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AN UNEQUIVOCAL DISTINCTION BETWEEN "*cis*" AND "*trans*" ISOMERS IN THE COMPLEXES π-$C_5H_5Mo(CO)_2\{P(CH_3)_2C_6H_5\}X$ WHERE X=HALOGEN

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SUMMARY

NMR studies on a series of dimethylphenylphosphine complexes of molybdenum(II) provide an unambiguous proof of stereochemistry.

Use has been made, particularly by Shaw[1] and co-workers, of the ligand dimethylphenylphosphine (I) to determine the stereochemistry of octahedral transition-metal complexes. We wish to report the use of (I) to solve a stereochemical problem of a different nature.

The complex π-$C_5H_5Mo(CO)_3Cl$ has been shown[2] to possess a roughly square-pyramidal shape, with the four monodentate ligands as the square base of the pyramid and the group π-C_5H_5 at the apex. Replacement of one carbonyl ligand by an alkyl or aryl phosphine (L) to give π-$C_5H_5Mo(CO)_2LCl$ can give complexes of two different stereochemistries, according to whether the ligand L is "*trans*" to the chloride ligand in the square base of the pyramid, or "*cis*".

Distinction between "*cis*" and "*trans*" isomers has hitherto been based either on the method of Manning[3] (relative intensities of the two C–O stretching modes), which has however been criticized by Brown and Darensbourg[4], or on a rule of thumb (singlet NMR resonance for π-C_5H_5 protons in a "*cis*" isomer: doublet resonance, due to coupling with phosphorus, for a "*trans*" isomer).

In the case of the complex, π-$C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]Cl$, an unequivocal distinction is however possible. Simple symmetry arguments show that the two methyl groups of (I) will be equivalent in the "*trans*" isomer but non-equivalent in

TABLE 1

NMR SPECTRA[a] OF COMPLEXES π-$C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]X$

X	$\tau(\pi\text{-}C_5H_5)$	$\tau(CH_3)$
Cl	4.68, singlet	two doublets, 8.15 and 8.17, $J=9.8$ Hz
Br	4.70, singlet	two doublets, 8.04 and 8.06, $J=9.8$ Hz
I, *cis*	4.73, singlet	two doublets, 7.91 and 7.95, $J=9.8$ Hz
I, *trans*	4.98, doublet, $J=2$ Hz	one doublet, 8.06, $J=9.7$ Hz

[a] Excluding phenyl protons, which yielded no stereochemical information.

the "*cis*" isomer. The NMR spectrum in $CDCl_3$ solution (see Table 1) shows two distinct doublets for the methyl groups, indicating that the complex exists purely in the "*cis*" form. There is only one signal for the π-cyclopentadienyl protons: a sharp singlet. This is in agreement with the rule of thumb mentioned above.

The analogous bromo complex can also be assigned "*cis*" stereochemistry by the same method. In the case of the iodo complex, both "*cis*" and "*trans*" isomers are present in solution. Approximately 80% of the complex (at 40°) is in the "*cis*" form, giving rise to two doublets for the ligand methyl groups and a singlet for the π-cyclopentadienyl protons. The remainder is in the "*trans*" form, for which a single doublet is observed for the two equivalent methyl groups and a doublet (rule of thumb again correct) for the π-cyclopentadienyl protons.

All spectra were recorded in $CDCl_3$ solution on a Perkin-Elmer R-10 spectrometer. The spectra did not alter between $+50°$ and $-50°$, apart from minor changes in the *cis/trans* ratio in the iodo complex. This indicates that isomerization is slow on the NMR time scale at all temperatures used. Correct integrations were obtained for the chloro and bromo complexes, and for each isomer of the iodo complex. Satisfactory analytical data were obtained for all three complexes. Further details on these and other complexes with (I) will be reported later.

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