Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

STUDY OF THE EXCHANGE PHENOMENON BETWEEN TWO ISOMERS OF PHOSPHINE SUBSTITUTED CARBONYL-π-CYCLOPENTADIENYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

II*. STERIC INFLUENCE OF BULKY GROUPS IN PHOSPHINES

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(Received April 6th, 1970)

SUMMARY

A variable temperature magnetic resonance study of π-$C_5H_5M(CO)_2LH$ complexes, shows the existence of intramolecular exchange between two isomers. Kinetic data have been obtained by line-shape analysis for rates of isomerisation with the Kubo–Sack matrix method, and thermodynamic data have been established. The structure of the transition state is discussed. Starting from these, special attention has been given to determine the steric influence of bulky groups in various phosphines.

INTRODUCTION

The π-$C_5H_5M(CO)_2LH$ complexes[2-6] (where M = Mo, W; L = phosphine, arsine or stibine) are of interest owing to the existence of two isomers[1,2,4-10]. The PMR spectra of such hydride complexes***,[4,6] have been assigned to each of the isomers empirically on account of IR results. It was possible, however, to distinguish the isomers only by PMR study[7,12]. Both forms are usually present in solution and undergo an interconversion process. This exchange phenomenon leads as often as not to averaged spectra at ambient temperature and therefore require a lower temperature for correct detection and identification of the isomers.

On the other hand, examining the values of the mean coupling constants $J(P-CH_3)$ in the $P(CH_3)_3$ ligand, $J(W-H)$ and $J(P-W-H)$[1,7,8] suggests that no breakage† of the W–H and W–P bonds occurs. In addition, the fact that in the π-$C_5H_5W(^{13}CO)(CO)_2H$ complex the (^{13}CO)–H coupling constant is still observed

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*For Part I see ref. 1. Portions of the present work were presented at the Fourth International conference on Organometallic Chemistry, Bristol, England, July–August 1969.

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***In fact, the first study about such sort of problems, concerned compounds like π-$C_5H_5M(CO)_2LI$[11].

†In fact, the existence of free ligand resulting from breakage of a bond but having a very short lifetime, as in the case of an associative mechanism within a solvent cage, would not influence the observed mean coupling constants.

in the averaged spectrum[10], is inconsistent with a breakage of CO groups. Lastly, complete breakage of the π-C_5H_5–M bond does not seem likely to occur. Consequently, the interconversion process must be intramolecular[1,7,8,10].

We have determined the thermodynamic data for some of these compounds and obtained the kinetic data by line-shape analysis employing the method of Kubo[13] and Sack[14–16].

In the present paper we discuss these data in terms of transition state structure. As we have studied a series of compounds ($M=W$ and $L=PMe_3$, PEt_3, $P(Ph)_3$; $M=Mo$ and $L=PMe_3$) in which the basicities are of the same order whereas the variation of bulkiness is large, we have been able to approach the influence of the metal involved and of the ligand bulkiness on the exchange rates between the *cis* and *trans* isomers.

EXPERIMENTAL

Synthesis of the π-$C_5H_5M(CO)_2LH$ derivatives, where $M=Mo$ and $L=PMe_3$, $M=W$ and $L=PMe_3$ or PEt_3

Stoichiometric quantities of ligand L are added to a hexane solution of π-$C_5H_5M(CO)_3H$ [17]. When the stoichiometric quantity of carbon monoxide has been released, the product is crystallized at −20°. The solvent is removed, n-hexane is added and the solution is filtered over alumina. After recrystallization, the solvent is removed again and the product is dried under reduced pressure.

Synthesis of π-$C_5H_5W(CO)_2P(Ph)_3H$ complex

In this case, as the reaction is slower, it is better to reflux a solution of π-$C_5H_5W(CO)_3H$, for one hour, with three times the stoichiometric quantity of triphenylphosphine in heptane. After cooling, the solvent is removed and the product washed with pentane and dried under reduced pressure.

IR spectra

IR spectra were recorded on a Perkin–Elmer 225 grating instrument[1].

PMR spectra

The NMR tubes were carefully filled in an atmosphere of nitrogen. We have used hexamethyldisiloxane as external reference in a coaxial capillary tube in order to prevent the possibility of an influence of the reference substance upon the complexes. Concerning the solvent we have preferred toluene or toluene-d_8 to chloroform in order to prevent formation of a chloro derivative[3,4,6].

Spectra were obtained with a Varian HA-100 instrument. Temperature control was carried out by means of a V 4343 variable temperature controller. The temperature scale was calibrated using the shift of methanol[18]. Spectra were recorded within the range −50° to +90°.

For the ligand and cyclopentadienyl resonances the sweep-widths were 100 Hz and the sweep-times 500 or 250 sec; for the hydride resonance the sweep widths were 250 Hz and the sweep times 500 or 250 sec. See Table 1.

TABLE 1

PMR CHARACTERISTICS AT TEMPERATURES *T* AND CO STRETCHING FREQUENCIES OF THE ISOMERS STUDIED

Compound	Population (at 25°)	Isomers	IR ν(CO) (cm^{-1})	PMR data[a]						
				C_5H_5		L		H		
				δ	J(P–C_5H_5)	δ	J(P–CH_3)	δ	J(P–M–H)	J(W–H)
π-$C_5H_5Mo(CO)_2HPMe_3$	≃0.54	*cis*	1947 1864	−4.60	< 0.3	−0.83	9.4	6.59	66.6	
$T = -38°$	≃0.46	*trans*	1938 1864	−4.47	1.0	−0.85	9.0	5.89	23.0	
π-$C_5H_5W(CO)_2HPMe_3$	≃0.53	*cis*	1941 1855	−4.38	0.5	−0.78	9.3	8.32	68.3	48.0
$T = -28°$	≃0.47	*trans*	1933 1855	−4.23	1.2	−0.79	9.5	7.51	24.0	48.0
π-$C_5H_5W(CO)_2HPEt_3$	≃0.72	*cis*	1937 1864	−4.69	< 0.3	[c]	[c]	8.31	64.3	47.5
$T = -28°$	≃0.28	*trans*	1937 1864	−4.55	0.8	[c]	[c]	7.76	22.4	47.5
π-$C_5H_5W(CO)_2HPPh_3$	≃0.70	*cis*	1944 1865	−4.33	< 0.3	[c]	[c]	6.97	66.1	[b]
$T = -27°$	≃0.30	*trans*	1944 1865	−4.23	0.8	[c]	[c]	7.19	21.4	[b]

[a] Chemical shifts δ in ppm, coupling constants J in Hz. [b] Too small a signal to noise ratio prevents the measurements of the constants. [c] Not measured.

RESULTS

Thermodynamic data

According to the conventional thermodynamic method of determining the ΔH, ΔS and ΔG values, it is necessary to measure the *cis*/*trans* ratio against T^{-1}. At low temperature this is easily done as the various resonances are clearly observed. But when the temperature is raised, because of the broadening of signals and of their coalescence, it is no more possible to obtain a sufficient accuracy in the measurement of signal intensities. Since, at low temperature, when the exchange is slow, the coupling constants $J(\text{P–M–H})_{cis}$ or $J(\text{P–M–H})_{trans}$ are neither temperature nor solvent sensitive and since this also presumably occurs at high temperature, the proportions of both isomers are computed from the mean constants $J(\text{P–M–H})$. From the plot ln $[cis]/[trans]$ against T^{-1}, a straight line is obtained; this involves less error as more points are obtained at high temperature, *i.e.* calculated from the mean values of the coupling constant. This accounts for the various changes in the mean errors of Table 2.

TABLE 2

THERMODYNAMIC DATA

Compound	ΔH(*trans*→*cis*) (cal)	ΔS(*trans*→*cis*)[a] (e.u.)	ΔG(*trans*→*cis*)[b] (cal)
$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2\text{PMe}_3\text{H}$	435 ± 5	1.84 ± 0.02	−113 ± 1
$\pi\text{-C}_5\text{H}_5\text{W(CO)}_2\text{PPh}_3\text{H}$	126 ± 15	2.09 ± 0.04	−497 ± 3
$\pi\text{-C}_5\text{H}_5\text{W(CO)}_2\text{PEt}_3\text{H}$	216 ± 8	2.58 ± 0.02	−553 ± 2
$\pi\text{-C}_5\text{H}_5\text{W(CO)}_2\text{PMe}_3\text{H}$	264 ± 8	1.08 ± 0.03	− 61 ± 1

[a] Calculated at 25°. [b] Determined from the plot (at 25°).

Kinetic data

We have computed spectra corresponding to various values of lifetimes with the Kubo–Sack matrix method by means of IBM 7044 computer program. In our measurements we have preferred to use the cyclopentadienyl resonances, because the shift differences between the resonances of the isomers at the phosphine level are too small and also the signals of the hydride resonances are too flat and therefore little apparent in a rather wide range of temperatures. We have taken into account the two $J(\text{P–C}_5\text{H}_5)$ couplings, which are of same sign, and the absence of any change in spin states. We can write the equations with a principal matrix (4,4):

$$I(\nu) = \text{Re}(P_A P_A P_B P_B) \begin{pmatrix} \alpha_A^- & 0 & 1/\tau_A & 0 \\ 0 & \alpha_A^+ & 0 & 1/\tau_A \\ 1/\tau_B & 0 & \alpha_B^- & 0 \\ 0 & 1/\tau_B & 0 & \alpha_B^+ \end{pmatrix}^{-1} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

with

$$\begin{aligned} P_A &= [cis]/\{[cis]+[trans]\} \\ P_B &= [trans]/\{[cis]+[trans]\} \\ J_A &= |J(\text{P–C}_5\text{H}_5)\,cis| \\ J_B &= |J(\text{P–C}_5\text{H}_5)\,trans| \end{aligned}$$

$$\begin{aligned} \tau &= \tau_A \cdot P_B = \tau_B \cdot P_A \\ \alpha_A^{\mp} &= -[2\pi i(\nu_A \pm \tfrac{1}{2}J_A - \nu) + 1/T_2(A) + P_B/\tau] \\ \alpha_B^{\mp} &= -[2\pi i(\nu_B \pm \tfrac{1}{2}J_B - \nu) + 1/T_2(B) + P_A/\tau] \end{aligned}$$

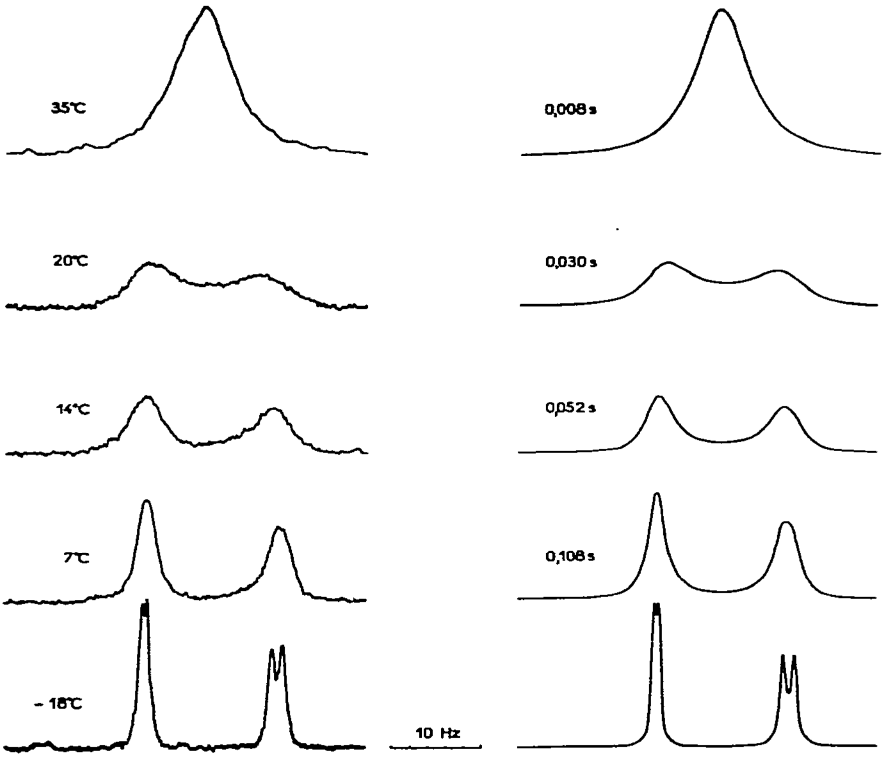

Fig. 1. Experimental and calculated spectra for π-$C_5H_5W(CO)_2PMe_3H$.

Visual comparison between experimental and calculated spectra (Figs. 1 and 2) gives a first relation between lifetime and temperature. In fact, the correspondance thus obtained is a rough approximation. With a view to obtain further accuracy, it is necessary to consider each lifetime value and compute again a spectrum taking into account the proportions P_A and P_B at the temperature and the life-time involved in the first relation. From $\ln 1/\tau_A \cdot T$ or $\ln 1/\tau_B \cdot T$ *vs.* T^{-1}, a straight line is obtained; the various mean errors are indicated in Table 3 together with ΔH^*, ΔS^* and ΔG^* values.

DISCUSSION

These results show that the *cis* compounds are thermodynamically more stable than the *trans* compounds. In addition, it appears that the stability of complexes should not depend on the basicity of ligands but on the steric bulkiness of the ligands: in the trimethylphosphine derivative, the difference between *cis* and *trans* isomers is smaller than in other complexes. Nevertheless, the influence of electronic factors is not to be rejected since *cis*-triethylphosphine is more stable than *cis*-triphenylphosphine relative to the corresponding *trans*-isomers.

Concerning kinetic data, we have to emphasize that the temperature is the principal cause of uncertainty: this is of little significance in the determination of enthalpies of activation but it is important in entropies of activation. Owing to those uncertainties, it is sufficient to consider as significant the classification order of the

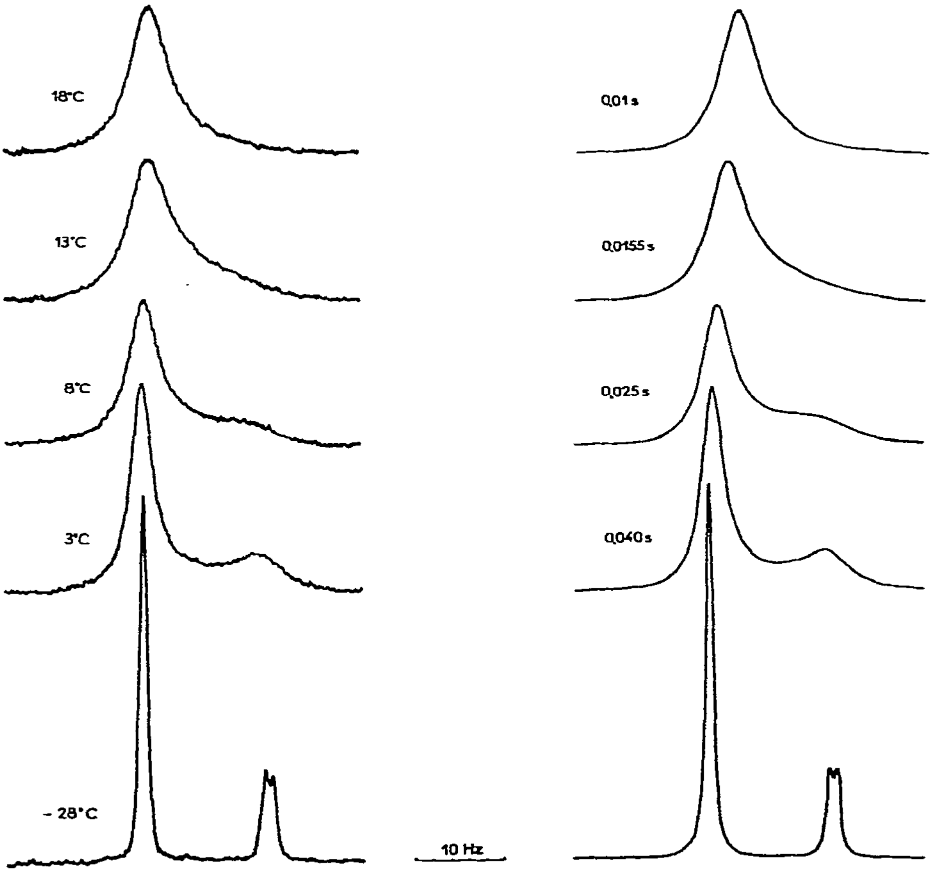

Fig. 2. Experimental and calculated spectra for π-$C_5H_5W(CO)_2PEt_3H$.

TABLE 3

KINETIC DATA

Compound	Conversion	ΔH^* (kcal·mole^{-1})	ΔS^* (e.u.)	ΔG^* (at 25°) (kcal·mole^{-1})
π-$C_5H_5Mo(CO)_2PMe_3H$	*trans*→*cis*	12.54±0.06	−5.00±0.26	14.029±0.010
	cis →*trans*	12.19±0.07	−6.60±0.25	14.153±0.007
π-$C_5H_5W(CO)_2PPh_3H$	*trans*→*cis*	13.41±0.05	−2.96±0.17	14.295±0.003
	cis →*trans*	13.32±0.03	−4.95±0.10	14.795±0.002
π-$C_5H_5W(CO)_2PEt_3H$	*trans*→*cis*	14.63±0.10	−0.36±0.32	14.737±0.002
	cis →*trans*	14.45±0.08	−2.80±0.27	15.287±0.002
π-$C_5H_5W(CO)_2PMe_3H$	*trans*→*cis*	15.40±0.17	−0.17±0.47	15.448±0.005
	cis →*trans*	15.16±0.12	−1.17±0.40	15.503±0.004

various complexes. We shall therefore consider only the signs and relative values of those data.

The entropies of activation are negative in the first three compounds as in the case of π-$C_5H_5Mo(CO)_2PPh_3H$ complex[8]. Under these conditions, the transition state exhibits a greater symmetry than the isomers themselves. Thus we can reject the assumption of isomers with a 3/3/1 structure, *i.e.* with the cyclopentadienyl group in one apical position, three ligands in a plane and the fourth ligand in the opposite apical position. The two "*trans*" compounds should have the two CO groups equatorially positioned (the two CO groups making an angle of 120°), the "*cis*" compounds should have a CO group in one of the apical positions (the two CO groups at right angles).

Consequently, we can consider, as Faller *et al.*[10] did, that the exchange involves isomers of 3/4 structure with the cyclopentadienyl group occupying three positions and four other ligands at the corners of a square pyramid with the metal at the apex, and involves a transition state 3/3/1.

As it is very likely that these configurations for isomers and transition state exist in the four envisaged cases, consequently the ΔS^* value relative to the π-$C_5H_5W(CO)_2PMe_3H$ complex is negative. It can be seen from Table 3 that the free enthalpy of activation decreases when the ligand bulkiness increases. Therefore, the transition state involving the phosphine in a plane is very likely to occur, or else, if the phosphine moved to an apical position, the activation energy needed for the complex to revert to a 3/4 structure, should increase along with the ligand bulkiness. This recalls the conventional S_N1 reactions, in which a carbonium ion is formed and in which the reaction speed varies according to bulkiness.

Though the present study provides no experimental evidence allowing to decide which of the two ligands CO or H move to the apical position, we believe, as suggested by Faller's results[8,10], that the H ligand behaves in this way.

On the other hand, taking into account kinetic results concerning the π-$C_5H_5Mo(CO)_2PPh_3H$ complex[8], we may come to the conclusion that, if the complexes are taken in the order from PMe_3 to PPh_3, the enthalpies and free enthalpies of activation decrease when molybdenum or tungsten are used; in addition, despite of the nearly equivalent bulkiness of the two metals, molybdenum enters the transition state more readily than tungsten.

It finally seems of interest to indicate that some linear relationship exists between the variations of activation energies ($\Delta\Delta H^*$) and the variations in the amount of reaction heat ($\Delta\Delta H$). The compounds mentioned above should point to Polanyi's relation[19], which recalls the similar ratios between the potential energy areas in the reactions involved.

CONCLUSION

In the π-$C_5H_5M(CO)_2LH$ complexes, an intramolecular exchange phenomenon occurs between the two so called *cis* and *trans* isomers with a 3/4 structure. The transition state assumes a 3/3/1 structure with the phosphine ligand in the plane. In the cases under investigation this exchange phenomenon is easier when the ligand bulkiness is greater; moreover, the rate of isomerization is greater with molybdenum complexes.

ACKNOWLEDGEMENTS

We are thankful to Professor Barrans of the University of Toulouse for the use of his PMR spectrometer.

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