Journal of Organometallic Chemistry, 441 (1992) 441–448
Elsevier Sequoia S.A., Lausanne
JOM 23005

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

III *. 1,3-Metallotropic shifts of sulphur coordination sites

Edward W. Abel, Keith G. Orrell, Haji Rahoo and Vladimir Šik
Department of Chemistry, University of Exeter, Exeter, Devon, EX4 4QD (UK)

(Received May 22, 1992)

Abstract

The dithioether complexes $[W(CO)_5RSCH_2SR']$ ($R = R' = Et$, ^iPr, ^tBu; $R = Me$, $R' = {}^iPr$, ^tBu) exhibit 1,3-metallotropic shifts of the S coordination sites at above-ambient temperatures. Energies of these fluxional shifts in the symmetrical ligand complexes were in the range 74–84 kJ mol^{-1}, the S–alkyl dependence being $Me > Et > {}^iPr > {}^tBu$. The energies for the two different directions of shift in the unsymmetrical dithioether complexes were related to the differences in the tungsten–S–alkyl bond strengths.

Introduction

The earlier parts of this series [1,2] have described the solution stereodynamics of metal pentacarbonyl complexes of general type $[M(CO)_5L]$ ($M = Cr$, W; $L =$ symmetrical dithioethers, $RSCH_2SR$, or unsymmetrical analogues $MeSCH_2SR$). At ambient temperatures the coordinated sulphur atoms under pyramidal inversion which is rapid on the nuclear magnetic resonance (NMR) timescale, but this effect can be arrested at low solution temperatures to reveal the static invertomers of the complexes. Activation energy data for the pyramidal inversion process were rationalised in terms of the nature of the S–alkyl or S–aryl groups.

These complexes exhibit additional intramolecular rearrangements at elevated temperatures (> 50°C) which consist of a commutation of a $W(CO)_5$ moiety between the two sulfur atoms of the dithioether ligand via a 1,3-shift mechanism. This type of fluxional movement has been observed previously in cyclic sulphur ligand complexes of types $[W(CO)_5(SCH_2SCH_2SCH_2)]$ [3], and $[W(CO)_5(SCH_2$

Correspondence to: Dr. K.G. Orrell.

* For Part II, see ref. 2.

$SCH_2SCH_2SCH_2)$] [4], and in open chain ligand complexes of types [$W(CO)_5(MeECH_2E'Me)$] ($E = E' = S$, Se; $E = S$, $E' = Se$) [5,6] and [$W(CO)_5(CH_3S)_nCH_{4-n}$] ($n = 2$–4) [7]. Also, there is evidence for its occurrence in the complexes [$M(CO)_5(MeSCH_2SCH_2SMe)$] before dissociation sets in [8]. In all the above open chain ligand complexes the metal moiety commutes between S-methyl groups. The present paper describes the influence of different S-alkyl groups on the rates and energies of 1,3-commutations of the $W(CO)_5$ moiety. In the complexes of unsymmetrical dithioethers $MeSCH_2SR$, ($R = {}^iPr$, ${}^tBu$), when an equilibrium of MeS → W and RS → W bonded species exists in solution, the energies of the two different directions of shift, namely MeS → W ⇌ RS → W allow an assessment of the relative strengths of the W–S–alkyl bonds.

Experimental details

Preparations of the complexes [9–12] were described in the preceding papers [1,2]. All ^1H NMR spectra were recorded on a Bruker AM 250 spectrometer operating at 250.13 MHz. Shifts are quoted relative to internal Me_4Si. Spectra were recorded on solutions of the complexes in tetrachloroethane-d_2, DCl_2CCCl_2D. Solution temperatures were measured as previously [1], and bandshape analyses utilized the authors' version of the DNMR3 program [13].

Results

[$W(CO)_5RSCH_2SR$] ($R = Et$, ${}^iPr$, ${}^tBu$)

On warming solutions of all complexes of symmetrical dithioethers exchange was observed between the hydrogen signals of R groups attached to coordinated and uncoordinated sulfur atoms, indicative of a 1,3-shift process causing magnetization transfer between the two R environments (Fig. 1). Chemical shifts of these environments at room temperature are given in Table 3 of Part I [1]. Special features of individual spectra are described below.

(a)[$W(CO)_5EtSCH_2SEt$]. Above 70°C the pairs of methyl and methylene signals of the two ethyl groups broadened, coalesced and finally sharpened to averaged multiplets. The triplet signals of the methyl hydrogens coalesced around 105°C. Substantial decomposition of the complex commenced at temperatures above 90°C and so the higher temperature coalescence of the methylene signals was not clearly seen. Total bandshape analysis was performed on the methyl signals, and an approximate value for the activation energy $\Delta G^\ddagger$ was also obtained from the coalescence point of the methyl signals. Satisfactory agreement between the two values was obtained (Table 1).

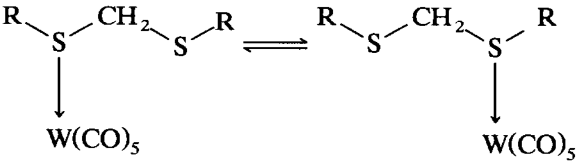

Fig. 1. The 1,3-metallotropic shift in the complexes [$W(CO)_5RSCH_2SR$]. Fast S inversion is assumed.

Table 1

Relative ground state energies and 1,3-shift activation energies of [W(CO)$_5$L] complexes

L	Process		Populations[b]		$\Delta G^{\ominus}$[c] (kJ mol^{-1})	$\Delta G^{\ddagger}$[d] (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
	A → B		p_A	p_B				
MeSCH$_2$SMe	MeS → W	MeS → W	0.50	0.50	0.0	84.65 ± 0.66[e]	–	–
EtSCH$_2$SEt	EtS → W	EtS → W	0.50	0.50	0.0	83.1 ± 1.6	84.4 ± 9.6	5 ± 27
						83.9[f]		
^{i}PrSCH$_2$S^{i}Pr	^{i}PrS → W	^{i}PrS → W	0.50	0.50	0.0	79.6[g]	–	–
						78.1[h]		
^{t}BuSCH$_2$S^{t}Bu	^{t}BuS → W	^{t}BuS → W	0.50	0.50	0.0	73.8 ± 0.2	89.3 ± 1.6	52 ± 5
MeSCH$_2$S^{i}Pr	MeS → W	^{i}PrS → W	0.75	0.25	2.7	81.7 ± 0.2	86.5 ± 1.2	16 ± 4
	^{i}PrS → W	MeS → W	0.25	0.75	−2.7	78.9 ± 0.2	86.5 ± 1.2	25 ± 4
MeSCH$_2$S^{t}Bu	MeS → W	^{t}BuS → W	0.91	0.09	5.7	78.3 ± 0.2	65.5 ± 1.5	−43 ± 5
	^{t}BuS → W	MeS → W	0.09	0.91	−5.7	72.5 ± 0.2	65.5 ± 1.6	−24 ± 4

[a] In CDCl$_2$ CDCl$_2$ solvent. [b] No temperature dependence detected. [c] $\Delta G^{\ominus} = -RT \ln(p_B/p_A)$ with $T = 298.15$ K. [d] At 298.15 K. [e] Ref. 5. [f] Based on coalescence of Me signals at 403 K. [g] Based on coalescence of Me signals at 333 K. [h] Based on coalescence of CH signals at 393 K.

(b) [W(CO)$_5$^{i}PrSCH$_2$^{i}SPr]. Hydrogen-1 spectra were recorded in the range 30–120°C. Signals of the isopropyl group commenced broadening at *ca.* 50°C, with coalescence at 60°C for the methyl protons and at *ca.* 120°C for the methine protons. However, decomposition of the complex started at *ca.* 100°C, leading to the observation of free ligand signals which precluded any total bandshape analysis on the methine signals. Instead, an approximate $\Delta G^{\ddagger}$ value for the 1,3-shift was obtained from the coalescence temperature spectrum of the methine protons. Bandshape analysis proved to be also unfeasible for the CH$_3$ region of the spectrum on account of the small chemical shift difference between coordinated and uncoordinated isopropyl methyl doublets which led to very little dynamic broadening (Fig. 2). However, an approximate $\Delta G^{\ddagger}$ value based on the coalescence temperature was again estimated (Table 1).

(c) [W(CO)$_5$^{t}BuSCH$_2$S^{t}Bu]. Above ambient temperature NMR spectra of this complex were analysed without difficulty. The t-butyl singlets broadened, coalesced at 37°C, and sharpened to an averaged signal at *ca.* 75°C. Bandshape analysis was carried out for the temperature range 50–70°C and reliable activation energy data for the fluxion obtained (Table 1).

[W(CO)$_5$MeSCH$_2$SR] (R = ^{i}Pr, ^{t}Bu)

Tungsten pentacarbonyl complexes of unsymmetrical dithioether ligands exist in solution as equilibrium mixtures of MeS → W bonded and RS → W bonded species (Fig. 3). The MeS → W bonded species are significantly more favoured presumably due to the smaller steric requirement of methyl compared to isopropyl or tert-butyl. In the complex [W(CO)$_5$MeSCH$_2$S^{t}Bu], the sulphur attached to ^{t}Bu is so sterically shielded that the ^{t}BuS → W bonded species is only 10% abundant in CDCl$_2$CDCl$_2$ solution.

(a) [W(CO)$_5$MeSCH$_2$S^{i}Pr]. At room temperature the MeS → W and ^{i}Pr → W bonded species were clearly identified by their different methylene, methine and methyl (MeS and ^{i}PrS) signals. (See Table 3, Part III.) On elevation of solution temperature all pairs of signals of corresponding protons for the two species

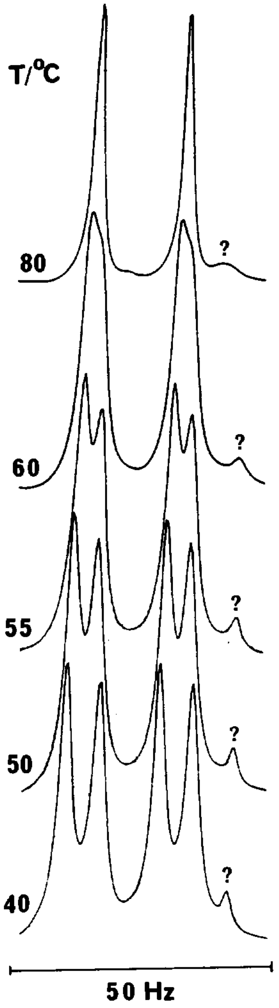

Fig. 2. Experimental ^1H NMR spectra of the methyl region of $[W(CO)_5{}^iPrSCH_2S^iPr]$ showing the coalescence of the methyl doublets due to the 1,3-shift process.

exhibited dynamic broadening. In view of the tendency of the complex to decompose above 100°C, the closely separated methylene signals were chosen for band-shape analysis as they coalesced at 65°C and gave a fairly sharp weighted-averaged signal at 70°C, before any significant complex dissociation occurred. Spectra were fitted in the usual way and rate constants, k_A, for the 1,3-shift from the more

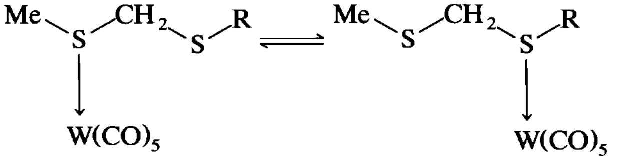

Fig. 3. The 1,3-metallotropic shift in the complexes $[W(CO)_5MeSCH_2SR]$ showing exchange between the MeS → W and RS → W bonded species.

populated MeS → W bonded species (A) to the less populated ^{i}PrS → W bonded species (B) were obtained. Activation parameters for this process were calculated accordingly (Table 1). Similar parameters for the reverse direction of the 1,3-shift were obtained from the reverse rate constants, k_B, using the kinetic equilibrium relationship $p_A k_A = p_B k_B$, where p_A, p_B are the populations of the appropriate species.

(b) [W(CO)$_5$MeSCH$_2$S^{t}Bu]. Both coordination species were distinguished by the different ^{1}H chemical shifts and relative intensities of their –SCH$_2$S–, MeS– and ^{t}BuS–signals. On warming the solution of the complex, all corresponding pairs of signals displayed exchange broadening. The ^{t}BuS– and –SCH$_2$S– singlets

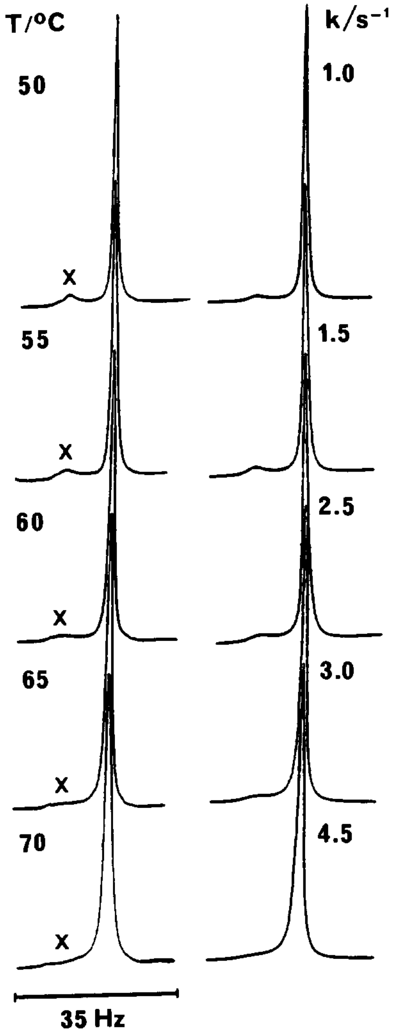

Fig. 4. Experimental and computer simulated ^{1}H spectra of the ^{t}Bu signals of [W(CO)$_5$MeSCH$_2$S^{t}Bu] showing the effects of the 1,3-shift. X denotes the minor ^{t}BuS → W bonded complex. Rate constants refer to the shift from major to minor species.

Table 2

Activation energies for 1,3-shifts in [W(CO)$_5$L] complexes [a]

R	$\Delta G^{\ddagger}$ (kJ mol^{-1})	$\Delta\Delta G^{\ddagger}$ (kJ mol^{-1})
(a) RS $\rightarrow$ W $\rightarrow$ RS $\rightarrow$ W		
Me	84.7	
Et	83.1	
^{i}Pr	79.6 [b]	
^{t}Bu	73.8	
(b) MeS $\rightarrow$ W $\rightarrow$ RS $\rightarrow$ W		
Me	84.7	
		3.0
^{i}Pr	81.7	
		3.4
^{t}Bu	78.3	

[a] $\Delta G^{\ddagger}$ values calculated at 298.15 K. [b] Based on coalescence of Me signals 333 K.

coalesced at *ca.* 70°C, and the MeS singlets at > 100°C when complex dissociation rather masked the effect. The ^{t}BuS region was chosen for the bandshape analysis and satisfactory fittings were obtained up to 70°C (Fig. 4). Above the temperature the spectra became insensitive to the chosen rate constants because of the very unequal populations of the two coordination species.

Discussion

The Eyring activation parameters for the 1,3-shift process in all the [W(CO)$_5$L] complexes studied here are shown in Table 1. This table also includes the previously published data for [W(CO)$_5$MeSCH$_2$SMe] [5]. The reliability of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data for all these complexes is only modest because of difficulties in some of the bandshape analyses arising from the limited thermal stability of most of the complexes in solution, and, in the case of the MeSCH$_2$SR complexes, the great disparity in solution populations of the two different coordination species. Discussions of energy trends will therefore be restricted to $\Delta G^{\ddagger}$ values which are less prone to systematic error [14].

Energy values are all relatively high, being in the range 72–85 kJ mol^{-1}. The most notable trend is that for shifts taking place between degenerate coordination species where $\Delta G^{\ddagger}$ values steadily decrease as the steric size of the alkyl group increases (Table 2(a)). The most likely explanation of this trend is that bulky S–alkyl groups will distort the pyramidal geometry of the sulfur atoms towards a geometry required for access to the pseudo-7-coordinate transition state of the 1,3-shift process (Fig. 5). This will raise the ground state energy of the complex and lead to a concomitant lowering of its activation energy.

This effect is also apparent in cases where the shift involves a movement from a MeS $\rightarrow$ W bonded species to an RS $\rightarrow$ W bonded species. As the alkyl group R changes from Me to ^{i}Pr to ^{t}Bu, $\Delta G^{\ddagger}$ values for the shift again decrease, but to only about half the extent observed for the symmetrical dithioether complexes. This may be interpreted as due to the bulky R groups distorting the geometry of the single uncoordinated S atom towards its required transition state geometry.

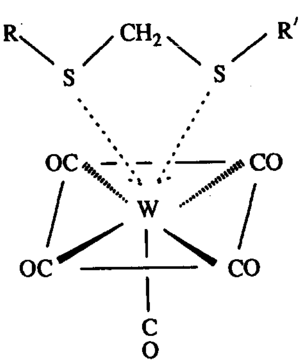

Fig. 5. Proposed pseudo-seven-coordinate intermediate structure for the 1,3-fluxional shift.

The relative abilities of the R groups in this respect are represented by the first differences in the activation energies, $\Delta\Delta G^{\ddagger}$, in Table 2(b).

The $\Delta G^{\ddagger}$ values for the different directions of 1,3-shift (Table 1) clearly depend on the different solution populations or ground state energies of the MeS → W and RS → W bonded species. These can be calculated from the usual thermodynamic relationship $\Delta G^{\ominus} = -RT \ln(p_B/p_A)$ where p_A and p_B are the populations of the MeS → W and RS → W species respectively. Ground state energy differences, $\Delta G^{\ominus}$, of both species in the two $MeSCH_2SR$ complexes were calculated (Table 1), and their values found to be virtually identical to the difference in the $\Delta G^{\ddagger}$ values for either direction of 1,3-shift. These $\Delta G^{\ddagger}$ differences can therefore be equated to the difference in ground state energies of the two coordination species of either $MeSCH_2SR$ complex, and as these differ primarily in the type of sulfur–tungsten bonding, the relative strengths of MeS → W, ^{i}Pr → W and ^{t}Bu → W bonds can be assessed. Calculated magnitudes are as follows:

$\Delta E(\text{MeS} \rightarrow \text{W}-{}^{t}\text{BuS} \rightarrow \text{W}) = 5.8 \text{ kJ mol}^{-1}$

$\Delta E(\text{MeS} \rightarrow \text{W}-{}^{i}\text{PrS} \rightarrow \text{W}) = 2.8 \text{ kJ mol}^{-1}$

$\Delta E({}^{i}\text{PrS} \rightarrow \text{W}-{}^{t}\text{BuS} \rightarrow \text{W}) = 3.0 \text{ kJ mol}^{-1}$

The present work provides no new insight into the nature of the transition state species for the 1,3-shift process, but following a previous study [15], a pseudo-seven-coordinate tungsten species is proposed with the $W(CO)_5$ moiety retaining a rigid square-pyramidal geometry. Support for the latter assumption comes from the absence of any axial/equatorial carbonyl exchange during the 1,3-shift in $[W(CO)_5MeSCH_2SMe]$ as evidenced by ^{13}C 2D-EXSY NMR experiments [15]. Such spectra were not possible in the present complexes, but the same shift mechanism is proposed, namely lateral movements of a rigid square-pyramidal $W(CO)_5$ unit relative to the dithioether ligand.

References

1 E.W. Abel, K.G. Orrell, H. Rahoo, V. Šik, M.A. Mazid and M.B. Hursthouse, J. Organomet. Chem., 437 (1992) 191.

2 E.W. Abel, K.G. Orrell, H. Rahoo, and V. Šik, J. Organomet. Chem., 441 (1992) 255.

3 E.W. Abel, M. Booth, K.G. Orrell and G.M. Pring, J. Chem. Soc., Dalton Trans., (1981) 1944.

4 E.W. Abel, G.D. King, K.G. Orrell, G.M. Pring, V. Šik and T.S. Cameron, Polyhedron, 2 (1983) 1117.

5 E.W. Abel, S.K. Bhargava, T.E. MacKenzie, P.K. Mittal, K.G. Orrell and V. Šik, J. Chem. Soc., Chem. Commun., (1982) 983.

6 E.W. Abel, S.K. Bhargava, T.E. MacKenzie, P.K. Mittal, K.G. Orrell and V. Šik, J. Chem. Soc., Dalton Trans., (1987) 757.

7 E.W. Abel, T.E. MacKenzie, K.G. Orrell and V. Šik, Polyhedron, 6 (1987) 1785.

8 E.W. Abel, M.Z.A. Chowdhury, K.G. Orrell and V. Šik, J. Organomet. Chem., 262 (1984) 293.

9 W.A. Schlenk and M. Schmidt, Z. Anorg. Allg. Chem., 416 (1975) 311.

10 W.A. Schlenk and M. Schmidt, Naturwissenschaften, 58 (1971) 96.

11 H.G. Raubenheimer, S. Lotz, H.W. Viljeon, and A.A. Chalmers, J. Organomet. Chem., 152 (1978) 73.

12 G.M. Pring, Ph. D. Thesis, University of Exeter, 1981.

13 D.A. Kleier and G. Binsch, DNMR3 Program 165, Quantum Chemistry Program Exchange, Indiana University, USA, 1970.

14 G. Binsch and H. Kessler, Angew. Chem., Int. Ed. Engl., 19 (1980) 411.

15 E.W. Abel, I. Moss, K.G. Orrell, K.B. Qureshi, V. Šik and D. Stephenson, J. Chem. Soc., Dalton Trans., (1988) 1489.