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STUDY OF THE EXCHANGE PHENOMENON BETWEEN TWO ISOMERS OF HYDRIDODICARBONYL(TRIMETHYL- OR TRIMETHOXYPHOSPHINE)CYCLOPENTADIENYLTUNGSTEN

PHILIPPE KALCK AND RENÉ POILBLANC
Department of Inorganic Chemistry, University of Toulouse, Toulouse-31 (France)

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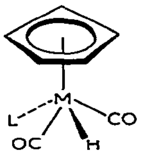
SUMMARY

A variable temperature study of. π-$C_5H_5W(CO_2)HP(CH_3)_3$ and π-$C_5H_5W(CO)_2HP(OCH_3)_3$ complexes, in proton magnetic resonance, shows an exchange phenomenon between two isomers. Kinetical and thermodynamical data suggest a mechanism of isomerization related to interconversion without breakage of bonds.

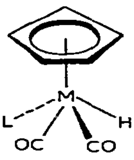
INTRODUCTION

A recent note of Faller and Anderson[1] describes a phenomenon of exchange between two isomers of π-$C_5H_5Mo(CO)_2LR$. Such a phenomenon has prevented these isomers from correct detection and identification at usual temperatures by NMR methods. This report prompts us to publish our results on analogous compounds. In fact the problem is the following.

In recent papers, which describe the direct or indirect synthesis of the π-$C_5H_5M(CO)_2LH$ complexes[2-6] where M = Mo or W, L = phosphines, some experimental facts show the existence of two isomers, (I) and (II), with respect to the following arguments.



(I) *trans*



(II) *cis*

Assuming the isomers to be pure, infrared spectra exhibiting two C–O stretching vibrations are expected; isomer (I) would have the more intense and isomer (II) the weaker absorption in the lower frequency. From variable ratios of those intensities generally observed, it may be concluded that a mixture of isomers is present in solution.

This has also been confirmed[2,4-6] by PMR spectra exhibiting two signals for the π-cyclopentadienyl radical and two for the ligand. Nevertheless, it is surprising that the hydrido resonance and the coupling constant phosphorus–hydrogen would be the same[4].

Faller and Anderson[1] suggest that this anomaly may be explained with an exchange phenomenon. Our present paper confirms this point of view and deals with structural and kinetical results* obtained using NMR at variable temperature and using infrared spectroscopy in the case of π-$C_5H_5W(CO)_2HP(CH_3)_3$ and π-$C_5H_5W(CO)_2HP(OCH_3)_3$ complexes.

RESULTS AND DISCUSSION

The proton nuclear magnetic resonance spectra at low temperature of these compounds exhibit two sets of easily distinguishable signals due to the two isomers that we will momentarily call A and B (Fig. 1 and 2, Table 1).

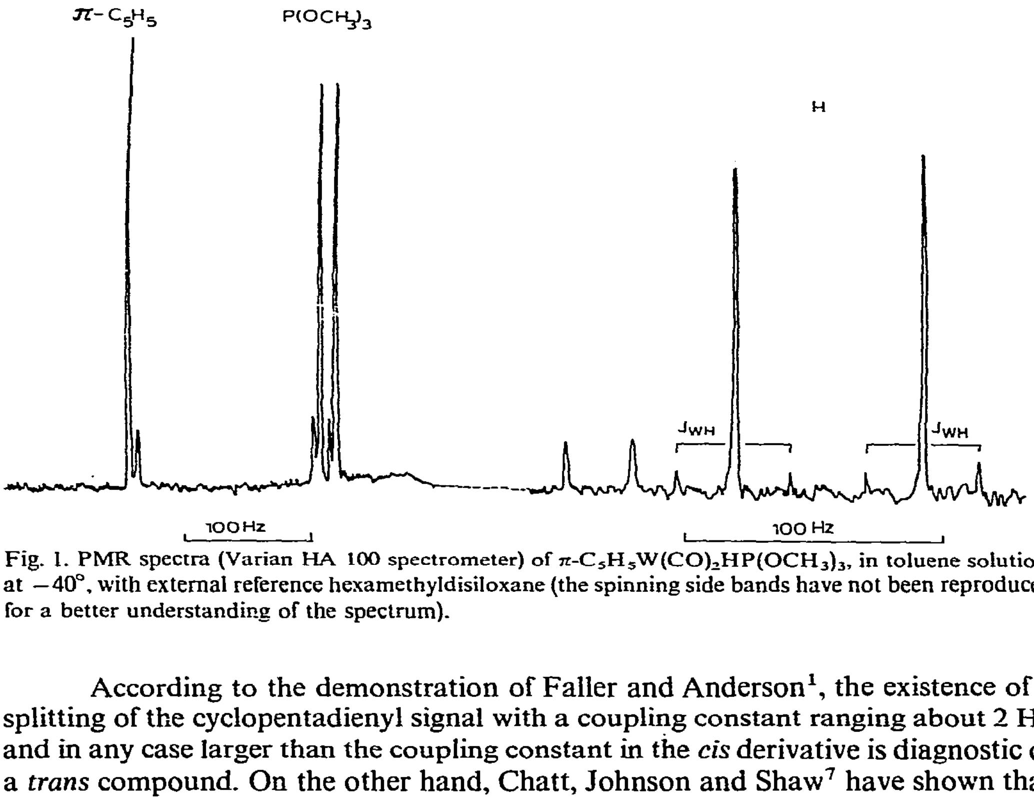


Fig. 1. PMR spectra (Varian HA 100 spectrometer) of π-$C_5H_5W(CO)_2HP(OCH_3)_3$, in toluene solution, at −40°, with external reference hexamethyldisiloxane (the spinning side bands have not been reproduced for a better understanding of the spectrum).

According to the demonstration of Faller and Anderson[1], the existence of a splitting of the cyclopentadienyl signal with a coupling constant ranging about 2 Hz and in any case larger than the coupling constant in the *cis* derivative is diagnostic of a *trans* compound. On the other hand, Chatt, Johnson and Shaw[7] have shown that the phosphorus–hydrogen coupling through a transition metal is greater with atoms in *trans* rather than in *cis* positions. This remark may be tentatively used for the purpose of identification in our case. Thus these two considerations would lead to opposite conclusions and in fact may both be subject to criticism. The former consideration may be criticized because the states of the bonds P–M–C_5H_5 would not necessarily be comparable in all isomers (I) and all isomers (II) of any of the π-C_5H_5M-

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* When this paper was being sent for publication, a preliminary note[15] of Faller, Anderson and Chin-Chun Chen appeared concerning compounds like π-$C_5H_5Mo(CO)_2HP(Ph)_3$. By means of variable temperature measurement, these authors reach conclusions quite similar to ours.

$(CO)_2LR$ complexes; consequently the coupling constant P–C_5H_5 may be, in some cases, of greater value in isomers (II). The later consideration may be criticized because isomers (I) and (II) are not strictly comparable to *trans* and *cis* isomers of the hexacoordinated complexes which were studied by Chatt, Johnson and Shaw[7]. Nevertheless, we will accept the arguments of Faller and Anderson as better stated, and consequently the compounds A, in which the coupling constant $J(P\text{–}C_5H_5)$ are larger, are the *trans* derivatives (I) and compounds B are the *cis* derivatives (II).

In other respects, in infrared spectra (Fig. 3) the observed splitting of the higher frequency C–O absorption band in π-$C_5H_5W(CO)_2HP(CH_3)_3$ confirms the existence of these two isomers. In addition, as the PMR spectra show that both isomers exist

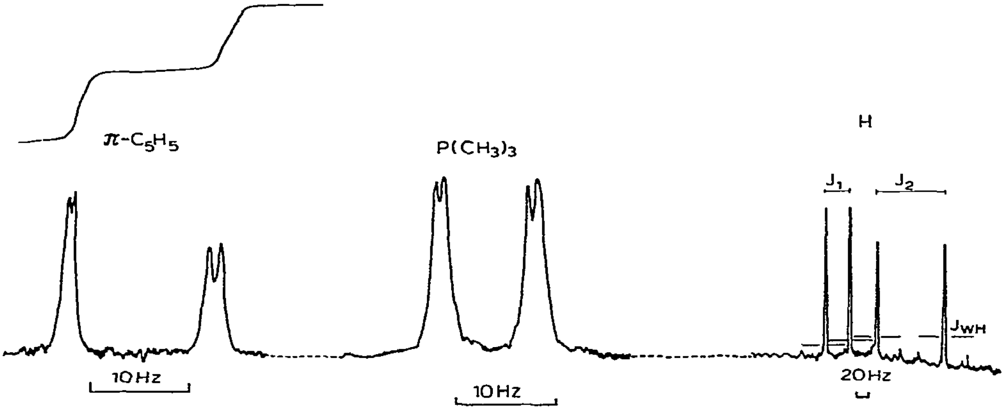

Fig. 2. PMR spectra (Varian HA 100 spectrometer) of π-$C_5H_5W(CO)_2HP(CH_3)_3$ in toluene solution, at −18° (the spinning side bands have not been reproduced for a better understanding of the spectrum).

TABLE 1

NMR CHARACTERISTICS AND C–O STRETCHING FREQUENCIES OF THE STUDIED ISOMERS
Chemical shifts in ppm, coupling constants J in Hertz, infrared frequencies in cm^{-1}.

Ligand L	Isomer	PMR[a]			IR ν(C–O)
		π-C_5H_5	L	H	
$P(OCH_3)_3$	A	$\delta = -4.32_5$ $J(P\text{–}C_5H_5) = 2$	$\delta = -2.89$ $J(P\text{–}CH_3) = 12$	$\delta = 7.66$ $J(P\text{–}W\text{–}H) = 26$ $J(W\text{–}H) = 44$	1954 1883
	B	$\delta = -4.39$	$\delta = -2.83$ $J(P\text{–}CH_3) = 12$	$\delta = 8.55$ $J(P\text{–}W\text{–}H) = 73$ $J(W\text{–}H) = 44$	1954 1883
$P(CH_3)_3$	A	$\delta = -4.26_4$ $J(P\text{–}C_5H_5) = 1.2$	$\delta = -0.81_8$ $J(P\text{–}CH_3) = 9.5$	$\delta = 7.51_7$ $J(P\text{–}W\text{–}H) = 24$ $J(W\text{–}H) = 48$	1933 1855
	B	$\delta = -4.41_4$ $J(P\text{–}C_5H_5) = 0.5$	$\delta = -0.81_0$ $J(P\text{–}CH_3) = 9.3$	$\delta = 8.31_0$ $J(P\text{–}W\text{–}H) = 68.3$ $J(W\text{–}H) = 48$	1941 1855

[a] Measured at −40° for π-$C_5H_5W(CO)_2HP(OCH_3)_3$; −18° for π-$C_5H_5W(CO)_2HP(CH_3)_3$.

in solution in equal quantities, observed intensities of the two bands under consideration are proportional to specific intensities of each isomer. Due to the smaller value of the angle between CO groups in the *cis* isomer, we can assign the more intense band in higher frequency (1941 cm^{-1}) to the *cis* derivative and the other one (1933 cm^{-1}) to the *trans* derivative.

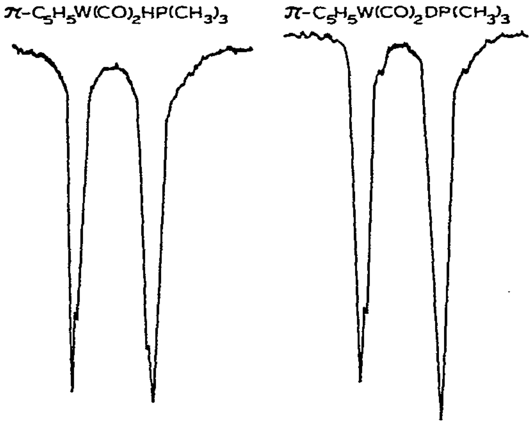

Fig. 3. IR spectra (Perkin-Elmer 225 spectrometer) of π-$C_5H_5W(CO)_2HP(CH_3)_3$ and π-$C_5H_5W(CO)_2$-$DP(CH_3)_3$.

Concerning the splitting of the lower frequency band, we have admitted[3] that it is due to a resonance phenomenon between a C–O stretching vibration and the W–H stretching vibration. This has been studied in the case of both derivatives. In fact, it is observed that, for the corresponding deutero complexes, the phenomenon disappears (Fig. 3) and that *a band assigned to the W–D vibration appears* at *ca.* 1320 cm^{-1}. As the ratio of intensities of the higher frequency bands remains unchanged, from π-$C_5H_5W(CO)_2HP(CH_3)_3$ to π-$C_5H_5W(CO)_2DP(CH_3)_3$, the ratio of concentrations surely remains unchanged by deuteration. Consequently, we admit that the different aspects in low C–O frequency region (Fig. 3) for the hydrido and deutero complexes result only from a resonance phenomenon occurring between a C–O and the W–H vibration. This is confirmed by the fact that, from the value of W–D frequency, the W–H stretching band is just only assumed to occur at 1860 cm^{-1}. Low C–O frequency bands in both isomers are finally assumed to be common to both isomers (I) and (II) (Table 1).

In fact, we cannot specify the repulsion effect[8] on frequencies of the C–O and W–H vibrations; the observed effect is an energy transfer of the former to the later vibration. This phenomenon would be concerned more probably with the *cis* isomer in which H and a CO group are respectively in a *trans* position[8]. The resonance may not be forbidden in this compound because the C–O stretching mode concerned is not to be considered as an antisymmetrical one in a compound in which no symmetry operation allows correspondance between the two CO groups.

Due to its spectral characteristics, π-$C_5H_5W(CO)_2HP(CH_3)_3$ derivative allows us to perform kinetical experiments by means of PMR studies and thermodynamical experiments by means of IR spectroscopy as well as by PMR studies.

In nuclear magnetic resonance, it is well known[9] that a coalescence of signals may be observed when a magnetic nucleus undergoes exchange between two sites of different chemical environments. And yet, at usual temperature, this phenomenon prevents observation of the two isomers.

In the case of the two isomers of π-$C_5H_5W(CO)_2HP(CH_3)_3$ which are present in equal quantities in solution, we can apply the simplified results of Gutowsky and Holm[10] and obtain the free enthalpy of activation (ΔG^*) from the coalescence temperature, T_c, and the difference, $\Delta\nu$, between the chemical shifts of the nucleus under consideration in each of the two sites.

$$k_c = \frac{\pi}{\sqrt{2}}\Delta\nu$$

$$\Delta G^* = 4.57\ T_c \cdot \left(10.32 + \log_{10}\frac{T_c}{k_c}\right)$$

Coalescence temperature is determined by extrapolation when $\Delta\nu = 0$. The different values of both T_c and k_c, obtained with the three signals of π-C_5H_5, $P(CH_3)_3$ and H for the free enthalpy of the isomerization studied lead to the values: $\Delta G^* = 15.8 \pm 0.3$ kcal·mole^{-1}†.

On the other hand, particularly of interest is the observation of coupling constants. The observed mean coupling constant $J(P{-}CH_3)$ in the $P(CH_3)_3$ ligand (9.4 Hz) is almost the average of coupling constants in both isomers (9.3 and 9.5 Hz; Table 1). Consequently the free phosphine [$J(P{-}CH_3) = 2.6$ Hz] seems to have no part in the isomerization process which would occur, therefore, without breakage of the W–P bond.

We can also observe a coupling between hydrogen and tungsten-183 ($I = \frac{1}{2}$, relative abundance 14.40%); this coupling constant is clearly observed at +80° and +90° and is equal to 48 Hz. This value is an average of the coupling constants in both isomers [$J(W{-}H) = 48$ Hz; Table 1] and strongly suggests that any breakage of the W–H band occurs.

The observed mean coupling constant of phosphorus and hydrogen through the metal, $J(P{-}W{-}H)$, is almost the average of coupling constants in the *cis* [$J(P{-}W{-}H) = 68.3$ Hz] and *trans* isomers [$J(P{-}W{-}H) = 24$ Hz]*. This observation corroborates the two first points. From a similar observation, in the case of $IrH(CO)_2L_2$ complexes, Yagupsky and Wilkinson[11] concluded that the isomerization process is intramolecular.

Concerning the complexes presently being studied, these preceding results imply only the absence of breakage of both W–H and W–P bonds**.

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† This value is surprisingly higher than the result of Faller, Anderson and Chin-Chun Chen in the case of π-$C_5H_5Mo(CO)_2HP(Ph)_3$. This may be taken as a proof of the fact that the steric influence of bulky groups is not to be considered as preponderant.

* We notice that in both isomers the coupling constants $J(P{-}W{-}H)$ have the same sign, in contrast with the case of $IrH(CO)_2L_2$ derivatives studied by Yagupsky and Wilkinson[11]. Likewise the $J(P{-}CH_3)$ coupling constant keeps also the same sign in both products (I) and (II).

** From a strict point of view, however, we have yet to remark that the existence of free ligand resulting from breakage of a bond but having a very short lifetime in solution, would not influence the observed mean coupling constants.

On the other hand, concerning the breakage of CO groups, an intermolecular exchange process seems to be inconsistent with the fact that, in the presence of a large amount of phosphine, when an exchange between the two isomers is effectively observed, any further substitution of CO by the phosphine occurs. Indeed in these conditions, breakage of a W–CO bond would lead to a S_N1 substitution process.

Lastly, it seems difficult to admit a simple breakage of the bond of the cyclopentadienyl radical; but an intramolecular transformation of the nature of the C_5H_5 bond is not strictly excluded. By means of some rearrangement, like the *pentahapto–trihapto–monohapto* transformation proposed by Cotton[12], the isomerization could be facilitated. In any case, the isomerization would imply an intramolecular process.

From a thermodynamical point of view, the P–H mean coupling constant J(P–W–H) remains unchanged between +70° and +90°. Likewise, between −25° and +25°, the relative intensities of the two infrared stretching bands at higher frequency, as well as the relative intensities of PMR cyclopentadienyl signals, remain practically constant. Our measurements give the proportion:

$$cis\% = 51.4 \pm 1.4$$

$$trans\% = 48.6 \pm 1.4$$

Consequently, $K = [cis]/[trans] = 1.06 \pm 0.06$ and the value of the free enthalpy is surely smaller than 70 cal·mole^{-1}. The conditions of a reversible system are certainly approached, and we can conclude that the equilibrium constant is almost unchanged between −25° and +90°. Under the conditions of our experiments, the absolute value of the enthalpy of isomerization is low and in any case smaller than 150 cal·mole^{-1}.

Concerning the mechanism of this isomerization process, we think that there is no real reason to reject some sort of interconversion process, following the mechanism of Berry[13], but our interest is now to determine whether the hydride complexes have particular behavior, in comparison with π-$C_5H_5M(CO)_2LR$ compounds of bulkier R groups. In fact, with respect to its smallness, following the hypothesis of Anderson and Faller[1], it is possible that hydride ligand does occupy easily apical position in the transition state.

EXPERIMENTAL

The compound π-$C_5H_5W(CO)_3H$ has been prepared using the previously published method[14]. All reactions are conducted in an atmosphere of nitrogen.

Synthesis of π-$C_5H_5W(CO)_2LH$ derivatives, where L = $P(CH_3)_3$ and $P(OCH_3)_3$

Stoichiometric quantities of ligand L are added to a hexane solution of π-$C_5H_5W(CO)_3H$ at 0°. When the stoichiometric quantity of carbon monoxide is evolved, 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 *in vacuo*.

Spectra

PMR spectra were recorded on a Perkin–Elmer R 10 instrument (60 MHz) at 35° or on JEOL and Varian HA 100 (100 MHz) instruments at variable temperature; infrared spectra were recorded on a Perkin–Elmer 225 grating instrument.

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