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Static and dynamic structures of pentacarbonylchromium(0) and -tungsten(0) complexes of dithioether ligands

II *. Unsymmetrical dithioether ligand complexes of general type [M(CO)$_5$(MeSCH$_2$SR)]

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Abstract

All six transition metal complexes of type [M(CO)$_5$MeSCH$_2$SR)] (M = Cr, W; R = ^{i}Pr, ^{t}Bu, Ph) have been synthesized. In CDCl$_3$ or CD$_2$Cl$_2$ solvents, the complexes exist as an equilibrium mixture of MeS-bonded and RS-bonded isomers, with the MeS-bonded species predominating. Variable temperature ^{1}H NMR studies have identified pyramidal inversion of the coordinated sulphur atoms and activation energy data have been obtained. $\Delta G^‡$ (298.15 K) values for the process are in the range 38–44 kJ mol^{-1}, and vary with the attached alkyl group (Me > ^{i}Pr ≈ ^{t}Bu).

Introduction

Part I of this series [1] described the syntheses and NMR characterization of the chromium(0) and tungsten(0) complexes of type [M(CO)$_5$L] where the ligands (L) were symmetrical dithioethers of the general type RSCH$_2$SR (R = Me, Et, ^{i}Pr and ^{t}Bu). In this paper, we describe the results of similar NMR studies on the unsymmetrical dithioether complexes of [M(CO)$_5$(MeSCH$_2$SR)] (R = ^{i}Pr, ^{t}Bu, Ph) which, in organic solvents, exist as mixtures of both possible S-bonded isomers. Energy values for pyramidal inversion of the coordinated S atoms are compared with those obtained from the analogous symmetrical ligand complexes.

Experimental

General

All preparations involving air-sensitive materials were performed by standard Schlenk techniques [2]. All solvents were freshly distilled under nitrogen.

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* For Part I, see ref. 1.

Table 1

^1H and $^{13}C-\{^1H\}$ chemical shifts for the ligands $MeSCH_2SR$ [a]

Ligands	$-SCH_2S-$		$-SCH_3$ $-SCH(CH_3)_2$ $-SC(CH_3)_3$		$-SCH(CH_3)_2$ $-SC(CH_3)_3$ $-SC_6H_5$	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
$MeSCH_2S^iPr$	3.66 (s)	36.40	2.17 (s), 3.12 (sp)	14.65, 41.46	1.29 (d)	22.94
$MeSCH_2S^tBu$	3.68 (s)	34.01	2.21 (s)	15.22, 43.22	1.37 (s)	30.92
$MeSCH_2SPh$	4.01 (s)	–	2.24 (s)	–	7.40 (m)	–

[a] Ligands diluted in $CDCl_3$. s, singlet; d, doublet; sp, binomial septet; m, multiplet.

Melting points of the solid complexes were measured with a digital Gallenkamp apparatus and were uncorrected. Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex. Infrared spectra of chloroform solutions of the complexes were recorded on a Perkin–Elmer Model 881 spectrometer.

The ^1H and $^{13}C-\{^1H\}$ NMR spectra were recorded on a Bruker AM 250 spectrometer operating at 250.13 and 62.90 MHz, respectively; all chemical shifts are quoted relative to internal Me_4Si. All spectra were recorded at ambient temperatures as $CDCl_3$ solutions, and at low temperatures as CD_2Cl_2 solutions. NMR probe temperatures were measured as previously described [1]. Bandshape analyses were performed by use of the authors' version of the DNMR3 program [3].

Synthesis of ligands

The unsymmetrical dithioether ligands $MeSCH_2SR$ ($R = {}^iPr$, ^tBu, Ph) were synthesized in a similar way to the symmetrical ligands $RSCH_2SR$ [1] by the reaction of chloromethylmethylsulphide and the appropriate mercaptan RSH ($R = {}^iPr$, ^tBu, Ph). Repeated vacuum distillation gave the desired product. Yields were in the range 20–35%, with the exception of $MeSCH_2SPh$ which was obtained in *ca.* 50% yield. NMR characterization data of the three ligands are given in Table 1.

Synthesis of complexes

All complexes were prepared by the general method reported for the symmetrical dithioether ligand complexes [4–7]. Analytical and IR data for the complexes are summarized in Table 2.

Results

Room temperature NMR studies

The ^1H NMR spectra of the six complexes of the series $[M(CO)_5MeSCH_2SR]$ (M = Cr, W; $R = {}^iPr$, ^tBu or Ph) could be interpreted on the basis of mononuclear, octahedral metal complexes with monodentate ligands (Fig. 1). In the spectra of $[W(CO)_5MeSCH_2S^tBu]$ (**1**) (Fig. 2), $[W(CO)_5MeSCH_2S^iPr]$ (**3**) and $[Cr(CO)_5MeSCH_2S^iPr]$ (**4**) the signals due to $-SCH_2S-$, SMe and $S-{}^iPr$ or $S-{}^tBu$ hydrogens comprised high and low intensity pairs, indicative of a mixture of isomers arising from the two types of S-coordination species, namely the Me–S

Table 2

Analytical and IR data of the pentacarbonyltungsten(0) and-chromium(0) complexes of unsymmetrical dithioether ligands [a]

Complex	Yield (%)	m.p. (°C)	ν(C=O) (cm^{-1})	Analytical data (%)			
				Found		Calculated	
				C	H	C	H
1 [$W(CO)_5MeSCH_2S^tBu$]	41	51–52	2076s, 1985s,b, 1948s,b	27.8	2.8	27.9	3.0
2 [$Cr(CO)_5MeSCH_2S^tBu$]	64	48.9–49.5	2070s, 1989s, 1947s,b, 1939sh,w	38.7	4.0	38.6	4.1
3 [$W(CO)_5MeSCH_2S^iPr$]	52	38	2076s, 1984s, 1938s,b, 1915sh	25.2	2.5	26.1	2.6
4 [$Cr(CO)_5MeSCH_2S^iPr$]	71	Oil	2070s, 1984s, 1944s,b, 1915sh	Not obtained			
5 [$W(CO)_5MeSCH_2SPh$]	42	38–39	2076s, 1982s, 1938s,b, 1915sh	31.6	2.1	31.6	2.0
6 [$Cr(CO)_5MeSCH_2SPh$]	65	Oil	2070s, 1986s, 1940s,b, 1915sh	Not obtained			

[a] Solvent chloroform-*d*. s, sharp; b, broad; sh, shoulder; w, weak.

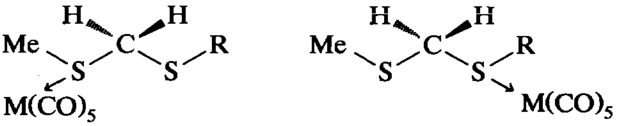
bonded and R–S bonded types (Fig. 1). The ^1H chemical shift data for the complexes (Table 3) enabled the isomers to be unambiguously identified and the measured isomer populations are contained in Table 3. It will be seen that the Me–S bonded isomers are invariably dominant and indeed are the only solution species detected in the cases of the complexes [$M(CO)_5MeSCH_2SPh$] (M = Cr, W) (**5**, **6**). Clearly in these two complexes, the bulk of the aryl group and perhaps its electronic influence preclude coordination at the aryl-S site.

In the room temperature spectra of all the complexes (Table 3), it should be noted that the signals due to the $-SCH_2S-$ protons are sharp singlets, indicating rapid pyramidal inversion of the coordinated S atom which is causing an averaging of the prochiral methylene environments.

Low temperature NMR studies

Such studies were carried out on all the complexes except [$Cr(CO)_5MeSCH_2S^tBu$] (**2**) and [$Cr(CO)_5MeSCH_2SPh$] (**6**), these being insufficiently stable in solution for any extended NMR measurements.

[$W(CO)_5MeSCH_2S^tBu$] (1). The room temperature spectrum of this complex in $CDCl_3$ was described previously (Fig. 2). When a CD_2Cl_2 solution of the complex is cooled to *ca.* −70°C the main methylene singlet signal changes to the expected AB quartet as a result of the arrest of the inversion of the S-methyl group and reveals the diastereotopic pair of methylene hydrogens (Fig. 3). The signal due to the minor $^tBuS \rightarrow W$ isomer broadens on cooling, appears to go through a coalescence point at *ca.* −70°C (Fig. 3), but is not clearly visible at this lowest temperature as a result of unfortunate band overlap with the major AB quartet. As the minor $^tBuS \rightarrow W$ bonded species was not clearly identified in its low tempera-



(a) (b)

Fig. 1. The two isomers of [$M(CO)_5MeSCH_2SR$] complexes.

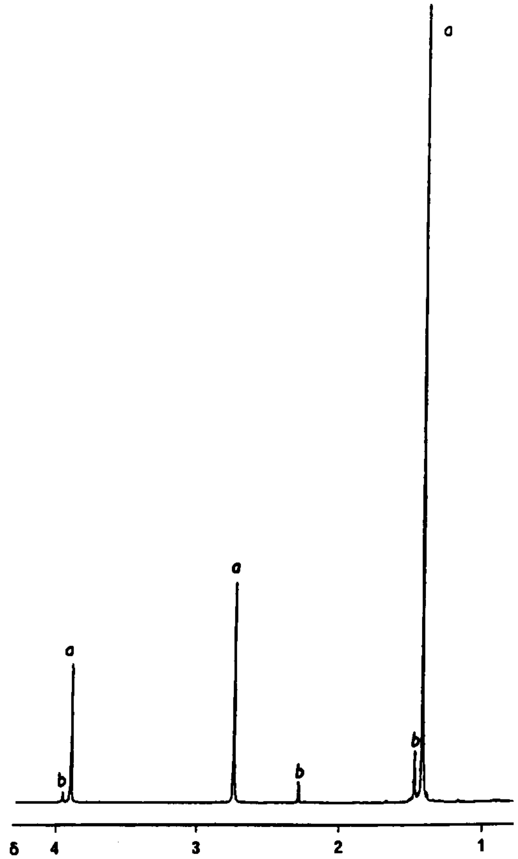


Fig. 2. Room temperature ^1H NMR spectrum of [$W(CO)_5MeSCH_2S^tBu$] showing the abundant MeS → W bonded (a) and minor ^tBu → W bonded (b) isomers.

ture limit, bandshape analysis was restricted to the major MeS → W bonded signals. These were fitted in the usual way and good visual matches between experimental and theoretical spectra obtained (Fig. 3).

[$W(CO)_5MeSCH_2S^iPr$] (3). This complex had a more favourable distribution of isomers for the detection of both solution species. However, their chemical shift distinction in the $-SCH_2S-$ region was very small (~ 0.01 ppm) so that on cooling the solution to effectively freeze the sulphur inversion process, two almost overlapping AB quartet patterns were obtained (Fig. 4). It proved impossible to perform any accurate total bandshape analysis of this region. Instead, approximate values of the energy barriers to the inversion in both isomers were measured from their band coalescence phenomena, using the standard formula [8].

[$Cr(CO)_5MeSCH_2S^iPr$] (4). For this complex, there was a somewhat greater distinction between the MeS-bonded and ^iPrS-bonded isomers than in the tungsten complex (3). This led to two distinguishable AB quartets at −90°C for the $-SCH_2S-$hydrogens in the two complex species, and total bandshape fittings were performed on both.

Table 3

^{1}H NMR and isomer population data [a] for the complexes [$M(CO)_5MeSCH_2SR$] in $CDCl_3$ solution at room temperature

No.	Complex	% Population	$-SCH_2S-$	$-SCH_3$	$-SCH(CH_3)_2$	$-SC(CH_3)_3$	$-SC_6H_5$
1a	[$W(CO)_5MeSCH_2S^tBu$] [c] ($MeS \rightarrow W$)	91	3.86 (s)	2.71 (s)	-	1.38 (s)	-
1b	[$W(CO)_5MeSCH_2S^tBu$] [c] ($Bu^tS \rightarrow W$)	9	3.92 (s)	2.24 (s)	-	1.44 (s)	-
2	[$Cr(CO)_5MeSCH_2S^tBu$]	[b]	3.69 (s)	2.41 (s)	-	1.39 (s)	-
3a	[$W(CO)_5MeSCH_2S^iPr$] ($MeS \rightarrow W$)	75	3.85 (s)	2.72 (s)	3.14 (sp) 1.34 (d)	-	-
3b	[$W(CO)_5MeSCH_2S^iPr$] ($Pr^iS \rightarrow W$)	25	3.84 (s)	2.26 (s)	3.43 (sp) 1.32 (d)	-	-
4a	[$Cr(CO)_5MeSCH_2S^iPr$] [d] ($MeS \rightarrow Cr$)	80	3.71 (s)	2.42 (s)	3.11 (sp) 1.32 (d)	-	-
4b	[$Cr(CO)_5MeSCH_2S^iPr$] [d] ($Pr^iS \rightarrow Cr$)	20	3.68 (s)	2.22 (s)	3.45 (sp) 1.37 (d)	-	-
5	[$W(CO)_5MeSCH_2SPh$] [d] ($MeS \rightarrow W$)	~ 100	4.21 (s)	2.75 (s)	-	-	7.2–7.6 (m)
6	[$Cr(CO)_5MeSCH_2SPh$] ($MeS \rightarrow Cr$)	~ 100	3.96 (s)	2.40 (s)	-	-	7.2–7.5 (m)

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[a] Shifts measured as δ values relative to internal Me_4Si. [b] Not measurable due to paramagnetic broadening effects. [c] $CDCl_2$ $CDCl_2$ solution. [d] CD_2Cl_2 solution. s, singlet; d, doublet; sp, binomial septet; m, multiplet.

Table 4

Activation energy data for pyramidal sulphur inversion in complexes $[M(CO)_5MeSCH_2SR]$[a]

No.	Complex	E_a (kJ mol^{-1})	$\log_{10}$ (A s^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})[b]	Ref.
1a	$[W(CO)_5MeSCH_2S^tBu]$ (MeS → W)	63.5 ± 2.7	16.2 ± 0.6	61.6 ± 2.7	59 ± 12	44.1 ± 0.9	[c]
1b	$[W(CO)_5MeSCH_2S^tBu]$ (^{t}BuS → W)	–	–	–	–	~ 35[d]	[c]
3a	$[W(CO)_5MeSCH_2S^iPr]$ (MeS → W)	–	–	–	–	39 ± 1[e]	[c]
3b	$[W(CO)_5MeSCH_2S^iPr]$ (^{i}PrS → W)	–	–	–	–	35 ± 1[f]	[c]
4a	$[Cr(CO)_5MeSCH_2S^iPr]$ (MeS → Cr)	61.1 ± 0.9	16.6 ± 0.2	59.3 ± 0.9	66 ± 4	39.5 ± 0.3	[c]
4b	$[Cr(CO)_5MeSCH_2S^iPr]$ (^{i}PrS → Cr)	42.6 ± 8.3	13.5 ± 2.4	41.0 ± 8.3	9 ± 47	38.4 ± 5.6	[c]
5	$[W(CO)_5MeSCH_2SPh]$ (MeS → W)	56.1 ± 2.6	15.1 ± 0.6	54.8 ± 2.6	38 ± 12	43.6 ± 0.9	[c]
	$[W(CO)_5MeSCH_2SMe]$	53.5 ± 2.7	14.8 ± 0.6	51.7 ± 2.7	32 ± 12	42.2 ± 0.9	1
	$[W(CO)_5{}^iPrSCH_2S^iPr]$	51.7 ± 0.6	15.8 ± 0.2	50.1 ± 0.6	52 ± 3	34.4 ± 0.3	1
	$[W(CO)_5{}^tBuSCH_2S^tBu]$	52.2 ± 1.5	16.8 ± 0.4	55.5 ± 1.5	71 ± 7	34.3 ± 0.6	1

[a] In CD_2Cl_2 solvent. [b] At 298.15 K. [c] This work. [d] Approx. estimate. [e] Calculated from coalescence temperature (−50°C). [f] Calculated from coalescence temperature (−70°C).

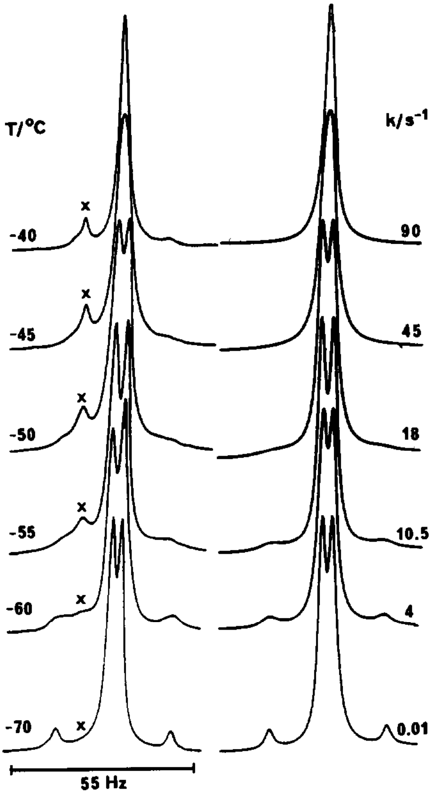

Fig. 3. Variable temperature and computer simulated spectra of the methylene hydrogens in [W(CO)$_5$MeSCH$_2$S^{t}Bu] showing the effects of the pyramidal sulphur inversion. Best-fit rate constants are shown alongside the theoretical spectra. The signal due to the minor ^{t}Bu → W isomer is denoted by X. This broadens on cooling and is present as a very broad coalesced signal at −70°C.

[W(CO)$_5$MeSCH$_2$SPh] (5). This complex exists in CDCl$_3$ or CD$_2$Cl$_2$ solutions as only the MeS-bonded isomer. The single–SCH$_2$S–signal at ambient temperatures changes to a single AB quartet at −70°C. The bandshape change was analysed in the usual way.

Discussion

The data in Tables 3 and 4 allow certain general points to be made regarding the relative ground state and transition state energies of the complexes **1–5**.

Firstly, in all cases the MeS-bonded isomers are favoured over the ^{i}PrS, ^{t}BuS and PhS-bonded isomers, the order of preference being MeS ≫ ^{i}PrS > ^{t}BuS ≫ PhS. Indeed, no evidence for PhS bonded species was found in the complexes **5** and **6** in the solvents studied (*viz.* CD$_2$Cl$_2$ or CDCl$_3$). Clearly, the steric size of the R group attached to sulphur is the prime influence of the coordinating strength of the S atom. Secondly, regarding relative magnitudes of S inversion energies, the appropriate comparisons of $\Delta G^\ddagger$ values in Table 4 lead to certain generalizations. For S atoms coordinated to W, inversion energies decrease in the order MeS > ^{i}PrS ≈ ^{t}BuS, following a similar trend noted previously [9] for the complexes

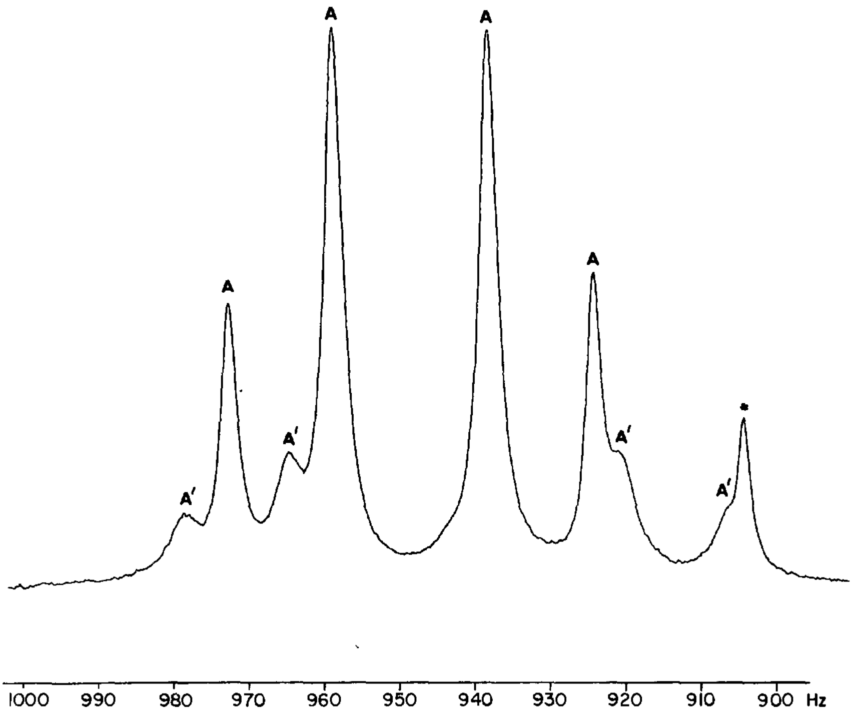

Fig. 4. ^1H NMR spectrum (methylene region) of [W(CO)$_5$MeSCH$_2$S^{i}Pr] at −90°C showing the AB quartet signals of the major MeS → W bonded isomer (A) and minor ^{i}PrS → W bonded isomer (A'). Impurity signal (*).

[W(CO)$_4$(RSCH$_2$CH$_2$SR)] (R = Me, Et, ^{i}Pr, ^{t}Bu). This trend is most easily rationalized in terms of the steric requirements of the alkyl groups. As these increase, a considerable distortion towards a planar S geometry will occur, thereby affording easier access to the planar transition state associated with the S inversion process, and leading to a reduction in $\Delta G^\ddagger$ energy values. In the present open chain ligand complexes, the magnitudes of the inversion energies, 34–44 kJ mol^{-1}, are notably lower (by *ca.* 9–10 kJ mol^{-1}) than those for the chelate complexes mentioned above [9].

The variation of S inversion energies with metal (*i.e.* Cr or W) is inconclusive in the present work as can be seen by comparing the $\Delta G^\ddagger$ data for complex **4a** with **3a** or **4b** with **3b**. The values suggest that S → Cr inversion is slightly less favoured over S → W inversion, but the quality of the data for complex **3** is not high, and as this suggested trend runs counter to trends observed in other complexes, *i.e.* [M(CO)$_5$(SCH$_2$SCH$_2$SCH$_2$)] (M = Cr, W) [10] and [M(CO)$_5$(MeSCH$_2$SCH$_2$SMe)] (M = Cr, W) [11], then it would be unwise to draw any firm conclusion from the new data.

We had hoped to be able to measure the influence of the uncoordinated SR group on the inversion energy of the coordinated S atom. Thus, a comparison was made between the MeS inversion energy in [W(CO)$_5$(MeSCH$_2$SMe)] [1] and the corresponding inversion energies in [W(CO)$_5$(MeSCH$_2$S^{t}Bu) (**1**), [W(CO)$_5$(MeSCH$_2$S^{i}Pr)] (**3a**) and [W(CO)$_5$MeSCH$_2$SPh)] (**5**). However, the values in Table 4 show no well defined trend although energies are slightly higher for the unsymmetrical ligand complexes with the exception of complex (**3a**), where the anomaly may be result of the approximate nature of this energy value.

The main conclusions of this work are that the nature of the alkyl or aryl group attached to sulphur in these unsymmetrical dithioether ligands greatly influence the coordinating strength of the S atom. Inversion energies are clearly, but rather less strongly, influenced by the nature of this group.

The third part of this series of papers [12] will deal with the question of whether these influences are carried over into the high temperature fluxional regime of these complexes, where 1,3-metallotropic shifts [13] of S-coordination sites occur.

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