Stereochemical Rigidity of the Square-pyramidal W(CO)$_5$ Moiety during 1,2- and 1,3-Metallotropic Shifts in Sulphur Ligand Complexes

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N.m.r. studies of tungsten pentacarbonyl complexes of type [W(CO)$_5$L] where L refers to open-chain ligands ($PhCH_2SSCH_2Ph$ or $MeSCH_2SMe$) and cyclic ligands (β-SCHMeSCHMeSCHMe, or $SCMe_2SCH_2CH_2$) have revealed no evidence of carbonyl scrambling accompanying the tungsten–sulphur 1,2- or 1,3-metallotropic shifts. This implies stereochemical rigidity of the square-pyramidal W(CO)$_5$ moiety, on the two-dimensional ^{13}C n.m.r. time-scale, during these intersulphur–metal commutations, energy barriers ($\Delta G^{\ddagger}$) for any carbonyl rearrangement being in excess of *ca.* 90 kJ mol^{-1}. The results further indicate that the metallotropic shifts involve lateral movements of the rigid W(CO)$_5$ moieties with no tendency to distort to seven-co-ordinate tungsten(0) species in the transition states.

The discovery of the widespread occurrence of metal carbonyl scrambling in organometallic chemistry has been largely the outcome of ^{13}C n.m.r. investigations.[1,2] In many bi-, tri-, and poly-metallic compounds, carbonyl exchange between bridging and terminal sites often occurs with ease by a variety of mechanisms most of which can be conveniently followed by standard dynamic n.m.r. techniques. Most mononuclear systems of type [M(CO)$_5$L] involving only terminal carbonyl environments appear to be stereochemically rigid at room temperature.[1] Studies above room temperature, however, are often severely restricted by the thermal instabilities of many [M(CO)$_5$L] complexes, and so the existence of slow, high-energy CO scrambling such as occurs in [W(CO)$_5$(CS)],[3] cannot be discounted with any certainty. Since two-dimensional exchange spectroscopy (2D-EXSY) spectra [4–6] are sensitive to slower dynamic exchange processes than one-dimensional bandshape n.m.r. methods, we have applied 2D-EXSY methodology [7] to a variety of [W(CO)$_5$L] complexes.

We chose to study complexes which were either previously known, or expected, to undergo metallotropic shifts, since our concern was not simply to test for the existence of CO fluxionality in [M(CO)$_5$L] systems, but to establish any correlation of CO movement within the M(CO)$_5$ moiety with metal–ligand movement. Accordingly, we have investigated the tungsten pentacarbonyl complex of dibenzyl disulphide [W(CO)$_5$($PhCH_2SSCH_2Ph$)],[8] which is known to undergo 1,2 tungsten–sulphur shifts,[8–11] the 2,4-dithiapentane complex [W(CO)$_5$($MeSCH_2SMe$)],[12,13] and the β-2,4,6-trimethyl-1,3,5-trithiane complex [W(CO)$_5$(β-SCHMeSCHMeSCHMe)],[14,15] the latter two complexes being known to undergo 1,3 tungsten–sulphur shifts.[12–18] In addition, we have examined the 2,2-dimethyl-1,3-dithiolane complex [W(CO)$_5$($SCMe_2SCH_2CH_2$)] the stereodynamics of which have not previously been established, but where a 1,3-metal shift was thought likely to occur, albeit at a slow rate due to the steric interactions of the ring methyls.

Table 1. Rate constants for the 1,2 tungsten–sulphur shift in [W(CO)$_5$($PhCH_2SSCH_2Ph$)]

T/K	Method	k/s^{-1}
353	*a*	80[b]
343	*a*	38[b]
333	*a*	15[b]
323[c]	*a*	5.0[b]
313[c]	*d*	1.82 ± 0.2
303[c]	*d*	0.51 ± 0.04
293[c]	*d*	0.154 ± 0.012

[a] One-dimensional ^{1}H bandshape analysis. [b] Uncertainty *ca.* ±10%. [c] Two-dimensional ^{13}C EXSY spectra recorded at this temperature contained no carbonyl cross-peaks. [d] Two-dimensional ^{1}H exchange spectroscopy.

Experimental

Materials.—Dibenzyl disulphide, $PhCH_2SSCH_2Ph$, was obtained commercially (BDH Ltd.). 2,4-Dithiapentane, $MeSCH_2SMe$, was prepared by a literature method,[19] as was β-2,4,5-trimethyl-1,3,5-trithiane.[20] 2,2-Dimethyl-1,3-dithiolane was prepared by treating a mixture of AnalaR acetone (7.9 g, 0.13 mol, 10 cm^3) and benzene (100 cm^3) with ethane-1,2-dithiol (1.28 g, 0.13 mol, 11.5 cm^3) in the presence of *p*-toluenesulphonic acid (0.2 g). The mixture was heated under reflux for 9 h at 65 °C, during which time water (2.1 cm^3, 0.116 mol) was collected using a Dean and Stark apparatus. The benzene was removed from the product by distillation at 80 °C, and the required product obtained by distillation of the residue under reduced pressure. Yield: 12 g, 65.9%; b.p. 50 °C, 10 mmHg (*ca.* 1 330 Pa).

The complex [W(CO)$_5$($PhCH_2SSCH_2Ph$)] was prepared by an established procedure[21] using the tungstate salt, NEt_4[W(CO)$_5$Br], in the presence of a Lewis acid.

The other three complexes were prepared in essentially the same way as follows. Tungsten hexacarbonyl (1.53 mmol) in dry tetrahydrofuran (thf) was irradiated by a Hanovia 450-W mercury lamp in a water-cooled jacket for 12 h under dry nitrogen. The yellow solution of [W(CO)$_5$(thf)] was filtered and added to the appropriate ligand (1.53 mmol) in a Schlenk tube. The mixture was stirred for 2 h at room temperature. All volatiles were removed leaving the required product. Recrystallisation was carried out from hexane with cooling to *ca.* −20 °C.

N.M.R. Spectra.—Spectra were measured using a Brüker AM250 spectrometer operating at 250.13 (^{1}H) and 62.9 MHz (^{13}C). The standard Brüker accessory was used to control and measure the probe temperatures which are accurate to ±1 °C.

Table 2. Carbon-13 carbonyl chemical shifts and ^{183}W–^{13}C coupling constants for $[W(CO)_5L]$ complexes

	CO Axial		CO Equatorial	
L	δ[a]	$^1J(^{183}W-^{13}C)$/Hz	δ	$^1J(^{183}W-^{13}C)$/Hz
$PhCH_2SSCH_2Ph$	200.10	160.5	196.68	129.5
$MeSCH_2SMe$	199.98	157.8	197.09	128.8
SCHMeSCHMeSCHMe	199.02	156.9	196.83	128.9
$SCMe_2SCH_2CH_2$	199.52	*b*	196.75	129.4

[a] Relative to $SiMe_4$. Solvent, $CDCl_3$. [b] Satellites not detected.

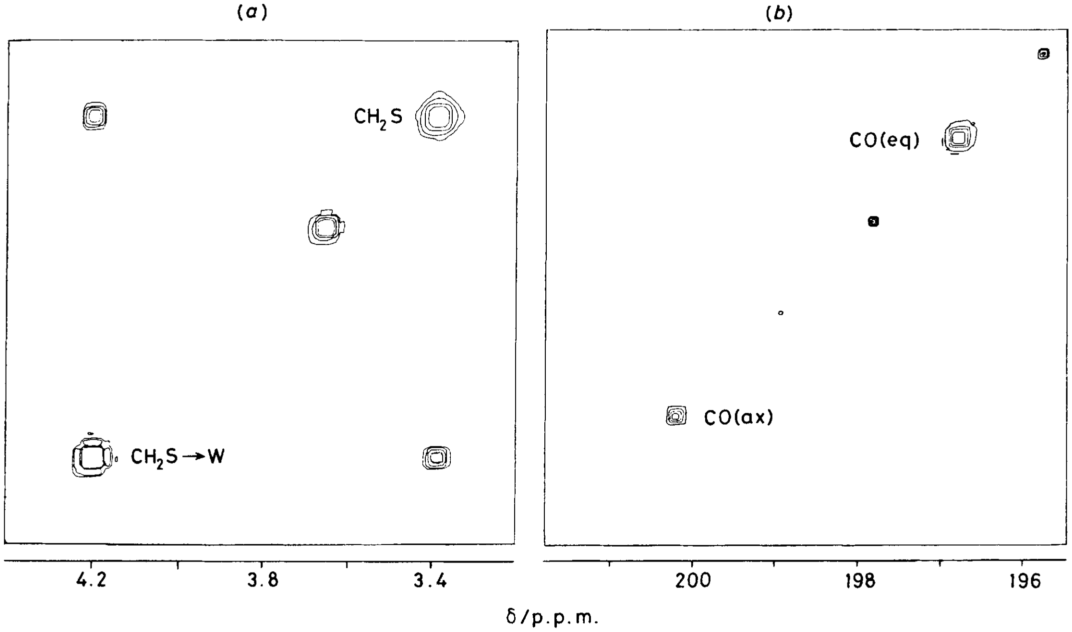

Figure 1. Two-dimensional EXSY spectra of $[W(CO)_5(PhCH_2SSCH_2Ph)]$ in $CDCl_3$ at 303 K. (*a*) Proton n.m.r. spectrum of methylene signals, τ_m = 0.5 s. Signal at δ 3.66 is due to free-ligand impurity. (*b*) ^{13}C-$\{^1H\}$ N.m.r. spectrum of carbonyl signals, τ_m = 2 s, showing the absence of CO cross-peaks

Two-dimensional ^1H and ^{13}C-$\{^1H\}$ EXSY spectra were obtained using the Brüker automation program NOESY. An initial relaxation delay of 3 s and a mixing time of 1—2 s was employed for all the ^{13}C EXSY experiments. Mixing times for the ^1H EXSY experiments were in the range 0.1—1 s because of the wide temperature range used. The F_1 data table for ^{13}C contained 64 words and for ^1H spectra 128 words, both being zero-filled to 512 words. For all experiments the F_2 domain contained 1 024 words, and was not zero-filled. Data were Fourier transformed using a Gaussian window function of 0.5 Hz and magnitude spectra calculated. For ^1H two-dimensional spectra, four scans per experiment were used, giving a total experimental time of *ca.* 40 min; for ^{13}C two-dimensional spectra, 144 scans per experiment were employed, resulting in a total experimental time of *ca.* 15 h. Rate constants and their uncertainties were calculated from two-dimensional signal intensities using the previously described D2DNMR program.[7]

Results

$[W(CO)_5(PhCH_2SSCH_2Ph)]$.—This complex undergoes 1,2 tungsten–sulphur shifts as revealed by its ^1H one-dimensional spectra in the temperature range 323—353 K. The methylene region consists of two signals (δ 3.4 and 4.2) which underwent exchange broadening on raising the temperature. Bandshape fittings were performed in the usual way.[8] Two-dimensional ^1H EXSY spectra were then obtained at temperatures down to 293 K in order to extend the temperature range in which rate constants for the 1,2-shift process were calculated (Table 1). The 2D-EXSY spectrum at 303 K of the methylene signals obtained with a mixing time (τ_m) of 0.5 s is shown in Figure 1. An Eyring plot of the results gave a $\Delta G^\ddagger$ (298.15 K) value of 76.00 ± 0.09 kJ mol^{-1} which compares closely to the value of 74.2 ± 0.02 kJ mol^{-1} obtained previously[10] for the related complex $[W(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$.

In order to obtain high-quality two-dimensional ^{13}C-$\{^1H\}$ EXSY spectra of $[W(CO)_5(PhCH_2SSCH_2Ph)]$ the complex was prepared from ^{13}CO-enriched hexacarbonyltungsten. From the relative intensities of the individual components of the ^{13}C carbonyl signals, arising from singly and multiply labelled ^{13}CO species ($^2J_{CC}$ ~ 2.5 Hz), the sample was assessed to have a 27% enrichment of ^{13}CO. High-sensitivity ^{13}C-$\{^1H\}$ EXSY spectra of the carbonyl region were recorded in the temperature range 293—323 K. In all cases two diagonal carbonyl signals

Table 3. Values of $\Delta G^{\ddagger}$ for fluxional processes in $[W(CO)_5L]$ complexes

L	W–S shift/ kJ mol^{-1}	Carbonyl scrambling[a]/ kJ mol^{-1}
$PhCH_2SSCH_2Ph$	76.00 ± 0.09[b]	>90
$MeSCH_2SMe$	84.65 ± 0.66[c]	>89
SCHMeSCHMeSCHMe	68.47 ± 0.02[d]	>86
$SCMe_2SCH_2CH_2$	77.75 ± 0.46	>86

[a] Lower limiting values; $\Delta S^{\ddagger}$ values assumed zero. [b] Ref. 8. [c] Ref. 12. [d] Ref. 14.

with ^{183}W satellites were detected due to the *cis*(equatorial) and *trans*(axial) carbonyls (Table 2) but no carbonyl cross-peaks were observed, even using relatively long mixing times. The spectrum at 303 K (Figure 1) using a mixing time of 2 s illustrates this point. At this and other temperatures in the range 293—323 K the rates of 1,2-metal shifts are appreciable (Table 1), and intense carbonyl cross-peaks would have been produced if correlated CO scrambling were occurring. The absence of such cross-peaks implies not only that the 1,2-metal commutation is not correlated with any tungsten carbonyl movement, but that the $M(CO)_5$ unit itself is remarkably rigid, any *cis–trans* CO exchange being too slow on the two-dimensional ^{13}C n.m.r. time-scale for detection. From the conditions used to obtain the 2D-EXSY spectra, rate constants for any CO scrambling in the temperature range 293—323 K would have to be $< 10^{-2}$ s^{-1} and the activation energy ($\Delta G^{\ddagger}$) for the process >90 kJ mol^{-1} (Table 3).

$[W(CO)_5(MeSCH_2SMe)]$.—A previously published[12] bandshape analysis of the one-dimensional ^1H spectrum of this complex yielded a $\Delta G^{\ddagger}$ (298.15 K) value for the 1,3-tungsten shift of 84.65 ± 0.66 kJ mol^{-1} (Table 3). 2D-EXSY experiments were performed at 297 and 313 K on the methyl protons and on the carbonyl carbons. At both temperatures cross-peaks were detected between the two methyl signals giving rate constants for the 1,3-metal shift of 0.013 s^{-1} at 297 K and 0.127 s^{-1} at 313 K. The $\Delta G^{\ddagger}$ value calculated from these two data points was found to be 83.4 kJ mol^{-1} in good agreement with the bandshape-analysis results. The reliability of the 2D-EXSY approach to the dynamic problem is thus confirmed. However, at neither temperature were cross-peaks detected between the axial and equatorial carbonyl carbons. Assuming a rate of 10^{-2} s^{-1} or more could be detected by these ^{13}C EXSY experiments, any carbonyl scrambling in the $W(CO)_5$ moiety must be associated with a $\Delta G^{\ddagger}$ value of >89 kJ mol^{-1}.

$[W(CO)_5(SCHMeSCHMeSCHMe)]$.—Proton bandshape analysis of this complex in the approximate temperature range −10 to 60 °C gave a $\Delta G^{\ddagger}$ (298.15 K) value of 68.5 kJ mol^{-1}. A ^{13}C 2D-EXSY experiment at 303 K on the carbonyl region showed no evidence of axial–equatorial CO exchange, again indicating high rigidity of the $W(CO)_5$ moiety even in the transition states associated with the 1,3 tungsten–sulphur shifts.

$[W(CO)_5(SCMe_2SCH_2CH_2)]$.—This newly synthesised complex has recently been investigated by variable-temperature ^1H n.m.r. spectroscopy. A total bandshape analysis of the methylene region, to be reported more fully elsewhere,[22] established the existence of inversion of the co-ordinated sulphur atom at below-ambient temperatures and 1,3-tungsten–sulphur shifts at above-ambient temperatures. Rate constants for the 1,3-metal shift process were measured for the temperature range 323—363 K. From these data the rate constant at ambient temperature (303 K) was predicted to be 0.26 s^{-1}. If any correlated CO scrambling were occurring during this 1,3-shift process, then this would be clearly displayed in a ^{13}C 2D-EXSY spectrum at 303 K of the carbonyl region. When such an experiment was performed, no carbonyl cross-peaks were observed, confirming again the rigidity of the $M(CO)_5$ moiety, this time when it forms part of a fluxional five-membered ring complex.

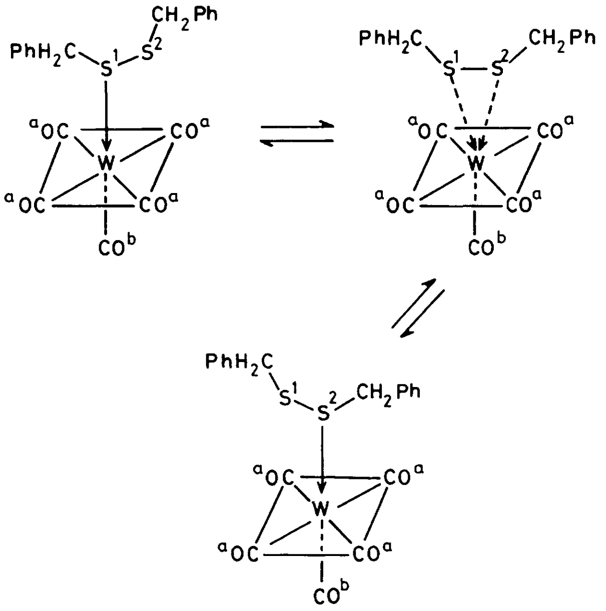

Figure 2. The 1,2-metallotropic shift of $[W(CO)_5(PhCH_2SSCH_2Ph)]$ showing the proposed intermediate structure

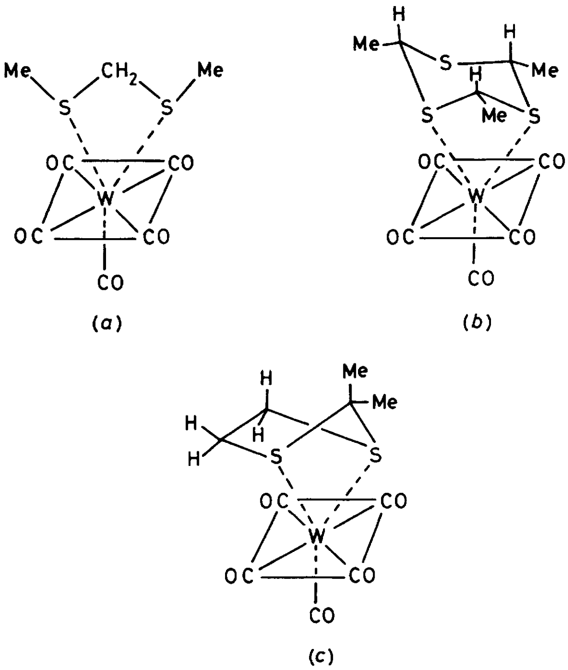

Figure 3. Proposed intermediate structures for the 1,3-metallotropic shifts of (*a*) $[W(CO)_5(MeSCH_2SMe)]$, (*b*) $[W(CO)_5(SCHMeSCHMeSCHMe)]$, and (*c*) $[W(CO)_5(SCMe_2SCH_2CH_2)]$

Discussion

The absence of any carbonyl cross-peaks in the ^{13}C 2D-EXSY spectra of the four complexes studied indicates the high degree of stereochemical rigidity of these $[W(CO)_5L]$ complexes. The absence of any tendency for carbonyl–ligand exchange in these complexes parallels the work of Darensbourg and co-workers[23–25] which has established that *cis–trans* isomerism of selectively ^{13}CO-labelled complexes of type $[M(CO)_5(PR_3)]$ (R = OMe or Ph) occurs at rates of *ca.* 10^{-5} s^{-1}. Such slow rates, which were measured by time-dependent ^{13}C n.m.r. spectroscopy, were attributed to a non-dissociative intramolecular rearrangement of these 18-electron $[M(CO)_5L]$ species, *via* either a trigonal-prismatic or bicapped tetrahedron intermediate or transition state, with the M–L bond remaining intact.

Our n.m.r. results extend this description a stage further by implying that, for tungsten–sulphur complexes at least, even when the nature of the W–S bonding is altered during an intramolecular 1,2- or 1,3-metallotropic shift, the $W(CO)_5$ group remains rigid. The square-pyramidal geometry of $W(CO)_5$ in these circumstances therefore appears to be intrinsically very stable, as has been predicted by crystal field stabilisation energy or molecular orbital stabilisation energy arguments,[26] with no tendency to distort to a highly fluxional, formally seven-co-ordinate species at the transition state of the 1,2- or 1,3-metallotropic shift. Suggested transition-state structures for the four complexes are shown in Figures 2 and 3.

Furthermore, it is evident that the $W(CO)_5$ group remains bonded to the ligand in some formal sense throughout the metal-shift processes. There is no indication of the intermediacy of a 'naked' $W(CO)_5$ moiety[27] which would be expected to be fluxional *via* a trigonal-bipyramidal geometry in a manner analogous to pentacarbonyliron.[27] The 1,2- and 1,3-metallotropic shifts described here may therefore be described as lateral movements of a rigid square-pyramidal $W(CO)_5$ unit relative to the sulphur ligand. The case of $[W(CO)_5(PhCH_2SSCH_2Ph)]$ is depicted in Figure 2, where the CO labelling implies retention of axial–equatorial CO distinction throughout the process. No distinction between the four equatorial CO groups is implied, and indeed this was never observed, presumably due to rapid rotation of the ligand about the W–S bond in all cases.

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