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III* ELECTRONIC EFFECTS IN THE TRICARBONYLCHROMIUM (BENZOYLCYCLOPENTADIENYL) MANGANESE TRICARBONYL ANION AND SOME SUBSTITUTED DERIVATIVES**

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SUMMARY

The ESR spectra of the tricarbonylchromium (benzoylcyclopentadienyl) manganese tricarbonyl anion and some substituted derivatives have been determined. The results show that the $Cr(CO)_3$ group withdraws spin density from both the phenyl protons and the manganese atom to the extent where A(H) is reduced by about one half and A(Mn) by about one third. Comparison of the experimental results with extended Hückel calculations shows that there is extensive delocalization of spin density throughout the organic system and that there is considerable π-overlap between the Cr atom and the phenyl ring. The conclusions are in general agreement with those resulting from IR and ^{1}H-NMR measurements. The ESR results for the -Cl and $-OCH_3$ derivatives without a $Cr(CO)_3$ group are also reported.

INTRODUCTION

In the previous paper [1] of this series ESR studies and extended Hückel molecular orbital calculations on substituted benzoylcyclopentadienylmanganese tricarbonyl anions were reported. We now wish to report and discuss studies on the tricarbonylchromium derivatives. A preliminary report on this work was given previously [2]. This is the first reported

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[*] For part II see ref. 1.

[**] Taken in part from the Ph.D. thesis of Chit Kay Chu, Memorial University of Newfoundland, 1974.

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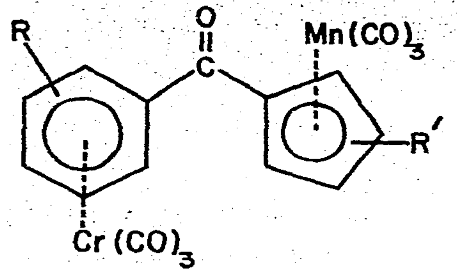

Fig 1.

ESR study of compounds with a tricarbonylchromium group bonded to a benzene ring and such studies will help in elucidating the nature of the metal-ring interaction. Since our preliminary report, Ceccon et al. [3] have published an account of the ESR spectrum of (t-butyl phenyl ketone) chromium tricarbonyl and this will be referred to in our discussion.

The results will also be discussed in relation to the anions without a tricarbonylchromium group [1] and in relation to the results obtained by other spectroscopic methods [4,5]. The general background to this work and references to other relevant work can be found in the previous papers of this series [1,6].

EXPERIMENTAL

The preparation of the parent neutral complexes has been reported previously [4,5]. The method used to prepare the anion radicals was described in the first paper of this series [6]. The spectroscopic methods and the general details of the calculations, both simulations and molecular orbital (M.O.), are the same as those given in the previous paper of this series [1].

RESULTS

Solutions ($2\text{-}10 \times 10^{-3}$M) of the neutral complexes (Figure 1) in 1,2-dimethoxyethane are orange in color. After reduction with potassium these turn dark greenish-yellow and do not give well resolved spectra until made very dilute. If reduction is continued with excess potassium a red species is obtained which does not give an ESR spectrum.

The spectrum of tricarbonylchromium (benzoyl β-methylcyclopentadienyl)-manganese tricarbonyl is shown in Figure 2(a). Computer simulation including proton and ^{55}Mn lines and dipolar broadening accounts for most of the spectrum's characteristics except for a line on each side of the spectrum. Allowance for 10% abundance of ^{53}Cr gives these extra two lines and a stick diagram based on computer simulation is shown in Figure 2(b). Computer simulation was used in making the assignments for all the spectra.

The experimental results for the methoxy and chloro-substituted anions without the tricarbonylchromium group are given in Table 1. As

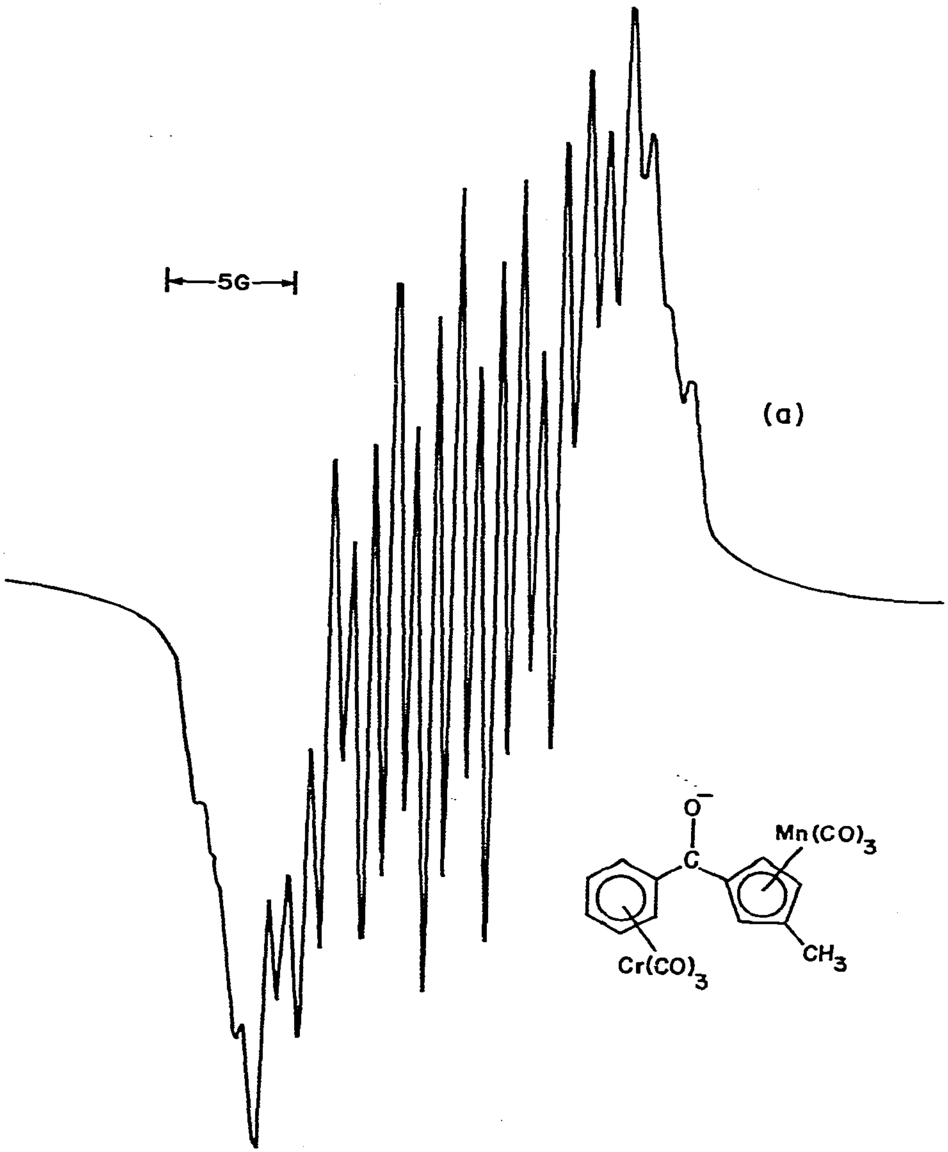

Fig 2. (a) ESR spectrum of $(CO)_3CrC_6H_5COC_5H_3(\beta\text{-}CH_3)Mn(CO)_3$ obtained at 22°C; microwave freq. 9.19292GHz; mod. width 0.32G microwave power 3mW.

indicated previously [5], we were unable to prepare the tricarbonylchromium derivatives of the chloro-substituted complexes. The experimental results for the tricarbonylchromium complexes, together with appropriate results [1] from compounds without the tricarbonylchromium group, are given in Table 2 and the experimental and theoretical spin densities are given in Table 3. Line broadening prevented the observance of possible small proton

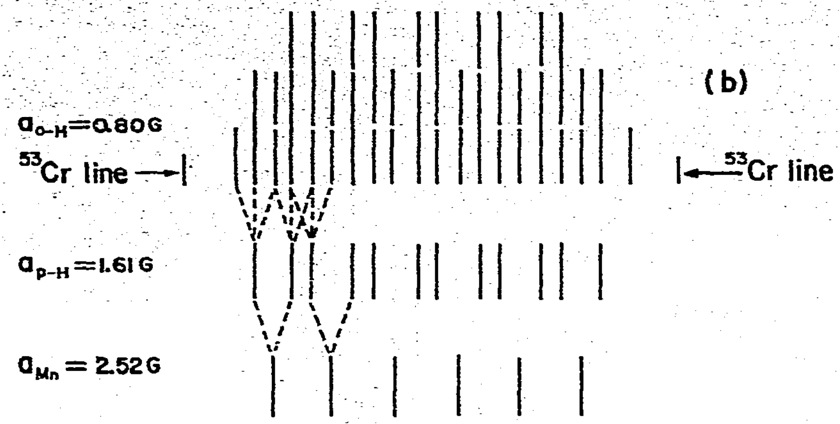

Fig 2. (b) "Stick" diagram reconstruction based on computer simulation.

TABLE 1

Experimental Values of g and the Hyperfine Coupling Constants[a] (gauss) for the Anion Radicals of $C_6H_4RCOC_5M_3R'Mn(CO)_3$

R	R'	g	A(Mn)
p-OCH_3	H	1.9989	10.55
p-OCH_3	α-CH_3	1.9985	10.44
p-OCH_3	β-CH_3	1.9990	10.66
o-Cl	H	2.0026	7.32
o-Cl	α-CH_3	2.0028	one broad band
o-Cl	β-CH_3	2.0031	7.22

[a] Experimental error 0.02 to 0.03 gauss. Line widths vary from 2.5 to 4.7 gauss.

splittings in some cases. The experimental spin densities were calculated as described previously [1] using the equation $A = Q\rho$ with values of Q(H) = -23G and Q(Mn) = 28G giving the best fit. The theoretical (M.O.) method used did not extend to the calculations on molecules having a methoxy or chloro substituent. Because of molecular size the tricarbonylchromium group was incorporated in the M.O. calculation as a point perturbation on the system using charge values of 0.14 for Cr and -0.18 for CO [7].

DISCUSSION

The results in Table 1 and those given previously [1] show that variation of phenyl substituents causes A(Mn) to decrease in the order

TABLE 2

Experimental Values of g and the Hyperfine Coupling Constants[a] (gauss) for the Anion Radicals of $(CO)_3CrC_6H_4RCOC_5H_3R'Mn(CO)_3$. Values for the corresponding $C_6H_4RCOC_5H_3R'Mn(CO)_3$ complexes are given in parentheses.[b]

R	R'	g	A(Mn)	A(p-H)	A(o-H)	A[H(CH$_3$)]	line-width
H	H	1.9998	2.41(7.67)	1.63(2.91)	0.80(1.03)	-	0.32
H	α-CH_3	2.0002	A non-symmetrical broad band				
H	β-CH_3	2.0001	2.52(7.77)	1.61(3.00)	0.80(1.04)	-	0.22
o-CH_3	H	1.9994	5.11(11.81)	-	-	1.01	0.80
o-CH_3	α-CH_3	2.0001	on broad band				18
o-CH_3	β-CH_3	1.9994	5.20(-)	-	-	1.06	0.82
m-CH_3	H	1.9995	2.24(8.10)	1.53(-)	0.78(-)	-	0.51
m-CH_3	β-CH_3	1.9995	2.51(8.17)	1.65(-)	0.83(-)	-	0.27
p-CH_3	H	1.9997	3.05(9.02)	-	-	1.52(-)	0.48
p-CH_3	α-CH_3	1.9996	1.62(7.73)	-	-	1.75(2.60)	1.50
p-CH_3	β-CH_3	1.9994	3.13(9.05)	-	-	1.54(2.41)	0.36
p-OCH_3	H	1.9989	4.28(10.55)	-	1.35(-)	-	0.33
p-OCH_3	α-CH_3	1.9982	4.45(10.44)	-	2.70(-)	-	0.48
p-OCH_3	β-CH_3	1.9998	4.40(10.66)	-	1.43(-)	-	0.38

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[a] Experimental error 0.01 to 0.04 gauss.

[b] From ref. 1.

$\underline{o}$-CH_3>$\underline{p}$-OCH_3>$\underline{p}$-CH_3>$\underline{m}$-CH_3>H>$\underline{o}$-Cl for the anions without a tricarbonylchromium group. The order for the tricarbonylchromium derivatives (Table 2) is $\underline{o}$-CH_3>$\underline{p}$-OCH_3>$\underline{p}$-CH_3>$\underline{m}$-CH_3≈H which is essentially the same as above. The one exception is the p-CH_3,α-CH_3 derivative which has a very low value attributable to the rings being twisted substantially out of plane due to steric hindrance of the CH_3 groups. These results show that substituent effects are transmitted from phenyl through to the manganese atom. It is clear that spin densities on manganese are affected in the same way as overall electron densities; the -OCH_3 group pushes electrons onto the phenyl and in turn through the system onto the manganese. Conversely the -Cl withdraws electrons from phenyl and in turn from the manganese.

The effect of the tricarbonylchromium group is striking. On complexation, the A(H)'s of phenyl are reduced to about one half of the original value and the A(Mn)'s to about one third. This is consistent with the tricarbonylchromium group withdrawing spin density from phenyl and in turn from the manganese. This substantial withdrawal of spin density from the benzoylcyclopentadienylmanganese system as a whole can only be explained satisfactorily if one assumes substantial conjugation through the system. In turn, this means that there must be substantial π-orbital overlap between chromium and phenyl.

Substantial spin density on chromium is further supported by the considerable reduction in total spectrum width (from 43 to 15G) on complexation and by the much improved simulation when ^{53}Cr satellites are incorporated. The results in Table 2 also demonstrate that the assignments given earlier [1] are correct.

It is interesting to attempt to apply the arguments put forward by Ceccon et al. [3], to our results. They reject the mechanism where π spin density is transferred to Cr orbitals on the grounds that they observe no ^{53}Cr hyperfine splittings, that the g-values they observe are not as low as others observe in cases [8] where there is a singly occupied $3d_{z^2}$ Cr orbital and that the small line-widths indicate too small a spin-orbit interaction.

In our case, however, ^{53}Cr hyperfine splittings are observed. In addition, unlike the cases [8] referred to by Ceccon et al. which are d^5 systems, the compounds reported here do not have a singly occupied Cr orbital of mainly $3d_{z^2}$ character. They are d^6 systems with no more than 0.4 additional electrons from the unpaired electron on Cr as the ketonic CO has between 0.4 and 0.5 of the unpaired electrons and the manganese and carbon atoms together have at least 0.2 of the unpaired electron. This would also explain a relatively small spin-orbit coupling.

Ceccon et al. [3] also consider and reject the argument that the ketonic CO group is twisted out of the plane of the ring causing σ-delocalization. We also reject this argument as our splitting patterns disagree with this explanation.

The third proposal put forward by these workers and the one favoured by them is rehybridization of the carbon atoms following complexation by the tricarbonylchromium group causing a small but sufficiently large distortion to enable the unpaired electron function not to vanish at the proton positions. This in turn could result in a positive contribution to the proton coupling which could cancel or slightly overcome the spin polarization contribution. Although this might explain a reduction in proton hyperfine splittings it cannot explain the large reduction we observe in the ^{55}Mn splittings. Based on steric arguments it is highly unlikely that the manganese atom could be affected in a direct way by the tricarbonylchromium group. We thus strongly favour a mechanism where a significant portion of the spin density resides on the chromium atom.

A comparison of experimental and theoretical spin densities is given in Table 3. Although there are some discrepancies, most of the trends in the experimental results are also reflected in the theoretical calculations. The agreement is not as good as for the compounds without a tricarbonylchromium group. This is because the tricarbonylchromium group is treated as a point perturbation in the M.O. calculations.

Following these results a general picture of the electron distribution in these systems becomes clearer. The I.R. results given earlier for the neutral complexes show that for both the compounds with [5] and without [4] a tricarbonylchromium group the substituents on phenyl do not affect the ν_{CO} of the tricarbonylmanganese group in any substantial or regular fashion. However, the effect on the tricarbonylchromium group is as expected. As regards the ^{1}H-NMR, the only significant substituent effect is an upfield shift of the cyclopentadienyl resonances when the phenyl is <u>o</u>-substituted [4,5]. This is interpreted as steric hindrance reducing π-overlap. As discussed above, substituents on phenyl markedly affect A(Mn) showing that electronic effects are transmitted through the system. Whether such effects are transmitted as far as the CO groups or the cyclopentadienyl protons cannot be determined as yet by these techniques.

Complexation with a tricarbonylchromium group has only a small effect on ν_{CO} of the tricarbonylmanganese group [5]. However, ^{1}H-NMR resonances of the cyclopentadienyl protons are shifted downfield consistent with π-electron withdrawal. This parallels the effect on the A(Mn) noted above. The effect of steric hindrance resulting in poorer π-overlap is also noticed in the A(Mn) values.

TABLE 3

Comparison between Experimental and Theoretical Spin Densities of $\{(CO)_3CrC_6H_4RCOC_5H_3R'Mn(CO)_3\}^-$

		Experimental				Theoretical			
R	R'	ρ(Mn)	ρ(p)	ρ(o)	ρ(CH$_3$)	ρ(Mn)	ρ(p)	ρ(o)	ρ(CH$_3$)
H	H	0.086	0.071	0.035		0.102	0.071	0.037	
H	β-CH$_3$	0.090	0.070	0.035	<0.009	0.105	0.070	0.040	0.008
o-CH$_3$	H	0.182	<0.007	<0.009	0.044	0.189	0.011	0.017	0.042
o-CH$_3$	α-CH$_3$	<0.042	<0.009	<0.008	<0.009	0.092	0.011	0.013	0.012
o-CH$_3$	β-CH$_3$	0.186	<0.007	<0.008	0.046	0.190	0.012	0.015	0.049
m-CH$_3$	H	0.080	0.066	0.034	<0.009	0.099	0.075	0.032	0.009
m-CH$_3$	β-CH$_3$	0.090	0.072	0.037	0.009	0.098	0.080	0.041	0.007
p-CH$_3$	H	<0.110	<0.006	0.008	0.066	0.100	0.012	0.012	0.081
p-CH$_3$	α-CH$_3$	<0.058	<0.006	0.008	0.076	0.051	0.012	0.012	0.075
p-CH$_3$	β-CH$_3$	<0.112	<0.006	0.008	0.067	0.112	0.009	0.021	0.071

CONCLUSION

The ESR results demonstrate that there is extensive electron delocalization throughout the chromium-benzoylcyclopentadienylmanganese system, which can only be explained satisfactorily by considerable π-overlap between the metal and the ring and π-conjugation within the aromatic system. The principal effect of the tricarbonylchromium group is to withdraw spin density from the system as a whole including withdrawal from the manganese atom. These results and interpretations agree with those obtained by ^{1}H-NMR of the neutral complexes.

ACKNOWLEDGMENTS

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REFERENCES

1. N.J. Gogan, C.K. Chu and P.A. Narayana, J. Organometal. Chem., 92 (1975) 207.
2. N.J. Gogan, C.K. Chu and P.A. Narayana, Proc. Int. Conf. Coord. Chem., 16th (1974) p: 2.5b.
3. A. Ceccon, C. Corvaja, G. Giacometti and A. Venzo, J. Chim. Phys. 72 (1975) 23.
4. N.J. Gogan and C.K. Chu, J. Organometal. Chem., 93 (1975) 363.
5. N.J. Gogan and C.K. Chu, J. Organometal. Chem., 132 (1977) 103.
6. N.J. Gogan, C.K. Chu and G.W. Gray, J. Organometal. Chem., 51 (1973) 323.
7. D.A. Brown and R.M. Rawlinson, J. Chem. Soc. A, (1969) 941.
8. C. Elschenbroich, F. Gerson and F. Stohler, J. Amer. Chem. Soc., 95 (1973) 6956.