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PROTONATION OF METAL CARBONYL COMPLEXES

II. A PMR SPECTROSCOPIC STUDY OF PROTONATION IN ARENECHROMIUM TRICARBONYLS AND ARENECHROMIUM DICARBONYL TRIPHENYLPHOSPHINES

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SUMMARY

From PMR spectroscopic studies, it has been shown that $C_6H_6Cr(CO)_3$, $CH_3C_6H_5Cr(CO)_3$, $CH_3OC_6H_5Cr(CO)_3$ and 1,3,5-$(CH_3)_3C_6H_3Cr(CO)_3$ protonate at the chromium atom in a mixture of $BF_3 \cdot H_2O$ and CF_3COOH (1/1), $H_0 \approx -7$ as a solvent, while $CH_3C_6H_5Cr(CO)_2P(C_6H_5)_3$, $CH_3OC_6H_5Cr(CO)_2P(C_6H_5)_3$ and 1,3,5-$(CH_3)_3C_6H_3Cr(CO)_2P(C_6H_5)_3$ protonate at the metal in CF_3COOH ($H_0 \approx -3$) as a solvent.

The effect of substituents in the π-bonded benzene ring of $ArCr(CO)_3$ and $ArCr(CO)_2P(C_6H_5)_3$ upon the ability of the complexes to protonate at the metal atom has been investigated, and it has been shown that electron-releasing groups enhance while electron-attracting groups hinder the protonation of these complexes.

Substitution of the carbonyl ligand in $ArCr(CO)_3$ by a triphenylphosphine group results in an increase in the basicity of the complex and facilitates its protonation in acidic media.

INTRODUCTION

We have shown previously that the IR data for arenechromium dicarbonyl triphenylphosphine complexes indicate that they undergo protonation in trifluoroacetic acid. In the present paper the results of a PMR study of the protonation of $ArCr(CO)_2P(C_6H_5)_3$ and $ArCr(CO)_3$ are reported.

RESULTS AND DISCUSSION

Protonation of $ArCr(CO)_2P(C_6H_5)_3$ and $ArCr(CO)_3$ in acidic medium may occur at one of the three reaction centres. Thus, protons may add on at the π-bonded benzene ring, at the chromium atom or at the carbonyl group. Use of PMR spectroscopy should allow these three possibilities to be distinguished.

Protonation of arenechromium dicarbonyl triphenylphosphine complexes at the phosphorus atom is less probable since the lone pair electrons in the phosphorus atom participate in donor–acceptor bonding with the chromium atom. Addition of a proton to benzene or to its homologues should result in a σ-complex capable of detection at low temperature in the PMR spectrum.

Olah[2] has shown that the PMR spectrum of protonated benzene exhibits a signal corresponding to the CH_2-protons ($\delta = 3.6$ ppm) together with signals for the CH aromatic protons at δ 8.8, 7.5 and 7.2 ppm, respectively. We suggest that the signal of a proton bonded to the carbonyl group of the complex should be located in the low field region of the spectrum, a suggestion which is supported by the observation that the signal associated with the addition of a proton to the CO group during the protonation of cyclic ketones occurs at δ 12–14 ppm[3].

In contrast, the combination of hydrogen with a metal generally results in a signal shifted to a higher field value relative to that of the tetramethylsilane signal[4]. In this present work, it was always found that the addition of a proton to a metal atom results in negative values of δ on the particular scale of chemical shifts employed.

That arenechromium tricarbonyls add protons at the metal atom is supported by the work of Wilkinson *et al.*[5], who have shown that these materials in boron trifluoride hydrate exhibit a PMR spectrum with a signal in the high field region with $\delta = (-3.55) - (-4.27)$ ppm.

In this study, the PMR spectra of arenechromium tricarbonyls have been measured using a mixture of trifluoroacetic acid and boron trifluoride hydrate (equal volumes) ($H_0 \approx -7$), as a solvent. The PMR parameters of the compounds investigated are listed in Table 1.

From the data in Table 1, it is seen that the PMR spectra of benzenechromium tricarbonyl, toluenechromium tricarbonyl, anisolechromium tricarbonyl and mesityl-

TABLE 1

PMR DATA FOR $ArCr(CO)_3$ COMPLEXES[a]

Compound	*In CS_2*		*In $BF_3 \cdot H_2O/CF_3COOH$ (1/1)*					$\Delta\delta^c$ (*ppm*)
	$\delta(H)$ (ppm)		*$\delta(H)$ (ppm)*			*Line width $\Delta\nu$ (Hz)*		
	Subst.	*Benz. ring*	*Subst.*	*Benz. ring*	*Cr–H*	*Cr–H*	*C_6H_{12}*	
$C_6H_6Cr(CO)_3$		5.23		6.79	−4.05	42	5	1.56
$CH_3C_6H_5Cr(CO)_3$	2.20 ($CDCl_3$)	5.25 (*o,p*) 5.42 (*m*)	2.50	6.71	−4.08	45	9	
$1,3,5$-$(CH_3)_3C_6H_3Cr(CO)_3$	2.19	4.76	2.50	6.37	−4.16	10	3	1.61
$CH_3OC_6H_5Cr(CO)_3$	3.68	4.76 (*p*) 4.99 (*o*) 5.41 (*m*)	4.12	6.15 (*p*) 6.55 (*o,m*)	−4.12	10	3	
$(CH_3)_2NC_6H_5Cr(CO)_3$	2.87	4.72 (*o,p*) 5.49 (*m*)	3.48	5.70	No			
$(COOH)C_6H_5Cr(CO)_3^b$				5.57 (*m*) 6.24 (*p*) 6.48 (*o*)	No			

[a] Studied earlier in $CDCl_3$[9–11]. [b] Assigned by analogy with $(CH_3OOC)C_6H_5Cr(CO)_3$. [c] Difference between chemical shifts of the benzene ring protons in acidic medium and CS_2.

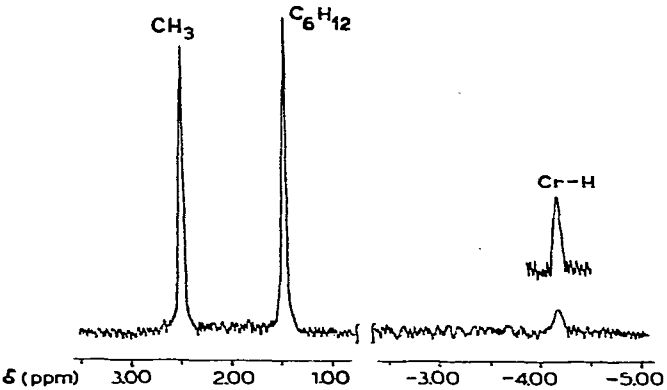

Fig. 1. The PMR spectrum of mesitylene chromium tricarbonyl in a 1/1 mixture of CF_3COOH and $BF_3 \cdot H_2O$ as a solvent at 34°.

enechromium tricarbonyl when dissolved in a mixture of $BF_3 \cdot H_2O$ and CF_3COOH exhibit an additional signal in the region of $\delta = (-4.05) - (-4.12)$ ppm alongside the proton signals normally obtained for the aromatic ligand. The PMR spectrum of mesitylenechromium tricarbonyl measured in a mixture of CF_3COOH and $BF_3 \cdot H_2O$ at 34° is shown in Fig. 1. If a mixture of the deuterohydrate of boron trifluoride and deuterotrifluoroacetic acid is used then the PMR spectra of the complexes mentioned above show no upfield signal, thus demonstrating that this signal must be associated with the proton transferred from the medium to the $ArCr(CO)_3$ complex.

In contrast, the PMR spectrum of $(CH_3)_2NC_6H_5Cr(CO)_3$ and $(COOH)C_6H_5$-$Cr(CO)_3$ in a mixture of $BF_3 \cdot H_2O$ and CF_3COOH exhibits no signals corresponding to the bonding of protons to the metal atom. These results, as far as $(COOH)C_6H_5$-$Cr(CO)_3$ is concerned, may be explained by the fact that electron-attracting substituents such as the COOH group inhibit protonation of $ArCr(CO)_3$ at the metal atom. For (dimethylaniline)chromium tricarbonyl, protonation in this particular medium obviously involves the nitrogen atom (to give the dimethylammonium group $(CH_3)_2N^+H$, which is a strong electron acceptor) rather than the metal atom.

The PMR spectra of arenechromium dicarbonyl triphenylphosphine complexes in trifluoroacetic acid have also been studied. The PMR data for these complexes measured in CF_3COOH and CS_2 are given in Table 2. Arene(triphenylphosphine)chromium dicarbonyls appear to protonate much more readily at the metal atom than arenechromium tricarbonyls, for in this case protonation takes place even in pure trifluoroacetic acid at $H_0 \approx -3$. Not unexpectedly, the replacement of one carbonyl group by a triphenylphosphine leads to an increased basicity of the resulting complex since, in contrast to the carbonyl group, the triphenylphosphine ligand is a stronger donor and a weaker acceptor.

The data in Table 2 also demonstrate that the introduction of substituents into the π-bonded benzene ring of $ArCr(CO)_2P(C_6H_5)_3$ has a considerable influence on the ability of these complexes to undergo metal protonation in an acidic medium. This effect is very similar to the action of substituents in the $ArCr(CO)_3$ series. Under the experimental conditions employed in this study the PMR spectrum of benzene(triphenylphosphine)chromium dicarbonyl measured in CF_3COOH showed no proton signal in the high-field region. When donor substituents were introduced into

TABLE 2

PMR DATA FOR $ArCr(CO)_2P(C_6H_5)_3$ COMPOUNDS

Compound	*In carbon disulfide*				*In trifluoroacetic acid*							$\Delta\delta$[a] *(ppm)*
	$\delta(H)$ (ppm)			*$J(P-H)$ (Hz) of benzene protons*	*$\delta(H)$ (ppm)*				*$J(P-H)$ (Hz) Cr proton*	*Line width $\Delta\nu$ (Hz)*		
	Subst.	*π-Bonded benzene ring*	*$P(C_6H_5)_3$*		*Subst.*	*π-Bonded benzene ring*	*$P(C_6H_5)_3$*	*Cr–H*		*Cr–H*	*C_6H_{12}*	
$C_6H_6Cr(CO)_2P(C_6H_5)_3$		4.58	7.32	3.5		6.20	7.68					1.62
$CH_3C_6H_5Cr(CO)_2P(C_6H_5)_3$	2.08	4.29 (*o*+*p*) 4.54 (*m*)	7.29		2.46	5.99	7.64	−4.27	63	8	1.5	
1,3,5-$(CH_3)_3C_6H_3Cr(CO)_2$-$P(C_6H_5)_3$	1.91	4.16	7.36	1.7	2.26	5.80	7.70	−4.08	67	7	2.5	1.64
$CH_3OC_6H_5Cr(CO)_2$-$P(C_6H_5)_3$	3.52	4.21 (*o*+*p*) 4.65 (*m*)	7.29		3.95	5.86	7.64	−4.56	69	6	1.8	
$(CH_3)_2NC_6H_5Cr(CO)_2$-$P(C_6H_5)_3$	2.76	3.87 (*o*) 4.31 (*p*) 4.73 (*m*)	7.43		2.98 3.42	5.19	7.61	No				
$(CH_3OOC)C_6H_5Cr(CO)_2$-$P(C_6H_5)_3$	3.69	4.47 (*m*+*p*) 5.36 (*o*)	7.31		4.01	4.99 (*m*+*p*) 5.97 (*o*)	7.52	No				0.52 (*m*+*p*) 0.61 (*o*)

[a] Difference between chemical shifts of the π-bonded benzene ring protons in CF_3COOH and CS_2.

the π-bonded benzene ring, however, this signal appeared as a doublet at $\delta = (-4.08) - (-4.56)$ ppm. The spectrum of mesitylene(triphenylphosphine)chromium dicarbonyl in CF_3COOH at 34°, which clearly demonstrates this, is shown in Fig. 2.

The introduction of electron-attracting substituents such as the carbomethoxy group and the protonated dimethylamino group, on the other hand, does not lead to enhanced protonation of $ArCr(CO)_2P(C_6H_5)_3$ at the metal atom.

The splitting of the signal corresponding to the proton associated with the metal atom into a doublet due to a spin-spin coupling with ^{31}P nucleus and the large value of coupling constant (J(P–H) = 63–69 Hz) provides further evidence that in these complexes proton addition occurs at the metal atom rather than at the aromatic ring. Furthermore, a comparison of integral intensities of the metal proton signal and those of the aromatic protons indicates that, within the accuracy of the integration, only one proton adds at the metal atom.

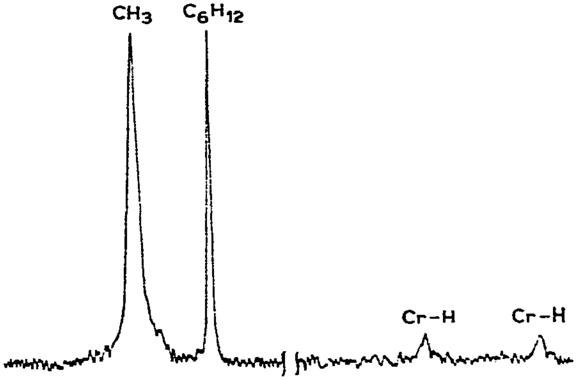

Fig. 2. The PMR spectrum of mesitylene chromium dicarbonyl triphenylphosphine in CF_3COOH as a solvent at 34°.

The introduction of substituents in the π-bonded benzene rings of $ArCr(CO)_3$ and $ArCr(CO)_2P(C_6H_5)_3$ affects the shape of the signal corresponding to the proton associated with the metal atom. Thus the broad signal of the metal proton in benzenechromium tricarbonyl and toluenechromium tricarbonyl (the halfwidth of the signal is equal to ~45 Hz) is considerably narrowed in the spectrum of mesitylenechromium tricarbonyl ($\Delta\nu$ 10 Hz). On the other hand, the broadening of signal of the metal proton in $C_6H_6Cr(CO)_3$ and $CH_3C_6H_5Cr(CO)_3$ is probably related to exchange processes. With three methyl groups in the benzene ring, the bond strength of the Cr–H bond increases and the exchange of protons between the medium and the metal is hindered.

Protonation of $ArCr(CO)_3$ and $ArCr(CO)_2P(C_6H_5)_3$ at the metal atom in acidic medium also affects the proton chemical shifts of the π-bonded benzene ring. In all the complexes studied, the signals of the aromatic protons are considerably downfield ($\Delta\delta$ 1.6 ppm) with respect to those measured in carbon disulfide, and since all these signals are very much broadened, accurate $\Delta\delta$ values were only measured for those complexes which exhibited a singlet corresponding to the aromatic protons in their spectra. After protonation, the proton signals for the π-bonded benzene ligands were found to be shifted even further downfield in comparison to the neutral solvents, and this must be attributed to the appearance of a positive charge in the complex upon protonation.

For $CH_3OOCC_6H_5Cr(CO)_2P(C_6H_5)_3$, which shows no upfield signal in CF_3COOH, the shift of the aromatic proton signals would be smaller when carbon disulfide is replaced as a solvent by trifluoroacetic acid, ($\Delta\delta$ 0.5–0.6 ppm). However, in benzene(triphenylphosphine)chromium dicarbonyl, which also exhibits no upfield PMR signal in CF_3COOH, the value of $\Delta\delta$ was found to be 1.62 ppm. Apparently in this latter case, protonation of the complex occurs at the chromium atom but the signal of the metal proton is very broad so that the PMR spectrum cannot be recorded at room temperature. This suggestion is supported by the IR data[1] for this compound, which indicate that in CF_3COOH as a solvent $C_6H_6Cr(CO)_2P(C_6H_5)_3$ exists in its protonated form.

The PMR spectra of $CH_3OC_6H_5Cr(CO)_3$ and $(CH_3)_3C_6H_3Cr(CO)_3$ in pure trifluoroacetic acid reveal no upfield signals, unlike the corresponding spectrum using a mixture of trifluoroacetic acid and $BF_3 \cdot H_2O$ as a solvent, and the difference in chemical shifts of the aromatic protons in CF_3COOH and CS_2 is only 0.3 ppm. This suggests that no protonation of arenechromium tricarbonyls occurs in pure trifluoroacetic acid.

It is interesting to compare the data on protonation of $ArCr(CO)_3$ and $ArCr(CO)_2P(C_6H_5)_3$ (obtained by two different methods *viz.* IR and PMR spectroscopy) with the rates of their hydrogen isotopic exchange measured in the same media.

According to PMR data, $ArCr(CO)_3$ adds a proton at the metal atom in a 1/1 mixture of CF_3COOH and $BF_3 \cdot H_2O$ when Ar = C_6H_6, $CH_3C_6H_5$, $CH_3OC_6H_5$ and $(CH_3)_3C_6H_3$. These complexes also undergo hydrogen isotopic exchange in the same media[6,7]. Unfortunately, corresponding data for the reactivities of $(CH_3)_2NC_6H_5Cr(CO)_3$ and $(COOH)C_6H_5Cr(CO)_3$ are not at present available. According to both IR and PMR data arenechromium tricarbonyls are not protonated in trifluoroacetic acid. No hydrogen–deuterium exchange processes occur with these complexes in CF_3COOD at room temperature.

From PMR spectra in trifluoroacetic acid the complex $ArCr(CO)_2P(C_6H_5)_3$ protonates at the metal if Ar = $(CH_3)_3C_6H_3$, $CH_3OC_6H_5$, $CH_3C_6H_5$ and apparently C_6H_6, but undergoes no protonation if Ar = $(CH_3OOC)C_6H_5$ and $(CH_3)_2NC_6H_5$. IR data in CF_3COOH indicate that the first four complexes exist only in the protonated form, while the compound $(CH_3OOC)C_6H_5Cr(CO)_2P(C_6H_5)_3$ is a mixture of both protonated and non-protonated forms. From this it follows that both IR and PMR methods indicate similar substituent effects regarding the protonation of the complexes. Of all the complexes investigated, only $ArCr(CO)_2P(C_6H_5)_3$ to date has been shown to undergo hydrogen isotopic exchange with deuterotrifluoroacetic acid[6,7]. No information is, as yet, available regarding hydrogen–deuterium exchange involving $(CH_3)_2NC_6H_5Cr(CO)_2P(C_6H_5)_3$. However, there is no direct dependence between the ability of the complexes to protonate at the metal atom and their rate of hydrogen exchange in an acidic medium. Thus, PMR data for $(CH_3OOC)C_6H_5Cr(CO)_2P(C_6H_5)_3$ indicate that protonation does not occur in CF_3COOH and IR data indicate that if protonation does occur its rate is somewhat slower than that of $C_6H_6Cr(CO)_2P(C_6H_5)_3$. In contrast, it has been found that the rate of hydrogen exchange of $(CH_3OOC)C_6H_5Cr(CO)_2P(C_6H_5)_3$ with CF_3COOD is approximately an order of magnitude greater than that of $C_6H_6Cr(CO)_2P(C_6H_5)_3$[8].

EXPERIMENTAL

All PMR spectra were recorded on a Perkin–Elmer R 12 spectrometer (60 MHz). Solutions of all compounds were prepared under an argon atmosphere, and spectra were measured in all cases using freshly prepared solutions. Cyclohexane was used as a standard (δ 1.48 in CF_3COOH).

REFERENCES

1 B. V. Lokshin, V. I. Zdanovich, N. K. Baranetskaya, V. N. Setkina and D. N. Kursanov, *J. Organometal Chem.*, 37 (1972) 331.
2 G. A. Olah, *J. Amer. Chem. Soc.*, 87 (1965) 1103.
3 G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, 90 (1968) 938.
4 *Trans. Metal Chem.*, *Vol. I*, *h.* 3, New York, 1965.
5 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1962) 3653.
6 D. N. Kursanov, V. N. Setkina, N. K. Baranetskaya, V. I. Zdanovich and K. N. Anisimov, *Dokl. Akad. Nauk SSSR*, 190 (1970) 1103.
7 V. N. Setkina, V. I. Zdanovich, N. K. Baranetskaya, A. I. Jurtanov, K. N. Anisimov and D. N. Kursanov, *Zh. Obshch. Khim*, 41 (1971) 1338.
8 D. N. Kursanov, V. N. Setkina, N. K. Baranetskaya, E. I. Fedin, E. I. Misov and K. N. Anisimov, *Dokl. Akad. Nauk SSSR*, in press.
9 W. McFarlane and S. O. Grim, *J. Organometal. Chem.*, 5 (1966) 147.
10 J. T. Price and T. S. Sorensen, *Can. J. Chem.*, 46 (1968) 515.
11 R. V. Emanuel and E. W. Randall, *J. Chem. Soc. A*, (1969) 3002.