A Bonding Model for Bent Bis-(π-cyclopentadienyl) Metal Compounds

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Summary An alternative to the Balhausen and Alcock models for bis-(π-cyclopentadienyl)metal systems, based on new structural data, is described.

Two descriptions for the bonding in bent bis-(π-cyclopentadienyl)metal systems have been proposed. Balhausen and Dahl[1] described bis-(π-cyclopentadienyl)molybdenum dihydride and, in order to account for the basic properties of this compound, suggested that the d^2 electrons were located in a 'lone pair' between the two hydrogens, see Figure 1(a). Alcock[2] observed that in the compound (π-C_5H_5)(C_5H_5Me)ReMe$_2$ the Me–Re–Me angle of 79° was too small to accommodate the lone pair that should be present if the Balhausen model was correct. He therefore suggested that d^2 electrons in this system were located in an orbital which lay largely outside the ReMe$_2$ system, [Figure 1(b)].

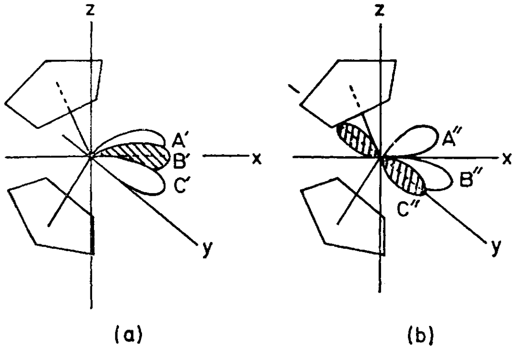

FIGURE 1 (a). *Location of orbitals suggested by Balhausen and and Dahl.*[1] (b) *Location of orbitals suggested by Alcock.*[2]

The crystal structures of the compounds (π-C_5H_5)$_2$M(SMe)$_2$,[3] where M = Ti or V and (π-C_5H_5)$_2$ZrX$_2$,[4] where X = F or I show that the X–M–X angle decreases in going from a d^0 system (Ti or Zr) to a d^1 (V) system.

TABLE

Some distances and angles in (π-C_5H_5)$_2$MX$_2$ *compounds*

Compound		X–M–X	d(M–X)	M–Cp[f]
(π-C_5H_5)$_2$Mo(SnBr$_3$)Br[a]	d^2	80·2(2)	2·606(9)[e]	1·99(2)
(π-C_5H_5)$_2$MoCl$_2$[b]	d^2	82·0(2)	2·471(5)	1·99(1)
[(π-C_5H_5)$_2$ReBr$_2$]$^+$BF$_4^-$[b]	d^2	82·0(1)	2·565(5)	1·89(1)
(π-C_5H_5)$_2$V(SPh)$_2$[c]	d^1	89·3	—	—
[(π-C_5H_5)$_2$MoCl$_2$]$^+$BF$_4^-$[b]	d^1	87·9(1)	2·382(2)	1·98(1)
(π-C_5H_5)$_2$NbCl$_2$[b]	d^1	85·6(1)	2·470(4)	2·09(1)
[(π-C_5H_5)$_2$NbCl]$_2$O^{2+}·2BF$_4^-$[b]	d^0	96·2(9)	2·370(4)	2·10(1)
(π-C_5H_5)$_2$ZrCl$_2$[b]	d^0	97·1(2)	2·441(5)	2·21(1)
(π-C_5H_5)$_2$ZrF$_2$[d]	d^0	96·2(3)	1·98(1)	2·21(1)
(π-C_5H_5)$_2$ZrI$_2$[d]	d^0	96·2(1)	2·832(2)	2·19(1)
(π-C_5H_5)$_2$Ti(SPh)$_2$[c]	d^0	95·0	—	—

[a] ref. 5; [b] ref. 6; [c] ref. 3; [d] ref. 4; [e] Mo–Br; [f] perpendicular distance from metal atom to cyclopentadienyl ring.

We have determined the crystal structures of seven new (π-C_5H_5)$_2$MX$_2$ compounds,[5,6] where the metal is a d^0, d^1 or d^2 system. All analyses were based on diffractometer data and refined to R values of 2·6—9·0%. The data (Table) show that there is a strong and wide-spread correlation between the X–M–X angle and the number of 'non-bonding' d-electrons on the metal.

This crystal structure evidence strongly supports the Alcock model for the compounds (π-C_5H_5)$_2$MX$_2$. On the other hand, the basic properties of the hydrides (π-C_5H_5)$_2$MH$_2$, M = Mo or W, and (π-C_5H_5)$_2$ReH and the structure of the trihydrides (π-C_5H_5)$_2$MH$_3$, M = Nb or Ta, seem to support the Balhausen description.

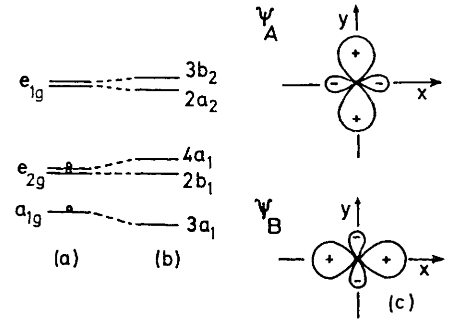

FIGURE 2 (a). *The highest filled and lowest empty M.O.'s in ferrocene.* (b) *The proposed M.O.'s in a bent* (π-C_5H_5)$_2$M *system.* (c) *Representation of the proposed hybrid orbitals* ψ_A *and* ψ_B *formed from the metal* $d_{x^2-y^2}$ *and* d_{z^2} *orbitals.*

These apparent differences may be resolved by a bonding model which incorporates features of both Alcock and Balhausen models as follows.

We have found that the photoelectron spectrum[7] of the complex (π-C_5H_5)$_2$MoH$_2$ suggests that there is a strong resemblance between the metal–ring bonding in this compound and in ferrocene. Therefore, it seems reasonable to generate the M.O. diagram for the bent bis-(π-cyclopentadienyl) metal system by 'bending' the ferrocene system to C_{2v} symmetry. This is shown in Figure 2(a) and (b) where the upper essentially non-bonding orbitals of ferrocene, the

e_{2g} and a_{1g} orbitals become the $3a_1$, $2b_1$, and $4a_1$ orbitals in the bent system.

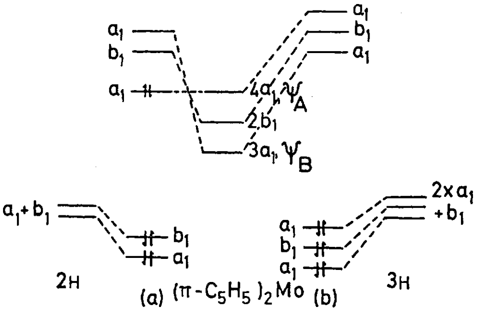

FIGURE 3 (a). *The M.O.'s resulting from interaction between the* $(\pi\text{-}C_5H_5)_2Mo$ *system and two hydrogen ligands, showing the 'lone pair' in the* ψ_A *(Alcock) orbital.* (b) *The M.O.s resulting from interaction between the* $(\pi\text{-}C_5H_5)_2Mo$ *system and three hydrogen ligands, showing that all three metal orbitals are employed. For simplicity, all other M.O.'s arising from the* $(\pi\text{-}C_5H_5)_2Mo$ *system are omitted.*

Assuming these orbitals are largely located on the metal then they can be said to arise primarily from the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} metal orbitals. Whilst the $2b_1$ orbital may be regarded as being essentially d_{xy} in character the $4a_1$ and $3a_1$ would mix and it can be envisaged that they might give rise to two new orbitals, ψ_A and ψ_B, see Figure 2. The ψ_A orbital resembles the $\psi_{C''}$ orbital of the Alcock model and the ψ_B orbitals resembles the $\psi_{B'}$ orbital of the Balhausen model, in their localisation.

This model may be used to describe the bonding in both compounds of the type $(\pi\text{-}C_5H_5)_2MX_2$ showing the highest filled orbital as the ψ_A orbital [Figure 3(a)] whereas when the bent bis-(π-cyclopentadienyl) metal system interacts with three ligands as in $[(\pi\text{-}C_5H_5)_2MoH_3]^+$ there are now three bonding M.O.s and there are now no 'lone pair' electrons [Figure 3(b)]. It follows from the above model that in binuclear systems of the type $(\pi\text{-}C_5H_5)_2MX_2ML_2$ the occurrence of an acute angle for X–M–X suggests the absence of M–M′ bonding and in compounds where $M = d^2$ the electrons would be located in the ψ_A type orbital. If X–M–X is obtuse this implies that a M–M′ bond is present. This correlation is in accord with present experimental evidence on bond angles in M–(μ-X_2)–M′ systems.[8]

Further support for this model is derived from the observations that (*a*) the perpendicular distances from the metal to the $(\pi\text{-}C_5H_5)$ ring decreases steadily with increasing nuclear charge [Zr (2·2 Å) > Nb (2·1 Å) > Mo (2·0 Å) > Re (1·9 Å)] but for a given central metal atom is independent of electron occupancy [*e.g.* $(\pi\text{-}C_5H_5)_2MoCl_2(d^2)$ (1·99 Å) ≈ $(\pi\text{-}C_5H_5)_2MoCl^+(d^1)$ (1·98 Å)] whereas (*b*) the M–Cl bond length is roughly constant with nuclear charge, $[(\pi\text{-}C_5H_5)_2ZrCl_2$ (2·441 Å) ≈ $(\pi\text{-}C_5H_5)_2NbCl_2$ (2·470 Å) ≈ $(\pi\text{-}C_5H_5)_2MoO_2$ (2·471 Å)] but for a given central metal atom decreases with decreasing electron occupancy, [*e.g.* $(\pi\text{-}C_5H_5)_2MoCl_2(d^2)$ (2·471 Å) > $(\pi\text{-}C_5H_5)_2MoCl_2^+(d^1)$ (2·382 Å)].

(*Received, 24th January* 1972; *Com.* 096.)

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