

***N*-METHYL-3-AROYLPYRROLE Cr(CO)₃ COMPLEXES. IR, ¹H NMR AND SCC-MO STUDIES**

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Summary

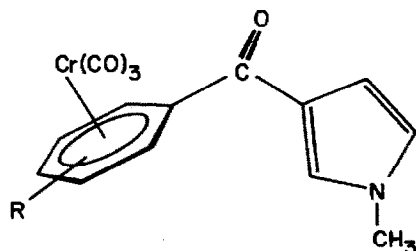
IR and ¹H NMR spectra have been measured for a series of *N*-methyl-3-aroypyrrole Cr(CO)₃ complexes (CH₃NC₄H₃COC₆H₄RCr(CO)₃; R = H, *p*-CH₃, *o*-CH₃, *p*-OCH₃, *p*-Cl) and the results interpreted with the assistance of SCC-MO calculations. The trend in the CO(Cr) stretching frequencies agrees with the Mulliken populations of the CO bond. The ¹H NMR resonances are affected by the substituents but the resonances of the pyrrole ring show little variation. This agrees with the calculated charges which are based on the pyrrole ring being at a 90° angle to the plane of the benzoyl group. Thus, there is little electron delocalization between the two rings.

Introduction

Previous studies in this laboratory have dealt with π -complexes of ligands containing two carbocyclic aromatic rings joined by a ketone or other simple groups. The two largest series have been metal tricarbonyl complexes of benzoylcyclopentadienyls [1] and benzophenones [2]. The work has focussed on determining the extent of electron delocalization throughout the compounds using various spectroscopic techniques coupled with molecular-orbital calculations.

The presence of a heteroatom in one of the aromatic rings could have a substantial influence on the electron distribution in these molecules. Some time ago we reported that the reaction of 2-benzoylpyrrole with Cr(CO)₃ yielded only a σ -complex [3]. We have recently reported that a similar reaction of 3-benzoylpyrrole, in contrast, gives only the π -complex in which a Cr(CO)₃ group is attached to the benzene ring [4]. This result has enabled us to prepare a series of complexes similar to the earlier ones mentioned above but containing a heteroatom in one of the rings.

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In this paper we report the preparation, IR and ^1H NMR spectra of a series of *N*-methyl-3-arylpyrrole $\text{Cr}(\text{CO})_3$ complexes together with self consistent charge and configuration molecular-orbital (SCCC-MO) calculations carried out to assist in the interpretation of the spectroscopic results in terms of electron distribution. The NCH_3 compounds were chosen because the hydrogen atom attached to the pyrrole nitrogen tends to be labile in some of the studies which we typically carry out on complexes.

Experimental

Melting points are uncorrected. Elemental analyses were performed by Canadian Microanalytical Service, Vancouver, B.C. The IR spectra were recorded on a Perkin-Elmer 283 spectrometer in CHCl_3 solution. The ^1H NMR spectra were determined using a Bruker WP-80 instrument and are expressed in ppm (δ -values) relative to tetramethylsilane as internal reference in CDCl_3 . Mass spectra were recorded on a VG Micromass 7070 HS spectrometer.

The preparation and characterization of the 3-arylpyrroles has been previously reported [5]. The tricarbonylchromium complexes were prepared as described previously for 3-benzoylpyrrole $\text{Cr}(\text{CO})_3$ [4] and the pyrrole NCH_3 derivatives were obtained using the method of Wang et al. [6]. The ligands were *N*-methylated in a similar fashion for comparison of spectroscopic results.

Computational Details

Electronic structures of both the complexes and ligands were determined by the SCCC-MO method using the QCPE 256 program [7]. Richardson's functions [8] were used for the metal orbitals and Clementi and Raimondi functions [9] were used for all other orbitals. The valence state ionization potentials [10] form the basis in calculating the non-diagonal elements using

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$$

where S_{ij} is the overlap integral and $K = 1.75$. Computer iteration to convergence was carried out for all the ligands and complexes. Standard geometries with little alterations were used as follows; $r[\text{Cr}-\text{C}(\text{H})]$ 2.20, $r(\text{C}-\text{H})$ 1.08, $r(\text{C}-\text{C})$ 1.42, $r[\text{Cr}-\text{C}(\text{O})]$ 1.85, r ketone (C-O) 1.15, $r[\text{N}-\text{C}(\text{C}_4\text{N})]$ 1.38 Å and OC-Cr-CO 90.0°.

A planar ligand arrangement would result in some non-bonding interatomic distances being less than normal bond lengths. For example, in the unsubstituted case the *ortho*-hydrogen (*o*-H) on the benzene ring and the alpha-hydrogen (α -H) on the pyrrole ring almost coincide resulting in great repulsion. In addition, the calculated parameters for the planar ligand did not agree with experiment. Preliminary calculations were carried out by rotating the benzene ring by 90°, the pyrrole ring by 90° and other angles in between. The arrangement where the pyrrole ring is at 90° to the plane of the benzoyl group gives close agreement with experiment and the values so calculated are the ones quoted in the tables. Detailed calculations were also carried out for the arrangement with the benzene ring at 90° to a plane containing the pyrrole and CO. These did not agree with experimental parameters.

Results and discussion

The complexes are orange crystals which melt without decomposition and have elemental analyses in agreement with the calculated values (Table 1). They exhibit the expected IR spectra with one ketonic $\nu(\text{CO})$ and two $\nu(\text{CO})$ in the (Cr)C–O region corresponding to the A_1 and E modes of an ideal local C_{3v} symmetry of a $\text{Cr}(\text{CO})_3$ group (Table 2). The ^1H NMR spectra (Table 3) show the usual upfield shift of the arene proton resonances on complexation whereas the pyrrole proton resonances show little or no change from the ligand values. All the mass spectra have m/e values corresponding to the molecular ions, successive loss of 3CO groups and other expected ions similar to those reported for 3-benzoylpyrrole $\text{Cr}(\text{CO})_3$ [4]. This evidence confirms the structure shown in the figure in which a $\text{Cr}(\text{CO})_3$ group is symmetrically bonded to the benzene ring in each case.

Variation of $\nu(\text{CO})$ [$\text{Cr}(\text{CO})_3$] with benzene ring substituents is well established [12] and the 3-arylpyrrole series follows the usual trend of electron-withdrawing groups giving CO absorptions at higher energies than electron-donating substituents. Theoretical calculations of bond orders using Mulliken populations have been carried out on arene metal tricarbonyls and have shown agreement between $\nu(\text{CO})$ and bond orders. The Mulliken populations for the 3-arylpyrrole $\text{Cr}(\text{CO})_3$

TABLE 1
ELEMENTAL ANALYSIS AND MELTING POINTS OF SOME $\text{C}_4\text{H}_3\text{N}(\text{CH}_3)\text{COC}_6\text{H}_4\text{RCr}(\text{CO})_3$ ^a

R =	M.p. (°C)	Analyses (Found (calcd.) (%))		
		C	H	N
H	109–110	55.98 (56.08)	3.61 (3.45)	4.31 (4.36)
<i>p</i> -CH ₃	140–141	57.37 (57.32)	4.15 (3.91)	4.17 (4.18)
<i>o</i> -CH ₃	73–75	57.15 (57.32)	4.15 (3.91)	4.04 (4.18)
<i>p</i> -OCH ₃	95–97	54.85 (54.71)	4.36 (3.73)	4.17 (3.99)

^a The chloro derivative gave an unsatisfactory analysis. The mass spectrum and other spectroscopic evidence, however, confirms that it has the same structure as the other members of the series.

TABLE 2

IR (cm^{-1} , CHCl_3) OF $\text{C}_4\text{H}_3\text{N}(\text{CH}_3)\text{COC}_6\text{H}_4\text{RCr}(\text{CO})_3$

R =	$\nu(\text{CO})$ (CrCO_3)		Mulliken ^b populations	$\nu(\text{CO})$ (ketone)
	A ₁	E		
H	1986	1914	1.4410	1630 (1631) ^a
<i>p</i> -CH ₃	1981	1908	1.4407	1632 (1631)
<i>o</i> -CH ₃	1977	1905	1.4407	1632 (1633)
<i>p</i> -OCH ₃	1978	1903	1.4403	1633 (1628)
<i>p</i> -Cl	1993	1925	1.4417	1632 (1633)

^a Numbers in parentheses are the ligand values. ^b Mulliken populations for C–O [$\text{Cr}(\text{CO})_3$].

TABLE 3

¹H NMR CHEMICAL SHIFTS (δ , ppm) OF $\text{C}_4\text{H}_3\text{N}(\text{CH}_3)\text{COC}_6\text{H}_4\text{RCr}(\text{CO})_3$

R	Arenic ring			R	Pyrrole ring ^b		
	<i>o</i>	<i>m</i>	<i>p</i>		α	β	CH ₃ (N)
H	6.095 (–1.74) ^a	5.34 (–2.15)	5.56 (–1.81)	–(–0.11)	6.68 (0.02)	7.40 (0.21)	3.73 (0)
<i>p</i> -CH ₃	6.18 (–1.61)	5.23 (–2.0)	–	2.30 (–0.11)	0.67 (0.07)	7.40 (0.28)	3.73 (–0.03)
<i>o</i> -CH ₃	5.72 (–1.68)	5.15 (–2.14)	5.45 (–1.45)	2.27 (–0.06)	6.60 (0.07)	7.38 (0.06)	3.68 (0.07)
<i>p</i> -OCH ₃	6.32 (–1.55)	5.20 (–2.0)	–	3.8 (–0.05)	6.68 (0.04)	6.97 (0.02)	3.75 (0.08)
<i>p</i> -Cl	6.20 (–1.56)	5.45 (–2.0)	–	–	6.65 (0.03)	7.15 (0)	3.72 (0.02)

^a Numbers in parentheses are Δ values where $\Delta = \delta(\text{complex}) - \delta(\text{ligand})$. ^b $\alpha = 4.5$; $\beta = 2$.

complexes are given in Table 2 and show essential agreement in trends with the observed $\nu(\text{CO})$ values.

Mulliken populations $p\text{-Cl} > \text{H} > p\text{-CH}_3 = o\text{-CH}_3 > p\text{-OCH}_3$
 $\nu(\text{CO})$ (E mode) $p\text{-Cl} > \text{H} > p\text{-CH}_3 > o\text{-CH}_3 > p\text{-OCH}_3$

The E mode was chosen for comparison because it is more sensitive to changes in substituents. This agreement is an indication of reliability of the calculations*.

In contrast to the benzoylcyclopentadienyl series [1] where the value decreases significantly ($8\text{--}18\text{ cm}^{-1}$) from the corresponding ligands, the ketonic $\nu(\text{CO})$ shows very little shift from the ligand values. This indicates that there is little or no interaction of the ketonic CO electrons with those of the benzene ring.

Complexation of a benzene ring by a $\text{Cr}(\text{CO})_3$ group causes an upfield shift of the ring protons as observed for the previous series [1,2]. Similar shifts are observed here (Table 3). The pyrrole proton resonances, however, show little or no shift from the ligand values indicating little interaction between the two rings and supporting the lack of planarity of the ligand system.

Calculated charges on various parts of the molecules are given in Table 4. The charge on the ketonic group in each case is almost the same as the ligand and shows little variation with benzene ring substituent. Similarly there is little variation in charge on the pyrrole ring with changing substitution on the benzene ring. Both

* Calculations based on the benzene ring at 90° to a plane containing the pyrrole and CO gave the order: $p\text{-Cl} > \text{H} > o\text{-CH}_3 > p\text{-OCH}_3 > p\text{-CH}_3$.

TABLE 4
CHARGES ON VARIOUS PARTS OF $C_4H_3N(CH_3)COC_6H_4RCr(CO)_3$

q^b	H	<i>o</i> -CH ₃	<i>p</i> -CH ₃	<i>p</i> -OCH ₃	<i>p</i> -Cl
A	0.088 (0.093) ^a	0.088 (0.068)	0.089 (0.075)	0.166 (0.165)	0.164 (0.176)
CO	-0.211 (-0.211)	-0.214 (-0.213)	-0.214 (-0.221)	-0.218 (-0.229)	-0.213 (0.217)
B	-0.028 (-0.027)	-0.032 (-0.037)	-0.031 (-0.032)	-0.032 (-0.037)	-0.028 (-0.031)
CH ₃	0.146 (0.146)	0.145 (0.145)	0.146 (0.145)	0.146 (0.145)	0.146 (0.146)
R	-	0.016 (0.045)	0.013 (-0.008)	-0.062 (-0.043)	-0.085 (-0.074)
Cr	0.360	0.359	0.359	0.361	0.363
(CO) ₃	-0.355	-0.361	0.361	-0.359	-0.345
Cr(CO) ₃	0.005	-0.002	-0.002	-0.002	0.018
ACOBRCCH ₃	-0.005	0.003	0.003	0.000	-0.016

^a Ligand values are shown in parentheses. ^b A = C₆H₄, B = C₄NH₃, R = H, *o*-CH₃, *p*-CH₃, *p*-OCH₃.

TABLE 5
TOTAL GROSS ORBITAL POPULATIONS AT VARIOUS PARTS OF $C_4H_3N(CH_3)COC_6H_4RCr(CO)_3$

	R = H	R = <i>o</i> -CH ₃	R = <i>p</i> -CH ₃	R = <i>p</i> -OCH ₃	R = <i>p</i> -Cl
<i>Ring A</i>					
C ₆ σ	18.437 (0.460) ^a	18.412 (0.460)	18.360 (0.384)	18.206 (0.483)	18.273 (0.492)
π	5.462 (-0.486)	4.475 (-0.500)	5.536 (-0.433)	5.633 (-0.510)	5.560 (-0.509)
Total C	23.899 (-0.026)	23.900 (-0.041)	23.985 (-0.048)	23.838 (-0.027)	23.833 (-0.016)
Total A	28.912 (0.005)	27.912 (-0.020)	27.911 (-0.025)	27.834 (-0.002)	27.836 (0.012)
<i>Ring B</i>					
C ₄ N σ	16.114 (-0.029)	16.116 (0.004)	16.115 (0.003)	16.116 (0.001)	16.115 (0.003)
π	4.925 (-0.002)	4.926 (-0.002)	4.926 (-0.003)	4.926 (-0.003)	4.925 (-0.002)
Total C ₄ N	21.040 (0.070)	21.042 (0.002)	21.041 (0.000)	21.042 (-0.002)	21.040 (0.001)
Total	24.038 (0.078)	24.032 (0.000)	24.031 (-0.002)	24.032 (-0.005)	24.030 (-0.001)
C ₄ NH ₃					
CO σ	8.091 (0.011)	8.093 (0.018)	8.092 (0.018)	8.089 (0.020)	8.090 (-0.000)
π	2.120 (-0.017)	2.121 (-0.021)	2.124 (-0.024)	2.129 (-0.031)	2.123 (-0.01)
Total CO	10.211 (-0.006)	10.214 (-0.003)	10.214 (-0.007)	10.218 (-0.012)	10.213 (-0.005)

^a The numbers in parentheses are δ , the complex population - the ligand population.

these results agree with the observed experimental results for $\nu(CO)$ (ketone) and ¹H NMR δ -values of the pyrrole ring*.

The charge on the chromium atom shows little variation (0.004) with ring substitution but the benzene ring charges vary by 0.078 with the greatest being the OCH₃ compound. This difference in charge is mainly at the expense of the (CO)₃ part of the molecule, thus the Cr atom seems to transmit the charge from one part of the molecule to another.

Table 5 shows gross orbital populations on the ring and CO groups. Complexation results in loss of π -electrons from the benzoyl ring which are donated to the Cr

* Calculations based on the benzene ring at 90° to a plane containing the pyrrole and CO showed substantial difference in charges between complex and ligand in disagreement with the experimental observations.

but there is a substantial back-donation of σ -electrons. The CO groups show similar donation and back-donation. The values of δ (complex populations – ligand populations) show that in each complex the benzene ring donates more π -electrons than it receives by σ back-donation. The absolute value of the difference $|\pi - \sigma|$ is least for the Cl case, is more for H and still greater for the other substituents. Thus in the Cl case the metal is left with more charge which it donates to the CO groups resulting in higher $\nu(\text{CO})$. Conversely less charge is donated in the other cases resulting in lower $\nu(\text{CO})$.

The values of δ_π or δ_σ for the pyrrole ring are very small and in agreement with observations that there is little electron delocalization into the pyrrole ring from the benzene ring.

Conclusion

The spectroscopic results coupled with the theoretical calculations show that there is little electron delocalization between the benzene and pyrrole rings. This is most likely due to the pyrrole ring being in a plane at a substantial angle (possibly as much as 90°) to the plane of the benzene ring. The result is in contrast to that obtained for similar cyclopentadienyl complexes [1] where there is significant interaction between the two rings.

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