*Journal of Organometallic Chemistry*, 99 (1975) 297—304

# THE $^{31}P$ NMR SPECTRA OF $ArCr(CO)_2P(C_6H_5)_3$ COMPOUNDS IN NEUTRAL AND ACIDIC MEDIA

L.A. FEDOROV, P.V. PETROVSKII, E.I. FEDIN, N.K. BARANETSKAYA, V.I. ZDANOVICH, V.N. SETKINA* and D.N. KURSANOV

*Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)*

(Received May 12th, 1975)

## Summary

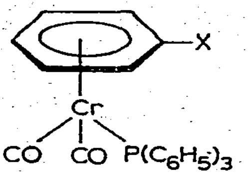
The $^{31}P$ NMR spectra of $C_6H_5XCr(CO)_2P(C_6H_5)_3$ (X = H, $CH_3$, $OCH_3$, $N(CH_3)_2$, $COOCH_3$) (I), $p$-$C_6H_4X_2Cr(CO)_2P(C_6H_5)_3$ (X = $COOCH_3$) (II) and $C_6H_3X_3Cr(CO)_2P(C_6H_5)_3$ (X = $CH_3$) (III) complexes in neutral and acidic media were investigated. The protonation of complexes I and III in trifluoroacetic acid results in the greater upfield shielding of $^{31}P$—{$^1H$} signal. In this case the complexes I (X = H, $CH_3$, $OCH_3$) are completely protonated at the metal, complex I (X = $COOCH_3$) is partially protonated, while no protonation occurs in the case of complex II.

Temperature-dependence of the $^{31}P$—{$^1H$} NMR spectra was investigated for complexes I (X = H, $OCH_3$) in a 1/10 mixture of trifluoroacetic acid and toluene and for complexes I (X = $COOCH_3$) and II in trifluoroacetic acid. The degree of protonation was found to increase with decreasing temperature.

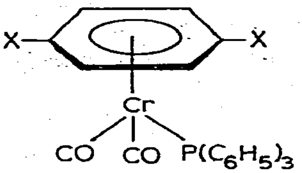
$^{13}C$ NMR spectroscopy has been used in the study of some aspects of the electronic and geometric configurations of the $\pi$-arenechromium complexes [1-3]. However the $^{31}P$ spectra of these complexes with phosphorous ligands have not been recorded up to the present time. This work is concerned with a $^{31}P$ NMR investigation of the electronic and geometric structures of arenechromium dicarbonyl triphenylphosphines with various substituents in the $\pi$-aromatic ring (compounds I-III) in neutral and acidic media*. Carbon disulfide was used as the neutral solvent and trifluoroacetic acid as acid.

---

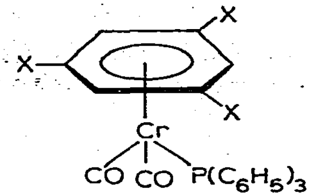
* The complexes I and III have been found to undergo hydrogen exchange with $CF_3COOD$ [4].



(I) a: X = H
b: X = $CH_3$
c: X = $OCH_3$
d: X = $N(CH_3)_2$
e: X = $COOCH_3$



(II) X = $COOCH_3$



(III) X = $CH_3$

All compounds I-III show a narrow singlet in the $^{31}P-\{^1H\}$ spectra in carbon disulfide at 20°C, showing that sufficiently fast internal rotation about the Ar—Cr π-bond takes place that no separate rotational isomers are observed under these conditions [5-6]. The $^{31}P-\{^1H\}$ spectra of complexes I-III in $CF_3COOH$ at room temperature also show a singlet shifted upfield with respect to that in $CS_2$. Addition of toluene to the acid affords two signals in some cases.

The $^{31}P$ chemical shifts of the complexes investigated in $CS_2$ and $CF_3COOH$ at 20°C are listed in Table 1. Table 2 combines the temperature-dependences of the $^{31}P-\{^1H\}$ spectra of compounds Id and IIb in $CF_3COOH$ and compounds Ia and Ib in a 1/10 mixture of $CF_3COOH$ and toluene.

Analysis of the data obtained shows that coordination of the triphenylphosphine ligand with chromium atom in complexes I-III causes a sharp downfield shift of the $^{31}P$ signal with respect to $PPh_3$. This shift depends on various factors (the medium, substituent in the π-aromatic ligand, etc.) and is about 90-100 ppm in carbon disulfide. A similar phenomenon is known for many other types of transition metal coordination compound [7].

Interesting behaviour was observed on the effects of the π-arenic ligand substituents on $^{31}P$ shielding. In I and III in carbon disulfide the electron donor substituents ($CH_3$, $OCH_3$, 1,3,5-$(CH_3)_3$, and $N(CH_3)_2$) produce a deshielding

TABLE 1

THE $^{31}P$ CHEMICAL SHIFTS OF $ArCr(CO)_2P(C_6H_5)_3$ IN $CS_2$ AND $CF_3COOH$ AT 20°C [a]

| Ar | δ ($^{31}P$) (ppm) | | Δδ [δ($^{31}P$)($CF_3COOH$) — δ($^{31}P$)($CS_2$)] (ppm) |
|---|---|---|---|
| | $CS_2$ | $CF_3COOH$ | |
| $H_3COOCC_6H_4COOCH_3$-p | —82.32 | —75.01 | 7.31 |
| $C_6H_5COOCH_3$ | —87.04 | —79.59 | 7.45 |
| $C_6H_6$ | —91.12 | —70.93 | 20.19 |
| $C_6H_5CH_3$ | —91.97 | —72.02 | 19.95 |
| $C_6H_5OCH_3$ | —92.21 | —72.26 | 19.95 |
| 1,3,5-$(CH_3)_3C_6H_3$ | —92.55 [b] | —73.19 | 19.36 |
| $C_6H_5N(CH_3)_2$ | —93.74 | —78.12 | 15.62 [c] |

[a] For $P(C_6H_5)_3$ δ($^{31}P$) = 6.0 [7]. [b] Spectrum was recorded at 10°C. [c] A decrease of Δδ from 20 to 15.62 may be explained by protonation at $N(CH_3)_2$ group.

TABLE 2

TEMPERATURE-DEPENDENCE OF $^{31}$P NMR SPECTRA OF $ArCr(CO)_2P(C_6H_5)_3$

| Ar | Conditions | | Protonated form ($^{31}$P) (ppm from 85% $H_3PO_4$) | $\Delta\nu$ (Hz) | Non-protonated form ($^{31}$P) (ppm from 85% $H_3PO_4$) | $\Delta\nu$ (Hz) |
|---|---|---|---|---|---|---|
| | Medium | $T$ (°C) | | | | |
| $COOCH_3C_6H_4COOCH_3$-$p$ | $CF_3COOH$ | 40 | | | −74.5 | 16.7 |
| | $CF_3COOH$ | 20 | | | −75.0 | |
| | $CF_3COOH$ | −10 | | | −74.5 | 8.4 |
| $C_6H_5COOCH_3$ | $CF_3COOH$ | 40 | −78.2 [a] | 192 | −78.2 [a] | 192 |
| | $CF_3COOH$ | 20 | −79.6 [a] | 171 | −79.6 [a] | 171 |
| | $CF_3COOH$ | −10 | −67.9 | 20.8 | | |
| $C_6H_6$ | $CF_3COOH$—toluene (1/10) | 40 | | | −89.8 | 47 |
| | $CF_3COOH$—toluene (1/10) | −10 | −73.0 | 100 | −89.9 | 50 |
| | $CF_3COOH$—toluene (1/10) | −30 | −72.6 | 50 | −90.1 | 17 |
| $C_6H_5OCH_3$ | $CF_3COOH$—toluene (1/10) | 40 | −85.0 [a] | 292 | −85.0 [a] | 292 |
| | $CF_3COOH$—toluene (1/10) | 20 | −74.6 | 167 | −86.9 | 317 |
| | $CF_3COOH$—toluene (1/10) | −30 | −74.7 | 17 | −92.2 | 33 |

[a] The signals of protonated and non-protonated forms are unresolved.

effect on the $^{31}P$ nuclei in the triphenylphosphine ligand: the downfield signal shift with respect to unsubstituted Ia is 1-2 ppm. On the other hand the electron attractive group $COOCH_3$ affords additional shielding of the $^{31}P$ nuclei: a 4 ppm upfield shift is observed. The data of Table 1 for compounds II and III demonstrate also that introduction of the new substituents into the π-aromatic ring enhances their shielding effect on the $^{31}P$ nuclei.

It should be noted that qualitatively the effect of various π-arenic ring substituents in complexes I on $^{31}P$ shielding is similar to that on $^{13}C$ of carbonyl ligands in these derivatives and in the compounds $(\pi\text{-}C_6H_5X)Cr(CO)_3$ [2,3] and in $(\pi\text{-}C_5H_5X)Mn(CO)_3$ [8].

Actually, the same sequence is always observed for the change of shielding of the indicator nucleus with the character of substituents in neutral solvents: $N(CH_3)_2 < OCH_3 < CH_3 < H < COOCH_3$; an increase of shielding of $^{31}P$ (in $PPh_3$ ligand) and $^{13}C$ (in CO ligands).

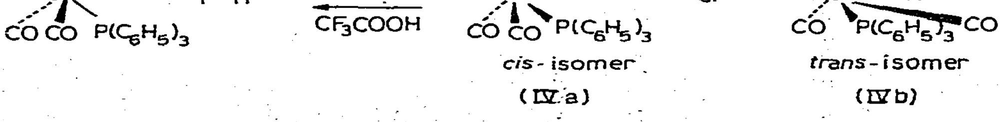
However, the $^{31}P$ nuclei are more sensitive than $^{13}C$ to the substituent effects. More rigorous estimations need special analysis.

Earlier we found by PMR and IR that at room temperature the derivatives I with electron donor substituents, benzenechromium dicarbonyl triphenylphosphine (Ia), and complex III in $CF_3COOH$ are entirely protonated at the metal atom [9]. However, under the same conditions complex Id is protonated only partially while no protonation occurs in the case of II.

We continued the study of the protonation complexes I-III in acidic medium using $^{31}P$ NMR. It was shown that in $CF_3COOH$ the $^{31}P$ signals of the triphenylphosphine ligand in I-III are shifted essentially upfield with respect to those observed in neutral $CS_2$ (the value of shift is equal to 7-20 ppm (Table 1). Earlier, similar behaviour was observed in the $^{31}P$ NMR study of protonation of π-cyclopentadienylmanganese complexes with phosphorus ligands [10].

In principle the effect of $CF_3COOH$ may be due to a dual solvent effect: a non-specific solvation of the complexes by acid molecules or/and specific solvation including protonation. For elucidating a non-specific solvation by $CF_3COOH$ in the total solvent effect we measured the $^{31}P$ spectrum of compound II, whose IR spectrum showed no protonation in this acid. Thus the value $\Delta\delta = \delta(^{31}P)(CF_3COOH) - \delta(^{31}P)(CS_2)$ for complex II of 7 ppm provides some evidence of the size of effect of the non-specific solvation.

The $^{31}P$ spectrum of III taken without proton decoupling shows two equally intense signals instead of one as in the $^{31}P\text{—}\{^1H\}$ spectrum. Probably the splitting is due to $^{31}P\text{—}^1H$ spin coupling; the value of 63 Hz obtained (as found earlier [9]) shows that in III and obviously in Ia-e the acid proton adds to the metal atom with formation of P—Cr—H.



*cis*-isomer (IVa)

*trans*-isomer (IVb)

(1)

It should be pointed out that the $^{31}P\text{—}Cr\text{—}^1H$ spin coupling is evidence of the sufficiently high lifetime of the Cr—H bond (in excess solvent) on the NMR time scale. In turn this also shows that in excess $CF_3COOH$ the protonation of III and Ia-e (eqn. 1) is shifted entirely to the right. Since in many cases the $^{31}P$—$\{^1H\}$ NMR spectrum shows only one signal we may assume the formation of one isomer: *cis* or *trans* with square pyramidal structure (IVa, IVb) in the protonation of these complexes. The configuration of this isomer may be deduced on the basis of data for transition metal compounds with similar structure, in particular the neutral compounds $\pi$-$C_5H_5M(CO)_2PR_3H$ (M = Mo, W, R = alkyl, $C_6H_5$ etc.) [10-14]. Earlier was found [9] that the 63 Hz splitting is in agreement with *cis* structure IVa.

Unlike the derivatives III and Ia-d under such conditions ($CF_3COOH$, room temperature) complex Ie is only protonated partially. Actually the value of 7.5-9.0 ppm at 20-40°C gives no clear evidence of the protonation. However the signal width (170-190 Hz) (Figs. 1a and b) under these conditions shows that Ie participates in some dynamic reaction, probably protonation (eqn. 1). However, when the temperature is decreased to —10°C the $^{31}P$ signal of this compound is narrower by an order of magnitude and shifted essentially upfield (Fig. 1b) and the value $\Delta\delta$ attains $\approx$19 ppm. Such temperature-dependence is practically absent (Table 2) in the spectrum of II unprotonated in $CF_3COOH$. Thus one may conclude that at room temperature Ie is only partially protonated [16].

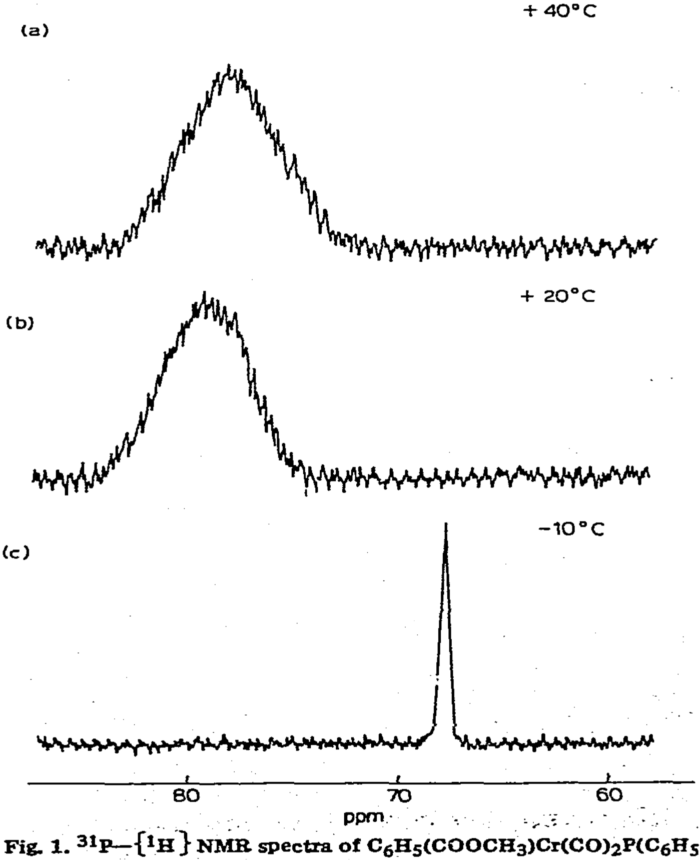


Fig. 1. $^{31}P$—$\{^1H\}$ NMR spectra of $C_6H_5(COOCH_3)Cr(CO)_2P(C_6H_5)_3$ in $CF_3COOH$ at various temperatures.

With decrease of temperature, however, the equilibrium is shifted markedly towards the protonated form.

For elucidating the protonation of compounds Ia-e and in particular for determining their relative affinities for proton addition, reaction 1 was investigated in $CF_3COOH$—toluene (1/10) mixture (Table 2). Fig. 2 shows the temperature-dependence of $^{31}P-\{^1H\}$ NMR spectra of complex Ia in this mixture. At 40°C the spectrum contains a rather narrow singlet which chemical shift indicates an unprotonated compound, Ia, under such conditions (Fig. 2a). With decrease of temperature the second signal of the protonated compound appears (Figs. 2b and c). We note that at —10°C the signal intensities corresponding to both forms are nearly the same, while at —30°C an increase in the signal intensity of the protonated form is four-fold.

The spectrum of complex Ic at 40°C in the mixture of solvents shows a broad singlet with an intermediate chemical shift (Table 2) demonstrating an

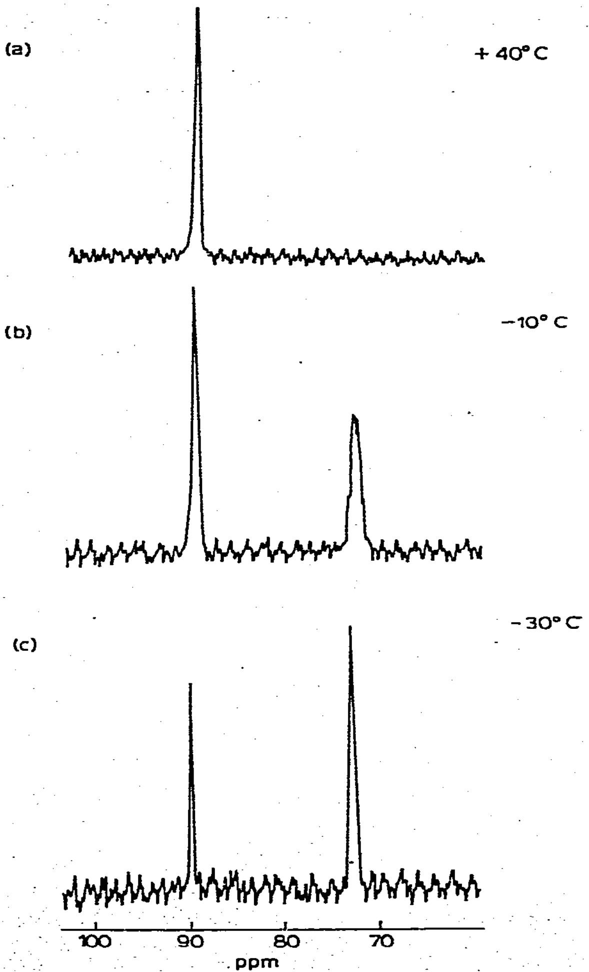
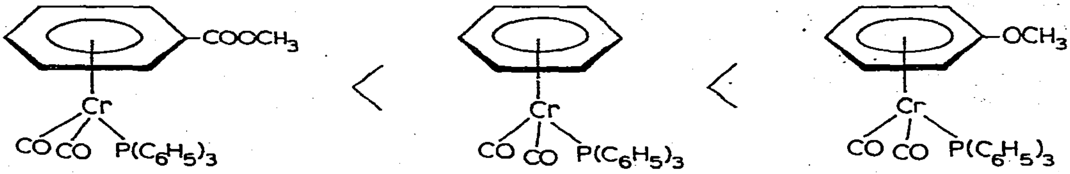


Fig. 2. $^{13}P-\{^1H\}$ NMR spectra of $C_6H_6Cr(CO)_2P(C_6H_5)_3$ in $CF_3COOH$—toluene (1/10) mixture at various temperatures.

equilibrium of close quantities of the protonated and non-protonated forms and the lifetime of C—H bond is comparable to the difference of their chemical shifts. At the lower temperature (—30°C) the spectrum shows two (instead of one) narrow singlets, corresponding to protonated and non-protonated forms. It should be noted that in this case the ratio of signals corresponding to the protonated and non-protonated forms is 14/1. This allows us to conclude that under the same conditions the methoxy derivative Ic is more readily protonated than Ia, with the unsubstituted π-arenic ring.

The following series of proton affinities of compounds I may be proposed on the basis of the qualitative data:



It may be readily seen that this series is consistent with the above-mentioned series of substituent effects on $^{31}$P shielding in the triphenylphosphine ligand. One may thus assume that the change of chromium affinity for a proton depends on the charge distribution over a molecule and thus on the type of substituent (donor or acceptor) in the π-aromatic ring.

The temperature dependence of $^{31}$P—{$^1$H} spectra of $ArCr(CO)_2P(C_6H_5)_3$ in acidic media shows that metal protonation is facilitated at lower temperatures. Probably the protonated form of these compounds is thermodynamically more favourable when the temperature is low.

## Experimental

$ArCr(CO)_2P(C_6H_5)_3$ compounds were obtained from $ArCr(CO)_3$ and $P(C_6H_6)_3$ by a previously used method [17]. The compounds were identified by their m.p.'s and IR spectra. The solutions of $ArCr(CO)_2P(C_6H_5)_3$ in $CS_2$, $CF_3COOH$ and $CF_3COOH$—toluene (1/10) were prepared under argon. The $^{31}$P NMR spectra were registered on a Bruker HX-90 spectrometer with Fourier transform and proton decoupling with noise modulation. The operating frequency was 36.43 MHz. 85% $H_3PO_4$ was used as an external standard.

## References

1 B.E. Mann, Chem. Commun., (1971) 976.
2 L.A. Fedorov, P.V. Petrovskii, E.I. Fedin, N.K. Baranetskaya, V.I. Zdanovich, V.N. Setkina and D.N. Kursanov, Dokl. Akad. Nauk SSSR, 209 (1973) 404.
3 G.M. Bodner and L.F. Todd, Inorg. Chem., 13 (1974) 360, 1335.
4 V.N. Setkina, V.I. Zdanovich, N.K. Baranetskaya, A.I. Yurtanov, K.N. Anisimov and D.N. Kursanov, Zh. Obshch. Khim., 41 (1971) 1338.
5 L.A. Fedorov, Usp. Khim., 42 (1974) 1481.
6 M.M. Crutchfield, C.H. Dungan, J.H. Letcher, V. Mark and J.R. Van Wazer, Topics Phosphorus Chem., 5 (1967) 19.
7 J.F. Nixon and A. Pidcock, Ann. Rev. NMR Spectrosc., 2 (1969) 345.
8 P.V. Petrovskii, E.I. Fedin, L.A. Fedorov, A.G. Ginsburg, V.N. Setkina and D.N. Kursanov, Dokl. Akad. Nauk SSSR, 210 (1973) 605.

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

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

11 J.W. Faller and A.S. Anderson, J. Amer. Chem. Soc., 91 (1969) 1550.

12 P. Kalck and R. Poilblanc, J. Organometal. Chem., 19 (1969) 115.

13 J.W. Faller, A.S. Anderson and C.-C. Chen., J. Organometal. Chem., 17 (1969) P7.

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

15 P. Kalck, R. Pince, R. Poilblanc and J. Roussel, J. Organometal. Chem., 24 (1970) 445.

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

17 W. Strohmeier and D. Hobe, Z. Naturforsch. B, 18 (1963) 981.