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POSSIBLE INTERACTION BETWEEN GROUP III TRIARYLS AND TRANSITION METALS

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The triphenyl derivatives of the Group III elements are all high melting crystalline compounds and have unusually large heats of sublimation[1,2]. Although the crystal structures of these compounds have not yet been investigated it is plausible to suppose that the molecules are almost planar and lie parallel to each other in the crystal, a situation which prevails in the crystals of many polynuclear organic compounds[3]. The magnitude of the heats of sublimation can then reasonably be ascribed to powerful dipolar forces. Compounds such as these, with closed electronic shells, cannot dimerise in their singlet ground states; such interaction can only lead to repulsive electronic forces. However there is no reason why two monomers should not interact with a *third* entity interposed between them as in ferrocene[4] and dibenzenechromium. The triphenyls of the Group III elements have a π-electron system extending over the whole of the molecule: hence it seems worthwhile to examine possible bonding patterns with central transition elements.

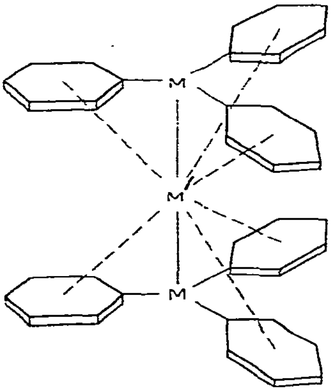

Fig. 1. Transannular molecule, D_{3h} (eclipsed symmetry).

The pivotal supposition is that the three central atoms are aligned in a colinear fashion (Fig. 1); then because the molecules are laterally extensive, substantially similar stabilising dipole forces should be retained. There are several secondary possibilities superimposed on this basic situation *e.g.* the phenyl rings could be noncoplanar with the Group III atom (as is almost certainly the case in the monomers) or the two sets of rings could be eclipsed or staggered with respect to each other (*i.e.*

D_{3h} or D_{3d} symmetry). With regard to the latter possibility the bonding patterns with a third entity would be essentially similar (see later) and the former may readily be accounted for by a perturbation treatment, indeed for small ring twisting angles it should have little effect.

MOLECULAR ORBITAL PATTERN (D_{3h} SYMMETRY)

We will consider first the π molecular orbitals of the two Ph_3M units. The π MO's of planar *monomeric* Ph_3M are all antisymmetric to reflection in the plane of the molecule (σ_h) and transform like the representations $5a_2''+6e''+2a_1''$ of group D_{3h}. In each monomer part the positive z axes are directed towards the other moiety. The MO's of the whole unit are then of symmetry, $5a_1'+5a_2''+6e'+6e''+2a_1''+2a_2'$. The two sets are distinguished by their behaviour to reflection in the new horizontal mirror plane (σ_h').

Under D_{3h} symmetry the orbitals of a transition metal atom or ion belong to representations as follows,

$$s, d_{z^2}, a_1'; \quad p_z, a_2''; \quad p_x, p_y, e'; \quad d_{xy}, d_{x^2-y^2}, e'; \quad d_{xz}, d_{yz}, e'';$$

Hence the totally symmetric a_1' orbitals of the two rings combine with a linear combination (or hybrid) of s and d_{z^2} orbitals. The bonding which results from this will be important in stabilising the new molecule because these a_1' ring MO's contain large contributions from the (initially empty) p_z orbital on M^5. They then bring about direct 'σ-type' bonding between M and M'. The p_z orbital of the transition metal will bond with the a_2'' linear combinations of the ring π systems which also contain an appreciable mixing coefficient for the Group III atom. These two bonding orbitals are the only ones which provide a direct link between M and M' and should be the most important ones as this particular bond distance is the shortest between M' and the triphenyl moiety. This means that the radial overlap is more likely to be favourable.

The d_{xz}, d_{yz}, d_{xy} and $d_{x^2-y^2}$ orbitals of the central atom bond with the e'' and e' MO's respectively, which are both localised on the phenyl rings. Now the d_{xz}, d_{yz} pair are directed in space towards the rings whereas d_{xy}, $d_{x^2-y^2}$ lie in a plane parallel to them hence the former should bring about stronger direct bonding with the rings.

ORBITAL OVERLAP

In triphenylboron half the carbon atoms of the rings lie outside a radius of 2.25 Å from the B atom and so bonding interactions between these carbons and M' can be discounted. This means that bonding of M' will be due mainly to interaction between it and the central Group III atom and with the nine carbons adjacent to the latter. The rest of the carbon atoms merely help determine the forms of the π ring MO's *i.e.* their constituent atomic orbital coefficients. Actually the overlap between the ring orbitals of a_1' and a_2'' symmetry and the transition metal atom will be dominated by that between the three co-linear central atoms because s orbitals are non-directional and the p_z orbital is defined along this particular axis. The d_{xy}, $d_{x^2-y^2}$ and p_x, p_y orbitals of the central atom are directed in a plane parallel to the rings and so may, in addition to the distance factor, also be discounted on the basis of small angular overlap with the phenyl rings. They may hence be regarded as non-bonding.

The d_{xz}, d_{yz} pair are directed towards the rings but the angular overlap can not be optimised because the latter lie at 120° to each other whereas the *d*-orbitals are an orthogonal degenerate pair. Moreover because the distance between M′ and the members of the nearest group of carbon atoms is somewhat long then the radial overlaps with the orbitals will also be to some extent diminished. Hence it seems that the orbitals of primary importance in bonding will be s, p_z, d_{z^2}, d_{xz}, d_{yz}, and the a_2'', a_1' and e'' MO's of the planar groups. Finally the magnitude of the overlaps between the ring orbitals and any of the transition metal orbitals is independent of whether the symmetry of the whole complex is D_{3d} or D_{3h}, (*i.e.* rings staggered or eclipsed); in either case the d_{xz}, d_{yz} pair cannot be oriented such that the overlap with the ring orbitals is as great as would be obtained under symmetries deriving from the cube.

SIZE EFFECTS

In the absence of an atom sandwiched between them the two monomer aryl units can approach to a distance of about 3.5 Å of each other. (There are numerous examples of planar molecules where the rings are mutually separated transannularly by such a distance in the unit cell)[3]. This therefore does not impose any limit on the size of the central atom (M′) that can be accommodated. Now if strong London dispersion forces are to remain operative the monomers should approach as closely as possible; this will be governed by (*a*) the M–M′ bond length which is, in turn, dependent on the size of the particular transition metal atom sandwiched inside the dimer unit and (*b*) by the particular group III atom. Iron is the smallest of the former type and has a radius of 1.24 Å whilst boron is the smallest of the latter group. These figures lead to an interring distance of ~4 Å if the iron and boron atoms are electrically neutral in the compound. Closer approach would be allowed if the Fe atom were effectively ionised and the charge transferred via boron to the rings.

However for an appreciable effect of this kind ionisation of Fe to something like Fe^{++} would be required and also if boron receives the major part of the transferred charge it would itself increase in size and the net bond shortening would be lessened, *e.g.* using Slater orbitals $B^{0.5-}$–Fe^{+}–$B^{0.5-}$ has almost the same Fe–B bond distance as does Fe^0–B^0. These considerations suggest that it might be advantageous to insert a transition metal *ion* in the centre and to convert the whole complex into a coordinated cation. The difficulty here is that the valence state ionisation potential of M′ would then undergo a disproportionate increase with concomitant loss of stability of the whole ion. (See later).

We conclude that small atoms like iron or nickel are the optimum choices because (*a*) larger dipole forces between the rings can be retained and (*b*) stronger radial overlap results between the *s*, *p*, and *d*-orbitals of the central atom with those of the boron and the nearest nine carbon atoms. Furthermore the outer orbitals of first row transition metals are more "compatible" with the 2*p* orbitals of carbon and boron because their principal quantum numbers are close to the latter.

Some points of distinction from the ferrocene case are worth noting. In the latter the rings are 3.38 Å apart[4] and the iron atom is accommodated by the central "hole" in the cyclopentadienyl ring. Thus it lies within "easy" bonding distance of all the ten carbon atoms. The chief bonding orbitals here are the doubly degenerate e_{1g} and e_{1u} set, the totally symmetric a_{1g} set figuring less prominently than in the present situation. Furthermore reverse delocalisation of electrons from Fe to the cyclopentadienyl ring is less important in ferrocene. This is because the e_{2g}, e_{2u} antibonding orbitals of the cyclopentadienyl ring are considerably displaced in energy from that of the *d*-orbitals of iron. This contrasts with the arylboron case where the acceptor orbitals are relatively close in energy.

ENERGY CONSIDERATIONS

In view of the foregoing discussion, the particular case of triphenylboron will be considered. This system has 19 π molecular orbitals of which nine are doubly filled. The orbitals which would be expected to mix most strongly with those of the transition metal are the set which lie closest in energy to the latter. Because of the low electronegativity of the central atom (M′) the most important potential bonding orbitals of Ph_3B will be the highest filled and the lowest antibonding orbitals. There are ~11 of these and they lie in the range -1.7 eV to -10.9 eV from the ionisation limit[5]. The most stable antibonding level has energy -2.81 eV and is non-degenerate. This level is perhaps the most significant because it contains a large contribution from the boron p_π orbital and is markedly displaced in energy from that of the original benzene e_{2u} π orbitals. It is also stabilised by ~1.7 eV with respect to the initial energy of the p_π orbital of the boron atom. This molecular orbital gives rise to two new ones which are symmetric and antisymmetric linear combinations of the two aryl units. These interact strongly with the s, d_{z^2} and p_z orbitals respectively of the metal M′. The electron affinity of the triarylborane is determined by this orbital (Koopmans' Theorem[6]) and because of its stability it is ideally situated to accept electrons from a source such as a transition metal atom having a number of these. To a first approximation the suggested compound could, in fact, be considered to result from electron transfer from the transition metal into this vacant orbital on each ring system. Such a situation would be energetically viable if the outer electrons of the central atom possessed low ionisation potentials and indicates that a first row transition element is most likely to form a stable compound. On the other hand a boron triaryl is little favoured over its aluminium analogue because the first antibonding orbital has similar energy in both cases[5]. Hence the chief advantage in the former is that the smaller size of boron allows closer mutual approach of the rings as discussed previously.

The energy of a model of this kind, neglecting covalency, may be obtained for some limiting cases from the formula,

$$E = \sum_i I_i - 2A - C$$

where I_i is the valence state ionisation potential of the i'th electron, A the electron affinity of the triaryl, and C the Coulomb attraction term. Appropriate values for I_1 and I_2 are lacking but the use of experimental values[7] is unlikely to introduce gross error. These are $I_1 = 7.90$, and $I_2 = 16.2$ eV. The three models B^-–Fe^{++}–B^- (Fe–B, 2.12 Å), $B^{0.5-}$–Fe^+–$B^{0.5-}$ (Fe–B, 2.12 Å), and B^-–Fe^{++}–B^- (Fe–B, 1.7Å, r_{max} of Fe^{++} calculated from Slater orbitals) possess net stabilisation energies of -8.4,

-1.7 and -15.2 eV respectively. The charge separation in models 1 and 3 is no doubt overestimated and case 2 is probably nearer to what the real situation might be.

Further stability should be conferred by mixing between the e'' type orbitals on the rings and those of the same symmetry on the central atom. The charge-transfer approach certainly oversimplifies the situation but it does lead to the prediction that such compounds may well be capable of preparation. Thus their stability would result primarily from the bonding between the s, d_{z^2} and p_z orbitals of the transition element and the low-lying antibonding orbitals of the triaryl unit. The rings of the latter augment the situation favourably by raising the electron affinity of the Group III atom and by introducing strong dispersion forces between the two ring systems. The overlap of the degenerate ring orbitals with the d-orbitals of the central atom is governed largely by the radial functions and this bonding is expected to influence less markedly the stability of the final compound.

SUMMARY

The possibility of new compounds formed by transannular interaction between transition metals and the triaryl of a Group III element is discussed. The conclusion is that such compounds may well be stable.

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