Proton Nuclear Magnetic Resonance Study of Electronic Transmission Effects and Fluxional Behaviour in Aryldiazenidotris(dimethyldithiocarbamato)molybdenum

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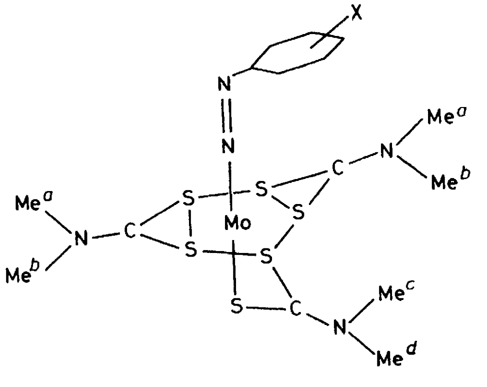
The rate of *N*-methyl exchange in a series of aryldiazenidomolybdenum complexes has been studied by ^{1}H n.m.r. spectroscopy as a function of temperature and of substitution in the aromatic ring. The results indicate a fluxional rearrangement characterised by a single first-order rate constant. The aromatic-substituent effect shows a better Hammett correlation with σ than with σ^+ values. The ρ factor is -0.64. Implications for the geometry of the system are discussed.

We have recently prepared a long series of aryldiazenido-complexes of molybdenum, $[Mo(N_2R)(S_2CNMe_2)_3]$ (R = aryl).[1] These complexes are seven-co-ordinate, and have a pentagonal-bipyramidal structure in the solid state as represented below.[2] The complex $[TiCl(S_2CNMe_2)_3]$ has an analogous structure and is fluxional in solution down to −90 °C,[3] but an extended study of the temperature dependence of the ^{1}H n.m.r. spectrum of $[Mo(NO)(S_2CNMe_2)_3]$ has been reported[4] and the spectral properties are rather similar to those of the diazenido-complexes discussed below.



A non-fluxional structure such as that shown would be expected to have four different kinds of methyl group, *a*—*d*, present in the ratio 2 : 2 : 1 : 1, and indeed in the ^{1}H n.m.r. spectrum at low temperatures, in the appropriate solvent, four singlet resonances in the ratio 1 : 2 : 1 : 2 assignable to the methyl protons are usually observed. The spectra are, however, temperature and solvent dependent, and as the temperature is increased the methyl spectrum changes in a fashion indicating interchange of methyl-group positions (see Figure 1). At sufficiently high temperatures the methyl-proton resonances collapse to a single peak, at which point the exchange process or processes cause(s) all the methyl groups to experience the same time-averaged chemical shift. Further, the rate of interchange is dependent on the substituent X in the aryl group C_6H_4X. Now the mechanism of methyl-group interchange could be one or more of several processes. For example, the groups *a* and *b* could interchange by rotation about the C–N bonds. This process would cause partial collapse of the methyl-proton spectrum, but is insufficient to reduce it to a single peak. Interchange of the dithiocarbamate groups themselves would cause general scrambling of all the methyl groups, and could result in the observation of a single signal attributable to all the methyl groups in the ^{1}H n.m.r. spectrum. Such an interchange could proceed (*i*) through complete dissociation of a S_2CNMe_2 or of a diazenide ligand from the complex, or (*ii*) through a S_2CNMe_2 ligand becoming unidentate in the transition state, thus allowing the remaining S_2CNMe_2 ligands to rearrange themselves, or (*iii*) through a fluxional rearrangement of bidentate S_2CNMe_2 ligands. This study was undertaken in order to clarify the mechanism of rearrangement and to determine the mode of transmission of substituent effects.

RESULTS AND DISCUSSION

(*a*) *Solvent Dependence.*—The ^{1}H n.m.r. spectrum of $[Mo(N_2Ph)(S_2CNMe_2)_3]$ in nitrobenzene at 15 °C shows the 1 : 2 : 1 : 2 pattern in the S_2CNMe_2 methyl region consistent with the pentagonal-bipyramidal structure (Table 1). However, in other solvents, the spectrum can be very different. A selection of spectra of $[Mo(N_2C_6H_4NO_2\text{-}m)(S_2CNMe_2)_3]$ in various solvents measured at −3 °C is shown in Figure 2. In both

Table 1

Hydrogen-1 n.m.r. spectra of $[Mo(N_2C_6H_4X)(S_2CNMe_2)_3]$ in the methyl region [a]

X	Shift (τ) and assignment [b]
m-NO_2	6.52 (*cd*), 6.57 (*ab*), 6.68 (*cd*), 6.76 (*ab*) [c]
p-NO_2	6.49 (*cd*), 6.61 (*ab*), 6.71 (*cd*), 6.79 (*ab*)
p-Cl	6.52 (*cd*), 6.66 (*ab*), 6.71 (*cd*), 6.82 (*ab*)
H	6.54 (*cd*), 6.68 (*ab*), 6.72 (*cd*), 6.87 (*ab*)
p-Me	6.50 (*cd*), 6.66 (*ab*), 6.70 (*cd*), 6.84 (*ab*), 7.56 (*p*-Me)
p-OMe	6.52 (*cd*), 6.67 (*ab*), 6.69 (*cd*), 6.85 (*ab*), 6.20, 6.21 (*p*-OMe)

[a] All the spectra were run in nitrobenzene solution at 15 °C with tetramethylsilane as internal standard. [b] See diagram for significance of *a*—*d*. [c] A spectrum run on a sample diluted two-fold gave the same chemical shifts.

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[1] M. W. Bishop, G. Butler, J. Chatt, J. R. Dilworth, and G. J. Leigh, *J.C.S. Dalton*, in the press.

[2] G. Butler, J. Chatt, G. J. Leigh, A. R. P. Smith, and G. Williams, *Inorg. Chim. Acta*, 1978, **28**, L165; M. G. B. Drew, *Progr. Inorg. Chem.*, 1977, **23**, 67.

[3] A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark, and S. H. Strauss, *Inorg. Chem.*, 1974, **13**, 886.

[4] R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. M. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 994.

nitrobenzene and benzonitrile the pentagonal-bipyramidal structure is indicated. In CD_3CN the spectrum is a 1 : 1 doublet which could indicate an end-capped trigonal-prismatic structure, although such a stereochemistry is very rare, even in the solid state.[5] In C_5D_5N, $CDCl_3$, CD_2Cl_2, and $(CD_3)_2CO$ a multiplet, *ca.* 1 : 2 : 3, is observed. On warming the $(CD_3)_2CO$ solution from −3 to 28 °C the spectrum changes *via* the 1 : 2 : 3 multiplet to the doublet, suggesting that the different solvents are enforcing configurations of different energies.

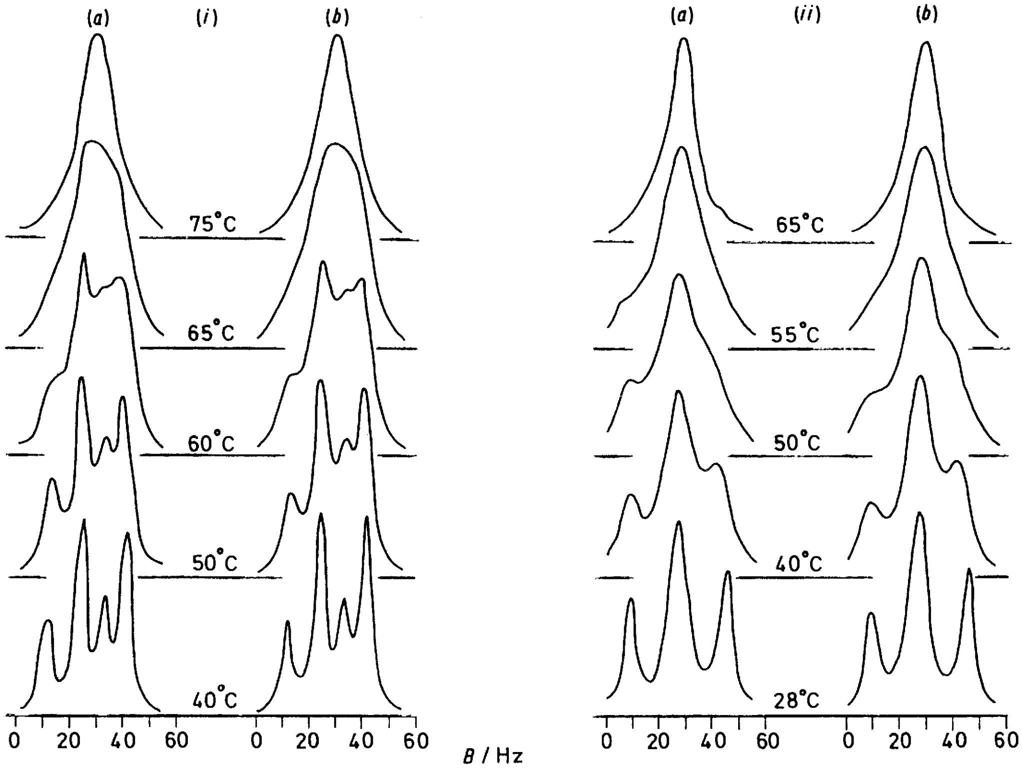

FIGURE 1 Examples of experimental (*a*) and calculated (*b*) exchange-broadened methyl-proton signals for (*i*) the complex with highest free energy of activation (*p*-NO_2 substituent), and (*ii*) for the complex with lowest free energy of activation (*p*-OMe substituent). The spectra are reproduced from ICL 1934 type 2 graph-plotter output

TABLE 2

Solvent properties and the effect on the ^1H n.m.r. spectrum of $[Mo(N_2C_6H_4NO_2\text{-}m)(S_2CNMe_2)_3]$

Solvent	Qualitative order of ease of methyl interchange [a]	Solvent viscosity (cP) [b]	Donor number [c]	Acceptor number [c]	Dielectric constant [d]
$PhNO_2$	1	2.03 (20)	4.4	14.8	34.8
PhCN	2	1.24 (25)	11.9	15.5	25.2
C_5D_5N	3	0.97 (20)	33.1	14.2	12.3
$CDCl_3$	4	0.58 (20)		23.1	4.8
$(CD_3)_2CO$	5	0.32 (25)	17.0	12.5	20.7
CD_2Cl_2	6	0.39 (30)		20.4	9.1
CD_3CN	7	0.35 (25)	14.1	18.9	38.0

[a] Judged from the form of the ^1H n.m.r. spectrum (see text); $PhNO_2$ is slowest. [b] The temperature (in °C) is given in parentheses. 1 P = 10^{-1} Pa s. [c] V. Gutmann, *Electrochim. Acta*, 1970, **21**, 661. [d] From 'Handbook of Chemistry and Physics,' 55th edn., ed. R. C. Weast, Chemical Rubber Company, Cleveland, Ohio, 1974, E-55.

Neither pyridine nor acetonitrile form stable solvates when the complexes are recrystallised from them. This suggests no strong solvent–metal interaction. Treatment with PMe_2Ph in toluene did not lead to an adduct. In contrast, $[Ru(S_2CNMe_2)_3]$ does react with NO to form $[Ru(S_2CNMe_2)_3(NO)]$ in which one S_2CNMe_2 is unidentate.[6] The oxidation potential of $[Mo(N_2C_6H_4NO_2\text{-}m)(S_2CNMe_2)_3]$ in dimethylformamide solution is not affected by the addition of pyridine. Thus there is little direct evidence apart from the ^1H n.m.r. spectra for solvent interaction and the best correlation with any solvent property appears to be that with viscosity (Table 2). Therefore the solvent–complex interaction probably consists of a physical interaction, and not a chemical bonding, and an interpretation in

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[5] R. Hofmann, B. F. Beier, E. R. Muetterties, and A. R. Rossi, *Inorg. Chem.*, 1977, **16**, 511.

[6] L. Combi and L. Malatesta, *Rend. Inst. Lombardo Sci.*, 1938, **71**, 118; A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 1966, 476.

terms of different configurations is probably premature.

(*b*) *Temperature Dependence*.—The ^1H n.m.r. spectra of a series of complexes $[Mo(N_2C_6H_4X)(S_2CNMe_2)_3]$ ($X = p$-Cl, H, *p*-Me, *p*-OMe, *p*-NO_2, or *m*-NO_2) were obtained from solutions in nitrobenzene over the range 40—90 °C.

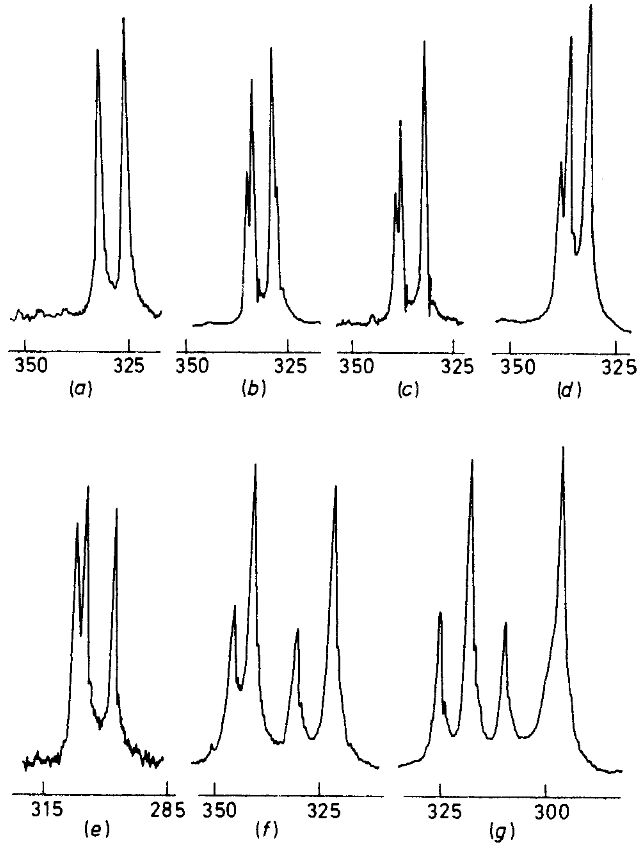

FIGURE 2 Hydrogen-1 n.m.r. spectra of the methyl region of $[Mo(N_2C_6H_4NO_2\text{-}m)(S_2CNMe_2)_3]$ in various solvents at −3 °C: (*a*) CD_3CN, (*b*) CD_2Cl_2, (*c*) $(CD_3)_2CO$, (*d*) $CDCl_3$, (*e*) C_6D_5N, (*f*) $PhNO_2$, and (*g*) PhCN. Shifts in Hz measured at 100 MHz, downfield from $SiMe_4$

In the case of one complex ($X = m$-NO_2) the spectra were repeated on 50% dilution of the original sample. The line shape at a given temperature was unchanged, confirming our expectation that the rearrangement process(es) were kinetically first order, and also showing that the chemical shifts were not significantly altered on dilution.

Details of computer simulation of the spectra are given in the Experimental section and examples of calculated and experimental spectra are shown in Figure 1. Chemical shifts were not varied during the iteration, and were selected on a trial-and-error basis. This presented no problem except for high-temperature spectra consisting of a single, broadened, featureless line, for which the combination of shift differences and rate constant giving a satisfactory fit is not unique. However, no significant (⩾0.5 Hz) variation of chemical shifts with temperature was found either from exchange-broadened spectra with multiplet structure, or from slow-exchange spectra at still lower temperatures (0—20 °C). The invariance with temperature was therefore reasonably assumed to apply to the high-temperature spectra also. Table 1 shows the observed chemical shifts.

TABLE 3

Thermodynamic and Arrhenius activation parameters

Aryl substituent	$\Delta G^\ddagger$/ kJ mol^{-1} [a,b]	$\Delta S^\ddagger$/ J K^{-1} mol^{-1} [b]	$E^\ddagger$/ kJ mol^{-1}
p-OMe	73.2 ± 0.2	−11 ± 30	72 ± 10
p-Me	73.9 ± 0.2	17 ± 30	82 ± 10
H	74.1 ± 0.2	10 ± 30	80 ± 10
p-Cl	75.4 ± 0.2	69 ± 30	100 ± 10
m-NO_2	77.2 ± 0.2	18 ± 30	86 ± 10
p-NO_2	77.4 ± 0.2	8 ± 30	83 ± 10

[a] $\Delta G^\ddagger$ for $[Mo(S_2CNMe_2)_3(NO)]$ has been reported to be 77.5 ± 0.8 kJ mol^{-1}, although a dissociative path is preferred for its apparently similar rearrangement.[4] [b] At 50 °C.

In every case (both of complex and of temperature) it was found possible to reproduce closely the appearance of the experimental spectrum by assuming a single constant *k* (reciprocal mean lifetime) for the interchange of all the pairs of methyl groups. The Arrhenius plots (see Figure 3) are linear within experimental error, as required for a single kinetic process. Thermodynamic and Arrhenius activation parameters are given in Table 3. Despite the large estimated error in the entropies of activation, the equality of these to zero within experimental error militates against the dissociative mechanisms, and is in best accord with the fluxional rearrangement (*iii*).

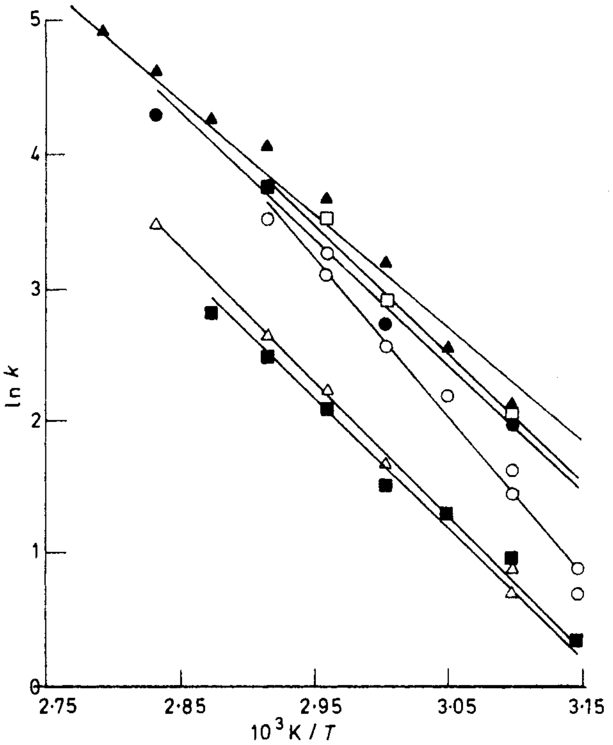

FIGURE 3 Arrhenius plots for the six compounds $[Mo(N_2C_6H_4X)(S_2CNMe_2)_3]$: $X = p$-OMe (▲), *p*-Me (□), H (●), *p*-Cl (○), *m*-NO_2 (△), and *p*-NO_2 (■). The lines for each complex are linear least-squares regression lines through the rate data

Furthermore, since mechanisms (*i*) and (*ii*) would probably lead to faster exchange averaging between the Me^c and Me^d signals than between other pairs, we interpret our results as evidence for the simultaneous fluxional exchange of all three dithiocarbamate ligands, *i.e.* mechanism (*iii*).

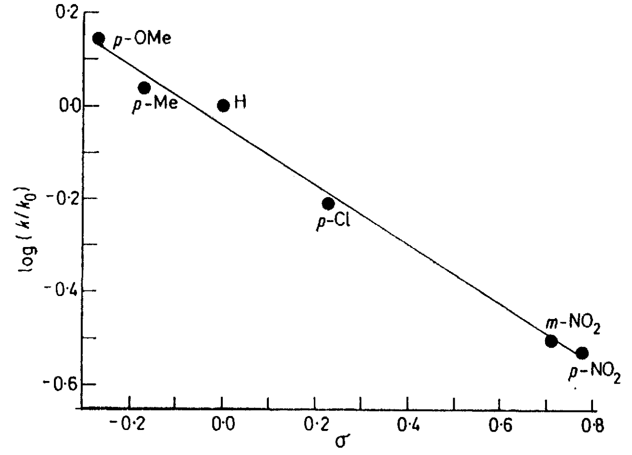

FIGURE 4 Plot of log (k/k_0) *versus* σ at 50 °C showing the linear least-squares regression line

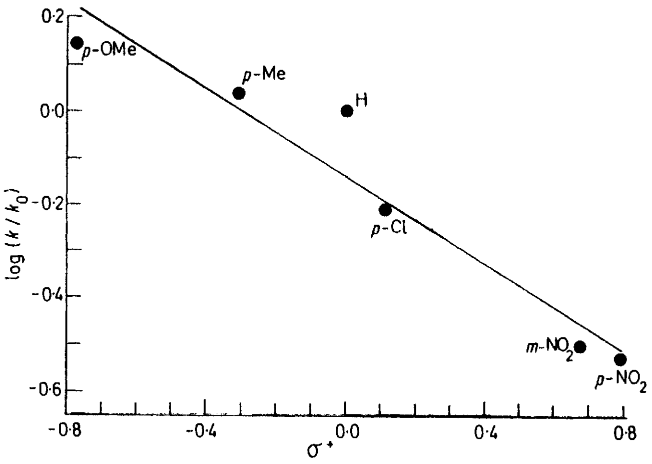

FIGURE 5 Plot of log (k/k_0) against σ^+ at 50 °C showing the linear least-squares regression line

Inspection of the Arrhenius plots and Table 3 shows a clear substituent effect on the free energy of activation, although partition of this between enthalpy and entropy terms is uncertain (variation of $\Delta S^‡$ alone would require parallel Arrhenius plots, whereas that of $\Delta H^‡$ or $E^‡$ alone would require convergence of such plots at $T^{-1} = 0$). The apparently anomalous gradient of the plot for the *p*-chlorophenyl complex is not regarded as proven beyond experimental error. In an attempt to rationalise the substituent effects, Hammett plots of log (k/k_0) (where k_0 = the rate constant for the unsubstituted compound, R = Ph) against both σ and σ^+ substituent constants[7] have been constructed (Figures 4 and 5). The rate constants used are those at 50 °C from the best-fit Arrhenius plots. In that region all the spectra are significantly broadened, yet retain some structure so that the values are the most reliable. The computed least-squares linear fit is shown both for the σ and σ^+ plots, and is clearly better for σ (correlation coefficient, $r = -0.996$) than for σ^+ ($r = -0.962$). The reaction constant, from the gradient of the former graph ($\rho = -0.64$), indicates a rather small substituent effect, the rearrangement being facilitated by electron-releasing, and retarded by electron-withdrawing, groups. The magnitude and sign of ρ indicates a small degree of positive-charge formation at the reaction site during rearrangement. σ^+ constants refer to reactions in which generation of a positive charge at the reaction site is facilitated by resonance interaction with the aromatic ring. On the other hand the normal σ constants are derived from ionisation of the corresponding benzoic acids, in which the electronic effects of the substituent are both mesomeric and inductive within the aromatic ring, but are relayed to the side chain containing the reaction site by an inductive mechanism alone. The linearity of an experimental σ plot therefore indicates that the substituent effect is entirely inductive, even though the metal atom is formally conjugated to the aromatic ring *via* the azo double bond.

We have considerable evidence to show that this is indeed so. For example, the oxidation potentials for the process (1) also correlate with the inductive Hammett σ.[8]

$$[Mo(N_2C_6H_4X)(S_2CNMe_2)_3] - e^- \longrightarrow [Mo(N_2C_6H_4X)(S_2CNMe_2)_3]^+ \quad (1)$$

On the other hand, the ^{13}C n.m.r. chemical shifts of the S_2CNMe_2 methyl carbons are invariant and independent of X, suggesting that the influence of X does not proceed further than the molybdenum[1] where it must modify the Mo–S interactions. In the solid state the phenyl groups of both $[Mo(N_2Ph)(S_2CNMe_2)_3]$ and $[Mo(N_2C_6H_4NO_2\text{-}m)(S_2CNMe_2)_3]$ are both so twisted as to hinder conjugation between the phenyl rings and the azo-nitrogens.[2] The small ρ value, facilitation by electron release from X, and the small entropy of activation are all consistent with only a small development of charge in the transition state, which confirms that the rearrangement process does not involve dissociation (with consequent high charge separation) but is a fluxional rearrangement of the ligands. It is possible that one of the intermediate structures in the process is an end-capped trigonal prism, but further work will be required to confirm this.

EXPERIMENTAL

The preparation of compounds is described elsewhere.[1]

N.M.R. Spectra.—The spectra were obtained from a JEOL JNM-PS-100 continuous-wave spectrometer fitted with a variable-temperature proton probe. The probe temperature was monitored during each experiment using a

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[7] See, for example, T. H. Lowry and K. S. Richardson, 'Mechanism and Theory in Organic Chemistry,' Harper and Row, New York, San Francisco, and London, 1976.

[8] G. Butler, J. Chatt, G. J. Leigh, and C. J. Pickett, *J.C.S. Dalton*, in the press.

Comark 3000 digital thermometer, and the temperature found to be stable to at least the ±1 °C accuracy of the thermometer. Samples were prepared in n.m.r. tubes (outside diameter 5 mm) as saturated solutions in nitrobenzene (0.5 cm^3). The complex containing a *p*-methyl substituent dissolved very slowly at room temperature, and required mild heating to obtain sufficient concentration. In this case, spectra were obtained from a solution that was probably supersaturated. All the spectra obtained were the result of unlocked single-field sweeps of 250 s duration.

Line-shape Analysis.—The kinetic analysis was achieved *via* spectra simulation on an ICL 1904S computer using an iterative line-shape analysis program, INMR, due to W. B. Jennings.[9] Input to the program for each spectrum consisted of a trial value for the reciprocal mean lifetime, line positions in Hz relative to an arbitrary origin, the digitised experimental spectrum measured relative to the same arbitrary origin, natural linewidth in Hz for each line, and the relative population of each site. Additionally, a probability matrix, with elements representing the probability of magnetisation transfer between sites, was required. The program output consisted of a best-fit rate constant in the range one half to twice the input value, a normalised best-fit spectrum in digital form, and a measure of the quality of the fit between experimental and theoretical spectra in the form of a standard deviation. The version of INMR used in this study included a subprogram to plot the experimental and best-fit theoretical spectra on an ICL 1934 type 2 graph plotter.

We thank the S.R.C. for the award of a Studentship (to D. O.).

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[9] W. B. Jennings, *Chem. Comm.*, 1971, 867.