Journal of Organometallic Chemistry, 81 (1974) 201—205
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PROTONATION OF METAL CARBONYL COMPLEXES

VII*. PROTON NMR SPECTRA AND STEREOCHEMISTRY OF PROTONATED FORMS OF π-CYCLOPENTADIENYLPHOSPHINEMANGANESE COMPLEXES

A.G. GINZBURG, P.O. OKULEVICH, V.N. SETKINA, G.A. PANOSYAN and D.N. KURSANOV

nstitute of Organo-Element Compounds, Academy of Sciences, Moscow, Vavilova 28, 117813 U.S.S.R.)

Received June 3rd, 1974)

Summary

^{1}H NMR measurements show that protonation of the complexes π-C_5H_5Mn-$(CO)_{3-n}(PR_3)_n$ (n = 1 and 2) with CF_3COOH occurs at the manganese atom, the spectra revealing "hydride" signals at δ values of —4 to —6 ppm. The stereochemistry of the protonated forms has been determined from the ^{1}H — ^{31}P coupling pattern.

---

ntroduction

Some previous communications by us report IR [1,3,4] and NMR [2] evi-ence of reversible protonation of π-arene chromium complexes, and of π-cyclopentadienyl-manganese, -vanadium, -niobium and -rhenium complexes, under the action of trifluoroacetic acid in CH_2Cl_2 solution. Most likely, the metal tom in these complexes is the most basic site subject to proton attack. In the ase of chromium complexes, the formation of a Cr—H bond has been demon-trated by the presence of the "hydride" hydrogen signal in the ^{1}H NMR spectra t higher fields [2, 5]. With π-cyclopentadienylmanganese complexes, the rotonation also occurs at the metal atom, as shown by ^{13}C and ^{31}P NMR [6]. n this paper we report on the protonation of these manganese compounds as tudied by ^{1}H NMR.

Results and discussion

Addition of excess trifluoroacetic acid to solutions of compounds I-VII in CH_2Cl_2 or in CH_2ClCH_2Cl at —20 to +20° gives rise to the Mn—H proton NMR ignal in the high field region (δ = —4 to —6 ppm) (see Table 1).

For Part VI, see ref. 6.

TABLE 1

NMR SPECTRAL DATA

Compound		Mn — H chemical shift (δ, ppm)	J (H — P) (Hz)	Proton chemical shift of C_5H_5 (δ, ppm)		
				In CH_2Cl_2	In CH_2Cl_2/CF_3COOH	$\Delta\delta$ (ppm)
I	$C_5H_5Mn(CO)(PPh_3)_2$	−6.25 t	89	3.70	4.50	0.8
II	$C_5H_5Mn(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$	−7.0 t	72			
III	$C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$	−5.1 d	90	4.10	4.50	0.4
IV	$C_5H_5Mn(CO)(Ph_2P\ CH_2\ PPh_2)$	−5.2 dd	$\begin{cases}82\\30\end{cases}$	4.35	4.75	0.4
V	$C_5Et_5Mn(CO)_2PPh_3$	−3.9 d	70			
VI	$C_5H_5Mn(CO)_2P(iso\text{-}C_3H_7)_3$	−5.6 d	51	4.40	4.90	0.5
VII	$C_5H_5Mn(CO)_2P(C_6H_{11})_3$	−5.7 d	51	4.40	5.0	0.6

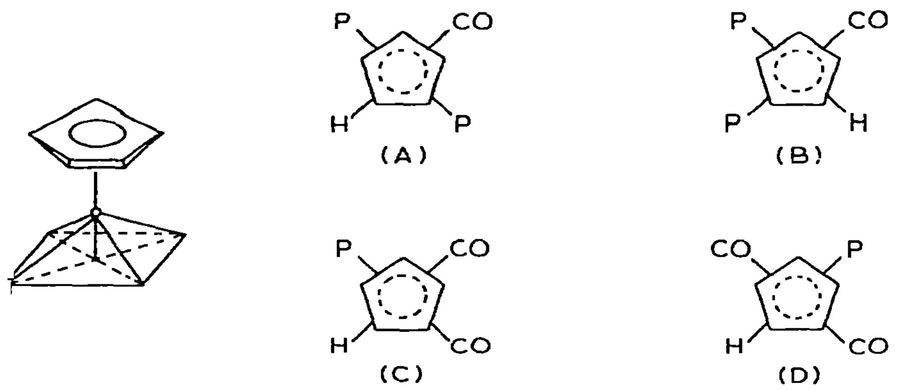

Fig 1. Possible configurations for the protonated diphosphine (A and B) and monophosphine (C and D) π-cyclopentadienylmanganese complexes.

In the case of monophosphine complexes V-VII, the Mn—H signal splits into a doublet, through $^{1}H - Mn - {}^{31}P$ coupling, with the constants J of 70 and 51 Hz. Note that for compound V the J value obtained from ^{1}H NMR spectrum is practically the same as that obtained earlier in the ^{31}P study [6].

In the case of diphosphine complexes I-IV, the Mn—H splitting pattern depends significantly on the geometry of the diphosphine ligand. All the observed multiplicities arise from coupling with the phosphorus nuclei, since the application of the phosphorus-decoupled heteronuclear $^{1}H - {}^{31}P$ technique transforms the signals to singlets with line-widths at half-height of 10 to 15 Hz (the broadening is due to the coupling with ^{55}Mn nuclei, spin $I = 5/2$, 100% content, and to the fine structure).

Analysis of the values of coupling constants $J(^{1}H - Mn - {}^{31}P)$, and of the type of splitting allowed us to determine the stereochemistry of the protonated forms of I-VII. The initial neutral complexes possess a "piano stool" configuration similar to $C_5H_5Mn(CO)_3$. Evidently, proton addition at the manganese

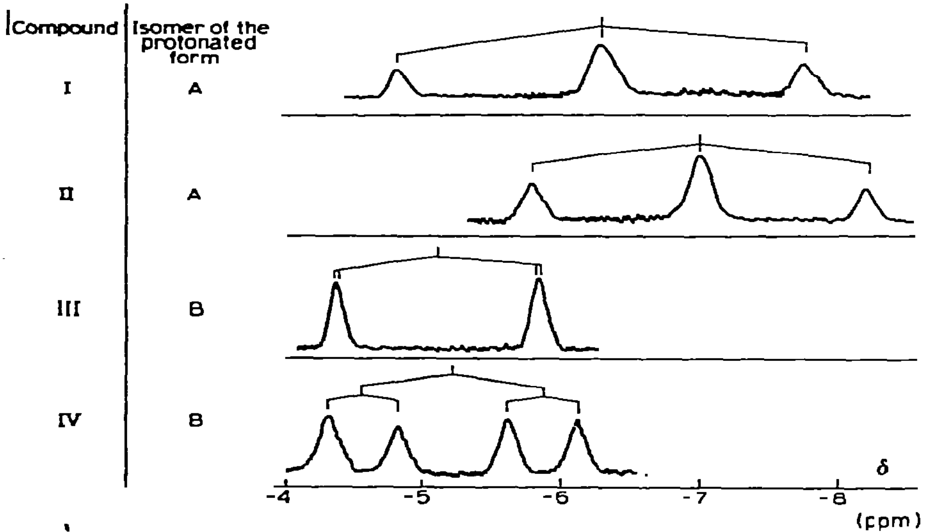

Fig. 2. ^{1}H NMR spectra of the diphosphine complexes in the Mn—H proton field.

atom will result in a square pyramidal structure with a Cp ligand on the apex. In this case two isomers may exist for both mono- and di-phosphine species (Fig. 1). In Fig. 2, proton NMR spectra of diphosphine complexes I-IV are shown in the region of the hydride shifts. The protonated forms of I and II possess structure A since the Mn—H protons give symmetrical 1/2/1 triplets indicative of the coupling with two equivalent ^{31}P nuclei (part X of the A_2X spectrum). The spectra yield *J* values of 70 to 90 Hz for *cis*-arranged ^{1}H and ^{31}P nuclei. This conclusion is in good agreement with published data on other transition metal π-cyclopentadienyl complexes. Thus, in the series of iron complexes $C_5H_5Fe(CO)(PR_3)H$ where no isomers can exist and ^{1}H is *cis* to ^{31}P, *J* ranges from 75 to 94 Hz [7]. In the case of the structurally related π-cyclopentadienylmolybdenum complexes $C_5H_5Mo(CO)_2(PR_3)H$, which can be regarded as neutral models for the protonated forms of V-VII, *J* values show a pronounced dependence on the configuration. Isomers with structure C give *J* in the range 64 to 73 Hz, while configuration D leads to *J* values of 21 to 29 Hz [8].

The Mn—H splitting pattern of compound IV is consistent with the couplin involving two non-equivalent ^{31}P nuclei (part X of the ABX spectrum). In this case the protonated form possesses structure B with ^{1}H — ^{31}P coupling constants *J*(*cis*) of 82 and *J*(*trans*) of 30 Hz. Accordingly, the ^{31}P — {^{1}H} NMR spectrum of IV comprises an AB quartet with *J*(P — P) of 160.0 Hz and the difference Δδ in the phosphorus chemical shift of 7.56 ppm (the centre of the multiplet is 30.96 ppm downfield relative to external 85% H_3PO_4).

It appears that the structure of the protonated compound III must also be B. However, in this case *J*(*cis*) is 90 Hz, while *J*(*trans*) is much smaller than that found for compound IV, and does not exceed the half-width of the line (⩽ 5 to 8 Hz). The ^{31}P — {^{1}H} spectrum consists of a single line with half-width of 40 Hz The broadening depends on both coupling with ^{55}Mn and fine structure contributions. Simulation of the NMR spectrum of compound III has been carried out to show that the variation in phosphorus chemical shifts in the range 0 to 0.6 ppm and in *J*(P — P) in the range 0 to 18 Hz yields a good agreement between experimental and calculated spectra, both ^{1}H and ^{31}P, thus confirming configuration B. The difference in *J*(*trans*) values for III and IV seems to result from changes of the valency angles around the phosphorus atom, as caused by the elongation of the polymethylene bridge by one CH_2 unit. It seems probable that isomer B is formed in III and IV due to the small length of the bridge, which hinders *trans* arrangement of the phosphorus atoms. On the contrary, with compound II the three CH_2 unit chain proves long enough to make configuration A possible. Realization of structure A for I is probably related to the significant steric hindrance caused by the occurrence of two bulky PPh_3 ligands.

As for the stereochemistry of protonated monophosphine complexes V-VII, these are likely to possess structure C, to judge from *J*(P — H) values of 51 and 70 Hz. We believe that earlier-studied π-arenechromium complexes π-$C_6H_5RCr(CO)_2PPh_3$, which exhibit *J*(P — H) values of 63 to 69 Hz, are characterized by the same configuration [2].

One more effect of the protonation at the metal atom lies in a downfield shift of the signal of the π-cyclopentadienyl protons. The shift, Δδ = 0.4 to 0.8 ppm, is considerably smaller than in the case of benzene protons of proton-d π-benzenechromium complexes ($\Delta\delta \approx 1.5$ ppm [2]). Besides, small down-ld shifts of C—H and C—CH_3 signals from the P(iso-C_3H_7) ligand ($\Delta\delta$ of 0.4 d 0.1 ppm respectively) and of C_6H_{11} signals from the $P(C_6H_{11})_3$ ligand ($\Delta\delta$ of 2 ppm for the centre of multiplet) have been observed in the protonation of mpounds VI and VII.

nclusion

Thus the overall results demonstrate that the metal protonation of carbonyl-iosphine -manganese and -chromium complexes produces the following changes their spectra:

(i) Higher frequency shift of the CO stretching vibrations, $\Delta\nu$ = 100-140 cm^{-1} [1, 3].

ii) Mn—H and Cr—H hydride signals appear at δ of -4 to -6 ppm (the present communication, and also refs. 2 and 5);

ii) A5 to 9 ppm downfield shift of ^{13}C NMR signal of the cyclopentadienyl ligand [6];

v) A 10 to 20 ppm upfield shift of the NMR signal from ^{31}P nuclei of the phosphine ligands [6].

xperimental

^1H NMR spectra were recorded on a RYa-2305 instrument (60 MHz) for .0 to 20% solutions of compounds I-VII in methylene chloride or dichloro-thane in the presence 8-10 fold excess of trifluoroacetic acid. Measurements vere taken at 0 to 20° for I-IV and at —30° for compounds V-VII. Chemical hifts were measured relative to CH_2Cl_2 (δ = 5.25 ppm from TMS) or to internal yclohexane (δ = 1.43 ppm from TMS). $^{31}P - \{^1H\}$ NMR FT spectra were obtained using a Brucker HFX-90 spectrometer. Simulation of the spectra were carried out on a Digital PDP-12 computer using a MMRSIM programm.

Acknowledgement

The authors are indebted to Drs. E.I. Fedin, P.V. Petrovskii and B.D. Lavrukhin for valuable consultations and discussions.

References

1 B.V. Lokshin, V.I. Zdanovich, N.K. Baratnenskaya, V.N. Setkina and D.N. Kursanov, J. Organometal. Chem., 37 (1972) 331.

2 D.N. Kursanov, V.N. Setkina, P.V. Petrovskii, V.I. Zdanovich, N.K. Baratnenskaya and I.D. Rubin, J. Organometal. Chem., 37 (1972) 339.

3 B.V. Lokshin, A.G. Ginzburg, V.N. Setkina, D.N. Kursanov and I.B. Nemitovskaya, J. Organometal. Chem., 37 (1972) 347.

4 B.V. Lokshin, A.A. Pasinsky, N.E. Kolobova, K.N. Anisimov and Yu.V. Makarov, J. Organometal. Chem., 55 (1973) 315.

5 C.P. Lillya and P.A. Sahatjan, Inorg. Chem., 11 (1972) 889.

6 A.G. Ginzburg, L.A. Fedorov, P.V Petrovsky, E.I. Fedin, V.N. Setkina and D.N. Kursanov, J. Organometal. Chem., 73 (1974) 77.

7 P. Kalck and R. Poilblanc, C.R.Acad. Sci., Paris, Ser. C, 274 (1972) 66.

8 J.W. Faller and A.S. Anderson, J. Amer. Chem. Soc., 92 (1970) 5852.