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# ESR OF ORGANOMETALLICS

## I. THE ANION OF (BENZOYLCYCLOPENTADIENYL)MANGANESE TRICARBONYL AND SOME METHYL SUBSTITUTED DERIVATIVES

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### SUMMARY

The radical anions of (benzoylcyclopentadienyl)manganese tricarbonyl, (1-benzoyl-2-methylcyclopentadienyl)manganese tricarbonyl and (1-benzoyl-3-methylcyclopentadienyl)manganese tricarbonyl have been prepared by alkali metal and electrolytic reduction in 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF). The best ESR spectra are obtained by potassium reduction in DME. Each anion shows a major splitting from the $^{55}$Mn nucleus and smaller splittings from the *p*- and *o*-protons of the phenyl ring.

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### INTRODUCTION

There have been several reports of ESR studies of radical anions produced from stable transition metal organometallic compounds. The major contributions in this area have come from Dessy and coworkers[1] who have extensively studied the electrochemical behaviour of organometallic compounds and have included ESR studies of many of the radicals produced. Another important contribution in this area is that of Elschenbroich and Cais[2] who studied substituted ferrocene radical anions. There have not been however, any ESR spectra of radical anions derived from compounds of the aromatic ring–metal carbonyl type. We are particularly interested in the electron distribution in these systems[3] and ESR is a valuable tool in such investigations. Dessy *et al.*[1] have studied the electrochemical behaviour of simple systems of this type. Their results showed no evidence of reversible one-electron reductions. Because of this we have studied a system which has a functional group, the ketonic carbonyl group, that readily undergoes reversible one-electron reductions. In addition the benzoyl group tends to add to the stability of the one-electron reduction product and our system, (benzoylcyclopentadienyl)manganese tricarbonyl is quite analogous in this respcct to benzophenone. In this paper we will describe ESR studies on the radical anions of (benzoylcyclopentadienyl)manganese tricarbonyl (I), (1-benzoyl-2-methylcyclopentadienyl)manganese tricarbonyl (II) and (1-benzoyl-3-methylcyclopentadienyl)manganese tricarbonyl (III).

## EXPERIMENTAL

ESR spectra were obtained using a JEOLCO ME 3X spectrometer operating on X-band. The field was measured with an NMR gaussmeter. The microwave frequency was measured by the beat method using a Micro-Now system. Both frequencies were measured with a TS1 385-R counter. NMR spectra were obtained in $CDCl_3$ solution on a Varian A-60 spectrometer, IR spectra on a Perkin–Elmer 457 spectrometer and mass spectra on a Hitachi Perkin–Elmer RMU-6E spectrometer.

### *Cyclopentadienylmanganese tricarbonyl*

This was prepared from sodium cyclopentadienide and bromomanganese pentacarbonyl in refluxing tetrahydrofuran (THF).

### *(Benzoylcyclopentadienyl)manganese tricarbonyl (I)*

(I) was prepared by Friedel–Crafts acylation of cyclopentadienylmanganese tricarbonyl using benzoyl chloride and aluminum chloride in refluxing methylene chloride. Yield 72% m.p. 74° (lit. 73.5–74.5°[4]).

### *Methyl substituted derivatives*

These were prepared in a similar way as above, using (methylcyclopentadienyl)-manganese tricarbonyl (Strem). The yield was almost quantitative and consisted in an approximately 1/1 ratio of the isomers. The isomers were separated by fractional recrystallization from petroleum ether (60–80°). (1-Benzoyl-2-methylcyclopentadienyl)manganese tricarbonyl (II) has a m.p. 118–119°. Its NMR has one cyclopentadienyl proton resonance at $\tau$ 4.85 and the remaining two at $\tau$ 5.28. (1-Benzoyl-3-methylcyclopentadienyl)manganese tricarbonyl (III) has a m.p. 55°. Its NMR has one cyclopentadienyl proton at $\tau$ 5.28 and the remaining two at $\tau$ 4.67. The mass spectra of all the complexes show the expected molecular ions and ions corresponding to successive loss of CO groups as well as other major fragment ions.

### *Tetrapropylammonium perchlorate (TPAP)*

TPAP was prepared from 10% tetrapropylammonium hydroxide (Eastman) in water by neutralization with 70% perchloric acid. It was recrystallized from 20% acetonitrile in water and dried in a vacuum desiccator over phosphorus pentoxide.

### *Tetrabutylammonium perchlorate (TBAP)*

TBAP was prepared from tetrabutylammonium bromide (Eastman) by reaction with 70% perchloric acid in water. After washing free of acid it was recrystallized from acetone/water solution and dried in a vacuum desiccator over phosphorus pentoxide.

### *Solvent purification for reductions*

1,2-Dimethoxyethane (DME) (Ansul) was dried over molecular sieves for a day and then distilled. It was then stirred with potassium metal for at least a day and distilled under $N_2$ into a flask containing fresh potassium metal. This flask was attached to the vacuum line and the solvent was distilled into another flask containing a potassium mirror and allowed to stand for several hours at room temperature. The solvent was then transferred on to a fresh potassium mirror and let stand, repeating the process several times until a strong blue color of the solvated electron was obtained at dry ice/acetone temperatures.

Tetrahydrofuran (THF) (Baker G. C., spectrophotometric grade) was stirred with sodium metal for several days. It was then distilled under $N_2$ on to potassium and purified further as described above for DME.

Hexamethylphosphoramide (HMPA) (Aldrich) was dried with molecular sieves. After decantation into a vacuum distillation apparatus it was degassed at 0.05 mmHg, distilled (52° at 0.15 mmHg) and then stored under an $N_2$ atmosphere.

### *Preparation of anions*

Alkali metal reductions were carried out in a reaction tube (length 7 cm diameter 1 cm) fitted with a quartz ESR tube and a small (1.5 cm) side arm for the initial reception of the alkali metal. About $10^{-4}$ mol of the reductant were placed at the bottom of the reaction tube and a small piece of freshly cut and washed alkali metal was placed in the small side arm. The reaction tube was then attached to the vacuum line using a stopcock adapter and the apparatus was evacuated. The alkali metal was then heated and formed a mirror on the reaction tube leaving behind any oxides in the side arm. The reaction tube was placed in liquid nitrogen and a small amount (usually 1 to 1.5 ml) of the freshly purified solvent was distilled into the reaction flask. The reaction vessel was then pumped on for about 5 min. After this the stopcock was closed and the apparatus was removed from the vacuum line. The apparatus was warmed up and the reduction reaction was allowed to proceed. The reaction rate was controlled by cooling in dry ice/acetone or liquid nitrogen baths.

Electrolytic reductions were carried out in a vacuum cell *in situ*. The cell design was similar to that used for alkali metal reductions except that it had no small side arm and the ESR tube was detachable and was fitted with two platinum electrodes. The apparatus was charged with reductant and supporting electrolyte and the solvent distilled in the same way as described above. A d.c. potential was applied between the electrodes and was increased until an ESR signal was observed.

## RESULTS

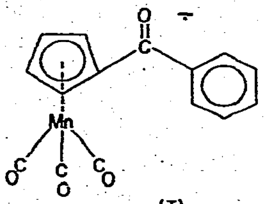
### *Alkali metal reductions*

Solutions of (I) ($2$–$8 \times 10^{-3}$ *M*) in DME are light yellow in color. These react with potassium mirrors at temperatures from $-80°$ to room temperature to give purple solutions. At low temperatures these solutions give an ESR spectrum consisting of six broad lines of approximately equal intensity which show no further hyperfine structure (hfs). When the temperature is increased the signal strength increases and further splitting of the six lines is observed. The best resolved and most intense spectra are observed in the 0° to 20° region. When dilute solutions (less than $10^{-3}$ *M*) are reacted with potassium a pink color is obtained which shows no ESR spectrum. A red color is also obtained when more concentrated solutions are left standing after reaction for prolonged periods. Presumably, the pink or red color is due to a diamagnetic dinegative ion while the purple solution contains the mononegative radical ion. It was found that the best resolved spectra were obtained by using the more concentrated solutions and reacting these until dark purple solutions were obtained. These concentrated solutions were then diluted in the ESR tube away from contact with the potassium mirror. A typical spectrum is shown in Fig. 1.

A similar pattern of behaviour is observed when sodium is used. However, in this case, each of the six lines is split into many more lines than in the potassium case due to the splitting from the $^{23}$Na nucleus.

THF can also be used as solvent but the spectra obtained are not quite as well resolved as in DME.

The spectrum shown in Fig. 1 is not fully resolved although it is well enough resolved to show all the major splittings. This line broadening could be due to ion pair formation. In an attempt to overcome this problem HMPA was used as solvent, both on its own and in mixtures with DME or THF. However, in all these attempts, only the red or pink color was seen and no ESR signal was observed.



(I)

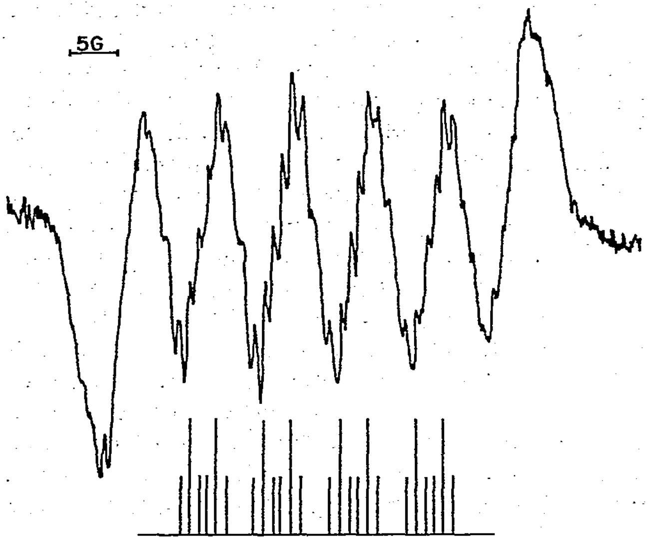


Fig. 1.

An IR spectrum was run of the sample residue after reduction with potassium in DME. It was found that the ketonic CO stretching vibration observed at 1640 cm$^{-1}$ was considerably reduced in intensity as compared to the metal CO stretching vibrations observed at 2020 cm$^{-1}$ and 1930 cm$^{-1}$. This is consistent with reduction at the ketonic carbonyl group and subsequent hydrolysis when the sample is exposed to the atmosphere.

The general behaviour of (II) and (III) was similar to above. The reduction proceeded somewhat more rapidly than for the unsubstituted case but the colors obtained were similar. Again the ratio of the intensity of the ketonic carbonyl stretching absorption to the metal carbonyl stretching absorptions in the IR was less after reduction than before.

*Electrolytic reductions*

Several combinations of electrodes, solvents and supporting electrolytes were tried in the attempted electrolytic reduction of these complexes. Spectra were obtained in DME or DME/THF mixtures with TBAP as supporting electrolyte and platinum electrodes. However, the resolution was poorer than that obtained by potassium reduction. Reduction was carried out in the −50 to +20° range. The signal strength was lower at the lower temperatures and the resolution was poor at all temperatures tried.

Attempts at reduction using acetonitrile or DMF resulted in no spectra being obtained. The use of a mercury electrode was also unsuccessful. Changing the supporting electrolyte to TPAP gave no improvement.

## DISCUSSION

The spectrum shown in Fig. 1, obtained by potassium reduction of (I) has a *g*-value of 2.00006. It consists of 6 lines of equal intensity with a separation of 7.68 gauss. This splitting arises from the single $^{55}$Mn nucleus in the molecule. Each of the six lines is further split into a doublet of triplets. This splitting is not as clear on the "wing" lines as on the other four. The doublet splittings are 2.91 gauss and the triplet splittings are 1.03 gauss.

By analogy with benzophenone[5], the doublet is most likely due to the *p*-proton and the triplet to the *o*-protons of the phenyl ring. This interpretation is also in accord with the work of Elschenbroich and Cais[2] who calculated that for benzoylferrocene, the unpaired electron density is expected to be mainly on the metal atom, non-magnetic nuclei and the *p*- and *o*-protons of the phenyl ring. Their experimental results agreed with this although their metal atom, unlike that in the present case, was non-magnetic.

The results obtained for the methyl substituted derivatives, (II) and (III), agree with the above interpretation for (I). The hyperfine splittings for the three compounds are given in Table 1. When there is a methyl group in the 3 position of the cyclopentadienyl ring the observed spectrum is very similar to the unsubstituted case, and only minor differences in the hfs are observed. With a methyl group in the 2 position of the cyclopentadienyl ring the hfs is a little different but the order of splitting constants is the same. This shows that the doublet and triplet splitting come from the phenyl ring.

TABLE 1

ESR OF $C_6H_5COC_5H_3RMn(CO)_3$ IN DME[a]

| *R* | $A_{Mn}$ | $A_{H(p)}$ | $A_{H(o)}$ |
|---|---|---|---|
| H | 7.67 ± 0.03 | 2.91 ± 0.03 | 1.03 ± 0.06 |
| 2-$CH_3$ | 6.16 ± 0.07 | 3.46 ± 0.05 | 0.85 ± 0.04 |
| 3-$CH_3$ | 7.77 ± 0.06 | 3.00 ± 0.03 | 1.04 ± 0.07 |

[a] Produced by potassium reduction *in vacuo*.

Therefore the unpaired electron density seems to be largely on the Mn atom, the phenyl ring and perhaps non-magnetic nuclei such as the ketonic carbonyl group. It must also be partially on the cyclopentadienyl ring although not to a sufficient extent to show proton splittings.

## ACKNOWLEDGEMENTS

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