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TEMPERATURE-DEPENDENCE OF THE NMR SPECTRA OF π-CYCLOPENTADIENYL COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

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SUMMARY

The relatively simple room temperature NMR spectra of complexes π-$C_5H_5M(CO)L_2X$ [M=Mo, W; L=phosphorus(III) ligand; X=halogen] become more complicated at lower temperatures. Two possible interpretations of the spectra and the change in their appearance with temperature are put forward: one involves the assumption of *trans*-stereochemistry for all the complexes, and restricted rotation of one or more of the ligands about the metal–ligand bond at low temperatures, while the other attributes the changes in spectra to *cis*⇄*trans* isomerization and/or *cis*⇄*cis* interconversion within the complexes, these processes being rapid at room temperature (so that averaged spectra are obtained) but relatively slow at the lowest temperatures reached.

INTRODUCTION

A recent X-ray crystallographic determination of the structure of the compound π-$C_5H_5Mo(CO)(PPh_3)_2NCO$ has shown[1] that its stereochemistry is related to those of complexes π-$C_5H_5Mo(CO)_3X$[2] and π-$C_5H_5Mo(CO)_2LX$[3,4] (X^-=anionic ligand; L=uncharged ligand), with the four monodentate ligands as the base of an approximate square pyramid which has the cyclopentadienyl ligand as its apex. As in the case of complexes π-$C_5H_5Mo(CO)_2LX$, this raises the possibility that compounds π-$C_5H_5Mo(CO)L_2X$ may exist in two isomeric forms. These can be labelled *cis* and *trans* according to the relative positions of the two ligands L in the base of the pyramid.

NMR spectra of complexes π-$C_5H_5Mo(CO)L_2X$ with suitable ligands L should allow a distinction to be made between the two isomers, since in *cis*-isomers the two ligands L are inequivalent while in *trans*-isomers they are equivalent. The situation is complicated by the fact that in both *cis*- and *trans*-isomers the Mo–L bonds do not lie in planes of symmetry through the molecule. If L is, for example, PMe_2Ph or $P(OMe)_2Ph$, the two methyl groups on a given ligand will, as a result, be inequivalent.

In a preliminary communication[5], we reported that the proton NMR spectrum of the complex π-$C_5H_5Mo(CO)(PMePh_2)_2Cl$ varied with temperature. In this paper we describe the behaviour of a number of complexes π-$C_5H_5M(CO)L_2X$ [M=Mo, W; L=phosphorus(III) ligand; X=Cl, I] and discuss possible interpretations of their spectra.

RESULTS AND DISCUSSION

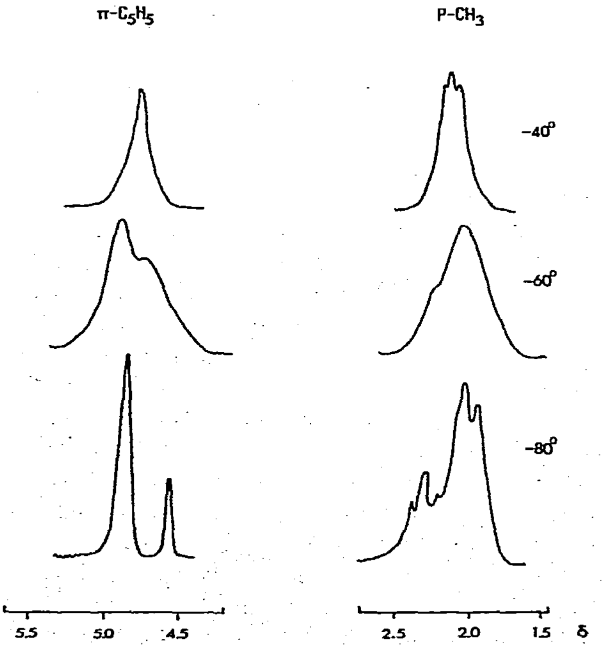
The proton NMR spectra of several complexes π-$C_5H_5M(CO)L_2X$ in $CDCl_3$ solution at 25° are given in Table 1. The effects of changes in temperature on the spectra of the complexes π-$C_5H_5Mo(CO)(PMePh_2)_2Cl$, π-$C_5H_5Mo(CO)[P(OMe)Ph_2]_2Cl$ and π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2I$ are shown in Fig. 1, 2 and 3. The behaviour of

TABLE 1

NMR SPECTRA OF COMPLEXES π-$C_5H_5M(CO)L_2X^a$

Complex	*C_5H_5*	*CH_3*
π-$C_5H_5Mo(CO)(PMePh_2)_2Cl$	4.85 (5)	2.15 (6)
π-$C_5H_5W(CO)(PMePh_2)_2Cl$	4.95 (5)	2.15 (6)
π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$	4.75 (5)	1.85 (12)
π-$C_5H_5Mo(CO)[P(OMe)Ph_2]_2Cl$	5.07 (5)	3.60 (6)
π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2Cl$	5.13 (5)	3.55 (6), 3.30 (6)
π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2I$	5.08 (5)	3.53 (6), 3.20 (6)

[a] Excluding resonances due to phenyl protons. Chemical shifts are given on the δ(ppm) scale. Spectra were recorded on $CDCl_3$ solutions of the complexes at 25°, using TMS as an internal standard. Figures in parentheses represent the relative areas of the peaks.



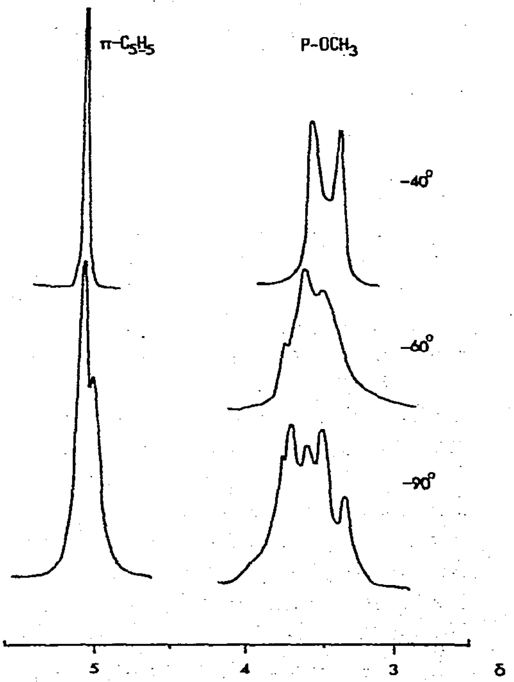


Fig. 1. The effect of changes in temperature on the NMR spectrum of π-$C_5H_5Mo(CO)(PMePh_2)_2Cl$ in $CD_2Cl_2/CDCl_3$.

Fig. 2. The effect of changes in temperature on the NMR spectrum of π-$C_5H_5Mo(CO)[P(OMe)Ph_2]_2Cl$ in CD_2Cl_2.

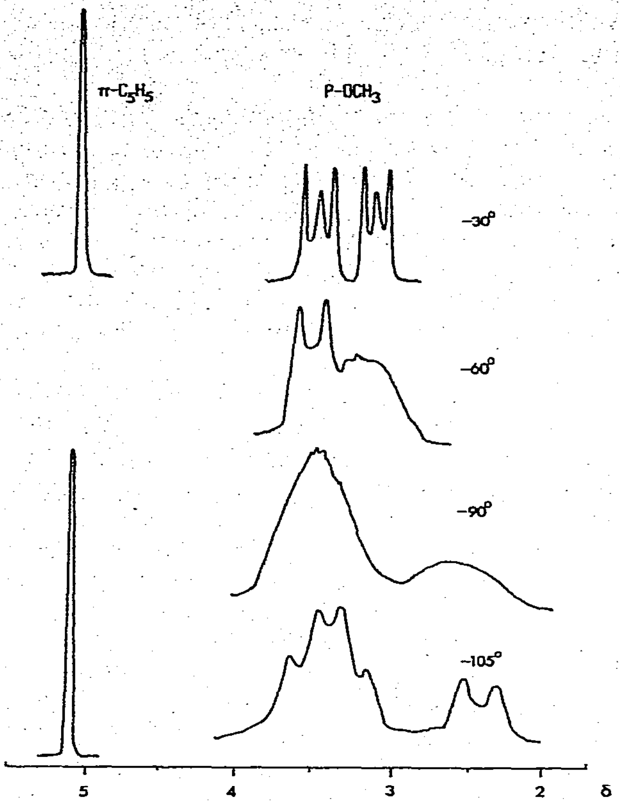


Fig. 3. The effect of changes in temperature on the NMR spectrum of π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2I$ in $CHFCl_2$.

the complex π-$C_5H_5W(CO)(PMePh_2)_2Cl$ was similar to that of its molybdenum analogue, while the changes in the spectrum of π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2Cl$ resembled those for the iodo complex, but occurred at lower temperatures. The complex π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$ is mentioned later. The lower limit of the temperature range used in each case was imposed by the solubility of the complex in the available solvents. All changes in spectra with temperature were reversible.

All the spectra recorded at 25° exhibited a single resonance for the cyclopentadienyl protons, although in some cases this was rather broad. In all cases, the resonances for the methyl protons in the ligand L were characteristic of "intermediate coupling"[5,6] rather than the 1/2/1 triplets expected for a "virtual coupling" situation[7]. In Table 2, the number of resonances observed for the methyl protons in the ligands L in the spectra recorded at 25° is compared with those expected for *cis*- and *trans*-stereochemistry.

If one ignores the changes in spectra at lower temperatures, the spectra at 25° appear to be easy to interpret. Whereas they do not seem to be compatible with *cis*-structures for the complexes, in all cases but one they match those expected for *trans*-isomers. The one discrepancy [one resonance instead of two for the methyl protons in π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$] could be attributed to an accidental superimposition of resonances due to formally inequivalent sets of methyl protons (although from our experience with complexes containing the ligand PMe_2Ph we would regard this as most unusual).

This apparent uniform preference for a *trans*-arrangement is surprising after the delicate balance between *cis*- and *trans*-stereochemistries for the related complexes π-$C_5H_5Mo(CO)_2LX$[8,9]. It could perhaps be rationalized on the grounds that it minimizes repulsion between the two phosphorus ligands, but such an argument ignores the steric requirements of the halogen ligand, which must be considerable in the case of the iodo-complex π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2I$. It is also odd that the complex π-$C_5H_5Mo(CO)(PPh_3)_2NCO$, where repulsion between the phosphorus ligands should be particularly marked, has been reported to exist in solution in both *cis*- and *trans*-forms[1].

Any consideration of the stereochemistry of the complexes π-$C_5H_5M(CO)L_2X$ must also take into account the changes in NMR spectra with decreasing temperature. Assuming that the assignment of *trans*-structures to all the complexes is correct, the changes in spectra on cooling must be ascribed to restricted rotation of one or more of the ligands about the metal–ligand bond. Examples of restricted rotation of both the π-cyclopentadienyl ligand and phosphorus(III) ligands appear to be rare, except where the phosphorus ligand bears very bulky substituents such as the tert-butyl group[10]. One awkward feature of the spectra, from the restricted rotation point of view, is that in some cases [π-$C_5H_5Mo(CO)L_2Cl$, L = $PMePh_2$, PMe_2Ph and $P(OMe)Ph_2$; π-$C_5H_5W(CO)(PMePh_2)_2Cl$] both the cyclopentadienyl resonance and the resonances due to the methyl protons in the phosphorus(III) ligands broaden as the temperature is lowered, whereas in the case of the complexes π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2X$ (X = Cl, I) the resonances due to the methoxy-protons broaden but that due to the cyclopentadienyl protons does not alter in appearance. There appears to be no obvious reason why steric effects within these two complexes should differ sufficiently from those in the remaining complexes to produce this result.

If the theory that the changes in spectra are due to restricted rotation of the ligands is not accepted, it is necessary to abandon the assumption that the spectra at 25° are those of pure *trans*-isomers. An alternative explanation for the relatively simple appearance of these spectra would be that they are averages of the spectra of different forms of the complexes which, at this temperature, are undergoing rapid intramolecular interconversion in a manner reminiscent of the behaviour of the monosubstituted complexes π-$C_5H_5Mo(CO)_2LX$ at higher temperatures[9]. Two types of rearrangement are possible, one a *cis*$\rightleftarrows$*trans* isomerization and the other a *cis*$\rightleftarrows$*cis* interconversion which does not pass through the *trans*-isomer but has the effect of interchanging the identities of the two phosphorus(III) ligands. Whereas the *cis*$\rightleftarrows$*cis* interconversion would presumably take place in any system which was undergoing *cis*$\rightleftarrows$*trans* isomerization, it would also be possible for *cis*$\rightleftarrows$*cis* interconversion to occur in complexes where the *trans*-isomer was appreciably less stable than the *cis*-, thus ruling out *cis*$\rightleftarrows$*trans* isomerization.

The type of spectrum to be expected from each of the complexes assuming (*a*) that the complex exists as a mixture of rapidly interconverting *cis*- and *trans*-isomers or (*b*) that the complex exists entirely as a *cis*-isomer which is undergoing rapid *cis*$\rightleftarrows$*cis* interconversion is shown in Table 2. One important point to note is that for complexes containing the ligands PMe_2Ph and $P(OMe)_2Ph$ the inequivalence of the two methyl

TABLE 2

NUMBER OF RESONANCES OBSERVED AT 25° FOR THE METHYL PROTONS IN THE LIGANDS L OF COMPLEXES π-$C_5H_5M(CO)L_2X$ COMPARED WITH THE NUMBER EXPECTED IN VARIOUS CIRCUMSTANCES

Complex	*Observed*	*Expected for*			
		cis-isomer	*trans-isomer*	*interconverting cis and trans isomers*	*cis-isomer undergoing cis$\rightleftharpoons$cis interconversion*
π-$C_5H_5Mo(CO)(PMePh_2)_2Cl$	1	2	1	1	1
π-$C_5H_5W(CO)(PMePh_2)_2Cl$	1	2	1	1	1
π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$	1	4	2	1	2
π-$C_5H_5Mo(CO)[P(OMe)Ph_2]_2Cl$	1	2	1	1	1
π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2Cl$	2	4	2	1	2
π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2I$	2	4	2	1	2

groups in a given ligand is retained in a *cis*$\rightleftharpoons$*cis* interconversion process. It can be seen that the 25° spectra of the complexes π-$C_5H_5M(CO)(PMePh_2)_2Cl$ (M = Mo, W) and π-$C_5H_5Mo(CO)[P(OMe)Ph_2]_2Cl$ could be produced by either type of interconversion, whereas *cis*$\rightleftharpoons$*trans* isomerization is required by the simple spectrum of π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$ and ruled out by the more complex spectra of π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2X$ (X = Cl, I), which can only be produced by *cis*$\rightleftharpoons$*cis* interconversion.

With falling temperature, the decrease in rate of the interconversion processes must eventually lead to broadening of the resonances due to the methyl protons, as observed. A change in the appearance of the resonance due to the cyclopentadienyl protons, however, is only to be expected if the complex is undergoing *cis*$\rightleftharpoons$*trans* isomerization, and not for a *cis*-isomer undergoing *cis*$\rightleftharpoons$*cis* interconversion. For the complexes π-$C_5H_5M(CO)(PMePh_2)_2Cl$ (M = Mo, W) and π-$C_5H_5Mo(CO)[P(OMe)Ph_2]_2Cl$, broadening of the resonances due to the methyl protons is accompanied by broadening of that due to the cyclopentadienyl protons, and at the lowest temperatures reached, separate resonances for the cyclopentadienyl protons in the *cis*- and *trans*-isomers are visible. In the case of π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$, broadening of the resonance due to the methyl protons is only observed at very low temperatures, but here again there is a corresponding change in the cyclopentadienyl proton resonance. In contrast, the broadening of the methyl proton resonances in the complexes π-$C_5H_5Mo(CO)[P(OMe)_2Ph]X$ (X = Cl, I) is not accompanied by a change in the appearance of the cyclopentadienyl proton resonance. This is exactly what one would expect from the spectra of the complexes at 25°: evidently these complexes, unlike the others, exist solely as the *cis*-isomers in solution, and undergo *cis*$\rightleftharpoons$*cis* interconversion at a rate which is sufficiently rapid at 25° to make the two $P(OMe)_2Ph$ ligands appear equivalent.

Of the two hypotheses suggested to account for the NMR spectra and their variation with temperature, we are inclined to favour the "rapid interconversion" rather than the "restricted rotation" theory. On this basis, the ligands $PMePh_2$,

PMe_2Ph and $P(OMe)Ph_2$ are seen to yield mixtures of *cis*- and *trans*-isomers of complexes π-$C_5H_5M(CO)L_2X$, while $P(OMe)_2Ph$ yields pure *cis*-isomers. This trend is what one would expect, since $P(OMe)_2Ph$ is less bulky than $PMePh_2$ and $P(OMe)Ph_2$, and a better π-acceptor than $PMePh_2$ and PMe_2Ph.

One drawback to the "rapid interconversion" theory is that it requires rearrangement to be much faster at a given temperature for complexes π-$C_5H_5Mo(CO)L_2X$ than for the monosubstituted complexes π-$C_5H_5Mo(CO)_2LX$, suggesting that ligand rearrangement is favoured by increased crowding (perhaps because the crowding is less severe in the activated state than in the *cis*- and *trans*-isomers themselves). This then has to be reconciled with the fact that within the series π-$C_5H_5Mo(CO)L_2X$ the rate of interconversion at a given temperature decreases as the bulkiness of the ligands X and L increases. This is shown by comparison of the spectra of π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$ and π-$C_5H_5Mo(CO)(PMePh_2)_2Cl$ and of π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2Cl$ and π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2I$, and by the fact that the complex π-$C_5H_5Mo(CO)(PPh_3)_2NCO$ is reported to exhibit separate resonances for the cyclopentadienyl protons in the *cis*- and *trans*-isomers at all temperatures studied[1].

EXPERIMENTAL

The complexes π-$C_5H_5M(CO)L_2X$ were prepared by heating the halo-compounds π-$C_5H_5M(CO)_3X$[11-13] with slightly more than the required amount of the phosphorus(III) ligand L under reflux in petroleum ether (b.p. 100–120°) for two to three days. In some cases, analytically pure crystals of the product were obtained on concentrating the solution, while in others the residue after removal of the solvent required recrystallization from dichloromethane/petroleum ether (b.p. 40–60°). Yields were generally between 50 and 60%. Analytical data and IR spectra in the C–O stretching region are given in Table 3. (The single C–O stretching band observed cannot be regarded as evidence for the presence of one isomer of each product only, since it is known that the C–O stretching bands of *cis*- and *trans*-isomers of the related complexes π-$C_5H_5Mo(CO)_2LX$ are almost always exactly superimposed[14].)

NMR spectra were recorded on a Perkin–Elmer R10 60 MHz spectrometer fitted with a variable temperature probe attachment (except for the tungsten complex,

TABLE 3

ANALYTICAL DATA AND IR SPECTRA OF COMPLEXES π-$C_5H_5M(CO)L_2X$

Complex	*Found*			*Calculated (%)*			*ν(C–O)*[a] *(cm⁻¹)*
	C	*H*	*X*	*C*	*H*	*X*	
π-$C_5H_5Mo(CO)(PMePh_2)_2Cl$	61.36	5.02	5.73	61.52	5.00	5.67	1810[b]
π-$C_5H_5W(CO)(PMePh_2)_2Cl$	53.91	4.38	4.92	53.93	4.38	4.97	1790[b]
π-$C_5H_5Mo(CO)(PMe_2Ph)_2Cl$	52.70	5.37	7.16	52.75	5.44	7.08	1801[b]
π-$C_5H_5Mo(CO)[P(OMe)Ph_2]_2Cl$	58.72	4.88	5.42	58.51	4.76	5.40	1848[c]
π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2Cl$	45.84	4.76	6.33	46.78	4.82	6.28	1845[b]
π-$C_5H_5Mo(CO)[P(OMe)_2Ph]_2I$	39.90	4.17	19.45	40.26	4.15	19.34	1863[b]

[a] IR spectra recorded on a Perkin–Elmer 257 spectrophotometer. [b] Hexane solution. [c] Dichloromethane solution

where the spectra at temperatures other than 25° were recorded by Dr. D. F. Ewing of Hull University on a JEOL 100 MHz spectrometer). The solvent employed for the low temperature studies on the complexes whose spectra are not illustrated in Fig. 1–3 was CD_2Cl_2.

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REFERENCES

1 A. T. McPhail, G. R. Knox, C. G. Robertson and G. A. Sim, *J. Chem. Soc. A*, (1971) 205.
2 S. Chaiwasie and R. H. Fenn, *Acta Crystallogr. B*, 24 (1968) 525.
3 M. A. Bush, A. D. U. Hardy, Lj. Manojlović–Muir and G. A. Sim, *J. Chem. Soc. A*, (1971) 1003.
4 R. H. Fenn and J. H. Cross, *J. Chem. Soc. A*, (1971) 3312.
5 G. Wright and R. J. Mawby, *J. Organometal. Chem.*, 29 (1971) C29.
6 R. K. Harris, *Can. J. Chem.*, 42 (1964) 2275.
7 J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, (1963) 279.
8 R. J. Mawby and G. Wright, *J. Organometal. Chem. (London)*, 21 (1970) 169.
9 J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 92 (1970) 5852.
10 B. E. Mann, C. Masters, B. L. Shaw and R. E. Stainbank, *Chem. Commun.*, (1971) 1103.
11 C. White and R. J. Mawby, *Inorg. Chim. Acta*, 4 (1970) 261.
12 E. W. Abel, A. Singh and G. Wilkinson, *J. Chem. Soc.*, (1960) 1321.
13 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
14 A. R. Manning, *J. Chem. Soc. A*, (1967) 1984.