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IV *. ANIONS OF MONOSUBSTITUTED BENZOPHENONECHROMIUM TRICARBONYL COMPLEXES

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Summary

The radical anions $RC_6H_4COC_6H_4R^1Cr(CO)_3^-$ (R = H, *o*-CH_3, *p*-CH_3, *p*-OCH_3, *p*-Cl, *p*-F and R^1 = H; R = H, R^1 = *o*-CH_3, *p*-CH_3) were prepared by potassium reduction in 1,2-dimethoxyethane and their ESR spectra measured. Each has a spectrum width of about half that of the corresponding ligand. Both coordination isomers of the *o*-CH_3 complexes and the ligand have spectra consisting of four lines assigned to splittings from the *para*- and *ortho*-protons of the unsubstituted ring with $A_p = A_o$. The *p*-CH_3 complexes both have 7-line spectra assigned to splittings from the two sets of *o*-protons one set having half the hyperfine splitting of the other. The reduction in hyperfine splitting of the uncomplexed as well as the complexed ring protons is an indication that the unpaired electron density is delocalized throughout the ligand system.

Introduction

Previous papers in the series [1,2,3] dealt with complexes of benzoylcyclopentanienyls. Those studies afforded an opportunity to examine a substantial number of complexes and of assessing the effect of complexation by a $Cr(CO)_3$ group. There were however two main disadvantages in that the completely uncomplexed organic ligand could not be studied for comparison and that the point of attachment of the $Cr(CO)_3$ group could not be varied for the same ligand. The present study was undertaken to overcome these disadvantages and to evaluate further the nature of the benzene—$Cr(CO)_3$ interaction. The principal complexes studied are 2-methylbenzophenone—$Cr(CO)_3$ and 4-methylben-

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* For part III see ref. 3.

zophenone—$Cr(CO)_3$. Some results are also given for benzophenone—$Cr(CO)_3$ and its 4-F, 4-Cl and 4-OCH_3 derivatives. In an earlier paper [4] the ^{13}C NMR spectra and SCCCMO calculations on these latter four complexes were discussed. The preparation, characterization, IR spectra and ^1H NMR spectra for the full series are being published in a separate paper.

Very few reports have appeared in the literature dealing with ESR spectra of arene—$Cr(CO)_3$ complexes. Apart from our work the only papers reporting such studies have been by Ceccon et al. [5,6]. The second of these papers included a discussion of a benzophenone complex and this provides an interesting comparison to our work.

Experimental

Radical anions were prepared by the method described previously [1] using potassium reduction in 1,2-dimethoxyethane (DME). Computer simulations of the spectra were carried out by the method described in the second paper of this series [2].

Results

Many ESR studies on the benzophenone radical anion (ketyl) have been published [7]. In addition, the ESR spectra of the 2-methylbenzophenone [8] and the 4-fluorobenzophenone [9] radical anions have been published. All the ligand spectra were also recorded by us so that valid comparisons could be made for the experimental conditions used for the complexes. The colorless solutions of the benzophenones in DME ($2—10 \times 10^{-3}$ *M*) turned blue on reduction except for the 4-chloro derivative which turned green.

Solutions ($2—10 \times 10^{-3}$ *M*) of the neutral complexes in DME are yellow or orange in color. After reduction with potassium they turn green or blue. The ESR spectra of these solutions were recorded in the temperature range of —15 to +25° C. In general, the best resolved and most intense spectra were obtained in the 0—25° C range. Reductions were also carried out in tetrahydrofuran (THF) and DME/THF mixtures but the spectra obtained were either inferior or no better than those obtained in DME.

In order to test for any ligand modification in the complex during reduction, the sample was allowed to decompose. After a prolonged period of time, typically 16 h, the solution was again allowed to react with the potassium and the spectrum of the original ligand was obtained.

2-Methylbenzophenone—$Cr(CO)_3$

The radical ion of 2-methylbenzophenone produced by potassium reduction was reported by Maruyama et al. [8] to give an ESR spectrum consisting of four lines with relative intensities 1/3/3/1. These splittings are assigned to the *para*- and *ortho*-protons of the unsubstituted ring with $A_p = A_o$. This assignment was confirmed by Okubo [10] using selective deuterium labelling and C_6H_5MgBr as the reducing agent. The four line pattern was also observed in the present study. The lack of observed splitting from other protons has been attributed to a rapid twisting vibration of the *o*-tolyl group [10].

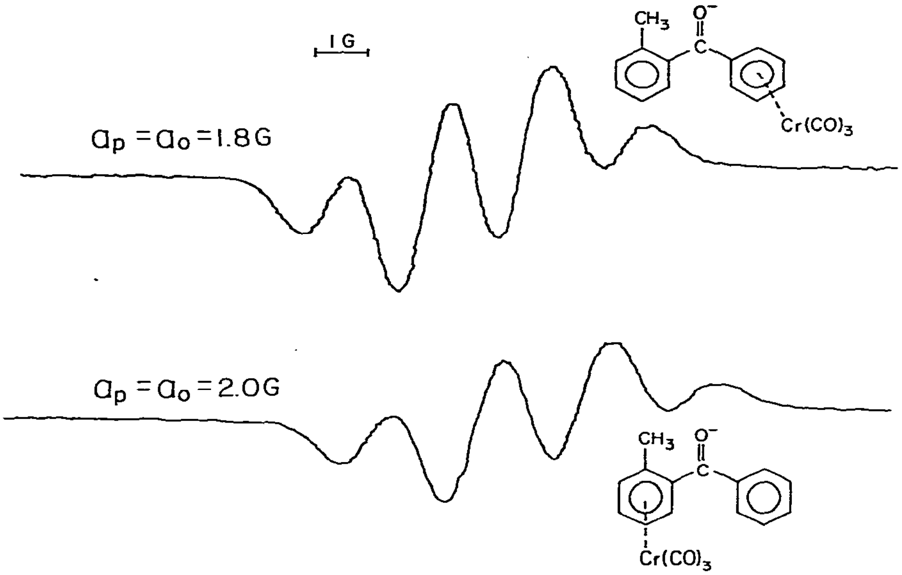

Fig. 1. ESR spectra of the radical anions of the 2-methylbenzophenone $Cr(CO)_3$ complexes.

The ESR spectra of the two coordination isomers of the $Cr(CO)_3$ complex are shown in Fig. 1. Both consist of four lines with intensity ratios 1/3/3/1. The hyperfine splittings (hfs) are however different as indicated in Fig. 1. The splittings are attributed to the *ortho-* and *para-*protons of the unsubstituted ring in both cases in accordance with the assignments for the ligand.

4-Methylbenzophenone—$Cr(CO)_3$

Again both coordination isomers give ESR spectra with the same general appearance each consisting of seven lines with smaller splittings superimposed. The seven lines, with intensity ratios of 1/2/3/4/3/2/1, can be assigned to two sets of two protons with one hfs being approximately half the other. The small splittings appear to be doublets split into quartets.

The spectrum of the isomer with the substituted ring complexed (Fig. 2 curve b) has more lines than the spectrum of the other isomer resulting in over-

TABLE 1

HALF THE ESR SPECTRUM WIDTH (GAUSS) OF THE RADICAL ANIONS OF $RC_6H_4COC_6R'Cr(CO)_3$

R	R	Complex	Ligand	Ligand/complex
H	H	5.5	11.5	1.80
H	*p*-CH_3	6.9	10.6	1.54
p-CH_3	H	5.9	10.6	1.80
p-OCH_3	H	4.9	10.4	2.12
p-Cl	H	5.7	12.0	2.11
p-F	H	6.3	13.0	2.06
o-CH_3	H	4.3	10.6	2.47
H	*o*-CH_3	4.8	10.6	2.21

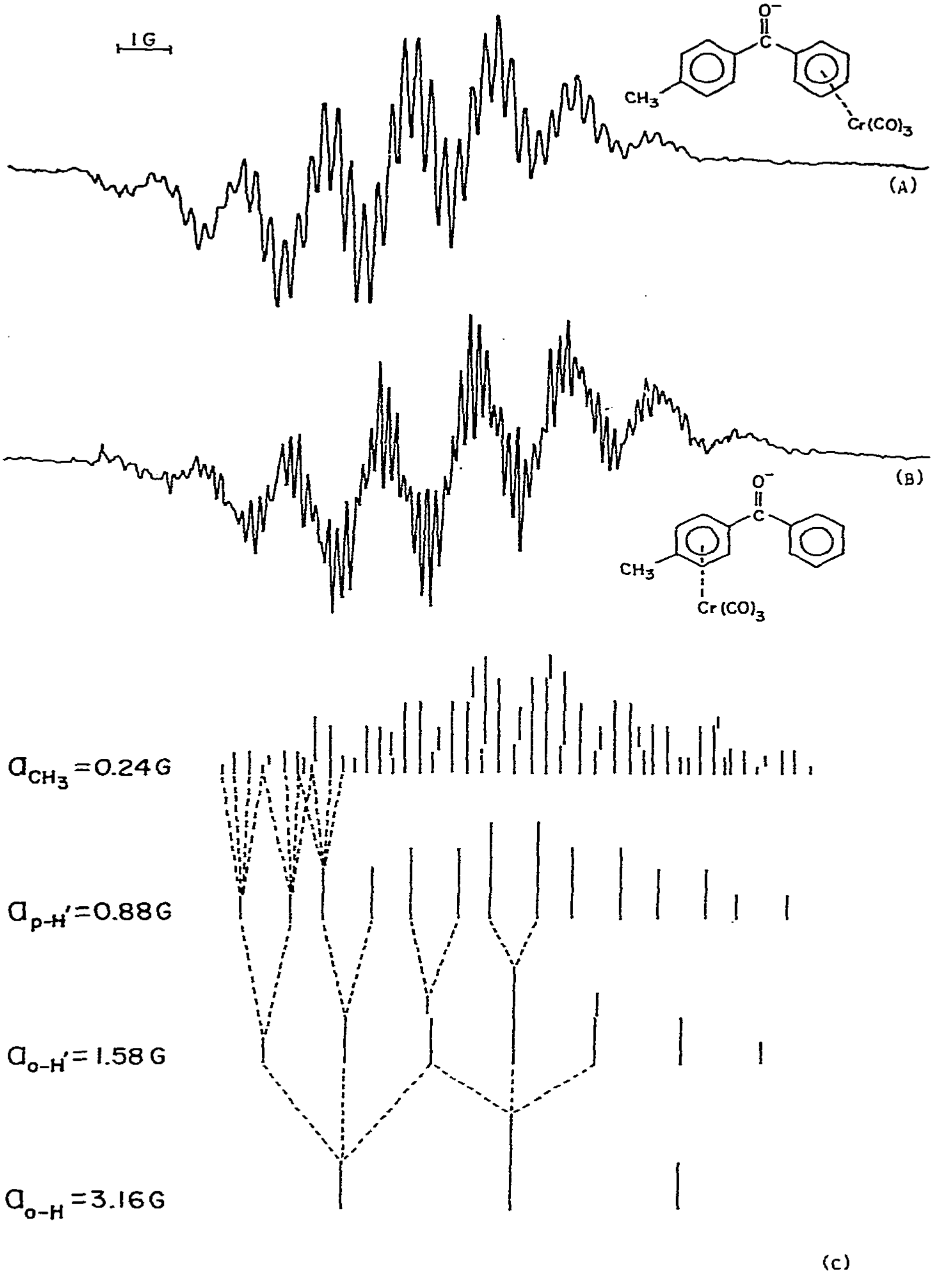

Fig. 2. ESR spectra of the radical anions of the 4-methylbenzophenone $Cr(CO)_3$ complexes. "A" and "B" are the recorded spectra. "C" is a "stick" diagram reconstruction of spectrum "A" based on a computer simulation.

lap of lines. This prevented accurate computer simulation. Computer simulation of the spectrum or the other isomer (Fig. 2 curve a) gave the following hfs constants 3.16 G (2), 1.58 G (2), 0.88 G (1), 0.24 G (3). The numbers in parentheses gives the number of protons to which the splitting constants apply.

Other compounds

Benzophenone—$Cr(CO)_3$ and its 4-F, 4-Cl and 4-OCH_3 derivatives gave spectra which were either too complex or too poorly resolved to analyse. Ceccon et al. [6] also reported that the spectrum of benzophenone—$Cr(CO)_3$ was too complex to analyze. Table 1 gives the half spectrum width for all the complexes in the series together with the values for the corresponding ligand.

Discussion

An examination of Table 1 shows a very substantial reduction in spectrum width on complexation in all cases. The reduction is about a factor of two, similar to that obtained for the phenyl protons in the benzoylcyclopentadienyl series [3] and, on average, similar to that obtained by Ceccon et al. [6] for the t-butyl compound. The explanation for this reduction is discussed in the paper dealing with the benzoylcyclopentadienyl compounds [3].

There is however an interesting difference from one coordination isomer to another. The ratios are 1.54 and 1.80 for the 4-methyl derivatives and 2.21 and 2.47 for the 2-methyl compounds. For each pair of substitution isomers the smaller values are observed when the substituted rings are complexed: that is a methyl group on the complexed ring causes the reduction of spectrum width to be less. In addition electron-withdrawing substituents on the uncomplexed ring cause a greater reduction in spectrum width than electron-donating substituents. Both these observations indicate that spin densities are affected the same way as electron densities in general and are in agreement with the results obtained for the benzoylcyclopentadienyl series [3].

Ceccon et al. [6] reported the spectrum of tetra-t-butylbenzophenone—Cr-$(CO)_3$. Because of the four t-butyl groups they obtained a much simpler spectrum than that obtained for either the unsubstituted benzophenone—$Cr(CO)_3$ or the *para*-monosubstituted derivatives. Their line assignments were a doublet due to the *para*-proton of the uncomplexed ring (A = 3.76 G), a triplet due to the *ortho*-protons of the uncomplexed ring (A = 1.90 G) and a triplet due to the *ortho*-protons of the complexed ring (A = 1.61 G). The splitting due to the *para*-proton splitting of the complexed ring was too small to measure. This they attribute to the complexed ring being twisted out of the plane containing the uncomplexed ring and the ketonic carbonyl group. If there is no such twisting the usual relatively large *para*-proton splitting would be expected.

The same pattern of assignments may be made in the case of the isomer of 4-methylbenzophenone—$Cr(CO)_3$ where the unsubstituted ring is complexed. The splitting of 3.16 G is assigned to the *ortho*-protons of the uncomplexed ring and that of 1.58 G to the *ortho*-protons of the complexed ring. The doublet splitting (0.88 G) is assigned to the *para*-proton of the complexed ring and the quartet (0.24 G) to the methyl group which would be expected to have a significant spin density. An attempt was made to confirm these assignments using selective deuteration. Unfortunately there was very substantial scrambling of the isotopes in solution which made the results meaningless.

The observation in our case of a *para*-proton splitting intermediate between the two extremes (i.e. coplanar rings and the complexed ring twisted through 90°) suggests that the complexed ring is partly twisted out of the plane containing the uncomplexed ring and the ketonic carbonyl group. The twisting is not great enough, however, to prevent substantial π-electron delocalization between two rings. The *para*-proton splitting observed for 4-methylbenzophenone—$Cr(CO)_3$ (0.88 G) is greater than half the value for the comparable benzoylcyclopentadienyl compound (1.61 G) and much greater than that observed by Ceccon for the tetra-t-butyl compound (<0.1 G).

Perhaps the most unusual result is the similarity of splitting patterns for both coordination isomers. This occurs for both substitution isomers. It might have been expected that the complexed ring would suffer substantially more reduction in splitting constants than the uncomplexed ring. That this is not observed suggests that the $Cr(CO)_3$ group does not substantially disrupt the electron distribution pattern in the ligand.

Acknowledgements

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