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^{13}C NMR AND SCCCMO STUDIES ON SUBSTITUTED BENZOPHENONETRICARBONYLCHROMIUM COMPLEXES

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Summary

^{13}C NMR studies on benzophenonetricarbonylchromium and its p-F, p-Cl and p-OCH_3 derivatives, with the substituents on the uncomplexed ring, show a small substituent effect on the complexed ring and on the carbons of the $Cr(CO)_3$ group. The SCCCMO calculations show π-electron donation from the ring to the metal but greater σ-electron back-donation which leaves the ring more negatively charged than before complexation. The chromium atom is more positively charged than it is in benzenetricarbonylchromium. The trends in calculated C—O bond orders are in agreement with the trends in C—O infrared stretching frequencies.

Introduction

The nature of the bonding in tricarbonylarenemetals has been a topic of considerable interest in the chemical literature [1—5]. The transmission of electronic effects can be useful in elucidating this bonding [6—8]. Complexes of ligands with two aromatic rings linked by various groups are particularly interesting because parts of the molecule can be studied separately. A series of such complexes containing benzene and cyclopentadienyl rings has been studied by various techniques [9,10], and a series of complexes containing two benzene rings joined by various groups has been studied by ^{13}C NMR [11]. This latter group included benzophenonetricarbonylchromium. More recently, Coletta et al. [12] also reported the ^{13}C NMR and ^{1}H NMR of benzophenonetricarbonylchromium as well as of fluorenonetricarbonylchromium and interpreted their results using a CNDO calculation on benzenetricarbonylchromium.

This present study was undertaken to examine the transmission of electronic effects in benzophenonetricarbonylchromium and some of its substituted derivatives and the SCCCMO method was used as an aid in interpreting the results.

Experimental

The complexes were prepared by the method of Nicholls and Whiting [13] using commercially available ligands and hexacarbonylchromium in refluxing di-n-butyl ether in a nitrogen atmosphere.

The NMR spectra were obtained on a JEOL 100-S PFT NMR spectrometer at an observation frequency of 25.15 MHz in $CDCl_3$ solution. The IR spectra were obtained on a Perkin—Elmer 283 spectrometer using CCl_4 solutions and water vapour and polystyrene as calibrants.

Calculations

The previously described [14] self-consistent charge and configuration molecular orbital method (SCCCMO) was used except that the Cusachs [15] approximation was employed in calculating the off-diagonal H terms.

A planar geometry was assumed for benzophenone and the bond lengths and angles were based on standard geometries.

Results and discussion

^{13}C *NMR*

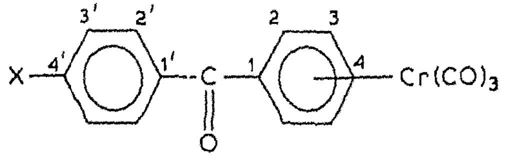
The chemical shifts of the complexes together with the differences, $\Delta\delta$-(ligand — complex), are given in Table 1. The assignments for benzophenone and its $Cr(CO)_3$ complex were given previously [11]. The resonances of the substituted derivatives were assigned using the corresponding benzene derivatives as models [16] and the assignments for 4-fluorobenzophenone are in essential agreement with the results of Sterk and Fabian [17].

When an arene ring is complexed with a $Cr(CO)_3$ group its resonances are shifted upfield. In the case of benzophenone the average upfield shift of the complexed ring is 37.5 ppm compared to 34.5 for benzene. For the F, Cl and OCH_3 derivatives the values are 37.5, 37.6 and 37.1 ppm respectively. This trend (i.e. the H, F and Cl upfield shifts being about the same and the OCH_3 derivative shifts being significantly less) is seen for each carbon of the complexed ring. Thus the upfield shift effect of the $Cr(CO)_3$ group is enhanced by the COC_6H_4X substituent. This is opposite to the effect observed by Bodner and Todd [18] who found that substituents, both electron-withdrawing and electron-donating, decrease the upfield shift compared to unsubstituted benzene.

The effect of the $Cr(CO)_3$ group on the ketonic carbon resonance is moderate, with the upfield shift ranging from 2.5 ppm for benzophenone to 3.4 ppm for the OCH_3 derivative. Again the H, F and Cl upfield shifts are close in value. The effect on the uncomplexed ring is small with the C(2') differences following

TABLE 1

^{13}C CHEMICAL SHIFTS (ppm) WITH THE UPFIELD SHIFTS ON COMPLEXATION ($\Delta\delta$) SHOWN IN PARENTHESES



	C(Cr)	C(1)	C(2)	C(3)	C(4)	C=O	C(1')	C(2')	C(3')	C(4')
H	230.4	96.0(41.5)	95.6(34.3)	89.4(38.7)	94.5(37.7)	193.6(2.5)	136.5(1.0)	128.5(1.4)	128.5(−0.4)	132.3(−0.1)
F	230.4	96.2(41.3)	95.6(34.2)	89.5(38.8)	94.5(37.9)	192.1(2.8)	132.6(1.2)	131.3(1.3)	115.9(−0.5)	165.3(0)
Cl	230.3	95.5(41.6)	95.5(34.3)	89.5(38.8)	94.6(37.9)	192.4(2.6)	134.7(1.1)	130.1(1.2)	128.9(−0.4)	138.8(−0.1)
OCH_3	230.7	98.0(40.3)	95.7(34.0)	89.6(38.5)	94.4(37.4)	191.8(3.4)	128.9(1.2)	131.4(1.0)	113.9(−0.4)	163.4(−0.2)

the sequence H > F > Cl > OCH_3 with a decrease from 1.4 ppm to 1.0 ppm in steps of 0.1 ppm. It is interesting to note that this trend is approximately opposite to that found for the ketonic carbon. The other uncomplexed ring carbons show small values of $\Delta\delta$ which vary only by a total of 0.1 or 0.2 ppm.

Small but significant substituent effects are observed in the unsubstituted (complexed) ring with OCH_3 showing the most substantial effect. As mentioned above the ketonic carbon upfield shift is in the order OCH_3 > F > Cl > H. The $\Delta\delta$ values for C(1) give almost the reverse trend of Cl > H > F > OCH_3 with a variation from 41.6 to 40.3 ppm. The other carbons in this ring give little or no variation with any observable trend being the same as for C(1). For each carbon, however, the $\Delta\delta$ value for the OCH_3 derivative is less than for the other substituents.

In the unsubstituted ring of each ligand the chemical shifts follow the same order, i.e., C(1) > C(4) > C(2) > C(3). In each complex, however, the order is C(1) > C(2) > C(4) > C(3). Thus each carbon does not appear to bond to the chromium to the same extent. In the uncomplexed ring the order of chemical shifts is the same for the complexes and the ligands even though this order is not the same for each substituent.

A small substituent effect is also observed for the carbons of the $Cr(CO)_3$ group with resonances at 230.7 ppm for the OCH_3 derivative and at 230.3 or 230.4 for the others. The difference between these values and those for the benzene complex (233.3 ppm) or its simple monosubstituted derivatives (232—235 ppm) [18] is significant.

SCCCMO

These are the first reported MO calculations on benzophenonetricarbonylchromium complexes. The σ and π electron populations on the various parts of the complex molecules together with Δ (complex population — ligand population) are given in Table 2. The results for benzenetricarbonylchromium, using the same method, are also given for comparison. It can be seen in all cases that the complexed ring donates π-electrons to the metal and that the metal back-donates σ-electrons to the ring. This σ-back-donation is greater than the π-donation leaving the complexed ring more negatively charged than before complexation. The ketonic group gains a small amount of σ-electron density on complexation and there is some redistribution of π-electron density. In the Cl case there is a net loss of π-electron density from the ketonic group. The uncomplexed ring gains σ and π electron density in each case, while the Cl substituent loses some electron density.

The chromium atom carries a +0.645 charge in the H and F cases, a +0.644 charge in the Cl case, and a +0.656 charge in the OCH_3 case. This is significantly higher than the benzene case where the charge is +0.639. The CO groups carry a net negative charge of between —0.538 and —0.559 which is lower than in the benzene case (—0.578).

It is tempting to rationalize the major ^{13}C NMR result, i.e., the upfield shift of the carbons bonded to the $Cr(CO)_3$ group, on charge arguments alone. The increased negative charge should increase the shielding at the carbon nucleus and move the resonances upfield. However, this explanation is inadequate for several reasons, one of which is that different MO treatments give different

TABLE 2

GROSS ORBITAL ELECTRON POPULATIONS

(Ring A complexed, ring B substituted with X (Δ = complex population—ligand population in parentheses)

X		H	F	Cl	OCH$_3$	C$_6$H$_6$Cr(CO)$_3$
Ring A						
6C	σ	18.502(0.432)	18.497(0.436)	18.507(0.438)	18.506(0.434)	18.493(0.452)
	π	5.523(—0.388)	5.519(—0.386)	5.520(—0.394)	5.526(—0.392)	5.574(—0.426)
Total C		24.025(0.044)	24.016(0.040)	24.027(0.044)	24.032(0.042)	24.067(0.026)
5H		4.961(0.034)	4.959(0.035)	4.957(0.031)	4.960(0.032)	5.994(0.035) (6H)
Total Ring A		28.986(0.078)	28.975(0.075)	28.984(0.075)	28.992(0.074)	30.061(0.061)
Ketonic CO						
C	σ	2.960(0.010)	2.957(0.010)	2.956(0.007)	2.959(0.011)	
	π	0.983(—0.004)	0.982(—0.004)	0.988(—0.004)	0.990(—0.004)	
O	σ	5.069(0.000)	5.070(0.000)	5.066(—0.002)	5.067(0.000)	
	π	1.196(0.004)	1.191(0.004)	1.198(0.001)	1.204(0.004)	
Total CO		10.208(0.010)	10.200(0.010)	10.208(0.002)	10.220(0.011)	
Ring B						
6C	σ	18.063(0.003)	17.807(0.002)	17.891(0.014)	17.851(0.006)	
	π	5.916(0.004)	6.005(0.006)	6.029(0.014)	6.064(0.001)	
Total C		23.979(0.007)	23.812(0.008)	23.920(0.028)	23.915(0.007)	
4H		3.937(0.002)	3.911(0.004)	3.930(0.005)	3.902(—0.002)	
X		0.990(0.001)	7.205(0.002)	7.050(—0.012)	13.066(0.000)	
Total Ring B		28.906(0.010)	34.928(0.014)	34.900(0.021)	40.883(0.005)	
Cr		5.355	5.355	5.356	5.344	5.361
3C		11.982	11.982	11.994	11.999	12.006
3O		18.556	18.556	18.556	18.560	18.572
Total (CO)$_3$		30.538	30.538	30.550	30.559	30.578

TABLE 3

CARBONYL OVERLAP POPULATIONS (BOND ORDERS) AND IR STRETCHING FREQUENCIES (cm^{-1}) IN $(CO)_3CrC_6H_5COC_6H_4X$

X	CO(Cr)	ν(CO)	CO(ketonic)	ν(CO)
H	0.673	1991	0.493	1663
F	0.673	1992	0.494	1664
Cl	0.673	1993	0.492	1652
OCH_3	0.672	1992	0.492	1655
$C_6H_6Cr(CO)_3$		1983 [a]		

[a] From ref. 6.

results. The ab initio calculations of Guest et al. [3] show both a σ and π electron drift from the chromium to the ring leaving the chromium with a charge of +2.08 clearly contrary to the obvious covalent nature of the molecule. Calculations by the CNDO method [3,5,12] give a σ-donation from the ring to the metal with a π-back-donation from the metal to the ring at variance with the generally accepted picture of π-donation from the ring to the metal. The SCCCMO calculations reported earlier [14] are in agreement with the picture presented here. The other reasons why a simple charge explanation is inadequate were also given in this latter paper.

It is difficult to calculate the various parameters in the Pople—Karplus equation [19] for such a large and unsymmetrical molecule. However, an estimation of the major parameter $(\Delta E)^{-1}$ for the carbon atoms of $Cr(CO)_3$ shows a lower value (0.347) than in the benzene case in keeping with the smaller downfield shift of the benzophenone complex (230.4 ppm) compared to the benzene complex (233.3) [14].

The infrared CO stretching frequencies and the corresponding bond orders (carbonyl overlap populations) are given in Table 3. It can be seen that the CO bond orders in the $Cr(CO)_3$ group show no significant change with substituent in agreement with the IR evidence which shows that frequencies do not change appreciably on substitution.

The ketonic CO bond orders are in the order $F > H > OCH_3 = Cl$. The CO stretching frequencies are 1664, 1663, 1655 and 1652 cm^{-1} for the F, H, OCH_3 and Cl compounds, respectively, in keeping qualitatively with the above trend.

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