

Stereochemical Rigidity of the Square Pyramidal $W(CO)_5$ Moiety During 1,2-Metallotropic Shifts in Disulphide Complexes

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N.m.r. studies of the complex $[W(CO)_5(PhCH_2SSCH_2Ph)]$ have revealed the absence of any carbonyl group scrambling accompanying the tungsten-sulphur 1,2-metallotropic shift; this implies stereochemical rigidity, on the two-dimensional ^{13}C dynamic n.m.r. timescale, of the square pyramidal $W(CO)_5$ unit during these intersulphur metal commutations.

Metal carbonyl scrambling is a widespread fluxional phenomenon in organometallic chemistry, and has been extensively studied by ^{13}C n.m.r. spectroscopy.^{1,2} In general, it occurs with ease in many bi-, tri-, and poly-metallic systems by a variety of mechanisms, most of which may be conveniently followed by standard dynamic n.m.r. techniques. Mononuclear systems of the type $[M(CO)_5L]$ do, however, appear to be stereochemically rigid at room temperature.¹ Nevertheless, since studies above ambient temperature have been limited by the thermal instabilities of many of the complexes, the existence of very slow high-energy carbonyl scrambling, such as occurs in $[W(CO)_5CS]$,³ cannot be discounted. We have now examined whether two-dimensional ^{13}C n.m.r. exchange spectroscopy can reveal carbonyl group scrambling in a $[M(CO)_5L]$ system at a rate too slow to produce exchange broadening in its one-dimensional n.m.r. spectra.

We chose to study $[W(CO)_5(PhCH_2SSCH_2Ph)]$ since we wished to test, not simply for the existence of CO fluxionality, but also for any correlation of such fluxionality inside the $M(CO)_5$ moiety with the 1,2-metal commutation known to occur in such disulphide complexes.⁴ The complex was prepared by an established procedure,⁵ and initially studied by one-dimensional 1H n.m.r. spectroscopy at a variety of temperatures between 323 and 353 K. The methylene region of the spectrum revealed two sharp signals (δ 3.40 and 4.20; solvent $CDCl_3$) at 303 K which underwent exchange broadening at higher temperatures owing to the 1,2-tungsten sulphur shift. Bandshape fittings were obtained in the usual way, and rate constants obtained (Table 1). Two-dimensional (2D) 1H

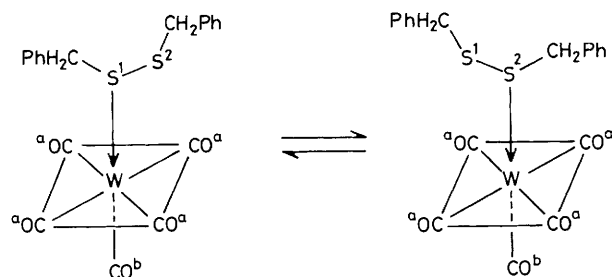
NOESY (EXSY)⁶ spectra obtained at below-ambient temperatures extended the range over which reliable k values could be computed. The resulting value of ΔG^\ddagger (298.15 K) for the 1,2-shift process was 76.00 ± 0.09 kJ mol⁻¹ which compared closely with the value of 74.2 ± 0.02 kJ mol⁻¹ previously obtained⁴ for the related complex $[W(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$.

In order to obtain 2D ^{13}C - $\{^1H\}$ EXSY spectra of $[W(CO)_5(PhCH_2SSCH_2Ph)]$, the complex was prepared from ^{13}C enriched hexacarbonyltungsten. Our disulphide complex contained a 27% enrichment of ^{13}C , this being assessed from the relative intensities of the individual components of

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

<i>T</i> /K	Method	<i>k</i> /s ⁻¹
353	1D-BS ^a	80
343	1D-BS	38
333	1D-BS	15
323 ^c	1D-BS	5.0
313 ^c	2D-EXSY ^b	1.82
303 ^c	2D-EXSY	0.51
293 ^c	2D-EXSY	0.154

^a One-dimensional bandshape analysis. ^b Two-dimensional exchange spectroscopy. ^c Two-dimensional ^{13}C -EXSY spectra recorded at these temperatures contained *no* carbonyl cross-peaks.



Scheme 1

the ^{13}C carbonyl signals, due to singly and multiply labelled ^{13}CO species ($^2J_{\text{CC}} \approx 2.5$ Hz). High quality $^{13}\text{C}\{-^1\text{H}\}$ EXSY spectra of the complex in the range 293 to 323 K consisted of diagonal carbonyl signals at δ 196.68 [$^1J(^{183}\text{W}\text{-}^{13}\text{C})$ 129.5 Hz] and 200.10 [$^1J(^{183}\text{W}\text{-}^{13}\text{C})$ 160.5 Hz] due to *cis*- and *trans*-carbonyl groups respectively, but contained no carbonyl cross-peaks. At these temperatures the rates of the 1,2-metal shifts were appreciable (Table 1), and intense carbonyl cross-peaks would have been produced if correlated CO scrambling was occurring during the process. The absence of such cross-peaks thus showed not only that the 1,2-shift fluxion was not correlated with any metal carbonyl movement, but that the $[\text{M}(\text{CO})_5]$ unit itself was remarkably rigid, any *cis*-*trans*-CO exchange being too slow on the 2D ^{13}C dynamic n.m.r. time-scale for detection. From the conditions used to obtain the 2D EXSY spectra,⁶ it is estimated that any rate constants for CO scrambling in the temperature range 293 to 323 K would have to be $<10^{-2} \text{ s}^{-1}$ and ΔG^\ddagger for the process $>90 \text{ kJ mol}^{-1}$.

This result is compatible with the work of Darensbourg *et al.*⁷⁻⁹ which has established that the *cis*-*trans*-isomerism of selectively ^{13}C labelled complexes $[\text{M}(\text{CO})_5\text{PR}_3]$ occurs at rates of the order of 10^{-5} s^{-1} . Such slow rates, which were measured⁹ by time-dependent ^{13}C n.m.r. studies, were attributed to a non-dissociative, intramolecular rearrangement of these 18-electron $[\text{M}(\text{CO})_5\text{L}]$ complexes, in which the M-L bond remains intact.

Our results, however, imply that even when the M-L bond is broken in an intramolecular metallotropic shift the $\text{M}(\text{CO})_5$ group remains rigid. Thus the square pyramidal geometry of $\text{M}(\text{CO})_5$ in these circumstances is intrinsically very stable,¹⁰ with no tendency to distort to a highly fluxional, formally seven-co-ordinate species at the transition state of the 1,2-metallotropic shift. Similarly it can be argued that there is no indication of the intermediacy of a 'naked'¹¹ $\text{W}(\text{CO})_5$ moiety, which would be expected here to be fluxional *via* a trigonal bipyramidal geometry in a manner analogous to pentacarbonyliron.¹²

The 1,2-metallotropic shift is thus the lateral movement of a rigid square pyramidal $\text{M}(\text{CO})_5$ unit relative to the ligand (Scheme 1). This conclusion, in addition to casting further light on the intramolecular nature of these 1,2-metallotropic shifts, has important mechanistic implications in metal carbonyl chemistry.

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