THE USE OF CIRCULAR DICHROISM FOR THE DETERMINATION
OF THE ABSOLUTE CONFIGURATION OF CHIRAL
BUTADIENE-TRICARBONYL IRON COMPLEXES

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Abstract - The circular dichroism spectra of functionalized butadiene-tricarbonyliron complexes can be used to predict the absolute configuration of these organometallic derivatives.

The use of chiral butadiene-tricarbonyl iron complexes for the synthesis of optically active compounds has developped a great deal during the last few years [1]. One of the key advantages of these complexes is that the strong stereo-inducing effect of the $Fe (CO)_3$ moiety allows, in most cases, the prediction of the absolute configuration of the newly created stereogenic centers, *provided that the absolute configuration of the starting complex has been unambiguously established.* For these butadiene-tricarbonyl iron complexes it has been suggested, by analogy with other transition metal derivatives, that the sign of the circular dichroism (c.d.) maximum at long wavelenghts attributable to d-d transitions should be related to their absolute configuration [2] [3]. The purpose of this letter is to report that this empirical rule can be useful in the prediction of absolute configuration of complexes having a general formula 1.

$$R^1 - \underset{\substack{Fe \\ (CO)_3}}{\overset{2 \quad 5}{\diagdown / }} - R^2 \qquad 1$$
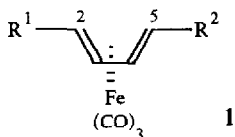
R¹ , R² see table

For such a study it is necessary to start with a compound whose structure has been unambiguously established, for instance, by x-ray analysis as in the case of complex 1a [4] (fig. 1) which is the first diastereoisomer obtained by fractional crystallisation during the resolution of (±) 1b by reaction with (-)

Ephedrine (of known 1R,2S absolute configuration). As shown on fig. 1, it has a 2S, 5R absolute

Fig. 1
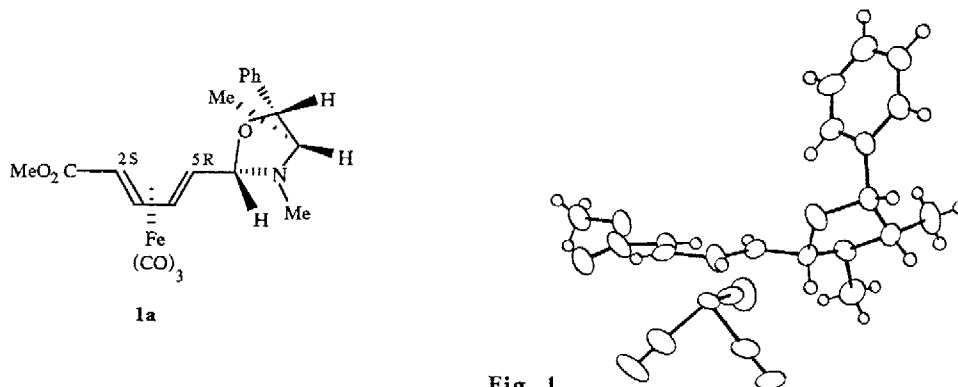
configuration. The hydrolysis of the oxazolidine leads without racemization to the aldehyde **1b**. <u>All</u> the other complexes (see table) have been prepared starting from this key intermediate [5] [6]. The results of the c.d. spectra are given in the table. Several points are worth noting :

1 - The presence of a chromophore directly linked to the complex is necessary to obtain a characteristic spectrum. All the derivatives without a carbonyl group (**1k**, **1l** and **1n** for instance) show no intense and significant band in the c.d. spectrum.

2 - For the complexes bearing only one chromophore *the circular dichroism spectrum appears characteristic of the absolute configuration of the carbon atom bearing this group*. All the complexes with a carbonyl function on the 2S carbon exhibit a strong negative band at long wavelength (around 400 nm) (compounds : **1a**, **1c**, **1d**, **1e**, **1f**, **1g**). Those having the carbonyl group on the 5R carbon [7] (see **1i**, **1j**, **1o**, **1p**) have a positive band at this position. Furthermore, although there are small shifts in the position of the maxima and variations in the intensity of the bands, this result is independent of the exact nature (ester, ketone or aldehyde) of the carbonyl group. The presence of other asymmetric centers (in the case of **1a**, **1d** or **1e** for instance) does not influence significantly the shape of the spectra and strong negative bands around 400 nm are obtained in each case.
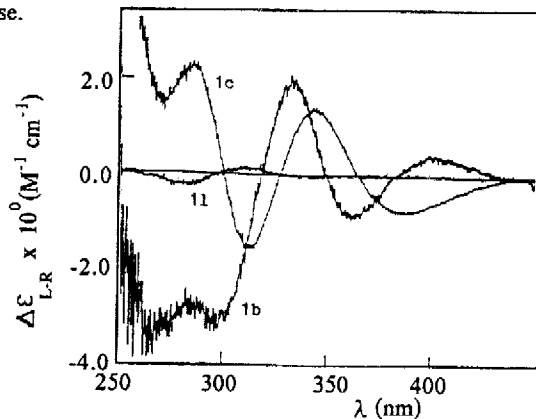
The strong similarity between the c.d. spectrum of the methyl sorbate complex **1r** [2] [8] and compounds **1a** to **1g** allows the indicated absolute configuration to be assigned to the dextrorotatory enantiomer which is obtained by direct resolution of the corresponding acid [2] [8].

Table - Summary of the c.d. spectra [a] and specific rotations [b] of complexes 1.

N°	R^1	R^2	λ_1 ($\Delta\varepsilon_1$)	λ_2 ($\Delta\varepsilon_2$)	λ_3 ($\Delta\varepsilon_3$)	λ_4 ($\Delta\varepsilon_4$)	$[\alpha]_D^{25}$
1a	MeO_2C-	- Oxazol.	387(-0.94)	339(1.84)	311(-0.25)	286(2.39)	+100(0.07)
1c	MeO_2C-	- $CH(OMe)_2$	386(-0.76)	342(1.92)	312(-1.56)	284(2.29)	+165(0.10)
1d	MeO_2C-	- CH(OH)Me 6R	384(-1.21)	339(1.65)	308(-0.87)	282(2.67)	+210(0.11)
1e	MeO_2C-	- CH(OH)Me 6S	385(-1.7)	339(2.90)	311(-1.45)	283(2.65)	+234(0.09)
1f	MeO_2C-	- CH_2OH	388(-0.52)	341(1.99)	310(-1.48)	281(2.34)	+193(0.10)
1g	MeO_2C-	- CH_2OMe	387(-0.73)	341(1.41)	309(-1.23)	282(2.00)	+179(0.29)
1i	HOH_2C-	- CHO	396(1.17)	353(-1.84)	322(1.68)	286(-3.80)	-105(0.10)
1j [c]	ROH_2C-	- CHO	397(1.32)	352(-2.89)	323(0.48)	288(-4.22)	- 79(0.12)
1m	OHC-	- CH_2OMe	400(-1.00)	354(+1.00)	325(-1.00)	284(2.56)	+ 78(0.14)
1o [c]	ROH_2C-	- COMe	391(1.82)	334(-5.97)		296(-5.08)	-193(0.10)
1p	HOH_2C-	- COMe	392(1.57)	335(-4.83)		291(-4.57)	-308(0.11)
1r	MeO_2C-	- CH_3	388(-1.54)	338(2.25)		285(3.04)	+205(0.10)
1l	HOH_2C-	- CH_2OMe			312(0.12)	282(-0.22)	-4 (0.45)
1k [c]	ROH_2C-	- CH(OH)Me 6R	364(-0.14)		301(-0.28)		-9.4(0.34)
1n [c]	ROH_2C-	- CH(OH)Me 6S	364(0.11)		310(-0.65)		+10.1(0.29)
1b	MeO_2C-	- CHO	398(0.47)	360(-0.89)	331(2.04)	296(-3.27)	+ 62(0.10)
1h	MeO_2C-	- COMe	396(0.64)	333(-2.61)	305(-2.71)		-120(0.12)
1q	OHC-	- COMe	379(0.50)	332(-4,34)		287(-1.05)	- 209(0.06)

[a] C.D. : solvent : methanol ; λ nm ; $\Delta\varepsilon_{L\text{-}R}$ (M^{-1} cm^{-1}).

[b] Specific rotation $[\alpha]^{25}_D°$ (concentration in g/100 cm^3 of methanol).

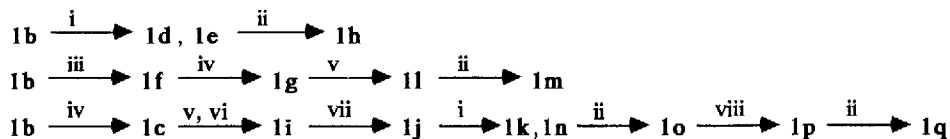[c] **1j** ; **1o** ; **1k** ; **1n** : R = $tBuPh_2Si$-.

Finally, it is interesting to point out that recent examples indicate that this rule also holds for complexes substituted in the 2-position [3].

3 - The situation is more complicated in the case of the complexes bearing one carbonyl function on the R carbon atom and another on the S atom. The three possible derivatives (**1b**, **1h** and **1q**) have been prepared and large changes in the position and intensity of the bands have been observed. However, the results obtained can be accommodated within the preceeding rule if the following preference order is accepted : ketone > aldehyde > ester.

In conclusion, for these acyclic [9] butadiene-tricarbonyl iron complexes bearing functionnal groups there is a clear correlation between the c.d. spectrum (notably the sign of the vague at long wavelength) and the absolute configuration of the carbon atom of the complex bearing the carbonyl substituent. Although empirical, this simple rule can be useful in predicting the absolute configuration of many complexes and designing strategies for the synthesis of chiral molecules starting from these derivatives.

References and notes.

1 - Grée R., Synthesis (in print) and ref. therein.

2 - Musco A., Palumbo R., Paiaro G., Inorg. Chim. Acta, 1971, 5, 157.

3 - For a very recent example see : Alcock N.W., Crent D.H.G., Henderson C.M., Thomas S.E., J. Chem. Soc. Chem. Commun., 1988, 746.

4 - Monpert A., Martelli J., Grée R., Carrié R., Tetrahedron Lett., 1981, 22, 1961.

5 - All these complexes have physical data in full agreement with their structures ; the details of their preparation will be reported in a full paper. An overview of the syntheses is given below :

$$\textbf{1b} \xrightarrow{\text{i}} \textbf{1d, 1e} \xrightarrow{\text{ii}} \textbf{1h}$$

$$\textbf{1b} \xrightarrow{\text{iii}} \textbf{1f} \xrightarrow{\text{iv}} \textbf{1g} \xrightarrow{\text{v}} \textbf{1l} \xrightarrow{\text{ii}} \textbf{1m}$$

$$\textbf{1b} \xrightarrow{\text{iv}} \textbf{1c} \xrightarrow{\text{v, vi}} \textbf{1i} \xrightarrow{\text{vii}} \textbf{1j} \xrightarrow{\text{i}} \textbf{1k, 1n} \xrightarrow{\text{ii}} \textbf{1o} \xrightarrow{\text{viii}} \textbf{1p} \xrightarrow{\text{ii}} \textbf{1q}$$

i) CH$_3$MgI, THF, - 40°C ; ii) PDC, 4 Å Mol. Sieves, - 40° to - 20°C ; iii) KBH$_4$, MeOH, 0°C ; iv) HC(OMe)$_3$, MeOH, TsOH, RT ; v) Dibal, - 50°C ; vi) SiO$_2$, H$^+$; vii) (tBu)Ph$_2$SiCl, Im, RT ; viii) nBu$_4$N$^+$F$^-$.

6 - For many of these complexes the corresponding enantiomers have also been prepared. As expected, symmetrical c.d. curves are obtained in those cases.

7 - The numbers 2 and 5 of the carbon atoms in the complex **1a** have been kept for consistency in all the derivatives.

8 - Jaenicke O., Kerber R.C., Kirsch P., Koerner Von Gustorf E.A., Rumin R., J. Organomet. Chem., 1980, 187, 361 ; de Montarby L., Mosset P., Grée R., Tetrahedron Lett., 1988, 29, 3937.

9 - Several studies have recently dealt with troponoid derivatives : Sotokawa H., Tajiri A., Morita N., Kabuto C., Tasoa, Tetrahedron Lett., 1987, 28, 5873 and 6465 ; bismethylene exocyclic derivatives have also been extensively studied : Gabioud R., Vogel P., Pinkerton A.A., Helv. Chim. Acta, 1986, 69, 271 ; Gabioud R., Vogel P., Helv. Chim. Acta, 1986, 69, 865 and ref. therein.

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