The Fluxional Behaviour of Some Nitrosyl Bis(cyclopentadienyl) Molybdenum Sulphur Complexes

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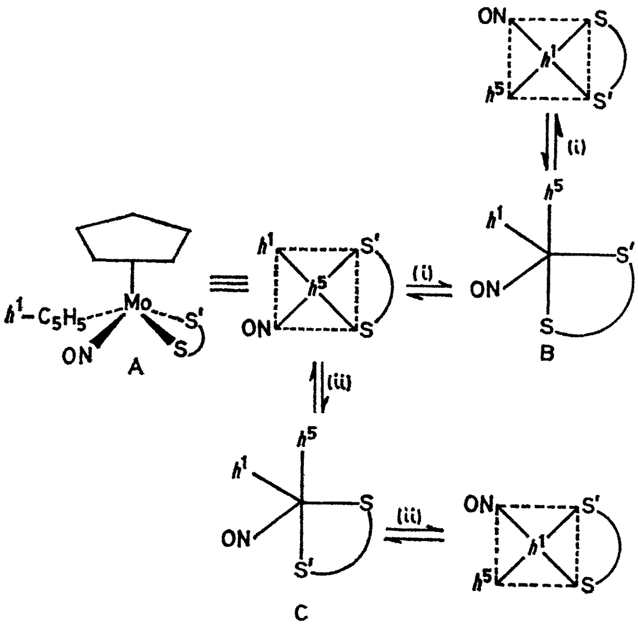
Summary The ^{1}H n.m.r. spectra of $[Mo(C_5H_5)_2(NO)(S_2CNMe_2)]$, (I), and of $[Ph_4P][Mo(C_5H_5)_2(NO)\{S_2C_2(CN)_2\}]$, (II), have been studied over the temperature range −80 to +130°: the limiting low-temperature spectra are consistent with the structure $[Mo(h^5\text{-}C_5H_5)(h^1\text{-}C_5H_5)(NO)\text{–}(S\text{–}S)]$ (S–S = sulphur ligand); at intermediate temperatures, the *monohapto*-ring is fluxional, and at high temperatures the rings in (I) undergo site exchange, and the methyl groups become equivalent.

IF the complexes $[Mo(C_5H_5)_2(NO)X]$ (X = I or Me)[1] and $[Mo(C_5H_5)_3(NO)]$[2,3] contain two *pentahapto*-cyclopentadienyl rings,† they are relatively unusual in that the metal atom may be regarded formally as having a "20-electron configuration." It has been suggested[3,4] that a more acceptable "18-electron configuration" could be achieved by regarding one of the cyclopentadienyl rings as being asymmetrically bonded to the metal atom *via* a *trihapto* (π-allylic) arrangement, leaving a double bond formally non-bonded, *e.g.* $[Mo(h^5\text{-}C_5H_5)(h^3\text{-}C_5H_5)(NO)X]$. It has been suggested that the observed ^{1}H n.m.r. equivalence of the cyclopentadienyl ring protons in $[Mo(C_5H_5)_2(NO)I]$ from −55 to +33° can be accounted for by invoking temperature independent interligand resonance, *viz.* $[Mo(h^5\text{-}C_5H_5)(h^3\text{-}C_5H_5)(NO)I] \rightleftharpoons [Mo(h^3\text{-}C_5H_5)(h^5\text{-}C_5H_5)(NO)I]$, and by assuming that the rings were also fluxional.[4] The ^{1}H n.m.r. spectrum at −110°,[2] and the molecular structural determination,[3] of $[Mo(C_5H_5)_3(NO)]$ revealed that the instantaneous structure of the molecule consisted of one *monohapto*-cyclopentadienyl ring and two other rings which bore almost identical structural relationships to the metal atom but were magnetically non-equivalent.‡



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We reasoned that, if the "20-electron configuration" was a stable one for these complexes, by replacing X with a bidentate ligand, one of the rings might adopt a rigid asymmetrically-bonded configuration, and accordingly have prepared $[Mo(C_5H_5)_2(NO)(S_2CNMe_2)]$, (I), and $[Ph_4P][Mo(C_5H_5)_2(NO)\{S_2C_2(CN)_2\}]$, (II).

The ^{1}H n.m.r. spectrum of (I) at −80° consisted of an ABCDX spectrum typical of a rigid *monohapto*-C_5H_5 ring, a sharp singlet assigned to an h^5-C_5H_5 ring, and a doublet due to the inequivalent methyl protons of the bidentate S_2CNMe_2 group.§ This inequivalence of the methyl groups, and of the protons in the h^1-C_5H_5 group, arises because of the asymmetry of the complex. On warming to probe temperature (+20°), the h^1-C_5H_5 ring became fluxional, undergoing, presumably, a series of 1,2-shifts similar to those in $[Fe(h^5\text{-}C_5H_5)(h^1\text{-}C_5H_5)(CO)_2]$, *etc.*[5] The spectrum of (II) over the range −60 to +30° was essentially similar to that of (I), except that the h^1-C_5H_5 protons at −60° constituted an ABCC'X group.

On warming (I) from +30° to +60° *both* the h^1- (τ 3·80, C_2Cl_4) and the h^5-C_5H_5 (τ 4·98, C_2Cl_4) signals broadened and collapsed until, at +70°, they had coalesced. Between +70 and +80° the coalesced C_5H_5 resonance (it occurred exactly mid-way between the original C_5H_5 signals) sharpened, but the methyl signals of the S_2CNMe_2 group remained a sharp doublet (separation 3·5 Hz). At *ca.* +90°, the methyl proton signals began to broaden and at +100° had coalesced, and the complete spectrum of (I) between +100 and +120° consisted of only two signals (τ 4·39 and 6·61; relative areas 5 : 6). At +130° (I) decomposed, but between −80 and +120°, the spectral changes were thermally reversible. Between +30 and +60°, the spectrum of (II) behaved similarly to that of (I) (in the C_5H_5 region), but the complex decomposed at *ca.* +65°.

The spectral data at low temperatures in themselves could be consistent either with an h^5/h^1- or an h^5/h^3-C_5H_5 bonding scheme. However, the former seems more likely in view of the spectral similarities between the new compounds and $[Fe(h^5\text{-}C_5H_5)(h^1\text{-}C_5H_5)(CO)_2]$[5] and because of the structure of $[Mo(C_5H_5)_3(NO)]$;[3] the metal atoms in (I) and (II) would then have "18-electron configurations.¶" The spectra of (I) between +30 and +90° may be interpreted in terms of a rapid exchange between h^1-C_5H_5 and h^5-C_5H_5 groups, and similar behaviour has been observed in the spectra of $[Ti(h^5\text{-}C_5H_5)_2(h^1\text{-}C_5H_5)_2]$.[6]

A pseudo-rotational mechanism (Scheme) can be used to

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† For an explanation of the nomenclature, see F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 6231.

‡ The n.m.r. spectrum consisted of an ABCDX multiplet due to the h^1-C_5H_5 ring, and two sharp lines due to the other rings (ref. 2).

§ Mesomeric release of electrons from NMe_2 causes the C–N bond in $S_2C\text{–}NMe_2$ to acquire partial double-bond character.

¶ An h^3-C_5H_5 ring system would also give an asymmetric spectrum perhaps similar to that of an h^1-ring, but the metal would then have a formal "22-electron configuration."

rationalise the high-temperature spectral behaviour of (I). If (I) has, essentially, an instantaneous five-co-ordinate, square-pyramidal structure, A,[††] the h^1- and h^5-C_5H_5 rings can be made to exchange sites without simultaneously permitting the generation of equivalent methyl groups *only via* the trigonal bipyramidal intermediate, B,[‡‡] and pathway (i); no other intermediate (*e.g.* C) can give rise to h^1/h^5-ring exchange alone. Pseudo-rotation *via* the intermediate C and pathway (ii) can give rise to simultaneous ring and methyl group exchange, which may account for the spectra of (I) above +90°. However, the methyl groups may become equivalent by other pseudo-rotational pathways (which may, or may not, lead also to ring site exchange), or by allowing the sulphur ligand to become monodentate, thereby relieving the partial double bond character of the S_2C–NMe_2 link permitting free rotation of the NMe_2 group. The crux of the mechanism used to describe the h^1/h^5-ring interchange is that the energy barrier to the formation of B from A is lower than that of C from A, *i.e.* that the sulphur atom "*trans*" to the NO group in A is more strongly bound to the Mo atom than the sulphur atom "*trans*" to the *monohapto*-ring.

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[††] For the argument, the h^5-C_5H_5 ring is regarded as occupying one co-ordination site; S and S′ are so labelled to permit easy visual identification.

[‡‡] S–M–S bond angles vary between 80° and 90° in most dithiocarbamato and related metal complexes, and it is therefore unlikely that any trigonal bipyramidal intermediate will contain the sulphur ligand occupuing two equatorial sites.

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[5] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, 1968, **88**, 4371.
[6] J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, 1970, **92**, 3801.