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# The Substituent Angle in $C_nR_n$ - Transition Metal π Complexes

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*Received June 30, 1967*

*When an unsaturated hydrocarbon is complexed with a transition metal ion its σ framework is usually distorted. In this paper the angular displacement of R groups in cyclic $C_nR_n$ system bonded to a transition metal is explained in terms of the non-orthogonality of the ligand σ framework with the orbitals of the metal atom. The principle of maximum overlap leads to equations which relate the σ and π overlap integrals to experimentally observed angles. Reasonable agreement is obtained when the theory is compared with experiment.*

## Introduction

A useful general qualitative approach to the problem of the nature of the bonding between a transition metal and an unsaturated hydrocarbon is now well established. The readily polarizable π-electron cloud of the ligand is partially delocalized onto the metal atom with a simultaneous, synergic, back transfer from the metal to the ligand. The general pattern of the stabilizing interaction is usually made fairly evident by group theoretical (and/or overlap) and qualitative energetic considerations. However, there are features of the bonding which are readily overlooked. For example, when only part of the conjugated system of an unsaturated hydrocarbon is bonded to the transition metal ion the presence of the non-bonded, but formally conjugated, part of the hydrocarbon will modify the molecular orbital pattern of the bonded fragment and so the detail of the hydrocarbon-metal interactions. Alternatively, the formally conjugated groups may rotate so as to lose conjugation with the metal-bonded fragment. In this case the geometry of the hydrocarbon in the complex differs markedly from that in the free ligand. We have discussed examples of these effects elsewhere.[1] Even when the entire unsaturated system is bonded to the transition metal the simple picture of the bonding is incomplete. This is evidenced by the fact that it rarely happens that the geometry of the hydrocarbon σ framework is unmodified on coordination. That is, the metal-ligand interactions involve not only the ligand π electrons but the ligand σ electrons also. It is pertinent to note that, for example, the frequently facile interchange between a (formally) π-bonded allyl group and a (formally) σ-bonded one strongly suggests that interactions between the transition metal and the ligand σ framework cannot, in general, be neglected. The nature of the energetic factors governing the preferred (ligand σ or π) interaction has been discussed by Orgel.[2] In the present paper we discuss the same problems in terms of the relative overlap integrals between the metal orbitals and ligand framework σ and π orbitals. Although the discussion may be extended to other cases* we restrict the discussion in this paper to ligands in which the π (and σ) molecular orbital coefficients are unambiguous (i.e. determined by symmetry), for these cases admit of a more rigorous mathematical treatment.

The common feature of structural organometallic chemistry which we discuss in this paper is the observation that a substituent R in a $C_nR_n$ ring is bent out of the plane of the $C_n$ ring. When n is small (4, 5) the bend is away from the transition metal[4] but as n increases the angle of bend decreases. So, for n = 6, approximate co-planarity has been observed.[3] This general behaviour does not seem to be explicable simply in terms of steric interactions between metal and R-group although this suggestion has been made for individual cases.[4]

In the isolated $C_nR_n$ ligand the operation of reflection in the plane of the ring carbon atoms is an allowed symmetry operation. However, when the ring is bonded to a transition metal this is no longer an allowed symmetry operation; so that the distinction between ligand orbitals which are symmetric and antisymmetric with respect to such a reflection is no longer applicable. That is, σ-π mixing can, and in general will, occur. In contrast, the operation of reflection in any of the n mirror planes (for a $C_nR_n$ ring) remain allowed symmetry operations — certainly in terms of local symmetry if not from the point of view of molecular symmetry. It follows that at each of the n ring carbon atoms the only important σ-π mixing will occur between the «$p_\pi$» orbital and that «$p_\sigma$» orbital directed radially from the centre of the $C_n$ ring.

As is well known, the stabilising interaction between the ring system and the metal atom way be one of several possible types. The three main interactions we shall denote as $A_1$, $E_1$ and $E_2$. These are, respectively, interactions involving $C_n$ ring group orbitals with zero, one and two nodal planes perpendicular to the plane of the ring. These basic symmetry labels are correct for all the $C_{nv}$ point groups, but additional suffixes may

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(1) S. F. A. Kettle, to be published.

(*) For example, complexes involving the π methallyl group (see R. Mason and D. R. Russell, *Chem. Comm.*, 26 (1966) ).

(2) L. E. Orgel, «An introduction to Transition Metal Chemistry», Methuen (London), p. 138 (1960).

(3) M. F. Bailey and C. F. Dahl, *Inorg. Chem.*, *4*, 1298 (1965).

(4) J. D. Dunitz, H. C. Mez, O. S. Mills and H. H. H. Shearer, *Helv. Chim. Acta*, *45*, 647 (1962).

have to be specified for molecules for higher symmetry. The main interaction types may, in general, be subdivided according to whether s, p or d orbitals on the metal atom are involved in the bonding. We shall consider only the involvement of d orbitals; these interactions will usually be the most important. Inclusion of the metal s and p orbitals would give equations with more unknowns than observables; it is, however, possible to qualitatively discuss their effect. For example, metal s-orbital-ligand interactions will be maximised when $\theta_1+\theta_2 = 90°$ (Figure 2) and therefore will tend to tilt a substituent towards the metal.

It is evident that any metal d-orbital will, in general, have a non-zero overlap integral with both the $p_\pi$ and $p_\sigma$ (radial) orbitals of each carbon atom in the $C_n$ ring (Figure 1).* In order to discuss these interactions

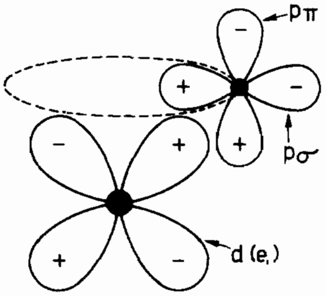

Figure 1.

theoretically one may solve an appropriate 3×3 secular determinant. The problem may be reduced to one of dimension 2, however, by considering that linear combination of $p_\pi$ and $p_\sigma$ (radial) which has a maximum overlap with the appropriate metal orbital. The orthogonal $p_\pi/p_\sigma$ (radial) combination then interacts solely with the substituent R, and, assuming bond following,[5] the angle $\theta_2$ (Figure 2), through which the substituent R has moved in passing from the free to the complexed ligand is to be correlated with the $p_\pi$-$p_\sigma$ (radial) mixing coefficients.

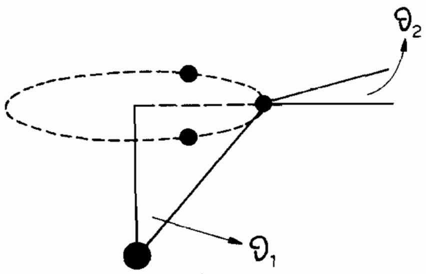

Figure 2.

Thus far the argument may be advanced with some confidence: bending of ring substituents out of the plane of the $C_n$ ring is a consequence of interactions between the metal orbitals and $\sigma$ framework of the ring system. Now, as we have noted, all of the metal d-orbitals may be involved in interactions with ring system, and maximum overlap with the ring orbitals will be achieved at different $\theta_2$ values for each of them (except for metal orbitals which transform as a pair). This means that the observed $\theta_2$ will be some compromise; at best we may hope that one interaction predominates.

**Table I.** I Values of $\theta_1$ for $3 \leqslant n \leqslant 8$

| Ring size (n) | Approximate $\theta_1$ for first row transition metals | Approximate $\theta_1$ for second and third row transition metals |
|---|---|---|
| 3 | 24° | 22° |
| 4 | 30° | 28° |
| 5 | 37° | 34° |
| 6 | 45° | 41° |
| 7 | 55° | 49° |
| 8 | 68° | 59° |

Consider Figure 2, which depicts a cyclic $C_n$ ring $\pi$ bonded to a transition metal atom. It is found experimentally that the angle $\theta_1$ is determined by the value of n together with a M-C bond length $\simeq$ 2.05 Å (for a first row transition element) and a C-C bond length $\simeq$ 1.42 Å. Values of $\theta_1$ for $3 \leqslant n \leqslant 8$ are given in Table I.

As we have noted, maximum overlap between the metal d orbital and the $p_\pi$ orbitals of the carbon ring system is achieved by varying $\theta_2$ i.e. by mixing of «$p_\pi$» and «$p_\sigma$». Now the group overlap integral between a metal and ring orbital is a function of $\theta_1$, $\theta_2$, $S_\sigma$ and $S_\pi$, the latter being the diatomic overlap integrals of $\sigma$ and $\pi$ symmetries. It is sufficient to require that the overlap integral between an appropriate metal d orbital and any carbon $p_\pi$ orbital is maximised (to maximise the *group* overlap integral would require that another angle, $\Phi$ say, be introduced. The angles $\Phi$ are, however, invariants of the system when the ligand molecular orbital coefficients are determined by symmetry).

From the general formulae we have given elsewhere[6] the individual overlap integrals in Table II may be obtained. The condition $\dfrac{dS}{d\theta_2} = 0$ leads to expressions also given in Table II and represent the maximum overlap condition provided that $\dfrac{d^2S}{d\theta_2^2} > 0$. It is readily seen that if the turning points given in Table II are maxima for $E_1$ and $E_2$ interactions then that for the $A_1$ is a minimum. This corresponds to the fact that in the situation depicted in Figure 1 if the $\sigma$ component of $d_{z^2}$-$p_\pi$ interaction is bonding then $\pi$ component is antibonding (or *vice versa*). The equations in Table II show that the ratio $S_\pi/S_\sigma$ can be obtained from the observed valued of $\theta_1$ and $\theta_2$, *provided that the predominant bonding interaction can be identified* and is of either $E_1$ or $E_2$ type. These are rather severe restrictions, but fortunately most detailed calculations on ferrocene-type systems indicate that they are at least approximately satisfied. Further, the comparison of this theory with experiment, which we give in the next section, is rather encouraging.

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(*) Overlap with the carbon 2s and other 2p orbital may also be non-zero. However, by applying arguments analagous to those developed in this paper, it is readily seen that their involvement will not affect the attitude of the ring substituent.

(5) L. Burnelle and C. A. Coulson, *Trans. Faraday Soc.*, 53, 403 (1957).

(6) S. F. A. Kettle, *Inorg. Chem.*, *4*, 1821 (1965).

**Table II.** Overlap relationships. (Tables of the functions listed in column 4 may be obtained from the author)

| Species of interaction | Metal orbital | Overlap integral | $\frac{dS}{d\theta_2} = 0$ condition |
|---|---|---|---|
| $A_1$ | $d_{z^2}$ | $(\cos^2\theta_1 - \frac{1}{2}\sin^2\theta_1) . \cos(\theta_1+\theta_2) . S_\sigma -$ | $\frac{S_\pi}{S_\sigma} = \frac{-1}{\sqrt{3}}\tan(\theta_1+\theta_2) .$ |
| | | $\frac{\sqrt{3}}{2}\sin 2\theta_1, \sin(\theta_1+\theta_2) . S_\pi$ | $(\cot\theta_1 - \frac{1}{2}\tan\theta_1)$ |
| | $d_{xz}$ | $\frac{\sqrt{3}}{2}\sin 2\theta_1 . \cos(\theta_1+\theta_2) . S_\sigma +$ | $\frac{S_\pi}{S_\sigma} = \frac{\sqrt{3}}{2}\tan 2\theta_1 .$ |
| $E_1$ | | | |
| | $d_{yz}$ | $\cos 2\theta_1 . \sin(\theta_1+\theta_2) . S_\pi$ | $\tan(\theta_1+\theta_2)$ |
| | $d_{x^2-y^2}$ | $\frac{\sqrt{3}}{2}\sin^2\theta_1 . \cos(\theta_1+\theta_2) . S_\sigma +$ | $\frac{S_\pi}{S_\sigma} = \frac{\sqrt{3}}{2}\tan\theta_1 .$ |
| $E_2$ | | | |
| | $d_{xy}$ | $\frac{1}{2}\sin 2\theta_1 . \sin(\theta_1+\theta_2) . S_\pi$ | $\tan(\theta_1+\theta_2)$ |

## Comparison with Experiment

Although there is an abundance of structural data available concerning complexes containing $C_n$ rings π bonded to a metal, rather little of it is suitable for comparison with the theory outlined above. This is usually because the only ring substituent is hydrogen, the position of which is not determined. The ideal ring substituent is probably the methyl group. Any potential substituent which either conjugates with the $C_n$ ring or is bulky enough for steric factors to interfere must be excluded, as must $C_n$ ring systems without a local $C_n$ rotation axis. Two molecules suggest themselves as potentially suitable for comparison with the theory. The first, hexamethylbenzene chromium tricarbonyl, has recently been studied by Bailey and Dahl;[3] the methyl groups are co-planar with the $C_6$ ring. It is difficult to decide whether, for this molecule, the $E_1$ or $E_2$ interactions predominate. The present work strongly suggests the latter. If the $E_1$ interactions predominate then for $\theta_1 = 45°$, $\theta_2 = 0°$ the ratio $\frac{S_\pi}{S_\sigma}$ is large, i.e. $S_\sigma \sim 0$, a conclusion quite inconsistent with the data in Table III.

If the $E_2$ interaction predominates then $\frac{S_\pi}{S_\sigma} = 0.9$, a value entirely consistent with the date in Table III.

**Table III.** Comparison of theoretical overlap integral ratios with the «experimental» for $Me_6C_6Cr(CO)_3$. For references see Table IV.

| Atomic orbitals | $S_\pi$ | $S_\sigma$ | $S_\pi/S_\sigma$ |
|---|---|---|---|
| «Experimental» ($E_2$ interaction) | | | 0.9 |
| Clementi and Raimondi S.C.F. | 0.028 | 0.223 | 0.39 |
| Slater | 0.175 | 0.218 | 0.78 |
| Slater modified | 0.206 | 0.071 | 0.94 |
| Richardson S.C.F. (zerovalent metal) | 0.144 | 0.172 | 0.84 |

The second molecule is the tetramethyl cyclobutadiene nickel dichloride dimer, the crystal structure of which was determined by Dunitz et al.[4] It appears reasonable to suppose that the $E_1$ interactions are the most important in this molecule so, with $\theta_1 = 30°$ and $\theta_2 = 6.5°$ (the average of the experimental values) we conclude that $\frac{S_\pi}{S_\sigma} = 1.1$. This value is to be compared with that calculated for various forms of the atomic orbitals (Table IV).

**Table IV.** Comparison of theoretical overlap integral ratios with the «experimental» for $(NiMe_4C_4Cl_2)_2$

| Atomic orbitals | $S_\pi$ | $S_\sigma$ | $S_\pi/S_\sigma$ |
|---|---|---|---|
| «Experimental» ($E_1$ interaction) | | | 1.1 |
| Clementi and Raimondi S.C.F.[a] | 0.026 | 0.035 | 0.74 |
| Slater[b] | 0.061 | 0.123 | 0.50 |
| Slater modified[c] | 0.076 | 0.134 | 0.57 |
| Richardson S.C.F.[d] | 0.080 | 0.132 | 0.61 |
| Richardson S.C.F.[e] | 0.057 | 0.108 | 0.53 |

[a] E. Clementi and D. L. Raimondi, *J. Chm. Phys.*, *38*, 2686 (1963). [b] J. C. Slater, *Phys. Rev.*, *36*, 57 (1937). [c] The carbon orbital exponent was taken as 1.42; *cfr.* A. Jucys, *Proc. Roy. Soc.*, *173A*, 59 (1939) and R. Mason, *Proc. Roy. Soc.*, *258A*, 302 (1960). [d] J. W. Richardson, W. C. Nieuwpoort, R. R. Powell and W. F. Edgell, *J. Chem. Phys.*, *36*, 1057 (1962), the nickel atom is assumed to be zerovalent. [e] The nickel atom is assumed to carry unit positive charge.

The closest fit to the «experimental» values is obtained with Clementi and Raimondi's S.C.F. orbitals, but the individual overlap integrals in this case seem much too small. Orbitals based on Richardson et. al's analysis of Watson's S.C.F. functions are little better than Slater orbitals. However, the presence of an appreciable E contribution to the bonding ($\frac{S_\pi}{S_\sigma} = 0.4$), would give better agreement between theory and experiment.

## Conclusion

It has become common practice to use some form of S.C.F. orbitals, in discussions on the electronic-properties of transition metal complexes. In this paper we have suggested a novel method of testing the accuracy of these orbitals which may be compared with the more detailed theoretical approach of Brown and Fitzpatrick.[7,8]

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(7) D. A. Brown and N. J. Fitzpatrick, *J. Chem. Soc.*, (A), 441 (1966).
(8) D. A. Brown and N. J. Fitzpatrick, *J. Chem. Soc.*, (A), 316 (1967).