Journal of Organometallic Chemistry, 149 (1978) 401—406

MOLECULAR ORBITAL CALCULATIONS ON TRANSITION METAL COMPLEXES

XIX *. π-CYCLOPENTADIENYL-π-CYCLOPROPENYLNICKEL

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(Received October 31st, 1977)

Summary

INDO SCF molecular orbital calculations for π-cyclopentadienyl-π-cyclopropenylnickel indicate a formally d^{10} configuration for the metal. Calculations of the ionisation energies show that electron loss should take place first from the occupied closely grouped set of dominantly *d*-orbitals, and then from a mainly π-cyclopentadienyl *e* orbital, this being the highest occupied ligand level. This latter level shows however only a slight mixing with the metal *d*-orbitals, resulting in a small ligand→metal electron donation; the dominant interaction is that between the higher lying π-cyclopropenyl *e* level and the metal $3d_{xz}$ and $3d_{yz}$ orbitals which leads to a substantial metal→ligand charge donation. The behaviour of the π-cyclopropenyl ligand is discussed using the calculated charge distributions.

Introduction

For the elements of the first transition metals series a wide variety of mixed sandwich compounds have been reported. Thus the species CpCrCh, CpMnBz, and CpCoCb (Cp = π-C_5H_5, Bz = π-C_6H_6, Ch = π-C_7H_7, and Cb = π-C_4H_4) are all well established, and with the well known $FeCp_2$ constitute an isoelectronic series with a formal d^6 configuration at the metal, using the ligand field formalism [1] and regarding the ligands as Ch^+, Bz^0, Cp^-, and Cb^{2-} respectively. Furthermore we have recently shown [2—5] that the dominant features of the bonding in all these systems can be ascribed to the metal 3*d*—ligand π-orbital interactions, and that the effect of variation of the size of the ligand ring can be rationalised in terms of the simple picture, put forward by Fischer [6] as long ago as 1963,

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* For Part XVIII see ref. 5.

based on the H^{core} terms of the e type ligand π-levels becoming progressively more negative with increasing ring size. However, in 1971 the first synthesis was reported [7] of a similar complex containing a three-membered carbocyclic ring, π-cyclopentadienyl-π-(triphenyl)cyclopropenylnickel, for which X-ray measurements [8] confirmed the sandwich structure, and it therefore appeared useful to extend our molecular orbital calculations to such a system. In addition, although the parent molecule, CpNiCpr (Cpr = π-C_3H_3), is formally isoelectronic with the other mixed sandwich compounds listed above, it seems more reasonable to regard the Cpr ligand as Cpr^+ than as Cpr^{3-} so that a d^{10} rather than a d^6 configuration at the metal would be anticipated.

We have therefore carried out full basis set INDO SCF MO calculations on the parent system, CpNiCpr; as yet only the triphenyl derivative has been synthesised but we believe our results for CpNiCpr should reflect satisfactorily the main features of the bonding, especially since the phenyl groups are known to be significantly rotated with respect to the plane of the Cpr ring. From our results we have attempted to assess the relative importance of the possible contributions to the bonding as discussed by Tuggle and Weaver [8], and to rationalise the fact that the metal to carbon bond length found for the Cpr ring is markedly shorter (0.14 Å) than for the Cp ring. Information has also been derived concerning the formal d configuration on the metal, and the splitting pattern and ionisation energies for the orbitals of dominantly metal $3d$ character.

Method

The all valence electron INDO SCF MO method previously described [9] was used for the calculations. The basis set spanned the metal $3d$, $4s$, and $4p$, the carbon $2s$ and $2p$, and the hydrogen $1s$ orbitals, and the molecular geometry was based upon that given by Tuggle and Weaver [8] for π-cyclopentadienyl-π-(triphenyl)cyclopropenylnickel.

Results and discussion

Although the X-ray diffraction measurements show the triphenyl derivative to have a symmetry no higher than C_s, it is nevertheless convenient to consider the parent CpNiCpr system as being formed by fusion at the metal atom of two fragments, CpNi and CprNi, of C_{5v} and C_{3v} symmetry respectively. Thus, although both the σ- and the π-frameworks of the ligand rings are involved in the bonding, the major interaction proves to be that between the metal $3d$ orbitals and the π-orbitals of the ligands, and this is illustrated in Fig. 1 in which we show the appropriate energy levels at the H^{core} stage of the calculation. The π-orbitals of the Cp and Cpr rings yield respectively the symmetry combinations $a_1 + e_1 + e_2$ and $a_1 + e$, as shown, but for the molecular orbitals of the complex the symmetry labels of the lower point group are appropriate; thus both the d_{xz}, d_{yz} (e_1 in C_{5v}) and $d_{x^2-y^2}$, d_{xy} (e_2 in C_{5v}) pairs transform as e and may therefore in principle be mixed.

In fact the H^{core} results do indicate a substantial degree of mixing between the two e pairs, and of the mainly metal d-orbitals one e level is bonding with respect to the Ni H^{core} term with the other e level and the a_1 orbital anti-bond-

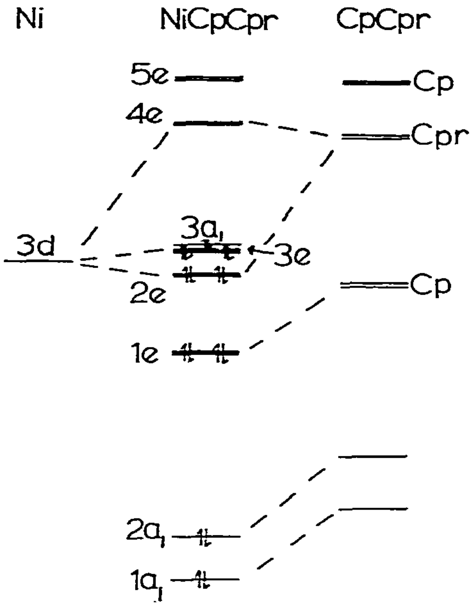

Fig. 1. H^{core} diagram for 3*d*—Ligand π-interaction in CpNiCpr.

ing. Both the *e* orbitals show rather more $d_{x^2-y^2}$, d_{xy} than d_{xz}, d_{yz} character, but the lower level exhibits the greater d_{xz}, d_{yz} contribution; in both cases the only significant ligand interaction takes place via the π-Cpr orbitals, the π-Cp orbitals being only weakly admixed. As will be seen from the SCF results (vide infra) the d_{xz}, d_{yz} orbitals appear to be much more delocalised than the $d_{x^2-y^2}$, d_{xy} pair, so that the H^{core} sequence for the mainly *d*-orbitals is equivalent to $d_{xz}, d_{yz} < d_{x^2-y^2}, d_{xy} < d_{z^2}$.

The interaction between the metal and the ligand π-orbitals, shown in Fig. 1, involves altogether eighteen electrons, and the resulting molecular orbitals are filled up to and including the $3a_1$ level. Since the metal d_{xz}, d_{yz} orbitals are strongly mixed with the e π-Cpr level a considerable accession of electron density from the metal to the Cpr ligand will ensue, and it should be noted that this in fact follows as a consequence of the Cpr ring size. Thus for the five-membered Cp ring the π-e_1 level lies well below the metal 3*d* level at H^{core}, but the *e* levels of *n*-membered ring π-systems become progressively higher in energy with decrease in *n*. Consequently, for the three-membered ring, the only *e* level now lies above the metal 3*d* orbitals and admixture therewith leads to metal to ligand electron donation.

In considering the nature of the bonding in the CpNiCpr complex it is of course more meaningful to examine the SCF rather than the H^{core} results, and we accordingly now treat those features of the results in which significant differences between the two stages are evident, as well as giving a more general discussion. In Table 1 therefore are shown the SCF compositions of the occupied orbitals, together with those of the virtual 4*e* and 5*e* levels, the dominant contributions and the other smaller admixtures being expressed as percentages.

From the Table it is seen that there is now no significant cross-mixing between

TABLE 1

COMPOSITIONS OF THE MOLECULAR ORBITALS MAINLY INVOLVED IN THE METAL $3d$—LIGAND π-ORBITAL INTERACTION IN CpNiCpr

Orbital	ϵ_{SCF} (a.u.)	Composition (%)
$5e$ [a]	+0.236	π-Cp (58.4), σ-Cp (25.0), H—Cp (12.7)
$4e$ [a]	+0.206	π-Cpr (47.7), $3d_{xz,yz}$ (36.0), π-Cp (10.2)
$3e$ [b]	—0.249	$3d_{xz,yz}$ (51.3), π-Cpr (35.1), $4p_{x,y}$ (4.0), σ-Cpr (4.0)
$2e$ [b]	—0.308	$3d_{x^2-y^2,xy}$(93.5), π-Cp (2.0), π-Cpr (1.0)
$3a_1$	—0.313	$3d_{z^2}$ (93.4), H—Cpr (1.8), H—Cp (1.5), $4s$ (1.5)
$1e$	—0.510	π-Cp (59.8), σ-Cpr (19.7), $3d_{xz,yz}$ (6.8), $4p_{x,y}$ (3.4)
$2a_1$	—0.765	π-Cpr (72.0), π-Cp (7.8), H—Cpr (7.2), σ-Cpr (5.9), $4s$ (2.3)
$1a_1$	—0.948	π-Cp (54.5), H-Cp (11.3), σ-Cp (9.2), π-Cpr (8.2), $4s$ (3.2)

[a] Virtual levels. [b] The $2e$ and $3e$ levels at SCF correspond approximately to the $3e$ and $2e$ levels respectively at H^{core}.

the $d_{x^2-y^2}$, d_{xy} and the d_{xz}, d_{yz} e pairs, and that only the mainly d_{xz}, d_{yz} level is appreciably mixed with any of the ligand orbitals. In contrast both the mainly $d_{x^2-y^2}$, d_{xy} and the mainly d_{z^2} levels are very largely localised on the metal. The ϵ_{SCF} ordering actually corresponds to the sequence $d_{z^2} < d_{x^2-y^2}, d_{xy} < d_{xz}, d_{yz}$ with an energy spread of about 0.064 a.u. (cf. 0.033 a.u. at H^{core}), but it is well known that Koopmans' theorem cannot be relied upon for metal sandwich systems because of the extensive reorganisation effects which accompany ionisation: thus the energies corresponding to electron loss must be calculated from the differences in total energy between the ground state of the neutral molecule and those of the resulting cationic species. When this is done we find that within the accuracy of our calculations electron loss from any of the dominantly metal $3d$ levels ($3a_1$, $2e$, and $3e$) requires approximately the same energy, some 5.5 eV.

From Table 1 it is also evident that the only occupied ligand orbital which is significantly mixed with the metal $3d$ levels is the $1e$ level which is predominantly ligand π-Cp in character; here the metal $3d_{xz}$, $3d_{yz}$ contribution represents some 7% of the molecular orbital, and results in a small drift of electron density from the Cp ring onto the metal. However, the salient feature of the bonding is clearly the very substantial mixing between the metal $3d_{xz}$, $3d_{yz}$ orbitals and the π-Cpr orbitals observed for the $3e$ (SCF) level, which only just shows more than 50% metal character. This results in a very significant release of electron density from the metal onto the Cpr ring, and contrasts with the behaviour of the metal $3d_{x^2-y^2}$, $3d_{xy}$ and $3d_{z^2}$ orbitals which are only rather slightly mixed with the ligands and whose resulting molecular orbitals ($2e$ (SCF) and $3a_1$ respectively) correspond to almost completely localised metal levels. Thus both the $2e$ and the $3a_1$ levels show about 94% metal character, and only for the former is there any appreciable (2%) contribution from the π-Cp orbitals.

The appreciably greater involvement of the π-Cpr orbitals, rather than those of the Cp ring, in the bonding scheme is moreover fully consistent with the much shorter Ni—C(Cpr) distance observed [8] in the triphenyl derivative (1.961 Å as against 2.100 Å for Ni—C(Cp)), whilst the drift of electrons from the Cp ring to the metal and more markedly from the metal to the Cpr ring is just what would be anticipated for the formulation of the complex as a d^{10} system, $Cp^-Ni^0Cpr^+$. It is however instructive to consider in more detail the

TABLE 2

ELECTRONIC POPULATIONS FOR THE FREE CpCpr SYSTEM AND THE COMPLEX CpNiCpr

Orbitals	Free CpCpr	Complex CpNiCpr
Cp(π), C, $2p_z$	5.930	5.105
Cpr(π), C, $2p_z$	2.070	3.306
Cp(σ), C, $2s$, $2p_{x,y}$	2.910 (X 5)	2.854 (X 5)
Cpr(σ), C, $2s$, $2p_{x,y}$	3.118 (X 3)	2.838 (X 3)
Cp, H, $1s$	1.090 (X 5)	1.012 (X 5)
Cpr, H, $1s$	0.882 (X 3)	0.969 (X 3)
Ni, $3d_{z^2}$	—	1.958
Ni, $3d_{xz,yz}$	—	2.504
Ni, $3d_{x^2-y^2,xy}$	—	3.876
Ni, $4s$	—	0.598
Ni, $4p$	—	1.886

electron distribution calculated for the CpNiCpr system, and to compare it with that derived for the uncomplexed CpCpr entity (at the same internuclear distances), and with that obtaining for the d^6 CpCrCh system [2], which can also be written as $Cp^-M^0Ch^+$.

The orbital populations for the cyclopentadienyl and cyclopropenyl rings before and after complexation with the nickel atom are given in Table 2, from which it is clearly appropriate to ascribe essentially unit positive and negative charges to the Cpr and Cp rings respectively in the uncomplexed system. However, the coordination of a cyclopentadienyl ring to a transition metal is usually regarded as taking place via electron donation from its π-orbitals into suitable vacant metal d-orbitals (viz. d_{xz}, d_{yz}), and if one treats the CpNiCpr complex as containing Ni^0 ($3d^{10}$) all the metal d-orbitals are fully occupied, thus apparently precluding this simple donation mechanism. Nevertheless, the electron populations show that a significant amount of π-electron density is lost from the Cp ring (0.825 electrons), whilst the wave functions reveal that only a small amount of this π-density is lost to the metal $4s$ and $4p$ orbitals, which acquire most of their electron density from the ring σ-systems.

In fact the most significant change in orbital population occurs for the cyclopropenyl ring π-orbitals where an overall increase of 1.236 electrons results on complexation, the whole of this increase arising through back-donation from the filled metal $3d_{xz}$, $3d_{yz}$ orbitals by interaction with the vacant e π-level of the Cpr ring. Thus the metal d_{xz}, d_{yz} orbitals are stabilised by this bonding interaction with the three-membered ring, but these same metal orbitals also mix with the highest filled (e_1) π-cyclopentadienyl level, which is thereby stabilised (as the $1e$ level). Thus, because of this metal contribution to level $1e$ a small amount of electron density (0.26 electrons) is effectively lost from the e_1 Cp π-orbital. However, the calculations show that the $3e$ (SCF) molecular orbital which is largely $3d_{xz}$, $3d_{yz}$ in character, is essentially non-bonding with respect to the metal and the Cp e_1 π-orbital, whilst the virtual $4e$ molecular orbital, which is mainly π-Cpr, contains the anti-bonding interaction between d_{xz}, d_{yz} and the Cp ring π-orbitals. Thus, despite the formal $3d^{10}$ metal configuration there results a small net bonding interaction between the Cp ring e_1 π-orbital and the metal $3d$ levels ($Cp \rightarrow Ni$ donation), which is however more than offset by a much larger donation from the same metal orbitals to the e π-Cpr level. The metal $3d_{z^2}$ and $3d_{x^2-y^2}$, $3d_{xy}$ orbitals remain essentially localised, contributing little to the bonding, and the resultant metal d-orbital population is $d^{8.34}$ made up as $(d_{z^2})^{1.96}(d_{xz}, d_{yz})^{2.50}(d_{x^2-y^2}, d_{xy})^{3.88}$, with an overall charge on the metal of -0.822.

Finally, it is interesting to compare the changes in electron density which occur on complexation in CpNiCpr with those found [2] for CpCrCh, which may also formally be regarded as containing a neutral metal, Cr^0 ($3d^6$), with one positively charged (Ch^+) and one negatively charged (Cp^-) ligand. Remarkably we find that for all the six types of ligand orbitals listed in Table 2 exactly parallel changes in populations are found on complexation for CpCrCh. Thus for Cp(π) there is electron loss from 6.00 to 5.35, but for Ch(π) electron gain from 6.00 to 7.65, whilst for Cp(σ) there is a small loss of density from 2.904 to 2.885 and for Ch(σ) a rather large decrease from 3.027 to 2.855. Moreover, the H densities also follow a similar pattern, decreasing from 1.095 to 1.018 for the Cp ring but increasing from 0.974 to 1.033 for the Ch ligand, whilst the total d-electron density of 4.37 falls short of the formal d^6 configuration by an amount almost exactly equal to the shortfall for CpNiCpr (8.34 for a formal d^{10} configuration).

Our calculations thus serve to reflect both the similarities and the differences in the bonding schemes for CpNiCpr and the CpMCh systems, and also satisfactorily indicate the stronger bonding of the Cpr ligand in CpNiCpr suggested by the shorter experimental bond length for the three-membered ring in the triphenyl derivative.

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