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MOLECULAR ORBITAL CALCULATIONS ON TRANSITION METAL COMPLEXES

XXIII *. ^{1}H NMR SHIFTS IN SANDWICH, MIXED SANDWICH, AND RELATED TRICARBONYL COMPLEXES

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Summary

INDO SCF MO calculations have been carried out for a variety of diamagnetic sandwich, mixed sandwich, and related tricarbonyl complexes of the 3*d* series, and for the free ligand systems of the cyclopentadienyl anion (Cp^-), the neutral benzene molecule (Bz), and the cycloheptatrienyl cation (Ch^+). The π bond orders for the C—C linkages of the ligand rings all show significant, but broadly comparable, reductions on complexation, and the ^{1}H NMR shift for a given ring proton, relative to that for the appropriate free ligand, $\Delta\tau$, shows a good linear correlation with the corresponding change in the charge density at that proton, $\Delta P_{\mu\mu}(H)$. The plot of $\Delta\tau$ against $\Delta P_{\mu\mu}(H)$ shows a positive (upfield) intercept of about 2.5 ppm on the $\Delta\tau$ axis, and it is concluded that the results provide evidence for an appreciable diminution in the aromatic character of the ligand rings on complex formation.

Introduction

Recently [1] we have attempted, by INDO SCF molecular orbital calculations, to make some quantative estimates of the strengths of the metal—ligand interactions in transition metal sandwich and mixed sandwich complexes; thus, for these species, we have evaluated the bond orders per ring relating to the bonding of the various metal orbitals (3*d*, 4*s*, and 4*p*) to those of the ligand rings (carbon 2*s* and $2p_{x,y}$ (σ) and $2p_z$ (π)). For such systems effective pseudo-axial symmetry obtains, and in general the most significant interactions were found to be those involving the metal e_1 (d_{xz}, d_{yz}) and e_2 ($d_{x^2-y^2}$, d_{xy}) orbitals with the appropriate symmetry combinations of the π ($2p_z$) orbitals of the

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* For part XXII see ref. 29.

ligand rings. These results, together with our earlier calculations [2—6] on a variety of sandwich systems, showed clearly that the importance of the e_2 interaction increased progressively with increasing size of the ligand ring, whilst the e_1 bonding became less important. Consequently, since the dominant bonding mechanism in such species proved to involve the conjugated π-systems of the ligand rings, it appeared desirable to investigate the influence of the metal—ligand interactions on the extent of π-bonding, or aromaticity, within the ligand rings, as compared with that existing for the corresponding free ligands.

It is well known that the positions of the ^{1}H NMR peaks for the protons of conjugated cyclic systems depend significantly upon the magnitudes of the ring currents within such rings, and thence upon the aromaticity thereof [7]. These resonances are in fact shifted to lower frequencies (downfield) by ring current effects, but are also dependent upon the charge density at the proton in question, increasing electron density leading to an upfield shift. Moreover, the magnitude of the ring current for a given cyclic system is dependent to the first order on the ring C—C π bond orders.

We have therefore carried out calculations for systems containing π-C_5H_5 (Cp), π-C_6H_6 (Bz), and π-C_7H_7 (Ch) rings, and for the corresponding free ligands, Cp^-, Bz, and Ch^+. In all cases we have evaluated the electron density, $P_{\mu\mu}(H)$, at the proton and the π bond orders, P_{ij}(C—C), for the ring linkages, and compared these quantities for the listed complexes with the values obtained for the free ligands. Thus it should be possible to determine whether or not any correlation exists between the experimentally reported ^{1}H NMR frequencies and the calculated quantities, and also to ascertain whether and to what extent the aromaticities of the ligand rings are affected by complex formation.

Method

The INDO SCF molecular orbital method previously described [8] was used throughout. The basis set employed included the metal $3d$, $4s$, and $4p$ orbitals, together with the hydrogen $1s$ orbitals and the carbon (and, where appropriate, oxygen) $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals; thus both σ- and π-bonding effects of the ligands were included.

Results and discussion

Our calculations were carried out for the seventeen complexes listed in Table 1, for all of which ^{1}H NMR data are available in the literature as shown. Of the eleven sandwich and mixed sandwich species two, CpTiCh and $TiBz_2$, represent formally d^4 systems, but the remainder correspond to d^6 configurations, as do all the six tricarbonyl systems studied. For these latter complexes the effective symmetry is lower than pseudo-axial, so that the $\Delta P_{\mu\mu}$ and ΔP_{ij} values listed are average quantities, but the calculated charges and bond orders for the ring atoms show only very small internal differences.

In this work we have deliberately restricted our attention to systems containing unsubstituted, homonuclear, ligand rings. Thus, any inductive or resonance effects due to substituents may be discounted, and contributions to the ^{1}H

TABLE 1

^{1}H CHEMICAL SHIFTS AND CALCULATED CHARGE DENSITIES AND BOND ORDERS

No.	Compound	$\Delta P_{\mu\mu}$(H)	$\Delta P_{\mu\mu}$(H)	ΔP_{ij}(C—C)	ΔP_{ij}(C—C)	$\Delta\tau$	$\Delta\tau$	Reference [b]
		Cp	C_nH_n	Cp	C_nH_n	Cp	C_nH_n	
1	$FeCp_2$	−0.088		−0.086		+1.40		13
2	$[CoCp_2]^+$	−0.110		−0.094		−0.38		14
3	CpMnBz	−0.080	+0.002	−0.084	−0.128	+1.50	+2.56	15
4	$[CpFeBz]^+$	−0.118	−0.056	−0.086	−0.088	+0.26	+0.78	16
5	CpCrCh	−0.088	+0.071	−0.074	−0.114	+1.75	+3.67	17
6	$[CpMnCh]^+$	−0.116	+0.017	−0.084	−0.090	+0.55	+2.10	18
7	CpTiCh	−0.092	+0.069	−0.067	−0.116	+0.48	+3.75	17
8	$CrBz_2$		+0.007		−0.124		+2.91	19
9	$[VBz_2]^-$		+0.056		−0.146		+3.99	19
10	$TiBz_2$		+0.005		−0.125		+2.19	20
11	CpCoCb	−0.106	[a]	−0.088	[a]	+0.64	[a]	21
12	$CpMn(CO)_3$	−0.089		−0.100		+0.85		13
13	$[CpFe(CO)_3]^+$	−0.126		−0.104		−0.34		22
14	$BzCr(CO)_3$		−0.011		−0.096		+2.00	23, 24
15	$[BzMn(CO)_3]^+$		−0.048		−0.090		+0.78	25
16	$ChV(CO)_3$		+0.068		−0.108		+4.58	26
17	$[ChCr(CO)_3]^+$		+0.025		−0.100		+2.62	27

Reference standards [28]	$P_{\mu\mu}$(H)	P_{ij}(C—C)	τ ^{1}H
Cp^-	1.106	0.648	4.50
Bz	1.026	0.667	2.73
Ch^+	0.962	0.642	0.80

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[a] Cb = π-C_4H_4, data not available. [b] Experimental data relate to several different solvents; resulting uncertainties estimated at 0.2 to 0.4 ppm.

NMR shift due to the magnetic anisotropy of neighbouring atoms are likely to be both small and more of less constant over the series. For proton NMR shifts any terms due to local paramagnetic effects will be very small so that for the systems chosen the effective contributions will be limited to those dependent on the charge density at the proton in question, together with any effects due to aromatic ring currents [7].

An initial inspection of the results of our calculations showed that there was a good correlation between the calculated changes in proton electron density on complexation, $\Delta P_{\mu\mu}$(H), and the observed changes in the positions of the ^{1}H NMR peaks, $\Delta\tau$. However, there was no apparent relationship between $\Delta P_{\mu\mu}$(H) and either the π electron density on the ring carbon atoms or the total density thereon. Moreover, for all the species studied the C—C π bond order for the rings showed an appreciable reduction, compared with the corresponding value for the free ligand. These quantities, ΔP_{ij}(C—C), did not vary widely from one system to another, and there was no apparent correlation with $\Delta\tau$.

It is, however, clear from Fig. 1 that the plot of $\Delta P_{\mu\mu}$(H) against $\Delta\tau$ affords a reasonably linear correlation, but the best straight line does not pass through the origin and instead yields an upfield intercept of some 2.5 ppm on the $\Delta\tau$ axis. It therefore follows that on complex formation the position of the ^{1}H NMR peak is effectively shifted to higher field, which in turn implies a reduction in the ring current contributions. Thus it may be concluded that complex-

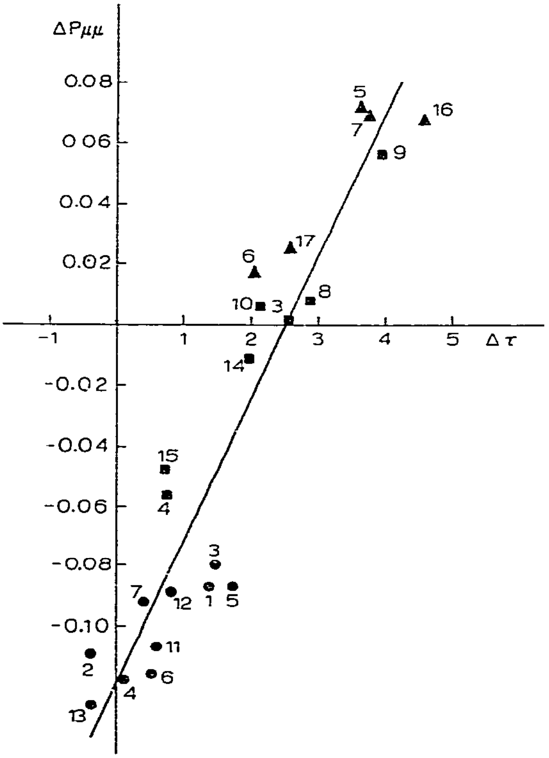

Fig. 1. Variation of relative chemical shift, $\Delta\tau$, with relative proton charge density, $\Delta P_{\mu\mu}$(H). (●) Cp, (■) Bz, (▲) Ch.

ation is accompanied by a significant diminution in the aromaticity of the ligand ring, which is of course also in agreement with the calculated decreases in P_{ij}(C—C).

It should, however, be noted that the reductions in the P_{ij}(C—C) values for the Cp, and the Bz and Ch, ligands on complexation arise via essentially different mechanisms. Thus the dominant interaction in the bonding of the Cp ligand to the metal is that involving the bonding e_1 π-orbitals of the ring with the metal d_{xz} and d_{yz} levels [1], leading to an accession of electrons from ligand to metal, and a decrease in the ring π bond order. On the other hand for the Bz and Ch ligands the decrease in P_{ij}(C—C) arises because the main metal—ligand interaction is that between the anti-bonding e_2 π-orbitals of the ring and the metal $d_{x^2-y^2}$ and d_{xy} levels [1], leading to a transfer of electrons from the metal into this ligand π^* level.

For the bis-benzene complexes the conclusion of reduced aromaticity in the ligand rings is in agreement with the results of ^{13}C NMR chemical shift measurements by Graves and Lagowski [9] for a wide range of substituted bis-benzene chromium complexes. Here no significant shift changes at the C(4) (*para*) position were observed with varying substituents, although the transmission of such effects had been well established [10] for the corresponding mono-substituted benzenes, and it was therefore concluded that resonance delocalisation in the ring system was effectively quenched on complex formation. It is, however, perhaps significant that the benzene ligands of the sandwich complexes listed in Table 1 generally show the largest decreases in P_{ij}(C—C) on complexation, whereas $BzCr(CO)_3$ and $[BzMn(CO)_3]^+$ show appreciably smaller decreases in P_{ij}(C—C), and it has been shown, also via ^{13}C NMR shifts [11], that for (arene)-$Cr(CO)_3$ systems substituent effects are fully transmitted to the *para* position. Furthermore, for the Cp ligands of Table 1 the calculated decreases in P_{ij}(C—C) are smaller again than for either the benzene sandwich and mixed sandwich species, or for the benzene metal tricarbonyls, and this accords with the more marked aromatic character of the ligand rings in the metallocenes than in the bis-benzene series [12]. However, the strong correlation between $\Delta P_{\mu\mu}$(H) and $\Delta\tau$, and the relative insensivity of the latter to small variations in ΔP_{ij}(C—C), suggest that as fas as the ^{1}H NMR shifts are concerned the charge density at the proton is the dominant consideration.

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