FORMATION OF GEOMETRICAL ISOMERS DURING PROTONATION OF CARBONYL COMPLEXES OF TRANSITION METALS: $(\eta^5\text{-}C_5H_5)Mn(CO)(Ph_2PCH_2CH_2PPh_2)$

B.V. LOKSHIN * and M. G. YEZERNITSKAYA

A.N. Nesmeyanov Institute of Organoelement Compounds, U.S.S.R. Academy of Sciences, Vavilov Str., 28, Moscow, 117813 (U.S.S.R.)
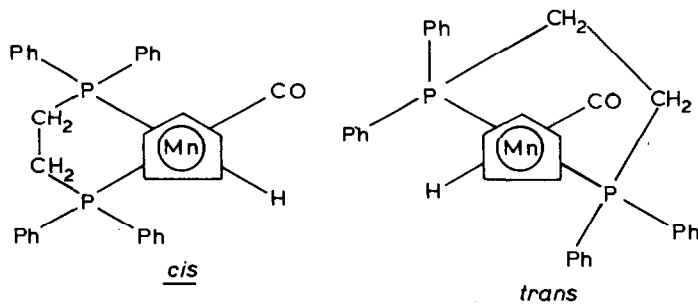
Summary

IR spectroscopic studies have been carried out to elucidate the factors responsible for formation of *cis* and *trans* isomers during protonation of $(\eta^5\text{-}C_5H_5)Mn(CO)\text{-}Ph_2P(CH_2)_2PPh_2$. The experimental results indicate that the conversion of the more rapidly formed *cis* isomer into the thermodynamically more advantageous *trans* isomer involves an intermolecular rather than intramolecular mechanism.

Introduction

The protonation of transition metal complexes has in recent years been intensively studied using IR and NMR spectroscopy. In particular, PMR studies have shown [1] that protonation at the metal atom of $(\eta^5\text{-}C_5H_5)Mn(CO)\text{-}Ph_2P(CH_2)_nPPh_2$-type complexes in CF_3COOH may lead to formation of *cis* and *trans* isomers, depending on the length of the polymethylene bridge in the chelated phosphine ligand. At $n = 1$ or 2, only *cis* isomers were found to form, whereas at $n = 3$ and in the case of $(\eta^5\text{-}C_5H_5)Mn(CO)(PPh_3)_2$ formation of only *trans* isomers was observed, which was ascribed to steric factors. However, as was found in IR spectroscopic studies of this type complexes at $n = 2$ [2], protonation yields both geometrical isomers with subsequent gradual conversion of the *cis* to the *trans* isomer. In the final analysis, only the *trans* isomer remained in the solution, which had not been revealed by NMR spectroscopy studies of this substance.

Such a difference in the results of IR and NMR spectroscopy prompted us to study more carefully the factors responsible for formation of geometrical isomers during protonation of the $(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2P(CH_2)_2PPh_2$ complex. The experimental data were used in postulating the isomerization mechanism.

The protonated complex $[(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2P(CH_2)_2PPh_2H]^+$ has the structure of a tetragonal pyramid. Two alternative mechanisms of mutual conversion of *cis* and *trans* isomers are possible: intramolecular and intermolecular. The intramolecular rearrangement proceeds without cleavage of the M–H bond through an intermediate with a geometrical ligand arrangement different from that in the cis and trans forms and taking the shape of a trigonal bipyramid. The intermolecular dissociative mechanism implies an M–H bond cleavage stage followed by formation of a new M–H bond with a different ligand arrangement.

Currently prevailing in the literature is the viewpoint, based on NMR data and developed in ref. 3, that the rearrangement proceeds intramolecularly. In this work neutral hydride complexes of the $(\eta^5\text{-}C_5H_5)Mo(CO)_2LH$ type, where L = PR_3, were studied and mutual conversions of *cis* and *trans* isomers were shown to occur in a CH_2Cl_2 solution. The conversions are rapid on the NMR time scale and were shown to involve an intramolecular mechanism. At low temperature, PMR spectra reveal two isomers differing in the magnitude of the $J(H^{31}P)$ constant of the signal due to the hydride proton at the phosphorus atom. When the temperature is raised, the signals coalesce but the spin-spin splitting persists, and its magnitude is intermediate between those observed in the case of *cis* and *trans* isomers, which is the chief argument in favour of the intramolecular mechanism of mutual conversion. Another important argument is the finding that the conversion rate is independent of concentration, which is indicative of first order reaction.

In contrast to neutral hydride complexes for which a dissociative mechanism is most unlikely, protonated complexes of transition metals in acid solutions may involve both intra- and inter-molecular dissociative mechanisms of rearrangement. The rapid exchange of protons in acid medium between protonated and unprotonated metal atoms in complexes of the $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ type is demonstrated in ref. 4. An important result of this work is establishment of a dependence of the exchange rate on the anion concentration, which supports the hypothesis that the proton is detached not by dissociation but through interaction with the anion: $MH^+ + A^- \rightleftarrows M + HA$.

However, NMR studies [5] of protonation of complexes of the $(\eta^6\text{-}C_6H_6)M(CO)_2L$ (M = Cr, Mo, W) and $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$ types, where L = PMe_2Ph and PMeBzPh, in acid medium suggest, with due account for the arguments similar to those used in ref. 3; that the *cis–trans* transitions of the proton in these compounds are of intramolecular nature. It should be admitted, though, that the investigators purposely created conditions (excessively high amounts of acid) hindering intermolecular exchange. Other investigators [1,6] also studied the protonation of the complexes $(\eta^6\text{-}C_6H_6)Cr(CO)_2L$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$ by the NMR method. As opposed to the previous results [5], only one geometrical isomer was revealed (proton in a *cis* position with respect to the substituent L). As was found in the case of $(\eta^5\text{-}C_5H_5)Re(CO)_2PPh_3$ [1], depending on its acidity, the solution contains either the *cis* form or a mixture of *cis* and *trans* isomers. The investigators believed that the rearrangement is based on an intramolecular mechanism, although no explanation is provided as to why the direction of the reaction is dependent on the acid concentration.

Although the hypothesis of the intramolecular rearrangement mechanism is prevalent in current literature, it does not account for the bulk of the presently available experimental data, including those presented in this work. In the case of protonation in acid media, one should not, in our opinion, rule out the possibility of an intermolecular isomerization mechanism.

Results and discussion

When CF_3COOH is added to a solution of $(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2P(CH_2)_2PPh_2$ in CH_2Cl_2, the $\nu(CO)$ band of the initial complex at 1835 cm^{-1} in the IR spectrum usually disappears, and two bands corresponding to the protonated form, shifted into the high-frequency region, appear at 1935 and 1965 cm^{-1}. As was shown earlier [2], the band at 1965 cm^{-1} corresponds to the *cis* isomer, while that at 1935 cm^{-1} is associated with the *trans* isomer. Figure 1 illustrates the IR spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2P(CH_2)_2PPh_2$ solutions (0.01 *M*) in CH_2Cl_2, taken immediately after addition of CF_3COOH (0.1 *M*), one hour later, then after two hours. The concentrations were selected such that the spectra feature the bands corresponding to both the initial substance and protonation products. Unlike most protonation reactions which proceed almost instantaneously, the process examined in this work lasted required minutes and even hours. Initially, the solution was found to contain the initial substance and a protonated *cis* form. The concentration of the *trans* form in the solution was low. Then, the *cis* form gradually passed into the *trans* form, the transition being accompanied by a decrease in the content of the initial substance. Finally, the *trans* form was virtually all that remained in the solution, while the initial complex had almost disappeared.

To gain a better insight into this process using IR spectroscopy we monitored the protonation reaction as a function of the complex concentration and the complex to acid ratio. The concentration of the complex in CH_2Cl_2 varied from 0.005 to 0.1 *M*,
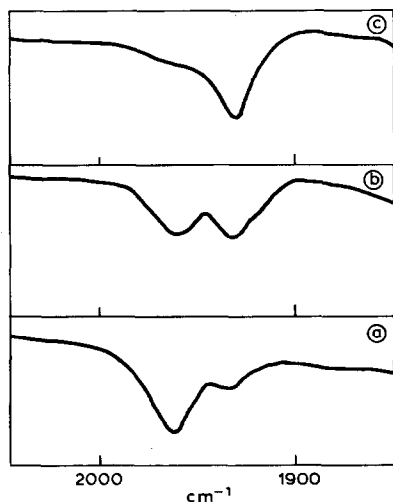

Fig. 1. IR spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2PCH_2CH_2PPh_2$ and CF_3COOH solutions in CH_2Cl_2. Complex concentration: 0.01 *M*; acid concentration: 0.1 *M*. (a) immediately after preparation; (b) one hour later; (c) after two hours.

while the molar complex to acid ratio varied from 1 : 1 to 1 : 40. In each case, we studied the changes occurring in the spectra in the course of time. The observation can be summed up as follows:

(a) At low concentrations and slight excesses of the acid, prominent in the spectra is only the low frequency band at 1935 cm^{-1}, corresponding to the *trans* isomer (Fig. 2a, b).

(b) At higher concentrations of the complex and the acid, two isomers emerge initially (Fig. 2c), corresponding to bands at 1935 and 1965 cm^{-1}. When the solution is allowed to stand, the *cis* isomer converts to the *trans* isomer (Fig. 2d), the conversion rate depending on the complex and acid concentrations.

(c) At high concentrations and large excesses of the acid (1 : 40) (Fig. 2e), as well as when the complex outweighs the acid, only a single high-frequency band is seen in the spectrum, no transition of the *cis* to *trans* isomer being observed in the meanwhile or, if it does take place, it is almost imperceptible (Fig. 2f). Thus, as the concentrations of the acid and the complex increase, the *cis* form is stabilized and formation of the *trans* isomer is hindered.

When the reaction is conducted in a more polar solvent, such as nitromethane, the process of *cis* to *trans* conversion is similar but much faster. In the case of protonation with perchloric acid, which is stronger than trifluoroacetic acid, in a nitromethane solution, formation of an isomer mixture was also observed initially, which was followed by complete *cis* to *trans* conversion. During protonation with much weaker acids (n-toluenesulfonic acid, n-xylene, n-nitrophenol), only the *trans* form emerged.

Addition of a small amount of ammonium trifluoroacetate (CF$_3$COONH$_4$) to a solution containing a mixture of *cis* and *trans* isomers appreciably speeds up the *cis–trans* isomerization (Fig. 3). This means that an increase in the anion concentration produces a tangible effect on the rate of rearrangement.

Finally, although only a *cis* isomer forms in a strongly acidic medium, addition of excess acid to a solution of the *trans* isomer does not lead to its conversion into the *cis* isomer. The implication is that the *trans* isomer is thermodynamically much more stable, and the *cis–trans* isomerization is virtually irreversible.

In contrast to other experiments [3,5], no rapid mutual conversion of both isomers was observed in our case. Depending on the conditions, a solution contains one or the other isomer, a mixture of isomers yielding, in the final analysis, only one isomer in a slow process. The lack of rapid mutual conversion may be due to the large difference in the energies of the isomers; this may also account for the difference in the ν(CO) frequencies of both isomers. According to ref. 3, the frequencies of stretching vibrations of the CO groups in both forms coincide, which, just as the rapid mutual conversion, may be due to the similarity of their energies.

The results also explain why protonation of (η^5-C$_5$H$_5$)Mn(CO)Ph$_2$PCH$_2$CH$_2$PPh$_2$ in a previous work [1] yielded only the *cis* isomer. The PMR spectra were examined only at high concentrations of the complex and the acid, that is under conditions when, as indicated by our results, no transition to the *trans* isomer takes place.

We shall now try to explain the results in terms of the intra- and inter-molecular mechanisms of rearrangement. Assume that the protonation yields only the *cis* form, while the *trans* isomer is the result of its intramolecular rearrangement. Then, the protonation step is rapid and reversible. The rearrangement into the *trans* isomer involves getting over a high potential barrier and is, therefore, a slow process. As the
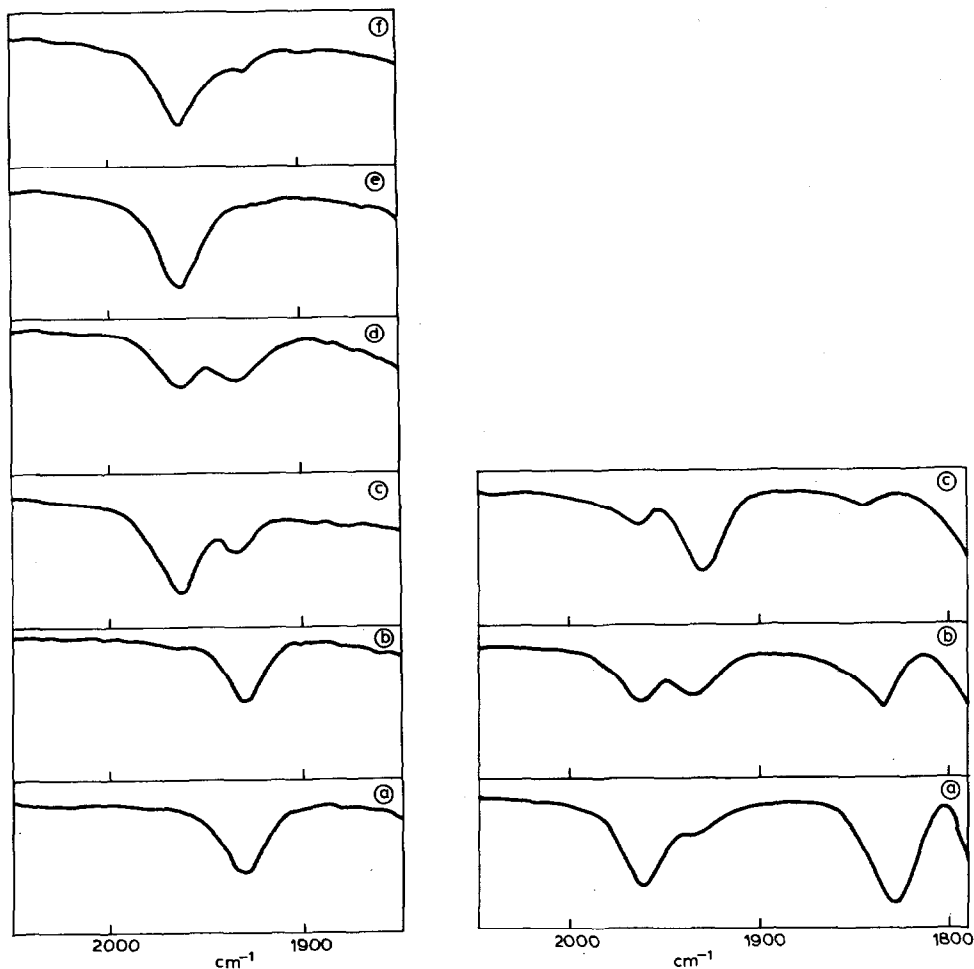
Fig. 2. Changes with time of the IR spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2PCH_2CH_2PPh_2$ and CF_3COOH solutions in CH_2Cl_2 at different concentrations. (a) complex concentration: 0.005 M; acid concentration: 0.1 M; (b) same solution after four hours; (c) complex concentration; 0.03 M; acid concentration: 0.6 M; (d) same solution after four hours; (e) complex concentration: 0.1 M; acid concentration: 4 M; (f) same solution after four hours.

Fig. 3. Effect of CF_3COONH_4 addition on the IR spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2PCH_2CH_2PPh_2$ and CF_3COOH solutions in CH_2Cl_2. Complex concentration: 0.01 M; acid concentration: 0.2 M. (a) immediately after preparation; (b) after two hours without addition of CF_3COONH_4; (c) after two hours in the presence of CF_3COONH_4.

cis form passes into the thermodynamically more stable *trans* isomer, the equilibrium shifts toward the protonated form, and the initial complex disappears from the solution. However, the intramolecular process must be a first order reaction and independent of concentration. Nor does this mechanism account for the stabilization of the *cis* isomer at high concentrations and the effect of the solvent polarity.

These facts could be explained in terms of formation in the solution of ion pairs between the protonated cation and acid anion. If it is assumed that the intramolecu-

lar rearrangement involves solvent-separated ion pairs, whereas formation of tight ion pairs hinders the rearrangement, then a decrease in the acid concentration and an increase in the solvent polarity will lead to an increase in the number of separated ion pairs and promote the rearrangement, which is consistent with the experimental data. However, addition of ammonium trifluoroacetate to the solution must, in this case, promote formation of tight ion pairs by virtue of increasing anion concentration and, thereby, hinder the rearrangement. In reality, the opposite is observed: addition of a salt to the solution speeds up the *cis–trans* conversion. Such a mechanism also fails to explain the stabilization of the *cis* isomer when the complex is present in excess with respect to the acid. Thus, the IR spectroscopic data obtained in experiments with protonation of the $(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2CH_2PPh_2$ complex are at variance with the possibility of an intramolecular mechanism of the *cis–trans* rearrangement being involved in the case of either a rapid reversible exchange or an irreversible conversion through a high potential barrier.

Consider now the available data in terms of a dissociative mechanism which presupposes two equilibria at a time between the initial complex and its two protonated forms:

$$A^- + MH^+_{trans} \rightleftarrows M + HA \rightleftarrows MH^+_{cis} + A^- \tag{1}$$

This mechanism seems to be consistent with the available experimental data if it is assumed that the rate of *cis* isomer formation is much higher than that of the *trans* isomer, yet the *trans* isomer is thermodynamically much more advantageous. The kinetic advantages of the *cis* form may be due to steric factors since the CF_3COOH molecule in organic solvents virtually does not undergo dissociation, and the acid molecule or even an associate of several molecules takes part in the protonation rather than the proton.

Increasing concentration of the initial substances is condusive to accumulation of the *cis* isomer in the solution, while solvation of the anion stabilizes the *cis* isomer and prevents dissociation, hence, its conversion into the thermodynamically more advantageous *trans* isomer. If the complex is present in excess, the equilibrium is also perceptibly shifted toward formation of the *cis* isomer, whereas a low concentration of the unprotonated form in the solution sharply slows down the *trans* isomer formation.

At lower acid concentrations as well as in the presence of CF_3COONH_4, anions increase in number. At the same time, the dissociation of the *cis* isomer, leading to appearance of the unprotonated form in the solution, becomes pronounced, which, in turn, brings about a gradual shift of equilibrium 1 towards formation of the *trans* isomer.

At complex concentrations ranging from 0.01 to 0.05 *M* and at complex to acid ratios varying from 1 : 20 to 1 : 40, the transition to the *trans* isomer is extremely slow (several tens of minutes or hours). As the concentration decreases to below 0.005 *M*, the formation of the *cis* isomer is virtually imperceptible in the IR spectrum, the only prominent feature being the band at 1935 cm^{-1}, corresponding to the *trans* isomer. Substitution of CF_3COOH for weaker acids acts upon the reaction similarly to decreasing the acid concentration.

Thus, the dissociative mechanism, as opposed to the intramolecular one, seems to be consistent with the experimental data. This conclusion, however, does not rule out the possibility of the intramolecular mechanism being involved in such reaction.

Apparently, depending on the nature of the transition metal complex and the conditions under which the reaction is conducted, the *cis–trans* conversion of the proton may proceed both intra- and intermolecularly. In the case under present investigation, the intermolecular dissociative mechanism seems more important.

Experimental

$(\eta^5\text{-}C_5H_5)Mn(CO)Ph_2PCH_2CH_2PPh_2$ was synthesized as described [7]. CF_3COOH was distilled under argon. The solutions were also prepared under argon. The IR spectra were recorded on an IR-75 spectrophotometer and a Bruker IFS-113V Fourier transform infrared spectrometer. CaF_2 cells were used.

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