# The Chemistry of Cyclopentadienyl Nitrosyl and Related Complexes of Molybdenum. Part 7.[1] The Fluxional Behaviour of Bis(cyclopentadienyl)dithiocarbamatomolybdenum Complexes, and the Application of Forsén–Hoffman Spin-saturation Method to the Nuclear Magnetic Resonance Spectra of a Five-spin System

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The synthesis, and $^1$H and $^{13}$C n.m.r. spectral behaviour over a temperature range, of $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNR_2)]^+$ (R = Me or Bu$^n$) is described. The species undergo three independent fluxional processes: (*i*) 1,2 shifts of the $\sigma$-$C_5H_5$ ring; (*ii*) $\sigma$–$\eta^5$ ring interchange; and (*iii*) C–N rotation of the $S_2C$–$NR_2$ group. Using Forsén–Hoffman spin-saturation techniques, it has been shown conclusively that the rate of 1,2 shifts of the $\sigma$ ring is significantly greater than that of 1,3 shifts. The mechanisms of ring hapticity interchange, their relation to the properties of $[Mo(C_5H_5)_2(NO)X]$ (X = unidentate ligand), and the synthetic implications of the presence of $\sigma$- or $\eta^3$-$C_5H_5$ rings in such complexes are discussed.

THE bis(cyclopentadienyl) complexes $[Mo(C_5H_5)_2(NO)X]$ (X = I, Me, or $\sigma$-$C_5H_5$) [2,3] are very unusual. Naïvely, one could imagine that the two rings are $\eta^5$-bonded and, if the Mo–N–O bond system is linear (*i.e.* NO behaves as a three-electron donor), then the metal atom *formally* has a 20-electron configuration. Such a situation, in the ground state, is extremely rare in organotransition-metal chemistry, an important and well characterised exception being $[Ni(C_5H_5)_2]$ ($S = \frac{3}{2}$).

However, there are several ways in which $[Mo(C_5H_5)_2(NO)X]$ may be accommodated within the more conventional '18-electron' pattern of behaviour, and two proposals have received serious consideration. King [2]

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[1] Part 6, J. A. McCleverty and J. Williams, *Transition Metal Chem.*, 1976, **1**, 288.

[2] R. B. King, *Inorg. Chem.*, 1968, **7**, 90.

[3] F. A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, 1968, **90**, 6232.

has suggested that the compounds with X = I or Me could be formulated as [$Mo(\eta^5-C_5H_5)(\eta^3-C_5H_5)(NO)X$]. The apparent equivalence of the two cyclopentadienyl rings on the $^1H$ n.m.r. spectral time scale over a modest temperature range (−55 to 33 °C) was explained by proposing that the $\eta^3$ rings rotated rapidly about the metal–ring axis and that the $\eta^5$ and $\eta^3$ rings were rapidly interchanging their hapticity; no actual mechanism was depicted. However, Cotton and his co-workers [4] examined crystallographically the species with X = Me and $\sigma-C_5H_5$ and discovered the structural equivalence but asymmetric attachment to the metal of the two rings in question. Cotton then suggested that the rings in this structural class of complex should be designated [5,6] as four-electron donors, thereby effectively representing the complexes as [$Mo(\eta^4-C_5H_5)_2(NO)X$] (the metal thereby attaining the 18-electron configuration). The concept of tetrahapticity has been used implicitly to explain the $^1H$ n.m.r. spectral equivalence of the ring protons in [$Mo(C_5H_5)_2(NO)X$] (X = Me, X, or I) and explicitly in the proposed mechanisms whereby $\eta^5$ and $\sigma$ rings undergo hapticity interchange in [$M(C_5H_5)_4$] (M = Ti, Zr, or Hf, but not Mo) and [$Mo(C_5H_5)_3(NO)$] (*i.e.* X = $\sigma-C_5H_5$).

Our interest in bis(cyclopentadienyl)molybdenum nitrosyl complexes, and in the way in which $\sigma$–$\eta^5$ ring-interchange occurs, was stimulated by our synthesis of [$Mo(C_5H_5)_2(NO)(S_2CNMe_2)$]. This molecule was expected, and shown both spectrally [7] and *X*-ray crystallographically,[8] to contain an $\eta^5$- and a $\sigma$-ring, an $\eta^2$-dithiocarbamate ligand, and a linear Mo–N–O bond system. Accordingly, the Mo atom has, in its ground state, an 18-electron configuration. The molecule is stereochemically non-rigid and exhibits three distinct fluxional processes: one associated with the $\sigma-C_5H_5$ ring, another with $\sigma$–$\eta^5$ ring interchange, and the third with the $\eta^2-S_2CNMe_2$ group. In our preliminary communication we suggested [7] a mechanistic path whereby the two rings could undergo *site* exchange, but this fails to explain how the rings interchange their hapticity. Recently, Cotton [6] ' has proposed an ostensibly superior mechanistic path, involving an intermediate containing $\eta^4-C_5H_5$ rings and a bent Mo–N–O system, *viz.* [$Mo(\eta^5-C_5H_5{}^*)(\sigma-C_5H_5)(NO^3)(\eta^2-S_2CNMe_2)$] $\rightleftharpoons$ [$Mo(\eta^4-C_5H_5{}^*)(\eta^4-C_5H_5)(NO^1)(\eta^2-S_2CNMe)$] $\rightleftharpoons$ [$Mo(\sigma-C_5H_5{}^*)(\eta^5-C_5H_5)(NO^3)(\eta^2-S_2CNMe_2)$].†

In this paper we describe the syntheses of [$Mo(C_5H_5)_2(NO)(S_2CNR_2)$] and the related [$Mo(\eta^5-C_5H_5)(NO)(\eta^2-S_2CNR_2)X$] (X = halide), and the $^1H$ and $^{13}C$ n.m.r. spectra of the complexes over a wide temperature range. Previous work has shown [6] that metals migrate around a $\sigma$-cyclopentadienyl ring *via* 1,2 rather than 1,3 or random shifts. However, it is still possible that 1,2 shifts may be occurring faster than 1,3 shifts but at a comparable rate. In order to investigate this possibility the Forsén–Hoffman spin-saturation method,[9] which has recently been extended to pulsed Fourier-transform $^{13}C$ n.m.r. spectroscopy,[10] has been applied for the first time to a five-site exchange problem. Previously, there has only been one application [11] of this method to a multisite system, which involved only three sites. This method permits the experimental determination of each of the five possible rates, the 1,2, 1,3, 1,4, and 1,5 shifts, and the movement of the Mo atom from one side of the ring to the other. It should be noted that, since the Mo atom is in an asymmetric environment, there is no reason why the rates of the 1,2 and 1,5 shifts should be equal. The rates are determined when they are comparable to the reciprocal of the spin–lattice relaxation times of the atoms involved, *e.g.* 1—10 $s^{-1}$. This method enables the determination of individual rates at relatively low temperatures. At higher temperatures we have used $^1H$ and $^{13}C$ line-shape analysis to determine the dominant 1,2-shift rate, and hence the activation energy for this process. The problem with [$Mo(\eta^5-C_5H_5)(\sigma-C_5H_5)(NO)(\eta^2-S_2CNR_2)$] is further complicated by the second slower process which interconverts the two rings. Finally, we comment on the interpretation of the data obtained in our analysis, on their chemical implications, and on our reservations about the concept of tetrahapticity in these systems.

## EXPERIMENTAL

The complex [$Mo(C_5H_5)_2(NO)I$] was prepared as described in the literature.[2] All the solvents were degassed with $N_2$ prior to use, and all the reactions were carried out under nitrogen. Yields are quoted relative to the molydenum-containing precursor, all m.p.s are uncorrected, and elemental analyses were by the Microanalytical Laboratory of this Department. Molecular weights were obtained osmometrically, mass spectra were recorded using an A.E.I. MS12 spectrometer, and $^1H$ n.m.r. spectra by using Varian HA100 and JEOL PS-100 spectrometers. The last instrument was used to obtain $^{13}C$ n.m.r. spectra, and the experimental procedure used for the dynamic $^{13}C$ n.m.r. spectral studies has been described previously.[10] Infrared spectra were obtained using Infracord 457 and PE180 instruments.

$\eta^5$-*Cyclopentadienyl*($\sigma$-*cyclopentadienyl*)(*dimethyldithiocarbamato*)*nitrosylmolybdenum*, [$Mo(\eta^5-C_5H_5)(\sigma-C_5H_5)(NO)(S_2CNMe_2)$].—The salt Na[$S_2CNMe_2$]·$2H_2O$ (0.6 g) was added to a solution of [$Mo(C_5H_5)_2(NO)I$] (1.0 g) in dichloromethane–ethanol (60 : 40, 60 $cm^3$). After stirring for 30 min the mixture was filtered off and the filtrate evaporated

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† The asterisk is intended to differentiate the two rings (note how they interchange their electronic roles), and the superscript attached to NO indicates the number of electrons donated by NO and therefore the effective Mo–N–O bond angle.

[4] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 1969, **91**, 2528; F. A. Cotton and G. A. Rusholme, *ibid.*, 1972, **94**, 402.

[5] J. L. Calderon, F. A. Cotton, B. G. deBoer, and J. Takats, *J. Amer. Chem. Soc.*, 1971, **93**, 3592.

[6] F. A. Cotton, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. F. A. Cotton and L. M. Jackman, Academic Press, New York, 1975.

[7] W. G. Kita, M. K. Lloyd, and J. A. McCleverty, *Chem. Comm.*, 1971, 420.

[8] N. A. Bailey, unpublished work.

[9] S. Forsén and R. A. Hoffman, *Acta Chem. Scand.*, 1963, **17**, 1787; *J. Chem. Phys.*, 1963, **39**, 2892.

[10] B. E. Mann, *J. Magnetic Resonance*, 1976, **21**, 17; 1977, **25**, 91; *J.C.S. Perkin II*, 1977, 84.

[11] S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, 1964, **40**, 1189.

to dryness. Dichloromethane (40 $cm^3$) was added to the yellow-brown residue, the mixture shaken for 5 min, and then centrifuged for another 5 min. The clear yellow solution was decanted, treated with ethanol (10 $cm^3$), evaporated *in vacuo* to low bulk (*ca.* 5 $cm^3$), and stored overnight at 0 °C. The yellow microcrystalline complex which formed was filtered off and washed twice with ethanol and three times with n-pentane (0.55 g, 56%), m.p. 152 °C (decomp. 125 °C) (Found: C, 41.8; H, 4.3; N, 7.4; S, 17.5%; *M* 390. Calc. for $C_{13}H_{16}MoN_2OS_2$: C, 41.5; H, 4.3; N, 7.5; S, 17.0%; *M* 378). The mass spectrum of the complex exhibited a molecular ion at *m/e* 378 ($[M]^+$), and ions at *m/e* 348 ($[M - NO]^+$), 313 ($[M - C_5H_5]^+$), 283 ($[M - NO - C_5H_5]^+$), 227 {$[Mo(C_5H_5)S_2]^+$}, and 195 {$[Mo(C_5H_5)S]^+$}.

*$\eta^5$-Cyclopentadienyl(σ-cyclopentadienyl)(di-n-butyldithiocarbamato)nitrosylmolybdenum*, $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNBu^n{}_2)]$.—The complex $[Mo(C_5H_5)_2(NO)I]$ (2.0 g) and $Na[S_2CNBu^n{}_2]\cdot 2H_2O$ (1.6 g) were stirred together in dichloromethane–ethanol (60 : 40, 100 $cm^3$) for 30 min. The resulting yellow-orange solution was evaporated to dryness under reduced pressure and the oily residue was redissolved in dichloromethane (40 $cm^3$). The solution was filtered, and the filtrate reduced to *ca.* 10 $cm^3$ *in vacuo*. The residue was chromatographed on dried degassed alumina using dichloromethane as eluant. The yellow band was collected and treated with ethanol (*ca.* 40 $cm^3$), the volume of the mixture being again reduced *in vacuo* until crystallisation began. The solution was then stored at −10 °C for *ca.* 48 h, and the resulting yellow-orange crystals were filtered off, washed with ethanol, and dried *in vacuo* (1.0 g, 50%) (Found: C, 61.0; H, 5.2; N, 5.4; S, 12.2. Calc. for $C_{27}H_{28}MoN_2OS_2$: C, 61.8; H, 5.3; N, 5.3; S, 12.2%).

*Bromo($\eta^5$-cyclopentadienyl)(dimethyldithiocarbamato)nitrosylmolybdenum*, $[MoBr(\eta^5\text{-}C_5H_5)(NO)(S_2CNMe_2)]$.—A mixture of $[\{MoBr_2(\eta^5\text{-}C_5H_5)(NO)\}_2]$ (3.0 g) and $Na[S_2CNMe_2]\cdot 3H_2O$ (1.3 g) was stirred in dichloromethane (70 $cm^3$) for 48 h. The mixture was filtered, treated with ethanol (40 $cm^3$), and evaporated *in vacuo* until crystallisation began. The brown crystals of $[MoBr(\eta^5\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ were collected by filtration, washed with ethanol, and dried *in vacuo* (2.5 g, 85%) (Found: C, 24.8; H, 3.1; Br, 20.5; N, 7.1. Calc. for $C_8H_{11}BrMoN_2OS_2$: C, 24.6; H, 2.8; Br, 20.4; N, 7.2%). The corresponding chloride was prepared similarly and isolated as orange crystals (Found: C, 27.9; H, 3.5; Cl, 10.1; N, 8.3. Calc. for $C_8H_{11}ClMoN_2OS_2$: C, 27.7; H, 3.2; Cl, 10.2; N, 8.1%).

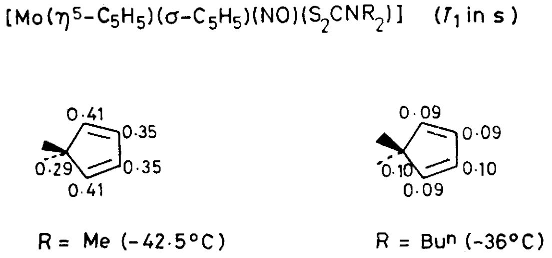
## THEORY AND RESULTS

It follows from Forsén's and Hoffman's treatment of the multisite exchange problem [11] that:

$$M_z{}^k(\infty) \sum_{\nu \neq k} k_{k\nu} - \sum_{\nu \neq k}{}_{\nu}\, k_{\nu k} M_z{}^{\nu}(\infty) = [M_z{}^k(0) - M_z{}^k(\infty)/T_{1k}] \quad (1)$$

Here $M_z{}^k(\infty)$ and $M_z{}^k(0)$ are the equilibrium magnetisations in the presence and absence, respectively, of a strong irradiating field at site Q, $k_{k\nu}$ is the exchange rate between the $k$th site and the $\nu$th site, and $T_{1k}$ is the spin-lattice relaxation time of the $k$th site. $M_z{}^k(0)$ can be measured in the absence of irradiation at site Q, and $M_z{}^{\nu}(\infty)$ can be measured in the presence of irradiation at site Q, provided that one waits at least $5(T_{1k}{}^{-1} + \sum_{\nu \neq k} {}_{\nu}K_{k\nu})^{-1}$ before commencing the measurement. $T_{1k}$ can be measured by the usual $(T_d - \pi - \tau - \frac{\pi}{2})$ pulse sequences provided that all the spin–lattice relaxation times are equal within what is an acceptable experimental error. For a general $n$-site exchange problem there are $n$ sites to irradiate, giving rise to $n(n - 1)$ such simultaneous equations and $n(n - 1)/2$ unknown rate constants. Thus, in all cases, the exchange rates can be calculated by solving the family of simultaneous equations given by (1).

In the case of $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ difficulties were encountered with the running of low-temperature spectra. The complex crystallised very readily from solution and there were significant differences in $T_1$ over the carbon atoms of the $\sigma\text{-}C_5H_5$ ring. Consequently there was a considerable danger of erroneous results in the measurement of $T_1$ by the $(T_d - \pi - \tau - \frac{\pi}{2})_n$ pulse sequence. In an attempt to improve the solubility properties, $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNBu^n{}_2)]$ was synthesised, and fortunately $T_1$ for each carbon atom in the σ ring became approximately equal. It is probable that the steric hindrance of the n-butyl groups reduces the rate of rotation of the σ ring about the Mo–C bond so that the rate is slow compared with the correlation time for the whole molecule.



*Hydrogen-1 N.M.R. Spectral Studies of* $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)]$.—(*i*) *Low-temperature spectra*. The room-temperature $^1H$ n.m.r. spectrum of the complex consisted of the following resonances: δ 6.17 (br, $\sigma\text{-}C_5H_5$), 5.03 (s, $\eta^5\text{-}C_5H_5$), 3.30 and 3.33 p.p.m. (s, $S_2CNMe_2$). On cooling the solution the broad signal at δ 6.17 p.p.m. collapsed and reappeared at *ca.* 0 °C in $CS_2$–$CDCl_3$ as an ill defined ABCDX multiplet, the ABCD group of signals being centred at δ 6.20 p.p.m. and the X signal occurring at δ 4.61 p.p.m. The other signals (at δ 4.87, 3.36, and 3.39 p.p.m. respectively) remained unchanged. Between 0 and −20 °C the ABCDX multiplet developed, with the upfield portion of the resonances gaining intensity and resolution faster than the low-field portion. In this respect, and as the temperature was further decreased to −70 °C, the spectral behaviour is very similar to that observed in other fluxional $\sigma\text{-}C_5H_5$ systems.[6] At −70 °C, below which no further spectral changes were observed (other than broadening presumably due to viscosity effects), the ABCDX system is fully resolved and it is clear that the molecule has the configuration consistent with its solid-state structure.

(*ii*) *High-temperature spectra*.—The spectra were recorded from 20 to 130 °C in $C_2Cl_4$, the respective chemical shifts at 20 °C being δ 6.14 (br, $\sigma\text{-}C_5H_5$), 4.80 (s, $\eta^5\text{-}C_5H_5$), 3.19 and 3.22 p.p.m. (two s, $S_2CNMe_2$). As the temperature was increased the sharp $\eta^5\text{-}C_5H_5$ signal began to broaden and collapse, the signal due to the $\sigma\text{-}C_5H_5$ protons also broadening somewhat. Both signals eventually coalesced at *ca.* 70 °C to a broad signal at δ 5.40 p.p.m. Further increase in temperature resulted in line narrowing and sharpening.

Up to 80 °C the methyl doublet remained sharp, but above this temperature it too began to broaden and collapse, coalescing to a singlet at *ca.* 110 °C ($\delta$ 3.20 p.p.m.). Above this temperature the spectrum of [Mo($\eta^5$-$C_5H_5$)($\sigma$-$C_5H_5$)(NO)($S_2CNMe_2$)] consisted of two singlets which continued to sharpen until decomposition occurred at *ca.* 130 °C.

*Carbon*-13 *N.m.r. Spectral Studies of* [Mo($\eta^5$-$C_5H_5$)($\sigma$-$C_5H_5$)(NO)($S_2CNBu^n_2$)].—The $^{13}C$ n.m.r. spectrum of the complex at −36 °C in $CD_2Cl_2$ is shown in Figure 1. The assignments for the $\sigma$-$C_5H_5$ ring are in agreement with those previously reported[6] for [Fe($\eta^5$-$C_5H_5$)($\sigma$-$C_5H_5$)$(CO)_2$]. Further confirmation of these assignments comes from the observation that the asymmetry at the Mo atom induces a greater chemical-shift difference between C(2) and C(5), which are closer to the metal atom than C(3) and C(4). If these assignments are reversed then, of course, all the arguments based on 1,2, as opposed to 1,3, shifts are reversed. The remainder of the assignments follow from known compounds and spin-saturation measurements: $NCS_2$, $\delta$ 201.1; $\sigma$-$C_5H_5$, C(1), 53.9, C(2), 142.3, C(3), 123.5, C(4), 122.2, C(5), 138.8; $\eta^5$-$C_5H_5$, 105.5; N–$CH_2$, 49.3 (d); $\beta$-$CH_2$ (of $Bu^n$), 29.2; $\gamma$-$CH_2$ (of $Bu^n$), 20.2; and $CH_3$ (of $Bu^n$), 14.0 p.p.m. The $\sigma$-ring gives five resonances because C(2) and C(5), and C(3) and C(4), are inequivalent as a consequence of the asymmetry at the metal atom. There are two signals due to the inequivalent N–$CH_2$ groups of the n-butyl residue. There are five sites for exchange, giving five (and not 10) rate constants, $k_{12}$, $k_{13}$, $k_{14}$, $k_{15}$, and $k_{inv.}$, as a consequence of the restrictions placed on the system by the ring, *e.g.* $k_{12} = k_{23} = k_{45} = k_{51}$; $k_{inv.}$ results from the possibility that the Mo atom can move from one side of the ring to the other, providing an additional mechanism for exchange of C(2) and C(5), and C(3) and C(4). A typical set of spectra is given in Figure 2. Qualitatively, these experiments confirm the dominance of 1,2 shifts. Irradiation of C(1) causes the signals of C(2) and C(5) to decrease most in intensity. The relative assignment of C(3) and C(4) is based on the dominance of 1,2 shifts and thus irradiation of C(2) causes the signals of C(1) and C(3) to decrease most in intensity. These spectra give rise to 12 simultaneous equations derived as shown above. A computer program, based on the NAG routing FO4AMF, was written to extract the best values of the rate constants from the data, and these are given in Table 1. It is considered that $k_{12} = k_{15}$ within experimental error, and that $k_{13}$, $k_{14}$, and $k_{inv.}$ are not significantly different from 0. The simultaneous equations were also solved with $k_{12} = k_{15}$ and $k_{13} = k_{14}$ and these results are also included in Table 1.

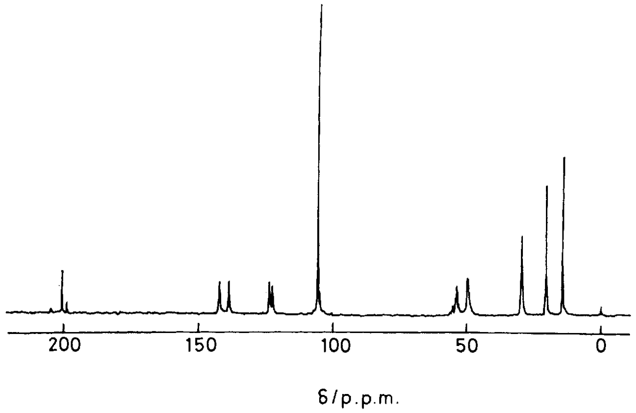


FIGURE 1 Carbon-13 n.m.r. spectrum of [Mo($\eta^5$-$C_5H_5$)($\sigma$-$C_5H_5$)(NO)($S_2CNBu^n_2$)] in $CD_2Cl_2$–$CH_2Cl_2$ at −36 °C

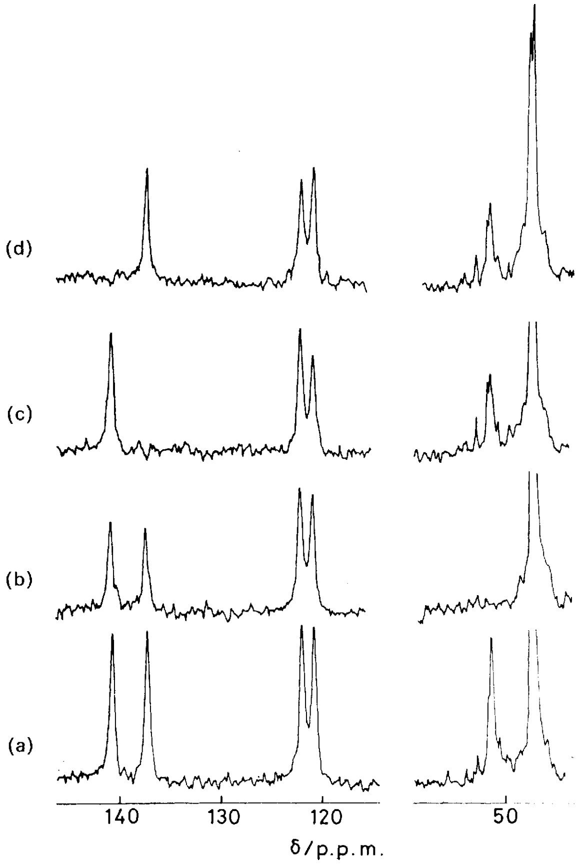


FIGURE 2 Partial $^{13}C$ n.m.r. spectrum of [Mo($\eta^5$-$C_5H_5$)($\sigma$-$C_5H_5$)(NO)($S_2CNBu^n_2$)] in $CD_2Cl_2$–$CH_2Cl_2$ at −27 °C, a 90° pulse angle, and a 1-s repetition time: (*a*) no irradiation; (*b*) irradiation at $\delta$ 53.9 p.p.m.; (*c*) irradiation at $\delta$ 138.8 p.p.m.; (*d*) irradiation at $\delta$ 142.3 p.p.m. Because of the closeness of the signals due to C(3) and C(4) it was not possible to irradiate one without partially irradiating the other. Irradiation causes the signal due to the irradiated nuclei to disappear

TABLE 1

Rate of $C_5H_5$ ring rotation on [Mo$(C_5H_5)_2$(NO)($S_2CNBu^n_2$)] in $CD_2Cl_2$

| $T$/K | $k$/s$^{-1}$ |
|---|---|
| 237 | 2.54 * |
| 246 | 6.89 * |
| 255 | 22.8 |
| 264.5 | 62 |
| 275.5 | 165 |
| 283 | 300 |
| 292.5 | 600 |
| 301 | 1 200 |
| 311 | 2 600 |

$\Delta H^\ddagger = 13.1 \pm 0.2$ kcal mol$^{-1}$, $\Delta S^\ddagger = -0.9 \pm 0.7$ cal K$^{-1}$ mol$^{-1}$.

* Determined by Forsén–Hoffman spin-saturation methods.

As a consequence of the Forsén–Hoffman spin-saturation measurements in $CD_2Cl_2$ solution, only one process, *viz.* 1,2 shifts, was considered for line-shape analysis. The spin-saturation experiments have shown that $k_{13}$, $k_{14}$, and $k_{inv.}$ are negligible, and a second exchange mechanism, which exchanges the $\sigma$- and $\eta^5$-$C_5H_5$ rings, does not occur at a rate sufficient to cause significant broadening of the $^{13}C$ n.m.r. spectral signal due to the $\eta^5$-$C_5H_5$ ring below the boiling point of $CD_2Cl_2$. Therefore, for the $CD_2Cl_2$ solution, the problem was treated as a five-site exchange problem with only one rate constant, $k_{12} = k_{15}$. The spectra are shown in Figure 3.

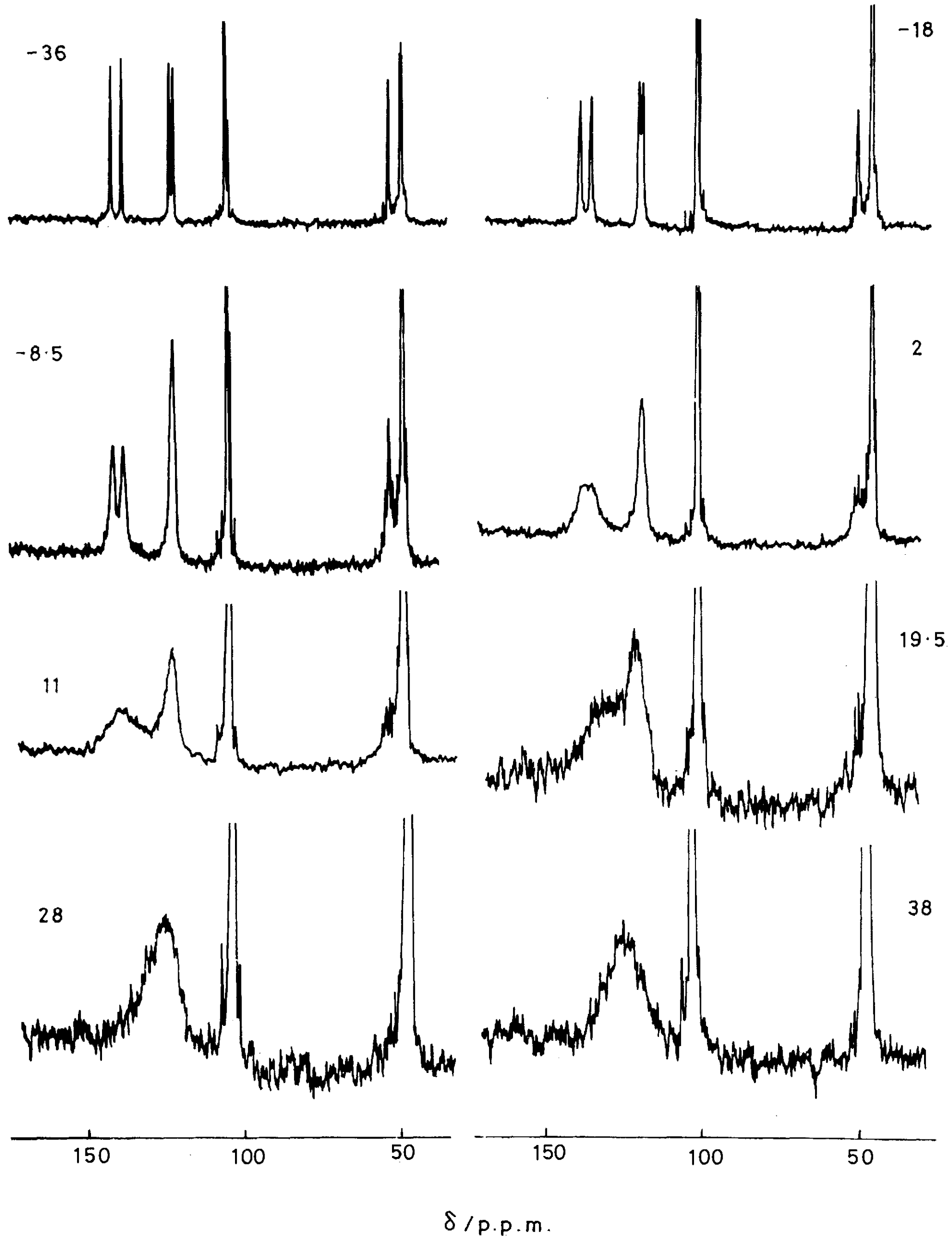


FIGURE 3 Partial $^{13}C$ n.m.r. spectrum of $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNBu^n_2)]$ in $CD_2Cl_2$–$CH_2Cl_2$ as a function of temperature ($\theta_c$/°C)

The results are given in Table 1, and from an Eyring rate plot $\Delta H^\ddagger = 13.1 \pm 0.2$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -0.9 \pm 0.7$ cal K$^{-1}$ mol$^{-1}$.† The accuracy of the activation parameters arises from the large range of rates examined as a result of using the Forsén–Hoffmann spin-saturation method. One standard deviation is given.

In order to investigate the slower process of exchange between $\sigma$- and $\eta^5$-$C_5H_5$ rings, [$^2H_8$]toluene was chosen as solvent. The major difficulty encountered was that it was impossible to get meaningful line shapes for the $\sigma$-$C_5H_5$ ring rotation on account of the signals due to the $C_6D_5CD_3$ carbon atoms. However, by 56 °C, the rate of $\sigma$-$C_5H_5$ ring rotation was sufficient to cause enough coalescence of the signals to produce a broad hump removed from the $C_6D_5CD_3$ signal and the rotation was followed up to 97 °C, but at this and greater temperatures $\sigma$—$\eta^5$ site exchange was sufficiently fast to make the line shape insensitive to $\sigma$-$C_5H_5$ ring rotation. The spectra are shown in Figure 4 and the rates are given in Table 2. An Eyring rate plot for the $\sigma$-$\eta^5$-ring interchange gave $\Delta H^\ddagger = 17.6 \pm 0.5$ kcal mol$^{-1}$ and $\Delta S^\ddagger = 1.5 \pm 1.5$ cal K$^{-1}$ mol$^{-1}$. It

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† Throughout this paper: 1 cal = 4.184 J.

should be noted that the rate of the σ-$C_5H_5$ ring rotation in toluene could not be reliably determined because of the restricted nature of the data and the risk of errors in determining one rate in the presence of a second dominating one at >86 °C.

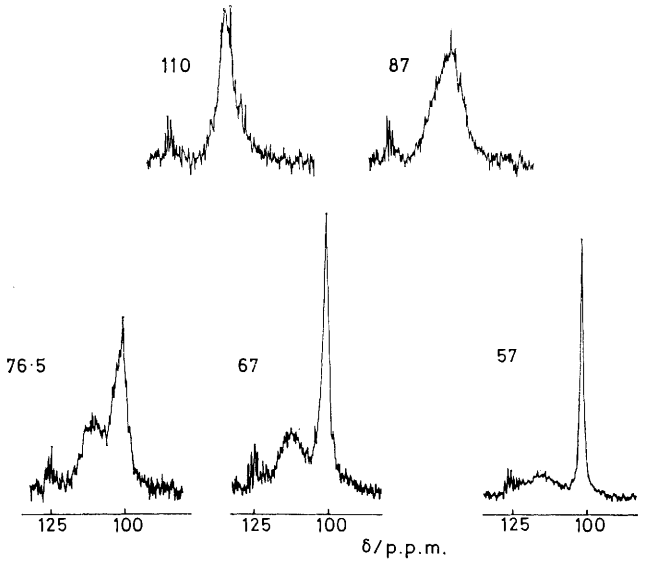

FIGURE 4 Partial $^{13}C$ n.m.r. spectrum of $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNBu^n{}_2)]$ in $[^2H_8]$toluene as a function of temperature ($\theta_c$/°C)

It is of particular relevance that, even at 10 °C, the rate of C–N bond rotation is slow on the $^{13}C$ n.m.r. time scale and two signals are still observed for the α-$CH_2$ carbon atoms, showing that the rate of rotation of the C–N bond is less than 20 $s^{-1}$ while the rate of σ–$\eta^5$ ring exchange is 1 440 $s^{-1}$.

TABLE 2

Rate of $C_5H_5$ ring exchange in $[^2H_8]$toluene

| $T$/K | $k$/$s^{-1}$ |
|---|---|
| 329 | 31 |
| 340 | 67 |
| 350 | 138 |
| 359.5 | 308 |
| 370 | 720 |
| 383 | 1 440 |

$\Delta H^\ddagger = 17.6 \pm 0.5$ kcal mol$^{-1}$, $\Delta S^\ddagger = 1.5 \pm 1.5$ cal K$^{-1}$ mol$^{-1}$.

## DISCUSSION

Of the three fluxional processes which $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNR_2)]$ undergoes, namely (*i*) 1,2 shifts of the σ-$C_5H_5$ ring, (*ii*) σ–$\eta^5$ ring interchange, and (*iii*) C–N bond rotation of the $S_2C\text{–}NR_2$ group, the first and the last are relatively common among σ-cyclopentadienyl and dithiocarbamate complexes. The second process is unusual and, so far as we know, is confined only to the species $[M(C_5H_5)_4]$(M = Ti, Zr, or Hf), $[Mo(C_5H_5)_3(NO)]$ and, presumably, $[Mo(C_5H_5)_2(NO)X]$ (X = I or Me).[6] As far as the first process is concerned we have shown by our work that the rate of 1,2 shifts about the σ-$C_5H_5$ ring is significantly greater than that of 1,3 shifts. This is the first time that this has been satisfactorily demonstrated, and little more needs to be said.

The C–N bond rotation process occurs with an activation energy entirely comparable with those calculated from coalescence temperatures obtained from $[Mo(\eta^5\text{-}C_5H_5)(NO)(S_2CNMe_2)X]$ [X = Cl, Br, I, σ-$C_3H_5$, or σ-$C_7H_5(CF_3)_2$]. We have also investigated the $^1H$ n.m.r. spectra of $[Mo(\eta^5\text{-}C_5H_5)(NO)I\{(p\text{-}MeC_6H_4)NNN(C_6H_4Cl\text{-}p)\}]$ $[Mo(\eta^5\text{-}C_5H_5)(NO)I(CF_3COCHCOMe)]$, and $[Mo(\eta^5\text{-}C_5H_5)(NO)(\sigma\text{-}C_3H_5)(S_2CNMe_2)]$, the $^{13}C$ n.m.r. spectrum of $[Mo(\eta^5\text{-}C_5H_5)(NO)I(O_2CPr^i)]$, and the $^{19}F$ n.m.r. spectrum of $[Mo(\eta^5\text{-}C_5H_5)(NO)I\{\sigma\text{-}C_7H_5(CF_3)_2\}]$ over a wide temperature range.[12] None of these molecules gave evidence of stereochemical non-rigidity other than that associated, where appropriate, with the dithiocarbamate ligand.† Accordingly, we are fairly certain that any mechanism which is devised to explain processes (*ii*) and (*iii*) in $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ will not involve Berry pseudo-rotation (as, for example, we suggested in our earlier communication).

Since our first attempts to explain the σ–$\eta^5$ ring interchange, Cotton [6] 'has suggested a mechanism, akin to a form of 'turnstile' rotation, whereby the two rings in our complex can interchange their roles without simultaneously interchanging the alkyl-group sites in the $S_2CNR_2$ ligand. This is shown below. The mechanism may be depicted as $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5{}^*)(NO^3)(S_2CNMe_2)] \rightleftharpoons [Mo(\eta^4\text{-}C_5H_5)(\eta^4\text{-}C_5H_5{}^*)(NO^1)(S_2CNMe_2)] \rightleftharpoons [Mo(\sigma\text{-}C_5H_5)(\eta^5\text{-}C_5H_5{}^*)(NO^3)(S_2CNMe_2)]$. This requires that both rings become $\eta^4$-bonded, while, simultaneously, the Mo–N–O bond angle bends, thereby converting the NO into a one-electron donor. In this way, the metal atom, in the transitory stages of this interchange, preserves its formal 18-electron configuration. Support for this mechanism rests essentially on the interpretation of Mo–C bond-length data obtained[4,15] from $[Mo(C_5H_5)_3(NO)]$ and $[Mo(C_5H_5)_2Me(NO)]$. Cotton proposed that the alternative mechanism involving dithiocarbamate chelate-ring opening, rather than Mo–N–O bond-angle bending, could be discounted, and we agree that this would be inconsistent with the clear difference in rates of interchange of the two rings and the alkyl-group sites.

Cotton's mechanism has much to commend it, but there is, in our opinion, one rather unattractive feature, namely the unsymmetrical (3 : 1) electron interchange involving $\eta^5\text{-}C_5H_5 \rightleftharpoons \eta^4\text{-}C_5H_5 \rightleftharpoons \sigma\text{-}C_5H_5$. Looking at the three sets of Mo–C(ring) distances mentioned earlier, we consider that two of these (spanning the range

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† This behaviour is in contrast to the '*cis*' ⇌ '*trans*' isomerism of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)X]$ (X = halide) [13] and the CO site-exchange process in $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(RNNNR')]$,[14] both of which appear to involve (non-dissociative) Berry pseudo-rotations.

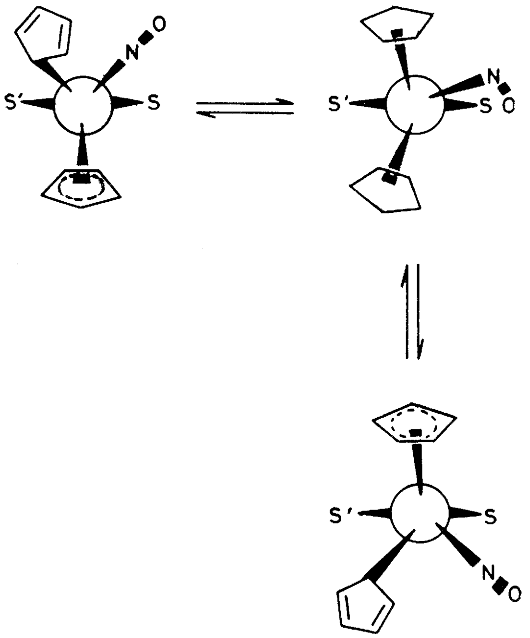
[12] M. M. Hunt, J. A. McCleverty, E. Pfeiffer, and K. Vrieze, unpublished work.

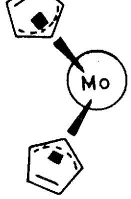
[13] K. W. Barnett and D. W. Slocum, *J. Organometallic Chem.* 1972, **44**, 1 and refs. therein.

[14] E. Pfeiffer, J. Kuyper, and K. Vrieze, *J. Organometallic Chem.*, 1976, **105**, 371.

[15] F. A. Cotton, *Discuss. Faraday Soc.*, 1969, **47**, 79.

2.32—2.46 Å) are certainly not inconsistent with $\eta^3$-bonding, and indeed structural data obtained[16] from comparable molybdenum allyl and benzyl complexes show that Mo–C(allyl) distances fall in the range 2.21—2.48 Å. The other C atoms in the bis(cyclopentadienyl) complexes are at distances of between 2.57 and 2.71 Å from the metal, which could be taken as essentially non-bonding. Hence, these rings might be thought of as bonding to the metal *via* an allylic mode, as in (I). It may be noted that this form of the isolated cyclopentadienyl ligand corresponds formally to the representation of the C $2p(\pi)$ molecular orbitals of $e_1$ symmetry. Further, Lauher and Hoffmann,[17] in their description of the bonding in the species $[M(C_5H_5)_2(CO)_2]$ (M = Mo or W) and $[M(C_5H_5)_2(NO)X]$, depict an important contribution to the bonding between the rings and the metal as involving just such an orbital.†





(I)

Accordingly, if we recognise the possibility of $\eta^3$ bonding by cyclopentadienyl rings, we can propose alternative mechanisms for $\sigma$–$\eta^5$ ring interchange *viz.*: $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO^3)(S_2CNR_2)] \rightleftharpoons [Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(NO^1)(S_2CNR_2)] \rightleftharpoons [Mo(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(NO^1)(S_2CNR_2)] \rightleftharpoons [Mo(\sigma\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(NO^3)(S_2CNR_2)]$; or $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO^3)(S_2CNR_2)] \rightleftharpoons [Mo(\eta^3\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(NO^3)(S_2CNR_2)] \rightleftharpoons [Mo(\sigma\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(NO^3)(S_2CNR_2)]$. The first of these two alternatives requires bending of the Mo–N–O bond angle, but involves a more symmetrical interchange of electrons. One cause for disquiet about this, or Cotton's mechanism, is that if Mo–N–O bond bending is necessary, and a normal facet of the dynamic stereochemistry of these systems, then perhaps we might expect $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_3H_5)(NO)(S_2CNMe_2)]$ to undergo 1,3 shifts associated with the allyl group. As we have stated above, this is not observed.

The second alternative does not require bending of the Mo–N–O bond angle. Indeed, exchange of the electronic role of the rings could even occur in one electron interchanges, *e.g.* $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNR_2)] \rightleftharpoons [Mo(\eta^4\text{-}C_5H_5)(\eta^2\text{-}C_5H_5)(NO)(S_2CNR_2)] \rightleftharpoons [Mo(\eta^3\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(NO)(S_2CNR_2)] \rightleftharpoons Mo(\eta^2\text{-}C_5H_5)(\eta^4\text{-}C_5H_5)(NO)(S_2CNR_2)] \rightleftharpoons [Mo(\sigma\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(NO)(S_2CNR_2)]$. It may be observed that $\eta^2$-bonded rings have been detected[18] in the structure of $[Ti(C_5H_5)_3]$. However, one disadvantage of this proposal lies in the observation of stereochemical rigidity in $[Mo(C_5H_5)_4]$. Cotton's explanation for this phenomenon, which contrasts sharply with the fluxionality of $[M(C_5H_5)_4]$ (M = Ti, Zr, or Hf), is that the Mo atom has an 18-electron ground-state electronic configuration and lacks the facility to provide a readily available empty orbital to assist ring interchange. The species $[M(C_5H_5)_4]$ have formal 16-electron ground-state configurations, and so potentially can provide an empty orbital. Similar interchange in the molybdenum nitrosyls is thought to be assisted by Mo–N–O bond bending which converts the NO from a three- into a one-electron donor and releases a vacant orbital on the metal. However, that ring interchange does not occur in $[Mo(C_5H_5)_4]$, but does in $[Mo(C_5H_5)_2(NO)(S_2CNMe_2)]$, need not depend on the ability of NO to withdraw an electron pair from the metal when necessary, but could be a reflection of the relative accessibility of other suitable low-lying orbitals in the latter, but not in the former.

Our comments on the electronic interchange of two rings may also apply to $[Mo(C_5H_5)_2(NO)X]$ (X = unidentate ligand). Thus, *in solution*, rapid ring interchange of the type $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5{}^*)(NO)X] \rightleftharpoons [Mo(\sigma\text{-}C_5H_5)(\eta^5\text{-}C_5H_5{}^*)(NO)X]$ could be facilitated by the potential existence of a vacant orbital in this formally 16-electron system (the NO group does not have to bend

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† *Note added in proof.* A very recent *X*-ray structural examination of $W(C_5H_5)_2(CO)_2$ has revealed the existence of an $\eta^5$- and an $\eta^3$-$C_5H_5$ ring. The latter is bent along its C(1)–C(3) axis by 20° and thus a 20-electron configuration at metal is avoided (G. Hüttner, H. H. Brintzinger, L. G. Bell, P. Friedrich, V. Bejenke, and D. Neugebauer, *J. Organometallic Chem.*, 1978, **145**, 529).

[16] F. A. Cotton, C. A. Murillo, and B. R. Stults, *Inorg. Chim. Acta*, 1977, **22**, 75; F. A. Cotton, B. A. Frenz, and C. A. Murillo, *J. Amer. Chem. Soc.*, 1975, **98**, 2118 and refs. therein; F. A. Cotton and M. D. la Prade, *ibid.*, 1968, **90**, 5418.

[17] J. W. Lauher and R. Hoffmann, *J. Amer. Chem. Soc.*, 1976, **98**, 1729.

[18] C. R. Lucas, M. L. H. Green, R. A. Forder, and K. Prout, *J.C.S. Chem. Comm.*, 1973, 97; R. A. Forder and C. K. Prout, *Acta Cryst.*, 1974, **B30**, 491.

in such a species). The low activation energy of this process ($<$ *ca.* 7 kcal $mol^{-1}$)† would also be a reflection of the electron-withdrawing nature of NO and X. It is also possible that a species of the type $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(X)S]$ (S = solvent) could exist, albeit transiently, in certain solvents. However, the intermediacy of $\eta^3\text{-}C_5H_5$ bonding modes cannot be discounted, and such a bonding situation has been invoked to account for the structure of the $\mu$-cyclopentadienyl species $[Pd_2(\mu\text{-}Br)(\mu\text{-}C_5H_5)(PPr^i_3)_2]$ [19] and in describing the mechanism of the displacement of ethylene from $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ by tertiary phosphines.[20] In the system $[Mo(C_5H_5)_2(NO)X]$, interconversions of the rings *via* an $\eta^5 \rightleftharpoons \eta^3 \rightleftharpoons \sigma$ path could occur without violation of the 18-electron configuration at the metal.

In conclusion, a unique and fully satisfactory interpretation of the method of hapticity interchange of the two rings in $[Mo(C_5H_5)_2(NO)X]$ and related species remains elusive. However, our proposals have some implications for the chemistry of such complexes, and these are discussed in subsequent papers.

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† The activation energy for ring interchange in $[Mo(C_5H_5)_2(NO)X]$ (X = I or Me) must be of this order since no resolution of the cyclopentadienyl proton signals was observed even at −100 °C.

[19] A. Ducruix, H. Felkin, C. Pascard, and G. K. Turner, *J.C.S. Chem. Comm.*, 1975, 615.

[20] R. Cramer and L. P. Seiwell, *J. Organometallic Chem.*, 1975, **92**, 245.