barrier, possibly through the angular form 5*:



Thus use of a chromium(tricarbonyl) group complexed to an aromatic ring has achieved our objective of being able to stabilise the syn-phanes with a group that is easily removable.

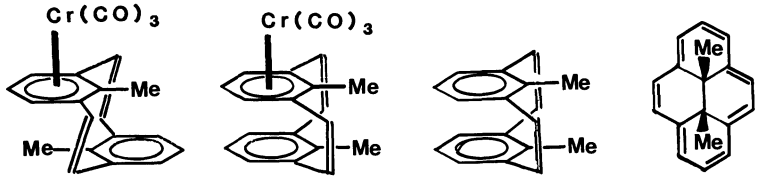
In order to put this to use in the methyl substituted phanes, we have attempted a controlled synthesis of the thiacyclophane itself. Thus cyclisation of the complexed salt 28 with the dithiol 29 yielded a 4:1 mixture of syn-16(R=Me)/anti-17(R=Me), a considerable improvement in syn/anti ratio to that obtained (1:7) using uncomplexed reactants. However, the poor yield of 8% obtained so far negates the gain in syn-isomer achieved over complexing the preformed thiacyclophanes. We have varied the leaving group ($-SMe_2$) in 28 without much success. Unfortunately -Br and -SH cannot be substituted in 28 for $-SMe_2$, since the compounds are then very unstable.



28 29 30 31

Attachment of a chromium(tricarbonyl) to a cyclophane has a further use, namely enabling study of the metacyclophane dienes: methylation and Stevens rearrangement (as above) of both 16 and 17 proceed without isomerisation to give syn-30 and anti-31 respectively, though the latter is more easily prepared by complexing the [2,2]phane. Hofmann elimination of anti-31 (ref. 2) gave the complexed anti-diene 32. Unlike 2, which spontaneously converts to the dihydropyrene 1, 32 is stable to above 130°C and will provide us an opportunity to study the chemistry of the diene bridges. The corresponding anti-diene 33 was similarly obtained from 20, and is also stable to 130°C. Its ^1H nmr spectrum is shown in Figure 7.

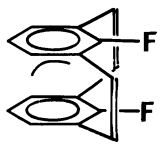
The substantial deshielding of H_a to δ 8.49 is of interest, as is the deshielding of H_x to 5.69. In comparison, in the saturated-bridge anti-phane 25 those protons are at δ 5.45 and 2.33 respectively, both some 3 ppm at higher field. This is a value similar to that found for comparison of 4 with 2(R=H) (ref. 12), and probably mainly reflects the dramatic change in ring current shielding as the geometry of the molecule changes, 25 being more stepped than 33 (4 more than 2).



32 34 35 36

We are also optimistic that syn-30 will likewise give the syn-diene 34, particularly since its uncomplexed form, 35 is unknown (it immediately valence isomerises into the syn-dimethyldihydropyrene 36 (ref. 2)).

In support of this we have very recently found that complexation of the difluoro compound 10(X=F), followed by the Stevens rearrangement/Hofmann elimination sequence in a similar manner to above has allowed synthesis of the unknown syn-difluoro-diene 37. In its ^{1}H nmr spectrum 37 shows the aromatic protons at δ 6.35-6.45 and the olefinic protons at δ 6.96, the reverse of those of the anti-diene 38, in which the aromatic protons are at δ 6.9-7.1 and the olefinic protons at δ 6.39. The co-facial shielding of the aryl protons in syn-37 is thus very evident. Moreover, the syn-diene 37, unlike its anti-isomer (ref. 22), does valence isomerise to the syn-difluorodihydropyrene 39, the first example of a dihydropyrene with internal halogen substituents. It is a deep green compound, similar to 1, and its ^{1}H nmr spectrum shows aromatic protons at δ 7.5-8.2.



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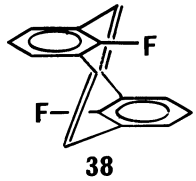

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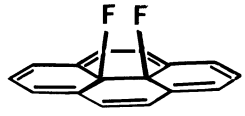

39

From the examples mentioned above, it is quite clear that attachment of a chromium-tricarbonyl to a cyclophane ring will considerably extend the knowledge and chemistry of these fascinating molecules.

ACKNOWLEDGEMENT

I am indebted to the skill of my many co-workers who have contributed to our groups chemistry over the years and made this talk possible. Those that have been most deeply involved with this project are listed as co-authors. I also wish to thank the University of Victoria and the Natural Sciences and Engineering Research Council of Canada for financial support.

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