

ORGANOMETALLIC ISOMERISM. THE CONFORMATION OF PHOSPHINE-SUBSTITUTED ACYLDICARBONYL- π -CYCLOPENTADIENYL-MOLYBDENUM COMPLEXES IN SOLUTION

P. J. CRAIG* and J. EDWARDS

School of Chemistry, City of Leicester Polytechnic, P.O. Box 143, Leicester, LE1 9BH (Great Britain)

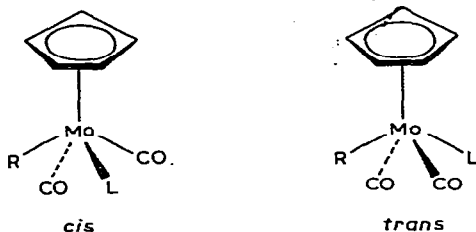
(Received April 27th, 1972; in revised form May 24th, 1972)

SUMMARY

NMR spectroscopy has been used to show that acyl complexes of the type $\text{RCOMo}(\text{CO})_2[\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2]-\pi\text{-C}_5\text{H}_5$ exist in solution in the *trans* form only, in contrast to the corresponding alkyl derivatives which give a mixture of *cis* and *trans* isomers.

INTRODUCTION

Phosphine-substituted alkyldicarbonyl- π -cyclopentadienylmolybdenum complexes, $\text{RMo}(\text{CO})_2(\text{L})-\pi\text{-C}_5\text{H}_5$, [$\text{R} = \text{C}_6\text{H}_5\text{CH}_2$, CH_3 ; $\text{L} = (\text{C}_6\text{H}_5\text{O})_3\text{P}$], have been shown to exist in solution in *cis* and *trans* forms, and undergo interconversion between



the two forms¹. The isomers have been distinguished empirically by (a) differences in the relative intensities of the $\nu(\text{C}\equiv\text{O})$ modes in the IR² and (b) the existence of a singlet or doublet $\pi\text{-C}_5\text{H}_5$ resonance in the NMR for *cis* and *trans* complexes respectively³. Method (a) has been criticised⁴ and Method (b) is arbitrary. For the benzyl complex a distinction based on the benzyl methylene protons has been made (they are equivalent in the *trans*, and non-equivalent in the *cis* isomer)¹.

RESULTS AND DISCUSSION

It might be expected that the corresponding acyl complexes would also give a mixture of isomers in solution. However we report that some new acyl complexes

* Author to whom correspondence should be addressed.

TABLE 1

SPECTRA OF COMPLEXES $\text{RMo(CO)}_2[\text{C}_6\text{H}_5\text{P(CH}_3)_2] - \pi\text{-C}_5\text{H}_5$

R	NMR data ^a			IR data ^c $\nu(\text{CO}) (\text{cm}^{-1})$
	$\tau(\pi\text{-C}_5\text{H}_5)^b$	$\tau[\text{P(CH}_3)_2]^b$	$\tau(\text{RCO})^b$	
CH_3CO	5.0 (d, J 1.2 Hz)	8.1 (d, J 9.1 Hz)	7.4 s	1919 s, 1828 vs
$\text{C}_2\text{H}_5\text{CO}$	5.1 (d, J 1.5 Hz)	8.1 (d, J 9.0 Hz)	7.0 (q, J 7.5 Hz), 9.1 (t, J 7.5 Hz)	1920 s, 1827 vs

^a s = Singlet, d = doublet, t = triplet, q = quartet. ^b CDCl_3 solution, 60 MHz. ^c CS_2 solution.

$\text{RMo(CO)}_2(\text{L})-\pi\text{-C}_5\text{H}_5$ [$\text{R} = \text{CH}_3\text{CO}, \text{C}_2\text{H}_5\text{CO}$; $\text{L} = \text{C}_6\text{H}_5\text{P(CH}_3)_2$] appear to exist in solution in one isomeric form which we have established unequivocally as the *trans* form (>99%). The method used for the assignment is that used for the halogen complexes [$\text{R} = \text{halogen}$; $\text{L} = \text{C}_6\text{H}_5\text{P(CH}_3)_2$]. In a *trans* isomer the two methyl groups in the phosphine are equivalent and give a doublet resonance in the NMR due to splitting by phosphorus. In a *cis* isomer the methyl groups are non-equivalent and two doublets are expected⁵. For each of these acyl compounds only one doublet assignable to the phosphorus methyl groups was observed at 33°. In neither case was there evidence for the occurrence of the additional doublet pair required if the *cis* isomer was present. Details of the spectra are given in Table 1.

The possibility that the observed results are caused by an interconversion at a rate rapid enough to give averaged spectra¹ (characteristic of the *trans* form) has been investigated. The NMR spectra were recorded at -40° when any interconversion occurring would probably be slowed to a detectable rate. There were no significant differences in the spectra at low temperature and we conclude the 33° spectra were not averaged. For the alkyl complexes averaged spectra were obtained only above 130° and it seems unlikely that acyl complexes would undergo a rapid interconversion at the much lower temperature of 33°. The corresponding acyl complexes of symmetric triphosphines have been reported and were assigned tentatively as *trans* isomers using the non-absolute methods (a) and (b) but an unequivocal assignment has not been made until now⁶.

The IR spectra of the complexes in the $\nu(\text{C}\equiv\text{O})$ region showed, both in the solid state and in solution, two peaks only, and for both these compounds the lower frequency peak was the more intense. This observation alone is not proof of the presence of a single isomer however, because cases are known where both *cis* and *trans* complexes have coincident absorption frequencies⁷.

The occurrence of only one isomer in the acyl case has implications for the mechanism of the interconversion reaction for the alkyls. If interconversion occurs without the breaking of the metal-alkyl bond¹ then it might be expected that both alkyl and acyl complexes would undergo isomerism at approximately similar rates. The metal-acyl bond is shorter than the metal-alkyl bond and has some double bond character⁸, so that if bond weakening or breaking occurs it might be expected that the activation energy would be higher for the acyl complexes, leading to slower interconversion or none at all depending on the temperature. We are currently investigating the steric and electronic factors responsible for this difference in behaviour between

the ostensibly similar alkyl and acyl complexes, and we are considering the possibility that a different mechanistic pathway for interconversion may exist between the alkyl and hydride ($R=H$; $L=R_3P$) complexes, where bond-breaking is thought not to occur⁹.

EXPERIMENTAL

The NMR spectra were run in $CDCl_3$ solution at 33° and -40° on a JEOL C-60HL 60 MHz spectrometer. Further spectra were taken using a 100 MHz Varian HA-100 machine at the Physico-Chemical Measurements Unit at Harwell in both $CDCl_3$ and $(CD_3)_2CO$ solution. The IR spectra were taken in the solid state (KBr disc) and in solution (CS_2) on a Perkin-Elmer 337 instrument and were calibrated with indene.

The complexes were prepared in a similar manner to the acyl complexes of symmetric phosphines⁶. Ethyl- or methyltricarbonyl- π -cyclopentadienylmolybdenum (0.5 g, ca. 1.3 mmoles), purified by sublimation, was dissolved in acetonitrile (ca. 25 cm³) under an inert atmosphere. The solution was stirred with a magnetic stirrer and the liquid $C_6H_5P(CH_3)_2$ (ca. 0.2 g, 1.5 mmoles) was introduced by injection from a syringe into the solution, which was stirred at room temperature for 3 h and then left for one week. (In fact the reaction is probably complete after 4 or 5 h and it is unnecessary to leave the solution for longer than this period). The acetonitrile was then evaporated at room temperature and the complexes were recrystallised from dichloromethane/n-hexane to give the products. $R=CH_3CO$, yield 85%. (Found: C, 51.6; H, 4.9; P, 8.0. $C_{17}H_{19}MoO_3P$ calcd.: C, 51.3; H, 4.8; P, 7.8%.) $R=C_2H_5CO$, yield 40%. (Found: C, 52.6; H, 5.7; P, 7.8. $C_{18}H_{21}MoO_3P$ calcd.: C, 52.4; H, 5.1; P, 7.5%.)

ACKNOWLEDGEMENT

The authors acknowledge the assistance of the Physico-Chemical Measurements Unit at Harwell in obtaining the 100 MHz NMR spectra.

REFERENCES

- 1 J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 92 (1970) 5852.
- 2 A. R. Manning, *J. Chem. Soc. A*, (1967) 1984.
- 3 R. B. King, *Inorg. Chem.*, 2 (1963) 923.
- 4 T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, 6 (1967) 971.
- 5 R. J. Mawby and G. Wright, *J. Organometal. Chem.*, 21 (1970) 169.
- 6 P. J. Craig and M. Green, *J. Chem. Soc. A*, (1968) 1978.
- 7 M. J. Mays and S. M. Pearson, *J. Chem. Soc. A*, (1968) 2291.
- 8 M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 7 (1968) 953.
- 9 J. W. Faller, A. S. Anderson and C. Chen, *J. Organometal. Chem.*, 17 (1969) P7.

J. Organometal. Chem., 46 (1972)