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CONFORMATIONAL STUDIES OF TRANSITION METAL CARBONYL COMPLEXES OF 1,5-DITHIACYCLOOCTANE (1,5-DTCO) AND CRYSTAL STRUCTURE OF [ReCl(CO)$_3$(1,5-DTCO)]

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Abstract—A new synthesis of the mesocyclic ligand 1,5-dithiacyclooctane (1,5-DTCO) is reported. Complexes of type [{W(CO)$_5$}$_n$(1,5-DTCO)] (n = 1,2) were isolated and their conformational and exchange dynamics in solution examined by NMR. The complex [W(CO)$_4$(1,5-DTCO)], where the ligand acts as a bidentate chelate, undergoes facile boat–chair $\rightleftharpoons$ chair–boat ring conformational exchange, NMR bandshape analysis of the motion yielding an activation energy, $\Delta G^{\ddagger}$ (298.15 K), of 25.1 ± 0.2 kJ mol^{-1}. The complexes [ReX(CO)$_3$(1,5-DTCO)] (X = Cl, Br) were isolated. An X-ray crystal structure of the X = Cl complex showed that the ligand adopts a boat–chair conformation, with a trans-annular S$\cdots$S contact distance of 3.277 Å. This ring conformation is retained in solution.

1,5-Dithiacyclooctane (1,5-DTCO) was first synthesized in 1934, in low yield, by Meadow and Reid.[1] The compound, in both its neutral and cationic forms, has a substantial coordination chemistry, in which it can adopt monodentate, bidentate or bridging ligand bonding modes. Examples have been reported of complexes with tin(IV),[2] iron(II),[3] nickel(II),[3,4] copper(II),[5,6] ruthenium(II)[7] and platinum(II).[8] The structures of many of these complexes have been deduced by X-ray crystallography. Three different ring conformations, namely boat–chair (BC), chair–chair (CC) and boat–boat (BB), exist in this selection of complexes. Where there are no severe steric constraints imposed by the metal moiety or other groups, the BC conformation is favoured, as it is for cyclooctane[9,10] and 1,5-DTCO itself.[11] In contrast, the BB conformation is favoured in the case of *trans*-[RuCl$_2$(1,5-DTCO)][7] to minimize interactions of the rings with the *trans* chlorides. In the case of the free ligand, 1,5-DTCO, there has been much interest in the unusually strong sulphur–sulphur lone pair interaction.[12] This causes a large splitting in the photoelectron spectrum of the ligand which suggests that the transannular sulphur atoms are much closer, namely 3.2–3.3 Å, than their van der Waals contact distance (3.70 Å).

There have been relatively few detailed studies of the solution dynamics of derivatives and metal complexes of 1,5-DTCO using NMR spectroscopy. This is probably a consequence of the limited solubility of many such species in suitable NMR solvents and the complex nature of many of their ^{1}H spectra. However, some ^{1}H NMR data have been reported for [Pt(PPh$_3$)$_2$(1,5-DTCO)](BF$_4$)$_2$[8] and ^{13}C

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data for ruthenium(II) complexes of 1,5-DTCO and 1,5-DTCO-1-oxide.[7] Unfortunately, the latter studies were complicated by partial dissociation of the complexes to new species. Our interest in 1,5-DTCO stems from our search for potentially fluxional transition metal complexes of sulphur ligands.[13] We have established the existence of 1,2-, 1,3- and, possibly, 1,5-metallotropic shifts in complexes of general type $[W(CO)_5L]$, where L are either thioethers of types RSSR,[14] $RSCH_2SR$,[15] $RSCH_2SR'$,[16] (R, R′ being alkyl groups), or cyclic thioligands such as $\overline{SCH_2SCH_2SCH_2}$[17,18] and $\overline{SCH_2SCH_2SCH_2SCH_2}$.[19] In view of the circumstantial evidence for a strong transannular S···S interaction in 1,5-DTCO (see above) it would seem likely that the complex $[W(CO)_5(1,5\text{-DTCO})]$ might exhibit a 1,5-metallotropic shift of the $W(CO)_5$ moiety. This complex was therefore synthesized together with the complex $[\{W(CO)_5\}_2(1,5\text{-DTCO})]$, where both sulphur donors are coordinated to the tungsten, and the solution stereodynamics of both complexes investigated by ^1H NMR spectroscopy. The role of 1,5-DTCO as a bidentate chelate ligand was also explored in the complexes $[W(CO)_4(1,5\text{-DTCO})]$ and $[ReX(CO)_3(1,5\text{-DTCO})]$ (X = Cl, Br).

This paper presents the first detailed NMR study of metal carbonyl complexes of 1,5-DTCO, and illustrates the insight that NMR can provide into their stereodynamics. An X-ray crystal structure is reported for $[ReCl(CO)_3(1,5\text{-DTCO})]$ and a comparison made between the solid state and solution structures of this complex.

EXPERIMENTAL

Materials

The mesocyclic ligand 1,5-DTCO was prepared by a new method involving a caesium thiolate intermediate. A mixture of caesium carbonate (24.01 g, 73.7 mmol) and freshly distilled dimethylformamide (DMF) (400 cm^3) was degassed in a 2 dm^3 flask. To this was added dropwise a degassed solution of 1,3-dibromopentane (14.82 g, 73.4 mmol) and 1,3-dithiapentane (7.89 g, 72.9 mmol) in DMF (200 cm^3). After vigorous stirring at 60°C for 48 h, the reaction mixture was filtered and solvent removed under reduced pressure to give an oily material. TLC analysis (silica plates, petroleum spirit–ethyl acetate, 10 : 1) indicated the presence of at least seven distinct cyclization products. Eluting with petroleum spirit on a neutral grade II alumina column (200 × 300 mm) gave the required compound (3.93 g, 26.5 mmol; yield 36%) as a highly viscous, yellow-tinged pungent oil.

Elution with petroleum spirit–ethyl acetate (5 : 1) gave 1,5,9-trithiacyclododecane (0.60 g, 2.7 mmol; 4%) as a white solid. Similar increments in solvent mixture polarity allowed isolation of three larger meso-cyclic compounds in a pure state (NMR spectroscopy).

Syntheses of the tungsten penta- and tetra-carbonyl complexes of 1,5-DTCO were achieved using standard Schlenk techniques[20] via the tetrahydrofuran (THF) precursor $[W(CO)_5(THF)]$ generated by UV radiation of $[W(CO)_6]$ in THF.[21,22] $[\{W(CO)_5\}_2(1,5\text{-DTCO})]$ was prepared by dropwise addition of a THF solution of $[W(CO)_5(THF)]$ to the ligand at −78°C. After stirring for *ca* 8 h at this temperature, the solvent was removed under reduced pressure to give an oily residue. This was washed with warm hexane, the collected washings being filtered and left at −20°C for 24 h. Recrystallization of the residue from dichloromethane–hexane (1 : 3) at −20°C gave crystals of $[\{W(CO)_5\}_2(1,5\text{-DTCO})]$. The yellow solid obtained by cooling the hexane washings was washed with cold hexane to remove free ligand and recrystallized from warm hexane to give yellow microcrystals of $[W(CO)_5(1,5\text{-DTCO})]$. The complex $[W(CO)_4(1,5\text{-DTCO})]$ was prepared by stirring $[W(CO)_5(THF)]$ with the ligand at ambient temperature for 24 h. Solvent was removed under reduced pressure and the residue subjected to chromatography (elution with dichloromethane). Removal of dichloromethane under reduced pressure gave a yellow solid which was vacuum sublimed. Recrystallization from dichloromethane–hexane (1 : 3) at −20°C gave yellow, needle-like crystals of the required complex (39% yield).

The complexes $[ReX(CO)_3(1,5\text{-DTCO})]$ (X = Cl, Br) were prepared by refluxing the ligand with $[ReX(CO)_5]$[23] in THF for several hours, the extent of reaction being monitored by IR spectroscopy.

Physical methods

Elemental analyses were completed by Butterworth Laboratories Ltd, Teddington, Middlesex, London. Uncorrected melting temperatures were recorded on a digital Gallenkamp apparatus. IR spectra were recorded in solution (usually dichloromethane) using matched CaF_2 solution cells on a Perkin–Elmer 881 spectrophotometer. ^1H NMR spectra were recorded at 250 MHz on a Bruker AM250 FT spectrometer in this department or at 400 MHz on a Bruker WH-400 spectrometer (University of Warwick). All chemical shifts are quoted relative to Me_4Si as an internal standard. A B-VT 1000 variable temperature unit was used to control the NMR probe temperature. Spectra were obtained using either $CDCl_3$, CD_2Cl_2 or C_6D_6 as solvents. Theoretical NMR spectra were simulated using the LAOCN3 program,[24] and bandshape analyses using the authors' version of the DNMR3 program.[25]

X-ray crystal structure

Crystals of [ReCl(CO)$_3$(1,5-DTCO)] were prepared from the preparative route above.

Crystal data. $C_9H_{12}O_3S_2ClRe$. $M = 453.98$, orthorhombic, space group $P2_12_12_1$, $a = 8.603(1)$, $b = 12.001(2)$, $c = 12.638(1)$ Å, $U = 1304.81$ Å^3, $Z = 4$, $D_c = 2.311$ g cm^{-3}, $F(000) = 856$, Mo-K_α radiation ($\lambda = 0.71069$ Å), $\mu = 99.43$ cm^{-1}.

Data collection and processing

Data were collected with a CAD4 diffractometer operating in the ω–2θ scan mode with graphite monochromated Mo-K_α radiation. A total of 6445 reflections ($1.5 \leqslant \theta \leqslant 27.0°$) were recorded, 2880 being unique and 2667 with $F_0 > 3\sigma(F_0)$.

Solution and refinement

The structure was solved by standard Patterson methods. Full matrix least squares refinement based on F_0 was performed with non-hydrogen atoms assigned anisotropic thermal parameters. Hydrogen atoms were experimentally located and freely refined with group U_{iso} values. The number of parameters in the least squares scheme was 146. Final R and R_G values were 0.026 and 0.030, respectively. Literature programs[26,27] were used for the solution and refinement of the structure. Full details of crystallographic data collection and structure refinement, atomic coordinates and thermal parameters have been deposited as supplementary material with the Editor.

RESULTS AND DISCUSSION

General

All complexes were isolated as yellow crystalline solids, which were characterized by elemental analysis, melting temperatures and IR spectroscopy (M—CO) stretching region (Table 1). Of the three IR signals [$(A_1)_1$, $(A_1)_2$ and E] predicted for [M(CO)$_5$L] complexes,[28] the strong $(A_1)_2$ and E bands were not resolved for the W(CO)$_5$ complexes in CH_2Cl_2 but were resolved for [W(CO)$_5$(1,5-DTCO)] in hexane at high dilution. Of the four signals [$(A_1)_1$, $(A_1)_2$, B_1 and B_2] expected for *cis*-[M(CO)$_4$(L—L)] complexes,[28] only three were observed for [W(CO)$_4$(1,5-DTCO)] in CH_2Cl_2 due to overlap. Three bands of comparable intensity in the spectra of [ReX(CO)$_3$(1,5-DTCO)] (X = Cl, Br) were consistent with a facial geometry of the metal moiety.[28]

1,5-DTCO *and* [W(CO)$_5$]$_n$ (1,5-DTCO)] (n = 1,2) *complexes*

The solution structures of the compounds were examined by their ambient temperature ^{1}H NMR spectra. The spectra of 1,5-DTCO and [{W(CO)$_5$}$_2$ (1,5-DTCO)] comprised two sets of signals with second-order multiplet splittings. The high frequency set (8H) is due to hydrogens α to the sulphur donors and the other set (4H) is due to the β-ring

Table 1. Synthetic, melting point, IR spectroscopic and analytical data for complexes of 1,5-DTCO

Complex	Yield (%)	M.p. (°C)	M—CO stretching wavenumber[a] (cm^{-1})	Elemental analysis[c] C (%)	H (%)
[W(CO)$_5$(1,5-DTCO)]	42	94.3–94.5	2075(w), 1938(vs)	28.1 (28.0)	2.6 (2.6)
[{W(CO)$_5$}$_2$(1,5-DTCO)]	37	147(d)	2076(w), 1937(vs), 1932(vs),[b] 2076(w), 1938(vs)	24.0 (24.2)	1.4 (1.5)
[W(CO)$_4$(1,5-DTCO)]	39	185(d)	2016(m), 1886(vs), 1856(s)	27.0 (27.1)	2.6 (2.7)
[ReCl(CO)$_3$(1,5-DTCO)]	78	191.1–191.7	2038(m), 1945(vs), 1900(vs)	23.8 (23.8)	2.6 (2.7)
[ReBr(CO)$_3$(1,5-DTCO)]	74	203.1–203.3	2040(m), 1945(vs), 1902(vs)	21.6 (21.7)	2.3 (2.4)

[a] In CH_2Cl_2 solvent.
[b] In hexane solvent.
[c] Calculated values in parentheses.
(d) Decomposed.

Table 2. ^{1}H NMR data[a] from the spectra of 1,5-DTCO and its W(CO)$_5$ complexes at 30°C

Parameters[b]	1,5-DTCO[c]	[{W(CO)$_5$}$_2$(1,5-DTCO)][c]	[W(CO)$_5$(1,5-DTCO)][d]
δ_A	2.76±0.01	3.18±0.1	2.45±0.1
δ_B	2.01±0.01	2.29±0.01	2.03±0.01
δ_C	—	—	1.33±0.01
$^2J_{AA'}$	−11.4±3.0[e]	−13.0±3.0[e]	−12.2[e]
$^2J_{BB'}$	−12.0±3.0[e]	−15.0±3.0[e]	−12.9[e]
$^2J_{CC'}$	—	—	−13.9[e]
$^3J_{AB}$	±3.7±0.3	±3.5±0.3	0
$^3J_{AB'}$	±8.1±0.3	±8.4±0.3	~0
$^3J_{AC}$	—	—	±2.9±0.3
$^3J_{AC'}$	—	—	±8.6±0.3
$^3J_{BC}$	—	—	±4.1±0.3
$^3J_{BC'}$	—	—	±8.1±0.3

[a] Chemical shifts (ppm) rel. to int. Me$_4$Si; *J* values in Hz.

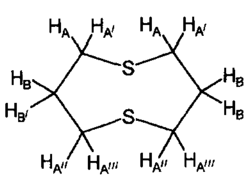
[b] By symmetry: $\delta_A = \delta_{A'} = \delta_{A''} = \delta_{A'''}$; $\delta_B = \delta_{B'}$; $\delta_C = \delta_{C'}$. The two magnitudes of vicinal couplings cannot be distinguished but the larger magnitudes were due to axial, axial $\rightleftharpoons$ equatorial, equatorial exchange, and the lower values to ax, eq $\rightleftharpoons$ eq, ax exchange.

[c] In CDCl$_3$ solvent.

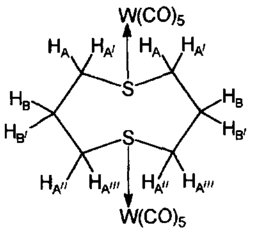
[d] In C$_6$D$_6$ solvent (Fig. 1).

[e] Very insensitive to iterative fitting.

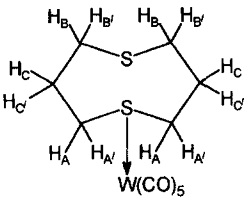
hydrogens. The observation of only two chemical shifts is consistent with time-averaged pseudo-planar ring conformations due to rapid ring reversal, most probably involving an interconversion of degenerate BC conformations (see later). Spectral simulations were performed on the basis of *AA'A''A'''BB'* or [[*A*]$_2$*B*]$_2$ spin systems[29] (**1** and **2**).



(1)



(2)



(3)

The 'best-fit' parameters are given in Table 2. Spectra were very insensitive to the geminal scalar couplings but sensitive to their difference in magnitudes, e.g. $|^2J_{AA'} - {}^2J_{BB'}| = 0.6 \pm 0.1$ Hz. Sums and differences of vicinal couplings could be measured accurately but it was not possible to distinguish between the two magnitudes of vicinal couplings. Excellent fits were achieved between the experimental 250 MHz spectrum and the simulated spectrum. A similarly good fit was achieved for the 100 MHz spectrum by reducing the chemical shift difference $|\nu_A - \nu_B|$ by a factor of 100/250, all *J* values remaining unchanged.

The ambient temperature ^{1}H NMR spectrum of [W(CO)$_5$(1,5-DTCO)] comprised three equal intensity, second-order multiplets compatible with an *AA'BB'CC'* or [*ABC*]$_2$ spin system[29] (**3**) due to the methylene hydrogens in α-, β- and γ-positions relative to the coordinating sulphur atoms. The spectrum was simulated using the LAOCN3 program[23] and a good fitting achieved (Fig. 1), despite the insensitivity of the spectra to the magnitudes of the geminal coupling constants (Table 2). The two magnitudes of vicinal couplings here, as in the spectra of **1** and **2**, are associated with rapid ring reversal

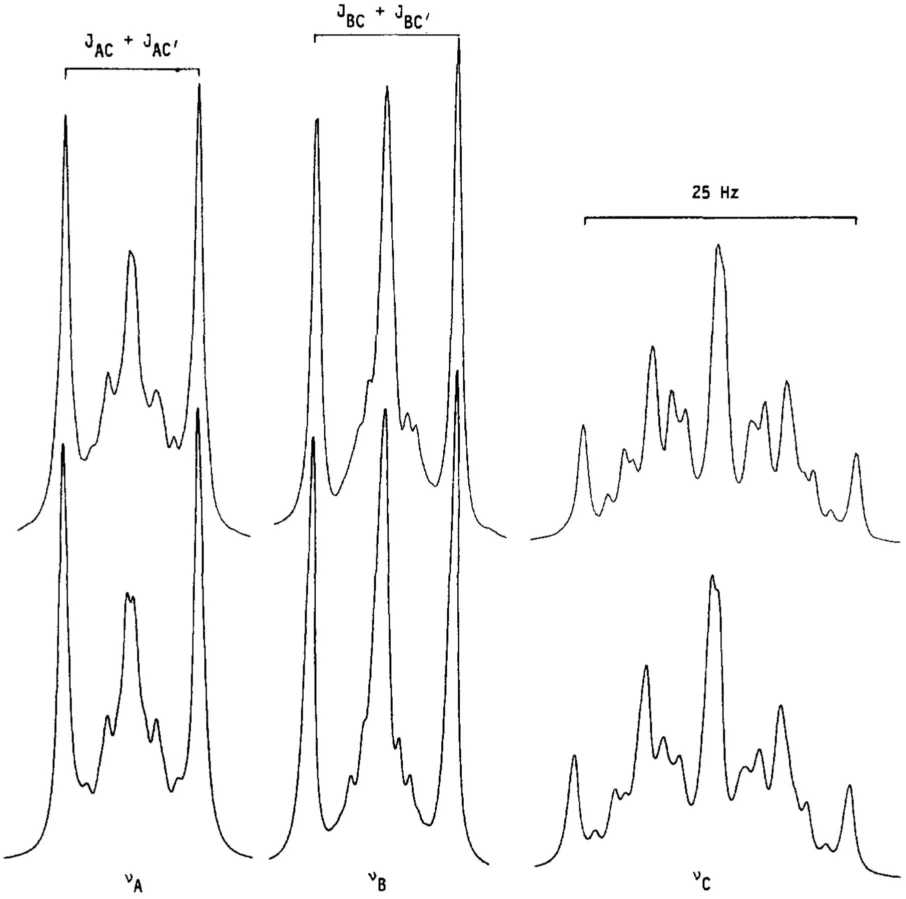


Fig. 1. Observed and computer simulated 250 MHz ^1H spectra of [$W(CO)_5$(1,5-DTCO)] in C_6D_6 at room temperature.

which leads to axial, axial $\rightleftharpoons$ equatorial, equatorial, and axial, equatorial $\rightleftharpoons$ equatorial, equatorial exchanges. The Karplus relationship[30] predicts a larger magnitude of averaged coupling for the ax, ax $\rightleftharpoons$ eq, eq exchange.

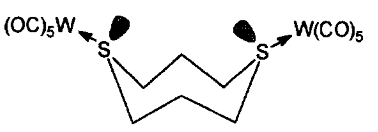
The room temperature ^1H spectrum of [$W(CO)_5$(1,5-DTCO)] was compatible with structure **3**, in which only one sulphur donor is coordinated to the metal moiety. In view of the strong transannular interaction between the two sulphur donors and the tendency for transition metal complexes to undergo metallotropic shifts,[13] it was thought likely that the $W(CO)_5$ moiety might undergo a 1,5-shift between the two sulphur atoms in 1,5-DTCO. Accordingly, a sample of the complex in C_6D_6 was warmed gradually to the boiling point of the solvent (80°C) and its ^1H spectrum measured. However, no sign of any intramolecular fluxion, which would have exchanged the AA' and B,B' environments of the ligand, was noted. All signals remained sharp throughout the temperature range, but their intensities changed and new signals appeared such that at *ca* 80°C signals due to the species [{$W(CO)_5$}$_2$(1,5-DTCO)], [$W(CO)_5$(1,5-DTCO)] and 1,5-DTCO itself, in an approximate population ratio of 3 : 1 : 1, were detected. This implies an equilibrium

$$2[\mathrm{W(CO)_5(1,5\text{-}DTCO)}] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\{\mathrm{W(CO)_5}\}_2(1,5\text{-}\mathrm{DTCO})] + 1,5\text{-}\mathrm{DTCO},$$

where the rate constants are such that $k_1 \gg k_2$. Thus, the $W(CO)_5$ moiety appears to undergo an intermolecular, as opposed to an intramolecular, exchange. The temperature dependence of the ^1H spectra suggests that the mononuclear metal complex is thermodynamically more stable than the dinuclear complex, but that the latter has an easily accessible ground state at above-ambient temperatures. The absence of any 1,5-intramolecular fluxion is likely to be due to a combination of skeletal flexibility of the eight-membered heterocyclic ring and sulphur atom pyramidal inversion, which interconverts conformers of similar ground state energy and modifies the ideal positioning of the sulphur lone pairs for $W(CO)_5$ fluxional shifts. Such factors appeared to pertain to the trithian complexes $[W(CO)_5(\overline{SCH_2SCH_2SCH_2})]$ and $[W(CO)_5(\overline{SCHMeSCHMeSCHMe})]$.[17,18] In the latter case, the fixed axial position of the $W(CO)_5$ group and the rigid conformation of the cyclic ligand with all methyl groups in equatorial positions greatly facilitates a 1,3-shift of the $W(CO)_5$ between the three fixed axial sulphur lone pairs. By contrast, in the unsubstituted trithian complex, the 1,3-shift process only occurs with difficulty at high temperatures as a result of the ligand flexibility.

A low temperature ^1H NMR study of a CD_2Cl_2 solution of $[\{W(CO)_5\}_2(1,5\text{-DTCO})]$ revealed some interesting changes. Below −80°C, the two sets of signals (Table 2) broadened significantly and each then split into unequal intensity pairs. The minor signals were to low frequencies of the main signals ($\Delta\delta \sim -0.2$) and had a relative intensity of 10–15% at −100°C. This low temperature spectrum suggested the presence of two different conformational isomers of this complex. On the assumption that the $W(CO)_5$ moieties are only attached in equatorial environments to minimize steric interactions with ring hydrogens, the major and minor species are thought to be due to BC and CC conformations, respectively (Fig. 2). Thus, cooling the complex to *ca* −100°C would appear to arrest the ring reversal process and reveal two distinct conformational isomers. The presence of both BC and CC conformations in solution is somewhat analogous to the solid state investigation of the compound $1,5\text{-DTCO}\cdot 2I_2$, in which crystals of both conformations were found to be present with S···S distances of 3.227 and 3.443 Å, respectively.[2]

eq - eq BC



eq - eq CC

Fig. 2. Proposed preferred conformational isomers of $[\{W(CO)_5\}_2(1,5\text{-DTCO})]$.

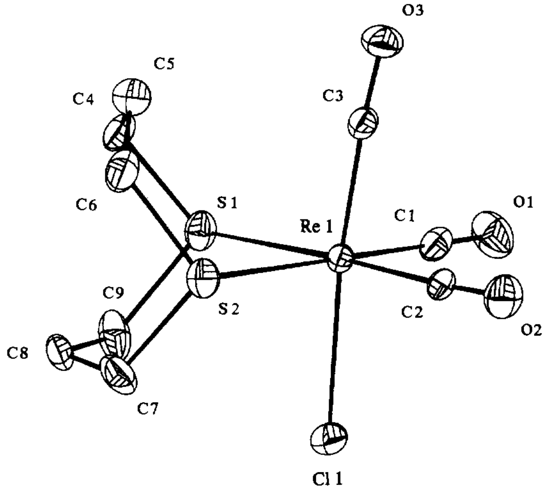


Fig. 3. X-ray structure of $[ReCl(CO)_5(1,5\text{-DTCO})]$ showing the atom labelling.

$[ReCl(CO)_3(1,5\text{-DTCO})]$

This complex was prepared in order to investigate the properties of 1,5-DTCO as a bidentate chelate ligand, and particularly to establish the conformation adopted by the eight-membered heterocyclic ring.

Prior to solution NMR studies, a single crystal X-ray determination of the structure was carried out. A view of the structure obtained is shown in Fig. 3. Selected bond lengths and angles are given in Tables 3 and 4. It is apparent that the ligand adopts one of two possible BC conformations when it chelates to $ReX(CO)_3$. This metal moiety possesses the expected *fac* geometry for the CO ligands and the boat section of the ligand ring is *cis* to halide but directed away to minimize β-ring methylene interactions. The other possible ring conformations CB or CC would have involved considerably larger chloride–β-methylene interactions. Such a structure is in accord with that deduced for *trans*-$[RuCl_2(1,5\text{-DTCO})_2]$, where the *trans* chlorides force the ligands to adopt BB conformations in order to min-

Table 3. Bond lengths (Å) for $[ReCl(CO)_3(1,5\text{-DTCO})]$

Cl(1)—Re(1)	2.488(4)	S(1)—Re(1)	2.496(4)
S(2)—Re(1)	2.499(4)	C(1)—Re(1)	1.903(11)
C(2)—Re(1)	1.902(9)	C(3)—Re(1)	1.884(10)
C(4)—S(1)	1.809(12)	C(9)—S(1)	1.821(11)
C(6)—S(2)	1.820(12)	C(7)—S(2)	1.811(11)
C(1)—O(1)	1.148(12)	C(2)—O(2)	1.164(10)
C(3)—O(3)	1.171(10)	C(5)—C(4)	1.525(17)
C(6)—C(5)	1.520(17)	C(8)—C(7)	1.518(15)
C(9)—C(8)	1.513(15)		

Table 4. Bond angles (°) for [ReCl(CO)$_3$(1,5-DTCO)]

S(1)—Re(1)—Cl(1)	87.1(2)	S(2)—Re(1)—Cl(1)	90.0(2)
S(2)—Re(1)—S(1)	82.0(2)	C(1)—Re(1)—Cl(1)	88.2(4)
C(1)—Re(1)—S(1)	92.5(3)	C(1)—Re(1)—S(2)	174.3(2)
C(2)—Re(1)—Cl(1)	91.3(3)	C(2)—Re(1)—S(1)	176.4(2)
C(2)—Re(1)—S(2)	94.7(4)	C(2)—Re(1)—C(1)	90.7(4)
C(3)—Re(1)—Cl(1)	174.2(3)	C(3)—Re(1)—S(1)	96.5(3)
C(3)—Re(1)—S(2)	95.0(4)	C(3)—Re(1)—C(1)	87.1(5)
C(3)—Re(1)—C(2)	85.3(4)	C(4)—S(1)—Re(1)	111.4(4)
C(9)—S(1)—Re(1)	109.7(4)	C(9)—S(1)—C(4)	99.4(6)
C(6)—S(2)—Re(1)	110.4(5)	C(7)—S(2)—Re(1)	109.7(5)
C(7)—S(2)—C(6)	99.9(5)	O(1)—C(1)—Re(1)	179.5(6)
O(2)—C(2)—Re(1)	177.4(6)	O(3)—C(3)—Re(1)	175.8(7)
C(5)—C(4)—S(1)	117.2(8)	C(6)—C(5)—C(4)	119.7(10)
C(5)—C(6)—S(2)	118.3(9)	C(8)—C(7)—S(2)	117.0(7)
C(9)—C(8)—C(7)	118.0(8)	C(8)—C(9)—S(1)	118.2(7)

imize β-methylene–chloride interactions. In the present complex the transannular S···S distance was calculated to be 3.277 Å. This value, which would appear to be the first reported for a chelate complex of 1,5-DTCO in which the ligand adopts a BC conformation, lies within the range expected for derivatives of 1,5-DTCO.[2–7] Its value is very similar to that of the monodentate complex *trans*-[SnCl$_4$(1,5-DTCO)$_2$], in which it is suggested[2] that the transannular S···S interaction is enhanced by the induced positive charge on the coordinated sulphur donor atoms. The S—Re—S 'bite' angle of 82.0° (Table 4) is the smallest reported for a chelate complex of 1,5-DTCO, the S—Ru—S angles of 84.9°

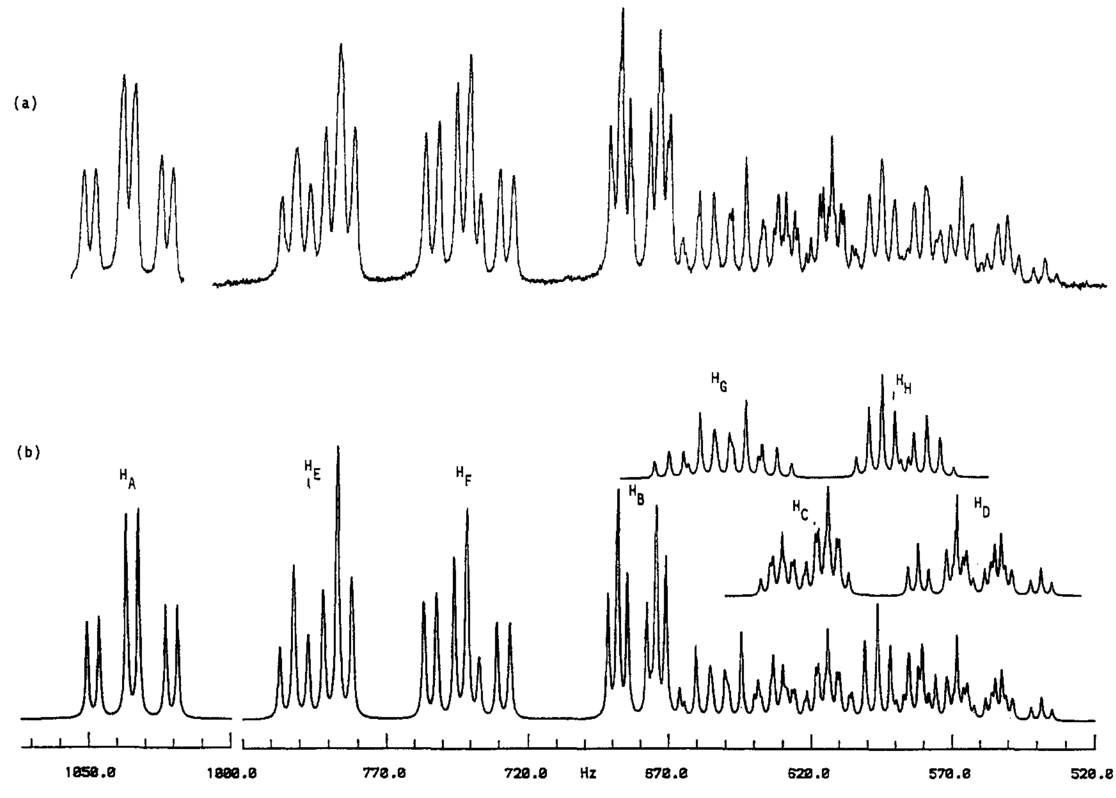
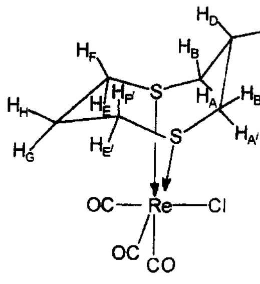
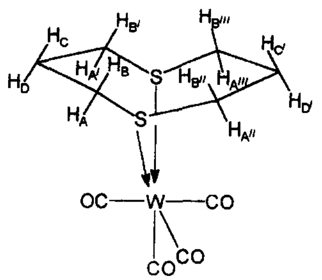


Fig. 4. Experimental (a) and computer simulated (b) 250 MHz ^{1}H spectra of [ReCl(CO)$_3$(1,5-DTCO)] in CDCl$_3$. The labelling refers to structure **4**. The simulated subspectra of H_C, H_D and H_G, H_H are shown separately.

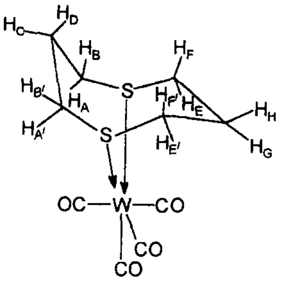
and 84.2° reported for *trans*-[$RuCl_2L_2$](L = 1,5-DTCO, 1,5-DTCO-1-oxide)[7] being at least partially determined by the BB ligand conformations. Inspection of the bond angles at the rhenium centre in the present complex reveals a significant deviation from regular octahedral geometry. It is particularly noteworthy that the Re—C(3)—O(3), 175.8(7)°, bonding is bent away from the local chair geometry, C(4)—C(5)—C(6), 119.7(10)°, of the ligand ring, C(3)—Re—S(1) and C(3)—Re—S(2) angles being 96.5(3) and 95.0(4)°, respectively.



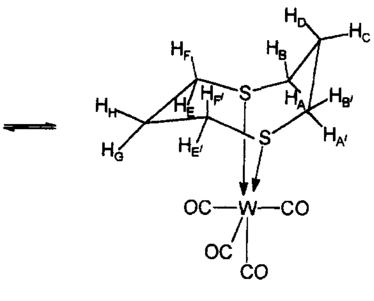
(4)



(5)



(5a)



(5b)

Solution state NMR studies of [$ReCl(CO)_3$(1,5-DTCO)] were undertaken to examine any differences in ligand ring conformation. In fact, none was detected, the ambient temperature ^{1}H spectra being amenable to analysis on the basis of a fixed BC ligand ring conformation (**4**). No evidence for other conformational isomers such as the chemically distinct CB and CC species was detected. The ^{1}H spectrum at 250 MHz was essentially first-order and of spin type $[AB]_2CD+[EF]_2GH$, with some overlap in the β-methylene region. The spectrum is depicted in Fig. 4a. The α-methylene region, consisting of two triplets of doublets (plus some second-order effects in one case) and two doublets of triplets, was most easily interpreted. Using the labelling in structure **4**, the two signals due to H_A and H_B (or $H_{A'}$ and $H_{B'}$) were identified by comparison with the spectra of [$ReBr(CO)_3$(1,5-DTCO)], where the different halide caused high frequency shifts in H_A and H_B, but not in H_E and H_F. Assignments within the geminal pairs were made on the basis of Karplus[30] predictions of magnitudes of vicinal couplings. Identification of the signals due to the β-methylene pairs H_C, H_D and H_G, H_H was aided by a ^{1}H 2D-COSY experiment which showed couplings to H_A, H_B, H_E and H_F. Assignments of signals within each pair were again achieved by the Karplus relationship. Hydrogen H_C, for example, was predicted to couple weakly to four *gauche* hydrogens (H_A, $H_{A'}$, H_B, $H_{B'}$), but more strongly to the geminal H_D, giving a doublet of quintets. In contrast, H_D was expected to show two weak *gauche* couplings (to H_B, $H_{B'}$), two large *trans* couplings (to H_A, $H_{A'}$) and a large geminal coupling (to H_C), giving an apparent quartet of triplets if $^3J_{DA} = {}^3J_{DA'} \approx {}^3J_{CD}$.

The $[AB]_2CD$ and $[EF]_2GH$ subspectra were simulated separately using the LAOCN3 program and then iterated on all magnetically non-equivalent chemical shifts and non-zero couplings. The final sets of parameters (Table 5) gave good fits

Table 5. ^{1}H NMR data[a] for [ReCl(CO)$_3$(1,5-DTCO)] and [W(CO)$_4$(1,5-DTCO)] at 30°C

Parameters	[ReCl(CO)$_3$(1,5-DTCO)][b]	[W(CO)$_4$(1,5-DTCO)][c]
δ_A	4.136 (0.029)	3.40
δ_B	2.724 (0.034)	2.72
δ_C	2.483 (0.040)	1.87
δ_D	2.245 (0.047)	2.11
δ_E	3.172 (0.034)	2.40
δ_F	2.967 (0.035)	2.82
δ_G	2.607 (0.050)	2.32
δ_H	2.357 (0.043)	2.11
J_{AB}	−13.88 (0.44)	[d]
J_{CD}	−16.00 (0.058)	[d]
J_{EF}	−15.15 (0.046)	[d]
J_{GH}	−16.03 (0.066)	[d]
J_{AC}	4.11 (0.045)	[d]
J_{AD}	13.88 (0.051)	[d]
J_{BC}	3.23 (0.050)	[d]
J_{BD}	3.65 (0.051)	[d]
J_{EG}	4.92 (0.050)	[d]
J_{EH}	4.70 (0.047)	[d]
J_{FG}	11.30 (0.054)	[d]
J_{FH}	4.44 (0.047)	[d]

[a] Chemical shifts rel. to Me$_4$Si ($\delta = 0$); scalar couplings in Hz.

[b] Values of iterative analysis of 250 MHz spectrum at 298 K. Probable errors in parentheses.

[c] Values from 400 MHz spectrum at 156 K.

[d] Not resolved due to residual dynamic broadening.

with the experimental spectra (RMS errors = 0.298 and 0.322 Hz, respectively). The total simulated spectrum is shown Fig. 4b, with the overlapping sub-spectra of H$_C$, H$_D$ and H$_G$, H$_H$ separated out.

[W(CO)$_4$(1,5-DTCO)]

The room temperature ^{1}H NMR spectra of this complex in CD$_2$Cl$_2$ or CDCl$_3$ consisted of two sets of well separated symmetrical multiplets in the intensity ratio 2 : 1 due to the α- and β-methylene ring hydrogens, respectively (Fig. 5a, c). The spectrum recorded in CD$_2$Cl$_2$ was analysed as a six-spin $[AB]_2CD$ system. This is consistent with a time-averaged BC $\rightleftharpoons$ CB ring or half-chair–half-chair structure (**5a**). The 'best-fit' parameters for the spectrum in CD$_2$Cl$_2$ were as follows: $\delta_A = 3.062$, $\delta_B = 2.975$, $\delta_C = 2.351$, $\delta_D = 2.286$, $J_{AB} = -16.4$ Hz, $J_{CD} = -14.6$ Hz, $J_{AC} = J_{A'C} = J_{AD} = J_{A'D} = 8.1$ and 3.7 Hz, $J_{BC} = J_{B'C} = J_{BD} = J_{B'D} = 8.1$ and 3.7 Hz. Spectra were very sensitive to the differences in chemical shifts $|\delta_A - \delta_B|$ and $|\delta_C - \delta_D|$, uncertainties being of the order of ±0.8 Hz, as illustrated by the significant differences in the multiplet structures on changing the solvent from CD$_2$Cl$_2$ to CDCl$_3$ (Fig. 5a, c).

On cooling the complex in CD$_2$Cl$_2$ solution to *ca* −100°C, its 250 MHz ^{1}H signals exhibited some dynamic broadening, but no decoalescence effects were observed. Spectra at 400 MHz were then obtained (by courtesy of the SERC service at the University of Warwick) in the hope that the larger chemical shift dispersion would aid the observation of the slowed dynamic effects. On cooling to *ca* −120°C, very significant changes did occur in most signals. At the lowest temperature attained before freezing of the CD$_2$Cl$_2$ solution, seven distinct signals were detected and attributed to the arresting of the BC $\rightleftharpoons$ CB ring process (**5a** $\rightleftharpoons$ **5b**). The signals were attributed to four α-methylene signals (H$_A$, H$_B$, H$_E$ and H$_F$; rel. intensity 8) and three β-methylene signals (H$_C$, H$_D$, H$_G$ and H$_H$; rel. intensity 4), with hydrogens H$_D$ and H$_H$ having identical shifts. A similar distribution of signals could be produced from a 1 : 1 mixture of BB and CC conformational isomers (each contributing two α-methylene and two β-methylene signals), but this possibility was ruled out since it is very unlikely

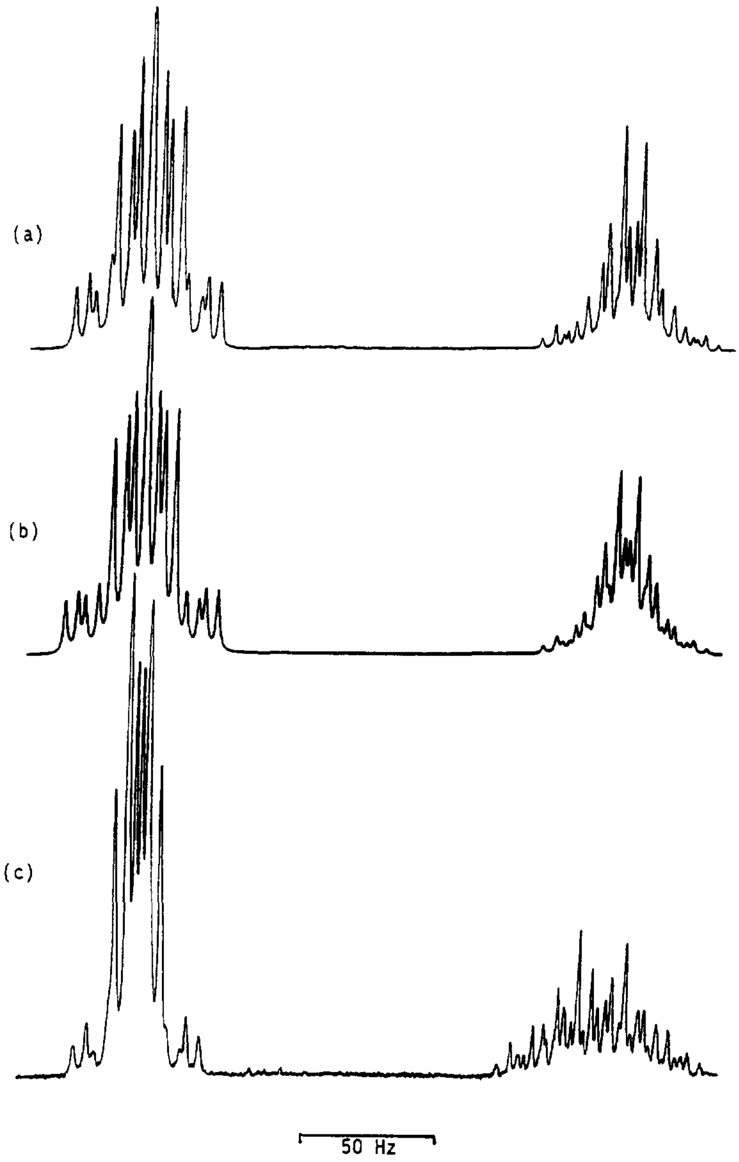


Fig. 5. 250 MHz ^{1}H NMR spectra of [W(CO)$_4$(1,5-DTCO)] in CD_2Cl_2 (a) and $CDCl_3$ (c). The computer simulated spectrum of (a) is shown in (b).

that both species would have identical ground state energies and hence solution populations. Indeed, the BB conformer would possess strong through-space interactions of β-methylene hydrogens and render it far less stable.

The variable temperature ^{1}H spectra of [W(CO)$_5$(1,5-DTCO)] represent a $[AB]_2CD \rightleftharpoons [EF]_2GH$ spin problem, if allowance is made for all possible scalar couplings. At a temperature of 156 K, the exchanging pairs of signals $A \rightleftharpoons E$, $B \rightleftharpoons F$ and $C \rightleftharpoons G$ can be readily identified. The other pair $D \rightleftharpoons H$ have virtually identical shifts at all temperatures and thus their combined signal shows no exchange broadening. The individual hydrogens of each pair cannot be assigned with any certainty, the assignments given in Fig. 6 and Table 5 being based on the relative ordering of corresponding shifts in the complex [ReCl(CO)$_3$(1,5-DTCO)]. Although scalar couplings were not resolved in the lowest temperature spectrum, the observed linewidths were considered to be comparable to the sums of the geminal and vicinal couplings for each hydrogen, in other words exchange broadening was judged to be very minimal and the experimental spectrum at 156 K closely approached the true 'static' spectrum. This may be illustrated for the signals of H_A and H_C, which have half-height-widths of 38 and 56 Hz, respectively.

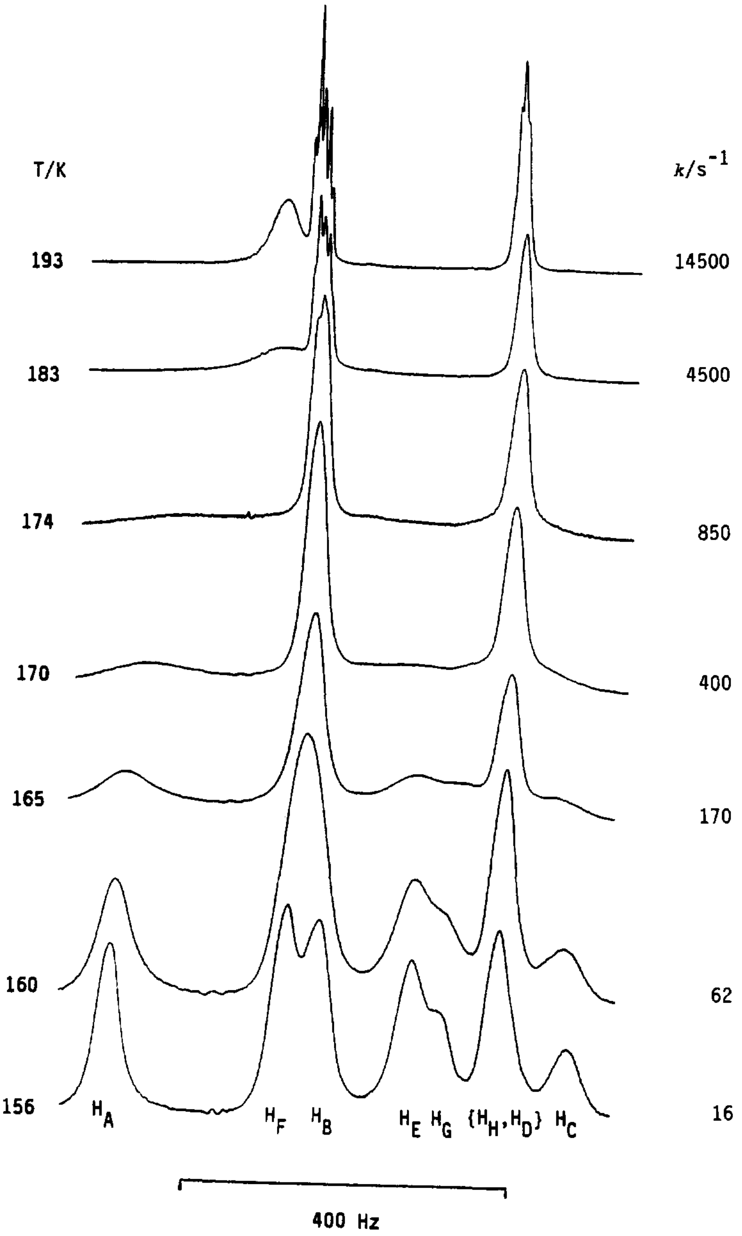


Fig. 6. 400 MHz ^{1}H NMR spectra of [W(CO)$_4$(1,5-DTCO)] in CD$_2$Cl$_2$ in the temperature range 150–193 K. Best-fit rate constants for the BC $\rightleftharpoons$ CB process are based on the exchanging H$_A$, H$_E$ signals.

Using the magnitudes of couplings from the spectrum of [ReCl(CO)$_3$(1,5-DTCO)], the breadths of multiplet structures of H$_A$ and H$_C$ are predicted to be 32 and 36 Hz, respectively. Thus, there would appear to be little exchange broadening in the spectrum of [W(CO)$_4$(1,5-DTCO)] at 156 K.

An approximate bandshape analysis was then carried out on the exchanging H$_A$ and H$_E$ signals. The DNMR3 program[25] was used firstly to simulate the lowest temperature spectrum using an effective transverse relaxation time, T_2^*, of 0.001 s. This corresponds to a linewidth of 32 Hz and was chosen to allow for the unresolved multiplicity due to scalar H–H couplings. On this basis a good fitting was achieved for a rate constant of 16 s^{-1}. Higher temperature spectra were fitted in a similar manner and rate data obtained for temperatures up to 193 K. No reliable fittings for temperatures between 170 and 183 K could be achieved because of the extreme broadness of the H$_A$ and H$_E$ bands (Fig. 6). The chemical shifts δ_A and δ_E (Table 5) showed virtually no temperature dependence over this range.

The activation energy data obtained from fittings of six spectra in the range 156–193 K were as follows:

$$E_a = 43.3 \pm 0.3 \text{ kJ mol}^{-1},$$

$$\log_{10}(A/\text{s}^{-1}) = 15.9 \pm 0.1,$$

$$\Delta H^{\ddagger} = 41.9 \pm 0.3 \text{ kJ mol}^{-1},$$

$$\Delta S^{\ddagger} = 56 \pm 2 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\text{and } \Delta G^{\ddagger} = 25.1 \pm 0.2 \text{ kJ mol}^{-1}.$$

These values must be treated with some caution, however, in view of the assumptions made in the fittings and of the rather high values of $\log_{10}(A/\text{s}^{-1})$ and $\Delta S^{\ddagger}$ calculated. The latter parameter is expected to be very small for a purely intramolecular rearrangement and the significantly positive value obtained here could be causing $\Delta G^{\ddagger}$ to be rather lower than the true value. Nevertheless, the magnitude of $\Delta G^{\ddagger}$ is clearly going to be significantly lower than those reported for ring reversal in cyclooctane-d_{15} (33.9 kJ mol^{-1}),[31] 1,1-difluorocyclooctane (31.4 kJ mol^{-1})[21] and 1,1,2,2-tetrafluorocyclooctane (43.1 kJ mol^{-1}),[31] all of which are known to exist in the BC or CB conformations at low temperatures with interconversion involving many possible intermediates, namely twist-boat, boat–boat, half-chair–chair, etc. In the present chelate complex of 1,5-DTCO it is more pertinent to consider the conformational process as reversals of trimethylene portions of two fused six-membered rings, with the S—W(CO)$_4$—S portion common to both rings being totally rigid. Thus, a more instructive comparison of energies is with that of cyclohexane ($\Delta G^{\ddagger} \sim 43$ kJ mol^{-1}).[31] In this six-membered ring the key intermediate, the half-chair form, is attained by geometric and electronic rearrangements of all C—C bonds in the ground state chair structure. To attain an analogous intermediate in the present W(CO)$_4$ complex, only individual trimethylene ring segments are involved and thus a substantially lower energy barrier than in cyclohexane would appear very reasonable.

The NMR method cannot provide any insight into the mechanism of the BC $\rightleftharpoons$ CB process, but chemical intuition would suggest that the process proceeded by a chair–chair intermediate at some stage, but this is unlikely to be the species whose relative energy is being measured by the NMR experiment.

In [W(CO)$_5$(1,5-DTCO)], the W(CO)$_4$ moiety clearly utilizes the 'inner' lone pairs on the sulphur atoms for coordination. In contrast, the W(CO)$_5$ moieties in [{W(CO)$_5$}$_n$(1,5-DTCO)] (n = 1,2) clearly use the 'outer' or equatorially directed lone pairs for bonding to minimize steric interactions. Such different choices of sulphur lone pairs have been noted previously[32] in connection with the structures of [{M(CO)$_5$}$_n$L] (M = Cr, W; n = 1, 2) where L is *cis*-1,4-cyclohexadienebisepisulphide $\overline{\mathrm{CHSC}}\mathrm{HCH_2}\overline{\mathrm{CHSC}}\mathrm{HCH_2}$.

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REFERENCES

1. J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.* 1934, **56**, 2177.
2. M. M. Olmstead, K. A. Williams and W. K. Musker, *J. Am. Chem. Soc.* 1982, **104**, 5567.
3. M. M. Olmstead, W. K. Musker and R. M. Kessler, *Acta Cryst.* 1984, **C40**, 1172.
4. N. L. Hill and H. Hope, *Inorg. Chem.* 1974, **13**, 2079.
5. M. M. Olmstead, W. K. Musker and R. M. Kessler, *Inorg. Chem.* 1984, **23**, 1768.
6. M. M. Olmstead, W. K. Musker and R. M. Kessler, *J. Am. Chem. Soc.* 1984, **23**, 3269.
7. B. W. Arbuckle, P. K. Bharadwaj and W. K. Musker, *Inorg. Chem.* 1991, **30**, 440.
8. A. S. Hirschon and W. K. Musker, *Transition Met. Chem.* 1980, **5**, 191.
9. J. B. Hendrickson, *J. Am. Chem. Soc.* 1961, **83**, 4537.
10. J. B. Hendrickson, *J. Am. Chem. Soc.* 1967, **89**, 7047.
11. W. N. Setzer, B. R. Coleman, G. S. Wilson and R. S. Glass, *Tetrahedron* 1981, **37**, 2743.
12. N. J. Leonard, T. W. Milligan and T. L. Brown, *J. Am. Chem. Soc.* 1960, **82**, 4075.
13. E. W. Abel, S. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem.* 1984, **32**, 1.
14. E. W. Abel, S. K. Bhargava, P. K. Mittal, K. G. Orrell and V. Šik, *J. Chem. Soc., Dalton Trans.* 1985, 1561.
15. E. W. Abel, T. E. MacKenzie, K. G. Orrell and V. Šik, *Polyhedron* 1987, **6**, 1785.
16. E. W. Abel, K. G. Orrell, H. Rahoo and V. Šik, *J. Organomet. Chem.* 1992, **441**, 441.
17. E. W. Abel, M. Booth, K. G. Orrell and G. M. Pring, *J. Chem. Soc., Dalton Trans.* 1981, 1944.
18. E. W. Abel, G. D. King, K. G. Orrell, G. M. Pring, V. Šik and T. S. Cameron, *Polyhedron* 1983, **2**, 1117.
19. E. W. Abel, G. D. King, K. G. Orrell and V. Šik, *Polyhedron* 1983, **2**, 1363.
20. D. F. Shriver, *Manipulation of Air-Sensitive Compounds.* McGraw-Hill, New York (1969).
21. W. Strohmeier, *Angew. Chem., Int. Edn Engl.* 1964, **3**, 187.
22. G. D. King, Ph.D. Thesis, University of Exeter (1983).
23. E. W. Abel, M. M. Bhatti, K. G. Orrell and V. Šik, *J. Organomet. Chem.* 1981, **208**, 195.

24. A. A. Bothner-By and S. M. Castellano, in *Computer Program for Chemistry* (Edited by D. F. De Tar). Benjamin, New York (1968).
25. D. A. Kleier and G. Binsch, Program DNMR3, Quantum Chemistry Program Exchange, Indiana University, U.S.A. (1970).
26. G. M. Sheldrick, SHELX 84, Program for Crystal Structure Solution, personal communication (1984).
27. G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination and Refinement, University of Cambridge (1976).
28. F. A. Cotton, *Chemical Applications of Group Theory*. Wiley-Interscience, New York (1971).
29. C. W. Haigh, *J. Chem. Soc.* (*A*) 1970, 1682.
30. M. Karplus, *J. Chem. Phys.* 1959, **30**, 11.
31. F. A. L. Anet and R. Anet, in *Dynamic Nuclear Magnetic Resonance Spectroscopy* (Edited by L. M. Jackman and F. A. Cotton), Ch. 14. Academic Press, New York (1975).
32. E. W. Abel, N. A. Cooley, K. Kite, K. G. Orrell, V. Šik, M. B. Hursthouse and H. M. Dawes, *Polyhedron* 1989, **8**, 887.