# Intramolecular Rearrangement in η-Allyl Complexes of Molybdenum(II) containing Unidentate Amine Ligands

By **David J. Bevan** and **Roger J. Mawby**,* Department of Chemistry, University of York, York YO1 5DD

Allyl and 2-methylallyl complexes [$Mo(CO)_2X(\eta$-$C_3H_4R)L_2$] (X = Cl, Br, or I; R = H or Me; L = $NC_5H_5$, $NC_5H_4Me$-4, or $NC_5H_3Me_2$-3,5) exist in solution at low temperatures in a single isomeric form in which the two carbonyl ligands, the two amine ligands, and the two ends of the allyl ligand are inequivalent. At higher temperatures, rearrangement (shown to be an intramolecular process) has the effect of removing all these inequivalences from the $^1H$ and $^{13}C$ n.m.r. spectra of the complexes. At a given temperature, the rearrangement rate is essentially independent of the nature of L, decreases with increase in the size of the halogen ligand, and is greater for the 2-methylallyl than for the allyl complexes. At the lowest temperatures studied, rotation of one amine ligand about the metal–nitrogen bond is restricted for the 2-methylallyl complexes only. Two structures are suggested for the complexes in solution: in one case (viewed as the more probable of the two) the variation in spectra can be attributed to a trigonal twist of the halogen and amine ligands relative to the remainder of the complex, and in the other to an oscillation of the allyl ligand about the metal–allyl axis.

ALTHOUGH it is now many years since the preparation of a range of η-allyl and η-2-methylallyl complexes [$Mo(CO)_2X(\eta$-$C_3H_4R)(L$–$L)$] (R = H or Me; X = Cl, Br, I, or NCS) containing the bidentate ligands L–L = 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) was reported,[1] corresponding complexes [$Mo(CO)_2X(\eta$-$C_3H_4R)L_2$] containing two unidentate pyridine or substituted-pyridine ligands L have received little attention. One such complex, [$Mo(CO)_2Br(\eta$-$C_3H_5)(NC_5H_5)_2$], was, however, prepared by tom Dieck and Friedel [2] in 1968.

Our interest in these complexes was two-fold. First, we have recently shown [3] that the η-allyl and η-2-methylallyl complexes [$Mo(CO)_2Cl(\eta$-$C_3H_4R)L'_2$], obtained in very rapid reactions between the ethanonitrile complexes [$Mo(CO)_2Cl(\eta$-$C_3H_4R)(NCMe)_2$] and the phosphorus ligands L′ = $PMe_2Ph$ or $PMePh_2$, undergo further reactions with these ligands which involve nucleophilic attack on the η-allyl ligand, giving [$C_3H_4RL'$]$^+$ and the molybdenum(0) complexes [$Mo(CO)_2L'_4$] or [$Mo(CO)_2(NCMe)L'_3$], and we wished to see whether complexes [$Mo(CO)_2Cl(\eta$-$C_3H_4R)L_2$] (L = pyridine or substituted pyridine) obtained in the same way would also be subject to attack by excess of the pyridine ligand L. Secondly, there have been several recent accounts [4–6] of rapid intramolecular rearrangement in η-allyl complexes of molybdenum(II), and we wished to see whether complexes [$Mo(CO)_2X(\eta$-$C_3H_4R)L_2$] would exhibit similar behaviour. If evidence of fluxional behaviour were obtained, we hoped to study the way in which the rate of rearrangement varied according to the presence or absence of the methyl substituent on the central carbon atom of the allyl ligand, the nature of the halogen ligand X, and the pattern of alkyl substitution around the pyridine rings.

## RESULTS AND DISCUSSION

(1) *Preparation of Complexes.*—Treatment of the complexes [$Mo(CO)_2Cl(\eta$-$C_3H_4R)(NCMe)_2$] (R = H or Me) with the ligands L = $NC_5H_5$, $NC_5H_4Me$-4, or $NC_5H_3Me_2$-3,5 in ethanol or propanone solution at room temperature yielded crystalline products [$Mo(CO)_2Cl(\eta$-$C_3H_4R)L_2$] in good yield. Bromo- and iodo-analogues of one of the chloro-complexes, [$Mo(CO)_2Cl(\eta$-$C_3H_5)(NC_5H_4Me$-4$)_2$], were prepared in the same way from [$Mo(CO)_2X(\eta$-$C_3H_5)(NCMe)_2$] (X = Br or I) and 4-methylpyridine. Under the mild conditions used, there was no evidence for nucleophilic attack by excess of amine on the allyl ligand: under more forcing conditions the complexes [$Mo(CO)_2X(\eta$-$C_3H_4R)L_2$] slowly decomposed, but there was no evidence that the decomposition reactions involved attack on the allyl ligand or formation of molybdenum(0) complexes.

Attempts to obtain complexes [$Mo(CO)_2Cl(\eta$-$C_3H_4R)L_2$] containing the ligands L = $NC_5H_3Me_2$-2,6 or $NC_5H_4Me$-2 were unsuccessful. Solid products were isolated from the reactions of [$Mo(CO)_2Cl(\eta$-$C_3H_4R)(NCMe)_2$] with these amines, but analytical data for these products were irreproducible and always in very poor agreement with the figures calculated for the desired complexes. Presumably the steric effects of the *ortho* substituents on the pyridine rings prevented the formation of stable complexes.

(2) *Variable-temperature N.M.R. Spectra of the Complexes.*—The $^1H$ and $^{13}C$ n.m.r. spectra of each of the complexes [$Mo(CO)_2X(\eta$-$C_3H_4R)L_2$] in $CDCl_3$ solution were recorded at a number of different temperatures. In every case the appearance of the spectra altered markedly with temperature, apparently as the result of some kind of rearrangement process. For this reason, Tables 1—3 of n.m.r. spectra give details not of spectra recorded at the ambient temperatures of the spectrometers but of those recorded at lower temperatures. For each complex, the temperature chosen was one at which the rearrangement had become slow enough to allow limiting low-temperature spectra to be obtained. It should, however, be added that in some instances the spectra obtained at the lowest temperatures used provided evidence for a separate phenomenon, namely the restricted rotation of one of the amine ligands about the metal–nitrogen bond. For these complexes, the spectra used to supply the information in the Tables were recorded at temperatures where the amine ligand

was still rotating fairly rapidly on the n.m.r. time scale: details of the changes in spectra observed on further cooling are given in the text.

TABLE 1

Proton n.m.r. spectra of complexes $[Mo(CO)_2X(\eta\text{-}C_3H_5)L_2]$ in $CDCl_3$ solution [a]

| Complex | $T$/K | $H^a$ | $H^s$ | $H^c$ | $H^2$ | $H^3$ | $H^4$ | $Me^3$ | $Me^4$ |
|---|---|---|---|---|---|---|---|---|---|
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_5)_2]$ | 263 | 1.49<br>1.52 | 2.86<br>4.08 | 3.82 | 8.91 [b] | 7.37 [b] | 7.88 [b] | | |
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 263 | 1.42<br>1.44 | 2.79<br>3.98 | 3.74 | 8.62<br>8.65 | 7.10 [b] | | | 2.37 [b] |
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_3Me_2\text{-}3,5)_2]$ | 263 | 1.41<br>1.45 | 2.78<br>3.99 | 3.73 | 8.43 [b] | | 7.42 [b] | 2.23<br>2.25 | |
| $[Mo(CO)_2Br(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 283 | 1.37<br>1.41 | 2.73<br>4.17 | 3.87 | 8.67 [b] | 7.08 [b] | | | 2.38 [b] |
| $[Mo(CO)_2I(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 283 | 1.27<br>1.37 | 2.63<br>4.38 | 4.01 | 8.66<br>8.71 | 7.05 [b] | | | 2.35<br>2.38 |

[a] In the allyl ligand, *anti*-proton ($H^a$) resonances were doublets [$^3J(H^a\text{–}H^c) = 9$ Hz], *syn*-proton ($H^s$) resonances were doublets of doublets [$^3J(H^s\text{–}H^c) = 6$, $^3J(H^s\text{–}H^{s\prime}) = 3$ Hz], and centre-proton ($H^c$) resonances were triplets of triplets. In the amine ligands, according to the substitution pattern, *ortho*-proton ($H^2$) resonances were either singlets or doublets [$^3J(H^2\text{–}H^3) = 6$ Hz], *meta*-proton ($H^3$) resonances were either doublets or doublets of doublets [$^3J(H^3\text{–}H^4) = 7$ Hz], and *para*-proton ($H^4$) resonances were either singlets or triplets. Methyl resonances were singlets. [b] Inequivalence too small to be detectable.

One feature of all the $^{13}C$ spectra (see Table 3) was that there was only a single resonance attributable to the central carbon atom, $C^c$, in the allyl ligand. In the case of the 2-methylallyl complexes, there was also only one resonance for the carbon atom in the methyl substituent, $Me^c$. Similarly, the $^1H$ spectra (see Tables 1 and 2) exhibited a single resonance for the proton, $H^c$, on the central carbon atom in the allyl complexes, and for those in the methyl substituent, $Me^c$, in the 2-methylallyl complexes. Thus there was no evidence that any of the complexes existed in more than one isomeric form in solution. In all cases separate resonances were observed for each of the carbon atoms in the carbonyl ligands, each of the carbon atoms $C^e$ at the ends of the allyl ligand, and for each *syn*($H^s$)- and *anti*($H^a$)-proton in the allyl ligand. The resonances for the *syn*-protons exhibited a doublet splitting due to the coupling between them (this was in addition to the doublet splitting caused by coupling to the central hydrogen atom in the allyl

TABLE 2

Proton n.m.r. spectra of complexes $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)L_2]$ in $CDCl_3$ solution *

| Complex | $T$/K | $H^a$ | $H^s$ | $Me^c$ | $H^2$ | $H^3$ | $H^4$ | $Me^3$ | $Me^4$ |
|---|---|---|---|---|---|---|---|---|---|
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_5)_2]$ | 243 | 1.37<br>1.41 | 2.79<br>3.68 | 2.03 | 8.79<br>9.04 | 7.31<br>7.38 | 7.79<br>7.87 | | |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_4Me\text{-}4)_2]$ | 243 | 1.34<br>1.37 | 2.75<br>3.66 | 2.05 | 8.62<br>8.83 | 7.08<br>7.13 | | | 2.38<br>2.42 |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_3Me_2\text{-}3,5)_2]$ | 233 | 1.32<br>1.36 | 2.76<br>3.61 | 2.00 | 8.31<br>8.55 | | 7.32<br>7.42 | 2.21<br>2.29 | |

* In the 2-methylallyl ligand, *anti*-proton ($H^a$) and methyl ($Me^c$) resonances were singlets; *syn*-proton ($H^s$) resonances were doublets [$^3J(H^s\text{–}H^{s\prime}) = 3$ Hz]. In the amine ligands, according to the substitution pattern, *ortho*-proton ($H^2$) resonances were either singlets or doublets [$^3J(H^2\text{–}H^3) = 6$ Hz], *meta*-proton ($H^2$) resonances were either doublets or doublets of doublets [$^3J(H^3\text{–}H^4) = 7$ Hz], and *para*-proton resonances were either singlets or triplets. Methyl resonances were singlets.

TABLE 3

Carbon-13 n.m.r. spectra of complexes $[Mo(CO)_2X(\eta\text{-}C_3H_4R)L_2]$ in $CDCl_3$ solution [a]

| Complex | $T$/K | $C^e$ | $C^c$ | $Me^c$ | $C^2$ | $C^3$ | $C^4$ | $Me^3$ | $Me^4$ | CO |
|---|---|---|---|---|---|---|---|---|---|---|
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_5)_2]$ | 263 | 59.2<br>62.5 | 72.9 | | 151.9<br>153.8 | 124.6<br>124.9 | 138.2<br>138.6 | | | 225.0<br>225.4 |
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 273 | 59.3<br>62.1 | 72.9 | | 151.3<br>153.2 | 125.4<br>125.8 | 150.2<br>150.7 | | 21.2 [b] | 225.3<br>225.6 |
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_3Me_2\text{-}3,5)_2]$ | 261 | 59.5<br>62.5 | 72.9 | | 149.1<br>151.0 | 133.6<br>134.1 | 139.5<br>139.8 | 18.4 [b] | | 225.4<br>225.6 |
| $[Mo(CO)_2Br(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 283 | 58.9<br>61.6 | 72.8 | | 152.0<br>153.9 | 125.3<br>125.9 | 150.1<br>150.7 | | 21.2 [b] | 225.2<br>225.4 |
| $[Mo(CO)_2I(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 298 | 58.0<br>60.6 | 72.1 | | 153.2<br>154.9 | 125.2<br>126.0 | 150.1<br>150.6 | | 21.2 [b] | 225.0<br>225.6 |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_5)_2]$ | 233 | 57.7<br>60.1 | 81.4 | 20.3 | 152.3<br>152.8 | 124.6<br>124.9 | 138.1<br>138.7 | | | 225.6<br>226.2 |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_4Me\text{-}4)_2]$ | 243 | 57.7<br>59.7 | 81.1 | 20.2 | 151.6<br>152.3 | 125.3<br>125.6 | 150.0<br>150.4 | | 21.1 [b] | 225.6<br>226.5 |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_3Me_2\text{-}3,5)_2]$ | 233 | 58.2<br>60.1 | 81.1 | 20.3 | 149.3<br>150.1 | 133.5<br>133.9 | 139.4<br>139.9 | 18.5 [b] | | 225.6<br>226.5 |

[a] All spectra were recorded under conditions of wide-band decoupling, and all resonances were therefore singlets. In the allyl ligand, $C^e$ represents the end carbon atoms, $C^c$ the central carbon atom, and (for the 2-methylallyl complexes) $Me^c$ the carbon atom in the methyl substituent. Labelling for amine carbon atoms is the same as for the corresponding protons (see Tables 1 and 2). [b] Inequivalence too small to be detected.

complexes). It was clear, therefore, that the structure adopted by the complexes in solution was one in which the two carbonyl ligands and the two ends of the allyl ligand were inequivalent. In addition, although not all the expected inequivalences were observed (presumably because some of the differences in chemical shift were too small to be detectable), it was clear that the two amine ligands were inequivalent in all of the complexes.

For each complex, as the temperature was raised, all the pairs of resonances in the low-temperature spectra were ultimately replaced by single resonances, indicating that some form of rearrangement was becoming fast enough to make the two carbonyl ligands, the two ends of the allyl ligand, and the two amine ligands appear equivalent. Thus, for example, the $^1$H n.m.r. spectrum of $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_5)_2]$ at 306 K, which may be compared with that recorded at 243 K (see Table 2), contained only one resonance for the *anti*-protons in the 2-methylallyl ligand (a singlet at δ 1.41) and one for the *syn*-protons (a singlet at δ 3.28: note the disappearance of the doublet splitting observed in the low-temperature spectrum, lost as the *syn*-protons become effectively equivalent). Similarly, only one set of resonances was observed for the pyridine-ring protons, a doublet $[^3J(H^2\text{–}H^3) = 6$ Hz] at δ 9.07 for the *ortho*-protons, $H^2$, a doublet of doublets $[^3J(H^3\text{–}H^4) = 7$ Hz] at δ 7.37 for the *meta*-protons, $H^3$, and a triplet at δ 7.85 for the *para*-protons, $H^4$. In the same way, one may compare the $^{13}$C spectrum of $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_5)_2]$ at 298 K with that obtained at 233 K. Details of the latter are given in Table 3: by contrast, the former contained only one resonance (at δ 59.2) for the carbon atoms at the ends of the allyl ligand, one each (at δ 152.6, 124.6, and 138.2 respectively) for the *ortho*-, *meta*-, and *para*-carbon atoms of the pyridine ligands, and one (at δ 226.0) for the carbonyl ligands.

In the case of the 2-methylallyl complexes the complete changeover from low- to high-temperature spectra could be studied in $CDCl_3$ solution, but for the allyl complexes the wide separation of the *syn*-proton resonances in the low-temperature spectra and (see below) the rather lower rate of rearrangement at any given temperature meant that an averaged *syn*-proton resonance could still not be seen at the boiling point of $CDCl_3$. A change of solvent to chlorobenzene solved this problem and also, by magnifying chemical-shift differences between pairs of inequivalent protons in the low-temperature spectra, made it easier to study the variation in spectra with temperature. Thus the $^1$H spectrum of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ in chlorobenzene solution at 263 K may be compared with that (see Table 1) obtained from a $CDCl_3$ solution at the same temperature. In chlorobenzene, the two *anti*-proton resonances were located at δ 1.42 and 1.59, the two *syn*-proton resonances at δ 2.72 and 4.36, and the two resonances for the methyl substituents in the amine ligands (not resolved from one another in $CDCl_3$) at δ 1.75 and 1.83. A rise in temperature to 306 K was sufficient to cause coalescence of both the *anti*-proton and methyl-proton resonances, and at 350 K a single averaged resonance [a somewhat broadened doublet with $^3J(H^s\text{–}H^c) = 6$ Hz] was observed for the two *syn*-protons. The resonance sharpened somewhat at higher temperatures.

Rough values for the coalescence temperatures for the various pairs of resonances were used * to obtain an indication of the relative rates of rearrangement for the various complexes in chlorobenzene solution. Change in the amine ligand had no significant effect on rearrangement rate, whereas increase in the size of the halogen ligand decreased the rate: at 294 K the rate of rearrangement for $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ was roughly five times as great as that for its iodo-analogue, with an intermediate rate for the bromo-complex. Much more marked, however, was the effect of introducing a methyl substituent on the central carbon atom of the allyl ligand: at 278 K the rates of rearrangement of the 2-methylallyl complexes were over 30 times greater than those for the analogous allyl complexes.

One feature of the spectra of the 2-methylallyl complexes was not shared by those of the allyl complexes. In the $^1$H n.m.r. spectrum of $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_5)_2]$ recorded at 243 K (see Table 2), the resonance for the *ortho*-protons in one pyridine ligand at δ 9.04 was slightly broader than that at δ 8.79 for those in the other pyridine ligand. Further decrease in temperature accentuated the difference: at 223 K the former resonance was a featureless hump, whereas the latter was still a sharp doublet. Similarly, in the $^{13}$C spectrum recorded at 233 K (see Table 3), the *ortho*-carbon resonance at δ 152.3 was somewhat broader than that at δ 152.8, and at 223 K the former had almost completely collapsed, whereas the latter remained sharp. It was concluded that both broadened resonances were for atoms in the same pyridine ligand, and that the broadening was due to restriction of rotation of this ligand about the metal–nitrogen bond.

Similar changes were observed for the *ortho*-carbon atoms and their associated hydrogen atoms in $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_4Me\text{-}4)_2]$. In the case of $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_3Me_2\text{-}3,5)_2]$, at 243 K the *ortho*-proton resonance at δ 8.57 was already markedly broader than that at δ 8.32, and at 233 K it had almost collapsed. At 217 K, separate resonances could be seen at δ 8.71 and 8.37 for each of the two *ortho*-protons on the ring whose rotation was restricted, whereas the observation of one sharp resonance at δ 8.30 for those on the other ring showed it still to be rotating freely.

(3) *Structure of the Complexes and Mechanism of the Rearrangement Process.*—The mechanism for the rearrangement could be either dissociative or intramolecular. A dissociative process could involve the partial dissociation of the η-allyl ligand to give a σ-allyl

---

* For the use of coalescence temperatures to determine rearrangement rates, see, for example, J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

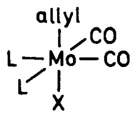
intermediate or reversible loss of an amine, carbonyl, or halogen ligand (either as halide ion or halogen atom). Reversible formation of a $\sigma$-allyl intermediate would result in scrambling of protons between *syn* and *anti* positions in the allyl ligand: this was not observed for any of the complexes, so a mechanism of this type was ruled out.

The complex $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_3Me_2\text{-}3,5)_2]$ was chosen for the test for reversible loss of an amine ligand because it contained the most bulky amine used. Free 3,5-dimethylpyridine was added to a chlorobenzene solution of the complex, and $^1H$ n.m.r. spectra recorded over a range of temperatures provided no evidence for rapid exchange between free and co-ordinated amine. A similar check was made for the 2-methylallyl complex $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_3Me_2\text{-}3,5)_2]$. At 299 K, which was above the coalescence temperature for all pairs of resonances in the complex, the spectrum still contained separate methyl-proton resonances for free and co-ordinated amine, again ruling out the possibility that the rearrangement occurred by way of amine dissociation. Interestingly, however, spectra recorded at higher temperatures provided evidence of a *separate* process involving amine exchange. At 313 K the resonances for free and co-ordinated amine had almost coalesced, and at 333 K a single, sharp, averaged resonance was observed. The rest of the spectrum remained unaltered. Given the high co-ordination number of the complex, it seemed likely that exchange occurred by a dissociative mechanism: certainly it did not proceed by way of a $\sigma$-allyl intermediate $[Mo(CO)_2Cl(\sigma\text{-}C_4H_7)(NC_5H_3Me_2\text{-}3,5)_3]$, since this would have resulted in exchange of *syn*- and *anti*-protons in the allyl ligand, and this did not occur.

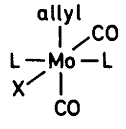
Dissociation of a carbonyl ligand was tested for by recording $^{13}C$ n.m.r. spectra of a mixture of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ and $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_4Me\text{-}4)_2]$ in $CDCl_3$ solution over a range of temperature. The pair of resonances for the two carbonyl ligands in the allyl complex coalesced independently of those for the 2-methylallyl complex, and at 313 K a single, sharp, carbonyl resonance was observed for each complex. The absence of rapid exchange of carbonyl ligands between the two complexes proved that rearrangement in the individual complexes did not involve dissociation of a carbonyl ligand.

In order to test for dissociation of the halogen ligand, the $^1H$ n.m.r. spectrum of a mixture of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ and $[Mo(CO)_2Br(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ in chlorobenzene solution was examined. Dissociation of the halogen ligands would result in halogen exchange between the two complexes, and hence in the observation of a *single* set of proton resonances for the two complexes at temperatures high enough for averaged resonances to be observed for each complex on its own. Many resonances in the spectra of the two complexes were virtually superimposed and hence useless for the test, but those for the *anti*-protons were sufficiently separated to be suitable. With increasing temperature, each pair of resonances coalesced independently, and at 343 K one sharp doublet was observed for each complex. Thus it was apparent that rearrangement did not involve dissociation of the halogen ligand.

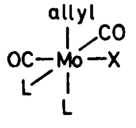
It was therefore clear that the rearrangement must occur by an intramolecular process, but the exact nature of the rearrangement necessary to produce the observed changes in spectra depended on the stereochemistry of the complexes. Assuming that, as in the case of those $\eta$-allyl molybdenum(II) complexes which have been studied by *X*-ray diffraction,[4,6–10] the ligands are arranged in an approximately regular octahedron around the metal, four structures, (I)—(IV), are compatible with the i.r. spectra of the complexes. Of these, (I) and (II) fit the low-temperature n.m.r. spectra only if it is assumed that rotation of the allyl ligand about an axis from the metal through the centre of the ligand is restricted at low temperatures, and if the preferred orientation of the ligand is an unsymmetrical one. For (III) and (IV) no such proviso is necessary.



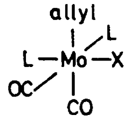
(I)



(II)



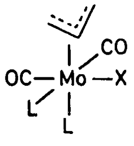
(III)



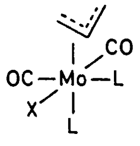
(IV)

Structure (I) is similar to that adopted by $[Mo(CO)_2(NCS)(\eta\text{-}C_3H_5)(bipy)]$ [7] and $[Mo(CO)_2(NCS)(\eta\text{-}C_4H_7)(phen)]$ [8] in the solid state, except that the structures of these complexes are essentially symmetrical, with the central carbon atom of the allyl ligand lying on the same side of the metal as the bidentate nitrogen ligand and approximately in the plane of symmetry which runs through the rest of the complex. The bipyridyl and phenanthroline ligands are, however, planar, making their steric interactions with the allyl ligand relatively unimportant. In contrast, the two pyridine rings in the complexes $[Mo(CO)_2X(\eta\text{-}C_3H_4R)L_2]$ can rotate independently of one another, and in structure (I) would (for steric reasons) be expected *not* to lie in the plane of the metal and the carbonyl ligands, so the allyl ligand might adopt an unsymmetrical orientation because of interactions with the amine ligands. There would automatically be a pair of such orientations, and the changes in n.m.r. spectra with temperature would be attributed to the increasing rate of the oscillatory movement of the allyl ligand about the metal–allyl axis which interconverts the two forms. Precedents for this type of restricted rotation of the allyl ligand in molybdenum(II) complexes come from the work of Davison and Rode [11] and Faller and Incorvia [12] on $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$, and, in particular, from the study by Faller and Haitko [5] of $[Mo(CO)_3(\eta\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)]^+$, which they believed to be undergoing interconversion between the two forms (VA) and (VB).

If (I) is the correct structure, one must consider why rearrangement is so much more rapid for the 2-methylallyl than for the allyl complexes, and why rotation of one of the amine ligands should be restricted for the 2-methylallyl but not for the allyl complexes. It may be that one orientation of the allyl ligand, with the central carbon atom fairly close to an amine ligand, is strongly preferred for the allyl complexes, so that the energy profile for rotation of the allyl ligand about the metal–allyl axis has a deep trough in it at this point. Introduction of a methyl substituent on the central carbon atom could then raise the energy of this structure because of the repulsion between methyl substituent and amine ligand, thus at the same time increasing the rate of rotation of the allyl ligand and restricting the rotation of the amine ligand concerned. One drawback of (I) is the fact that a change in the halogen ligand significantly affects the rearrangement rate whereas introduction of methyl substituents on the pyridine rings does not: given the ligand arrangement in (I), one might have expected the reverse.



(IIIA)



(IIIB)

Structure (II) is similar to that adopted by $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(PMe_2Ph)_2]$ in the solid state.[13] Here, however, the 2-methylallyl ligand adopts an approximately symmetrical position and, although this complex and others like it also have temperature-dependent n.m.r. spectra,[14] in these cases the two phosphorus ligands appear to be equivalent at all temperatures, as do the two ends of the allyl ligand. Also the rate of rearrangement is increased, not decreased, by removal of the methyl substituent in the allyl ligand. Finally it can be seen that no single movement of the ligands in (II) could result in all the changes in n.m.r. spectrum exhibited by the amine complexes. We therefore reject (II) as a structure for the complexes.

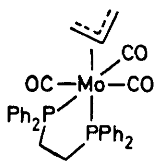
TABLE 4

Analytical data and i.r. spectra * for complexes $[Mo(CO)_2X(\eta\text{-}C_3H_4R)L_2]$

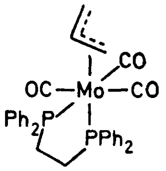
| Complex | Analysis (%) Found C | H | N | Calc. C | H | N | $\tilde{\nu}$(C–O)/cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_5)_2]$ | 46.3 | 4.00 | 7.55 | 46.6 | 3.90 | 7.25 | 1 920, 1 823 |
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 49.6 | 4.40 | 6.55 | 49.25 | 4.60 | 6.75 | 1 922, 1 824 |
| $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_3Me_2\text{-}3,5)_2]$ | 51.05 | 5.70 | 6.05 | 51.55 | 5.25 | 6.35 | 1 933, 1 820 |
| $[Mo(CO)_2Br(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 45.0 | 4.20 | 5.85 | 44.45 | 4.15 | 6.10 | 1 921, 1 821 |
| $[Mo(CO)_2I(\eta\text{-}C_3H_5)(NC_5H_4Me\text{-}4)_2]$ | 41.35 | 4.40 | 5.45 | 40.35 | 3.80 | 5.55 | 1 934, 1 832 |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_5)_2]$ | 47.65 | 4.50 | 7.00 | 47.95 | 4.30 | 7.00 | 1 910, 1 815 |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_4Me\text{-}4)_2]$ | 50.65 | 5.15 | 6.40 | 50.4 | 4.95 | 6.55 | 1 930, 1 826 |
| $[Mo(CO)_2Cl(\eta\text{-}C_4H_7)(NC_5H_3Me_2\text{-}3,5)_2]$ | 52.35 | 5.70 | 5.95 | 52.6 | 5.50 | 6.15 | 1 930, 1 825 |

* In the C–O stretching region only. Spectra were recorded on Nujol mulls of the complexes.

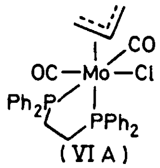
Structure (III) is related to that of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)]$, which also possesses a temperature-dependent n.m.r. spectrum. Faller *et al.*[4] proposed that this resulted from a reversible, 120°, trigonal twisting motion of the halogen and phosphorus ligands relative to the rest of the complex, *i.e.* (VIA) $\rightleftharpoons$ (VIB). An analogous twisting motion, (IIIA) $\rightleftharpoons$ (IIIB), would account for the changes in the n.m.r. spectra of the amine complexes with temperature. It is also easier than in the case of (I) to see why change in the halogen ligand should affect the rearrangement rate, and why rotation of only *one* of the two amine ligands (presumably that which is *cis* to the allyl ligand) should be restricted at low temperatures in the 2-methylallyl complexes. The explanation for the increase in rearrangement rate caused by the introduction of the methyl substituent in the allyl ligand must be similar to that proposed for structure (I).



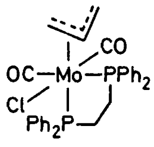
(VA)



(VB)



(VIA)



(VIB)

Finally, if the complexes possessed structure (IV), the variation in n.m.r. spectra with temperature could again be due to a trigonal twisting motion, in this instance of the carbonyl and halogen ligands. The disadvantages of (IV) are first that (so far as we are aware) no related η-allyl molybdenum(II) complex has been shown to adopt this particular ligand arrangement, and secondly that it is less obvious than in the case of (III) why the presence of a methyl substituent on the allyl ligand should restrict rotation of one amine ligand but not of the other.

Thus we believe that the structure of the complexes $[Mo(CO)_2X(\eta\text{-}C_3H_4R)L_2]$ (X = halogen, R = H or Me, L = amine) in solution is either (I) or (III), and, for reasons given above, we regard (III) as the more likely alternative.

## EXPERIMENTAL

All preparative work was carried out under dry nitrogen in dry, nitrogen-saturated solvents. The method used to prepare the complexes $[Mo(CO)_2Cl(\eta\text{-}C_3H_4R)(NCMe)_2]$ (R = H or Me) has been described earlier,[2,3] and the complexes $[Mo(CO)_2X(\eta\text{-}C_3H_5)(NCMe)_2]$ (X = Br or I) were prepared in the same way using 3-bromo- or 3-iodo-propene in place of 3-chloropropene. Details of the preparation of one of the complexes $[Mo(CO)_2X(\eta\text{-}C_3H_4R)L_2]$ are given below: the others were prepared in the same way.

$[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NC_5H_3Me_2\text{-}3,5)_2]$. A solution of $[Mo(CO)_2Cl(\eta\text{-}C_3H_5)(NCMe)_2]$ (0.20 g) in ethanol (40 cm$^3$) was treated with 3,5-dimethylpyridine (0.14 g). The solution rapidly became deep orange, and when the colour change was complete solvent was removed under reduced pressure until orange crystals started to form. The solution was then left under nitrogen until crystallisation was complete. The mother-liquor was removed, and the crystals were washed with ethanol and then with light petroleum (b.p. 313—333 K). This and the other complexes could also be satisfactorily prepared in propanone solution. Analytical data for the complexes are collected in Table 4.

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer, $^1$H n.m.r. spectra on a JEOL N-MH-100 spectrometer with the NM-VT-3B variable-temperature attachment, and $^{13}$C n.m.r. spectra on a JEOL FX-60 instrument with the NM-5471 variable-temperature attachment. Chemical-shift values are given on the $\delta$ scale, and were measured relative to tetramethylsilane, which was used as an internal standard.

We thank Mrs. B. Howard and Dr. A. J. G. Crawshaw for experimental assistance.

[9/1380 *Received*, 30*th August*, 1979

## REFERENCES

[1] C. G. Hull and M. H. B. Stiddard, *J. Organometallic Chem.*, 1967, **9**, 519.
[2] H. tom Dieck and H. Friedel, *J. Organometallic Chem.*, 1968, **14**, 375.
[3] D. A. Clark, D. L. Jones, and R. J. Mawby, *J.C.S. Dalton*, 1980, 565.
[4] J. W. Faller, D. A. Haitko, R. D. Adams, and D. F. Chodosh, *J. Amer. Chem. Soc.*, 1977, **99**, 1654.
[5] J. W. Faller and D. A. Haitko, *J. Organometallic Chem.*, 1978, **149**, C19.
[6] B. J. Brisdon and A. A. Woolf, *J.C.S. Dalton*, 1978, 291.
[7] A. J. Graham and R. H. Fenn, *J. Organometallic Chem.*, 1969, **17**, 405.
[8] A. J. Graham and R. H. Fenn, *J. Organometallic Chem.*, 1970, **25**, 173.
[9] R. H. Fenn and A. J. Graham, *J. Organometallic Chem.*, 1972, **37**, 137.
[10] F. Dawans, J. Dewailly, J. Meunier-Piret, and P. Piret, *J. Organometallic Chem.*, 1974, **76**, 53.
[11] A. Davison and W. C. Rode, *Inorg. Chem.*, 1967, **6**, 2124.
[12] J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, 1968, **7**, 840.
[13] L. Smart, personal communication.
[14] D. A. Clark, D. L. Jones, and R. J. Mawby, unpublished work.