Journal of Organometallic Chemistry, 336 (1987) 137–142
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ESR of organometallics

V *. Experimental and SCCC-MO studies on the anions of *N*-methyl-3-aroylpyrroles and their $Cr(CO)_3$ complexes

Niall J. Gogan, I. Sheila Jayasinghe and Pardeep K. Sayal **

*Department of Chemistry, Memorial University of Newfoundland, St. John's,
Newfoundland A1B 3X7 (Canada)*

(Received May 1st, 1987)

Abstract

The radical anions of $RC_6H_4COC_4H_3NCH_3$ (R = H, *o*-CH_3 and *p*-CH_3) and of their $Cr(CO)_3$ complexes were prepared by potassium reduction in 1,2-dimethoxyethane and their ESR spectra were measured. The widths of the spectra of the $Cr(CO)_3$ complexes are about half that of the corresponding ligands, consistent with the withdrawal of unpaired electron (upe) density by the $Cr(CO)_3$ groups. The parent complex and ligand give sufficiently well resolved spectra to enable analysis and show splittings from the *para* and *ortho* protons on the benzene ring. SCCC-MO calculations on the ligand show that the upe is primarily on the benzene ring, a little is on the CO group and very little is on the pyrrole ring. Calculations on the complex also result in almost no upe density on the pyrrole ring and the benzene ring has about half the upe density that it has in the ligand. The remainder of the upe density is mostly on the CO groups attached to the Cr atom.

Introduction

Over the past several years, studies have been carried out in this laboratory on complexes with extended ligand systems, usually consisting of two or more possible π-donor sites joined by a simple group. Radical anion formation and consequently ESR studies are facilitated when a CO group joins the two sites. For example, ESR studies of the anions of tricarbonylchromium benzoylcyclopentadienylmanganese tricarbonyl and benzophenonechromium tricarbonyl and various substitued deriva-

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* For part IV see ref. 2.

** Present address: Ganges Paints and Chemicals, E-54 Focal Point, Ludhiana, Punjab, India.

tives have given useful insights into electron distribution in these complexes [1,2]. In addition, Ceccon et al. [3,4] have also studied some benzophenonechromium tricarbonyl complexes.

Up to now no ESR spectra have been reported on anions of simple pyrroles or their complexes, although Rao and Symons [5] did report ESR results for some pyrrole cations. Recently we reported the preparation, IR, ^{1}H NMR and SCCC-MO studies on a series of *N*-methyl-3-aroylpyrrolechromium tricarbonyls [6]. In this paper we present the ESR spectra of anion radicals produced from these complexes and the corresponding ligands together with SCCC-MO calculations on the radical anions which were undertaken to help in the interpretation of the ESR results in terms of electron delocalization.

Experimental

The preparation and characterization of the ligands [7] and the complexes [6] have already been described. Radical anions were prepared by the method described previously [8] using potassium reduction in 1,2-dimethoxyethane (DME). ESR spectra were recorded at room temperature on a JEOLCO ME3X spectrometer.

Computational details

The general method, standard geometries and other parameters used for the self-consistent charge and configuration molecular-orbital (SCCC-MO) calculations are the same as those reported for the neutral complexes [6]. In these calculations the MO, ϕ_i, is expressed as a linear combination of atomic orbitals, ψ_i:

$$\psi_i = N\sum_j C_{ij}\phi_j$$

where N is the normalization constant and C_{ij} is the coefficient of the atomic orbital ϕ_j in the molecular orbital ψ_i.

The unpaired electron (upe) density $= |C_{ij}|^2$ and $\sum_j |C_{ij}|^2 = 1$ because of normalization. ESR simulations were carried out using QCPE210 [9].

Results

The colorless DME solutions (5–8×10^{-3} M) of *N*-methyl-3-benzoylpyrrole and its CH_3 derivatives turn dark blue or purple when treated with potassium. These anions are stable for several hours as indicated by their ESR spectra. The OCH_3 and Cl compounds turn orange and the anions are unstable. Solutions of the complexes (5–8×10^{-3} M in DME) turn yellow or orange when treated with potassium and the anions, except for the Cl, OCH_3 and *p*-CH_3 complexes, are stable in solution for 0.5–2 h. The Cl complex gives no ESR spectrum.

All of the spectra are substantially line-broadened even when the solutions are diluted to the limit of spectral observation. THF solutions give spectra that are even more line-broadened than those in DME. In an effort to obtain better spectra we repeated some measurements on a Varian E104B/E-E109B spectrometer with a Nicolet 1170 signal averager located in the Chemistry Department of Dalhousie University, Halifax, Nova Scotia. However the spectra obtained were only marginally better than those obtained with our own spectrometer.

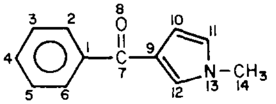
N-Methyl-3-benzoylpyrrole

The radical anion gives an ESR spectrum consisting of a doublet (A = 8.05 G) of triplets (A = 3.15 G). In keeping with the interpretation for the benzoylcyclopentadienylmanganese tricarbonyl anion [10] the doublet is assigned to the *para* proton and the triplet to two equivalent *ortho* protons. The spectrum of the anion produced from the compound with all five benzene protons replaced by deuteriums consists of a single line supporting the conclusion that all the hyperfine splitting (hfs) comes from the benzene ring protons.

The theoretically calculated upe densities are given in Table 1. The major portion of the density is on the benzene ring with substantial amounts at the *para* and *ortho* positions. There is very little (~ 1%) on the pyrrole ring. Table 2 shows a comparison between these theoretically calculated densities and those calculated from the experimentally observed hfs using the McConnell relationship [11]. A value of 26.7 G gives the best agreement. This value is in the usual range for aromatic compounds

Table 1

Unpaired electron densities calculated by SCCC-MO



	Phenyl ring			Pyrrole ring			Carbonyl group	
	Ligand	Complex		Ligand	Complex		Ligand	Complex
1	0.208	0.077	9	0.004	0.002	7	0.062	0.031
2	0.127	0.033	10	0.003	0.002	8	0.066	0.032
3	0.047	0.008	11	0.001	0.000			
4	0.298	0.135	12	0.002	0.001			
5	0.055	0.021	13	0.001	0.000			
6	0.119	0.099	14	0.000	0.000			
Total	0.854	0.373		0.011	0.005		0.128	0.063
3C		0.290	Cr		0.059			
3O		0.201						
	Total	0.491						

Table 2

Experimental and calculated upe densities (ρ) for $C_6H_5COC_4H_3NCH_3$ and its $Cr(CO)_3$ complex

	Ring position	ρ (calcd.)	ρ (found) [a]
Ligand	2	0.127	0.118
	4	0.298	0.302
	6	0.119	0.118
Complex	2	0.033	0.064
	4	0.135	0.135
	6	0.099	0.064

[a] ρ (found) = A/Q (Q = 26.7 G).

and gives further support to the interpretation that the splittings come from the *o*- and *p*-protons. It also indicates the self-consistency of the MO calculations.

N-Methyl-3-benzoylpyrrole chromium tricarbonyl

The ESR spectrum of this radical anion, like that of its parent ligand, consists of a doublet of triplets. Its appearance (Fig. 1), however, consists of five lines because the triplet hfs is approximately half the doublet value. The computer simulation is also shown in Fig. 1. As has been noted for other arene $Cr(CO)_3$ complexes [1–4], the hfs are very much reduced from the benzene ring of the parent. In this case A_p = 3.60 G and A_o = 1.70 G.

Table 1 lists the theoretically calculated upe densities and, like the ligand, there is substantial density on the benzene ring with concentration at the *ortho* and *para* positions. Again there is very little upe density on the pyrrole ring. The total upe density on the benzoylpyrrole part of the molecule is less than half that of the ligand in agreement with the experimental observation that the hfs is substantially reduced. The remainder of the unpaired electron is located primarily on the CO(Cr) groups (0.491) with very little on the Cr atom (0.059).

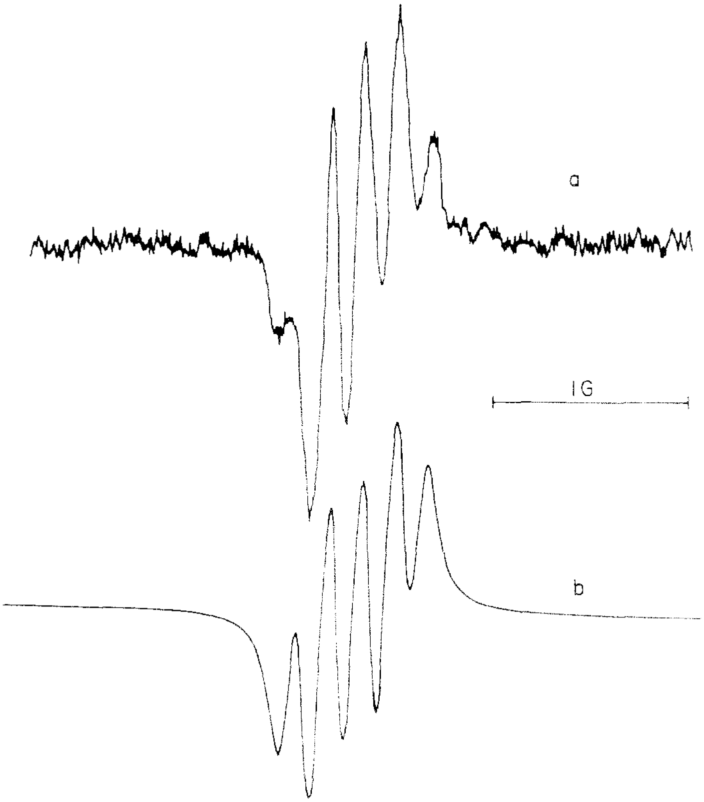


Fig. 1. ESR spectrum of $(CO)_3CrC_6H_5COC_4H_3NCH_3$. (a) ESR spectrum recorded at room temperature. (b) Computer simulation based on A_p = 3.60 G and A_o = 1.70 G.

Substituted N-methyl-3-benzoylpyrroles and their Cr(CO)$_3$ complexes

Computer simulation of the ESR spectrum of the *N*-methyl-3-(2-methylbenzoyl) pyrrole anion reveals two doublet splittings (7.30 and 3.30 G) and a quartet splitting (2.65 G). These are assigned respectively to the *p* and *o* ring protons and the *o*-methyl protons. Similarly the corresponding complex gives A_p = 3.8 G, A_o = 1.60 G and $A(o\text{-CH}_3)$ = 1.50 G.

In the *p*-CH_3 case both the ligand and complex radical anion spectra are too line-broadened to analyse. However their total spectral widths could be measured. The *p*-OCH_3 anions and the *p*-Cl ligand anion decomposed during the running of the spectra. As noted above, the *p*-Cl complex gave no ESR spectrum.

Discussion

Initial attempts at preparing radical anions of benzoylpyrroles and their Cr(CO)$_3$ complexes were unsuccessful. The characteristic colours (usually blue or purple) were not observed when solutions of the compounds in DME or THF were treated under vacuum with potassium nor were any ESR signals obtained. It was thought that the problem was with the lability of the hydrogen atom on the nitrogen and so the *N*-CH_3 compounds were prepared. These gave radical anions and ESR spectra under the usual conditions [8].

The ESR spectra of all the complexes show a substantial reduction in hfs from the corresponding ligand spectra. This is reflected in the total spectrum width and is a factor of approximately two (Table 3). The *o*-CH_3 complex shows the greatest reduction (2.73) and the unsubstituted compound the least (2.05) which is the same trend as in the benzophenone series [2]. The magnitude of the reduction is similar to that reported for other arene Cr(CO)$_3$ complexes [1–4].

We have already shown [1] that this reduction can be best explained if there is substantial conjugation through the system. This means that there is substantial π-overlap between the benzene ring and the Cr(CO)$_3$ group on the one hand and between the benzene ring and the CO group on the other. However, the lack of upe density on the pyrrole ring indicates that there is little or no π-overlap between the CO group and the pyrrole ring.

Because of the above results we assume in our calculations that the CO group is in the plane of the benzene ring. As discussed previously [6], for steric reasons this necessitates the pyrrole ring to be substantially out of the plane of the benzene ring. We have assumed that it is at a 90° angle.

Rieger and Fraenkel [12] have shown for aldehydes and ketones that when the CO group is in the plane of the benzene ring there is a large hfs from the *p*- and *o*-protons. A relatively small splitting is observed where the CO is substantially out

Table 3

ESR half spectrum width (G) of the radical anions of $RC_6H_4COC_4H_3NCH_3$

R	Ligand	Cr(CO)$_3$ complex	Ligand/complex
H	7.4	3.6	2.05
p-CH_3	13.0	4.8	2.70
o-CH_3	10.4	3.8	2.73

of the plane. We observe large hfs for the *p*- and *o*-protons. Indeed the magnitude is very similar to that observed by Rieger and Fraenkel. This further supports our conclusion that the CO groups is in the same plane as the benzene ring.

The reduction in upe density on the benzoylpyrrole moiety on complexation parallels the change in overall charge observed for the neutral compounds [6]. The shift in upe density primarily to the COs attached to the Cr is also similar to the shift in charge on complexation.

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada and to Memorial University for financial support. The advice and assistance of Dr. H.J. Anderson, Dr. C.E. Loader and Mr. L.C. Hopkins of this department are gratefully acknowledged. We thank Mr. R. McDonald for preparing the ligands. We also thank Dr. D. Arnold, Chemistry Department, Dalhousie University, N.S., Canada for allowing us to use the ESR spectrometer in his department.

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