

Preliminary communication

Stereochemical non-rigidity in a "crowded" molybdenum(II) complex

GILLIAN WRIGHT and R.J. MAWBY

Department of Chemistry, University of York, Heslington, York YO1 5DD (Great Britain)

(Received March 31st, 1971)

The complex $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{Cl}$ has approximate square pyramidal geometry, with the cyclopentadienyl ligand in the apical position and the other four ligands forming the base of the pyramid¹. Replacement of one carbonyl ligand by a phosphorus(III) ligand L can give rise to pairs of isomers $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2\text{LCl}$ with the remaining carbonyl groups either *cis* or *trans* to one another in the base². At high temperatures ($> 100^\circ$) intramolecular interconversion between the isomers is fast enough to average the NMR resonances of the individual isomers².

Similar *cis-trans* isomerism can be expected for complexes $\pi\text{-C}_5\text{H}_5\text{Mo(CO)L}_2\text{Cl}$. However, the NMR spectrum of the complex with $\text{L} = \text{PMePh}_2$ in CD_2Cl_2 at 25° exhibits only one resonance (δ 4.83) for the cyclopentadienyl protons and one (δ 2.12; ${}^2J(\text{P-H}) + {}^4J(\text{P-H}) = 8.6$ Hz; shape of resonance typical of "intermediate" P-P coupling³) for the methyl protons on the phosphorus ligands. At first sight, this would suggest that the complex exists only as the *trans*-isomer, since two resonances would be expected for the methyl protons in the *cis*-isomer.

That this is an oversimplification of the situation is shown by studying the NMR spectrum as a function of temperature. As the temperature is lowered, both the cyclopentadienyl and the methyl resonance broaden and then collapse. At -62° two distinct cyclopentadienyl resonances (at δ 4.58 and δ 4.88) can be observed, and further lowering of the temperature causes these resonances to sharpen. The two resonances, one presumably characteristic of *cis*- $\pi\text{-C}_5\text{H}_5\text{Mo(CO)(PMePh}_2)_2\text{Cl}$ and the other of the *trans* isomer, are unequal in area, and the relative areas vary somewhat with temperature, indicating a shift in the position of equilibrium. The spectrum of the methyl protons on the phosphorus ligands below the coalescence temperature is (as would be expected) distinctly complex, and interpretation is hindered by the overlapping of the resonances from the two isomers. It is clear from the observation of coupling between the phosphorus ligands at 25° that the isomerization does not involve dissociation of a phosphorus ligand.

It is remarkable that the replacement of one carbonyl ligand in $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2\text{LCl}$ by a phosphorus ligand has lowered the coalescence temperature by over 150° . (That this is not simply a steric effect is shown by our preliminary observation that the complex $\pi\text{-C}_5\text{H}_5\text{Mo(CO)(PMe}_2\text{Ph)}_2\text{Cl}$ (which contains a less bulky phosphorus ligand) has an even

lower coalescence temperature than $\pi\text{-C}_5\text{H}_5\text{Mo(CO)(PMePh}_2)_2\text{Cl}$.) Extrapolation back to the unsubstituted complex $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{Cl}$ would suggest that intramolecular exchange of carbonyl groups *cis* and *trans* to chlorine would be a relatively slow process: it would be of interest to check this experimentally.

Satisfactory analytical data have been obtained for the complexes mentioned. Each exhibits only one carbonyl stretching frequency in CH_2Cl_2 solution. This is not surprising since *cis* and *trans* isomers of many complexes $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2\text{LX}$ (X = Cl, Br and I) also have identical stretching frequencies^{2,4}. NMR spectra were recorded on a Perkin-Elmer R10 spectrometer. All changes observed in NMR spectra on cooling samples from 25° to -90° were reversible.

We thank British Petroleum Co. Ltd. for a grant to G.W.

REFERENCES

- 1 S. Chaiwasie and R.H. Fenn, *Acta Cryst., Sect. B*, 24 (1968) 525.
- 2 J.W. Faller and A.S. Anderson, *J. Amer. Chem. Soc.*, 92 (1970) 5852.
- 3 R.K. Harris, *Canad. J. Chem.*, 42 (1964) 2275.
- 4 A.R. Manning, *J. Chem. Soc. A*, (1967) 1984.

J. Organometal. Chem., 29 (1971) C29-C30